Quantum chemical approach to spin-orbit excitations and magnetic interactions in iridium oxides

Dissertation
zur Erlangung des akademischen Grades
Doctor rerum naturalium (Dr. rer. nat.)

vorgelegt von

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Dezember 2014
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Eingereicht am 17. Dezember 2014
Disputation am 05. Februar 2015
I would like to dedicate this thesis to BHAGAVAN SRI SATHYA SAI BABA.
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Nomenclature

Other Symbols

$\Gamma_{ij}$  Symmetric anisotropic tensor

$\Delta_t$  Tetragonal crystal field splitting

$\lambda$  Spin-orbit coupling strength

$J$  Isotropic exchange interaction

$K$  Kitaev-type exchange interaction

$Z$  Spin-orbit coupling operator

$\tilde{j}$  Effective total angular momentum

$\tilde{l}$  Effective orbital angular momentum

Acronyms / Abbreviations

AF  Antiferromagnetic

AO  Atomic Orbital

BR  Branching Ratio

CAS  Complete Active Space

CASPT2  Complete Active Space Perturbation Theory 2nd order

CASSCF  Complete Active Space Self Consistent Field

CF  Crystal Field

CI  Configuration Interaction

CISD  Configuration Interaction Singles and Doubles
<table>
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<td>Configuration State Functions</td>
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<tr>
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<tr>
<td>DFT</td>
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<td>DM</td>
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</tr>
<tr>
<td>DMFT</td>
<td>Dynamic Mean Field Theory</td>
</tr>
<tr>
<td>ECPs</td>
<td>Effective Core Potentials</td>
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<tr>
<td>ED</td>
<td>Exact Diagonalization</td>
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<tr>
<td>FCI</td>
<td>Full Configuration Interaction</td>
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<tr>
<td>FM</td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>FW</td>
<td>Foldy-Wouthuysen</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
</tr>
<tr>
<td>GTO</td>
<td>Gaussian Type Orbitals</td>
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<tr>
<td>KD</td>
<td>Kramers Doublet</td>
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<tr>
<td>KH</td>
<td>Kitaev Hiesenberg</td>
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<tr>
<td>LCAO</td>
<td>Linear Combination of Atomic Orbitals</td>
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<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
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<tr>
<td>MCSCF</td>
<td>Multi-Configurational Self-Consistent Field</td>
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<td>MO</td>
<td>Molecular Orbital</td>
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<td>NEVPT2</td>
<td>N-Electron Valence state Perturbation Theory</td>
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<tr>
<td>NN</td>
<td>Nearest Neighbor</td>
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<td>NR</td>
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Nomenclature

PC  Point Charge
QC  Quantum Chemistry
QDPT Quasi-Degenerate Perturbation Theory
RHF Restricted Hartree-Fock
RIXS Resonant Inelastic X-ray Scattering
ROHF Restricted Open Hartree-Fock
SCF Self-Consistent Field
SE Schrödinger Equation
SO Spin-Orbit
SOC Spin-Orbit Coupling
SOO Spin Other Orbit
SR Scalar Relativistic
SSO Spin Same Orbit
TIPs Total Ion Potentials
TM Transition Metal
UHF Unrestricted Hartree-Fock
WF Wave Function
XAS X-ray Absorption Spectroscopy
I am indebted to Dr. Liviu Hozoi and Prof. Dr. Jeroen van den Brink for a host of things, primarily for giving me an opportunity to work at IFW Dresden, for guidance on the topic, bountiful resources, encouragement and empathy.

Liviu introduced me to quantum chemical methods and their application to solid state systems. Apart from his constant encouragement to try out new things, he was always ready to share his expertise, be it related to Physics or a career in scientific research. I will never forget the help he offered while I was writing this thesis, especially the comments on content and style. Liviu, I am thankful to you for all your advice and thoughtful criticism, without which this thesis work would not have seen the light.

Jeroen has been excellent in coming up with relevant projects that can be investigated using quantum chemistry methods. His extensive reach and connections with the experimentalists gave me an opportunity to collaborate with several experimental groups. These collaborations led to a couple of impactful publications. He was generous enough to sponsor my trips to several conferences and workshops around the world. These in fact have helped me to broaden my scope on strongly correlated materials and condensed matter physics in general. Jeroen, I am deeply grateful for your support during the last few years.

I would like to express my gratitude to Dr. Viktor Yushankhai for his detailed explanations on the model Hamiltonian construction and superexchange theory relevant for iridates.

I wish to thank Prof. Dr. Hermann Stoll for promptly answering all my queries related to MOLPRO and quantum chemistry calculations in general.

Large part of this thesis would not have been possible without the help from Dr. Ioannis Rousochatzakis. He taught me how to play with spin Hamiltonians and their symmetry properties. At times, he took pains to explain some of the most fundamental concepts. Ioannis, your guidance was invaluable in extracting those anisotropic magnetic couplings in Chapter 6 and 7. The Mathematica code you have generously provided will serve me for many years to come.

Dr. Satoshi Nishimoto, I thank you for collaborating with us. Your ED calculations have added more value to the results obtained in this work.

Thank you Dr. Dmitry Efremov, discussions with you were helpful in solidifying my
concepts in solid-state physics.

Nikolay Bogdanov, my PhD comrade, was ever ready for a long discussion, whether it was about science, languages or even about food! Niko, I have learnt a lot of stuff from you, especially many software related things. Thanks for encouraging me to use open access programs.

I also want to take this opportunity to express my heartfelt gratitude to Grit Rötzer for helping me to deal with all the official paper work required during my stay at IFW. Grit, I appreciate your help in arranging the initial accommodation in Dresden and for the translations during my first days here.

To all my other colleagues, Danny, Judith, Katia, Ganesh, Alex, Frank, Andre, Sahinur and Ravi, your company was a lot of fun. The tea sessions we often had were really relaxing and beneficial. Danny, thank you for being so generous to donate your Desktop. Judith, whenever I work with Mathematica, I will definitely remember you, thanks for explaining all the tricks. Alex, thanks for lending me your notes on topological insulators.

Last but certainly not least, to my family who have stood by me with patience and love, I am forever grateful. Steffi, special thanks to you for reading through the thesis. I will make sure to keep in mind all those things, which you taught me during this period, in my future writings.
Chapter 1

Introduction

1.1 Electronic correlations and spin-orbit coupling in transition metal oxides

In the last few decades, transition metal (TM) oxides, especially those of the first row series, have been in the focus of solid state research for several reasons. These compounds possess extraordinary and intriguing properties that have been puzzling the scientific community to the present day. Unconventional superconductivity with high critical temperature (high-$T_c$), for instance, first discovered in copper oxide compounds in the mid 1980s [1], is one of these properties that still remains to be comprehended. Some of the other remarkable phenomena TM oxides exhibit are colossal magnetoresistance [2], enthralling phase transitions, e.g., metal-insulator transitions [3], and the occurrence of many compelling magnetic and non-magnetic phases.

All of the above-mentioned properties are to a large extent manifestations of strong electronic correlations in TM oxides. The latter arise due to large on-site Coulomb ($U$) and exchange interactions ($J_H$) among the TM valence electrons. Many $3d$ TM oxides show an insulating behavior even though the valence shells are only partially filled\(^1\). This is because the on-site Coulomb repulsion within the relatively compact $3d$ orbitals prevents double orbital occupation, required in the simplest picture for electronic conduction. In other words, when the on-site repulsion is much larger than the kinetic energy $W$ gained by the formation of “electron-hole” pairs ($U >> W$), the electrons would rather remain localized at their lattice sites and make the system insulating. Such an insulator is called Mott or Mott-Hubbard insulator [4, 5]. The large $U$ in these compounds also leads to localized magnetic moments at each of the TM lattice sites. The interactions between these moments (ferromagnetic [FM]

\(^1\)The Pauli’s exclusion principle prevents the movement of electrons in completely filled energy bands leading to band insulators.
and/or antiferromagnetic (AF)) give rise to fascinating magnetic phases either with or without long-range order [6]. Apart from the sign and strength of these magnetic interactions, certain geometries of the underlying lattice on which the spin-moments reside could lead to frustration [7]. For example in spin-liquids [8], although correlations between the spin-moments are large, no ordering of these moments occurs due to various frustrating and/or competing interactions.

Recently, in addition to 3d compounds, the interest in TM oxides with 4d and 5d valence electrons has grown immensely. This is partly the result of a search for new oxide materials hosting superior or even new properties. Indeed, novel and stimulating physics has lately been discovered in second and third series TM oxides. The electron-electron interactions are known to become progressively weaker when going to heavier TM elements, i.e., from 3d to 4d and 5d, mainly due to an increase in the radial extent of the d orbitals. Hence, a concomitant crossover to a weakly correlated electronic structure is naively expected. However, the relativistic spin-orbit coupling (SOC) follows the opposite trend – it increases progressively when going to heavier elements.

In 5d TM compounds, e.g., iridates and osmates, the intriguing situation arises where the spin-orbit and electron-electron interactions meet on the same energy scale. Interestingly, it turns out that the former can effectively enhance the latter, as explained in more detail in Chap. 2. This has created a new window of interest in such compounds since the interplay of crystal field (CF) effects, local multiplet physics, SOCs and intersite hopping can offer novel types of correlated ground states and excitations. Some of the most exotic examples are possible topological states in pyrochlore iridates, such as a topological Mott insulator, a Weyl semimetal, or an axion insulator [9], and the possible realization of the recently proposed Kitaev spin model with bond-dependent spin-spin interactions in 2D honeycomb-lattice iridium oxides [10–13]. 2D square-lattice iridates such as Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ are also appealing because of their perceived structural and magnetic similarity to La$_2$CuO$_4$, the mother compound of the cuprate high-T$_c$ superconductors. This has promoted the latter iridium oxide compounds as novel platforms for the search of high-T$_c$ superconductivity [14–16].

To put the above considerations on solid footing it is essential to quantify the different coupling strengths and energy scales, as they appear in effective model-Hamiltonian descriptions of these correlated electronic systems [16–18]. The work in this thesis deals with the \textit{ab initio} investigation of the essential valence-shell couplings and interactions defining the remarkable properties of 5d$^5$ iridium oxides.

### 1.2 Anisotropic exchange interactions in 5d$^5$ iridium oxides

The Heisenberg model $J \mathbf{S}_i \cdot \mathbf{S}_j$ of magnetic interactions between spin moments at sites $\{i, j\}$ has been successfully used as an effective minimal model to describe the cooperative mag-
1.2 Anisotropic exchange interactions in 5d$^5$ iridium oxides

Magnetic properties of both molecular and solid-state many-electron systems. For example, 2D square-lattice effective spin models based on the isotropic Heisenberg picture have been extensively investigated in relation to layered superconducting materials such as the copper oxides [1] and iron pnictides [19]. While in iron pnictides the nearest-neighbor (NN) and next-NN Heisenberg interactions are of the same magnitude and must be treated on equal footing [20, 21], in cuprates the NN exchange defines the dominant magnetic energy scale [22]. It has been shown, however, that the anisotropic intersite couplings are also important, in particular for correctly describing the AF ordering pattern in La$_2$CuO$_4$ [23] or in cuprate oxychlorides [24, 25].

The role of anisotropic interaction terms in d-metal oxide compounds has lately received a new impetus with recent insights into the basic electronic structure of 5d systems such as the 5d$^5$ iridium oxides. A subtle interplay between spin-orbit interactions and sizable electron correlations gives rise to insulating ground states in 5d$^5$ iridates. Due to the strong SOC, however, the magnetic moments are best described as effective pseudospin $\tilde{S} = 1/2$ entities [10, 14, 15, 26] and the effective anisotropic exchange parameters are orders of magnitude larger than in 3d TM compounds. For instance, in the square-lattice system Sr$_2$IrO$_4$, Dzyaloshinskii-Moriya (DM) interactions as large as one quarter of the NN AF superexchange have been predicted [27, 28]. Further, a less conventional spin model – the Kitaev model [29] – has been recently proposed for the 5d$^5$ materials Na$_2$IrO$_3$ and Li$_2$IrO$_3$, with 90$^\circ$ metal-oxygen-metal bonds on a honeycomb lattice [10]. The exchange couplings in this model are highly anisotropic, with different spin components interacting along different bond directions of the honeycomb network. Interestingly, the model hosts nontrivial topological phases with elementary excitations exhibiting Majorana statistics, which are relevant and much studied in the context of topological quantum computing [29–34].

Valuable insights into the role of different superexchange processes in correlated d-metal oxides come from the detailed analysis of extended multiorbital Hubbard-type models. The foundations of superexchange theory were laid as early as the 1950s with the works of Anderson, Goodenough and Kanamori [35–39]. Standard approaches within this theoretical framework proved to be extremely useful in better understanding the origin and relative strength of the anisotropic couplings in layered cuprates. On the other hand, in iridates, much less information is presently available on the magnitude of various electronic-structure parameters that enter the superexchange models. While estimates for these effective electronic-structure parameters are normally based on either experiments [10, 40–42] or density-functional band-structure calculations [18, 27, 28, 43, 44], here, in this thesis, we employ many-body quantum chemistry (QC) methods to obtain an ab initio assessment of the NN Heisenberg exchange and anisotropic couplings in 5d$^5$ iridates. Specific compounds we investigate are for example the 2D square-lattice materials Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ and the honeycomb-lattice systems Na$_2$IrO$_3$ and Li$_2$IrO$_3$. 
1.3 Wave-function-based quantum chemistry approach

The *ab initio* calculation of the electronic structure of a system of interacting electrons and nuclei is a challenging task. Currently, the most widely used computational approach for solids is density functional theory (DFT) and various approximations to it, e.g., the local-density and generalized-gradient approximations (LDA/GGA) [45]. Here, the translational symmetry of the solid is exploited by means of periodic boundary conditions and the ground state problem of the system is formulated and solved in momentum space\(^2\). Specific properties are then calculated from the ground state charge density. This approach has seen an unparalleled success in describing a variety of compounds in solid state physics, especially in estimating properties like lattice parameters, elastic constants, dielectric functions and phonon frequencies within a few percent of the experimental values [45]. It is, however, also known that DFT fails to correctly describe systems which contain \(d\) or \(f\) elements where the electrons are strongly correlated [47, 48]. This is because of the mean-field type of treatment of electron-electron interactions in present LDA/GGA formulations of DFT, where an individual electron is assumed to be moving in an effective field of the other electrons. However, in \(d\)- and \(f\)-electron systems the underlying physics is dominated by the mutual Coulomb repulsive interactions. The latter are due to the rather localized nature of the \(d\) and \(f\) orbitals. Although extensions of DFT by dynamical-mean-field theory (DMFT) [49] led to DFT+DMFT schemes that allow one to overcome some of the intrinsic limitations of DFT, the accuracy and predictive power of these calculations is to some extent restricted by the use of parameterizations such as the on-site Coulomb repulsion \(U\). It is therefore desirable to explore complementary techniques to treat the electronic correlation problem efficiently.

A different approach to *ab initio* electronic structure calculations is based on wave function methods and a real space formulation. Such methods have been extensively applied for calculating molecular electronic structures in the theoretical chemistry community [50]. An appealing characteristic of the wave-function-based approach is the ability to address the electron correlation problem in a systematic and controlled manner without using \textit{ad hoc} parameters. However, the calculation of the many-body wave function for a solid is computationally impracticable and has not been used traditionally. Algorithms based on many-body second-order perturbation [50–52] and multireference configuration interaction formalism [53, 54] have been developed only during the last few decades to explicitly treat electron correlations in solids. More recently, a method based on the quantum Monte-Carlo algorithm has been proposed for the calculation of full configuration interaction (FCI) wave functions [55].

One way to approach the computational hindrance is to use cluster approximations, where only a given, rather small, part of the actual crystal is treated explicitly with advanced many-

\(^2\)There are very few real space implementations of DFT, e.g., PARSEC [46]
body calculations and the rest of the solid environment is dealt with at an approximate level. Such local impurity-like models based on lattice model Hamiltonian as proposed by Anderson [56] were earlier used to describe various electronic properties of strongly correlated 3d systems [57, 58]. In such calculations, e.g., for Ni dihalides, the 3d-states of Ni were essentially treated as impurity states in a host band-structure that involves the TM 4s and ligand p bands [58]. A similar cluster approach with \textit{ab initio} wave-function-based quantum chemistry calculations [59–76] proved to be successful as well. Within the latter method, a cluster, large enough to compute the relevant “local” physics, is embedded in an effective potential that accounts for the solid state environment. The many-body problem within the cluster region is solved using either configuration interaction techniques or perturbation methods [50]. This approach has provided accurate estimates and predictions for properties like d-d excitations, ligand to metal charge transfer effects [74, 77, 78], quasi-particle band structures [54, 70, 73, 75, 76], core level spectra [79, 80] and Heisenberg spin interactions [66, 67, 81–85] in several insulating TM materials. More recently, anisotropic exchange interaction parameters in 3d TM compounds have also been extracted, see [86–88] and references therein.

1.4 Overview of this thesis

This thesis deals with the investigation of the electronic structure and magnetic properties of crystalline 5d\textsuperscript{5} iridium oxides. Wave-function-based many-body quantum chemical methods are employed for this purpose. By spin-orbit electronic structure calculations, we determine the character of the ground state wave functions as well as of the low-lying spin and charge excitations. This allows us to extract, for example, the strengths and signs of the NN magnetic exchange couplings, by mapping the quantum chemically computed magnetic spectrum of nearby iridium sites onto appropriate effective spin Hamiltonians. The isotropic (Heisenberg) and anisotropic (both symmetric and antisymmetric) exchange couplings derived this way are further used to analyze in detail the magnetic phase diagrams of some of these compounds.

In the following chapter (Chap. 2), an introduction to the physics of spin-orbit driven “Mottness” in iridium oxides is provided. In particular, we discuss in detail the formation of the effective total angular momentum $\vec{j} = 1/2$ ground state. Since most of the results are compared with resonant inelastic x-ray scattering (RIXS) measurements\textsuperscript{3}, a brief description of this experimental technique is also provided. In the subsequent chapter (Chap. 3), the many-body quantum chemical methods employed for the calculation of the above-mentioned properties are outlined.

In Chap. 4, we present results of both ground and excited state calculations for several

\textsuperscript{3}Nowadays, these methods are being used extensively to study charge and spin excitations in TM oxides.
insulating iridium oxides with different crystal structures. We begin with the much studied layered square-lattice $\text{Ae}_2\text{IrO}_4$ ($\text{Ae} = \text{Ba, Sr}$) 214 type of compounds and then move on to the honeycomb-lattice materials of $\text{A}_2\text{IrO}_3$ 213 type ($\text{A} = \text{Na, Li}$). We examine the composition of the spin-orbit coupled ground state wave function and characterize the Ir $d-d$ charge excitations. Our results for both classes of compounds are in excellent agreement with those observed in RIXS measurements. Moreover, the analysis of the wave functions provides a better understanding of the ground and excited states. In particular, we identify the precise mechanism responsible for a different order of the Ir $t_{2g}$ levels in Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$. This different order gives rise to subtle differences in the composition of the spin-orbit $j \simeq 1/2$ ground and $j \simeq 3/2$ excitonic states in the two 214 materials. We proceed to explore the same aspects in two additional compounds that exist in a lower crystal symmetry, Sr$_3$CuIrO$_6$ and Na$_4$Ir$_3$O$_8$, and discuss the competition between anisotropic crystal fields and spin-orbit couplings. In Chap. 5, the expectation value of the spin-orbit coupling operator is evaluated for a number of Ir $5d^5$ oxides. The results are compared with those extracted from the measured branching ratios (BR) in x-ray absorption experiments. We provide a quantitative explanation for the unusual large values of those BRs deduced from the measurements.

In the last two chapters, the magnetism in 214 (Chap. 6) and 213 (Chap. 7) iridates is discussed. We first describe the construction of the effective spin Hamiltonian by using the underlying symmetry of the system. The calculated two-site magnetic spectrum is then mapped onto the effective Hamiltonian and the exchange couplings are extracted. We further discuss the various contributions to the exchange mechanism, by carrying out calculations at different levels of theoretical sophistication and also by comparing the results with those obtained for idealized structural models. We find that the isotropic Heisenberg interaction is dominant in 214 compounds, although the anisotropic interactions are considerably large compared to, e.g., cuprates. For Ba$_2$IrO$_4$ we propose a compass-Heisenberg model for the magnetism within the 2D layers. By including additional inter-layer exchange couplings we explain the ground state magnetic order observed in experiments. For the 213 iridates our analysis shows that the symmetric anisotropic exchange interactions are dominant, especially the Kitaev type interaction in Na$_2$IrO$_3$. For Li$_2$IrO$_3$ we propose the formation of triplet dimers on one particular set of Ir-Ir bonds due to the large FM isotropic coupling extracted from our calculations for those particular links. A semiclassical analysis with second and third neighbor isotropic interactions between these triplet entities on the effective triangular lattice results in a magnetic phase diagram very similar to that obtained from cluster exact diagonalization calculations on the original honeycomb-lattice.
Chapter 2

Iridium oxides

In this chapter we give an introduction to the remarkably rich physics in iridium oxide compounds. Concepts like the quenching of orbital angular momentum, spin-orbit coupling, electron correlations and exchange are introduced and how the interplay of such effects and interactions leads to the spin-orbit coupled Mott insulating $\tilde{j} = 1/2$ states is discussed. In the last section an overview of various magnetic interactions occurring in $\tilde{j} = 1/2$ compounds is provided.

2.1 Tetravalent Ir 5$d^5$ systems

The electronic configuration of the iridium (Z=77) atom is [Xe]4$f^{14}5d^76s^2$. Because the 4$f$ electronic shell is rather compact, only the 5$d$ and 6$s$ subshells actively participate in the chemical bonding. In oxide compounds of iridium, the iridium ion sits in a cage of oxygen ions with sixfold coordination (Fig. 2.1a), e.g., in Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ [89, 90]. In a pure ionic picture, each iridium gives away four electrons to the neighboring oxygens, leading to Ir$^{4+}$ and O$^{2-}$ valence states. The five electrons in the 5$d$ subshell then occupy the orbitals formed by linear combinations of $|l,m_l\rangle$ states, with the orbital angular momentum $l = 2$ and the magnetic quantum number $m_l$ taking values from $-l$ to $l$. These orbital states can be expressed as:

\begin{align*}
    d_{xy} &= \frac{1}{i\sqrt{2}}(|2,2\rangle - |2,-2\rangle) \\
    d_{yz} &= -\frac{1}{i\sqrt{2}}(|2,1\rangle + |2,-1\rangle) \\
    d_{zx} &= -\frac{1}{i\sqrt{2}}(|2,1\rangle - |2,-1\rangle)
\end{align*}

(2.1)
\[ d_{z^2} = |2, 0 \rangle \]
\[ d_{x^2-y^2} = \frac{1}{\sqrt{2}} (|2, 2 \rangle + |2, -2 \rangle). \]

(2.2)

The Hund’s first rule [6] states that the energy of a half-filled \( d \) shell is minimum when the total spin momentum \( S = \sum_i s_i \) (\( s_i \) is spin of the \( i \)th electron) is maximized. Hence, each of the 5\( d \) levels will be occupied with one electron to give a high-spin \( S = 5/2 \) state\(^1\). Such a scenario occurs, however, only in the case of a free Ir\(^{4+} \) ion where the \( d \) orbitals are energetically degenerate. In oxides, the \( d \) orbitals are not degenerate due to interaction and orbital overlap with the neighboring ligands. This effect is described in the following section.

\section*{2.2 Crystal fields and \( d \)-level splitting}

In TM oxides, the charge distribution around the TM ion is not spherically symmetric. The arrangement of the negatively charged oxygen ligands around the TM cation lowers the symmetry depending on the lattice position of the ligands. The consequence is that each of the TM \( d \) orbital is affected differently, leading to a splitting of the \( d \)-level degeneracy. Two effects contribute to this \( d \)-level splitting: the electrostatic repulsion of the ligand ions and the hybridization of TM \( d \)-orbitals with the ligand \( p \)-orbitals [91, 92].

For an octahedrally coordinated compound (\( O_h \) point-group symmetry) as in iridium oxides (see Fig. 2.1a), the \( d \) levels of the TM ion are split into doubly degenerate \( e_g \) and triply degenerate \( t_{2g} \) subspaces (irreducible representations of \( O_h \) symmetry). This separation is called crystal field splitting/energy (\( \Delta_{CF} \)). Because the electron cloud of \( e_g \) (\( d_{z^2} \) and \( d_{x^2-y^2} \)) orbitals is directed towards the negatively charged O ions surrounding the TM ions (see Fig. 2.1b), the \( e_g \) electrons experience a strong repulsive Coulomb interaction with the oxygen ions. On the other hand, the three \( t_{2g} \) orbitals of the TM have their lobes directed along the diagonals in between the oxygens (see Fig. 2.1b). The \( t_{2g} \) levels therefore lie at lower energies than the \( e_g \) states. This is the essence of crystal field theory [91].

The other contribution to \( \Delta_{CF} \) is due to the hybridization of the \( d \)-orbitals of the TM ion with the \( p \)-orbitals of the oxygens. This causes a mixing of these orbitals and leads to the formation of molecular-like orbitals (MOs). The TM \( e_g \) orbitals have a strong \( \sigma \)-overlap with the symmetry equivalent O \( 2p \) orbitals, resulting in the formation of low energy bonding (dominantly O \( 2p \) character) and high energy antibonding (dominantly TM \( e_g \) character) MOs. The considerably weaker \( \pi \)-overlap of TM \( t_{2g} \) orbitals with those of the O \( 2p \) functions of the same symmetry results in a rather small upward shift of the \( \pi \) antibonding MOs, dominantly of TM \( t_{2g} \) character (see Fig. 2.1c). This leads to an enhancement of the splitting

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\(^1\)The Pauli’s exclusion principle precludes having two electrons with the same spin in a given orbital.
2.2 Crystal fields and d-level splitting

Fig. 2.1 (a) Ir ion in octahedral cubic environment of O ligands. (b) Angular distribution of the d-orbitals. (c) Crystal field splitting due to octahedral arrangement of the O ligands. The splitting due to electrostatic interactions as calculated by crystal field theory is referred to as 10Dq. The molecular orbital diagram shows the splitting of the 5d levels due to the d – p hybridization. The type of overlap is shown in the brackets, antibonding states are represented by an asterisk. The large σ-overlap of the Ir 5d e_g orbitals with the O 2p orbitals of the same symmetry leads to a very large separation between the bonding and antibonding e_g MOs. The relatively little overlap of the Ir 5d t_2g orbitals with the symmetry equivalent O 2p orbitals results in a smaller separation between the respective bonding and antibonding MOs. This gives rise to increased separation between the TM-like t_2g and e_g MOs.
between the upper, TM-like $t_{2g}$ and $e_g$ levels.

The order of the energy levels depends on the type of coordination, for instance, in a tetrahedrally coordinated compound, the $e_g$ orbitals have little overlap with the oxygen orbitals and hence have lower energy compared to the $t_{2g}$ orbitals whose lobes are pointing towards the oxygen ligands. This is exactly opposite to the situation occurring in octahedral coordination [6].

As the degeneracy of the $d$-orbitals is removed, the electrons first start to fill the low energy orbitals. The filling up of orbitals depends on the competition between the crystal field splitting and the Hund’s rule coupling (energy saved by aligning the spins in parallel in accordance with Pauli’s exclusion principle) [93]. The exact value of $\Delta_{CF}$ strongly depends on the type of anions and cations and the distance between them. In the case of iridium oxides, the large spatial extent of Ir 5$d$ orbitals gives rise to stronger $d-p$ interaction and larger splitting between the $t_{2g}$ and $e_g$ levels as compared to the splitting in, e.g., 3$d$ TM oxides. The crystal field splitting in iridates is estimated to be $\sim 3$ eV [94]. A much smaller Hund’s rule coupling in iridates ($\sim 0.3–0.5$ eV) results in a low-spin $S = 1/2$ configuration with the five electrons in the $t_{2g}$ subshell (see Fig. 2.1c).

The $t_{2g}$ orbitals remain degenerate as long as the crystal environment around the Ir$^{4+}$ ions is octahedral. Depending on the solid-state chemistry, various types of distortions may arise. In such cases, the $d$-level splittings become substantially more complex as the degeneracy of the $e_g$ and $t_{2g}$ groups of orbitals may also be removed. For example, when the two apical oxygens move away from the iridium ion, the energy of the $d_{x^2}$ level becomes lower than that of $d_{z^2−y^2}$. On the other hand, if the apicals are pushed towards the metal ion along the $z$-axis, the $d_{xy}$ ($t_{2g}$) and $d_{z^2−y^2}$ ($e_g$) are stabilized with lower energies as compared to the respective $z$ counterparts [6]. In Chap. 4, we discuss the effects of noncubic fields on the Ir $t_{2g}$ levels in a number of iridium oxide compounds.

### 2.3 5$d$ spin-orbit couplings

Spin-orbit (SO) interaction is the interaction between the orbital motion of an electron and its spin due to relativistic effects. It is rigorously derived from relativistic quantum mechanics [95] but can also be understood semiquantitatively in a classical framework (see App. A.1). In simple terms, SO interaction is the effect that the electron’s magnetic dipole moment experiences from the magnetic field generated by the electron’s orbital motion around the nucleus.

For a single electron in an atom, the SO Hamiltonian coupling the orbital and spin angular
momentum $l$ and $s$, respectively, can be written as (see App. A.1)

$$H_{\text{SO}}^{(1)} = \zeta l \cdot s,$$

with \(\zeta = \frac{\hbar^2 Z e^2}{2m^2c^2r^3}\) (2.3)

as the strength of SO interaction. The splitting due to SO coupling is given by

$$E_{\text{SO}}^{(1)} = \langle H_{\text{SO}}^{(1)} \rangle = \frac{Z^4e^2\hbar^2}{4m^2c^2} \left\{ \frac{j(j+1)-l(l+1)-s(s+1)}{l(l+1/2)(l+1)a^3n^3} \right\},$$

(2.4)

From Eq. 2.4, it can be seen that the SO interaction is proportional to \(Z^4\) and inversely proportional to the principal quantum number \(n\). For a many-electron atom the SO Hamiltonian can be obtained by summing over all electrons as

$$H_{\text{SO}} = \sum_i \zeta l_i \cdot s_i \approx \lambda \mathbf{L} \cdot \mathbf{S},$$

(2.5)

where \(\mathbf{L}\) and \(\mathbf{S}\) are the total orbital and spin angular momentum, respectively, of a particular state. \(\lambda\) here depends only on the values of \(\mathbf{L}\) and \(\mathbf{S}\) [92].

In magnetic oxides based on 3d TM ions, \(\lambda\) is substantially smaller than both \(\Delta_{\text{CF}}\) and the on-site Coulomb repulsion \(U\), e.g., in Cu \((Z=29)\), \(\lambda \sim 0.01\) eV and \(U \sim 5\) eV. Therefore, Hund’s rule determines the ground state values of \(\mathbf{L}\) (whenever it is not quenched) and \(\mathbf{S}\). SO interaction can be treated here as a small perturbation, which primarily gives rise to magnetic anisotropy [23]. In 4d and 5d TM oxides with larger \(Z\), the SO coupling is considerably stronger, e.g., in Ir \((Z=77)\) \(\lambda \sim 0.5\) eV [96], and in fact it plays a major role. In the presence of large SO interaction, the spin and orbital momentum quantum numbers are not conserved and the Hamiltonian in Eq. 2.5 does not commute with \(\mathbf{L}\) and \(\mathbf{S}\). However, the total angular momentum \(\mathbf{J} = \mathbf{L} + \mathbf{S}\) commutes with \(H_{\text{SO}}\) and hence \(\mathbf{J}\) becomes a good quantum number. In the JJ-coupling scheme, the \(d\)-levels are split into low energy \(J = 3/2\) and high energy \(J = 5/2\) states separated by \(5\lambda^2/2\) as shown on the right side in Fig. 2.2.

However, in 5d iridium oxide compounds the large crystal field separation \(\sim 3\) eV between the \(t_{2g}\) and \(e_g\) manifolds partially quenches the orbital angular momentum. Thus, one can treat the effect of SO interaction in the two manifolds separately [91]. Because the orbital angular momentum is completely quenched within the \(e_g\) states (see App. A.5), there is no first-order SO interaction within this manifold. On the other hand, the SO interaction within the \(t_{2g}\) manifold removes the three-fold degeneracy. Moreover, the off-diagonal matrix elements of the SO interaction couple the \(t_{2g}^{\pi}\) and \(t_{2g}^{\pi-\sigma}\) \(e_g^{\sigma}\) manifolds (see App. A.5 for such SO matrix elements).

Interestingly, a comparison of the matrix elements of the orbital angular momentum operators for \(t_{2g}^{\pi}/t_{2g}^{\pi-\sigma}\) configurations with those for \(p^1/p^5\) states of free atoms allows the mapping
of the \( t_{2g} \) states onto the atomic \( p \) states (see App. A.2) [91] as

\[
I(t_{2g}) = -I(p). \quad (2.6)
\]

This is sometimes called the \( T - P \) (\( t_{2g} - p \)) equivalence [91]. Provided that a large crystal field splitting separates the \( e_g \) and \( t_{2g} \) levels, the \( T - P \) equivalence allows one to treat the \( t_{2g} \) manifold as having an effective orbital angular momentum \( \tilde{l} = 1 \). These \( |\tilde{l}, m_l\rangle \) states in the \( d \)-orbital basis can then be written as [97]

\[
|1, 1\rangle = \frac{1}{\sqrt{2}} (-|d_{yz}\rangle + i|d_{xz}\rangle) \\
|1, 0\rangle = d_{xy} \\
|1, -1\rangle = \frac{1}{\sqrt{2}} (|d_{yz}\rangle + i|d_{xz}\rangle).
\]

In Chap. 5, we examine the effect of having a finite energy separation between the \( t_{2g} \) and \( e_g \) levels and the role of spin-orbit mediated \( t_{2g}^5 - t_{2g}^4 e_g^1 \) interactions.

The single unpaired electron in the \( t_{2g} \) manifold (\( \tilde{l} = 1 \)) of Ir\(^{4+} \) oxides also has a \( S = 1/2 \) spin. Within the LS-coupling scheme, we then have three Kramers doublets [98] with effective total angular momenta \( \tilde{j} = 1/2 \) (\( m_j = \pm 1/2 \)), \( \tilde{j} = 3/2 \) (\( m_j = \pm 1/2, \pm 3/2 \)). Here, due to the negative sign associated with the \( T - P \) mapping, the \( \tilde{j} = 1/2 \) doublet is higher in energy as compared to the quartet \( \tilde{j} = 3/2 \) states, as shown in Fig. 2.2. The energy difference between these SO coupled states is \( 3\lambda^2/2 \). The SOC strength \( \lambda \) can thus be obtained from the energy difference of the eigenvalues of \( H_{SO} \) within the \( t_{2g}^5 \) manifold (see App. A.3) [91]. The formation of \( \tilde{j} = 1/2 \) state can also be thought of as occurring due to the crystal field splitting.
of the $J = 5/2$ states formed in the JJ-coupling scheme\textsuperscript{2} (see Fig. 2.2).

The electronic states $|\tilde{j}, m_\tilde{j}\rangle$ can be derived in the $d$-orbital basis using Eq. 2.7 and the Clebsch-Gordan coefficients (see App. A.3) to add angular momenta ($\tilde{j} = \tilde{l} + S$). The $|\tilde{j}, m_\tilde{j}\rangle$ states are given as

\begin{align}
|\frac{1}{2}, \frac{1}{2}\rangle &= \frac{1}{\sqrt{3}} \left( |d_{yz}, -\frac{1}{2}\rangle + i |d_{zx}, -\frac{1}{2}\rangle + |d_{xy}, \frac{1}{2}\rangle \right) \\
|\frac{1}{2}, -\frac{1}{2}\rangle &= \frac{1}{\sqrt{3}} \left( |d_{yz}, \frac{1}{2}\rangle - i |d_{zx}, \frac{1}{2}\rangle - |d_{xy}, -\frac{1}{2}\rangle \right) \\
|\frac{3}{2}, \frac{1}{2}\rangle &= \frac{1}{\sqrt{6}} \left( |d_{yz}, -\frac{1}{2}\rangle + i |d_{zx}, -\frac{1}{2}\rangle - 2 |d_{xy}, \frac{1}{2}\rangle \right) \\
|\frac{3}{2}, -\frac{1}{2}\rangle &= \frac{1}{\sqrt{6}} \left( - |d_{yz}, \frac{1}{2}\rangle + i |d_{zx}, \frac{1}{2}\rangle - 2 |d_{xy}, -\frac{1}{2}\rangle \right) \\
|\frac{3}{2}, \frac{3}{2}\rangle &= \frac{1}{\sqrt{2}} \left( |d_{yz}, \frac{1}{2}\rangle + i |d_{zx}, \frac{1}{2}\rangle \right) \\
|\frac{3}{2}, -\frac{3}{2}\rangle &= \frac{1}{\sqrt{2}} \left( - |d_{yz}, -\frac{1}{2}\rangle + i |d_{zx}, -\frac{1}{2}\rangle \right). \tag{2.8}
\end{align}

The five electrons of the Ir$^{4+}$ ion then occupy the low energy $\tilde{j} = 3/2$ quartet states leaving one electron in the $\tilde{j} = 1/2$ levels. A schematic for the formation of this SO $\tilde{j} = 1/2$ ground state is shown in Fig. 2.2. Such a ground state has been recently confirmed by resonant x-ray diffraction experiments in IrO$_2$ [99] and in many other insulating iridium oxides (discussed in the next section).

So far we have considered a highly symmetric octahedral crystal field as the only contribution to the splitting of the Ir 5$d$ levels. However, various factors such as low dimensionality in layered structures or Jahn-Teller effects that distort the oxygen octahedra may give rise to noncubic crystal fields at the $d$-metal site. These noncubic fields effectively lift the degeneracy of the $t_{2g}$ and $e_g$ manifolds, further quenching the orbital angular momentum. This eventually alters the $\tilde{j} = 1/2$ ground state as the contribution from each of the $t_{2g}$ orbitals would be unequal (see Eq. 2.8) due to their dissimilar energies. Hence, the combined effects of noncubic crystal fields and SO interactions have to be considered simultaneously. The magnitude of the crystal field splittings (cubic and noncubic) and the study of their interplay with the SO coupling is a main topic of Chap. 4, where the ground and excited states of several iridates are analyzed in detail.

\textsuperscript{2}In the LS-coupling scheme, the spins-spin and orbital-orbital coupling is assumed to be stronger than the spin-orbit coupling. Whereas in the JJ-coupling scheme, the spin-orbit coupling is the strongest and hence $L$ and $S$ are first summed.
2.4 Electronic correlations, insulating $\tilde{j} = 1/2$ ground state

A single hole in the $\tilde{j} = 1/2$ levels should naively lead to metallic behavior, and in fact experiments find IrO$_2$ [99] and SrIrO$_3$ [100] to feature a $\tilde{j} = 1/2$ metallic ground state, in accordance with standard band-theory considerations. However, several other 5$d^5$ iridium oxides are found to be insulating, e.g., Sr$_2$IrO$_4$. Although band structure calculations find a metallic ground state for Sr$_2$IrO$_4$, the resistivity and optical measurements show a clear insulating behavior [89, 94]. The fact that Sr$_2$RhO$_4$, a 4$d$ analogue of Sr$_2$IrO$_4$, is a Fermi liquid [101] puzzled the scientific community even more.

Recently, using a combination of resonant x-ray scattering experiments and SO coupled, correlation corrected band-structure calculations, B. J. Kim et al. have shown that the insulating behavior originates due to a subtle interplay of SO interactions and electronic correlations [14, 15]. We outline this mechanism here through the sketch in Fig. 2.3. In 3$d$ TM oxides, an insulating gap can be induced in the valence band structure by including electron correlation effects described by the on-site Coulomb interaction $U$. The gap opens when $U$ is larger than the band width $W$. In 4$d$ and even more so in 5$d$ systems, the electron-electron interactions are known to be weaker due to the larger spatial extent of the $d$ orbitals. This more extended radial charge distribution also gives rise to larger $d − p$ orbital overlap and significantly larger band widths. Hence, a weakly correlated electronic behavior is expected in the simplest picture. Without the inclusion of SO coupling (see Fig. 2.3a), the width of the Ir $t_{2g}$ bands is so large that band-structure calculations with a reasonable Coulomb interaction

![Fig. 2.3 Schematic band picture of insulating 5$d^5$ iridates. According to band-structure calculations [14], the width $W$ of the $t_{2g}$ bands is much larger than the Hubbard $U$ if SO coupling is not considered and hence the system is metallic. With inclusion of SOC, the $t_{2g}^5$ manifold is split into $\tilde{j} = 1/2$ and $\tilde{j} = 3/2$ subbands whose widths are significantly narrower. Even a relatively small $U$ may then induce a finite Mott-like gap for the upper $\tilde{j} = 1/2$ states.](image-url)
2.5 Magnetic interactions

In insulating compounds, magnetism appears due to the exchange interactions between localized magnetic moments associated with individual ions. The exchange interaction is purely quantum mechanical. It is the result of electrostatic Coulomb interaction between the electrons and the Pauli exclusion principle that requires the wave function of a pair of electrons to be antisymmetric with respect to the exchange of an electron position. These symmetry-constrained Coulomb interactions have the effect of coupling the electronic spins (see App. B.1). The inter-ionic exchange depends on the overlap of the magnetically active orbitals and hence is strongly sensitive to the inter-atomic distances. It is this interaction that is responsible for the magnetic ordering of the ionic spins which are created by the intra-ionic exchange coupling \(^3\). The inter-ionic exchange between a pair of ions \(i\) and \(j\) can be in many cases reasonably well described by the Heisenberg Hamiltonian [6]

\[
H_{ij} = J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \tag{2.10}
\]

The Heisenberg exchange \(J_{ij}\) may couple the pair of spins either parallel (FM, \(J < 0\)) or antiparallel (AF, \(J > 0\)). This interaction can, in principle, extend to all pairs of ions but in TM oxides it is largely restricted to a few NN shells. The NN exchange parameters \(J_{<ij>}\) determine to a large extent the magnetic ordering temperature and the spin-wave dispersion relations in many insulating magnetic materials. An important difference between FM and AF interactions is that the latter are prone to frustration for certain types of lattices.

A direct magnetic exchange occurs when the magnetic ions are close enough to have a significant overlap of the wave functions. However, in TM oxide compounds, there is little direct overlap of the wave functions of the NN cations, instead they strongly overlap with the \(p\) orbitals of the neighboring \(O^{2-}\) ligand ions. The exchange interaction is now mediated via the bridging oxygen(s) due to the hybridization of the O \(2p\) and TM \(d\) orbitals. Such an interaction is termed superexchange. The superexchange mechanism was first suggested by Kramers [102] and the model was later developed by Anderson [103], Goodenough and Kanamori [104]. The superexchange interaction involves two virtual electron transfer processes. First, an electron is transferred from the bridging oxygen \(2p^6\) shell to an adjacent

---

\(^3\)The intra-ionic exchange, also known as \(J_H\) or Hund’s exchange, couples electrons in a partially filled shell of a particular ion so as to maximize the total spin (Hund’s first rule), see App. B.1.
TM ion leading to a virtual $d^{n+1}$ state at an energy cost $U$ (the repulsion of the transferred electron with the one already existing at this site). The $2p$ hole is then filled by an electron transferred from the other TM ion, which overlaps with the same O $2p$ orbital. This has the effect of coupling the spins of the two TM ions antiferromagnetically.

The simplest case with a single, half-filled $d$ orbital per TM site is shown in Fig. 2.4. A transfer of a $p \downarrow$ electron into an empty TM $d \downarrow$ state of TM$_1$ (Pauli’s principle forbids the transfer of an $\uparrow$ electron) leaves a $2p \downarrow$ hole, which can only be filled by a TM $d \downarrow$ electron from TM$_2$. Hence, a configuration with opposite spins on the two TM ions is lower in energy than the one with parallel spins because both electrons in the oxygen $2p$ orbital can be “spread out” into unoccupied TM $d$ orbitals when the TM ion spins are antiparallel. The superexchange interaction $J$ is therefore AF. Anderson [105] formulated the superexchange model using second order perturbation theory and showed that the AF alignment decreases the energy of the $d-p-d$ unit by $\Delta E = -4t^2/U$ (see App. B.2). Here, $t$ is the hopping matrix element for the transfer of an electron from the oxygen $p$ to the TM $d$ orbitals; $t^2$ appears because of the two virtual transfer processes. Since intersite $d-d$ hopping occurs via the ligand $p$ orbitals, the geometry of the corresponding bond is crucial. Goodenough and Kanamori [38, 39] designed a set of rules, later refined by Anderson [105], that synthetizes the basic features of superexchange interactions for different geometries of the TM-O-TM bonds (see App. B.3).

So far, we have ignored the spin-orbit coupling and only considered pure spin-spin interactions. In this case, the interaction is Heisenberg-like and isotropic. The presence of SOC, however, gives rise to anisotropic exchange interactions as the magnetic moments now contain both spin and orbital angular momenta.

Without SOC the exchange interaction is a scalar product of two spins (Eq. 2.10) and is SU(2)-invariant – spherically symmetric, but in general the exchange interaction is a convo-
2.5 Magnetic interactions

Solution of two pseudospin \( \tilde{S}_i \) and \( \tilde{S}_j \),

\[
\mathcal{H}_{ij} = \tilde{S}_i \cdot \hat{J} \cdot \tilde{S}_j = \sum_{\alpha\beta} J^\alpha_{\beta i j} \tilde{S}_\alpha \tilde{S}_\beta,
\]

(2.11)

where \( \alpha, \beta = x, y, z \) and \( J^\alpha_{\beta i j} \) is a \( 3 \times 3 \) tensor [106]. For diagonal \( \hat{J} \) with \( J^\alpha_{\beta i j} = J^\delta_{\alpha\beta} \), the interaction is isotropic and leads to the Heisenberg form of Eq. 2.10. More generally, however, \( J^\alpha_{\beta i j} \) may contain nondiagonal terms. This symmetric part of the intersite exchange can be diagonalized, for example, in tetragonal symmetry to

\[
\mathcal{H}^s_{ij} = J^\parallel \tilde{S}_z \tilde{S}_z + J^\perp (\tilde{S}_x^2 + \tilde{S}_y^2).
\]

(2.12)

We discuss this in detail with respect to the magnetic interactions in Ba\(_2\)IrO\(_4\) in Sec. 6.3.

The antisymmetric part of the exchange interaction can be written as

\[
\mathcal{H}^{as}_{ij} = D_{ij} \cdot \tilde{S}_i \times \tilde{S}_j.
\]

(2.13)

This interaction was first obtained by Dzyaloshinskii based on symmetry considerations [107] and later derived microscopically by Moriya [108].

Thus, the most general bilinear effective spin Hamiltonian for a pair of NN pseudospins \( \tilde{S}_i \) and \( \tilde{S}_j \) can be cast in the form

\[
\mathcal{H}_{ij} = J_{ij} \tilde{S}_i \tilde{S}_j + D_{ij} \tilde{S}_i \times \tilde{S}_j + \tilde{S}_i \cdot \Gamma_{ij} \cdot \tilde{S}_j,
\]

(2.14)

where \( J_{ij} \) is the isotropic Heisenberg exchange, the vector \( D_{ij} \) defines the Dzyaloshinskii-Moriya (DM) anisotropy [108, 109], and \( \Gamma_{ij} \) is a symmetric traceless second-rank tensor that describes the symmetric portion of the exchange anisotropy [108, 110]. Depending on various geometrical details and the choice of the reference frame, some or all of the elements of the DM vector and/or of the \( \Gamma_{ij}^{\alpha\beta} \) tensor may be zero.

Because the \( \tilde{j} = 1/2 \) moments in the SO Mott-insulating iridium oxides, e.g., Ba\(_2\)IrO\(_4\) and Sr\(_2\)IrO\(_4\), are an admixture of spin orbital components (see Eq. 2.8), the exchange interaction between them is expected to be highly anisotropic [10]. As a result, the magnetism in these compounds is strongly dependent on details of the lattice structure. For corner-sharing octahedral arrangement with Ir-O-Ir bond angle close to 180\(^\circ\), magnetic interactions of the \( \tilde{j} = 1/2 \) moments are predicted to be predominantly isotropic [10]. However, additional anisotropic interactions arise when introducing particular types of distortions. For example, in Sr\(_2\)IrO\(_4\), the rotation of the IrO\(_6\) octahedra around the \( c \) axis gives rise to antisymmetric DM anisotropy as large as one third of the isotropic interaction [10, 28]. In Chap. 6, we

\(^4\)Magnetic moments that contain both spin and orbital angular momentum components.
present the isotropic and anisotropic exchange interactions obtained from quantum chemistry calculations on $\text{Ba}_2\text{IrO}_4$ and $\text{Sr}_2\text{IrO}_4$.

Another class of $\tilde{j} = 1/2$ Mott-insulating iridates that have attracted considerable interest in the context of anisotropic magnetic interactions are the layered honeycomb-lattice compounds: $\text{Na}_2\text{IrO}_3$ and $\text{Li}_2\text{IrO}_3$. Here, the IrO$_6$ octahedra are edge-shared and the Ir-O-Ir bond angles are close to 90°. The magnetic interaction in these compounds is predicted to be highly anisotropic [10, 111] and resembles the exactly solvable Kitaev-honeycomb spin model [29], which hosts a spin-liquid phase. We deal with the magnetic exchange interactions in these compounds in Chap. 7 and show that they are indeed highly anisotropic.

### 2.6 RIXS spectroscopy

Resonant inelastic x-ray scattering (RIXS) is a second order “photon-in photon-out” spectroscopic process, in which the incoming photon excites a core hole state that consequently decays by the emission of a scattered photon. The scattering is inelastic, meaning the energy of the scattered photon is lower than the energy of the incoming photon. The resulting energy loss is transferred to the system leaving it in some kind of excited state [112]. This excited state holds a definite momentum as the incoming and outgoing x-ray momenta are not the same. Moreover, this momentum is comparable to the crystal momentum of the conduction electrons. RIXS can therefore probe both the energy and the momentum dependence of low-energy elementary excitations in condensed matter systems. These excitations can be, for instance, phonons, magnons, d-d or charge-transfer (CT) in nature. In this section, a brief overview is given on the kind of information that RIXS spectroscopy can provide on the valence electronic structure of d-metal compounds such as iridates.

In a typical RIXS experiment the energy $\omega_1$ of the incoming x-ray beam is tuned to a particular absorption edge to achieve resonance, i.e., $\omega_1$ is the energy required to scatter off a core electron to an excited state above the Fermi level (Fig. 2.5). For iridates, the Ir
2.6 RIXS spectroscopy

Fig. 2.6 (a) RIXS spectrum of Sr$_3$CuIrO$_6$ [116]. (b) Incident x-ray energy dependence of the RIXS spectrum at the Ir $L_3$ edge. Three low energy features at 0.28, 0.58, and 0.81 eV show similar resonant behavior, each peaking at 11.216 keV. More on this spectrum is discussed in Sec. 4.5.

$L_3$ absorption edge ($\omega \sim 11.217$ keV) is most frequently used$^5$ [114, 115], where the $2p_\frac{3}{2}$ core-electron is excited into the Ir $5d$ valence states and subsequently an electron out of this shell decays to fill the core-hole. In Ir$^{4+}$ oxide compounds, the $e_g$ states are empty because of the relatively large crystal field splitting but the $t_{2g}$ states also display finite hole density. The Ir $2p$ core-electron can thus be excited through dipole-allowed transitions into either $e_g$ or $t_{2g}$ unoccupied states to give rise to an intermediate $|n\rangle = |2p_{3/2}^0t_{2g}^5e_g^1\rangle$ or $|n\rangle = |2p_{3/2}^0t_{2g}^6\rangle$ configuration, respectively. A different $t_{2g}$ electron associated with the initial $t_{2g}^5$ configuration can then fill the $2p$ core-level, leaving the system in a final state $|f\rangle = |t_{2g}^4e_g^1\rangle$ or $|f\rangle = |t_{2g}^5e_g^0\rangle$ where a local $d$-$d$ excitation with energy $\omega = \omega_1 - \omega_2$ and momentum $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$ has been created. By measuring the energy loss $\omega$, excitation peaks corresponding to both intra-site $d$-$d$ and TM $d$ to ligand $p$ CT transitions can be obtained. A typical RIXS spectrum and its incident x-ray energy dependence measured for Sr$_3$CuIrO$_6$ is shown in Fig. 2.6 [116]. One can see that the three peaks at 0.28, 0.58, and 0.81 eV show the same resonant behavior as a function of the incident x-ray energy, indicating that they all originate from initial $2p \rightarrow 5d$ transitions into the same unoccupied states within the Ir $t_{2g}$ manifold. The character of these peaks is discussed in Sec. 4.5. The different loss energies of those three features have to do with the fact that the $5d \rightarrow 2p$ decay creates holes in different $t_{2g}$ levels, leaving the system in different excited states at the end of the respective RIXS process.

Using the angular momentum carried by the scattered photon, the electron excited into the valence shell can flip its spin. This is possible due to the fact that the spin-orbit coupling in the core level is very strong. As a result, the core electron carries both spin and orbital angular momentum. Depending on the symmetry of the system and the absorption edge selected, either a double spin-flip scattering [117] or direct spin-flip scattering [118] can occur. For

$^5$Oxygen K-edge RIXS has been also reported recently in, e.g., Ref. [113].
Fig. 2.7 RIXS energy loss spectra of Sr$_2$IrO$_4$ at low energies. The peak at less than 200 meV corresponds to the single-magnon peak whose dispersion can be seen on the right. From Ref. [40].

layered cuprates, for example, the latter can happen as long as the Cu spin has a non-zero projection on the CuO$_2$ plane [119]. Very recently, RIXS experiments were also used to probe magnetic excitations in Sr$_2$IrO$_4$ [40] and a single magnon dispersion was extracted. Fig. 2.7 shows RIXS spectra for Sr$_2$IrO$_4$. It is seen that the excitation below 200 meV corresponds to a single-magnon peak. This peak has a momentum dispersion that extends up to 205 meV [40].

2.7 Summary

To summarize, we have described the basic concepts that are relevant in understanding the spin-orbit coupled physics in iridium oxide compounds. We briefly discussed how the interplay of crystal-field energy splittings, electronic correlations and spin-orbit coupling leads to novel Mott-insulating effective $\tilde{j} = 1/2$ total-angular-momentum ground states in iridates. The origin/expressions for isotropic as well as anisotropic exchange interactions were also briefly addressed. Finally, we outlined the basic principles behind one of the experimental techniques, resonant inelastic x-ray scattering, that is being extensively and successfully used nowadays to investigate the electronic structure and magnetic properties of iridium oxide compounds.
Chapter 3

Quantum chemistry methodology

In this chapter, the wave-function-based electronic structure methods employed in the present work are described. After explaining the need and justifying the use of such methods, the construction of many-electron wave functions, starting from the Hartree-Fock to multireference configuration interaction methods, is detailed. A brief description of relativistic effects influencing the electronic structure is then provided. We also touch upon the implementation of these methods in the MOLPRO quantum chemistry package [120]. The latter is used for all the calculations presented in this thesis. The description of the various computational methods in this chapter follows from Ref. [50].

3.1 Introduction

Ab initio electronic structure calculations based on conventional DFT within, e.g., the LDA/GGA approximation, fail to correctly describe the open-shell TM oxides. This is due to the mean-field like approach these methods adopt to treat electron-electron interactions [47, 48]. In TM systems the latter play an essential role. Approaches such as LDA+$U$ [121–123] and LDA+DMFT (the LDA results are imported into many-body schemes based on model Hamiltonian and dynamical mean field approximation) [48], are commonly used to account for the correlation effects in TM systems. However, such methods to some extent are constrained by the underlying model Hamiltonian (e.g., Hubbard Hamiltonian in the LDA+DMFT approach) and invariably depend on parameterizations, e.g., the Coulomb repulsion $U$ and Hund’s coupling $J_H$\(^1\). Further, in the “DFT+DMFT” approach double counting needs to be avoided [125]. The latter arises due to the fact that DFT captures some of the interactions between strongly correlated, e.g., $d$ or $f$ electrons, which are explicitly included in DMFT

\(^1\)There are methods like constrained LDA/GGA [123] and constrained random phase approximation to evaluate $U$ and $J_H$ [124].
formalism, resulting in counting those correlations twice. Nevertheless, these methods, when used with appropriate parameters like on-site $U$, $J_H$ values and properly accounting for the double counting, have been successful in qualitatively explaining phenomena such as metal-insulator transitions [48, 126].

On the other hand, the Hartree-Fock (HF) method is based on molecular orbital theory and the explicit construction of the real space wave function [50]. The HF theory relies on single-particle picture as well, where the $N$-electron wave function is approximated as a product of $N$ one-electron wave functions (orbitals). Nevertheless, this wave function can be systematically improved to include electronic correlation effects using the post-HF quantum chemistry methods. Such an approach has been extensively used in the molecular chemistry community for several decades [50]. However, the calculation of many-body wave functions for a solid is a Herculean task and the computational complexity associated with this approach has constrained its usage for solids. It is only recently that algorithms have been developed to explicitly treat electronic correlations in solids using quantum chemistry methods [127, 128], and with present day computational facilities, many properties of solids can be studied, e.g., see Refs. [54, 67, 74, 77–80, 84, 86].

In the remaining part of this chapter, we briefly describe the basic principles behind the quantum chemistry methods that we employ for the investigation of the electronic structure in iridates. We begin by explaining the embedded cluster approach, commonly used to overcome the computational hindrance for the construction of many-body wave functions in solids. After outlining the HF theory, we further describe the configuration interaction methods that are often used to systematically improve the single-determinant HF wave function. At the end, theoretical aspects related to relativistic spin-orbit interactions and their inclusion in the calculations are presented.

### 3.2 Embedded cluster approach

Electronic correlations are most often short-ranged in nature [129]. In TM oxides, they can, for instance, be either intra-atomic correlations or Hubbard-like correlations among electrons on neighboring atoms. Thus, a local approach for the calculation of the $N$-electron wave function is a very attractive option in TM compounds. The general strategy in this approach is to use a finite atomic cluster cut out from the infinite solid and treat the ubiquitous strong electronic correlations using many-body quantum chemistry methods. The collection of atoms is “embedded” in a potential that accounts for the part of the crystal that is not treated explicitly.

Several embedding schemes have been developed over the years to ensure a proper connection of the cluster with the rest of the solid. The simplest approximation relies on the fully ionic model. In such a picture, the remaining part of the crystal is represented with
3.2 Embedded cluster approach

an array of point charges (PCs) at the lattice positions. In more advanced schemes, the crystalline environment is modeled as an effective potential obtained on the basis of prior periodic Hartree-Fock [54, 76, 130, 131] or DFT calculations [132–134].

In the PC embedding scheme, the interaction of the cluster with the surroundings is incorporated by calculating the Madelung field of the ions not included in the cluster and adding the potential to the cluster Hamiltonian. The external potential is obtained by first calculating the exact Madelung field by an Ewald summation [135] with formal charges at the experimentally determined lattice positions and then subtracting the contribution of the cluster ions. This external potential can be appended to the cluster Hamiltonian in several different ways. A straightforward method is to put formal charges at all lattice positions and sum their contributions to the potential. However, the Madelung potential of a finite set of PCs converges slowly in real space with respect to PC array size, requiring a very extensive number of charges to obtain sufficient accuracy. In some cases, such real space summation might not reproduce the exact Madelung potential due to the infinite crystal. The Evjen method [136], in which fractional PCs are assigned to the “terminal positions” of a PC array with the same symmetry as the bulk unit cell, ensures a much faster convergence. For example, in a cubic system, the Evjen scheme assigns half of the formal charge to sites on the faces, a quarter at the edges and one eighth at the vertices. In a different method, which is used in this work, the external potential is produced based on a fitting procedure. Here, the charge of a small set of PCs at lattice positions, within a certain radius from the cluster region, is adjusted such that an exact value of the Madelung potential at a large number of grid points in the cluster region is reproduced [137]. Klittenberg et al. have developed another method, where a set of formal charges are used at lattice positions, as in the Evjen scheme, up to a given radius from the cluster region, beyond which the charges are adjusted such that the calculated Madelung potential converges to that obtained by Ewald summation [138].

In the quantum mechanical Hartree-Fock embedding scheme, the crystalline environment is modeled as an effective one-electron potential that is extracted from a prior HF calculation for the periodic lattice. The embedding potential is constructed by using the self-consistent Fock operator of the periodic HF calculation and that associated with the density operator arising from orbitals of the cluster atoms alone [130] (see also Ref. [139]). Further, the orbital set associated with the cluster atoms is generated from the HF crystal Wannier orbitals. This embedding approach effectively provides a frozen HF environment for the subsequent correlation calculations.

In the present work, calculations are performed on clusters containing one or two TM-ligand octahedra (as central region) plus all the NN TM-ligand octahedra. Effectively, all atoms up to the third coordination shell of the central TM ion are included in such clusters. The inclusion of the NN octahedra is essential to account for short-range Pauli and exchange interactions of electrons in the central region with those of the immediate NNs finite charge
distribution. Although we attempted to construct the HF embedding potential to account for the crystal environment, due to technical limitations of the presently available CRYSTAL-MOLPRO interface program\(^2\) [130] regarding the usage of effective core potentials to represent the core electrons of iridium ions, we resolved to using the simpler PC embedding approach. Nevertheless, as we shall discuss later on, our results are in good to excellent agreement with available experimental measurements. Moreover, for the properties of interest in this thesis, we find in a 4\(d^5\) rhodium compound, closely related to the 5\(d^5\) iridates, that the results for excitation energies obtained with HF and PC embedding do not differ by more than \(\sim 15\%\) [141].

### 3.3 Many-electron wave function

A central aim in electronic structure theory is to find an approximate solution to the time-independent \(N\)-electron Schrödinger equation (SE)

\[
\hat{H} \Psi = E \Psi,
\]

that is nevertheless accurate enough to describe the electronic properties of the system. In Eq. 3.1, \(\hat{H}\) is the Hamiltonian of the system, \(\Psi\) is an eigenstate that depends on the space and spin coordinates of the \(N\) electrons and \(E\) is the associated energy eigenvalue.

One approach is to first construct an approximate solution \(\Psi\) that can qualitatively provide a correct description and thereby systematically improve it to be quantitatively precise. For many systems, the Hartree-Fock method provides such 0\(^{th}\) order approximate solution. In this method, a trial wave function is postulated as a product of \(N\) one-electron wave functions to form a Hartree product. Since the Pauli exclusion principle requires the wave function to be antisymmetric with respect to the interchange of the coordinates of any two electrons, the wave function is written in the form of a Slater determinant:

\[
\Psi(r_1, \cdots, r_N) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_n(r_1) \\ \psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_n(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_n) & \psi_2(r_n) & \cdots & \psi_n(r_n) \end{vmatrix}.
\] (3.2)

The spin-orbitals \(\psi_i\) are functions of three space and one spin coordinates, which in a nonrelativistic picture can be written as the product of an orbital and a spin function:

\[
\psi_i^\alpha = \phi_i(x, y, z) \alpha,
\]

\(^2\)The CRYSTAL-MOLPRO interface program constructs the embedding and the starting orbitals for correlated calculations with MOLPRO package, from the periodic HF output obtained from CRYSTAL program [140].
3.3 Many-electron wave function

\[ \psi_i^\beta = \phi(x,y,z)\beta. \] (3.3)

In the second quantization notation, the Slater determinant of Eq. 3.2 is represented as an occupation number (ON) vector \( |k\rangle \) of a set of molecular orbitals (MOs) \( \psi_j, j \in \{ 1, \cdots, M \} \):

\[ |k\rangle = |k_1, k_2, \ldots, k_M\rangle = \prod_p a_p^\dagger |\text{vac}\rangle, \] (3.4)

where \( a_p^\dagger (a_p) \) is a creation (annihilation) operator that creates ( annihilates) an electron in the \( p^{th} \) MO [50].

Within the Born-Oppenheimer approximation\(^3\), the nonrelativistic many-electron Hamiltonian can be written [50] as

\[ \hat{H} = \sum_{pq} h_{pq} \left( \sum_{\sigma} a_{p\sigma}^\dagger a_{q\sigma} \right) + \frac{1}{2} \sum_{pqrs} g_{pqrs} \left( \sum_{\tau} a_{p\tau}^\dagger a_{q\tau} a_{r\sigma} a_{s\tau} \right) + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{R_{ij}}, \] (3.5)

where \( h_{pq} \) and \( g_{pqrs} \) are molecular one- and two-electron integrals, respectively, given by

\[ h_{pq} = \int \psi_p^\ast (\mathbf{r}) \left( -\frac{1}{2} \nabla^2 - \sum_i \frac{Z_i}{r_i} \right) \psi_p (\mathbf{r}) \, d\mathbf{r} \] (3.6)

\[ g_{pqrs} = \int \int \psi_p^\ast (\mathbf{r}_1) \psi_q^\ast (\mathbf{r}_2) \frac{1}{r_{12}} \psi_s (\mathbf{r}_1) \psi_r (\mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2. \] (3.7)

\( Z_i \) are the nuclear charges, \( r_i \) electron-nucleus separations, \( R_{ij} \) inter nuclear separations and \( r_{12} \) is the electron-electron separation. The operator \( a_{p\sigma}^\dagger \) creates an electron in the \( p^{th} \) orbital with spin \( \sigma \in \{ \alpha, \beta \} \).

### 3.3.1 The Hartree-Fock equations

The simplest approximation to the many-electron wave function is the single Slater determinant of spin orbitals of Eq. 3.4. Such a wave function is obtained in Hartree-Fock theory by variationally minimizing the energy

\[ E = \min_k \langle k | \hat{H} | k \rangle \] (3.8)

of the Hamiltonian in 3.5. This leads to the Hartree-Fock equations [50]

\[ \hat{f} a_{p\sigma}^\dagger |\text{vac}\rangle = \varepsilon_p a_{p\sigma}^\dagger |\text{vac}\rangle, \] (3.9)

---

\(^3\)Due to the large differences in the electron and nuclear mass, the electron is assumed to be instantaneously following the motion of the nuclei.
where $\hat{f}$ is an effective one-electron operator called Fock operator,

$$\hat{f} = \sum_{pq} \left( h_{pq} + \sum_i \left( g_{pqii} - g_{piiq} \right) \right) E_{pq}. \quad (3.10)$$

Here $E_{pq} = d^\dagger p \alpha d_q \alpha + d^\dagger p \beta d_q \beta$ is the singlet excitation operator. The one-electron part $h_{pq}$ in Eq. 3.10 is the same as in the many-electron Hamiltonian 3.5 but the two-electron integrals are replaced by the effective one-electron equivalents $g_{pqii}$ and $g_{piiq}$, Coulomb and exchange terms, respectively. The Hartree-Fock equations are solved by diagonalizing the Fock matrix

$$f_{pq} = h_{pq} + \sum_i \left( g_{pqii} - g_{piiq} \right) \quad (3.11)$$

and the resulting eigenvectors are referred to as canonical (spin) orbitals of the system. The orbital energies are the eigenvalues of the Fock matrix $f_{pq} = \delta_{pq} \epsilon_p$. Because the Fock matrix in 3.11 is defined in terms of its own eigenfunctions (see expressions in 3.6), the canonical orbitals and energies can only be obtained through a self-consistent calculation.

In the restricted Hartree-Fock (RHF) approximation, the energy is optimized subject to the condition that the wave function is an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$ by restricting the sets of orbitals for $\alpha$ and $\beta$ spins to be identical. In the unrestricted Hartree-Fock (UHF) approach, no such restrictions on the one-electron functions are imposed. As a consequence, the wave function is not required to be an eigenfunction of the $\hat{S}^2$ operator [142].

The HF method very much simplifies the many-electron Schrödinger equation. However, solving the resulting equations numerically is still too expensive for most practical problems. Often, the spatial MO $\psi(r)$ are expanded as a linear combination of atomic orbitals (LCAOs),

$$\phi_k(r) = \sum_{\mu=1}^n C_{\mu k} \chi_{\mu}(r), \quad (3.12)$$

where $n$ is the number of atomic orbitals in the chosen basis set. The HF equations can then be written in a matrix form and the MO coefficients $C_{\mu k}$ of the above expansion can be used as variational parameters for minimizing the HF energy. The obtained matrix equation is commonly referred to as the Hartree-Fock-Roothaan set of equations and written as

$$fC = SC\epsilon. \quad (3.13)$$

\[4\] In the rest of the thesis we refer to spin-orbitals as just orbitals unless otherwise specified.

\[5\] These are a set of simple analytical one-electron functions, e.g., of Gaussian or Slater type in real-space formulations.
The elements of the Fock matrix in the atomic orbital (AO) basis are given by

\[ f_{\mu \nu}^{AO} = h_{\mu \nu} + \sum_i (2g_{\mu \nu \mu ii} - g_{\mu ii \mu ii}), \] (3.14)

the matrix \( S_{\mu \nu} = \langle \chi_{\mu} \mid \chi_{\nu} \rangle \) is the overlap of basis functions and \( \epsilon \) is a diagonal matrix containing orbital energies [50].

In the self-consistent field (SCF) procedure, one starts with an appropriate choice of initial MOs (guess orbitals) on the basis of which the Fock operator is constructed and further diagonalized to obtain the matrix \( C \) in Eq. 3.13. Using this \( C \), a new set of MOs are obtained according to Eq. 3.12, with which a new Fock matrix is built and solved again for an updated \( C \) matrix. This procedure is repeated until a satisfactory convergence is found, i.e., the orbitals and total energy no longer change within some threshold, at which point the MOs satisfy the Hartree-Fock equations in Eq. 3.13 [142].

### 3.3.2 Electron correlation energy

The single Slater determinant wave function obtained from the HF method is an uncorrelated wave function and the difference between the HF total energy, and the exact nonrelativistic energy is defined as correlation energy. There are two main contributions to this correlation energy. First, the HF method is based on the independent particle approximation where electrons are treated as moving in the average field of the other electrons. The detailed, “correlated” motion of electrons as induced by their instantaneous mutual repulsion is here not taken into account. The error in total energy due to this one-particle approximation is generally called dynamical correlation energy. The second contribution arises from the inability of a single HF configuration to describe the \( N \)-electron wave function. Configurations that lie close in energy often mix with the “leading” HF configuration [50]. A classic example of the failure of the RHF method is the inaccurate description of the dissociation energy of the \( H_2 \) molecule. The above discrepancy can be corrected by including additional configurations in the wave function [50]. The error caused due to the near-degeneracies among various configurations is often termed as non-dynamical (static) correlation energy as it is unrelated to the instantaneous repulsion between electrons. It should be noted that a clear demarcation between static and dynamic correlation effects is often not possible.

In many TM oxides, electron correlation effects become important due to their open-shell character as well as the localized nature of the \( d \) electrons. The former aspect leads to strong intra-atomic near-degeneracy correlation effects. The latter alone gives rise to dynamical correlation effects but in conjunction with the former also to Hubbard-like correlations which are a form of near-degeneracy effects. Thus, it is necessary to go beyond the single-determinant representation of the wave function to study TM oxide systems. In the following, we briefly
describe the configuration interaction expansion that is capable of capturing both static and dynamic correlations. In the next subsection, a description of the multiconfiguration wave function is given, which with a proper construction of the active orbital space may well account for the essential static correlations. Using a combination of the two methods, both static and dynamic correlation effects can be well described.

### 3.3.3 Configuration interaction (CI)

The single determinant HF method yields a finite set of orbitals within a finite basis set. For $n$ basis functions there are $2^n$ different orbitals, out of which the lowest $m$ in energy define the HF wave function $\Phi_0$. However, several different Slater determinants can also be formed by using the remaining $2^n - m$ orbitals. For example, the singly excited class of determinants, which corresponds to raising a single electron from an occupied orbital $\phi_k$ to a virtual orbital $\phi_a$, is defined as

$$\phi_k^a = \text{det} | \phi_1 \phi_2 \cdots \phi_a \phi_l \cdots \phi_m |,$$

and similarly in the doubly excited determinant $\phi_k^{ab}$ two electrons have been promoted, one from $\phi_k$ to $\phi_a$ and another from $\phi_l$ to $\phi_b$. It turns out that these determinants are eigenfunctions of only the projected spin $\hat{S}_z$ and not of the total spin $\hat{S}^2$. However, a linear combination of the above determinants can be constructed such that they are also eigenfunctions of $\hat{S}^2$ [50]. Such a linear combination of Slater determinants having the same spin symmetry are referred to as configuration state functions (CSFs). The CSFs can then be used in linear combination with $\Phi_0$ to improve the $N$-electron wave function. The exact ground (and excited) state wave functions can be expressed as a linear combination of all possible CSFs arising from a complete set of orbitals as

$$\Psi = C_0 \Phi_0 + \sum_{ia} C_i^a \Phi_i^a + \sum_{ijab} C_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{ijkabc} C_{ijk}^{abc} \Phi_{ijk}^{abc} + \cdots,$$

where $\{C\}$ is the set of expansion coefficients that are determined variationally by minimizing the energy functional

$$E(C) = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle},$$

leading to a set of secular equations referred to as the CI equations

$$\sum_j (H_{ij} - ES_{ij}) C_j = 0.$$

$H_{ij}$ and $S_{ij}$ are Hamiltonian and overlap matrix elements between configurations. The \textit{ab initio} approach in which the wave function is expressed as in Eq. 3.16 is referred to as the configuration interaction (CI) method. In a full CI (FCI) calculation all the CSFs of the
appropriate symmetry for a given finite basis set are used in constructing $\Psi$ and the associated energy is exact with respect to a given Hamiltonian. However, the number of determinants (CI space) in a FCI calculation grows very rapidly as the number of basis set functions and electrons increases, which makes this method computationally intractable for large systems. By far the most common CI approximation is the truncation of the CI space according to the excitation level relative to the reference state (see Eq. 3.16).

When a single determinant $\Phi_0$ is a qualitatively good approximation to the true wave function and can thus be selected as a zeroth order reference state, the widely used CI expansion is the one that contains only single and double (CISD) excitations on top of the HF wave function. Such an expansion is given by

$$
\Psi_{\text{CISD}} = C_0 \Phi_0 + \sum_{ia} C^a_i \Phi^a_i + \sum_{ijab} C^{ab}_{ij} \Phi^{ab}_{ij}.
$$

(3.19)

Since the Hamiltonian operator contains only one- and two-electron terms (see Eq. 3.5), at most doubly excited determinants can interact with each other. It turns out that only the double excitation configurations interact “directly” with the HF reference configuration\(^6\) [142], and the single excitations contribute corrections to the ground state via the interaction with doubly excited ones. Hence, a CISD wave function accounts for most of the dynamical correlation energy, e.g., > 95% in small molecules [143].

### 3.3.4 Multiconfiguration self-consistent field (MCSCF) and multireference CI expansion (MRCI)

The single Slater-determinant HF wave function is a poor starting reference wave function for the CI expansion in systems where multiple configurations are nearly degenerate. For example, the dissociation of the two-electron hydrogen molecule cannot be described by a single reference wave function. However, a two-configuration wave function containing the HF configuration $\sigma_2^g$ (bonding 1s) and the configuration $\sigma_2^u$ (corresponding to the antibonding 1s orbital) recovers almost all of the dissociation energy \([50]\)^7.

**MCSCF.** A self-consistent calculation that uses a wave function consisting of multiple configurations is referred to as multiconfigurational self-consistent field (MCSCF) method. In TM compounds the multiconfigurational mixing or near-degeneracy effects occur because of the open-shell nature of these systems. For example, in 5$d^5$ iridates, there is one hole in the Ir 5$d$ $t_{2g}$ levels that are (nearly) degenerate. All three configurations corresponding to a hole in each of the different orbitals are equally important and thus are needed to be

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\(^6\)According to Brillouin’s theorem, the singly excited determinants bring no correction directly to the HF wave function.

\(^7\)It is completely recovered with a CI wave function containing 10 CSFs.
treated on equal footing. In the MCSCF method, in addition to the CI coefficients in Eq. 3.16, the LCAO expansion coefficients (Eq. 3.12) are optimized as well, which makes it computationally more demanding than a HF calculation. However, the optimization of the orbitals partially compensates for truncation errors in the CI expansion to only single and double excitations (see the following subsection). Rather accurate results can be thus obtained by including only a relatively small number of CSFs.

The optimized CI and orbital expansion coefficients are obtained by a series of exponential transformations $U = e^R$ of the orbitals, where $R$ is an antisymmetric matrix of independent variational parameters [50, 142]. One approach based on this formulation is the Newton-Raphson (NR) method, where the energy $E$ is expanded as a Taylor series to second order in $R$ and $\Delta C$ (the changes in the CI coefficients). Minimization of this approximate energy expansion yields a system of linear equations for the parameters $R$ and $\Delta C$ [50]. The NR method has quadratic convergence when near the solution. An improved optimization procedure is used in the MOLPRO package, where an energy functional of $T = U - I$, correct to second order, $E(T^2)$ is minimized [144–147]. This method has a larger radius of convergence compared to the NR method although a set of non-linear equations are required to be solved at almost the same computational cost as in the NR scheme.

The complete active space self-consistent field (CASSCF) method [50] is an example of the MCSCF approaches. Here, the spin-orbitals are divided into three classes: inactive orbitals, the lowest energy spin-orbitals that are doubly occupied in all the determinants; virtual orbitals, which are unoccupied in all determinants; and active orbitals that often are energetically intermediate between the first two and whose occupation can be between 0 and 2. All possible combinations with the correct spatial and spin symmetries are allowed in the active space of a CAS wave function, hence corresponding to a FCI within that orbital space. Since none of the configurations that can be constructed from the occupied and virtual MOs are favored over others, the CASSCF calculations are always multiconfigurational. Thus, the multiconfigurational wave functions are capable of handling static correlation effects. Dynamic correlation effects are difficult to treat using MCSCF methods because active spaces can seldom be chosen large enough. In fact, the choice of the active space for a MCSCF calculation is not trivial and usually the MOs are selected either according to their occupation numbers obtained from a preceding single-reference CI calculation or by “chemical intuition”.

**Multireference configuration interaction (MRCI).** A CI expansion of the excited determinants that are formed from the set of reference configurations created at the MCSCF level leads to a MRCI wave function. In other words, for each of the reference configurations in the MCSCF wave function, electrons are moved from the occupied to unoccupied orbitals to create more determinants to be used in the CI expansion. A MRCI wave function with single

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8Restricted active space SCF (RASSCF) is another commonly used MCSCF method.
3.3 Many-electron wave function

and double substitutions can be written as

$$\Psi_{\text{MRCI(SD)}} = \sum_I C^I \Phi_I + \sum_{Sa} C^S_a \Phi^a_S + \sum_{Pab} C^{ab}_P \Phi^{ab}_P,$$  \hspace{1cm} (3.20)

where the sum over $I$ runs over all selected reference states, $a$ and $b$ denote external orbitals (those that are unoccupied in the reference configurations), and $S$ and $P$ denote internal $N-1$ and $N-2$ hole states. $\Phi_I$, $\Phi^a_S$ and $\Phi^{ab}_P$ are internal, singly external and doubly external configurations, respectively. The multiconfigurational reference determinants (generally including singly and doubly excited determinants from the HF wave function), combined with both the single and double excitations in MRCI(SD) lead to the inclusion of the most important determinants up to quadruple excitations. Therefore, the size-extensivity error\(^9\) that is commonly encountered in single-reference CISD is significantly reduced in MRCI(SD), and a large fraction of the exact correlation energy is achieved with a reasonable number of determinants. The computational effort for a MRCI(SD) calculation increases with $n_P \cdot N^4 + n_x^P \cdot N^3$, where $N$ is the number of external orbitals, $n_P$ the number of $N-2$ electron states $P$, and $1 < x \leq 2$.

Contraction schemes are in general used to reduce the number of variational parameters in the MRCI wave functions. An internally contracted CI scheme was developed and implemented by Werner et al. [148–150] in the MOLPRO package, where the configurations are generated by applying pair excitation operators to the reference wave function as a whole. In this contraction scheme, the number of internal states becomes independent of the number of reference configurations. It only depends on the number of correlated orbitals and hence the algorithm is computationally more efficient.

3.3.5 Perturbational methods

Dynamical electron correlation effects on top of a multiconfigurational reference wave function can also be captured by many-body perturbation calculations [142]. In perturbative methods, the Hamiltonian (Hilbert space) is partitioned into a zeroth-order (reference space) and a perturbation (secondary space). In multireference perturbative theories (MRPT), in the zeroth-order part $H_0$ all the electronic interactions in the active space are already included. The perturbation $V$ is designed in a way that it captures electron interactions also in the secondary space (rest of the Hilbert space).

The complete active space second-order perturbational scheme (CASPT2) [151] is the most widely used perturbational method to capture dynamic correlation effects. Here, the zero-order Hamiltonian is a sum of one-electron Fock operators that reduces to the Møller-Plesset operator [152] in case of a single-configuration reference wave function. The first order interacting space (FOIS) is spanned by an internally contracted expansion of all con-

\(^9\)A method is said to be size extensive if the energy calculated scales linearly with the number of particles.
configurations related to single and double substitution operators (excitations) on the reference CASCCF wave function $\Psi_0$.

In perturbation schemes based on Fock-type zeroth-order Hamiltonians, configurations can appear in the first-order wave function with an expectation value of $H_0$ which is very close to (or even lower than) the expectation value of the reference wave function, leading to a breakdown of the perturbational treatment [153]. As a result, intruder states, states that have large matrix elements with the reference wave function although their interaction is minimum, may appear. Level shifting techniques [154] are sometimes used to cure such problems. $N$-electron valence state perturbation theory (NEVPT) is another perturbational approach that has been recently devised by Angeli and co-workers to account for dynamical correlation effects devoid of intruder states [155, 156].

### 3.4 Spin-orbit coupling

So far we have outlined methods that can describe accurately the electronic structure of molecules and compounds containing light atoms in a nonrelativistic quantum mechanical framework. Relativistic effects on energies and other physical properties are proportional to the fourth power of the nuclear charge $Z^{10}$ (see Sec. 2.3). As a result, they begin to play a major role in heavy atoms and their compounds.

In atoms and molecules, relativistic effects may be divided into those having kinematical origin and those due to spin-orbit coupling [158]. The kinematical effects are caused by electrons moving with high velocity in the vicinity of a (heavy) nucleus leading to “contracted” orbitals, i.e., a more compact electron density distribution around the nucleus, with lowered orbital energies compared to the nonrelativistic calculations. These are mainly important for $s$ and $p$ shells, since those have appreciable amplitude in the vicinity of the nucleus. Orbitals with higher angular momentum are hardly directly affected by kinematical relativistic effects. However, the modified shielding of the nuclear charge by the contracted core orbitals results in an expansion of the valence, e.g., $d$ and $f$ orbitals. A detailed review can be found in Ref. [158–160]. The relativistic spin-orbit coupling on the other hand gives rise to subshell splittings due to the coupling of the orbital and spin degrees of freedom.

Relativistic QC calculations are much more expensive than the nonrelativistic analogue because relativistic theory has to consider for every particle also the degrees of freedom for its charge-conjugated particle on equal footing. The Dirac equation properly describes the motion for spin one-half particles using a four component formulation [95, 161]. In the following, we describe briefly the Dirac equation and the Breit-Pauli Hamiltonian that treats the electron-electron interactions and relativistic effects on the same footing. The use

$^{10}$Note that the valence electrons experience a reduce nuclear charge $Z_{\text{eff}}$ due to the Coulomb screening by the inner shell electrons [157].
of the Foldy-Wouthuysen (FW) transformation to reduce the problem to a two-component equation for positive energy solutions describing the electrons is also outlined. In the last subsection, we describe the quasi-degenerate perturbation method that is often implemented in QC packages to incorporate the spin-orbit coupling effects.

### 3.4.1 The Dirac equation

The relativistic analogue for the SE can be written using the energy-momentum relation $E^2 = p^2c^2 + m^2c^4$ as

$$\left(-\frac{1}{c^2}\frac{\partial^2}{\partial t^2} + \nabla^2\right)\psi = m^2c^2\psi.$$  \hspace{1cm} (3.21)

This is commonly referred to as the Klein-Gordan equation [162, 163]. Although this form is sufficient for the description of spinless particles, it suffers from the existence of negative energy solutions and probability density when spin degrees of freedom are included. To avoid the latter, Dirac suggested the equation [95, 161]

$$H_{\text{Dirac}}\psi = (c\mathbf{\alpha}.\mathbf{p} + \beta mc^2)\psi,$$  \hspace{1cm} (3.22)

which contains a set of four coupled first order differential equations. Here, $\alpha_i$ ($i = 1, 2, 3$) and $\beta$ are defined so as to satisfy $E^2 = p^2c^2 + m^2c^4$, yielding

$$\alpha_i = \left(\begin{array}{c} 0 & \sigma_i \\ \sigma_i & 0 \end{array}\right), \quad \beta = \left(\begin{array}{cc} I_2 & 0 \\ 0 & -I_2 \end{array}\right)$$  \hspace{1cm} (3.23)

in the Dirac-Pauli representation. $\sigma_i$ are the Pauli spin matrices and $I_2$ is a 2 $\times$ 2 unitary matrix.

The solution of the Dirac equation is a four-component entity, four-spinors that replace the scalar wave functions in nonrelativistic theory. The solution also contains negative energy solutions, but with positive probability density$^{11}$. The Dirac spinor can be divided into large- ($\psi_+$) and small-component ($\psi_-$) solutions,

$$\psi = \left(\begin{array}{c} \psi_+ \\ \psi_- \end{array}\right).$$  \hspace{1cm} (3.24)

The solutions $\psi_+$ correspond to the positive energy, i.e., electronic solutions, whereas solutions $\psi_-$ correspond to the positronic states.

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$^{11}$These were interpreted as electrons with positive charge (positron) that were later discovered experimentally [164].
3.4.2 The Breit-Pauli Hamiltonian

Since we are interested in a many-body quantum mechanical problem, it is important to incorporate many-body effects into the Dirac equation. The simplest way is to include the potential terms that describe the nuclear-electron and electron-electron Coulomb interactions. This leads to the Dirac-Coulomb (DC) Hamiltonian

$$H_{DC} = \sum_i H_{i}^{Dirac} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} + \sum_{i,K} \frac{1}{r_{iK}},$$

(3.25)

where $r_{ij}$ denotes the distance between electrons $i$ and $j$, and $r_{iK} = r_i - R_K$ is the position of the $i$th electron with respect to nucleus $K$. A Lorentz invariant\(^\text{12}\) form of the DC Hamiltonian is the Bethe-Salpeter equation \([165, 166]\), which is essentially a generalization of the Dirac equation for two particles. The Bethe-Salpeter equation is an integro-differential equation that features different time variables for the two particles. It is required for the Lorentz invariance and hence it is problematic to find a solution. An approximate relativistic many-body Hamiltonian, however, can be constructed from the Dirac Hamiltonian by adding the Breit term \([167]\)

$$H_{ij}^{Breit} = -\frac{1}{r_{ij}} \left[ \alpha_i \cdot \alpha_j - \frac{(\alpha_i \cdot r_{ij})(\alpha_j \cdot r_{ij})}{2r_{ij}^2} \right],$$

(3.26)

consisting of the leading terms in the series obtained from the Bethe-Salpeter equation. The Breit Hamiltonian describes other pairwise additive interactions than the standard Coulomb interaction of electrons $i$ and $j$, the first being the magnetic Gaunt term \([158]\) and the second being a term that describes retardation (finite “speed” of interaction). With the above term, the Dirac-Coulomb-Breit (DCB) Hamiltonian is written as

$$H_{DCB} = \sum_i H_{i}^{Dirac} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} + \sum_{i,K} \frac{1}{r_{iK}} + \frac{1}{2} \sum_{i \neq j} H_{ij}^{Breit}.$$

(3.27)

It implicitly includes all relativistic effects on the kinetic energy as well as the spin-orbit interaction.

Solving the DCB Hamiltonian is computationally too expensive for most of the purposes. Since only positive energy solutions of the Dirac equation are relevant in electronic structure theory, decoupling the positive and negative energy components of Eq. 3.24 to give a two-component equation for the positive energy solutions is highly desirable. Foldy and Wouthuysen \([168]\) introduced a systematic procedure for decoupling the large and small components by finding a unitary transformation that block-diagonalizes the four-component Hamiltonian.

\(^{12}\)Lorentz invariance is required by Einstein’s theory of special relativity.
The Foldy-Wouthuysen (FW) transformation gives rise to the Pauli Hamiltonian \[ H_{\text{Pauli}} = V + \frac{p^2}{2} - \frac{1}{8c^2}(p^4 - \nabla^2 V) + \frac{1}{4c^2} \sigma \cdot (\nabla V \times p). \] (3.28)

The first two terms of the above correspond to the nonrelativistic Hamiltonian, the third and fourth represent the mass-velocity and Darwin corrections, respectively, also referred to as scalar relativistic (SR) corrections. The last term is the spin-orbit coupling term. The Breit-Pauli Hamiltonian is obtained from the DCB Hamiltonian in Eq. 3.27 for two-electron systems through the FW transformation and a generalization of that for \( N \) electrons [170, 171].

The spin-orbit part of the Breit-Pauli Hamiltonian can be written as

\[ H_{\text{BP SO}} = \sum_i h_i + \frac{1}{2} \sum_{i \neq j} h_{ij}, \] (3.29)

where the one- and two-electron terms are respectively

\[ h_i = + \frac{1}{4c^2} \sum_K \frac{Z_K}{r_{iK}^3} \sigma_i \cdot (r_{iK} \times p_i), \] (3.30)

\[ h_{ij} = - \frac{1}{4c^2} \frac{\sigma_i \cdot (r_{ij} \times p_i) - \sigma_j \cdot (r_{ij} \times p_j)}{r_{ij}^3} - \frac{1}{2c^2} \frac{\sigma_i \cdot (r_{ij} \times p_j) - \sigma_j \cdot (r_{ij} \times p_i)}{r_{ij}^3}. \] (3.31)

The one-electron part describes the interaction of an electron spin with the potential produced by the nuclei. The first term in the two-electron part (Eq. 3.31) is the spin-same orbit (SSO) coupling that describes the interaction of the electron with its own orbital momentum and the second term is the spin-other orbit (SOO) coupling which describes the interaction of an electron spin with the orbital momenta of other electrons.

The presence of the complicated two-electron part in the \( H_{\text{SOC}}^{\text{BP}} \) Hamiltonian makes its usage computationally quite demanding. In most quantum chemistry packages, e.g., MOLPRO, the SOC matrix elements are computed for an effective one-electron spin-orbit Fock operator that is obtained directly from the two-electron integrals [172, 173].

For heavy elements, relativistic effects of the core electrons are often incorporated in the effective core potentials (ECPs) that are used to reduce the computational effort by limiting the number of electrons treated explicitly [174]. They are included by parameterization with respect to suitable relativistic all-electron reference calculations. For instance, the ECPs used in this thesis were adjusted in two-component multiconfiguration calculations to valence-energy spectra derived from fully relativistic four-component multiconfiguration
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3.4.3 Quasi-degenerate perturbation theory

A straightforward and least demanding approach to the evaluation of the approximate eigenvalues and eigenfunctions of the total Hamiltonian that includes both nonrelativistic and relativistic terms is to use Rayleigh-Schrödinger perturbation theory [177]. One starts with the nonrelativistic solution $\Psi_0^i$ and $E_0^i$ of Hamiltonian $H_0^i$ obtained from, e.g., a CI calculation. The spin-orbit Hamiltonian $V = H_{SO}^{BP}$ acts in this case as a perturbation to this nonrelativistic solution. The perturbed wave function and energy $E$ must satisfy the equation

$$(H_0^i + V)\Psi = E\Psi. \quad (3.32)$$

In degenerate perturbation theory, for a $p$-fold degenerate energy level, the eigenvalue problem of the perturbation operator $V$ is first solved in the basis of the eigenfunctions of $H_0^i$ that span the degenerate space associated with the energy level $E_0^i$

$$Vc = (E - E_0^i)c, \quad (3.33)$$

where the matrix elements $V_{ij} = \langle \Psi_0^i | V | \Psi_0^j \rangle$ and $c$ are the expansion coefficients. The first order corrections to the energy and zero-order wave functions, with expansion coefficients $c$, are obtained as eigenvalues and eigenfunctions of Eq. 3.33. The $p$ different eigenvalues of $V$ correspond to the (partial) splitting of the reference state. The second order corrections to energy and the corresponding first order wave functions are then obtained by solving the eigenvalue problem of matrix $V$ with elements $V_{ik}$ (the degenerate states are ordered as the first $p$ states)

$$V_{ik} = \langle \Psi_0^i | V | \Psi_0^k \rangle + \sum_{j>p} \frac{\langle \Psi_0^i | V | \Psi_0^j \rangle \langle \Psi_0^j | V | \Psi_0^k \rangle}{E_0^i - E_0^j} \quad (3.34)$$

$$\Psi = \sum_{i=1}^{p} c_i \left( \Psi_0^i + \sum_{j>p} \frac{\langle \Psi_0^j | V | \Psi_0^i \rangle}{E_0^i - E_0^j} \Psi_0^j \right). \quad (3.35)$$

The above treatment is reasonable when the spin-orbit coupling is only a small perturbation with respect to the electron-electron repulsive interactions. Moreover, in cases where several nonrelativistic electronic states with different spin multiplicities accidentally lie close to each other (near degeneracy effects), one needs to use a method where both spin-orbit coupling and electron-electron correlations are treated on equal footing.

Quasi-degenerate perturbation theory (QDPT) is an extension of degenerate perturbation
3.5 Basis sets

theory 3.33 and 3.34, that allows the inclusion of not only the strictly degenerate eigen-
functions of the unperturbed Hamiltonian but also a number of other eigenfunctions that are
nearly degenerate with them in the initial diagonalization of Eq. 3.33. Thus, a more general
eigenvalue problem similar to Eq. 3.33 can be written as

\[(H^0 + V)c = Ec\] (3.36)

\[H^0_{ij} = \langle \Psi^0_i | H^0 | \Psi^0_j \rangle = E_i \delta_{ij}.\] (3.37)

The elements of the matrices \(H\) and \(V\) are here evaluated in the basis \(\{\Psi^0\}\).

Thus, in the basis of the precalculated nonrelativistic states \(\Psi^{SM_i}\) of spin multiplicities \(S\),
QDPT implies the construction and diagonalization of the Hamiltonian \(H^{NR} + H^{BP}_{SOC}\),

\[\langle \Psi^{SM_i} | H^{NR} + H^{BP}_{SOC} | \Psi^{SM_j} \rangle = \delta_{ij} \delta_{SS'} \delta_{M_i M_j} E^{(S)}_i \langle \Psi^{SM_i} | H^{BP}_{SOC} | \Psi^{SM_j} \rangle.\] (3.38)

The size of the resulting matrix depends on the number of nonrelativistic states considered
in the spin-orbit treatment. After diagonalization, the resulting eigenvalues yield the SO
splittings and complex eigenvectors which can be employed in further property calculations.

### 3.5 Basis sets

There are three general features that determine the accuracy of a quantum chemical calcula-
tion: the choice of the Hamiltonian, the type of electron correlation treatment (truncation of
the CI space) and the description of the one-particle space, i.e., the kind of basis set used.
The choice of the basis set is an important factor determining the quality of a quantum chem-
ical calculation. For instance, an insufficiently large basis set could yield erroneous results
regardless of the level of theory employed, whereas using sufficient basis functions may pro-
vide qualitatively correct results already at the (MC)SCF level of theory.

The most common choice for the \(\chi\), the basis functions in Eq. 3.12, is to use Gaussian
type orbitals (GTO) centered at the atomic nuclei,

\[\chi^l_{\rho}(r, \theta, \phi) = Y_{lm}(\theta, \phi)r^l e^{-\zeta r^2}.\] (3.39)

\(Y_{lm}(\theta, \phi)\) are the spherical harmonics for angular momentum quantum number \(l\), \(r\) the
distance from the nucleus and \(\zeta\) are the exponents that are optimized separately for each element.
GTOs are sometimes also expressed in Cartesian coordinates. While physically more real-
istic basis sets, e.g., the Slater-type orbitals, exist, the ability to calculate the two and three
centered integrals analytically made the GTOs very popular. An elaborate discussion can be
found in Ref. [50]. Contracted GTOs (CGTO) are often used to increase the efficiency of
Quantum chemistry methodology

In a segmented contraction, each GTO contributes only to a single CGTO and in a general contraction such a restriction is relaxed. The Pople/Mc-Lean-Chandler basis sets [178, 179] and the Karlsruhe basis sets [180, 181] are some of the most popular segmented contracted GTOs. The correlation-consistent (cc) basis sets by Dunning et al. [182], optimized using correlated (CISD) wave functions, are the most widely used generally contracted basis sets. The polarized valence cc-PVxZ basis sets (x=D,T,Q,5,6 corresponds to the number of contracted Gaussian type functions used to represent the particular Slater type of orbital) can be augmented with additional diffuse functions. The atomic natural orbital (ANO) basis sets by Roos et al. [183] provide another general contraction scheme. In this case, the contraction coefficients are natural orbital coefficients, which are obtained by diagonalization in the basis set optimization process. In the calculations in this thesis, cc-type and ANO basis sets are used.

3.6 Summary

In this chapter, a brief overview of the computational methods employed in this thesis was provided. The embedded cluster approach, where only a fragment of the periodic crystal is explicitly considered at the quantum mechanical level, was succinctly explained. In such an approach, the remaining part of the crystal is modeled at a coarser level, for example by embedding the cluster in an effective potential that captures the electrostatic effects of the crystal environment. The mean-field Hartree-Fock method that may form in some cases a good starting point for subsequently constructing correlated many-body wave functions was first described. The configuration interaction based methods to systematically improve the HF wave function to include electronic correlation effects were also outlined. The single reference CI captures most of the correlations when the HF reference wave function is a good approximation. However, in cases when several configurations are (nearly) degenerate, a CI expansion on top of MCSCF (CASSCF) reference wave functions is necessary. The MCSCF method is designed to capture static correlations related to near-degeneracy effects. In the last part, the relativistic Dirac equation was introduced and the simplified Breit-Pauli form of SO coupling commonly used in quantum chemistry packages was described. The quasi-degenerate perturbation theory approach that treats both the SOC and electronic correlations on the same footing was also outlined at the end.

The CASSCF + MRCI(SD) expansion is a very suitable way to include both static and dynamical electronic correlations in the description of the electronic structure of TM oxides. Nondynamical correlation effects, which in the 5d5 iridates we thoroughly investigate in this thesis, are related to both having the triply degenerate Ir t2g levels and couplings between the t2g and eg shells, are accounted for by CASSCF wave functions that are constructed with active spaces containing either three (t2g) or five (t2g + eg) orbitals. The remaining
3.6 Summary

Electronic correlations, due to configurations involving charge transfer like states with holes in the oxygen $p$-orbitals, are estimated by MRCI(SD) expansions of the wave function.
Electronic structure: ground state and 
d-d excitations in Ir$^{4+}$ compounds

The ground state and on-site d-d excitations of several insulating iridium 5d$^5$ oxides, Sr$_2$IrO$_4$, Ba$_2$IrO$_4$, Na$_2$IrO$_3$, Li$_2$IrO$_3$, Sr$_3$IrCuO$_6$ and Na$_4$Ir$_3$O$_8$, are discussed in this chapter. We analyze the interplay of crystal field d-level splittings and spin-orbit coupling by detailed quantum chemistry calculations and further examine the formation of \( \tilde{j} \approx 1/2 \) ground states. Additionally, the admixture of \( \tilde{j} = 3/2 \) character into the ground state wave functions of all these compounds is quantified. The excitation energies computed for the \( \tilde{j} \approx 3/2 \) spin-orbit exciton and the \( t_{2g}^5 \) to \( t_{2g}^4e_1^1 \) transitions compare very well with available resonant inelastic x-ray scattering data.

4.1 Introduction

In 5d$^5$ oxide compounds, the intriguing situation arises where the on-site Coulomb interaction and the SO coupling meet on the same energy scale. It turns out that for the 5d$^5$ electron configuration, in particular, the SO interaction can effectively enhance that way the effects of electronic correlations. This renewed interest in these compounds since the interplay of crystal field effects, local multiplet physics, SOC and inter-site hopping can offer novel types of correlated ground states and excitations.

Some of the most intensely studied iridate compounds are the layered square-lattice, 214 family $Ae_2$IrO$_4$ ($Ae$=Sr,Ba) [89, 90] and the layered honeycomb-lattice, 213 family $A_2$IrO$_3$ ($A$=Li,Na) [186, 187]. The structural similarity of the 214 iridates to some of the high-T$_c$ superconducting cuprates, e.g., La$_2$CuO$_4$, and the realization of a novel, SO coupled Mott-

insulating ground state has attracted major scientific interest in this class of materials. On the other hand, the honeycomb 213 family has been proposed to host a spin-liquid phase arising from the presence of highly anisotropic magnetic interactions of Kitaev type [10]. Along with these two families of iridates, other iridium oxides like Na$_4$Ir$_3$O$_8$ and the pyrochlore 227 compounds $L_2$Ir$_2$O$_7$ ($L =$ Y, Eu, Pr etc.) have been proposed to harbor similarly exciting spin-liquid or topological phases.

The prerequisite for all the remarkable properties and phases put forward in iridates is the entangled SO $\tilde{j} = 1/2$ ground state. Since the realization of this state depends on the balance between the crystal field and SO coupling effects, it is of utmost significance to calculate by ab initio means the relevant microscopic energy scales and investigate in detail the characteristics of 5$d^5$ ground state configuration. In this regard, we study the local electronic structure of the Ir ion using quantum chemistry (QC) methods.

In the next section, the computational approach we employed and further numerical details are described. The detailed nature of the SO ground states of both Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ is discussed in Sec. 4.3.1 and Sec. 4.3.2, along with the calculated d-level excitations. Using the microscopic energies obtained from QC calculations in a simple model Hamiltonian setting, we analyze the admixture of $\tilde{j} = 1/2$ and $\tilde{j} = 3/2$ states in the ground state. Then, we move on to discuss the calculated on-site excitations in layered honeycomb compounds, Na$_2$IrO$_3$ and Li$_2$IrO$_3$, and compare the results with RIXS measurements. In Sections 4.5 and 4.6, we present the results of QC calculations for compounds with low crystal symmetry and examine the case when the low-symmetry crystal field splittings are comparable or even larger than the strength of SOC. We provide in the end a summary of our findings.

4.2 Computational scheme

The essential physics of iridium oxides mainly concerns the Ir 5$d$ and the oxygen 2$p$ levels. Hence, the material model we consider is a cluster consisting of one (central) IrO$_6$ octahedron surrounded by the NN IrO$_6$ octahedra and the adjacent closed-shell metal ions, e.g., Sr in Sr$_2$IrO$_4$. We find in our investigation that it is essential to include the NN octahedra in the actual cluster [74, 188] as the large spatial extent of the Ir 5$d$-orbitals requires a good description of the nearby charge distribution. To simulate the effect of the farther solid-state environment, a point charge (PC) embedding scheme (see Sec. 3.2) is employed. In this scheme the cluster is embedded in a large array of PCs at the lattice positions, whose values are adjusted to reproduce the ionic Madelung field in the cluster region.

Energy-consistent relativistic pseudopotentials were used for the Ir [175], alkali [189] and alkaline-earth ions [190], with Gaussian-type valence basis functions [50] from the MOLPRO [120] library. Basis sets of quadruple-ζ quality were applied for the central Ir ion [175] and triple-ζ basis sets for the NN Ir sites [175]. The oxygen ligands of the central octahedron
were represented by all electron triple-\(\zeta\) basis functions \[182\]. For the central Ir ions we also used two polarization \(f\) functions \[175\]. For farther oxygens around the NN Ir sites minimal atomic-natural-orbital basis sets \[183\] were applied. All occupied shells of the alkali and alkaline-earth ions were incorporated in the large-core pseudopotentials and the outermost (ionized) \(s\) orbitals were described by a single contracted Gaussian function \[189, 190\].

Two separate sets of calculations were carried out, having the Ir\(^{4+}\) 5\(d^5\) NN’s modeled in two different ways. The most natural way is to treat all the Ir sites in the cluster to be equivalent, with an open-shell \(d^5\) configuration. However, if \(t_{2g}\) to \(e_g\) or/and intersite excitations are to be included, the number of relevant multiplets increases drastically and the calculations become cumbersome for more than two Ir\(^{4+}\) \(d^5\) sites. Moreover, the analysis of the \(N\)-electron wave functions turns out to be tedious. A simpler approach, which provides good results especially for single-site properties like the on-site \(d-d\) excitations, is to cut off the (spin) couplings of the central Ir with the NN’s by modeling the NN Ir\(^{4+}\) (5\(d^5\)) sites with closed-shell Pt\(^{4+}\) (5\(d^6\)) ions. This is a usual procedure in QC studies on TM systems, see e.g., Refs. \[68, 87, 188\]. Nevertheless, we performed calculations with both open-shell and closed-shell NNs and the results are compared in the following.

The step-by-step procedure followed for the calculations of both ground state and on-site excitations is outlined below:

1. A scalar-relativistic\(^1\) closed-shell HF calculation was first performed on the chosen cluster with the restriction that all the orbitals are doubly occupied. In this calculation the central Ir ion was also considered to have a closed-shell \(d^6\) \((t_{2g}^6\) configuration.

2. The resulting HF orbitals were next separated into frozen, inactive, active and virtual orbital groups using the orbital localization module in MOLPRO \[191\] and the Jmol \[192\] plotting program, for subsequent MCSCF calculations. The 5\(d\) orbitals (either \(t_{2g}\) or \(t_{2g}+e_g\), depending on the number of states computed by CASSCF) of the central Ir site\(^2\) are grouped as active, the Ir 5\(s\)5\(p\) along with the O 1\(s\)2\(s\)2\(p\) orbitals of the central octahedron as inactive\(^3\) orbitals. All doubly occupied orbitals belonging to the NN IrO\(_6\) octahedra were frozen in the subsequent CASSCF calculations and all the empty orbitals are labeled as virtual.

3. Next, in the multiconfiguration (CASSCF) calculations, for excitations within the Ir \(t_{2g}\) manifold, an active space CAS[5,3] (5 electrons in 3 \(t_{2g}\) orbitals) was considered. In this calculation, the coefficients in the LCAO expansion of active and inactive orbitals as well as the CI coefficients of the multiconfiguration wave function were used as

\(^1\)Scalar-relativistic effects are implicitly included in the effective core potentials.

\(^2\)These are the highest occupied (only \(t_{2g}\)) molecular orbitals. The O 2\(p\) orbitals are immediately below the Ir 5\(d\) levels.

\(^3\)These are doubly occupied but still optimized in the subsequent CASSCF calculation.
variational parameters to optimize the CAS wave function. For excitations from $t_{2g}$ to $e_g$ and O 2$p$ to Ir 5$d$, the active space was enlarged with Ir 5$d$ $e_g$ and a few O 2$p$ orbitals, respectively.

In those calculations where the NN Ir$^{4+}$ sites were treated as open-shell, the $t_{2g}$ orbitals of the NN Ir sites were also included in the active space. However, the corresponding 5$s$5$p$ remained frozen as at the HF level. The CASSCF calculation was performed in two steps. First, the active space consisted of three $t_{2g}$ orbitals and five electrons of each of the iridium sites in the cluster. In the second set of calculations, the doubly occupied molecular-like $t_{2g}$ orbitals of the NN Ir sites were frozen and only the NN Ir 5$d$ orbitals that are singly occupied were included in the active space, along with the central Ir 5$d$ orbitals.

4. In the subsequent MRCI(SD) calculations performed to capture dynamic correlation effects, starting from the CAS reference wave functions, configurations involving single and double excitations from the active and inactive space to the virtual orbitals were also taken into account. Active here are the central Ir $t_{2g}$ or $t_{2g} + e_g$ orbitals, while the inactive space contains the O 2$p$ orbitals of the central octahedron.

5. The relativistic SO interaction was later on included within quasi-degenerate perturbation theory. Here, the SO Hamiltonian is constructed in the basis of MRCI wave functions and is then added to the scalar-relativistic Hamiltonian. Diagonalizing the resulting matrix provides the SO coupled eigenstates whose eigenfunctions are an admixture of MRCI states of different spin and space symmetries. A simpler approach is to use CASSCF wave functions and replace the diagonal energies of the SO Hamiltonian by MRCI energies [193]. However, we find that the use of MRCI wave functions is crucial in correctly estimating the anisotropic magnetic exchange couplings discussed in Chap. 6 and 7.

4.3 Spin-orbit ground state and excitations in square-lattice iridates

4.3.1 Sr$_2$IrO$_4$

Sr$_2$IrO$_4$ is one of the first iridium oxide compounds that has attracted attention due to its structural similarity with some of the high-T$_c$ cuprate superconductors. Although it was already synthesized in 1956 [194] and thought to exist with a K$_2$NiF$_4$-type crystal structure similar to Sr$_2$RuO$_4$ with I$4/mmm$ space group symmetry, it was only after four decades that a complete crystal structure analysis was reported. X-ray, electron and neutron diffraction
experiments concluded a low symmetry tetragonal $I4_1/acd$ crystal structure [89, 195, 196]. In this layered perovskite structure, Ir-O$_2$ planes alternate with Sr-O planes and each Ir$^{4+}$ ion (formal charge) is octahedrally coordinated with oxygen ligands. The IrO$_6$ octahedra are corner-shared and give rise to a 2D square lattice of Ir$^{4+}$ ions. In addition, the octahedra are rotated around the $c$-axis by about 11.5° (Fig. 4.1) in a staggered fashion, removing the inversion symmetry at the midpoint of the Ir-Ir bonds along the $\langle100\rangle$ and $\langle010\rangle$ directions. This lack of inversion symmetry gives rise to Dzyaloshinskii-Moriya (DM) interactions between the magnetic moments on NN Ir ions. This aspect is dealt with briefly in Chap. 6.

Early transport measurements showed that Sr$_2$IrO$_4$ is insulating, with significant anisotropy between the $a/b$ and $c$ axes [15, 197, 198]. The optical gap is 0.3 eV [94]. The optical excitations above 1.5 eV were interpreted to be charge transfer excitations from the O 2$p$ to the Ir 5$d$ levels. A gap that is roughly consistent with the optical gap is also found by angle resolved photoemission spectroscopic measurements [14]. The insulating behavior of Sr$_2$IrO$_4$ was ex-

![Crystal structure of Sr$_2$IrO$_4$. Corner-sharing IrO$_6$ octahedra are alternately rotated clockwise and anti-clockwise around the $c$-axis by about 11.5° (right) [89]. For this reason the unit cell consists of octahedra in four successive layers (left).](image-url)
plained to be originating from the formation of a novel $\tilde{j} \simeq 1/2$ ground state [15]. The latter is the result of a subtle interplay of crystal field splittings, SOC, and electron correlations. In particular, the SO interactions effectively enhance the electron correlations to open up a Mott-like insulating gap [14].

4.3.1.1 Ground state and on-site excitations

The ground state electronic configuration and on-site $d$-$d$ excitations in Sr$_2$IrO$_4$ were calculated on a cluster consisting of five IrO$_6$ octahedra (1 central + 4 NN) and the neighboring ten Sr$^{2+}$ ions. Crystal structure parameters as reported in Ref. [89] at 13 K were used. Apart from the staggered rotation of the IrO$_6$ octahedra, the individual octahedra are not perfectly cubic but elongated along the $c$-axis. The out-of-plane (apical) Ir-O bond lengths are larger than the in-plane Ir-O distances, 2.057 vs 1.979 Å. As a result, the symmetry of the solid-state environment around the Ir atom is lowered from octahedral $O_h$ symmetry to tetragonal $D_{4h}$. This lowering of the symmetry lifts the degeneracy of the Ir $t_{2g}$ (and $e_g$) orbitals.

**Splittings within the $t_{2g}$ levels.** We first investigated the effect of noncubic crystal fields by computing the scalar-relativistic ground state and the low-energy crystal field excitations. Two sets of calculations were performed. In the first calculation the NN Ir sites were modeled as closed-shell Pt$^{4+}$ $t_{2g}^6$ ions, as described in Sec. 4.2. The active space consisted of the three $t_{2g}$ orbitals and five electrons corresponding to the central Ir site (CAS[5,3]). With such an active space, the lowest energy term for idealized octahedral ($O_h$) symmetry is $^2T_{2g}$ ($t_{5g}^5$) [91]. Although the actual point-group symmetry is lower than octahedral, for convenience, we still use, however, notations corresponding to $O_h$. In the CASSCF calculations, the orbitals were optimized for an average of the split $^2T_{2g}$ states. The calculated relative energies of these $^2T_{2g}$ ($t_{5g}^5$) states are given in Table 4.1a.

In the second set of calculations, all five Ir sites were modeled as Ir$^{4+}$ species with open

<table>
<thead>
<tr>
<th>Orbital occ.</th>
<th>CASSCF</th>
<th>MRCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{x^2-y^2}$</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>$d_{xy}$</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>$d_{x^2-y^2}$</td>
<td>0.120</td>
<td>0.155</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Orbital occ.</th>
<th>CASSCF</th>
<th>MRCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{x^2-y^2}$</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>$d_{xy}$</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>$d_{x^2-y^2}$</td>
<td>0.078</td>
<td>0.110</td>
</tr>
</tbody>
</table>

**Table 4.1** $^2T_{2g}$ ($t_{5g}^5$) states in Sr$_2$IrO$_4$, as obtained in the two sets of calculations that differ in the way the NN sites are modeled (see text), at CASSCF and MRCI levels of theory. For a cubic octahedral environment these states are degenerate. However, the tetragonal symmetry in Sr$_2$IrO$_4$ splits this degeneracy.
shell $d^5$ configuration. Here, the CASSCF calculations were performed in two steps. First, all 12 Ir $t_{2g}$ orbitals (3 central + 4 × 3 NN) and 15 Ir 5$d$ electrons were considered as active (CAS[15,12]). All these Ir 5$d$ orbitals and the 2$p$ orbitals of oxygens belonging to the central octahedron were optimized for the high spin $S_{\text{tot}}=5/2$ state. In the next step, the doubly occupied molecular-like $t_{2g}$ orbitals of the NN Ir were frozen. Only the singly occupied NN Ir $t_{2g}$-like orbitals along with the three $t_{2g}$ orbitals of the central Ir ion were considered to be active (CAS[9,7]). The $^2T_{2g}$ ($t_{2g}^5$) states associated to the central Ir ion were computed by keeping the NN Ir spins high-spin coupled to the central site. The associated Ir $t_{2g}$ splittings are shown in Table 4.1b.

It can be seen from Table 4.1 that the tetragonal crystal field splits the Ir $t_{2g}$ orbitals into a doublet $e_g'$ and a singlet $b_{2g}$, if notations corresponding to $D_{4h}$ point group symmetry are to be used. The scalar-relativistic ground state is doubly degenerate, with a hole either in the $d_{xz}$ or $d_{yz}$ orbitals and an energy of 0.155 eV is required to excite a hole into the $d_{xy}$ orbital\(^4\). This implies that the in-plane $d_{xy}$ orbital is lower in energy compared to the out-of-plane $d_{xz}/d_{yz}$ orbitals. Within ligand-field theory for transition-metal complexes [92] with elongated TM$\text{O}_6$ octahedra, it is, however, the out-of-plane $d_{xz}/d_{yz}$ orbitals that are stabilized (see Fig. 4.2 (left)). Our splittings in Table 4.1 suggest the opposite, as depicted in Fig. 4.2 (right), a scenario that corresponds to a compression of the Ir$\text{O}_6$ octahedra.

To understand the origin of the negative tetragonal splittings\(^5\) even for an elongated Ir$\text{O}_6$ octahedra, it is instructive to look at the orbital energies for a hypothetical crystal structure

\(^4\)We use hole representation in this thesis unless otherwise specified.

\(^5\) Conventionally $\Delta_t = E(d_{xy}) - E(d_{xz/yz})$ [91].
in which the O cage around the Ir\(^{4+}\) ion is perfectly cubic, i.e., all the Ir-O bond lengths are equal (set to 1.975 Å, average of the Ir-O bond lengths in Sr\(_2\)IrO\(_4\)) but the relative distances between the Ir and Sr layers are kept the same as in the actual experimental structure of Sr\(_2\)IrO\(_4\). In Table 4.2, the relative energies of the three states of the \(^2T_2\) \((t_{2g}^5)\) term are provided. Here, as in Table 4.1, the lowest energy state contains a hole in the \(d_{xz}/d_{yz}\) orbitals. However, the splitting between the \(d_{xy}\) and \(d_{xz}/d_{yz}\) hole orbital states is much larger now. The splitting of the \(t_{2g}\) levels even in a cubic octahedral oxygen environment is unexpected and suggests that the field generated by ions beyond the oxygen ligands also plays an important role on the precise order of the \(d\) levels. We will discuss the actual origin of this non-trivial behavior in Sec. 4.3.3.

The splittings computed in the two cases, which differ in the way the NN Ir sites are modeled (see Table 4.1a and 4.1b), are slightly different by \(<\leq 0.05\) eV. Nevertheless, the order of the \(d\)-levels is the same. It should be noted that in the case of open-shell NNs the energies were computed for a high-spin \((S_{\text{tot}} = 5/2)\) configuration, although spins in Sr\(_2\)IrO\(_4\) couple antiferromagnetically \([40, 196]\). Calculating the on-site excitations in a low-spin configuration is cumbersome as there would also be additional excitations corresponding to the coupling of spins of the NN sites. In the rest of the calculations discussed in this chapter, we used a cluster with NNs modeled as closed-shell Pt\(^{4+}\) \(t_{2g}\) ions.

Although the electronic structure illustrated until now in this section does not consider the SO interaction, the energy splittings presented here are important in understanding the SO ground state and excitations. Besides, these Ir \(t_{2g}\) splittings constitute basic parameters used in model Hamiltonian calculations \([199]\) and play a crucial role in the interpretation of experimental observations \([200, 201]\).

**Spin-orbit excitations.** The SO interaction was first included only within the \(t_{2g}\) manifold, neglecting off-diagonal SOCs that couple the \(t_{2g}\) and \(e_g\) states. This corresponds to the case where the \(e_g\) levels are assumed to be infinitely separated from the \(t_{2g}\) manifold and the \(T\)-\(P\) equivalence (see App. A.2) can be invoked. In fact, the large majority of theoretical models presently used in the literature are based on this assumption, see, e.g., Ref. \([10, 28]\).

The SO admixes the three \(^2T_2\) \(t_{2g}\) states of the \(\bar{t}_{2g}\) configuration and gives rise to three Kramers doublets \([10]\). The relative energies of these are shown in Table 4.3. Both CASSCF +SOC and MRCI+SOC calculations find the ground state doublet to be separated from the other two Kramers doublets by at least 0.66 eV. The SO wave functions indicate that the

<table>
<thead>
<tr>
<th>Orbital occupation</th>
<th>Relative energies (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{xy}^2 d_{xz}^1 d_{yz}^2)</td>
<td>CASSCF 0.00, MRCI 0.00</td>
</tr>
<tr>
<td>(d_{xy}^2 d_{xz}^2 d_{yz}^1)</td>
<td>CASSCF 0.00, MRCI 0.00</td>
</tr>
<tr>
<td>(d_{xy}^3 d_{xz}^2 d_{yz}^2)</td>
<td>CASSCF 0.29, MRCI 0.33</td>
</tr>
</tbody>
</table>

The splittings from Table 4.2 are shown in Table 4.3. Both CASSCF +SOC and MRCI+SOC calculations find the ground state doublet to be separated from the other two Kramers doublets by at least 0.66 eV. The SO wave functions indicate that the...
4.3 Spin-orbit ground state and excitations in square-lattice iridates

Table 4.3 Relative energies of the three Kramers doublet states associated with the $\tilde{j} = 1$ and $S = 1/2$ quantum numbers of the $\text{Ir}^{4+} t_{2g}^6$ configuration in $\text{Sr}_2\text{IrO}_4$. The NN Ir sites are modeled as closed shell $\text{Pt}^{4+} t_{2g}^6$ ions. CASSCF and MRCI results are shown. The composition of the SO wave functions in the $t_{2g}$-orbital basis at the CASSCF level is also provided.

<table>
<thead>
<tr>
<th>SO state</th>
<th>Relative energy (eV)</th>
<th>CASSCF WF composition (%)</th>
<th>CASSCF+SOC</th>
<th>MRCI+SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{j} = \frac{1}{2}, m_j = \pm \frac{1}{2}$</td>
<td>0.00</td>
<td>25.0</td>
<td>37.5</td>
<td>37.5</td>
</tr>
<tr>
<td>$\tilde{j} = \frac{3}{2}, m_j = \pm \frac{3}{2}$</td>
<td>0.67</td>
<td>0.00</td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td>$\tilde{j} = \frac{3}{2}, m_j = \pm \frac{1}{2}$</td>
<td>0.75</td>
<td>75.0</td>
<td>12.5</td>
<td>12.5</td>
</tr>
</tbody>
</table>

ground state is close to the $\tilde{j} = 1/2$ state and the higher lying states correspond to the (split) $\tilde{j} \simeq 3/2$ quartet. The contribution to the spin-orbit ground state of the configuration with a hole in the $d_{xy}$ orbital is $\approx 8\%$ smaller than the $33.33\%$ expected for a pure $\tilde{j} = 1/2$ state. This is due to the lower energy of the $d_{xy}$ orbital compared to $d_{yz} / d_{zx}$, arising from the noncubic crystal fields (see Table 4.1). Furthermore, the splitting of the $t_{2g}$ levels results in a slight admixture of the $\tilde{j} = 3/2, m_j = \pm 1/2$ and $\tilde{j} = 1/2, m_j = \pm 1/2$ Kramers doublets, leading to a splitting of the $\tilde{j} \simeq 3/2$ quartet states into two doublets by 0.11 eV at the MRCI level. An estimation of this admixture can be made using a simple model Hamiltonian analysis as described below.

4.3.1.2 $\lambda - \Delta_t$ model

The effect of noncubic crystal fields, which remove the degeneracy of $t_{2g}$ levels, on the formation of the $\tilde{j} = 1/2$ ground state can be analyzed with a minimal model that describes both the splitting of the $t_{2g}$ levels and the SO interaction. If a noncubic crystal field separates the $d_{xy}$ states from $d_{yz}$ and $d_{zx}$ states by $\Delta_t$, then the corresponding Hamiltonian $H'_{\text{cf}}$ can be written as

$$H'_{\text{cf}} = -\Delta_t \sum_{\sigma = \pm \frac{1}{2}} |d_{xy}, \sigma \rangle \langle d_{xy}, \sigma| = -\Delta_t \sum_{\sigma = \pm \frac{1}{2}} |0, \sigma \rangle \langle 0, \sigma|.$$  (4.1)

We used the relations in Eq. A.19 to obtain the above expression. The sign of $\Delta_t$ in Eq. 4.1 is chosen in such a way that $\Delta_t > 0$ implies an elongation of the IrO$_6$ octahedra and the state with the hole in the $d_{xy}$ orbital is the lowest, see Fig. 4.2. The total Hamiltonian with the inclusion of SOC,

$$H = -\lambda \mathbf{L} \cdot \mathbf{S} + H'_{\text{cf}},$$  (4.2)
is block diagonal in the total angular momentum basis $|j,m_j\rangle$:

$$H = \begin{bmatrix} H_+ & 0 & 0 \\ 0 & H_- & 0 \\ 0 & 0 & H_3 \end{bmatrix}, \text{ with }$$

$$H_\pm = \begin{pmatrix} \frac{1}{2}, \pm \frac{1}{2} \\ \frac{3}{2}, \pm \frac{1}{2} \end{pmatrix} \begin{bmatrix} -\lambda - \frac{\Delta t}{\sqrt{3}} & -\frac{\sqrt{2}\Delta t}{3} \\ -\frac{\sqrt{2}\Delta t}{3} & -\lambda - \frac{2\Delta t}{3} \end{bmatrix} \text{ and } H_3 = \begin{pmatrix} \frac{3}{2}, \frac{3}{2} \\ \frac{3}{2}, -\frac{3}{2} \end{pmatrix} \begin{bmatrix} -\frac{\lambda}{2} & 0 \\ 0 & -\frac{\lambda}{2} \end{bmatrix}.$$  

Introducing the parameter $\delta = \frac{2\Delta t}{\lambda}$, the eigenvalues and eigenfunctions obtained by diagonalizing the two-dimensional matrices $H_\pm$ and $H_3$ are, respectively,

$$E_+ = \frac{\lambda}{4} \left( -1 - \delta \mp \sqrt{9 - 2\delta + \delta^2} \right),$$

$$E = \frac{\lambda}{2}$$

and

$$|a_{\pm \frac{1}{2}}\rangle = C_1 \begin{pmatrix} \frac{1}{2}, \pm \frac{1}{2} \\ \frac{3}{2}, \pm \frac{1}{2} \end{pmatrix} + C_2 \begin{pmatrix} \frac{3}{2}, \pm \frac{1}{2} \\ \frac{3}{2}, \pm \frac{1}{2} \end{pmatrix}, \text{ (E$_-$)}$$

$$|b_{\pm \frac{1}{2}}\rangle = C_1 \begin{pmatrix} \frac{3}{2}, \pm \frac{1}{2} \\ \frac{3}{2}, \pm \frac{1}{2} \end{pmatrix} - C_2 \begin{pmatrix} \frac{1}{2}, \pm \frac{1}{2} \\ \frac{1}{2}, \pm \frac{1}{2} \end{pmatrix}, \text{ (E$_+$)}$$

$$|c_+\rangle = \begin{pmatrix} \frac{3}{2}, \frac{3}{2} \end{pmatrix}, \text{ (E)}$$

$$|c_-\rangle = \begin{pmatrix} \frac{3}{2}, -\frac{3}{2} \end{pmatrix}, \text{ (E)},$$

with

$$C_1 = \sqrt{\frac{1}{2} \left( 1 + \frac{9 - \delta}{3\sqrt{9 - 2\delta + \delta^2}} \right)} \text{ and } C_2 = \sqrt{\frac{1}{2} \left( 1 - \frac{9 - \delta}{3\sqrt{9 - 2\delta + \delta^2}} \right)}.$$  

The eigenfunctions clearly show that the splitting of the $t_{2g}$ levels leads to an admixture of pure $j = 1/2, m_j = \pm 1/2$ and $j = 3/2, m_j = \pm 1/2$ states, whereas the $j = 3/2, m_j = \pm 3/2$ states remain unchanged. For $\delta = 0$, there is no mixing.

In Sr$_2$IrO$_4$, the splitting within the $t_{2g}$ levels is $\Delta \epsilon = -0.155$ eV (see Table 4.1) and a $\lambda = 0.468$ eV$^6$ gives rise to $C_1 = 0.995$ and $C_2 = 0.095$. Thus, the ground state in Sr$_2$IrO$_4$ is an admixture of $j = 1/2, m_j = \pm 1/2$ and $j = 3/2, m_j = \pm 1/2$ states with a percentage ratio

$^6$Evaluated in Chap. 5.
4.3 Spin-orbit ground state and excitations in square-lattice iridates

of 99.1 : 0.9. The splitting among the quartet states from Eq. 4.4 is \( E_\downarrow - E_\uparrow = 0.11 \text{ eV} \). This value closely matches with the \( t_{2g} \) splitting obtained from the \textit{ab initio} QC calculations (see Table 4.3), implying that the estimate of the ground state admixture from this simple model is reasonably good in this case.

**Excitations between the \( t_{2g} \) and \( e_g \) manifolds.**

Electronic excitations from the \( t_{2g} \) to \( e_g \) levels were calculated by considering an active space of all five Ir 5d orbitals (\( t_{2g} + e_g \)) and the five valence electrons (CAS[5,5]). Such an active space gives rise to several states belonging to three different spin multiplicities: 72 doublet and 24 quartet states associated with the configurations \( t_{2g}^4 e_g^1 \) and \( t_{2g}^3 e_g^2 \), and one sextet state that corresponds to the \( t_{2g}^3 e_g^2 \) configuration. Relative energies of the excited states up to 5 eV obtained from both CASSCF and MRCI calculations are shown in Table 4.4. Here, the CASSCF orbitals were optimized for an average of the \( 2^T_{2g} (t_{2g}^5) \) spin doublet, lowest \( 4^T_{1g}, \)

<table>
<thead>
<tr>
<th>( \text{Ir 5d}^3 ) splittings</th>
<th>( \text{Relative energies (eV)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CASSCF</td>
</tr>
<tr>
<td>( 2^T_{2g} (t_{2g}^5) )</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>0.11</td>
</tr>
<tr>
<td>( 4^T_{1g} (t_{2g}^4 e_g^1) )</td>
<td>2.51</td>
</tr>
<tr>
<td></td>
<td>2.65</td>
</tr>
<tr>
<td></td>
<td>2.65</td>
</tr>
<tr>
<td>( 4^T_{2g} (t_{2g}^4 e_g^1) )</td>
<td>3.23</td>
</tr>
<tr>
<td></td>
<td>3.36</td>
</tr>
<tr>
<td></td>
<td>3.36</td>
</tr>
<tr>
<td>( 2^A_{1g} (t_{2g}^4 e_g^1) )</td>
<td>3.66</td>
</tr>
<tr>
<td>( 2^T_{1g} (t_{2g}^4 e_g^1) )</td>
<td>3.82</td>
</tr>
<tr>
<td></td>
<td>3.82</td>
</tr>
<tr>
<td></td>
<td>3.85</td>
</tr>
<tr>
<td>( 2^T_{2g} (t_{2g}^4 e_g^1) )</td>
<td>4.05</td>
</tr>
<tr>
<td></td>
<td>4.20</td>
</tr>
<tr>
<td></td>
<td>4.20</td>
</tr>
<tr>
<td>( 2^E_{1g} (t_{2g}^4 e_g^1) )</td>
<td>4.31</td>
</tr>
<tr>
<td></td>
<td>4.45</td>
</tr>
<tr>
<td>( 6^A_{1g} (t_{2g}^2 e_g^2) )</td>
<td>4.09</td>
</tr>
</tbody>
</table>

Table 4.4: Excitations from the Ir \( t_{2g} \) to \( e_g \) levels in Sr\(_2\)IrO\(_4\). All states below 5 eV, at both CASSCF and MRCI level of theory, with and without SOC, are shown.
Electronic structure: ground state and \(d-d\) excitations in Ir\(^{4+}\) compounds

\(4T_{2g}\) quartet states and the \(6A_{1g} (t_{2g}^3e_{g}^2)\) sextet. We find that the inclusion of the higher energy \(6A_{1g}\) state is necessary in order to ensure quick convergence.

In the scalar-relativistic calculations, at both CASSCF and MRCI levels, the lowest \(t_{2g}^4e_{g}^1\) spin-quartets, \(4T_{1g}\) and \(4T_{2g}\), are at 2.64 – 2.73 and 3.14 – 3.4 eV, respectively. The lowest ten spin-doublet states (\(2A_{2g}, 2T_{1g}, 2T_{2g}, 2E_g\)) associated with the \(t_{2g}^4e_{g}^1\) configuration, start at 3.74 eV and extend up to 4.41 eV. The \(6A_{1g}\) state resulting from the \(t_{2g}^3e_{g}^2\) configuration is at 4.42 eV. Comparing the CASSCF and MRCI numbers, we can conclude that MRCI causes an increase in the splittings. The highest \(6A_{1g}\) state is shifted up by 0.33 eV (largest shift) and all the other states rise by 0.02 – 0.08 eV.

The SO interaction now couples the \(2T_{2g}\) \((t_{2g}^5)\) states with states associated with \(t_{2g}^4e_{g}^1\) configurations due to the off-diagonal SO matrix elements (see App. A.4). Interestingly, this gives rise to an increase in the separation between the ground state \(\tilde{j} \simeq 1/2\) doublet and \(\tilde{j} \simeq 3/2\) quartet states to 0.77 eV (MRCI+SOC), which is 0.11 eV larger than what is calculated when those \(t_{2g}^4e_{g}^1\) states are not included, see Table 4.3. More about the effect of these high energy states on the \(\tilde{j} = 1/2\) ground state is discussed in Chap. 5. The spin-quartet \((^4T_{1g} \text{ and } ^4T_{2g})\) and spin-doublet \((^2A_{1g}, ^2T_{1g}, ^2T_{2g} \text{ and } ^2E_{1g})\) states corresponding to \(t_{2g}^4e_{g}^1\) manifold are now pushed to higher energies by 0.4 – 0.7 and 0.6 – 1.0 eV, respectively and the \(6A_{1}\) state of \(t_{2g}^3e_{g}^2\) configuration has moved up in energy by as much as 1.1 eV.

### 4.3.2 Ba\(_2\)IrO\(_4\)

Soon after realizing that a \(\tilde{j} \simeq 1/2\) ground state is achieved in Sr\(_2\)IrO\(_4\), which explains the insulating nature of this compound, a lot of interest has been shown to synthesize new materials that can host a similar SO coupled ground state. Ba\(_2\)IrO\(_4\), a material nearly isostructural to Sr\(_2\)IrO\(_4\), was synthesized at high pressures of 6 Gpa [90] and has been characterized to occur with the \(I4/mmm\) space group symmetry. As in Sr\(_2\)IrO\(_4\), the Ir-O\(_2\) layers are separated by Ba-O planes giving rise to a quasi-2D layered structure. However, unlike in Sr\(_2\)IrO\(_4\), the Ir-O-Ir bonds in the square planar lattice of Ba\(_2\)IrO\(_4\) are straight (Fig. 4.3), without any rotation of the \(\text{IrO}_6\) octahedra. As a result, the inversion symmetry at the midpoint of Ir-O-Ir links is preserved and the DM interaction vanishes. In Fig. 4.3a, the stacking of Ir-O\(_2\) layers in Ba\(_2\)IrO\(_4\) is shown. Similar to Sr\(_2\)IrO\(_4\), the \(\text{IrO}_6\) octahedra are not perfectly cubic, but display tetragonal distortions. The apical-oxygen distance, 2.155 Å, exceeds the in-plane Ir-O length of 2.015 Å, implying a positive tetragonal distortion of 6.92%, almost two times larger than in Sr\(_2\)IrO\(_4\) (3.94%). This structural difference reflects in the \(t_{2g}\)-level splittings that are discussed later on in this section.

Due to the unrotated \(\text{IrO}_6\) octahedra in Ba\(_2\)IrO\(_4\), in the simplest picture the width of the Ir \(t_{2g}\)-bands would increase and drive the material into a metallic regime. However, a semi-conducting behavior with an activation energy of \(\sim 70\) meV was observed from resistivity...
4.3 Spin-orbit ground state and excitations in square-lattice iridates

Fig. 4.3 (a) Layered structure of Ba$_2$IrO$_4$. (b) The cluster used for the QC calculations. The Ba ions on top of each octahedron are not shown.

measurements [18]. Also here, the effect of the $5d$ SO interaction is strong enough to open, in cooperation with the $5d$ electronic correlations, a finite gap.

4.3.2.1 $d$-level electronic structure

A cluster of five IrO$_6$ octahedra and ten Ba ions was used to calculate the ground and excited states of a Ir$^{4+}$ $5d^5$ ion in Ba$_2$IrO$_4$ (see Fig. 4.3b). To cut off the spin couplings of the central Ir$^{4+}$ ion with the NNs, the latter were modeled with closed shell Pt$^{4+}$ $t^6_{2g}$ species. The calculated relative energies of the split Ir $t_{2g}$ levels, by both CASSCF and MRCI, are shown in Table 4.5. The lowest energy state implies a configuration with a hole in the in-plane $d_{xy}$ orbital and the states having the hole in the out-of-plane $d_{yz}/d_{xz}$ orbitals are at 0.07 eV higher in energy relative to the lowest state. This is in contrast to what was found in Sr$_2$IrO$_4$ – the lowest energy state features a hole in the $d_{yz}/d_{xz}$ orbitals. Although both compounds have positive tetragonal distortions (elongated apical Ir-O bonds), they thus show a different order of the Ir $t_{2g}$ levels. This difference can be understood from the fact that the magnitude of tetragonal distortion in Ba$_2$IrO$_4$ is large enough to overcome

<table>
<thead>
<tr>
<th>Orbital occupation</th>
<th>Relative energies (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CASSCF</td>
</tr>
<tr>
<td>$d_{xy}^1d_{xz}^2d_{yz}^2$</td>
<td>0.000</td>
</tr>
<tr>
<td>$d_{xy}^2d_{xz}^2d_{yz}^1$</td>
<td>0.070</td>
</tr>
<tr>
<td>$d_{xy}^2d_{xz}^1d_{yz}^2$</td>
<td>0.070</td>
</tr>
</tbody>
</table>
the field produced by farther neighbors (seemingly have an opposite effect, see Sec. 4.3.1.1),
eventually pushing the $d_{xy}$ orbital to higher energies, as canonical ligand-field theory pre-
dicts. In fact, a calculation of the $t_{2g}$ splittings for a hypothetical structure of $\text{Ba}_2\text{IrO}_4$, with
all Ir-O distances set to 2.015 Å (the in-plane Ir-O bond length in the actual $\text{Ba}_2\text{IrO}_4$ crystal
structure [18]), results in $\Delta t = -0.26$ eV, almost identical to the one obtained for an ideal-
ized $\text{Sr}_2\text{IrO}_4$ structure (see Table 4.2). In this hypothetical structure, only the single IrO$_6$
octahedron under investigation is made cubic. This way we can ensure that the solid-state
environment is same as in the experimental $\text{Ba}_2\text{IrO}_4$ structure.

The splittings resulting from the MRCI calculations (Table 4.5) are smaller by 5 meV
compared to the CASSCF values, suggesting that correlation effects involving the O 2$p$ –
Ir 5$d$ charge transfer (CT) states stabilize the $d_{xy}$ level as compared to the $d_{xz}/d_{yz}$ levels.
On the contrary, in $\text{Sr}_2\text{IrO}_4$ the MRCI treatment brings a 35 meV increase in the splitting,
see Table 4.1a. This is because in $\text{Sr}_2\text{IrO}_4$ the $d_{xy}$ orbital is the lowest in energy and a further
stabilization of the $d_{xy}$ level by CT-type correlation effects leads to an increase in the splitting.

With the inclusion of SOC, we find the ground state to be indeed close to the effective
$\tilde{j} = 1/2$ ground state in cubic environment and the excitations at 0.69 eV to be the (split) $\tilde{j} \approx
3/2$ states (see Table 4.6). This is reflected in the wave function composition for these three Kramers doublets. The $\tilde{j} \approx 3/2$ states are split by 0.05 eV, with the $m_{\tilde{j}} = \pm 1/2$ components
above the $m_{\tilde{j}} = \pm 3/2$, unlike in $\text{Sr}_2\text{IrO}_4$. This is due to the different sign of the $t_{2g}$
level splittings in the two compounds. With $\Delta t = 0.065$ eV, the admixture of $\tilde{j} = 1/2, m_{\tilde{j}} = \pm 1/2$
and $\tilde{j} = 3/2, m_{\tilde{j}} = \pm 1/2$ in the ground state is 99.8% : 0.2% (see Eq. 4.5). The splitting of the
$\tilde{j} \approx 3/2$ states from Eq. 4.6 turns out to be 0.04 eV, very similar to that deduced from the
MRCI+SOC results in Table 4.6.

The excitations into the $e_g$ levels are shown in Table 4.7. Without SO interactions we find
the quartet $^4T_{1g}$ ($t_{2g}^4 e_g$) states to be the lowest, at 2.07 eV (MRCI). The $^4T_{2g}$ ($t_{2g}^4 e_g$) states are
at 2.68 eV (MRCI), indicating a splitting of 0.61 eV between the $d_{z^2}$ and $d_{x^2−y^2}$ levels of the
$e_g$ symmetry. Interestingly, the $^4T_{2g}$ states are split into a lowest singlet and a higher doublet
in contrast to the $^4T_{1g}$ states that are split into a lower doublet and higher singlet. The lowest

<table>
<thead>
<tr>
<th>Table 4.6</th>
<th>Relative energies of effective total angular momentum Ir $t_{2g}^j$ states in Ba$_2$IrO$<em>4$. The composition of the SO coupled wave functions in the $t</em>{2g}$ orbital basis at CASSCF level is also shown.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO state</td>
<td>Relative energy (eV)</td>
</tr>
<tr>
<td>$\tilde{j} = 1/2, m_{\tilde{j}} = \pm 1/2$</td>
<td>0.000</td>
</tr>
<tr>
<td>$\tilde{j} = 3/2, m_{\tilde{j}} = \pm 1/2$</td>
<td>0.685</td>
</tr>
<tr>
<td>$\tilde{j} = 3/2, m_{\tilde{j}} = \pm 3/2$</td>
<td>0.726</td>
</tr>
</tbody>
</table>
4.3 Spin-orbit ground state and excitations in square-lattice iridates

doublet states $^2T_{1g}$ arising from the $t_{2g}^4 e_{g}^1$ configuration and the $^6A_{1g}$ sextet related to the $t_{2g}^3 e_{g}^2$ configuration occur at similar energies, 3.20 and 3.26 eV, respectively.

The SOC interaction (CASSCF+SOC & MRCI+SOC) now separates the $\tilde{j} \simeq 1/2$ and $\tilde{j} \simeq 3/2$ states by at least 0.84 eV, 0.15 eV higher compared to those obtained by neglecting off-diagonal SOCs (see Table 4.6) that bring into play the excited $t_{2g}^4 e_{g}^1$ configurations. The quartet and doublet states arising from the $t_{2g}^4 e_{g}^1$ configuration are also renormalized and raised to higher energies by 0.3 – 1.2 eV; the highest sextet state is pushed up by 1.04 eV to 4.30 eV.

**Table 4.7** Excitations between the Ir $t_{2g}$ and $e_g$ manifolds without (CASSCF & MRCI) and with inclusion of SOC (CASSCF+SOC & MRCI+SOC) in Ba$_2$IrO$_4$.

<table>
<thead>
<tr>
<th>Ir 5$d^4$ splittings</th>
<th>Relative energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CASSCF</td>
</tr>
<tr>
<td>$^2T_{2g}$ ($t_{2g}^5$)</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>0.071</td>
</tr>
<tr>
<td>$^4T_{1g}$ ($t_{2g}^4 e_{g}^1$)</td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td>2.05</td>
</tr>
<tr>
<td></td>
<td>2.05</td>
</tr>
<tr>
<td>$^4T_{2g}$ ($t_{2g}^4 e_{g}^1$)</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td>2.81</td>
</tr>
<tr>
<td>$^2T_{1g}$ ($t_{2g}^4 e_{g}^1$)</td>
<td>3.18</td>
</tr>
<tr>
<td></td>
<td>3.21</td>
</tr>
<tr>
<td></td>
<td>3.21</td>
</tr>
<tr>
<td>$^2A_{1g}$ ($t_{2g}^4 e_{g}^1$)</td>
<td>3.32</td>
</tr>
<tr>
<td>$^2T_{2g}$ ($t_{2g}^4 e_{g}^1$)</td>
<td>3.58</td>
</tr>
<tr>
<td></td>
<td>3.58</td>
</tr>
<tr>
<td></td>
<td>3.58</td>
</tr>
<tr>
<td>$^2E_{1g}$ ($t_{2g}^4 e_{g}^1$)</td>
<td>3.71</td>
</tr>
<tr>
<td></td>
<td>3.77</td>
</tr>
<tr>
<td>$^6A_{1g}$ ($t_{2g}^4 e_{g}^2$)</td>
<td>2.99</td>
</tr>
</tbody>
</table>
4.3.3 In-plane versus out-of-plane ionic charges, anomalous \( d \)-level splittings

To better understand the effect of longer-range crystal anisotropy in \( A_2\text{IrO}_4 \) (\( A=\text{Sr, Ba} \)), we performed additional calculations in which we changed the charges around the central \( \text{IrO}_6 \) octahedron. Doing this in a way that the total system stays charge neutral, we assigned the surrounding NN iridium ions a charge \( \text{Ir}^{(4-2\Delta q)+} \) and the \( A \)-site cations the valence \( A^{(2+\Delta q)+} \) (see Fig. 4.4). As illustrated in Fig. 4.4a, increasing \( \Delta q \) amounts to moving positive charge out of the \( \text{IrO}_2 \) plane into the inter-plane region. The \( \text{Ir} t_{2g} \) splittings \( (\Delta_t = E_{xy} - E_{xz/yz}) \), computed for different values of \( \Delta q \), are plotted in Fig. 4.4b. These were obtained from CASCI\(^7\) calculations using orbitals that were optimized for \( \Delta q = 0 \) (corresponds to the experimental scenario). The calculations show that \( \Delta_t \) increases upon moving charge out of the \( \text{IrO}_2 \) plane, i.e., this redistribution of charge counteracts the level inversion in \( \text{Sr}_2\text{IrO}_4 \) and further increases the already positive \( \Delta_t \) in \( \text{Ba}_2\text{IrO}_4 \). In \( \text{Sr}_2\text{IrO}_4 \) the perfectly cubic \( \tilde{j} = 1/2 \) limit occurs for \( \Delta q = 0.22 \). This effect can easily be understood: placing more positive charge out of the plane decreases the energy of out-of-plane \( t_{2g} \) orbitals, corresponding to the \( d_{zx}, d_{yz} \) orbital doublet, and thus increasing \( \Delta_t \). One can also perform the opposite and drive \( \Delta q \) negative. In this case more positive charge piles up in the \( \text{IrO}_2 \) plane, which is expected to lower

\[ \Delta_t (\text{eV}) \]

\[ \Delta_t (\text{eV}) \]

\[ \Delta_t (\text{eV}) \]

\[ \Delta_t (\text{eV}) \]

---

\(^{7}\) A CI expansion of the wave function within the active orbital space of the CASSCF calculation, i.e., the orbitals are not relaxed.
the energy of the \(d_{xy}\) orbital singlet, thus enhancing the inversion of Sr\(_2\)IrO\(_4\). This is indeed what happens, see Fig. 4.4b. What is more, driving \(\Delta q\) negative even causes a level inversion in Ba\(_2\)IrO\(_4\), when \(\Delta q < -0.25\). It is interesting to note that the slope of the \(\Delta\) versus \(\Delta q\) lines in Sr\(_2\)IrO\(_4\) is much steeper than in Ba\(_2\)IrO\(_4\), which is caused by the significantly smaller Ir-Ir distances in Sr\(_2\)IrO\(_4\).

To summarize this section, we have found that the Ir 5\(d_5\) ground state in Sr\(_2\)IrO\(_4\) and Ba\(_2\)IrO\(_4\) is close to the SOC \(\tilde{j} = 1/2\) state. The excitations into the \(\tilde{j} \simeq 3/2\) states at 0.66 eV in Sr\(_2\)IrO\(_4\) matches well the RIXS data in Ref. [40, 202]. Also the oxygen K-edge RIXS data on Ba\(_2\)IrO\(_4\) show multiple peaks at \(\sim 0.64\) eV [113], corresponding to excitations between the SO coupled \(\tilde{j} \simeq 1/2\) and \(\tilde{j} \simeq 3/2\) states. Importantly, the fine details of the resonant x-ray scattering data [200, 201] could only be understood with negative Ir \(t_{2g}\) splitting in Sr\(_2\)IrO\(_4\) and positive in Ba\(_2\)IrO\(_4\), as inferred from our \textit{ab initio} calculations [141].

### 4.4 Honeycomb-lattice iridates: Na\(_2\)IrO\(_3\) and Li\(_2\)IrO\(_3\)

The A\(_2\)IrO\(_3\) (A=Na,Li) [11, 12, 44, 111, 186, 203–205] family of iridate compounds have attracted much scientific interest in the context of Kitaev type of anisotropic magnetic interactions. These materials, showing insulating behavior [186, 204], were proposed to host a \(\tilde{j} = 1/2\) SO coupled ground state similar to the 214 square-lattice iridates. Due to their honeycomb-lattice structure with edge-sharing octahedra, they were put forward as ideal candidates for the realization of the Heisenberg-Kitaev model [11, 12, 111] that contains bond-dependent Kitaev interactions, which supports various types of topological phases relevant in quantum computing. Recent structural refinements find a sizable trigonal distortion of the IrO\(_6\) octahedra in these 213 compounds [42, 206] (see Fig. 4.5), which in principle may give rise to sizable splittings within the \(t_{2g}\) manifold. This loss of \(t_{2g}\) degeneracy could, in principle, drive the system away from the \(\tilde{j} = 1/2\) ground state. Theoretical studies have suggested that the ground state possibly contains large contributions from the \(\tilde{j} = 3/2\) high-lying states [207]. An \textit{ab initio} investigation and a detailed analysis of the ground state wave function and SO excitations in these materials is therefore highly desirable. A clear picture on the nature of the Ir on-site ground state configuration is essential for further understanding the magnetism of these compounds.

#### 4.4.1 Structural details

In Na\(_2\)IrO\(_3\) and Li\(_2\)IrO\(_3\), layers of edge-sharing IrO\(_6\) octahedra forming a hexagonal (honeycomb) arrangement of Ir ions are stacked alternatively along the \(c\)-axis (see Fig. 4.5(a)). The unit cell was first characterized to have a monoclinic \(C2/c\) space group symmetry [186, 208] with asymmetrically distorted IrO\(_6\) octahedra. However, later x-ray and neutron diffraction
experiments on single crystals of Na$_2$IrO$_3$ have concluded a monoclinic $C2/m$ unit cell [42] with more symmetric IrO$_6$ octahedra but nevertheless far enough from cubic. Fig. 4.5(c) shows the deviation of the O-Ir-O bond angles from $90^\circ$. This is due to the trigonal distortion of the IrO$_6$ octahedra, i.e., the O$_3$ faces of the IrO$_6$ octahedron perpendicular to the $c$-axis are pushed closer to the Ir ions. A similar structural refinement for Li$_2$IrO$_3$ after the initial reports led to the assignment of $C2/m$ space group symmetry [187]. Yet, the IrO$_6$ octahedra in Li$_2$IrO$_3$ are much more distorted (see Fig. 4.5(d)) than in Na$_2$IrO$_3$, with the Ir-O bonds differing in length by $\sim 10\%$. The lack of single-crystal samples of Li$_2$IrO$_3$ makes a detailed refinement of its structure difficult, especially the determination of the precise positions of ligand sites by x-ray structural probes as they are not particularly sensitive to light elements like oxygen [187, 208].

Fig. 4.5 (a) Layered structure of $A_2$IrO$_3$ ($A=$Na, Li), IrO$_2$ layers separated by Na/Li layers. The honeycomb arrangement of Ir ions is highlighted in red color. (b) Cluster with four IrO$_6$ octahedra and 15 Na/Li adjacent ions used in the QC calculations of $d$-level excitations. (c) The IrO$_6$ octahedron in Na$_2$IrO$_3$ [42]. The deviation of O-Ir-O bond angles from $90^\circ$ is due to trigonal distortion, i.e., the oxygen layers perpendicular to the $c$-axis are compressed towards the hexagonal Ir plane. (d) Ir-O bond lengths and O-Ir-O bond angles in the IrO$_6$ octahedron in Li$_2$IrO$_3$ [187] indicate that the octahedral distortions are much more stronger than in Na$_2$IrO$_3$. 
4.4 Honeycomb-lattice iridates: \( \text{Na}_2\text{IrO}_3 \) and \( \text{Li}_2\text{IrO}_3 \)

### 4.4.2 \( \text{Na}_2\text{IrO}_3 \): ground state and \( d \)-level excitations

Table 4.8 Relative energies (eV) of Ir \( d-d \) excitations in \( \text{Na}_2\text{IrO}_3 \). The first two columns (CASSCF and MRCI) show the splittings obtained without the inclusion of SOC; the last two columns (CASSCF+SOC and MRCI+SOC) show the SO splittings. The wave function composition of the SO \( t_{2g}^5 \) states obtained at the CASSCF level is also shown, in (b) and (c) (see text).

(a) Ir \( t_{2g} \) level excitations with the CAS[8,5] active space. The Ir NNs are modeled as \( \text{Ir}^{4+} t_{2g}^5 \) ions.

<table>
<thead>
<tr>
<th>( t_{2g} ) levels</th>
<th>no SOC</th>
<th>with SOC (( \times 2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CASSCF</td>
<td>MRCI</td>
</tr>
<tr>
<td>( E_0 )</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( E_1 )</td>
<td>0.000</td>
<td>0.009</td>
</tr>
<tr>
<td>( E_2 )</td>
<td>0.110</td>
<td>0.126</td>
</tr>
</tbody>
</table>

(b) Ir \( t_{2g} \) level excitations with a CAS[5,3] active space. The Ir NNs are modeled as closed-shell \( \text{Pt}^{4+} t_{6g}^2 \) ions.

<table>
<thead>
<tr>
<th>State</th>
<th>no SOC</th>
<th>with SOC (( \times 2 ))</th>
<th>WF composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CASSCF</td>
<td>MRCI</td>
<td>CASSCF+SOC</td>
</tr>
<tr>
<td>( E_0 )</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( E_1 )</td>
<td>0.000</td>
<td>0.027</td>
<td>0.673</td>
</tr>
<tr>
<td>( E_2 )</td>
<td>0.060</td>
<td>0.080</td>
<td>0.739</td>
</tr>
</tbody>
</table>

(c) Excitations among the \( t_{2g} \) and \( e_g \) manifolds obtained with a CAS[5,5] active space. The NN Ir ions are modeled as closed-shell \( \text{Pt}^{4+} t_{2g}^5 \) ions.

<table>
<thead>
<tr>
<th>State</th>
<th>no SOC</th>
<th>with SOC (( \times 2 ))</th>
<th>WF composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CASSCF</td>
<td>MRCI</td>
<td>CASSCF+SOC</td>
</tr>
<tr>
<td>( t_{2g}^5 e_g ):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_0 )</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( E_1 )</td>
<td>0.002</td>
<td>0.024</td>
<td>0.828</td>
</tr>
<tr>
<td>( E_2 )</td>
<td>0.059</td>
<td>0.073</td>
<td>0.885</td>
</tr>
<tr>
<td>( t_{2g}^4 e_g^1 ):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_3 )</td>
<td>2.26</td>
<td>2.44</td>
<td>2.66; 2.71</td>
</tr>
<tr>
<td>( E_4 )</td>
<td>2.29</td>
<td>2.48</td>
<td>2.85; 3.06</td>
</tr>
<tr>
<td>( E_5 )</td>
<td>2.33</td>
<td>2.53</td>
<td>3.11; 3.20</td>
</tr>
<tr>
<td>( E_6 )</td>
<td>2.90</td>
<td>3.00</td>
<td>3.71; 3.73</td>
</tr>
<tr>
<td>( E_7 )</td>
<td>3.03</td>
<td>3.13</td>
<td>3.80; 3.90</td>
</tr>
<tr>
<td>( E_8 )</td>
<td>3.10</td>
<td>3.21</td>
<td>3.98; 4.02</td>
</tr>
<tr>
<td>( t_{2g}^3 e_g^2 ):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_9 )</td>
<td>3.48</td>
<td>4.03</td>
<td>4.57; 4.58; 4.59; 5.03; 5.04; 5.04</td>
</tr>
</tbody>
</table>

The on-site Ir \( d-d \) excitations computed for \( \text{Na}_2\text{IrO}_3 \) are summarized in Table 4.8. The
calculations were performed on a cluster containing a central IrO$_6$ octahedron, the three adjacent NN IrO$_6$ octahedra and 15 NN Na ions (see Fig. 4.5(b)). The splittings within the $t_{2g}$ levels shown in Table 4.8a were obtained from calculations in which the NN Ir sites were modeled as open-shell Ir$^{4+}$ with a $t_{2g}^5$ configuration. The active space in the CASSCF calculations consisted of the three $t_{2g}$ orbitals, five electrons of the central Ir and the singly occupied molecular-like $t_{2g}$ orbitals of the three NN Ir sites (CAS[8,5]). In the scalar-relativistic calculation, the four Ir $S = 1/2$ sites can couple into quintet, triplet and singlet states. The splittings on the left without SO coupling correspond to the high-spin coupled state ($S = 2$). At the CASSCF level, one finds that two of the Ir $t_{2g}$ levels are degenerate. However, with the inclusion of dynamic correlation effects they are split by 9 meV. We find the highest state at 120 meV in MRCI calculations. The inclusion of SO interactions results in an electronic structure with the lowest charge excitation from the ground state at 0.66 – 0.70 eV. The finite spread of this state arises due to the coupling of the different spin multiplets entering the SOC calculations.

Table 4.8b shows the Ir $t_{2g}$ level splittings when the NN Ir sites are modeled as Pt$^{4+}$ with a $t_{2g}^6$ closed-shell configuration. The active space in this calculation consists of only the central Ir $t_{2g}$ orbitals and the five electrons in them (CAS[5,3]). Due to the additional spin interactions with the Ir NNs, the splittings in Table 4.8a are slightly larger than in Table 4.8b. However, the SO excitations do not differ by more than 10 meV. This allows us to consider the NN Ir sites to be closed-shell in further calculations. From the composition of the SO wave functions shown in the last three columns of Table 4.8b, it is clear that the ground state is in fact nearly $\tilde{j} = 1/2$ and that the states at 0.66 – 0.77 eV are the $\tilde{j} \approx 3/2$ quartet states. The latter are split by 0.11 eV into two Kramers doublets. Using the $\lambda - \Delta$ model, we find that the ground state is a mixture of $\tilde{j} = 1/2$ and $\tilde{j} = 3/2$ states by 99.4% : 0.6% and the splitting of the $\tilde{j} = 3/2$ states to be 0.07 eV. This estimation is slightly different from that obtained by QC calculations due to the limitations of the model employed, specifically that the QC calculations include the effect of high energy states such as those of the charge-transfer type.

In Table 4.8c, excitations within the $t_{2g}$ manifold and from the $t_{2g}$ to $e_g$ subspaces are presented. The NN Ir sites are closed-shell and the active space consists of five $d$ orbitals and five electrons of the central Ir (CAS[5,5]). With SOC switched on, we find an increase in the $\tilde{j} = 1/2 \rightarrow 3/2$ excitation energies by 0.16 eV. This is due to off-diagonal SOC matrix elements (see App. A.5) that admix the $t_{2g}^5$ and $t_{2g}^4 e_g^1$ states.

The excited $t_{2g}^4 e_g^1$ states without SOC start at 2.26 eV and extend up to 3.10 eV. With the inclusion of SO interactions, these states are shifted to higher energies by at least 0.5 eV. The MRCI+SOC calculations estimates them to be in the range 2.8 – 4.1 eV. The $t_{2g}^3 e_g^2$ state is positioned at 3.48 eV at the CASSCF level and the SO interactions pushes it to 4.6 eV. For this state, the MRCI (MRCI+SOC) brings as much as 0.5 eV change to the CAS (CAS+SOC) energy, shifting it to higher energies.
4.4 Honeycomb-lattice iridates: Na$_2$IrO$_3$ and Li$_2$IrO$_3$

### 4.4.3 Li$_2$IrO$_3$: mixing of $\tilde{j} = 1/2$ and $\tilde{j} = 3/2$ states

The QC results for the on-site $d$-$d$ excitations in Li$_2$IrO$_3$ are summarized in Table 4.9. Calculations were carried out on a cluster similar to the one used for Na$_2$IrO$_3$, with a central IrO$_6$ octahedron and three surrounding NN IrO$_6$ octahedra along with 15 nearby Li ions. The results in Table 4.9a were obtained from calculations where the three $t_{2g}$ orbitals and five $t_{2g}$ valence electrons of the central iridium were considered in the active space (CAS[5,3]). It can be seen that in the scalar-relativistic calculation the $t_{2g}$ levels are split by as much as 0.34 eV at the MRCI level. This large separation among the $t_{2g}$ levels results in a ground state that is an admixture of $\tilde{j} = 1/2, m_j = \pm 1/2$ and $\tilde{j} = 3/2, m_j = \pm 1/2$ states (see Eq. 4.5), when the SOC is included. This removal of the Ir $t_{2g}$ orbital degeneracy also causes a splitting of

| Table 4.9 Relative energies (eV) of Ir 5$d$ levels in Li$_2$IrO$_3$. The NN Ir sites are modeled as closed-shell Pt$^{4+}$ $t_{2g}^6$ ions. |
|---|---|---|---|---|
| **(a) Ir $t_{2g}$ levels calculated with the CAS[5,3] active space.** | | | |
| State | no SOC | with SOC (×2) | | |
| | CASSCF | MRCI | CASSCF+SOC | MRCI+SOC |
| $E_0$ | 0.000 | 0.000 | 0.000 | 0.000 |
| $E_1$ | 0.262 | 0.267 | 0.664 | 0.662 |
| $E_2$ | 0.309 | 0.341 | 0.816 | 0.833 |
| **(b) Ir $d$-$d$ excitation energies obtained with the CAS[5,5] active space.** | | | |
| State | no SOC | with SOC (×2) | | |
| | CASSCF | MRCI | CASSCF+SOC | MRCI+SOC |
| $t_{2g}^5$: | | | |
| $E_0$ | 0.00 | 0.00 | 0.00 | 0.00 |
| $E_1$ | 0.25 | 0.27 | 0.78 | 0.80 |
| $E_2$ | 0.30 | 0.33 | 0.95 | 0.97 |
| $t_{2g}^4e_g^1$: | | | |
| $E_3$ | 2.62 | 2.84 | 2.89; 3.11 | 3.05; 3.28 |
| $E_4$ | 2.82 | 2.93 | 3.29; 3.39 | 3.40; 3.53 |
| $E_5$ | 2.88 | 3.03 | 3.53; 3.59 | 3.67; 3.73 |
| $E_6$ | 3.61 | 3.65 | 4.06; 4.14 | 4.12; 4.20 |
| $E_7$ | 3.66 | 3.74 | 4.24; 4.40 | 4.31; 4.45 |
| $E_8$ | 4.27 | 4.31 | 4.91; 4.94 | 4.95; 4.97 |
| $t_{2g}^3e_g^2$: | | | |
| $E_0$ | 4.59 | 5.05 | 5.43; 5.44 | 5.45; 5.83 | 5.83 | 5.84 |
the $\bar{j} = 3/2$ quartet states. By MRCI+SOC calculations, the latter splitting was found to be 0.17 eV. From Eq. 4.6, an estimate of 10% of $\bar{j} = 3/2, m_j = \pm 1/2$ character in the ground state is obtained.

Excitations calculated with an active space consisting of all five Ir 5d orbitals and five electrons are shown in Table 4.9b. As for Na$_2$IrO$_3$, the splittings between the $\bar{j} \simeq 1/2$ and $\bar{j} \simeq 3/2$ states increase by 0.14 eV by increasing the active orbital space (see first three rows in the last column, MRCI+SOC, of Tables 4.9a and 4.9b). This is again the outcome of off-diagonal elements, $t_{2g}^5 - t_{2g}^{4}e_g^1$, of the SO matrix. A slight difference in this enhancement of the excitation energy of the $\bar{j} \simeq 3/2$ SO exciton in the two compounds, 0.16 eV in Na$_2$IrO$_3$ vs. 0.14 eV in Li$_2$IrO$_3$, is due to the slightly different $t_{2g} - e_g$ splittings, 2.44 (see Table 4.8c) vs. 2.84 eV (see next paragraph and Table 4.9b), respectively.

The $t_{2g}^{4}e_g^1$ states in Li$_2$IrO$_3$ start at 2.84 eV in the scalar-relativistic MRCI calculations. The inclusion of SOC shifts them to at least 3.05 eV. The $t_{2g}^{3}e_g^2$ ($^6A_{1g}$ in $O_h$ point group symmetry) state is at 5.05 eV without SOC and upon switching on the latter, the related SO state is pushed up to 5.84 eV.

4.4.4 Comparison with RIXS data

A comparison of the excitations calculated in the previous sections with RIXS measurements for the Na$_2$IrO$_3$ and Li$_2$IrO$_3$ compounds is shown in Fig. 4.6. It is seen that the MRCI+SOC data for Na$_2$IrO$_3$ (Table 4.8c) fit the RIXS spectrum reasonably well, with the peaks B and C corresponding to $\bar{j} \simeq 1/2 \rightarrow 3/2$ transitions. Interestingly, without including off-diagonal SO matrix elements that admix the $t_{2g}^{5}$ and $t_{2g}^{4}e_g^1$ states, the excitations corresponding to peak positions B and C are found at lower energies (see last column in Table 4.8b). This suggests that the coupling to $t_{2g}^{4}e_g^1$ states is essential to obtain the correct excitation energies for the $\bar{j} \simeq 3/2$ SO exciton in these compounds. Above 2.5 eV, the MRCI+SOC results indicate multiple

![Fig. 4.6 Left: RIXS spectrum for a single-crystal of Na$_2$IrO$_3$ and a powder sample of Li$_2$IrO$_3$ (for further details, see Ref. [185]). Right: Comparison of excitation energies obtained from MRCI+SOC calculations and the RIXS measurements.](image-url)
to $e_g$ excitations displaying a two-peak structure reminiscent of the D and E features in the RIXS spectra. Although a direct comparison is difficult due to the broad spectral width of the D and E excitations, the MRCI+SOC seems to somewhat overestimate the relative energies of those latter features. Still, for Li$_2$IrO$_3$ the calculations correctly reproduce the shift to higher energies of the Ir $t_{2g}$ to $e_g$ transitions relative to those in Na$_2$IrO$_3$. Some discrepancies between the experimental values and the MRCI+SOC results (e.g., peak C) could be caused by the uncertainty in the structural model used for this calculation (C2/m from Ref. [187]).

In conclusion, the ground state of the Ir$^{4+}$ ion in the 213 honeycomb iridate Na$_2$IrO$_3$ is predominantly $j = 1/2$, with an admixture of $j = 3/2, m_j = \pm 1/2$ character of less than 1%. In Li$_2$IrO$_3$, on the other hand, this admixture is as large as 10%, indicating a strong deviation from the $j = 1/2$ picture. Moreover, we find that the coupling due to the off-diagonal SO matrix elements is important to describe the $j = 1/2 \rightarrow 3/2$ excitations for both the compounds.

### 4.5 “Zero”-dimensional Sr$_3$CuIrO$_6$

The strong SOC limit assumes local cubic symmetry with perfect IrO$_6$ octahedra. However, compounds proposed for the realization of several theoretical models in general have non-ideal octahedra. As we have seen in the square-lattice (Ae$_2$IrO$_4$, Ae=Ba,Sr) and hexagonal lattice systems (A$_2$IrO$_3$, A=Li,Na), the $t_{2g}$ levels are split due to the noncubic crystal fields arising from the distortion of the O octahedra as well as farther crystal anisotropy. With the intention of better understanding the interplay of SOC and noncubic crystal fields, we here study the iridate compound Sr$_3$CuIrO$_6$. Although the IrO$_6$ octahedra in this material feature only small distortions, the noncubic crystal fields due to the highly anisotropic chain-like structure [209] influence the electronic structure of the Ir$^{4+}$ ion significantly.

Sr$_3$CuIrO$_6$ is a quasi-one-dimensional material with a monoclinic structure [209, 210]. Individual IrO$_6$ octahedra are linked by spin-1/2 Cu$^{2+}$ ions along one direction, forming a chain structure, see Fig. 4.7. Moreover, the open-shell $d_{x^2−y^2}$ orbitals at the NN Cu sites are essentially orthogonal to the $t_{2g}$ orbitals on the Ir site. This effectively suppresses the inter-site hopping. Even though correlation effects are reduced due to the large radial extent of the 5$d$ orbitals, this special crystallographic arrangement puts Sr$_3$CuIrO$_6$ in the strongly localized regime. Thus, this compound can be to a large extent regarded as a zero dimensional material.

A single Cu-Ir-Cu chain of Sr$_3$CuIrO$_6$ is shown in Fig. 4.7, with the local coordinates for a given IrO$_6$ octahedron marked. The O-Ir-O bonds are straight and of similar length, with differences of less than 2%. The distortion of the IrO$_6$ octahedra mainly consists of rotations of the O-Ir-O bonds – the in-plane bonds along the $x$ and $y$ directions, for instance, rotate towards each other (see the arrows in Fig. 4.7), reducing the angle from 90° to 80°. Further,
Electronic structure: ground state and \(d-d\) excitations in \(\text{Ir}^{4+}\) compounds

The QC calculations were carried out on a cluster which contains a central \(\text{IrO}_6\) octahedron, two NN \(\text{CuO}_4\) plaquettes and the adjacent Sr atoms, properly embedded in a large array of PCs to reproduce the Madelung crystal field in the cluster region. To cut off the spin-couplings of the Ir spins with the NN Cu spins, the \(\text{Cu}^{2+}\) ions were substituted with closed-shell Zn\(^{2+}\) \(d^{10}\) species. The effect of noncubic crystal fields was studied by first turning off the SO coupling. The results of such calculations are illustrated in Table 4.10. An active space consisting of the three Ir \(t_2g\) orbitals and the corresponding five electrons (CAS\([5,3]\)) was first used. Although the distortions of the IrO\(_6\) octahedra are small, all the \(t_2g\) levels are split. The states with lowest energies \(E_0\) and \(E_1\) have dominant contribution from the configurations with a hole in the \(d_{xz}\) and \(d_{yz}\) orbitals. The third state has large contribution from the configuration with a hole in the \(d_{xy}\) orbital and is separated from the lowest \(t_2g\) hole state by as much as 0.49 eV at the MRCI level. This significant noncubic crystal field splitting is comparable to the SOC strength and consequently has a strong effect on the relevant SO wave functions.

In Table 4.11, the calculated SO excitations and the percentage contributions of various Ir \(5d^5\) configurations to the respective wave functions are shown. Low-energy excitations within the \(t_2g^2\) manifold occur at 0.59 and 0.91 eV and the Ir \(t_2g^2\) to \(t_2g^1e_g^1\) excitations are between 3.2 and 4.9 eV. Further, excitation energies of \(\sim 5.9\) eV were calculated for the Ir \(t_2g^3e_g^2\) states. We also found O \(2p\) to Ir \(5d\) charger transfer transitions between 3.5 and 5.4 eV (not shown in the table).

**Table 4.10** Splittings within the Ir \(t_{2g}\) shell in \(\text{Sr}_3\text{CuIrO}_6\) without spin-orbit coupling. The active space consists of three \(t_{2g}\) orbitals and five electrons of the central Ir ion. The hole orbital that has a dominant contribution to the wave function is shown in brackets.

<table>
<thead>
<tr>
<th>(t_{2g}) levels</th>
<th>Relative energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_0 (d_{xz}))</td>
<td>0.00 (\text{CASSCF}) 0.00 (\text{MRCI})</td>
</tr>
<tr>
<td>(E_1 (d_{yz}))</td>
<td>0.11 (\text{CASSCF}) 0.13 (\text{MRCI})</td>
</tr>
<tr>
<td>(E_2 (d_{xy}))</td>
<td>0.44 (\text{CASSCF}) 0.49 (\text{MRCI})</td>
</tr>
</tbody>
</table>

The O-Ir-O bonds along the \(z\) axis are tilted towards the NN Cu atoms by \(\sim 4^\circ\).
4.5 “Zero”-dimensional Sr$_3$CuIrO$_6$

Table 4.11 Percentage contributions of various Ir 5$d^5$ configurations to the different excitations. The results are obtained from MRCI + SOC calculations.

<table>
<thead>
<tr>
<th>Config.</th>
<th>Energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>$d_{xy}^{2}, d_{xz}^{2}, d_{yz}^{1}$</td>
<td>37.1</td>
</tr>
<tr>
<td>$d_{xy}^{2}, d_{xz}^{1}, d_{yz}^{2}$</td>
<td>49.0</td>
</tr>
<tr>
<td>$d_{xy}^{1}, d_{xz}^{2}, d_{yz}^{2}$</td>
<td>13.9</td>
</tr>
<tr>
<td>$t_{2g}^4 e_{g}^{1}$</td>
<td></td>
</tr>
<tr>
<td>$t_{2g}^3 e_{g}^{2}$</td>
<td></td>
</tr>
</tbody>
</table>

The contributions of the different orbital configurations to the wave function of each SO state within the $t_{2g}^5$ manifold show significant deviation from the values corresponding to a pure $\tilde{j} = 1/2$ state. In the ground state, the contribution from the $d_{xy}$ orbitals is reduced by >40%. This significant modification affects the density profile of the ground state wave function, as shown in Fig. 4.8.

The comparison of the excitation energies calculated by QC methods with those found in the RIXS measurements is shown in Fig. 4.8a. It can be seen that the energy peak positions in the spectrum are nicely reproduced by QC calculations. This good agreement between the calculated values and the experimental observations confirms the reliability of our calculations for highly anisotropic systems.

Using the $\lambda - \Delta$ model introduced in Sec. 4.3.1.2, with a $\Delta_t = 0.49$ eV for Sr$_2$CuIrO$_6$, we obtain the mixing of $\tilde{j} = 1/2, m_j = \pm 1/2$ and $\tilde{j} = 3/2, m_j = \pm 1/2$ terms to be 88% : 12% for the ground state. The splitting between the two components of the $\tilde{j} \simeq 3/2$ quartet is 0.24 eV.

![Fig. 4.8](image-url) (a) RIXS spectra obtained for Sr$_3$CuIrO$_6$. For details, see [116]. Vertical and horizontal bars indicate the excited states listed in Table 4.11, as obtained from the MRCI+SOC calculations. (b) Density profile of the Ir $t_{2g}$ hole. Left: $\tilde{j} = 1/2$ density profile for perfect IrO$_6$ octahedra. Right: the modified wave function due to the noncubic crystal fields.
eV. This value is 0.08 eV smaller than what is found from the \textit{ab initio} QC calculations (see Table 4.11).

To conclude, our results for Sr$_3$CuIrO$_6$ reiterate that the long range crystal fields strongly influence the electronic structure of the Ir 5$d$ levels. Although the IrO$_6$ octahedra in this compound are moderately distorted, we find the splittings induced by the noncubic fields (due to both distortions in the oxygen cage and the anisotropic long range environment) to be of similar strength as the SO coupling. This drives the system away from the strong SO coupling limit ($\lambda \gg \Delta$) and significantly modifies the relevant wave functions, which then have important consequences for, e.g., the magnetic exchange interactions.

4.6 Na$_4$Ir$_3$O$_8$ – hyperkagome lattice

Proposed as a candidate material for hosting a spin-liquid phase [211], Na$_4$Ir$_3$O$_8$ has a three dimensional network of corner-sharing Ir$^{4+}$ triangles (see Fig. 4.9) forming a hyperkagome lattice [211]. Magnetic susceptibility measurements for $T \geq 1.8$ K showed no signs of magnetic ordering, despite the existence of strong AF interactions suggested by a large Curie-Weiss constant $\theta_W \sim -650$ K [211]. Initially, the SO interactions were ignored and the Ir$^{4+}$ ions were thought to host “pure” $S = 1/2$ spin moments (low-spin $t_2^5g$ configuration) [211]. Both classical and semiclassical simulations with Heisenberg interactions on the geometrically frustrated hyperkagome lattice show that the ground state is highly degenerate [213]. A 120° coplanar magnetically ordered state [214] obtained from a semiclassical model was found to lead to a gapped topological spin-liquid phase [214] with the inclusion of quantum fluctuations. The latter prediction, however, contradicts the experimental observation of a large $\chi$ and entropy at low temperatures, which indicate the survival of gapless spinful excitations for $T \ll \theta_W$ [211, 215]. A quantum spin-liquid phase with gapless spinon Fermi surfaces was later suggested as a favorable candidate for the ground state of the AF Heisenberg model on the hyperkagome-lattice [216, 217].

Later on, it was shown that the anisotropic exchange interactions induced by SO interactions that break the $SU(2)$ spin-rotation symmetry relieve frustration and may give rise to magnetic ordering at low temperatures [218]. In the strong spin-orbit coupling limit (with idealized IrO$_6$ octahedra) the proposed superexchange mechanism leads to an “unfrustrated” spin Hamiltonian, predicting an ordered state. On the other hand, in the weak spin-orbit coupling limit (SO interactions have only a perturbative effect), it was shown that it is the antisymmetric DM anisotropy that relieves the frustration in the Heisenberg model [218].

The exchange interactions depend crucially upon the relative magnitude of the SO cou-

\footnote{In the kagome structure the corner-sharing triangles lie in a plane, but in the hyperkagome arrangement they are arrayed in three dimensions [212].}

\footnote{The spin are treated as classical $O(N)$ vectors.
4.6 Na$_4$Ir$_3$O$_8$ – hyperkagome lattice

Fig. 4.9 (a) Hyperkagome lattice formed by the edge-sharing IrO$_6$ octahedra in Na$_4$Ir$_3$O$_8$. (b) The cluster used for the QC calculations. The IrO$_6$ octahedra have different Ir-O bond lengths and the O-Ir-O bond angles (not indicated) vary from 92.4° to 98.6°, making the O-cage crystal field noncubic.

pling strength $\lambda$ and the noncubic splittings of the Ir $t_{2g}^5$ multiplet. We here calculate the Ir$^{4+}$ crystal field parameters by ab initio QC methods and address the effect of the noncubic environment on the order of the electronic levels. Subsequently, the interplay of SO interactions and crystal field splittings in determining the local ground state electronic configuration in this interesting 3D spin-liquid candidate material is discussed.

The IrO$_6$ octahedra in Na$_4$Ir$_3$O$_8$ have three different Ir-O bond lengths, as shown in Fig. 4.9b. Moreover, the O-Ir-O bond angles strongly deviate from 90° and no two of them are equal. This makes the local crystal fields around the Ir ions highly anisotropic. The QC calculations were performed on a five-octahedra cluster (one central and four NN octahedra) that is embedded in an array of PCs, see Fig. 4.9b. The NN Ir sites were modeled as closed-shell Pt$^{4+}$ $t_{2g}^6$ ions. We used the unit cell parameters from Ref. [211].

The relative energies of the Ir $d$ levels calculated on such a cluster are summarized in Table 4.12. Those obtained from calculations with a CAS[5,3] active space (three $t_{2g}$ orbitals and five electrons of the central Ir) are shown in Table 4.12a. It can be seen that the $t_{2g}$ levels are split by 0.42 eV in the scalar-relativistic calculation. With the inclusion of SO coupling, the excitations into the split $\tilde{j} \simeq 3/2$ states are computed at 0.63 and 0.90 eV at the MRCI level. The ground state Kramers doublet is hence an admixture of SO coupled $\tilde{j} = 1/2$ and $\tilde{j} = 3/2$ states. The composition of the SO ground state wave function obtained from the $\lambda - \Delta$ model is 90 : 10 % admixture of $\tilde{j} = 1/2, m_{\tilde{j}} = \pm 1/2$ and $\tilde{j} = 3/2, m_{\tilde{j}} = \pm 1/2$ states, respectively. The estimate for the splitting between $\tilde{j} = 3/2, m_{\tilde{j}} = \pm 1/2$ and $\tilde{j} = 3/2, m_{\tilde{j}} = \pm 3/2$ of 0.22 from this model is close to the 0.27 eV value obtained from the QC calculations (see Table 4.12a). A 10% admixture of $\tilde{j} = 3/2$ states in the ground state
wave function may lead to considerable deviations in the magnetic exchange processes from those between $\tilde{j} = 1/2$ moments.

In Table 4.12b, relative energies obtained from calculations with an active space given by five electrons and five Ir $d$-orbitals (CAS[5,5]) are shown. As for the other Ir$^{4+}$ compounds discussed in this chapter, the excitation energy within the $t_{2g}$ states, $\tilde{j} \simeq 1/2 \rightarrow \tilde{j} \simeq 3/2$, is increased by 0.15 eV (24%) with this larger active space. However, the splitting of the $\tilde{j} \simeq 3/2$ states is decreased marginally to 0.25 eV at the MRCl level. In the scalar-relativistic MRCl calculations the $t_{2g}^4 \epsilon_{g}^{1}$ states were found to start at 2.78 eV and the $t_{2g}^3 \epsilon_{g}^{2}$ states at 4.85 eV (see Table 4.12b, third column). The MRCl+SOC calculations “renormalize” these states and shift them to higher energies to 3.00 and 5.4 eV, respectively.

In conclusion, we found the Ir$^{4+}$ ion in Na$_4$Ir$_3$O$_8$ to have an effective total-angular-momentum ground state that is predominantly of $\tilde{j} = 1/2$ character with 10% admixture

Table 4.12 Relative energies (eV) of Ir 5$d$-levels in Na$_4$Ir$_3$O$_8$.

(a) Ir $t_{2g}$ excitations with a CAS[5,3] active space.

<table>
<thead>
<tr>
<th>State</th>
<th>no SOC</th>
<th>with SOC (×2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CASSCF</td>
<td>MRCl</td>
</tr>
<tr>
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<td>0.00</td>
</tr>
<tr>
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<td>$E_2$</td>
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<td>0.42</td>
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(b) Ir $d$-$d$ excitation energies with a CAS[5,5] active space.

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<th>with SOC (×2)</th>
</tr>
</thead>
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<td>CASSCF</td>
<td>MRCl</td>
</tr>
<tr>
<td>$t_{2g}^5$:</td>
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<tr>
<td>$E_0$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$E_1$</td>
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<td>0.42</td>
</tr>
<tr>
<td>$t_{2g}^4 \epsilon_{g}^{1}$:</td>
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<td></td>
</tr>
<tr>
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</tr>
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<tr>
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<td>3.72</td>
</tr>
<tr>
<td>$t_{2g}^3 \epsilon_{g}^{2}$:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| $E_9$  | 3.92   | 4.54          | 4.85; 4.85 | 5.38; 5.39 | 5.40
of $\tilde{j} = 3/2, m_j = 1/2$ states. The compound should thus be considered as having a strong SO coupled ground state with perturbations driving it slightly away from the $\tilde{j} = 1/2$ state. Highly anisotropic exchange interactions are thus expected and all symmetry allowed anisotropic exchange couplings (symmetric and antisymmetric) must be taken into account apart from the isotropic Heisenberg interactions in the effective spin Hamiltonian in order to understand the intriguing magnetic behavior of Na$_4$Ir$_3$O$_8$.

### 4.7 Summary and conclusions

In this chapter, we have analyzed the electronic structure of six different iridium oxide compounds displaying four different types of lattice structures: 2D square-lattice Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$, layered honeycomb-lattice Na$_2$IrO$_3$ and Li$_2$IrO$_3$, chain-like Sr$_3$CuIrO$_6$ and hyperkagome Na$_4$Ir$_3$O$_8$. We first used scalar-relativistic QC calculations to compute the energies of the Ir 5$d$ levels and from there derived ab initio values for the crystal field splittings, parameters which are important to comprehend the SO ground state and excitations. The excitations obtained by relativistic SO calculations were then compared with the available RIXS data. Good to excellent agreement was found between theory and experiment.

We found that the presence of anisotropic crystal fields around the Ir ion in 2D square-lattice iridates such as Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$, due to the tetragonally distorted oxygen cages as well as longer-range crystal anisotropy, splits the $t_{2g}$ levels. In particular, the Ir $t_{2g}$ splitting in Sr$_2$IrO$_4$ were found to be negative, in spite of sizable positive tetragonal distortions. We further observed that the much stronger tetragonal distortion in Ba$_2$IrO$_4$ renders the tetragonal splitting positive. Nevertheless, the interesting situation arises that the magnitude of the Ir $t_{2g}$ splitting is largest in Sr$_2$IrO$_4$. The $d$-level inversion in Sr$_2$IrO$_4$ and the surprisingly small splitting in Ba$_2$IrO$_4$ have to do with the way the positive ionic charge is distributed between adjacent Ir$^{4+}$O$_2$ and A$^{2+}$O layers, having more positive charge in the TM-O planes. This is in contrast to the 214 cuprate superconductors, where the positive charge is distributed more evenly among in-plane Cu$^{2+}$ and out-of-plane R$^{3+}$ ions. This excess of in-plane positive charge in 214 iridates almost compensates the “local” tetragonal field arising from the $z$-axis elongation of the IrO$_6$ octahedra in Ba$_2$IrO$_4$ and over-compensates it in Sr$_2$IrO$_4$.

Yet, the SO ground state in both compounds is very close to the effective total angular momentum $\tilde{j} = 1/2$ state, with a very small admixture of $\tilde{j} = 3/2$ character in the range of only 1%. The fact that the order of the Ir $t_{2g}$ levels is different in the two compounds makes that the excited $\tilde{j} = 3/2, m_j = \pm 3/2$ state is lower than the $\tilde{j} = 3/2, m_j = \pm 1/2$ state in Sr$_2$IrO$_4$ and vice versa in Ba$_2$IrO$_4$.

In the honeycomb lattice compound Na$_2$IrO$_3$ we found Ir $t_{2g}$ splittings of 0.11 eV. The admixture of $\tilde{j} = 3/2, m_j = \pm 1/2$ states into the ground state wave function was calculated to be less than a percent. However, in Li$_2$IrO$_3$, the highly distorted IrO$_6$ octahedra give rise to
large $t_{2g}$ splittings, as high as 0.34 eV. As a result, the SO ground state wave function displays $\sim 10\% \ 3/2$ character. In these trigonally distorted compounds, we determined that the off-diagonal SO matrix elements which couple the $t^5_{2g}$ and $t^4_{2g}e^1_{g}$ manifolds are important and need to be considered to obtain good agreement with the experimentally measured (RIXS) excitation peaks.

In the last two compounds that we looked at, Sr$_3$CuIrO$_6$ and Na$_4$Ir$_3$O$_8$, we found the Ir $t_{2g}$ splittings to be of the same size as the strength of SOC. Nevertheless, the ground state is dominantly of $3/2$ character, $\geq 85\%$, and the “average” $j \simeq 1/2 - j \simeq 3/2$ energy separation is approximately the same as in other iridates. In fact, the calculated SO excitations agree perfectly with the RIXS measurements in Sr$_3$CuIrO$_6$. This validates the use of QC methods for low-symmetry compounds displaying highly anisotropic crystal fields.

In conclusion, the Ir $t_{2g}$ levels are sensitive to both the low-symmetry fields associated with the anisotropic extended surroundings and the local distortions of the oxygen cages. The SO ground state is nonetheless dominantly of $3/2$ character in the particular compounds we addressed in this chapter.
Chapter 5

Spin-orbit coupling observables: \( \langle Z \rangle \) operator and branching ratio

In this chapter, we address the origin of the large expectation values of the spin-orbit coupling operator \( \langle Z \rangle \) extracted from x-ray absorption experiments for the Ir\(^{4+} \) 5d\(^5 \) configuration. We present the \( \langle Z \rangle \) values obtained for Sr\(_2\)IrO\(_4\) and Ba\(_2\)IrO\(_4\) by quantum chemistry methods and further analyze the contributions of multiplet states arising from the different electronic configurations \( t_{2g}^5, t_{2g}^4e_g^1 \) and \( t_{2g}^3e_g^2 \) to \( \langle Z \rangle \).

5.1 Introduction

Due to the evidently important role played by SO coupling in iridium oxide compounds, it is necessary to quantify the effect of SO interactions on a particular ground state. One way to analyze this experimentally is by using x-ray absorption spectroscopy (XAS). Van der Laan and Thole [219–221] have pointed out that the ratio between the integrated intensities at the \( L_3 \) and \( L_2 \) 2p absorption edges, \( I_{L_3} \) and \( I_{L_2} \), also referred to as branching ratio, is directly related to the ground state expectation value of the angular part of the spin-orbit operator \( Z = \sum_i l_i \cdot s_i \), where \( l_i \) and \( s_i \) are one-electron orbital angular momentum and spin operators, respectively. Such XAS experiments have been recently employed to investigate the role of SO coupling in iridium oxide compounds [222, 223] and surprisingly large values of the branching ratios have been reported. However, different experimental studies have resulted in estimates that are significantly disagreeing with each other [222, 223]. To obtain a proper and systematic understanding of the evolution of these expectation values, quantum chemistry calculations are used in this chapter to calculate and analyze the respective quantities.

Large part of this chapter is published in Inorg. Chem. 53(10), 4833 (2014) [141].
Spin-orbit coupling observables: $\langle Z \rangle$ operator and branching ratio

specifically for the 2D square-lattice compounds Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$.

5.2 Branching ratio in x-ray absorption spectra and spin-orbit operator in 5$d^5$ iridates

In $L$ edge XAS experiments on Ir$^{4+}$ compounds, an electron is excited from the Ir 2$p$ to the Ir 5$d$ levels. The electron can be excited either from the 2$p_{\frac{1}{2}}$ or 2$p_{\frac{3}{2}}$ SO states, resulting in two absorption peaks (white lines$^2$) corresponding to the $L_2$ or $L_3$ edges, respectively. The integrated intensity of these white-line peaks is proportional to the local density of unoccupied final states in the system ($5d$ holes) [219–221]. The selection rules that govern the electric dipole transitions then allow the use of the relative intensities of the $L_2$ and $L_3$ peaks, the branching ratio

$$ BR = \frac{I_{L_3}}{I_{L_2}} $$

(5.1)

to extract information about the total angular momentum $J$ of the available 5$d$ hole states$^3$. Since $\Delta J = 0, \pm 1$ [224], the $L_2$ edge is sensitive to only those transitions involving $5d_{\frac{3}{2}}$ holes, while the $L_3$ edge is sensitive to both $5d_{\frac{3}{2}}$ and $5d_{\frac{5}{2}}$. Note that the $\tilde{j} = 1/2$ states are split off from the atomic-like $J = 5/2$ states due to the cubic crystal field splitting (see Fig. 2.2). In the limit of negligible SO coupling, the $J = 3/2$ and $J = 5/2$ multiplets are degenerate and the transition probabilities for $L_2$ and $L_3$ processes depend only on the density of the initial core-hole states. Thus a statistical $BR = 2$ is expected as the ratio of occupied $2p_{\frac{3}{2}}$ and $2p_{\frac{1}{2}}$ states is 2:1.

Thole et al. [225] have shown that the BR is related to the ground-state expectation value of the angular part of the SO coupling operator

$$ \langle \mathbf{L} \cdot \mathbf{S} \rangle = \langle \mathbf{L} \cdot \mathbf{S} \rangle $$

(5.2)

through the relation

$$ BR = \frac{2\langle n_h \rangle + \langle \mathbf{L} \rangle}{\langle n_h \rangle - \langle \mathbf{L} \rangle}, $$

(5.3)

where $n_h$ is the number of holes in the valence shell. $\mathcal{H}_{\text{SO}} = \sum \zeta i \cdot s_i$ is here the SO Hamiltonian while $\lambda = \pm \zeta / 2S$ and $\zeta$ are SO coupling parameters for a particular $d^n$ electron configuration ($\lambda$ is positive for less than half-filled shells and negative for more than half-filling) [92, 97].

---

$^2$They are called white lines for historical reasons: in the past, x-ray absorption spectra were recorded using photographic plates and the strong absorption of certain wavelength leads to an unexposed band on the photographic plates, which later develops in negative and appear as a white vertical stripe.

$^3$ The total angular momentum $J$ is obtained from $JJ$ coupling.
For quantum numbers \( l, s \) and \( j \), orbital, spin and total angular momentum, respectively, \( \langle Z' \rangle \) can be written as (see Eq. A.5 in App. A.1) \cite{97, 98}

\[
\langle Z' \rangle = \langle \mathbf{l} \cdot \mathbf{s} \rangle = -\frac{1}{2} [j(j+1) - l(l+1) - s(s+1)].
\]

(5.4)

In the Ir\(^{4+} \) compounds, one hole is present in the Ir \( t_{2g} \) orbitals and thus for a pure \( j = 1/2 \) ground state with \( s = 1/2 \) and the effective orbital quantum number \( \tilde{l} = 1 \), we have

\[
\langle Z' \rangle = -\langle \mathbf{l} \cdot \mathbf{s} \rangle
\]

\[
= -\frac{1}{2} [\tilde{j}(\tilde{j}+1) - \tilde{l}(\tilde{l}+1) - s(s+1)]
\]

(5.5)

It follows that with \( \langle Z' \rangle = 1 \), BR = 2.75 (Eq. 5.3) for an average number of holes in the 5d shell \( \langle n_h \rangle = 5 \). Without SO interactions Eq. 5.3 leads to BR = 2, consistent with the statistical BR.

Interestingly, for 5d\(^5 \) iridium oxides, branching ratios of approximately 4 and ground-state expectation values \( \langle Z' \rangle \) close to 2 have been derived from the XAS measurements \cite{222, 226, 227}. Such large values for BR and \( \langle Z' \rangle \) can only be accounted for by taking into consideration the sizable admixture of the leading ground-state configuration \( t_{2g}^5 \) with excited-state \( t_{2g}^4 e_g \) \((and t_{2g}^3 e_g^2)\) configurations \cite{222, 226} via SO coupling \cite{26, 96, 220, 221, 228, 229}. In other words, the Ir \( e_g \) levels should also be explicitly taken into consideration as they play an important role and particular attention should be paid when approximating them to be infinitely separated from the \( t_{2g} \) manifold.

\section{5.3 \( \langle Z' \rangle \) from \textit{ab initio} calculations}

In the presence of off-diagonal SO couplings that couple the \( t_{2g}^n \) and \( t_{2g}^{n-1} e_g^1 \) multiplets (see App. A.4), \( \langle Z' \rangle \) is most conveniently expressed as \cite{220, 221}

\[
\langle Z' \rangle = \zeta^{-1} (E_{LS}^0 - E_{LSJ}^0),
\]

(5.6)

where \( E_{LS}^0 \) is the energy of the lowest \( d^n \) state without SO treatment and \( E_{LSJ}^0 \) is the ground-state eigenvalue with SO interactions accounted for. SO matrix elements have been tabulated for the octahedral \( d^5 \) manifold by Schröder \cite{228} and the effect of off-diagonal SO interactions for Ir\(^{4+} \) 5d\(^5 \) ions was already anticipated a few decades ago by Thornley, Allen, Andlauer \textit{et al.} \cite{26, 96, 229}.

For evaluating the energies in Eq. 5.6, CASSCF and MRCI calculations were carried out.
on a cluster that contains a single central IrO₆ octahedron, the NN octahedra and the nearby alkaline-earth (Sr/Ba) ions. The solid-state surroundings were modeled as a large array of PCs fitted to reproduce the crystal Madelung field in the cluster region. The same basis sets as those used for the d-d excitation calculations (see Sec. 4.2) were employed. Since an explicit treatment of spins at the NN d sites is technically impracticable ⁴ for the calculation of the ground state ⟨Σ⟩, these sites were approximated as closed shell Pt⁴⁺ t₂g ions. For the computations with only t₂g orbitals in the active space, the CASSCF optimization was carried out for an average of the ²T₂g(t²g) terms. When both the t₂g and e_g orbitals are in the active space (see Table 5.1 and Table 5.2), the orbitals were optimized for an average of the ²T₂g(t²g), ⁴T₁₈(t⁴e_g), ⁴T₂g(t⁴e_g) and ⁶A₁g(t³e²_g) states⁵.

5.3.1 Evaluation of the spin-orbit coupling strength ζ

As the SO coupling constant ζ is not directly provided in MOLPRO, we extract this parameter by mapping the ab initio energies of the SO components originating from the ²T₂g(t²g) term onto the eigenvalues associated with the SO matrix elements tabulated in, e.g., Ref. [228]. This integral is determined for the Ir⁴⁺ 5d⁵ ion from the splitting of the ˜j = 1/2 and ˜j = 3/2 t²g terms. To avoid complications related to the lower point-group symmetry in Sr₂IrO₄ and Ba₂IrO₄ (see, e.g., the tables with Coulomb and SO matrix elements for D₄h symmetry in Refs. [230, 231]), the ˜j = 1/2 to ˜j = 3/2 excitation energy ΔE₁/₂→3/₂ is here obtained from a set of QC calculations for an idealized cubic perovskite compound, CaIrO₃. In this hypothetical structure the Ir-O distances were set to the average of Ir-O bond lengths in the post-perovskite crystal structure of CaIrO₃ [232]. In full cubic symmetry [26, 96–98, 228, 229],

\[ \zeta = \frac{2}{3} \Delta E_{1/2 \rightarrow 3/2}. \]  

(5.7)

With orbitals optimized for the ²T₂g(t²g) term, ζ(5d⁵) comes out this way as large as 0.468 eV. Additional test calculations have shown that these SO coupling constants change by not more than 1.5% if orbitals averaged over the ²T₂g(t²g), ⁴T₁₈(t⁴e_g), ⁴T₂g(t⁴e_g) and ⁶A₁g(t³e²_g) states are used. Further, the ζ determined from the splitting of the t³g ˜j = 1/2 and ˜j = 3/2 terms is found to be the same with the ζ obtained from the splittings of the j = 1/2, j = 3/2 and j = 5/2 terms arising from either the ⁴T₁₈(t⁴e_g) or ⁴T₂g(t⁴e_g) components [98, 228]. For the latter tests, the same set of averaged orbitals was used for expressing the various JLS states. To remove off-diagonal SO couplings with higher-lying terms, appropriate orbital occupation restrictions were applied. Finally, a value ζ = 0.468 eV was used for computing the ground-state expectation values of the Σ operator.

⁴The analysis of on-site excitations become cumbersome when intersite spin interactions are also present.

⁵Inclusion of the ⁶A₁g state in the CASSCF optimization ensures rapid convergence.
5.3.2 $\langle Z \rangle$ in square-lattice iridates: Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$

$\langle Z \rangle$ values are listed for the Ir$^{4+}$ $5d^5$ electronic configuration of Sr$_2$IrO$_4$ in Table 5.1 and for Ba$_2$IrO$_4$ in Table 5.2, for different active spaces. These expectation values were derived by using Eq. 5.6 and the eigenvalues provided by MOLPRO for the $^2T_{2g}(t^5_{2g})$ configuration state function and for the many-body SO ground state.

If the active orbital space in the CASSCF calculation is restricted to the three Ir $t_{2g}$ orbitals, $\langle Z \rangle$ is indeed approximately 1, in fact slightly lower than 1 due to the splitting of the $t_{2g}$ levels (they are split by 0.12 eV in Sr$_2$IrO$_4$ and 0.07 meV in Ba$_2$IrO$_4$, see the splittings in Tables 4.1a and 4.5). In octahedral symmetry, the $t^5_{2g}$ $j=1/2$ and $j=3/2$ terms fall in the double-group representations $\Gamma_7$ and $\Gamma_8$, respectively [97, 228, 229]. With tetragonal distortions (as experimentally found in Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$, see Chap. 4), two of the four components of the octahedral representation $\Gamma_8$ and the components of the octahedral representation $\Gamma_7$ give rise to the tetragonal double-group representation $\Gamma_7$, see e.g. Ref. [231], where off-diagonal SO matrix elements for some of the $d^5$ terms in $D_{4h}$ symmetry are provided. The admixture of $j=3/2$ character into the ground-state wave function yields ground-state expectation values $\langle Z \rangle < 1$ (see results for the $t^5_{2g}$ electron configuration in Tables 5.1, 5.2 and 5.3) because, for the “pure” $j=3/2 t^5_{2g}$ state the expectation value of the $Z$ operator is

$$\langle Z \rangle = \lambda^{-1} \langle \mathcal{H}_{so} \rangle = \langle \mathbf{L} \cdot \mathbf{S} \rangle = -1/2. \quad (5.8)$$

We note that for the $j=3/2 t^5_{2g}$ term, $\langle \mathcal{H}_{so} \rangle = \lambda \langle \mathbf{L} \cdot \mathbf{S} \rangle = \zeta/2$, where $\lambda = -\zeta$ for the $t^5_{2g}$ configuration [92, 97]. $\langle \mathcal{H}_{so} \rangle = \lambda \langle \mathbf{L} \cdot \mathbf{S} \rangle = -\zeta$ for the $j=1/2 t^5_{2g}$ term.

By enlarging the active space with Ir $e_g$ orbitals, $\langle Z \rangle$ dramatically increases, although the weight of the $t^4_{2g}e^1_{g}$ and $t^3_{2g}e^2_{g}$ configurations in the SO ground state wave function is not larger than 6% (see the wave function composition in Table 5.3). We first included in the SO treat-

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<th>MRCI</th>
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<td>1.46</td>
</tr>
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<td>1.66</td>
</tr>
<tr>
<td>9D, 8Q, 1S (60 KDs)</td>
<td>1.82</td>
<td></td>
</tr>
</tbody>
</table>
Spin-orbit coupling observables: $\langle Z \rangle$ operator and branching ratio

Table 5.2 $\langle Z \rangle$ ground-state expectation values for the Ir$^{4+}$ 5$d^5$ ion in Ba$_2$IrO$_4$. The CASSCF and MRCI calculations are carried out as for the results in Table 5.1. The separation between the lowest $t_{2g}^5$ and $t_{2g}^4e_g^1$ states is 2.07 eV by MRCI. The weight of the $t_{2g}^4e_g^1$ and $t_{2g}^5e_g^2$ configurations in the ground-state wave function is 10%.

<table>
<thead>
<tr>
<th>Number of states</th>
<th>CASSCF</th>
<th>MRCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D (3 KDs with SOC)</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>1D, 2Q, 1S (18 KDs)</td>
<td>1.63</td>
<td>1.54</td>
</tr>
<tr>
<td>5D, 2Q, 1S (27 KDs)</td>
<td>1.86</td>
<td>1.76</td>
</tr>
<tr>
<td>9D, 8Q, 1S (60 KDs)</td>
<td>1.91</td>
<td>–</td>
</tr>
</tbody>
</table>

The split $^2T_{2g}$ term related to the $t_{2g}^5$ configuration and additionally the (split) $^4T_{1g}(t_{2g}^4e_g^1)$, $^4T_{2g}(t_{2g}^4e_g^1)$, and $^6A_{1g}(t_{2g}^3e_g^2)$ components. The orbitals were optimized for an average of all these terms. Results from such SO calculations are listed on the second line in Tables 5.1 and 5.2. The doublet, quartet and sextet states that enter the SO treatment are labeled as D, Q and S, respectively. For the results in the third row in Tables 5.1 and 5.2, we further added to the SO calculation the low-lying $^2A_{2g}$, $^2T_{1g}$, $^2E_g$ and $^2T_{2g}$ components arising from the $t_{2g}^4e_g^1$ manifold. Calculations with even more excited states in the SO treatment (see the lowest line in Tables 5.1 and 5.2) show that the $\langle Z \rangle$ ground-state expectation values are more or less converged. For the latter set of results, the MRCI SO calculation is too expensive and only the CASSCF+SOC $\langle Z \rangle$ value is shown. All quartet $t_{2g}^4e_g^1$ ($^4T_{1g}$, $^4T_{2g}$), $t_{2g}^3e_g^2$ ($^4A_{1g}$, $2\times^4E_g$, $^4T_{2g}$, $^4T_{1g}$, $^4A_{2g}$) and doublet $t_{2g}^4e_g^1$ ($^2A_{2g}$, $2\times^2T_{1g}$, $2\times^2E_g$, $2\times^2T_{2g}$, $^2A_{1g}$) components are included here in the SO treatment.

$\langle Z \rangle$ values of 1.7 ± 1.8, (Table 5.1) are comparable with a result of 2.1 extracted from the XAS/XMCD data [226]. At the same level of theory, $\langle Z \rangle$ is slightly higher in Ba$_2$IrO$_4$, $\langle Z \rangle$ = 1.8 ± 1.9 (see Table 5.2), which reproduces the trend found in the XAS/XMCD measurements [226, 227]. The difference between the $\langle Z \rangle$ ground state expectation values in the two compounds mainly results from the different $t_{2g}$–$e_g$ energy separation, with $t_{2g}^5$ to $t_{2g}^4e_g^1$ excitation energies lower by 0.5 eV in Ba$_2$IrO$_4$ as compared to Sr$_2$IrO$_4$ (see the captions of Tables 5.1 and 5.2).

*X-ray magnetic circular dichroism.*
5.4 Perturbational analysis for contributions to $\langle \mathcal{Z} \rangle$ from $e_g$ states

The enhancement of the $\langle \mathcal{Z} \rangle$ expectation values with the inclusion of excited state configurations, $t_{2g}^5 e_g^1$ and $t_{2g}^4 e_g^2$, in the SO calculations can be understood from a simple perturbation analysis as described below. The off-diagonal SO matrix elements between the $t_{2g}^5$ and $t_{2g}^4 e_g^1$ manifolds result in the modification of the SO wave functions derived for the $t_{2g}^5$-only configuration. If one writes the total SO Hamiltonian as

$$
\mathcal{H}_{SO} = \lambda L' \cdot S' + \lambda' L'' \cdot S'' ,
$$

(5.9)

where the first term is the effective SO Hamiltonian within the $t_{2g}^5$ manifold and the second term describes SO interactions that couple states related to the $t_{2g}^5$ and $t_{2g}^4 e_g^1$ configurations, then

$$
\langle L \cdot S \rangle = \langle L' \cdot S' \rangle + \langle L'' \cdot S'' \rangle \quad \text{and}
\langle \mathcal{Z} \rangle = \langle \mathcal{Z}' \rangle + \langle \mathcal{Z}'' \rangle .
$$

(5.10)

$\lambda'$ is expected to be smaller than $\lambda$ for the following reason. The Ir $t_{2g}$ and $e_g$ orbitals are not pure atomic functions, but molecular-like orbitals due to the admixture with the neighboring oxygen 2$p$ orbitals. The covalency effects giving rise to this admixture are different for the $t_{2g}^5$ and $t_{2g}^4 e_g^1$ states as the strengths of the $\pi (t_{2g})$ and $\sigma (e_g) p - d$-coupling are different. Hence the matrix elements of the orbital angular momentum operator within the $t_{2g}$ and between $t_{2g}$ and $e_g$ (molecular-like) orbitals are renormalized differently. To take this difference into consideration, $\lambda'$ is used [97].

Within the $t_{2g}^5$ manifold, in the effective total angular momentum ($\tilde{j} = 1/2, 3/2$) basis,

$$
\mathcal{Z}' = - \sum_{m_j = \pm 1/2} \frac{1}{2} m_j \left\langle \frac{1}{2} m_j \right| + \frac{1}{2} \sum_{m_j = \pm 3/2} \frac{3}{2} m_j \left\langle \frac{3}{2} m_j \right| .
$$

(5.11)

The ground state with four electrons in the $\tilde{j} = 3/2$ and one in the $\tilde{j} = 1/2$ state can be written as (electron picture)

$$
|\Psi\rangle_{GS} = \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle \otimes \prod_{m_j = \pm \frac{3}{2}} \frac{3}{2} m_j \right\rangle .
$$

(5.12)

---

7See Section 5 of Chapter 20 in Ref. [97].
Thus, the contribution to $\langle 2' \rangle$ from the $t_{2g}^5$-only states is

$$
\langle 2' \rangle = -1 + 4 \times \frac{1}{2} = 1.
$$

(5.13)

In a single particle picture, where the SO interaction is considered only between the $^2T_{2g}$ term ($t_{2g}^5$) and $^2E_g$ term of $t_{2g}^4 eg$ configuration, the action of the residual SO Hamiltonian that contains off-diagonal SO matrix elements coupling these two terms (see App. A.5) on the total angular momentum $\tilde{j}$ states derived from the $t_{2g}^5$-only manifold is given by

$$
H_{SO}^{r} \left| \begin{array}{c}
\frac{1}{2}, \pm \frac{1}{2} \end{array} \right\rangle = 0
$$

$$
H_{SO}^{r} \left| \begin{array}{c}
\frac{3}{2}, \pm \frac{3}{2} \end{array} \right\rangle = \mp i\lambda \sqrt{\frac{3}{2}} \left| d_{z^2}, \mp \frac{1}{2} \right\rangle
$$

$$
H_{SO}^{r} \left| \begin{array}{c}
\frac{3}{2}, \pm \frac{1}{2} \end{array} \right\rangle = \mp i\lambda \sqrt{\frac{3}{2}} \left| d_{x^2-y^2}, \pm \frac{1}{2} \right\rangle.
$$

(5.14)

Using the above expressions we can write the second term in Eq. 5.9 as

$$
\mathcal{Z}'' = i \sqrt{\frac{3}{2}} \left( \left| d_{z^2}, \frac{1}{2} \right\rangle \langle d_{z^2}, -\frac{1}{2} | + \left| d_{z^2}, -\frac{1}{2} \right\rangle \langle d_{z^2}, \frac{1}{2} | \right)
$$

$$
+ i \sqrt{\frac{3}{2}} \left( - \left| d_{x^2-y^2}, \frac{1}{2} \right\rangle \langle d_{x^2-y^2}, -\frac{1}{2} | + \left| d_{x^2-y^2}, -\frac{1}{2} \right\rangle \langle d_{x^2-y^2}, \frac{1}{2} | \right),
$$

(5.15)

i.e., the two $e_g$ orbitals $|d_{z^2}, \pm \frac{1}{2}\rangle$ and $|d_{x^2-y^2}, \pm \frac{1}{2}\rangle$ only affect the $\tilde{j} = 3/2, \pm 3/2$ and $\tilde{j} = 3/2, \pm 1/2$ states respectively. The ground state wave function then becomes

$$
|\Psi\rangle_{GS} = \left| D_{\frac{3}{2}, \pm \frac{1}{2}} \right\rangle \otimes \prod_{m_j = -\frac{3}{2}}^{\frac{3}{2}} |D_{\frac{3}{2}, m_j} \rangle
$$

(5.16)

where the $D$s are wave functions of the doublet and quartet states that are perturbed due to the off-diagonal SO matrix elements. To first order in $\frac{\lambda'}{\Delta_{CF} + \frac{1}{2}}$, the modified $\tilde{j} \simeq 1/2$ and $\tilde{j} \simeq 3/2$ wave functions become

$$
\left| D_{\frac{3}{2}, \pm \frac{1}{2}} \right\rangle = \left| \frac{3}{2}, \pm \frac{3}{2} \right\rangle \mp i \sqrt{\frac{3}{2} / \Delta_{CF} + \frac{1}{2}} \left| d_{z^2}, \mp \frac{1}{2} \right\rangle
$$

$$
\left| D_{\frac{3}{2}, \pm \frac{1}{2}} \right\rangle = \left| \frac{3}{2}, \pm \frac{1}{2} \right\rangle \mp i \sqrt{\frac{3}{2} / \Delta_{CF} + \frac{1}{2}} \left| d_{x^2-y^2}, \mp \frac{1}{2} \right\rangle
$$

(5.17)

(5.18)

The energy separation between the $\tilde{j} = 3/2$ states of the SO split $t_{2g}^5$ configuration and the $e_g$ levels is given by $\Delta_{CF} + \frac{1}{2}$. 

---

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\begin{align*}
|D_{1/2^{\pm 1}}\rangle &= \frac{1}{\sqrt{2}} \left| \frac{1}{2} \pm \frac{1}{2} \right\rangle. \quad (5.19)
\end{align*}

Note that only wave functions of the $\tilde{j} = 3/2$ quartet states are modified and the $\tilde{j} = 1/2$ Kramers doublet is unperturbed in this single-particle picture. If the SO interactions between all the terms corresponding to $t_{2g}^4 e_g^1$ states are also taken into account, one finds that the $\tilde{j} = 1/2$ states are also modified.

Hence, the contribution to $\langle \mathcal{Z} \rangle$ from the $t_{2g}^4 e_g^1$ terms of $t_{2g}^4 e_g^1$ configuration is

\begin{align*}
\langle \mathcal{Z}'' \rangle &= \left\langle D_{3/2, m_j}\left| L'' \cdot S'' \right| D_{3/2, m_j} \right\rangle = 4 \times \frac{3\lambda'}{\Delta_{\text{CF}} + \frac{\lambda}{2}},
\end{align*}

and the total expectation value of $\mathcal{Z}$ is given by

\begin{align*}
\langle \mathcal{Z} \rangle &= \langle \mathcal{Z}' \rangle + \langle \mathcal{Z}'' \rangle \\
&= 1 + 4 \times \frac{3\lambda'}{\Delta_{\text{CF}} + \frac{\lambda}{2}}. \quad (5.21)
\end{align*}

Thus, to a first approximation, the contribution from the $t_{2g}^4 e_g^1$ states to the ground state expectation value of $\mathcal{Z}$ is inversely proportional to the energy separation of the $e_g$ levels from the SO split $t_{2g}$ manifold $\Delta_{\text{CF}} + \frac{\lambda}{2}$. $\Delta_{\text{CF}}$ is an order of magnitude larger than $\lambda/2$ in $5d^5$ iridates implying that it is the former quantity which significantly influences the $\langle \mathcal{Z} \rangle$ values. Trends as function of $\Delta_{\text{CF}}$ are discussed in the next section.

### 5.5 $\langle \mathcal{Z} \rangle$ in other $5d^5$ iridates

The Ir $5d$-level splittings, $\langle \mathcal{Z}' \rangle$ and $\langle \mathcal{Z}'' \rangle$ expectation values and the composition of the SO ground state wave function for several iridium oxide compounds are shown in Table 5.3. The $\langle \mathcal{Z}' \rangle$ values were obtained by including only the $2T_{2g}$ term of the Ir $t_{2g}$ configuration in the SO treatment while the $\langle \mathcal{Z}'' \rangle$’s were calculated by further adding the $4T_{1g}, 4T_{2g}, 2A_{2g}, 2T_{1g}, 2E_g, 2T_{2g} (t_{2g}^4 e_g^1)$ and $6A_{1g} (t_{2g}^4 e_g^2)$ components. In order to unambiguously estimate the individual contributions to the ground state SO wave function from the $t_{2g}^5, t_{2g}^4 e_g^1$, and $t_{2g}^3 e_g^2$ configurations, only the CASSCF results are shown.\(^9\)

The compounds in Table 5.3 are ordered in such a way that the Ir $t_{2g}$ energy splitting is increasing as one moves down the rows in the table. For CaIrO$_3$, a hypothetical idealized perovskite structure with degenerate Ir $t_{2g}$ levels, it can be seen that $\langle \mathcal{Z}' \rangle$ is exactly 1, as is expected.

\(^9\)The MRCI wave function would also contain contributions from those configurations with holes in the O 2p orbitals.
Table 5.3 Crystal field splittings within the $t_{2g}$ levels ($\Delta_t$) and between the $t_{2g}$ and $e_g$ manifolds ($\Delta_{CF}$) along with $\langle \mathcal{Z}^\prime \rangle$ and $\langle \mathcal{Z}^\prime\prime \rangle$ values in several iridium oxides, as obtained from QC calculations. Only the states below 5 eV are included in the SO treatment (in $O_b$ symmetry these are $^4T_{1g}$, $^4T_2$, $^2A_{2g}$, $^2T_1$, $^2E_g$ and $^2T_2$ corresponding to $t_{2g}^4 e_{g}^1$ and $^6A_{1g}$ of $t_{2g}^3 e_{g}^2$). $\langle \mathcal{Z}^\prime\prime \rangle$ values (see text) deduced from the CASSCF calculations and those obtained from Eq. 5.21 are also shown. Contributions (weights) to the ground state SO wave function from scalar-relativistic CASSCF states corresponding to the $t_{2g}^5$, $t_{2g}^4 e_{g}^1$ and $t_{2g}^3 e_{g}^2$ configurations are given in the last two columns.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta_t$ (eV)</th>
<th>$\langle \mathcal{Z}^\prime \rangle$ (eV)</th>
<th>$\langle \mathcal{Z}^\prime\prime \rangle$ (eV)</th>
<th>QC</th>
<th>Eq. 5.21</th>
<th>$t_{2g}^5$</th>
<th>$t_{2g}^4 e_{g}^1$ &amp; $t_{2g}^3 e_{g}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>idealized</td>
<td>0.00</td>
<td>1.00</td>
<td>1.79</td>
<td>0.96</td>
<td>1.06</td>
<td>87.47</td>
<td>12.53</td>
</tr>
<tr>
<td>CaIrO$_3$</td>
<td>0.06</td>
<td>0.96</td>
<td>2.26</td>
<td>0.90</td>
<td>0.87</td>
<td>90.28</td>
<td>9.72</td>
</tr>
<tr>
<td>Na$_2$IrO$_3$</td>
<td>0.07</td>
<td>0.91</td>
<td>2.04</td>
<td>0.94</td>
<td>0.95</td>
<td>88.82</td>
<td>11.18</td>
</tr>
<tr>
<td>Ba$_2$IrO$_4$</td>
<td>0.11</td>
<td>0.92</td>
<td>2.51</td>
<td>0.85</td>
<td>0.80</td>
<td>91.59</td>
<td>8.41</td>
</tr>
<tr>
<td>Sr$_2$IrO$_4$</td>
<td>0.20</td>
<td>0.82</td>
<td>2.45</td>
<td>0.85</td>
<td>0.81</td>
<td>91.08</td>
<td>8.92</td>
</tr>
<tr>
<td>BaIrO$_3$</td>
<td>0.28</td>
<td>0.84</td>
<td>2.91</td>
<td>0.80</td>
<td>0.70</td>
<td>92.79</td>
<td>7.21</td>
</tr>
<tr>
<td>Y$_2$Ir$_2$O$_7$</td>
<td>0.59</td>
<td>0.62</td>
<td>2.87</td>
<td>0.76</td>
<td>0.71</td>
<td>92.51</td>
<td>7.49</td>
</tr>
<tr>
<td>Sr$_3$CuIrO$_6$</td>
<td>0.59</td>
<td>0.62</td>
<td>2.87</td>
<td>0.76</td>
<td>0.71</td>
<td>92.51</td>
<td>7.49</td>
</tr>
</tbody>
</table>

for a pure $j = 1/2$ system. For finite Ir $t_{2g}$ splittings, $\langle \mathcal{Z}^\prime \rangle$ decreases due to the mixing of $j = 1/2$ and $j = 3/2$ terms in the ground state (see Sec. 5.3.2). In Sr$_3$CuIrO$_6$, it becomes as small as 0.62 for $\Delta_t$ larger than the SO coupling strength ($\lambda = 0.468$ eV).

With an enlarged active space to also include the $e_g$ orbitals, the $\langle \mathcal{Z}^\prime \rangle$ calculated for CaIrO$_3$ is 1.96. This implies that the contribution from $t_{2g}^4 e_{g}^1$ and $t_{2g}^3 e_{g}^2$ configurations is $\langle \mathcal{Z}^\prime\prime \rangle = (\langle \mathcal{Z}^\prime \rangle - \langle \mathcal{Z}^\prime\prime \rangle) = 0.96$. We note that by including more states in the SO treatment (see lowest line in Table 5.1 and 5.2), $\langle \mathcal{Z}^\prime \rangle$ increases to 2.05. Nevertheless, the contribution to the ground state wave function from $t_{2g}^4 e_{g}^1 + t_{2g}^3 e_{g}^2$ states is 12.53%. We also found that $\langle \mathcal{Z}^\prime\prime \rangle$ (sixth column in Table 5.3), as obtained from the QC calculations, decreases as $\Delta_{CF}$ increases, which implies that the coupling of the $t_{2g}^5$ and $t_{2g}^4 e_{g}^1$ states diminishes with growing separation between them. This trend is also reflected in the composition of the ground state wave function (see last column in Table 5.3).

Interestingly, the single particle perturbation analysis presented in Sec. 5.4 captures rather well the change in $\langle \mathcal{Z}^\prime\prime \rangle$ for different compounds. The values obtained from Eq. 5.20 are shown in the seventh row of Table 5.3. Since the unknown $\lambda'$ enters Eq. 5.20, its value is chosen by fitting $\langle \mathcal{Z}^\prime\prime \rangle$ to those calculated ab initio. A reasonable fitting leads to $\lambda' = 0.19$ eV, less than half of $\lambda$. Although $\lambda'$ is expected to be smaller than $\lambda$ due to a different degree of hybridization of the $t_{2g}$ and $e_g$ orbitals with O 2p functions, such a small value could be
attributed to the limitation of the single particle analysis that we employed here.

## 5.6 Conclusions

We analyzed the role of $t_{2g}-e_g$ many-body couplings mediated by SO interactions and showed that in Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ they give rise to sizable deviations from the canonical $\langle Z' \rangle = 1$ picture for a "pure" $\tilde{j} = 1/2$ system [14, 97]. The experimental trend, with a $\langle Z' \rangle$ ground-state expectation value that is larger for Ba$_2$IrO$_4$ than for Sr$_2$IrO$_4$ is reproduced in the \textit{ab initio} calculations and is assigned to the smaller $t_{2g}-e_g$ splitting in Ba$_2$IrO$_4$. The estimation of contributions to $\langle Z' \rangle$ due to $t_{2g}-e_g$ SO couplings from a single particle perturbation analysis explains rather well the trend observed in the QC results for several iridium oxide compounds. The value of $\lambda'$ extracted by mapping the QC data onto the perturbation model of Eq. 5.21 closely matches with those used in other works, see, e.g., Ref. [226].
\( \tilde{j} \simeq 1/2 \) square-lattice antiferromagnets – \( \text{Ba}_2\text{IrO}_4 \) and \( \text{Sr}_2\text{IrO}_4 \)

The magnetic properties of the layered square-lattice compounds \( \text{Ba}_2\text{IrO}_4 \) and \( \text{Sr}_2\text{IrO}_4 \) are discussed in this chapter. We compute the NN exchange interaction parameters, both isotropic and anisotropic within the 2D layer for \( \text{Ba}_2\text{IrO}_4 \) and further explain the experimentally observed magnetic order by analytical minimization of an extended Hamiltonian containing also interlayer exchange interactions. We also study the structural dependence of magnetic interactions in \( \text{Sr}_2\text{IrO}_4 \) by comparing the computed singlet-triplet energy splittings for strained \( \text{Sr}_2\text{IrO}_4 \) thin films with that of the bulk crystal.

6.1 Introduction

The magnetically active sites in most 5\(d^5\) iridates, the Ir\(^{4+}\) ions, possess an effective \( \tilde{j} \simeq 1/2 \) Kramers-doublet ground state, as described in Chap. 4. These pseudospin moments are fundamentally different from pure \( S = 1/2 \) spins as they encompass both spin and orbital angular momentum components. Because the latter is directional dependent, the magnetic exchange interactions between these pseudospin moments are no longer governed by the \( SU(2) \) symmetry alone and thus depend strongly on lattice geometries [10]. We here analyze and discuss the magnetic interactions between Ir\(^{4+}\) ions that are connected through one ligand site in two slightly different geometries as shown in Fig. 6.1. In \( \text{Ba}_2\text{IrO}_4 \), the Ir-O-Ir bond angle is 180° while in \( \text{Sr}_2\text{IrO}_4 \) it is significantly smaller than 180° due to rotations of the IrO\(_6\) octahedra about the \( c \) axis. Both isotropic Heisenberg-like and anisotropic exchange interaction pa-

---

1 We shall use the pseudospin notation \( \tilde{S} = 1/2 \) throughout this and the next chapters.
Fig. 6.1 Two slightly different bond geometries in 214 iridium oxides. a) 180° geometry occurring for corner-sharing oxygen octahedra in Ba$_2$IrO$_4$. b) 157° bond geometry in Sr$_2$IrO$_4$.

Parameters are extracted by mapping the magnetic spectrum obtained from QC calculations on units of two corner-sharing octahedra onto an appropriate effective spin Hamiltonian whose form is dictated by the symmetry of the crystal structure.

We begin by briefly explaining in Sec. 6.2 the way the QC calculations are carried out. In Sec. 6.3, we discuss the magnetic interactions in Ba$_2$IrO$_4$. The symmetry of the Ir-Ir link and the calculated spectrum show that the magnetic interactions within a single 2D square-lattice layer in this compound can be described by a compass-Heisenberg type of spin Hamiltonian. We also provide an explanation for the experimentally observed magnetic structure by deriving the magnetic phase diagram as a function of the interlayer anisotropic magnetic interactions. In Sec. 6.4, we move on to the square-lattice compound Sr$_2$IrO$_4$. The lack of inversion symmetry and sizable tetragonal crystal field splittings within the Ir $t_{2g}$ levels in this compound give rise to both antisymmetric and symmetric anisotropic interactions. Deriving hard values for all these effective parameters in Sr$_2$IrO$_4$ is not as straightforward as in the case of the higher-symmetry Ba$_2$IrO$_4$ system. Using the eigenvalues obtained by spin-orbit MRCI calculations, we nevertheless provide expressions for the anisotropic coupling constants as function of the isotropic Heisenberg exchange. In the last section, we show that the singlet-“triplet” splitting calculated for strained samples of Sr$_2$IrO$_4$ correctly explains the observed trend for the zone-boundary magnon energy values in RIXS experiments.
6.2 Magnetic spectrum of two NN sites

To obtain the magnetic spectrum of two NN Ir\(^{4+}\) sites, QC calculations were performed on embedded clusters made of two reference IrO\(_6\) octahedra. As in the single site calculations, it is important to describe the finite charge distribution at sites in the immediate neighborhood. Hence, the adjacent IrO\(_6\) octahedra and closest Ba/Sr cations around the reference [Ir\(_2\)O\(_{11}\)] fragment (see Fig. 6.2) were also included in the actual cluster. To make the analysis of the low-lying magnetic states tractable\(^2\), the spin couplings with the adjacent \(S = 1/2\) moments were cut off by replacing the open-shell Ir\(^{4+}\) 5\(d^5\) NNs with closed-shell Pt\(^{4+}\) \(t^6_{2g}\) species. Such a procedure is very often followed in QC studies on transition-metal systems \([68, 87, 188, 235, 236]\) and it allows a straightforward mapping of the \textit{ab initio} data onto an effective spin model. Another uncomplicated way is to use effective total ion potentials (TIPs) for the NN Ir sites \([237–239]\). The surrounding solid-state matrix was described as a finite array of point charges fitted to reproduce the crystal Madelung field in the cluster region.

Energy-consistent relativistic pseudopotentials from the MOLPRO library were used for Ir \([175]\) and the alkaline-earth cations \([190]\). The valence orbitals at the two central Ir sites were described by basis sets of quadruple-\(\zeta\) quality supplemented with two \(f\) polarization functions \([175]\), while for the ligands bridging the two magnetically active Ir ions quintuple-\(\zeta\) valence basis sets and four \(d\) polarization functions \([182]\) were applied. The other oxygens at the two central octahedra were modeled by triple-\(\zeta\) valence basis sets \([182]\). For the additional ligands coordinating the adjacent 5\(d\) sites minimal atomic-natural-orbital basis functions \([183]\) were employed. At those adjacent 5\(d\) sites triple-\(\zeta\) valence basis sets \([175]\) were used.

Scalar-relativistic restricted HF calculations without symmetry restrictions were first performed to obtain a set of suitable initial orbitals for the subsequent CASSCF calculations.

\(^2\)The number of spin-orbit coupled states dramatically increases with the number of Ir sites. With two Ir sites, one has 36 spin-orbit states associated with the Ir \(t_{2g}\) orbital space \((2\times3\text{ Ir } t_{2g}\text{ orbitals and } 2\times5\text{ electrons})\); with three of them, it increases to 162 states.
Since the six Ir$^{4+} t_{2g}^{5}$ ions surrounding the reference two-octahedra unit were all replaced by closed-shell Pt$^{4+} t_{2g}^{6}$ species, an active space of five electrons and three ($t_{2g}$) orbitals at each of the two magnetically active Ir sites (CAS[10,6]) was considered while freezing the orbitals at the NN IrO$_6$ octahedra as at the HF level. To separate the orbitals corresponding to the reference fragment and of those associated with the NN octahedra into different groups, the Pipek-Mezey orbital localization scheme [191] available in MOLPRO [120] was used. The orbitals were optimized for an average of the nine singlet and nine triplet states arising from the $t_{2g}^{5} - t_{2g}^{5}$ configuration.

In the MRCI treatment, single and double excitations from the six Ir $t_{2g}$ orbitals and the 2$p$ shell of the bridging ligand site were taken into account. Similar strategies of explicitly dealing only with selected groups of ligand orbitals were adopted in earlier studies on both 3$d$ [83, 240–242] and 5$d$ [184, 235, 236] compounds, with results in good agreement with the experiment [83, 184, 235, 241, 242]. The same Pipek-Mezey localization scheme [191] was used to separate the metal 5$d$ and various sets of O 2$p$ orbitals into different groups. The MRCI treatment was carried out for each spin multiplicity, singlet or triplet, as a nine-root calculation.

The spin-orbit treatment is then carried out within the quasi-degenerate perturbation theory framework [172]. Here, the matrix elements of the SO Hamiltonian are computed in the basis of the nine singlet and nine triplet states obtained at the MRCI level. The SO Hamiltonian is then added to the scalar-relativistic part. The resulting Hamiltonian is solved to yield 36 SO coupled states. Only the four low-lying states out of the 36 SO eigenfunctions are of direct relevance for the analysis of the NN magnetic interactions. The higher-lying states imply an excitation energy of at least 0.6 eV. The latter number corresponds to the $\tilde{j} \simeq 1/2$ to $\tilde{j} \simeq 3/2$ spin-orbit exciton transition. To determine the nature of each SO state, we explicitly computed with MOLPRO the dipole and quadrupole transition matrix elements within that manifold. The nonzero matrix elements of the respective operators and standard selection rules for dipole and quadrupole transitions [243] then clearly indicate which state is which (see App. C).

### 6.3 Ba$_2$IrO$_4$: realization of the compass-Heisenberg model

The exchange interactions between the Ir$^{4+} \vec{S} = 1/2$ pseudospin entities involve both isotropic Heisenberg and anisotropic terms. As described in Sec. 2.5, for a pair of NN pseudospins $\vec{S}_i$ and $\vec{S}_j$, the most general bilinear spin Hamiltonian can be cast in the form

$$\mathcal{H}_{ij} = J_{ij} \vec{S}_i \cdot \vec{S}_j + D_{ij} \vec{S}_i \times \vec{S}_j + \vec{S}_i \cdot \vec{\Gamma}_{ij} \cdot \vec{S}_j,$$  \hspace{1cm} (6.1)
where $J_{ij}$ is the isotropic Heisenberg exchange, the vector $D_{ij}$ defines the DM anisotropy, and $\Gamma_{ij}$ is a symmetric traceless second-rank tensor that describes the symmetric portion of the exchange anisotropy [108].

### 6.3.1 Symmetry of the $[\text{Ir}_2\text{O}_{11}]$ unit and effective spin Hamiltonian

For the square lattice of corner-sharing IrO$_6$ octahedra in Ba$_2$IrO$_4$, the symmetry of each block of two NN octahedra is $D_{2h}$, with inversion symmetry at the bridging oxygen site [244] (see Fig. 6.3b). Given the inversion center, the DM anisotropy vanishes. The remaining symmetry elements require that in the $(xyz)$ frame, with $x$ along the Ir-Ir link and $z$ orthogonal to the IrO$_2$ layers (see Fig. 6.3b), $\Gamma_{ij}$ is diagonal. The two-site effective spin Hamiltonian for an Ir-Ir link along the $x$ axis can then be written as

$$H_{ij}\parallel x = J \tilde{S}_i \cdot \tilde{S}_j + \Gamma_{\parallel} \tilde{S}_x^i \tilde{S}_x^j + \Gamma_{\perp} \tilde{S}_y^i \tilde{S}_y^j + \Gamma_{zz} \tilde{S}_z^i \tilde{S}_z^j,$$

(6.2)

with $\Gamma_{zz} = - (\Gamma_{\parallel} + \Gamma_{\perp})$ since $\Gamma$ is traceless. Due to the four-fold $z$-axis symmetry, we analogously have

$$H_{ij}\parallel y = J \tilde{S}_i \cdot \tilde{S}_j + \Gamma_{\parallel} \tilde{S}_y^i \tilde{S}_y^j + \Gamma_{\perp} \tilde{S}_x^i \tilde{S}_x^j + \Gamma_{zz} \tilde{S}_z^i \tilde{S}_z^j$$

(6.3)

for bonds along the $y$ axis. The eigenstates of the Hamiltonian in 6.2 are the singlet $|\Psi_S\rangle = \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}$ and the three “triplet” components $|\Psi_1\rangle = \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}$, $|\Psi_2\rangle = \frac{|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle}{\sqrt{2}}$, $|\Psi_3\rangle = \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}$. Here, $\uparrow$ and $\downarrow$ stands for pseudospins with $m_j = 1/2, -1/2$, respectively. The corresponding

![Fig. 6.3](image-url) (a) Layered crystal structure of Ba$_2$IrO$_4$. In-plane isotropic ($J$) plus interlayer isotropic ($J_{\text{out}}$) and anisotropic ($\Gamma_{\text{out}}$) exchange couplings are shown. (b) Schematics of two NN Ir sites in the $ab$-plane of Ba$_2$IrO$_4$. The point-group symmetry is $D_{2h}$. Symmetry elements are also indicated.
eigenvalues are

\[ E_2 = \frac{1}{4} J - \frac{1}{2} \Gamma_\perp, \quad E_3 = \frac{1}{4} J - \frac{1}{2} \Gamma_\parallel. \]

For \( D_{2h} \) symmetry of the two-octahedra unit, the four low-lying (spin-orbit) states, \( |\Psi_S\rangle, |\Psi_1\rangle, |\Psi_2\rangle \) and \( |\Psi_3\rangle \), transform according to the \( A_1g, B_2u, B_1u \) and \( A_1u \) irreducible representations, respectively (see App. C). This symmetry analysis is useful in determining the nature of each of the low-lying many-body states in the QC calculations.

### 6.3.2 Magnetic spectrum and effective exchange couplings from quantum chemistry calculations

A cluster containing two reference IrO\(_6\) octahedra, the six NN IrO\(_6\) octahedra along with the closest 16 Ba ions surrounding the reference [Ir\(_2\)O\(_{11}\)] fragment, was constructed using the crystal structure parameters reported by Okabe et al. [90] (see Fig. 6.2). The NN Ir sites in the calculations were modeled with closed-shell Pt\(^{4+}I\_) ions.

Of the 36 spin-orbit states that are obtained in the \textit{ab initio} calculations, the low-lying four corresponding to the magnetic spectrum are listed in Table 6.1. These four states were mapped onto the eigenvalues of the effective spin Hamiltonian in 6.2. Energy splittings and the associated effective magnetic couplings are provided at three levels of approximation: single-configuration ROHF (HF+SOC), CASSCF (CASSCF+SOC) and MRCI (MRCI+SOC). It can be seen that at all levels of theory two of the triplet components, \( \Psi_1 \) and \( \Psi_2 \), are degenerate\(^3\). Given the tetragonal distortions in Ba\(_2\)IrO\(_4\), with out-of-plane (z-axis) Ir-O bonds significantly stretched as compared to the in-plane (x/y) bonds [244], this degeneracy is somewhat surprising at first sight. Using Eqs. 6.4, this means that two of the diagonal elements of \( \Gamma \) are equal, \( \Gamma_{zz} = \Gamma_\perp \), which further implies \( \Gamma_\parallel = -2\Gamma_\perp = -2\Gamma_{zz} \). The interaction terms in the Hamiltonian 6.2 and 6.3 can then be rewritten as

\[
\mathcal{H}_{(ij)}^{(\parallel)} x = \bar{J} \bar{S}_i \cdot \bar{S}_j + \bar{\Gamma}_\parallel \bar{S}_i^x \bar{S}_j^x,
\]

\[
\mathcal{H}_{(ij)}^{(\parallel)} y = \bar{J} \bar{S}_i \cdot \bar{S}_j + \bar{\Gamma}_\parallel \bar{S}_i^y \bar{S}_j^y,
\]

where \( \bar{J} \equiv J + \Gamma_\perp \) and \( \bar{\Gamma}_\parallel \equiv -3\Gamma_\perp \). This Hamiltonian points to a compass-Heisenberg type of model [245].

QC results for \( \bar{J} \) and \( \bar{\Gamma}_\parallel \) are provided on the lowest line in Table 6.1. The value computed for the Heisenberg \( J \) within the ROHF approximation, \(-12 \text{ meV}\), is sizable and close to the

\(^3\)The energies of those two states differ by not more than 0.1 cm\(^{-1}\) in the spin-orbit ROHF, CASSCF and MRCI calculations.
6.3 Ba$_2$IrO$_4$: realization of the compass-Heisenberg model

Table 6.1 Energy splittings for the four lowest spin-orbit states of two NN IrO$_6$ octahedra and the corresponding effective coupling constants in Ba$_2$IrO$_4$, at different levels of approximation (all in meV).

<table>
<thead>
<tr>
<th>States/Method</th>
<th>HF+SOC</th>
<th>CASSCF+SOC</th>
<th>MRCI+SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Psi_S(A_{1g})$</td>
<td>12.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\Psi_3(A_{1u})$</td>
<td>0.0</td>
<td>37.5</td>
<td>65.0</td>
</tr>
<tr>
<td>$\Psi_1(B_{2u})$</td>
<td>0.2</td>
<td>38.2</td>
<td>66.7</td>
</tr>
<tr>
<td>$\Psi_2(B_{1u})$</td>
<td>0.2</td>
<td>38.2</td>
<td>66.7</td>
</tr>
<tr>
<td>$(J, \Gamma_\parallel)$</td>
<td>(-12.0, 0.4)</td>
<td>(37.5, 1.4)</td>
<td>(65.0, 3.4)</td>
</tr>
</tbody>
</table>

results computed in square-lattice 3$d^9$ Cu oxides (see, e.g., Ref. [83]). It accounts only for direct exchange, since no (intersite) excitations are allowed. In contrast to the ROHF $J$, the anisotropic $\Gamma_\parallel$ is AF by ROHF.

With correlated wave functions, CASSCF and MRCI, the singlet $\Psi_S$ becomes the ground state, well below the triplet components $\Psi_1$, $\Psi_2$ and $\Psi_3$. This shows that the largest energy scale is here defined by the isotropic Heisenberg exchange $J (J > 0)$. In the CASSCF approximation, only intersite $d$–$d$ excitations à la Anderson [35] are accounted for, i.e., polar $t_{2g}^6$–$t_{2g}^4$ configurations. Again, the CAS+SOC $J$, 37.5 meV, is very similar to the CASSCF $J$’s in layered 3$d^9$ cuprates [81–83]. It is seen in Table 6.1 that the configuration-interaction treatment, which now includes as well $t_{2g}^5$e$_g$–$t_{2g}^4$ and O $2p$ to Ir $5d$ charge-transfer virtual states, enhances $\tilde{J}$ by about 70% as compared to the CAS+SOC value, somewhat less spectacular than the ratio between the configuration-interaction and CASSCF $J$’s in layered cuprates. In the latter compounds, this ratio is 3 to 4 [83, 246].

If we include only the six Ir $t_{2g}$ orbitals in the MRCI treatment, $\tilde{J}$ is 49.1 meV (not shown in Table 6.1). The difference between the latter number and the CAS+SOC value given in Table 6.1 is indicative of the role of excitation processes via the Ir $5d$ e$_g$ levels. The further increase from 49.1 to 65 meV is due to excitations that additionally involve the bridging O $2p$ orbitals. The data in Table 6.1 also show that the correlation treatment very much enlarges the symmetric anisotropic coupling $\Gamma_\parallel$, from 0.4 by ROHF to 3.4 meV by MRCI.

6.3.3 Comparison to effective superexchange models

For the Mott-like insulating regime occurring in iridates [10, 14, 15], an effective superexchange model can be in a first approximation set up by considering the leading excited configurations with two holes at the same Ir site. With corner-sharing octahedra and straight Ir-O-Ir bonds along the x axis, the intersite $d$–$d$ hopping takes place via both in-plane $p_x$ and out-of-plane $p_z$ $\pi$-type O orbitals. The relevant effective hopping integrals are $t_1 = (t_{pd}^\pi)^2 / |\varepsilon_d^{xy} - \varepsilon_p^{xy}|$ for the in-plane, $xy$ pair of NN Ir $t_{2g}$ functions and $t_2 = (t_{pd}^\pi)^2 / |\varepsilon_d^{xz} - \varepsilon_p^{xz}|$ for the out-of-plane,
and the Coulomb repulsion integrals by $d$ we arrive at the pseudospin Hamiltonian in (6.2), with energy splitting.

For tetragonal distortions, $e_1 \neq e_2$, $\epsilon^y = \epsilon^z_p$ and therefore $t_1$ and $t_2$ may acquire quite different values. A hole hopping between NN Ir ions is then described by the Hamiltonian

$$H_{\text{hop}}^{ij} = \sum_{m=1,2} \sum_{\sigma=\uparrow,\downarrow} \left( t_{m\sigma} c_{im\sigma}^\dagger d_{jm\sigma} + h.c. \right), \quad (6.6)$$

where $d_{im\sigma}^\dagger$ ($d_{im\sigma}$) is the creation (annihilation) operator at site $i$ of a hole with spin $\sigma$ in the orbital $d_{xy}$ for $m=1$ and $d_{xz}$ for $m=2$. For a bond along the $y$ axis, $p_y$ is replaced by $p_x$, $d_{xz}$ by $d_{yz}$, $\epsilon^y = \epsilon^z_p$, $\epsilon_3 = \epsilon^y_{d} = \epsilon^z_{d} = \epsilon_2$, and the hopping Hamiltonian in (6.6) has the same form.

The interaction of two holes in the $t_2g$ subshell is described by Hund’s coupling $J_H$ and the Coulomb repulsion integrals $U_{mn'} \simeq U - 2J_H$, if $m \neq m'$, and $U_{mm} = U$. While the isotropic exchange is related to second-order processes that concern transitions between the lowest spin-orbit Kramers doublets, i.e., $J \sim t^{2}_{1/2}/U$, the symmetric anisotropy is entirely determined by third-order processes that involve excited Kramers doublets, i.e., is dependent on $t^{2}_{1/2}J_H/U^2$.

The lowest Kramers doublet wave functions

$$|\uparrow\rangle = \sin \theta |xy, \uparrow\rangle + \frac{\cos \theta}{\sqrt{2}} (i|xz, \downarrow\rangle + |yz, \downarrow\rangle)$$

$$|\downarrow\rangle = \sin \theta |xy, \downarrow\rangle - \frac{\cos \theta}{\sqrt{2}} (i|xz, \uparrow\rangle - |yz, \uparrow\rangle) \quad (6.7)$$

as well as those for the excited Kramers doublets are here parameterized as in Ref. [10], with the angle $\theta$ given by $\tan(2\theta) = 2\sqrt{2}\lambda/($ $\lambda - 2\Delta_i$) while $\Delta_i = \epsilon^{d}_{2} - \epsilon^{d}_{1}$ is the tetragonal $t_{2g}$ energy splitting.

By collecting the second- and third-order processes in this effective superexchange model, we arrive at the pseudospin Hamiltonian in (6.2), with

$$J = \frac{4}{U} \left( t_1 \sin^2 \theta + \frac{t_2}{2} \cos^2 \theta \right)^2 + \gamma,$$

$$\Gamma_{||} = -\eta \frac{3(t_1 - t_2)^2}{U} \sin^2 \theta \cos^2 \theta - \gamma,$$

$$\Gamma_{\perp} = -\eta \frac{3t^2_1}{U} \sin^2 \theta \cos^2 \theta - \gamma,$$

$$\Gamma_{zz} = -\eta \frac{3t^2_1}{2U} \cos^4 \theta - \gamma. \quad (6.8)$$

Here $\eta = J_H/U$ and $\gamma = -\frac{\eta}{2} \cos^2 \theta |(t_1 - t_2)^2 \sin^2 \theta + t_1^2 \sin^2 \theta + \frac{1}{2} t^2_2 \cos^2 \theta|$. Now, for $\Gamma_{zz} = \Gamma_{\perp}$, the model described by Eq. (6.5) displays uniaxial compass-like anisotropy [245].
That is obviously the case for perfect, cubic octahedra with $\Delta_0 = 0$, $t_1 = t_2 = t$, and $\cos \theta_c = \sqrt{2}/2$. In the cubic limit we further have from expressions 6.8:

$$J^c = (16/9)t_2^2/U + \gamma^c,$$
$$\gamma^c = -(4\eta/9)t_2^2/U,$$
$$\Gamma^c_\parallel = -\gamma^c,$$
$$\Gamma^c_\perp = \Gamma^c_{zz} = (-2\eta/3)t_2^2/U - \gamma^c.$$

For tetragonal distortions as found in Ba$_2$IrO$_4$ [244], $\Gamma_\perp = \Gamma_{zz}$ implies that $(t_2/t_1)^2 = 2\tan^2 \theta$. As a measure of how large the departure from the cubic limit is we can take the ratio between the tetragonal $t_{2g}$ splitting $\Delta_t$ and the strength of the spin-orbit coupling $\lambda$. The QC calculations yield $\Delta_t = 65$ meV in Ba$_2$IrO$_4$, (see Table 4.5 in Sec. 4.3.2,) and $\lambda = 0.47$ eV (see Sec. 5.3.1). The ratio $\Delta_t/\lambda$ is therefore rather small, $\approx 0.15$.

Estimates for the parameters that enter the effective superexchange model can be most easily obtained in the cubic limit. Using Eqs. 6.8 we find that $\tilde{\Gamma}_\parallel/\tilde{J} \approx (3/8)\eta$. The MRCI+SOC values of Table 6.1, $\tilde{\Gamma}_\parallel = 3.4$ and $\tilde{J} = 65$ meV, then lead to $\eta \approx 0.14$ and $4t_2^2/U \approx 149$ meV. Interestingly, estimates of the hopping integral $t$ from calculations based on density-functional theory in the generalized gradient approximation (GGA) are $t_{GGA} \approx 260$ meV, while the on-site Coulomb repulsion comes out from constrained calculations in the random phase approximation (cRPA) as $U_{cRPA} \approx 1.65$ eV [18]. The ratio $4t_{GGA}^2/U_{cRPA}$ is therefore $\approx 164$ meV, close to the result derived on the basis of the MRCI+SOC effective couplings listed in Table 6.1. On the other hand, the $\eta$ parameter extracted from the periodic GGA calculations [18] is $\eta_{GGA} \approx 0.08$, much smaller than the above value of 0.14. Using the latter value for $\eta$, $\eta_{GGA} \approx 0.08$, an estimate for the symmetric anisotropic coupling $\tilde{\Gamma}_\parallel = 3/8 \eta \tilde{J}$ would be significantly smaller than the MRCI result.

### 6.3.4 Ground state phase diagram

Having established the strength of the dominant in-plane exchange interactions, both isotropic and anisotropic, we now turn to the nature of the magnetic ground state of Ba$_2$IrO$_4$, focusing first on a single square-lattice IrO$_2$ layer. In the classical limit, the compass-Heisenberg model defined by Eqs. 6.5 has an accidental SO(2) ground-state degeneracy, with spins pointing along any direction in the basal $xy$-plane [245, 247, 248]. This degeneracy is eventually lifted via thermal [249–251] or quantum [251–254] order-by-disorder effects, whereby harmonic spin wave fluctuations select the states with spins pointing either along the $x$ or $y$ axis. This is, however, in sharp contrast to experiments, which show basal-plane AF order with magnetic moments along the [110] direction below $\sim 240$ K [227]. It indicates additional anisotropies in the system, large enough to overcome the energy gain from the order-by-
disorder mechanism.

The situation is actually analogous to several $3d^9$ Cu oxides with the same layered “214” crystal structure as $\text{Ba}_2\text{IrO}_4$. It has been shown that in cuprates that particular type of AF order is selected by a subtle interplay between in-plane and interlayer interactions, as discussed in detail in Ref. [252]. Assuming that qualitatively the same 3D mechanism is applicable to $\text{Ba}_2\text{IrO}_4$, we analyze below the main contributions to the expression of the 3D ground-state energy and derive a generic phase diagram. This exercise provides useful insights into the dependence of the ground-state spin configuration on various interaction parameters in 214 iridates.

It turns out that the most important effects competing with the in-plane NN interactions concern (i) the frustrating nature of the isotropic interlayer exchange and (ii) the symmetric part of the anisotropic exchange between layers. To show this, we proceed by parameterizing the global spin direction in each basal plane by an angle $\phi_n$, where $n$ is the layer index, and by writing down all relevant energy contributions.

The first contribution is the zero-point energy (per spin) coming from the order-by-disorder mechanism in each individual layer, $E_{\text{ZP},2D}(\{\phi_n\}) = \sum_n E_{\text{ZP},2D}(\phi_n)$, where

$$E_{\text{ZP},2D}(\phi) = \frac{1}{2N} \sum_\mathbf{q} (\omega_+(\mathbf{q}) + \omega_-(\mathbf{q}))$$

(6.10)

and $\omega_\pm(\mathbf{q})$ are the two spin wave branches, for which explicit expressions are provided in Appendix E.1. A numerical analysis of Eq. 6.10, using the $ab\ initio$ QC values for the in-plane NN effective couplings (see Sec. 6.3.2), shows that $\mathcal{E}_{\text{ZP},2D}(\phi)$ is almost identical to the expression

$$\mathcal{E}_{\text{ZP},2D}(\phi) = -K \cos(4\phi) + E_0,$$

(6.11)

with $K = 0.86 \mu\text{eV}$ and $E_0 = 56.55 \text{meV}$.

We now turn to the second contribution to the energy, which stems from the interlayer isotropic exchange $J_{\text{out}}$. Despite being the dominant portion of the interlayer interactions, its total contribution to the energy vanishes in the mean-field sense due to geometric frustration in the 214 structure, see Fig. 6.2a. Yet, quantum fluctuations driven by $J_{\text{out}}$ still give rise to a zero-point energy contribution

$$E_{\text{ZP},\text{3D}}(\{\phi_n\}) = -B \sum_n \cos(2\phi_n - 2\phi_{n+1}),$$

(6.12)

where $B = 0.032J_{\text{out}}^2/(2J_{\text{av}})$ and $J_{\text{av}} = J + (\Gamma|| + \Gamma\perp)/2$ [255]. Since $B$ is positive for any sign of $J_{\text{out}}$, this contribution favors collinearity of the staggered magnetization in adjacent layers.

The third contribution to the energy comes from the anisotropic portion of the interlayer
couplings. We first note that the antisymmetric DM component vanishes by symmetry since the midpoint of each of these out-of-plane NN Ir-Ir links is an inversion center. The remaining, symmetric portion can be described by a traceless second-rank tensor $\Gamma_{\text{out}}$. The structure of the latter is simplified by using the fact that the out-of-plane NN Ir-Ir links are $C_2$ axes, additionally perpendicular to reflection planes. Adding up the four tensors (related to each other by symmetry) from all four NN bonds above/below the reference layer gives [252]

$$E_{\text{aniso},3D} = -A \sum_n \sin(\phi_n + \phi_{n+1}),$$

(6.13)

where the constant $A$ is fixed by the elements of $\Gamma_{\text{out}}$.

The total energy now reads

$$E = E_{\text{ZP},2D} + E_{\text{ZP},3D} + E_{\text{aniso},3D}.$$  

(6.14)

It can be minimized analytically as described in Appendix E.2 by working it out for a bi-layer of Ba$_2$IrO$_4$. The resulting phase diagram in the $(A/K, B/K)$ plane is shown in Fig. 6.4 for positive $A$ (the phase diagram for $A < 0$ is identical, see Appendix E.2) and hosts three different phases, two collinear (phases I and II) and one noncollinear (phase III).

In phase I, the staggered magnetizations point along one of the ⟨110⟩ axes and the relative
directions between adjacent planes are regularly collinear or anticollinear. In phase III, the AF magnetization prefers one of the \( \langle 100 \rangle \) axes and the relative directions in adjacent planes are now perpendicular to each other. Finally, in phase II, the relative directions between adjacent planes are again either collinear or anticollinear but the staggered magnetizations in each layer rotate in the basal plane as a function of \( A/K \), see Appendix E.2. Importantly, the degeneracy is not completely lifted by the above couplings and all phases have an Ising degree of freedom per layer, which comes from the fact that the energy remains the same if we flip all spins within a given layer. This remaining macroscopic degeneracy may eventually be lifted via higher-order processes or farther-neighbor couplings, see for example the discussion in Ref. [255].

The collinear AF structure observed experimentally [227] in \( \text{Ba}_2\text{IrO}_4 \) can now be naturally explained provided that \( A \) and \( B \) fall into the broad region of phase I in the phase diagram of Fig. 6.4 and by taking into account the lifting of the macroscopic Ising degeneracy mentioned above.

In summary, our \textit{ab initio} calculation of effective magnetic exchange interactions in \( \text{Ba}_2\text{IrO}_4 \) reveal a dominant Heisenberg \( J \) and uniaxial anisotropy. However, the resulting compass-Heisenberg model is not enough to explain the experimentally observed AF ordering pattern with spins along the \( \langle 110 \rangle \) direction. One possible way to explain this ordering is by including interlayer exchange interactions in the effective Hamiltonian. The magnetic phase diagram obtained from such an extended model Hamiltonian does contain a large region with AF spin ordering as observed in the measurements.

### 6.4 Heisenberg interaction and antisymmetric anisotropy in \( \text{Sr}_2\text{IrO}_4 \)

#### 6.4.1 \( C_{2v} \) symmetry of the \( [\text{Ir}_2\text{O}_{11}] \) unit and the corresponding spin Hamiltonian

The crystal structure of \( \text{Sr}_2\text{IrO}_4 \) has a lower \( (I4_1/acd) \) symmetry compared to \( \text{Ba}_2\text{IrO}_4 \) (see Sec. 4.3.1), due to the staggered rotation of the \( \text{IrO}_6 \) octahedra. As a result, the symmetry of each block of two NN octahedra is \( C_{2v} \) (see Fig. 6.5), with no inversion symmetry at the midpoint of the Ir-Ir link. Consequently, the DM anisotropy in Eq. 6.1 is finite [10, 28]. In the reference frame with the \( x \) axis along the Ir-Ir link and \( z \) perpendicular to the \( \text{IrO}_2 \) layer, only the \( D_z \) component of the DM vector is non-zero [10]. Further, having the \( C_2 \) axis along the \( y \) direction, the \( \Gamma_{ij} \) in Eq. 6.1 is diagonal. Thus, the effective spin Hamiltonian for an Ir-Ir
6.4 Heisenberg interaction and antisymmetric anisotropy in Sr$_2$IrO$_4$

Fig. 6.5 Sketch of two NN Ir sites in the $ab$-plane of Sr$_2$IrO$_4$. The $z$-axis is perpendicular to the plane. The [Ir$_2$O$_{11}$] unit has $C_{2v}$ point-group symmetry.

The link along the $x$ axis can be written as

$$\mathcal{H}_{ij}\|_x = J \vec{S}_i \cdot \vec{S}_j + D_z (S_i^z S_j^z - S_i^z S_j^z) + \Gamma_{xx} (S_i^x S_j^x - S_i^y S_j^y) + \Gamma_{zx} (S_i^z S_j^y - S_i^y S_j^z),$$

(6.15)

where the traceless property of $\Gamma_{ij}$ is used to substitute $\Gamma_{yy} = - (\Gamma_{xx} - \Gamma_{zz})$. The eigenstates and the corresponding eigenvalues of the Hamiltonian 6.15 are

$$|\Psi_S\rangle = a |\Phi_S\rangle + b |\Phi_1\rangle, \quad E_S = -\frac{1}{4} \left( -\Gamma_{zz} - \zeta - J \right),$$

$$|\Psi_1\rangle = a |\Phi_S\rangle - b |\Phi_1\rangle, \quad E_1 = -\frac{1}{4} \left( -\Gamma_{zz} + \zeta - J \right),$$

$$|\Psi_2\rangle = |\Phi_2\rangle = \left| \uparrow \uparrow \rangle + \downarrow \downarrow \rangle \right\rangle / \sqrt{2}, \quad E_2 = \frac{1}{4} \left( -2 \Gamma_{xx} + J \right),$$

$$|\Psi_3\rangle = |\Phi_3\rangle = \left| \uparrow \uparrow \rangle - \downarrow \downarrow \rangle \right\rangle / \sqrt{2}, \quad E_3 = \frac{1}{4} \left( -2 (\Gamma_{xx} + \Gamma_{zz}) + J \right),$$

(6.16)

(6.17)

where $|\Phi_S\rangle = \left| \uparrow \downarrow \right\rangle - \left| \downarrow \uparrow \right\rangle / \sqrt{2}$, $|\Phi_1\rangle = \left| \uparrow \downarrow \right\rangle + \left| \downarrow \uparrow \right\rangle / \sqrt{2}$ and $\zeta = \sqrt{4D_z^2 + (\Gamma_{zz} - 2J)^2}$.

For $C_{2v}$ symmetry of the two-octahedra unit (Fig. 6.5), the four low-lying (spin-orbit) states, $|\Psi_S\rangle$, $|\Psi_1\rangle$, $|\Psi_2\rangle$ and $|\Psi_3\rangle$, transform according to the $A_1$, $A_1$, $B_1$ and $B_2$ irreducible representations, respectively (see App. C.3), implying that $|\Psi_S\rangle$ and $|\Psi_1\rangle$ are in principle allowed to be an admixture of the singlet $|\Phi_S\rangle$ and antisymmetric triplet $|\Phi_1\rangle$ states. The reason for this admixture is the antisymmetric DM interaction, in other words, $a$ and $b$ in Eq. 6.16 are functions of $D_z$. 
6.4.2 Two-site magnetic spectrum

The QC calculations were performed on a similar cluster to that used for Ba$_2$IrO$_4$. The lattice parameters were taken from Ref. [89]. The NN Ir sites in these calculations were modeled more accurately as compared to the study on Ba$_2$IrO$_4$, by using Ir$^{4+}$ 5$d^5$ effective total ion potentials [239] instead of approximating them with closed shell Pt$^{4+}$ $t^6$ $2g$ ions.

The four low-lying states describing the magnetic spectrum of two NN sites are listed in Table 6.2. Energy splittings at three levels of approximation, single-configuration ROHF (HF+SOC), CASSCF (CAS+SOC) and MRCI (MRCI+SOC) are provided. It can be seen that within the ROHF approximation, the triplet states are lower in energy as in Ba$_2$IrO$_4$. At the CASSCF and MRCI levels, the singlet becomes the ground state, with triplet states at $\approx 33$ and $\approx 56.5$ meV, respectively. The triplet states are split up due to the finite anisotropic couplings that are allowed in $C_2v$ symmetry.

The Hamiltonian 6.15 implies four unknown parameters, whereas the magnetic spectrum in Table 6.2 provides only three energy splittings. Deriving a unique set of coupling constants for the spin Hamiltonian 6.15 is therefore not possible with just the MRCI eigenvalues alone. One way to overcome this issue is to use the MRCI wave functions, also accessible in the QC outputs. In the present work, however, we do not carry out a thorough analysis of the MRCI wave spin-orbit functions, instead, the expressions for the relation between the isotropic and anisotropic exchange parameters are derived.

Rearranging the expressions for the eigenstates in 6.16 and expressing the anisotropic exchange parameters as a function of the isotropic interaction $J$, we have

\[
\begin{align*}
\Gamma_{zz} &= E_2 + E_3 - E_1 - J \\
\Gamma_{xx} &= \frac{5E_2 - 3E_3 + E_1 + J}{2} \\
\Gamma_{yy} &= \frac{- (3E_2 - E_3 - E_1 - J)}{2}
\end{align*}
\]

Table 6.2 Energy splittings for the four lowest spin-orbit states of two NN IrO$_6$ octahedra in Sr$_2$IrO$_4$, at different levels of approximation (all in meV). Due to the antisymmetric anisotropic exchange, $\Psi_S$ and $\Psi_1$ are admixtures of $\Phi_8 = (\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$ and $\Phi_1 = (\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2}$. The symmetry of each state is indicated in parentheses.

<table>
<thead>
<tr>
<th>States/Method</th>
<th>HF+SOC</th>
<th>CASSCF+SOC</th>
<th>MRCI+SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Psi_S(A_1)$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\Psi_1(A_1)$</td>
<td>-11.3</td>
<td>33.7</td>
<td>57.0</td>
</tr>
<tr>
<td>$\Psi_2(B_1) = (\uparrow\uparrow + \downarrow\downarrow)/\sqrt{2}$</td>
<td>-11.6</td>
<td>33.6</td>
<td>56.9</td>
</tr>
<tr>
<td>$\Psi_3(B_2) = (\uparrow\uparrow + \downarrow\downarrow)/\sqrt{2}$</td>
<td>-11.7</td>
<td>33.3</td>
<td>55.9</td>
</tr>
</tbody>
</table>
6.4 Heisenberg interaction and antisymmetric anisotropy in \( \text{Sr}_2\text{IrO}_4 \)

Fig. 6.6 (a) Dependence of the anisotropic exchange interactions on the Heisenberg \( J \) in \( \text{Sr}_2\text{IrO}_4 \), as obtained by mapping the MRCI+SOC energy spectrum (see Table 6.2) onto the eigenvalues (6.16) of the Hamiltonian 6.15. (b) Dependence of the exchange parameters \( J_i = J + \Gamma_{ii}, i \in \{x, y, z\} \), on the staggered rotation (\( \alpha \) in radians) of \( \text{IrO}_6 \) octahedra in \( \text{Sr}_2\text{IrO}_4 \), as obtained from superexchange model Hamiltonian calculations (taken from Ref. [28]).

\[
D_z = \sqrt{\left( \frac{E_1 + E_2 + E_3}{3} \right)^2 - \frac{(E_2 + E_3 - E_1 - 3J)^2}{2}}. \tag{6.18}
\]

By using the MRCI+SOC energies from Table 6.2, the variation of the anisotropic exchange interactions with the isotropic coupling \( J \) is plotted in Fig. 6.6a. It is seen that the DM interaction \( D_z \) is very sensitive to \( J \) (2 meV variation in \( J \) leads to a 18 meV change of \( D_z \)). The anisotropic exchange interaction parameters have also been calculated using model Hamiltonians based on superexchange theory [27, 28]. These studies indicate that, for the staggered rotation of \( \text{IrO}_6 \) octahedra by 11.5° (experimentally observed rotation angle), the DM interaction is roughly one third of \( J \). Further, they provide insights into the variation of the symmetric anisotropic interactions \( \Gamma_{ij} \) with the \( \text{IrO}_6 \) rotation angle \( \alpha \) [28]. A plot for the dependence of \( J_i = J + \Gamma_{ii}, i \in \{x, y, z\} \), taken from Ref. [28] is shown in Fig. 6.6b. For the point on the \( J \) axis in Fig. 6.6a with a ratio \( J_z/J_x \) that corresponds to \( \alpha = 0.201 \) rad (11.5°) in Fig. 6.6b, we find \( J = 55.32, D_z = 13.03, \Gamma_{zz} = 0.48, \Gamma_{xx} = 0.76 \) and \( \Gamma_{yy} = -1.24 \) meV. The ratio \( D_z/J = 0.24 \) we obtain this way is in fact very close to that estimated by various model Hamiltonian calculations and fits of the experimental data [10, 27, 28]. The value of the isotropic exchange \( J \) is also in excellent agreement with the value of 60 meV derived from RIXS experiments [40]. Apart from this remarkable agreement of \( J \) and \( D_z/J \) with experiments and model calculations, our analysis also provides the values of the symmetric anisotropic interactions. The latter are an order of magnitude smaller than the isotropic \( J \) and antisymmetric anisotropy \( D_z \).

The staggered rotation of the \( \text{IrO}_6 \) octahedra and the single-layer Hamiltonian in 6.15,
with a DM vector along the $z$ axis and a biaxial easy-plane symmetric anisotropy described by two independent diagonal components of $\Gamma$, correctly explain the canting angle of the basal-plane AF order [10, 28] but fails in predicting the AF vector alignment along one of the $\langle 110 \rangle$ axes. The reason is that the presence of two additional anisotropies, $D \parallel z$ and $\Gamma_{zz} \neq 0$, do not remove the SO(2) basal-plane ground-state degeneracy, at least not in the classical limit. This accidental degeneracy can, however, again be lifted via the 3D mechanism discussed for the case of $\text{Ba}_2\text{IrO}_4$, to arrive at an AF ordering pattern similar to that of $\text{Ba}_2\text{IrO}_4$ [227].

### 6.4.3 Magnetic interactions in strained samples of $\text{Sr}_2\text{IrO}_4$

To investigate the dependence of the magnetic properties on structural details of $\text{Sr}_2\text{IrO}_4$, we studied the magnetic interactions in thin films of $\text{Sr}_2\text{IrO}_4$ as experimentally grown on $\text{SrTiO}_3$ (SIO-STO) and $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (SIO-LSAT) substrates [256]. The films grown on SIO-STO substrates are characterized by a tensile strain of 0.45%. The films grown on SIO-LSAT substrates display the same amount of compressive strain. As a result, the lattice parameters change to $a = 3.900$, $c = 25.690$ and $a = 3.870$, $c = 25.910\text{Å}$ [256] in SIO-STO and SIO-LSAT, respectively, from $a = 3.878$, $c = 25.790\text{Å}$ in bulk $\text{Sr}_2\text{IrO}_4$ (SIO-bulk) [89].

Since the precise structural details of the thin film samples (e.g., Ir-O distances and Ir-O-Ir bond angles) are difficult to access experimentally, we used two different structural models to simulate the effects of strain. In model A, the Ir-O-Ir bond angles were kept the same as in the bulk and only the inter-atomic distances were changed with strain. In the second model (model B), the in-plane Ir-O bond lengths are fixed to the values measured in the bulk and

<table>
<thead>
<tr>
<th>Angle (°)</th>
<th>SIO-STO</th>
<th>SIO-LSAT</th>
<th>SIO-Bulk</th>
<th>SIO-STO</th>
<th>SIO-LSAT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir-O-Ir</td>
<td>157</td>
<td>157</td>
<td>157</td>
<td>160</td>
<td>155</td>
</tr>
<tr>
<td>Ir-Ir</td>
<td>3.90</td>
<td>3.87</td>
<td>3.88</td>
<td>3.90</td>
<td>3.87</td>
</tr>
<tr>
<td>4 × Ir-O</td>
<td>1.99</td>
<td>1.975</td>
<td>1.98</td>
<td>1.98</td>
<td>1.98</td>
</tr>
<tr>
<td>2 × Ir-O</td>
<td>2.05</td>
<td>2.07</td>
<td>2.06</td>
<td>2.06</td>
<td>2.06</td>
</tr>
<tr>
<td>$\Psi_S$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\Psi_1$</td>
<td>50.1</td>
<td>60.5</td>
<td>57.0</td>
<td>56.8</td>
<td>55.3</td>
</tr>
<tr>
<td>$\Psi_2$</td>
<td>50.0</td>
<td>60.5</td>
<td>56.9</td>
<td>56.6</td>
<td>55.2</td>
</tr>
<tr>
<td>$\Psi_3$</td>
<td>49.2</td>
<td>59.4</td>
<td>55.9</td>
<td>55.6</td>
<td>54.4</td>
</tr>
</tbody>
</table>

The precise structural details of the thin film samples (e.g., Ir-O distances and Ir-O-Ir bond angles) are difficult to access experimentally, we used two different structural models to simulate the effects of strain. In model A, the Ir-O-Ir bond angles were kept the same as in the bulk and only the inter-atomic distances were changed with strain. In the second model (model B), the in-plane Ir-O bond lengths are fixed to the values measured in the bulk and
for reproducing the strain-induced variation of the lattice parameters [256], the Ir-O-Ir bond angles were modified. In the upper half of Table 6.3, Ir-O distances and Ir-O-Ir bond angles are shown for both models A and B and compared with bulk data.

The magnetic spectra calculated for models A and B are presented in the lower half of Table 6.3. First, let us look at the energy scale of the singlet-triplet (average of the three triplet components) separation $\Delta E_{ST}$ in the two models (for the moment we neglect the anisotropic interactions). In model A, for the SIO-STO sample displaying in-plane expansion, $\Delta E_{ST}$ decreases to 49.8 meV, from a SIO-bulk value of 56.6 meV. For the compressed sample (SIO-LSAT), $J$ increases to 60.1 meV, see Table 6.4. In the case of model B, a larger Ir-O-Ir bond angle for SIO-STO leads to a $\Delta E_{ST}$ of 56.4 meV and a smaller Ir-O-Ir bond angle accommodating the compressive strain produces $\Delta E_{ST} = 55.0$ meV. One finds variations of $\Delta E_{ST}$ of 3.5 to 7 meV in model A and only 1.6 meV variation in model B, as compared to the bulk. Since the structure of the triplet components is always the same, with two of them nearly degenerate and the energy splitting between the lowest and highest triplet terms taking values in a narrow interval between 0.9 and 1.2 meV, we can safely conclude that for model A, the most important changes with strain concern the variation of the isotropic Heisenberg exchange $J$.

In Table 6.4, the experimental RIXS values for the zone-boundary magnon energy, which is proportional to $J$, is also shown for the strained samples [234]. With compressive strain the magnons are driven to higher energies, whereas with tensile strain it is lowered. This trend observed in the RIXS spectra is reproduced by the QC results for model A. In contrast, for model B, the variations of $\Delta E_{ST}$ are much smaller and do not follow the trend observed for $J$ by RIXS. This suggests that the most significant structural change that occurs in the epitaxial thin films is the modification of the Ir-Ir and Ir-O bond lengths.

In Fig. 6.7, the dependencies expressed by relations 6.18 are plotted for the two different types of strained samples of Sr$_2$IrO$_4$ using the MRCI+SOC values listed in Table 6.4. An instructive exercise is to now use the particular values that the $J_z/J_x$ ratio takes for either model A or model B for each of the two types of SIO films according to the calculations.

### Table 6.4 Effective singlet-triplet energy splittings $\Delta E_{ST}$ in bulk Sr$_2$IrO$_4$ and Sr$_2$IrO$_4$ thin films for two adjacent Ir ions (meV). MRCI+SOC results, see text. Experimental RIXS values for the zone boundary magnon energy (proportional to $J$) are also provided for comparison [234]. Strain-induced relative changes in the energy scales are listed in parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RIXS $E_{(\pi,0)}$</th>
<th>Model A $\Delta E_{ST}$</th>
<th>Model B $\Delta E_{ST}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIO-STO</td>
<td>172 (-3.4%)</td>
<td>49.8 (-12%)</td>
<td>56.4 (-0.4%)</td>
</tr>
<tr>
<td>SIO-Bulk</td>
<td>178</td>
<td>56.6</td>
<td>56.6</td>
</tr>
<tr>
<td>SIO-LSAT</td>
<td>196 (+10.0%)</td>
<td>60.1 (+5.8%)</td>
<td>55.0 (-2.8%)</td>
</tr>
</tbody>
</table>
based on superexchange theory of Ref. [28]. In particular, the authors of Ref. [28] find that $J_z/J_x = 0.995$ for $\alpha = 157^\circ$ (bulk SIO and SIO-STO/SIO-LSAT films in model A), $J_z/J_x = 0.98$ for $\alpha = 160^\circ$ (SIO-STO films in model B) and $J_z/J_x = 1.007$ for $\alpha = 155^\circ$ (SIO-LSAT films, model B), see Fig. 6.6b. Assuming such values for $J_z/J_x$, we can then provide estimates for $J$ and $D_z$ for each of the structural models employed in our study, see Fig. 6.7. In model A, both $J$ and $D_z$ increase with decreasing Ir-Ir distance (from tensile to compressive strain). However, the $D_z/J$ ratio remains almost the same, about 0.22. This confirms the earlier conclusion drawn from the singlet-triplet energy separation $\Delta E_{ST}$ alone. In model B, $J$ is smaller in both SIO-STO and SIO-LSAT, as compared to SIO-bulk. The $D_z/J$ ratio goes from 0.17 to 0.26.

![Graphs showing the dependence of anisotropic exchange interactions on the Heisenberg $J$ for Sr$_2$IrO$_4$ thin films. These plots are obtained by mapping the MRCl+SOC energy spectrum (Table 6.3) onto the eigenvalues (6.16) of the Hamiltonian 6.15. (a) and (b) are respectively for tensile (SIO-STO) and compressive (SIO-LSAT) structures as in model A; (c) and (d) are the same for structures in model B (see text). The ratio $J_z/J_x$ ($J = J_i + \Gamma_{ii}, i \in \{x,y,z\}$) is taken from Ref. [28], based on which the parameters $J$ and $D_z$ are extracted.](image)
6.5 Conclusions

In conclusion, we have employed \textit{ab initio} QC techniques to evaluate the magnetic exchange parameters in the corner-sharing octahedral square-lattice iridates Ba$_2$IrO$_4$ and Sr$_2$IrO$_4$. The \textit{ab initio} results reveal effective uniaxial anisotropy in Ba$_2$IrO$_4$, although the actual symmetry of each of the in-plane Ir-Ir links is lower than $D_{4h}$. The anisotropic effective coupling constants are as large as 3.5 meV, comparable in strength with the anisotropic Kitaev exchange in honeycomb Na$_2$IrO$_3$ (discussed in the next chapter). However, the largest energy scale is still defined here by the Heisenberg $J$, with $J \approx 65$ meV. This value agrees with estimates based on resonant inelastic x-ray scattering measurements on 214 iridates [40].

Due to the staggered rotation of IrO$_6$ octahedra, the inversion symmetry is lost in Sr$_2$IrO$_4$, leading to non-zero DM interaction. It turns out that just the relative energies of the four low-lying magnetic states in the two-site problem are insufficient to uniquely extract all the parameters in the effective spin Hamiltonian. Nevertheless, using the magnetic spectrum obtained from QC calculations, we derived relations expressing the anisotropic exchange coupling parameters as functions of the Heisenberg $J$. Further, using the insights from the model Hamiltonian study of Ref. [28], we could finally deduce unique values for all exchange couplings. The obtained isotropic $J \approx 55$ meV and a ratio $D_z/J \approx 0.24$ are in excellent agreement with experiments and phenomenological model calculations [10, 27, 28, 40]. The singlet-“triplet” energy separation, calculated for model structures that incorporate strain effects in thin film samples of Sr$_2$IrO$_4$, correctly reproduce the trend observed in the RIXS zone-boundary magnon energies. Moreover, the calculations suggest that the most significant structural change occurring in epitaxial thin films is the modification of the Ir-Ir and Ir-O bond lengths.
Chapter 7

Kitaev interactions in honeycomb Na$_2$IrO$_3$ and Li$_2$IrO$_3$

In this chapter, the essential magnetic interactions in honeycomb-lattice iridates, Na$_2$IrO$_3$ and Li$_2$IrO$_3$, are analyzed. We determine the signs and the strengths of the exchange coupling parameters using ab initio quantum chemistry methods. Our calculations reveal highly anisotropic exchange interactions in the two compounds, with the Kitaev-type terms being dominant in Na$_2$IrO$_3$. Remarkably, although the two compounds are isostructural, we find the magnetic ordering to be completely different in these systems.

7.1 Introduction

The Heisenberg spin model with isotropic interactions between localized spin moments has seen unprecedented success in describing the cooperative magnetic properties of many solid-state systems. A less conventional spin model – the Kitaev model [29] – has been recently proposed for honeycomb-lattice compounds with 90° metal-oxygen-metal bonds and strong spin-orbit interactions [10]. It has nontrivial topological phases with elementary excitations exhibiting Majorana statistics, which are relevant and much studied in the context of topological quantum computing [29–34]. Candidate materials proposed to host such physics are the honeycomb iridates Na$_2$IrO$_3$ and Li$_2$IrO$_3$ [10]. The magnetically active sites, the Ir$^{4+}$ species, display in these systems a 5$d^5$ valence electron configuration, octahedral ligand coordination and bonding of NN Ir ions through two ligands [42, 206]. The ground state electronic configuration at each of these Ir sites is a $t_{2g}^5$ effective $\tilde{j} \simeq 1/2$ spin-doublet [10, 14, 26, 97] (see also Sec. 4.4). The anisotropic, Kitaev-type coupling then stems from the particular form the superexchange between the Ir $\tilde{j} \simeq 1/2$ pseudospins takes for 90° bond angles on the Ir-O$_2$-Ir

Part of this chapter is published as a regular article in New J. Phys. 16, 013056 (2014) [13].
plaquette [10, 11, 111].

Recent measurements on Na$_2$IrO$_3$ [42, 206] indicate significant lattice distortions away from the idealized case of cubic IrO$_6$ octahedra and 90° Ir-O-Ir bond angles for which the Kitaev-Heisenberg (KH) model was proposed [10, 111]. Lower-symmetry crystal fields and distortions of the Ir-O-Ir bonds obviously give rise to finite Ir $t_{2g}$ splittings [44, 185] (see Chap. 4) and more complex superexchange physics [257, 258]. It has been actually shown that the interplay between “local” distortions of the O cage and longer-range crystal anisotropy is a key feature in 5$d$ oxides [235, 236, 259] and the outcome of this competition is directly related to the precise nature of the magnetic ground state [236]. Moreover, the lower symmetry characterizing a given [Ir$_2$O$_{10}$] unit of two edge-sharing octahedra allows in principle for nonzero anisotropic interaction terms beyond the Kitaev picture. Experimentally, both Na$_2$IrO$_3$ and Li$_2$IrO$_3$ have been found to order antiferromagnetically below 15 K [260, 261]. While inelastic neutron scattering [42], x-ray diffraction [262] and resonant inelastic x-ray scattering experiments [263] indicate an AF zigzag ordering pattern in Na$_2$IrO$_3$, the nature of the AF ground state of Li$_2$IrO$_3$ is to date unknown. The questions that arise are therefore (i) which magnetic instability preempts the formation of the spin-liquid state anticipated for spin-orbit coupled $\tilde{S} = 1/2$ honeycomb systems in Ref. [11, 111] and (ii) how close the system remains to a spin-liquid ground state. To clarify the signs and the strengths of the effective coupling constants in both Na$_2$IrO$_3$ and Li$_2$IrO$_3$, here we employ many-body ab initio techniques from wave-function-based quantum chemistry [50].

We begin by giving a brief description of the superexchange mechanism that leads to the Kitaev-Heisenberg model and then derive the relevant spin-Hamiltonian for A$_2$IrO$_3$ (A=Li,Na) compounds. We find that in the Kitaev reference frame, some of the off-diagonal terms of the symmetric anisotropic exchange-coupling tensor are allowed to be non-zero by symmetry. In Sec. 7.3, we first estimate the magnetic exchange parameters of an idealized Na$_2$IrO$_3$ structure with 90° Ir-O-Ir bond angles and compare them with those obtained for the reported $C2/m$ crystal structure of Na$_2$IrO$_3$ displaying distorted (rhombic) Ir$_2$O$_2$ plaquettes. Interestingly, we find the effective Kitaev coupling to be FM and dominant. The NN Heisenberg $J$, however, is AF and significantly weaker. For NN interaction parameters as derived in the QC study, exact diagonalization (ED) calculations including additionally finite AF second ($J_2$) and third ($J_3$) neighbor Ir-Ir Heisenberg couplings indicate the presence of zigzag AF order, in agreement with the experimentally observed spin texture [42, 206, 263].

In Sec. 7.4, we present QC exchange couplings for the sister compound Li$_2$IrO$_3$. Interestingly, the coupling parameters come out to be significantly different from those of Na$_2$IrO$_3$. The Heisenberg coupling in Li$_2$IrO$_3$ even has opposite signs on the two crystallographically inequivalent Ir-Ir links. Through an additional set of QC calculations, we demonstrate in Sec. 7.4.2, that this behavior follows a more general trend of $J$ and $K$ as functions of bond-angles and inter-atomic distances. We explain this way the difference in sign of the NN $J$
7.2 Symmetric anisotropy and the Kitaev-Heisenberg (KH) model

7.2.1 Edge-shared geometry: Kitaev-Heisenberg exchange

In the honeycomb structure of the A$_2$IrO$_3$ compounds, two NN IrO$_6$ octahedra share an O-O edge, as shown in Fig. 7.1. The magnetic coupling between these two NN $\tilde{S} = 1/2$ pseudospins can occur by superexchange processes mediated via the two oxygen ligands or through direct exchange caused by the direct overlap of the Ir $d$ orbitals.

The superexchange via oxygen ligands in the 90° Ir-O-Ir bond geometry leads in the simplest model to a peculiar situation where the isotropic Heisenberg interaction vanishes completely due to a destructive interference among the multiple superexchange paths. On the other hand, it gives rise to non-zero anisotropic interaction due to virtual hoppings into the excited $\tilde{S} = 3/2$ states that are coupled to the $\tilde{S} = 1/2$ ground state via Hund’s exchange [10]. This anisotropic exchange is Ising-like, coupling only components of the pseudospins that are perpendicular to the Ir$_2$O$_2$ plaquette. For example, only the $z$ components of the pseudospins couple in the geometry shown in Fig. 7.1b. On the honeycomb-lattice there are three different Ir-Ir links (see Fig. 7.1a) and for each of these links the bond dependent spin Hamiltonian can be written as [10]

$$H^{(\gamma)}_{ij} = -K_{ij}\tilde{S}^\gamma_i\tilde{S}^\gamma_j,$$ (7.1)

where $\gamma$ is perpendicular to the plane of Ir$_2$O$_2$ plaquette. This type of interaction exactly resembles the Kitaev spin-model [29], where along a particular bond on the honeycomb plane only one set of spin components is magnetically active. The Kitaev model is exactly solvable and hosts a spin-liquid state possessing anyonic excitations with fractional statistics [33].

The direct exchange due to the overlap of Ir $d$ orbitals gives rise to an AF isotropic Heisenberg interaction [111]. The total exchange Hamiltonian for a particular Ir-Ir link in Fig. 7.1a...
Kitaev interactions in honeycomb Na$_2$IrO$_3$ and Li$_2$IrO$_3$

Fig. 7.1 (a) Ir honeycomb layer in $A_2$IrO$_3$. An idealized model with cubic IrO$_6$ and AO$_6$ octahedra of equal size and 90° Ir-O-Ir bonds is shown. The two types of bonds B1 and B2 = B3 in the actual crystal structures of Na$_2$IrO$_3$ and Li$_2$IrO$_3$ are also indicated. (b) NN IrO$_6$ octahedra and the two different coordinate frames $(x,y,z)$ and $(X,Y,Z)$, see text, used to express the effective spin Hamiltonian.

Can then be written as [11, 111]

$$
\mathcal{H}^{ij} = J \tilde{S}_i \cdot \tilde{S}_j - K \tilde{S}_i^\alpha \tilde{S}_j^\alpha ,
$$

(7.2)

where $J$ is the isotropic interaction and $K$ is the Kitaev type of anisotropic exchange.

7.2.2 $A_2$IrO$_3$: symmetry of the [Ir$_2$O$_{10}$] unit and effective spin-Hamiltonian

In the $C2/m$ crystal structure of $A_2$IrO$_3$ [42, 187], there are two different types of NN Ir-Ir links. For the bonds along the crystallographic $b$ axis (B1 bonds), the Ir-Ir axis is a $C_2$ axis with an orthogonal mirror plane [42, 206], i.e., the symmetry of those [Ir$_2$O$_{10}$] units is $C_{2h}$ (see Fig. 7.1a). For the other Ir-Ir links (B2 and B3), the symmetry of these units is lowered to $C_i$, due to additional slight distortions of the IrO$_6$ octahedra that give rise to different Ir-O distances (see Fig. 4.5 in Sec. 4.4).

For a pair $\{i,j\}$ of magnetic sites in systems in which the midpoint of the $ij$ link displays inversion symmetry, the most general bilinear exchange Hamiltonian is

$$
\mathcal{H}^{(ij)\in b} = J^{(0)}_b \tilde{S}_i \cdot \tilde{S}_j + \sum_{\alpha,\beta \in \{X,Y,Z\}} \Gamma^b_{\alpha\beta} \tilde{S}_i^\alpha \tilde{S}_j^\beta ,
$$

(7.3)

where $\tilde{S}_i, \tilde{S}_j$ are pseudospin operators ($\tilde{S} = 1/2$) [10, 111], $J^{(0)}_b$ is the NN Heisenberg interaction and the elements $\Gamma^b_{\alpha\beta}$ form a traceless symmetric second-rank tensor. The index $b$ refers to the type of Ir-Ir link ($b \in \{B1,B2,B3\}$).

It is convenient to choose the $X$ axis along the Ir-Ir link ($C_2$ axis) and $Z$ perpendicular to
the plaquette defined by the two Ir ions and the two bridging ligands (see Fig. 7.1b). With such a choice of the coordinate system only $\Gamma_{YZ} = \Gamma_{ZY}$ are finite and so

$$\Gamma^b = \begin{pmatrix} A_b & 0 & 0 \\ 0 & B_b & C_b \\ 0 & C_b & -A_b - B_b \end{pmatrix}_{\{X,Y,Z\}}. \quad (7.4)$$

The fact that $Y$ and $Z$ are not $C_2$ axes is related to the configuration of the four adjacent Ir sites – two of those are below and two above the $XY$ plane, with no inversion center (see Fig. 7.2b) – and the trigonal squashing of the IrO$_6$ octahedra [42]. The eigenvalues and corresponding eigenstates of the Hamiltonian in 7.3 are then obtained from a straightforward diagonalization as

$$E_S = -\frac{3J_b^{(0)}}{4}, \quad \Phi_S = \frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}},$$

$$E_1' = \frac{J_b^{(0)} + A_b + \sqrt{(A_b + 2B_b)^2 + 4C_b^2}}{4}, \quad \Phi_1 = \frac{\uparrow\downarrow + \downarrow\uparrow}{\sqrt{2}},$$

$$E_2' = \frac{J_b^{(0)} + A_b - \sqrt{(A_b + 2B_b)^2 + 4C_b^2}}{4}, \quad \Phi_2 = \frac{\uparrow\uparrow + \downarrow\downarrow}{\sqrt{2}},$$

$$E_3 = \frac{J_b^{(0)} - 2A_b}{4}, \quad \Phi_3 = \frac{\uparrow\uparrow - \downarrow\downarrow}{\sqrt{2}}. \quad (7.5)$$

Here $\Phi_S$ is the two-site spin singlet state and $\Phi_{1-3}$ are combinations of the three triplet components. The latter are degenerate in the plain Heisenberg model. The above diagonalization procedure is equivalent with a rotation of the coordinate system $(X,Y,Z)$ around $X$ by an angle $\gamma$ to a new frame $(X',Y',Z')$ in which the symmetric anisotropic exchange matrix is diagonal [266]. For $C_{2h}$ point-group symmetry, the $\Phi_S$, $\Phi_1$, $\Phi_2$ and $\Phi_3$ SO wave functions transform according to the $A_g$, $B_u$, $B_u$ and $A_u$ irreducible representations, respectively (see App. C.2). Since states $\Phi_1$ and $\Phi_2$ belong to the same irreducible representation $B_u$, they are in general admixed, i.e., in the reference frame $(X,Y,Z)$ the corresponding eigenfunctions should be written as

$$\Psi_1 = \Phi_1 \cos \gamma + i\Phi_2 \sin \gamma,$$

$$\Psi_2 = i\Phi_1 \sin \gamma + \Phi_2 \cos \gamma. \quad (7.6)$$

The mixing parameter $\xi = \sin \gamma$ is given by

$$i\xi = \langle \Phi_2 | \Psi_1 \rangle = \langle \Phi_1 | \Psi_2 \rangle \quad (7.7)$$
and is explicitly obtained here from the QC data (see App. D). $(X', Y', Z')$ are also referred to as principal axes and the angle $\gamma$ is given by
\[
\tan(2\gamma) = \frac{2C_b}{A_b + 2B_b}.
\] (7.8)

Using Eqs. 7.5, 7.7 and 7.8 the effective coupling parameters of 7.3 are obtained as:
\[
J_b^{(0)} = \frac{1}{3}(E_1 + E_2 + E_3) - E_S,
\]
\[
A_b = \frac{2}{3}(E_1 + E_2) - \frac{4}{3}E_3,
\]
\[
B_b = \frac{1}{2} \left[ -A_b \pm \frac{2(E_1 - E_2)}{\sqrt{1 + \eta^2}} \right], \text{ with } \eta = \frac{2\bar{\xi}\sqrt{1 - \bar{\xi}^2}}{1 - 2\bar{\xi}^2},
\]
\[
C_b = \frac{\eta(A + 2B)}{2}.
\] (7.9)

Expressing the Hamiltonian in 7.3 in the Kitaev reference frame $(x, y, z)$ that has the $(x, y)$ coordinates rotated by 45° about the $Z = z$ axis as compared to $(X, Y)$ [10, 111], see Fig. 7.1b, $\Gamma$ then becomes
\[
\Gamma^b = \left( \begin{array}{ccc}
\frac{(A_b + B_b)}{2} & \frac{(A_b - B_b)}{2} & -C_b/\sqrt{2} \\
\frac{(A_b - B_b)}{2} & \frac{(A_b + B_b)}{2} & C_b/\sqrt{2} \\
-C_b/\sqrt{2} & C_b/\sqrt{2} & -(A_b - B_b)
\end{array} \right)_{\{x,y,z\}}.
\] (7.10)

The spin-Hamiltonian for $C_{2h}$ symmetry can thus be written as
\[
\mathcal{H}(ij)_{(b)} = J_b \hat{S}_i \cdot \hat{S}_j + K_b \hat{S}_i^{z_b} \hat{S}_j^{z_b} + \sum_{\alpha < \beta} \Gamma^b_{\alpha \beta} (\hat{S}_i^{\alpha} \hat{S}_j^{\beta} + \hat{S}_j^{\alpha} \hat{S}_i^{\beta}),
\] (7.11)

with the effective couplings for each of the Ir-Ir link given by
\[
J_b = J_b^{(0)} + \frac{A_b + B_b}{2}, \quad K_b = -\frac{3}{2}(A_b + B_b),
\]
\[
\Gamma^b_{xy} = \frac{A_b - B_b}{2}, \quad \Gamma^b_{yz} = \frac{C_b}{\sqrt{2}}.
\] (7.12)

Further lowering of the symmetry of the [Ir$_2$O$_{10}$] unit to $C_1$ leads to $|\Gamma_{yz}| \neq |\Gamma_{zx}|$.

### 7.3 Na$_2$IrO$_3$

The IrO$_6$ octahedra in Na$_2$IrO$_3$ display significant amount of trigonal distortion. These trigonal distortions lead to Ir-O-Ir bond angles different from 90°. Moreover, the two
7.3 Na$_2$IrO$_3$

(upper and lower) O$_3$ triangles perpendicular to the c-axis of each IrO$_6$ octahedron are rotated by the same amounts in opposite senses [42] (see honeycomb layer in Fig. 4.5), giving rise to slightly different Ir-O bond lengths. The Ir-Ir, Ir-O bond lengths and the Ir-O-Ir bond angles for the two different Ir-Ir links are provided in Table 7.1.

### Table 7.1 Ir-Ir distances and Ir-O-Ir bond angles for the two different types of NN Ir-Ir links in Na$_2$IrO$_3$. The symmetry of the [Ir$_2$O$_{10}$] unit is also shown in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>B1 (C$_{2h}$)</th>
<th>B2 (C$_i$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d$(Ir-Ir) (Å)</td>
<td>3.138</td>
<td>3.13</td>
</tr>
<tr>
<td>$d$(Ir-O) (Å)</td>
<td>2.056, 2.065, 2.083</td>
<td>2.065, 2.083</td>
</tr>
<tr>
<td>$\angle$(Ir-O-Ir) (deg)</td>
<td>99.45</td>
<td>97.97</td>
</tr>
</tbody>
</table>

#### 7.3.1 Exchange interactions in idealized structures of Na$_2$IrO$_3$

To obtain better insight into the nature of the NN magnetic couplings, we first considered two NN octahedra taken from an idealized crystalline model of Na$_2$IrO$_3$ without trigonal distortions and with all adjacent Ir and Na sites modeled to be identical. In this case, the overall symmetry is $D_{2h}$ and all off-diagonal couplings cancel by symmetry in the $(X, Y, Z)$ coordinate system with $X$ along the Ir-Ir link, see Fig. 7.2a. For an idealized [Ir$_2$O$_{10}$] unit displaying $D_{2h}$ symmetry, $C = 0$ and the spin Hamiltonian 7.11 reduces to

$$\mathcal{H}^{D_{2h}}_{(ij)\in b} = J_b \mathbf{\hat{S}}_i \cdot \mathbf{\hat{S}}_j + K_b \mathbf{\hat{S}}_i \mathbf{\hat{S}}_j + D_b \left( \mathbf{\hat{S}}_i \mathbf{\hat{S}}_j^y + \mathbf{\hat{S}}_j \mathbf{\hat{S}}_i^y \right),$$

(7.13)

where $K_b = -\frac{3}{2}(A_b + B_b)$, $J_b = J_b^{(0)} - K_b/3$ and $D_b = \frac{1}{2}(A_b - B_b)$. The off-diagonal $xy$ coupling, last term in (Eq. 7.13), is allowed by symmetry even for ideal octahedra at 90° Ir-O-Ir bonding but has been neglected in earlier studies on Na$_2$IrO$_3$ [10, 11, 44, 111, 264].

Results of SO calculations, both at the CASSCF (CASSCF+SOC) and MRCI (MRCI+SOC) levels, are listed for idealized [Ir$_2$O$_{10}$] $D_{2h}$ model clusters in Table 7.2. Such a cluster is highly charged, 12−. To ensure charge neutrality, a fictitious charge of +12/26 is assigned to each of the 26 adjacent Na and Ir sites (see Fig. 7.2a). In the simplest approximation, no farther embedding was used for these $D_{2h}$ clusters. The $ab$ initio calculations were performed for both i) cubic IrO$_6$ octahedra and 90° Ir-O-Ir bond angles and ii) distorted geometries with all ligands in the $xy$ plane pushed closer to the Ir-Ir axis and therefore larger Ir-O-Ir bond angles but keeping the $D_{2h}$ bond symmetry. The Ir-Ir distance $d$(Ir-Ir) and in the latter case the Ir-O-Ir angle were set to 3.133 Å and 98.5°, respectively, average values in the C2/m crystal structure reported in Ref. [42].

To determine the nature of each SO state, the dipole and quadrupole transition matrix elements among those four low-lying states describing the magnetic spectrum of two edge-sharing octahedra are explicitly calculated. Symmetry analysis reveals that the SO wave functions $\Psi_S, \Psi_1, \Psi_2$ and $\Psi_3$ defined in Table 7.2 transform according to the $A_g, B_{2u}, B_{1u}$ and $A_u$ irreducible representations, respectively (See App. C.1). Standard selection rules and the
Kitaev interactions in honeycomb Na$_2$IrO$_3$ and Li$_2$IrO$_3$

Fig. 7.2 (a) The two-octahedra cluster and +12/26 charges (yellow color) with $D_{2h}$ symmetry used for obtaining the energy spectrum and coupling parameters in Table 7.2. (b) Fragment of the Na$_2$IrO$_3$ crystal used in the QC calculations for extracting the effective magnetic couplings presented in Table 7.3.

nonzero dipole and quadrupole matrix elements in the QC outputs then clearly indicate which state is which (see App. C.2). We also carried out the transformation of the SO wave functions from the usual $\{L_1,M_{L_1},L_2,M_{L_2},S,M_S\}$ basis in standard QC programs to the $\{\tilde{S}_1,\tilde{S}_2,\tilde{M}_{S_1},\tilde{M}_{S_2}\}$ basis (see App. D). This allows the study of $\Psi_1$–$\Psi_2$ mixing when the point-group symmetry

<table>
<thead>
<tr>
<th>Method</th>
<th>CAS$\text{SCF}+\text{SOC}$</th>
<th>MRCI$\text{+SOC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Ir-O-Ir})=90^\circ:$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Psi_S = (\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\Psi_2 = (\uparrow\uparrow + \downarrow\downarrow)/\sqrt{2}$</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>$\Psi_3 = (\uparrow\uparrow - \downarrow\downarrow)/\sqrt{2}$</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>$\Psi_1 = (\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2}$</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>$(J,K,D)$</td>
<td>$(1.0,-0.6,0.0)$</td>
<td>$(1.1,-0.7,-0.7)$</td>
</tr>
<tr>
<td>$(\text{Ir-O-Ir})=98.5^\circ:$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Psi_2 = (\uparrow\uparrow + \downarrow\downarrow)/\sqrt{2}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\Psi_3 = (\uparrow\uparrow - \downarrow\downarrow)/\sqrt{2}$</td>
<td>1.2</td>
<td>2.1</td>
</tr>
<tr>
<td>$\Psi_S = (\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$</td>
<td>4.3</td>
<td>5.1</td>
</tr>
<tr>
<td>$\Psi_1 = (\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2}$</td>
<td>3.9</td>
<td>6.5</td>
</tr>
<tr>
<td>$(J,K,D)$</td>
<td>$(-0.4,-6.6,-1.2)$</td>
<td>$(1.4,-10.9,-2.1)$</td>
</tr>
</tbody>
</table>

Table 7.2 Energy splittings of the four lowest magnetic states and effective exchange parameters (meV) for two edge-sharing IrO$_6$ octahedra taken out of the idealized structural model with $D_{2h}$ bond symmetry. In a pure KH model, $\Psi_2$ and $\Psi_3$ are degenerate. $d$(Ir-Ir)=3.133 Å, see text.
is reduced to $C_{2h}$. Having the assignment of the states resolved, the $\Psi_5 - \Psi_1$ splitting provides $J_b$, the $\Psi_2 - \Psi_3$ splitting yields $D_b$, while the difference between the energy of $\Psi_1$ and the average of the $\Psi_2$ and $\Psi_3$ eigenvalues equals $-K_b/2$.

The QC data in Table 7.2 indicate AF $J$’s, FM $K$’s and off-diagonal anisotropic couplings comparable in strength to the isotropic $J$ interaction. Interestingly, the ab initio MRCI calculations indicate a much stronger $K$ for nonorthogonal Ir-O-Ir bonds. This shows that deviations from rectangular geometry on the Ir$_2$O$_2$ plaquette is not a negligible factor, as presently assumed in simplified superexchange models for Kitaev physics in honeycomb Na$_2$IrO$_3$ [10, 11, 111]. The effect of the MRCI treatment is also stronger for nonorthogonal Ir-O-Ir bonds: the CASSCF+SOC $K$ and $D$ coupling parameters are enlarged by more than 50% by including O 2$p$ to Ir 5$d$ charge-transfer effects, Ir $t_{2g}$ to $e_g$ excitations and additional correlations accounted for in MRCI while $J$ changes sign. This strong enhancement of the FM $K$ for nonorthogonal Ir-O-Ir bonds and the tiny effect of the MRCI treatment on the FM $K$ for rectangular geometry also disagrees with predictions of present approximate superexchange models that indicate the $t_{2g}$ to $e_g$ excitations and hopping as the dominant superexchange mechanism, giving rise to a large AF $K$ [11, 267].

### 7.3.2 Exchange couplings for experimental structure of Na$_2$IrO$_3$

Relative energies and the resulting effective coupling constants are next given in Table 7.3 for the experimentally determined $C2/m$ crystal structure of Ref. [42]. For this set of calculations, effective embedding potentials were used as described in Sec. 6.2. As already mentioned, there are two inequivalent Ir-Ir links in Na$_2$IrO$_3$, displaying different Ir-O-Ir bond angles and slightly different Ir-O and Ir-Ir distances [42] (see Table 7.1). While the [Ir$_2$O$_{10}$] block with larger Ir-O-Ir bond angles (upper part in Table 7.3) displays $C_{2h}$ symmetry, for the other unit of edge-sharing octahedra the point-group symmetry is even further reduced to $C_i$ (lower part in Table 7.3). The expressions of the SO wave functions in the transformed \{$\tilde{S}_1, \tilde{S}_2, \tilde{M}_S, \tilde{M}_{S'}$\} basis show, however, that the mixing of the $\Psi_i$ terms as expressed in the idealized $D_{2h}$ geometry is negligible in the $C2/m$ structure (see App. D.2). Therefore the ab initio data is mapped also in this case

![Fig. 7.3 Low-lying energy levels for two NN octahedra in Na$_2$IrO$_3$. The triplet components are split due to anisotropic exchange.](A2_4_largefont_xy_long.png)
on the effective model described by Eq. 7.13.

As for the idealized $D_{2h}$ configuration, the MRCI+SOC results indicate large FM Kitaev couplings, weaker AF Heisenberg superexchange and sizable $D$ anisotropic interactions. The latter are not included in the plain KH model [10, 11, 111, 264] while the signs of $K$ and $J$ that are computed here are different from those proposed in the recent model-Hamiltonian analysis of Ref. [11, 267]. We note that in agreement with our findings, relatively large FM Kitaev couplings $K$ have been earlier predicted by Kimchi and You [264] from the analysis of the phase diagram obtained by exact diagonalization on modest size clusters and by Foyevtsova et al. [44] on the basis of an effective superexchange model fed with electronic-structure parameters obtained from density-functional calculations for the same $C2/m$ structure [42]. However, the NN Heisenberg $J$ is also FM in the latter work, different from the small AF values that are found in the MRCI calculations. We also find that on each hexagonal Ir$_6$ unit the two Ir-Ir links along the $b$-axis have effective coupling constants significantly different from the set of parameters associated with the other four Ir-Ir “bonds” due to subtly different oxygen distortions. Together these findings stress the importance of lattice distortions and symmetry issues and lay the foundation for rigorous ab initio investigations of unusually large anisotropic interactions such as the Kitaev exchange in strongly SO coupled 5$d$ oxides.

Table 7.3 Energy splittings of the four lowest magnetic states and effective coupling parameters (meV) for two NN IrO$_6$ octahedra in the $C2/m$ structure of Ref. [42]. The weight of $(\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2}$ and $(\uparrow\uparrow + \downarrow\downarrow)/\sqrt{2}$ in $\Psi'_1$ and $\Psi'_2$, respectively, is $\approx 98\%$, see text.

<table>
<thead>
<tr>
<th>Method</th>
<th>CASSCF+SOC</th>
<th>MRCI+SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\angle$(Ir-O-Ir)$=99.45^\circ$, $d$(Ir$_1$-Ir$_2$)$=3.138$ Å ($\times 1$):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Psi'_2$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\Psi_3 = (\uparrow\uparrow - \downarrow\downarrow)/\sqrt{2}$</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>$\Psi_S = (\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$</td>
<td>4.4</td>
<td>5.5</td>
</tr>
<tr>
<td>$\Psi'_1$</td>
<td>6.3</td>
<td>10.5</td>
</tr>
<tr>
<td>$(J,K,D)$</td>
<td>(1.9,$-12.4,-0.2$)</td>
<td>(5.0,$-20.5,-0.5$)</td>
</tr>
<tr>
<td>$\angle$(Ir-O-Ir)$=97.97^\circ$, $d$(Ir$_2$-Ir$_3$)$=3.130$ Å ($\times 2$):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Psi'_2$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\Psi_3 = (\uparrow\uparrow - \downarrow\downarrow)/\sqrt{2}$</td>
<td>0.3</td>
<td>1.2</td>
</tr>
<tr>
<td>$\Psi_S = (\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$</td>
<td>4.6</td>
<td>6.7</td>
</tr>
<tr>
<td>$\Psi'_1$</td>
<td>5.8</td>
<td>8.2</td>
</tr>
<tr>
<td>$(J,K,D)$</td>
<td>(1.2,$-11.3,-0.3$)</td>
<td>(1.5,$-15.2,-1.2$)</td>
</tr>
</tbody>
</table>
7.3.3 Farther-neighbor interactions and magnetic phase diagram

It is known experimentally that Na$_2$IrO$_3$ displays zigzag AF order at low $T$’s [42, 206, 263]. It has also been argued that the longer-range magnetic interactions, up to the second and third Ir coordination shells, are sizable and AF [42, 44, 204, 264]. Phase diagrams obtained by exact diagonalization calculations performed for the model given in Eq. 7.3, supplemented with second and third neighbor couplings $J_2$ and $J_3$ (see Appendix B in Ref. [13]) and fed with the NN exchange interactions from Table 7.3, are shown in Fig. 7.4. The presence of two structurally and magnetically different sets of Ir-Ir links is disregarded in these ED calculations and approximately averaged values over all bonds were used, with $J = 3$, $K = -17.5$ and $D = -1$ meV. The phase diagram in Fig. 7.4a shows that the zigzag phase is indeed stable in the region of $J_2 J_3 > 2$ meV. We note that positive $J_2$ and $J_3$ values of 4–5 meV would be consistent with the experimentally observed Curie-Weiss temperature $\approx -125$ K [204] using $\theta_{\text{CW}} = -\tilde{S}(\tilde{S} + 1)(J + 2J_2 + J_3 + K/3)/k_B$ [42]. Thus an extended spin Hamiltonian based on the nearest-neighbor anisotropic exchange terms found from the *ab initio* QC calculations supplemented by farther-neighbor exchange integrals could provide a realistic starting point to explain the magnetism of Na$_2$IrO$_3$.

![Phase diagram for the effective spin model in (7.13) supplemented by second and third neighbor couplings $J_2$ and $J_3$, with $J = 3$ meV, $K = -17.5$ meV and $D = 0$ (a) or $D = -1$ meV (b), as found by exact diagonalization on a 24-site cluster [13].](image)
7.3.4 Conclusions

In sum, for the honeycomb iridate Na$_2$IrO$_3$, the ab initio QC calculations show that in a reference system with $X$ along the Ir-Ir link and $Z$ perpendicular on the Ir$_2$O$_2$ plaquette the $X$-$Y$ anisotropy is significant and gives rise in the rotated ($x$, $y$, $z$) Kitaev-type frame [10, 111] to off-diagonal anisotropic terms beyond the plain Kitaev-Heisenberg model. Nevertheless, the calculations predict that the largest energy scale is the Kitaev interaction, 10 to 20 meV, while the NN Heisenberg superexchange and the off-diagonal $xy$ coupling are significantly weaker. The QC data additionally establish that the Kitaev term is FM. Further, all NN couplings are highly sensitive to subtle distortions involving the O ions.

7.4 Li$_2$IrO$_3$

Li$_2$IrO$_3$ is isostructural [187] with Na$_2$IrO$_3$ and undergoes a transition to an AF state at the same temperature $T_N = 15$ K as Na$_2$IrO$_3$. However, the Curie-Weiss (CW) temperature and the frustration parameter$^2$ were reported to be quite different [204]. A similar type of zigzag magnetic ordering as in Na$_2$IrO$_3$ was proposed in Ref. [204], from calculations for a KH model with farther-neighbor couplings. It was also claimed that Li$_2$IrO$_3$ is on the verge of the Kitaev spin-liquid phase [204].

Other model Hamiltonian calculations [268, 269] suggested that the Kitaev spin-liquid phase can be obtained in Li$_2$IrO$_3$ on application of strain. Nevertheless, the ground state magnetic order in Li$_2$IrO$_3$ still remains to be understood. Here we present the results of QC calculations on this compound.

Table 7.4 Structural details concerning the two NN links B1 and B2 = B3 in Li$_2$IrO$_3$. The symmetry of the [Ir$_2$O$_{10}$] unit is shown in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>B1 ($C_{2h}$)</th>
<th>B2 ($C_i$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d$(Ir-Ir) (Å)</td>
<td>2.98</td>
<td>2.98</td>
</tr>
<tr>
<td>$d$(Ir-O-Ir) (Å)</td>
<td>2.01, 2.08, 1.97</td>
<td>95.3, 94.7</td>
</tr>
</tbody>
</table>

The honeycomb layer in Li$_2$IrO$_3$ has two inequivalent Ir-Ir links (B1 and B2 = B3) as in Na$_2$IrO$_3$ (see Fig. 7.1a). Although the Ir-Ir bond lengths are equal, these bonds differ with respect to the Ir-O-Ir bond angles (see Table 7.4) [187]. While in Na$_2$IrO$_3$ the Ir-O-Ir angles are in the range of 98-100°, in Li$_2$IrO$_3$ the bond angles are significantly smaller, around 95°, and the Ir-Ir distances are shorter too. The Ir-Ir link (B1) parallel to the crystallographic $c$ axis has $C_{2h}$ point-group symmetry. Slight distortions of the Ir$_2$O$_2$ plaquettes lower the symmetry to $C_i$ for the other Ir-Ir links, labeled B2 and B3.

$^2$Frustration parameter $f$ is defined as the ratio absolute value of Curie-Weiss temperature to ordering temperature, $f = \Theta_{CW}/T_N$. 

7.4.1 Magnetic spectrum and effective exchange couplings

Relative energies for the four low-lying states describing the magnetic spectrum of the two NN octahedra corresponding to bonds B1 and B2 in Li$_2$IrO$_3$ are shown in Table 7.5. These energies were obtained from CASSCF and MRCI calculations as described in Sec. 6.2. Subsequently, they are mapped onto the eigenvalues of the spin Hamiltonian 7.11, which contains all the exchange interaction terms allowed for a NN Ir-Ir link with $C_{2h}$ point-group symmetry. For this symmetry group, the triplet terms $\Phi_1$ and $\Phi_2$ belong to the same irreducible representation $B_u$ and hence they can be admixed (see Sec. 7.2.2). This mixing has to do with off-diagonal terms in the $\Gamma$ tensor, namely $\Gamma_{xz} (=\Gamma_{zx})$ and $\Gamma_{yz} (=\Gamma_{zy})$ (see Eq. 7.10). It can be obtained by transforming the SO wave functions $\{\Psi_i\}$ from the $\{L_1, M_{L_1}, L_2, M_{L_2}, S, M_S\}$ basis to the $\{\vec{S}_1, \vec{S}_2, \vec{M}_{S_1}, \vec{M}_{S_2}\}$ basis and by further projecting these eigenvectors onto the wave functions $\{\Phi_i\}$. The weight of $\Phi_1 = \frac{\uparrow\downarrow + \downarrow\uparrow}{\sqrt{2}}$ and $\Phi_2 = \frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}}$ in $\Psi_1$ and $\Psi_2$, respectively, is 73% for B1 and 89% for link B2 (see App. D).

The exchange parameters obtained from this mapping procedure are shown in the lower part of Table 7.5. For the B1 links both $J$ and $K$ are FM, in contrast to Na$_2$IrO$_3$, where $J$ is AF for all pairs of Ir NN’s [13] (see Sec. 7.3.2). For the B2 links, the \textit{ab initio} data show that the FM exchange is disfavored such that $J$ turns AF. Although the bond symmetry is lower for the B2 links (C$_i$), the analysis of the SO wave functions shows however negligible additional mixing effects and the \textit{ab initio} results are still mapped onto a $C_{2h}$ model with $\Gamma_{zx} = -\Gamma_{yz}$.

<table>
<thead>
<tr>
<th>Energies and effective couplings</th>
<th>$b =$ B1</th>
<th>$b =$ B2, B3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CASSCF</td>
<td>MRCI</td>
</tr>
<tr>
<td>$E_S(\Psi_S = \Phi_S = (\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2})$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$E_1(\Psi_1)$</td>
<td>-20.1</td>
<td>-17.1</td>
</tr>
<tr>
<td>$E_2(\Psi_2)$</td>
<td>-25.5</td>
<td>-24.8</td>
</tr>
<tr>
<td>$E_3(\Psi_3 = \Phi_3 = (\uparrow\uparrow - \downarrow\downarrow)/\sqrt{2})$</td>
<td>-23.9</td>
<td>-21.6</td>
</tr>
<tr>
<td>$J_b$</td>
<td>-22.0</td>
<td>-19.2</td>
</tr>
<tr>
<td>$K_b$</td>
<td>-3.4</td>
<td>-6.0</td>
</tr>
<tr>
<td>$\Gamma_b^b$</td>
<td>0.3</td>
<td>-1.1</td>
</tr>
<tr>
<td>$\Gamma_{\gamma_{b\gamma_b}} = -\Gamma^b_{\gamma_b\gamma_b}$</td>
<td>3.7</td>
<td>-4.8</td>
</tr>
</tbody>
</table>

For this symmetry group, the triplet terms $\Phi_1$ and $\Phi_2$ belong to the same irreducible representation $B_u$ and hence they can be admixed (see Sec. 7.2.2). This mixing has to do with off-diagonal terms in the $\Gamma$ tensor, namely $\Gamma_{xz} (=\Gamma_{zx})$ and $\Gamma_{yz} (=\Gamma_{zy})$ (see Eq. 7.10). It can be obtained by transforming the SO wave functions $\{\Psi_i\}$ from the $\{L_1, M_{L_1}, L_2, M_{L_2}, S, M_S\}$ basis to the $\{\vec{S}_1, \vec{S}_2, \vec{M}_{S_1}, \vec{M}_{S_2}\}$ basis and by further projecting these eigenvectors onto the wave functions $\{\Phi_i\}$. The weight of $\Phi_1 = \frac{\uparrow\downarrow + \downarrow\uparrow}{\sqrt{2}}$ and $\Phi_2 = \frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}}$ in $\Psi_1$ and $\Psi_2$, respectively, is 73% for B1 and 89% for link B2 (see App. D).

The exchange parameters obtained from this mapping procedure are shown in the lower part of Table 7.5. For the B1 links both $J$ and $K$ are FM, in contrast to Na$_2$IrO$_3$, where $J$ is AF for all pairs of Ir NN’s [13] (see Sec. 7.3.2). For the B2 links, the \textit{ab initio} data show that the FM exchange is disfavored such that $J$ turns AF. Although the bond symmetry is lower for the B2 links (C$_i$), the analysis of the SO wave functions shows however negligible additional mixing effects and the \textit{ab initio} results are still mapped onto a $C_{2h}$ model with $\Gamma_{zx} = -\Gamma_{yz}$.
7.4.2 Evolution of $J$ and $K$ with the Ir-O-Ir angle

Quite insightful here are the curves plotted in Fig. 7.5, displaying the dependence of the NN $J$ on the amount of trigonal distortion for simplified structural models of both Li$_2$IrO$_3$ and Na$_2$IrO$_3$. The trigonal compression of the O octahedra translates into Ir-O-Ir bond angles larger than 90°. Additional distortions giving rise to unequal Ir-O bond lengths (see Tables 7.1 and 7.4) were not considered in these idealized lattice configurations. Interestingly, for 90° bond angle – the case for which most of the superexchange models are constructed [10, 11, 44, 111] – both $J$ and $K$ are very small, $\lesssim$1 meV. Further, while $|K|$ monotonously increases with the Ir-O-Ir bond angle, $J$ displays a parabolic behaviour and changes sign around 98°.

Our investigation also shows that the large FM $J$ value obtained for the B1 Ir-Ir links in Li$_2$IrO$_3$ is the superposition of three different effects: an Ir-O-Ir bond angle smaller than the value of $\approx$98° where $J$ changes sign which in contrast to Na$_2$IrO$_3$ takes us into the FM regime, the shift to lower values of the minimum of the nearly parabolic $J$ curve in Li$_2$IrO$_3$, and further the additional distortions giving rise to three different sets of Ir-O bond lengths for each IrO$_6$ octahedron. The latter are significantly stronger in Li$_2$IrO$_3$, remove the degeneracy of the Ir $t_{2g}$ levels, and make that the NN B1 $J$ is even lower than the minimum of the parabola displayed in Fig. 7.5. It is also interesting that the offdiagonal $\Gamma_{yz}$ and $\Gamma_{zx}$ couplings have about the same strength with the Kitaev $K$ (see Table 7.5).

The fact that the unequal Ir-O bond lengths for the Ir-Ir link B2 leads to an AF $J$ is
illustrated in the inset of Fig. 7.5, where the evolution of the NN $J$ when in addition to trigonal distortions the bridging ligands on the Ir-O$_2$-Ir plaquette are gradually shifted in opposite senses parallel to the Ir-Ir axis is shown. For the reference equilateral plaquette, the Ir-O-Ir bond angle is set to the average value in the experimental structure, 95° [187]. It is seen that such additional distortions indeed enhance the AF contribution to the Heisenberg superexchange.

### 7.4.3 Longer range interactions, mapping onto an effective $S=1$ triangular lattice

The second and third neighbor Heisenberg interactions $J_2$ and $J_3$ in honeycomb iridates are known to be sizable [44] and to significantly influence certain properties [13, 42, 260, 264]. However, since correlated QC calculations for these longer range interaction terms are computationally much too demanding, their effect is investigated by calculations for extended effective Hamiltonians that use the \textit{ab initio} NN magnetic interactions listed in Table 7.5 and adjustable isotropic $J_2$, $J_3$ exchange couplings.

With strong FM exchange on the B1 bonds, a simple description of the system consists in replacing all B1 pairs of Ir 1/2 pseudospins by rigid triplet degrees of freedom. This mapping leads to an effective model of spin $T = 1$ entities on a triangular lattice, captured by the Hamiltonian

$$ \mathcal{H}_{\text{eff}} = \sum_R T_R \cdot \Gamma_1 \cdot T_R + J_\delta T_R \cdot T_{R+\delta} + T_R \cdot \Gamma_2 \cdot T_{R+\delta}. $$

(7.14)

It includes both on-site ($\Gamma_1$) and intersite ($J_\delta, \Gamma_{2,\delta}$) effective interaction terms. The essential features of the model are as follows. First, among the few different contributions to $\Gamma_1$, there is an effective coupling of the form $K \frac{\gamma}{2} (T_R^z)^2$. Since $K < 0$, this term selects the two triplet components with $T_z = \pm 1$ and therefore acts as an easy-axis anisotropy. Second, there are
Kitaev interactions in honeycomb Na$_2$IrO$_3$ and Li$_2$IrO$_3$

Fig. 7.7 (a) Classical phase diagram of the effective spin $T = 1$ model on the triangular lattice in the $J_2$-$J_3$ plane, found by a numerical minimization of the interaction matrix $\Lambda(k)$ in the BZ. (b) Quantum mechanical phase diagram for the original spin-1/2 model in the $J_2$-$J_3$ plane, found by exact diagonalization calculations on 24-site clusters. The NN couplings listed in Table 7.5 are used in both the calculations.

two different types of effective exchange couplings between NN triplets, see Fig. 7.6. This asymmetry reflects the constitutive difference between bonds B1 and B2/B3. Finally, there is also an effective longer-range exchange driven by the $J_3$ interaction in the original hexagonal model.

In momentum space, the effective model takes the form

$$\mathcal{H}_{\text{eff}} = \sum_{\alpha, \beta, k} T^\alpha_k \cdot \Lambda_{\alpha\beta}(k) \cdot T^\beta_{-k},$$

(7.15)

where $T_k = \frac{1}{N} \sum_{R} e^{i k \cdot R} T_R$. $N$ is the number of B1 and $\Lambda(k)$ is a symmetric $3 \times 3$ matrix. Since $T = 1$, the classical limit is expected to yield a rather accurate overall description of the phase diagram. The minimum eigenvalue $\lambda_Q$ of $\Lambda(k)$ over the Brillouin zone (BZ) provides a lower bound for the classical ground state energy [271–274]. As shown in Fig. 7.7a, there exist five different regions for $|J_{2,3}| \lesssim 6$ meV, three with commensurate (FM, diagonal zigzag and stripy) and two with incommensurate $Q$ (ICx and ICy, with $Q = (q, 0)$ and $(0, q)$, respectively). In all commensurate regions, the state $T_R = e^{iQ \cdot R} v_Q$ (where $v_Q$ is the eigenvector associated with $\lambda_Q$) saturates the above lower energy bound and in addition satisfies the spin length constraint $|T_R| = 1$ for all $R$.

\(^3\)see Appendix in Ref. [270].
The phase diagram obtained by exact diagonalization calculations on 24-site clusters for the original honeycomb spin-1/2 model, including the effect of \( J_2 \) and \( J_3 \) and periodic boundary conditions as in previous studies \([11, 13]\), is shown in Fig. 7.7b. Note that in the absence of \( J_2 \) and \( J_3 \), the system is in a spin-liquid phase characterized by a structureless \( S(Q) \) that is adiabatically connected to the Kitaev liquid phase for \( -K \gg J \) \([10]\). With finite \( J_2 \) and \( J_3 \), most of the classical phases of the effective spin-1 model are recovered, including the ICx phase, albeit with a smaller stability region due to finite-size effects. The result for rigid triplet degrees of freedom finds support in recent fits of the magnetic susceptibility data, which yield effective moments of 2.22 \( \mu_B \) for \( \text{Li}_2\text{IrO}_3 \) \([275]\), much larger than the value of 1.74 \( \mu_B \) expected for an isotropic 1/2 spin system.

Turning finally to the nature of the actual magnetic ground state of \( \text{Li}_2\text{IrO}_3 \), it should be first noted that the longer range couplings \( J_2 \) and \( J_3 \) are expected to be both AF \([42, 260]\) and to feature values not larger than \( 5 - 6 \) meV \([42]\) in honeycomb iridates, which suggests that \( \text{Li}_2\text{IrO}_3 \) orders either with a diagonal-zigzag or ICx pattern. Recent magnetic susceptibility and specific heat measurements show indeed that the ground state is very different from zigzag in \( \text{Li}_2\text{IrO}_3 \) \([261]\) while inelastic neutron scattering data \([265]\) indicate clear signatures of incommensurate Bragg peaks. These experimental findings provide strong support for the ICx spin configuration.

### 7.4.4 Conclusions

To summarize, we have established a microscopic spin model and zero-temperature phase diagram for the layered honeycomb iridate \( \text{Li}_2\text{IrO}_3 \), one of the proposed realizations of the spin-1/2 Kitaev-Heisenberg model with strongly spin-orbit coupled \( \text{Ir}^{4+} \) magnetic ions. \textit{Ab initio} QC electronic-structure calculations show that, in contrast to \( \text{Na}_2\text{IrO}_3 \), the structural inequivalence between the two types of Ir-Ir links has a striking influence on the effective spin Hamiltonian, leading in particular to two very different nearest-neighbor superexchange pathways, one weakly antiferromagnetic (\( \approx 1 \) meV) and another strongly ferromagnetic (\( -19 \) meV). The latter gives rise to rigid spin-1 triplets on a triangular lattice that remain well protected in a large parameter regime of the phase diagram, including a diagonal-zigzag and an incommensurate ICx phase. In view of these theoretical findings and of recently reported neutron scattering data \([265]\), we conclude that the magnetic ground state of \( \text{Li}_2\text{IrO}_3 \) lies in the incommensurate ICx phase.
This thesis project had two main objectives. First, to analyze the manifestation of the $\tilde{j} = 1/2$ spin-orbit coupled ground state and related low-energy charge excitations in several $5d^5$ iridium oxide compounds. The second goal was to understand the exchange interactions between the spin-orbit entangled $\tilde{j} = 1/2$ moments in layered square-lattice and honeycomb-lattice iridates. For this purpose, we used many-body quantum chemistry methods that provide a theoretical frame for the rigorous construction and systematic improvement of correlated $N$-electron wave functions. In the following, a summary of the results and observations derived from this work is provided.

In $5d$ transition-metal oxide compounds, the crystal field splittings, spin-orbit interactions and electronic correlations occur on the same energy scale, giving rise to interesting physics. The spin-orbit coupling in these compounds can effectively enhance the way electronic correlations manifest themselves. This led to a renewed interest in these compounds since the interplay of crystal field effects, spin-orbit interactions, local multiplet physics and intersite hopping can offer novel types of correlated electronic ground and excited states. In particular, insulating $5d^5$ iridium oxide compounds were proposed to host a spin-orbit entangled $\tilde{j} = 1/2$ ground state. Several exotic theoretical proposals were put forward based on this ground state. For example, topological Mott insulators, a Weyl semimetal and an axion insulator and the possible realization of the Kitaev spin model, with bond-dependent spin-spin interactions in 2D honeycomb-lattice iridates.

To better understand this novel $\tilde{j} = 1/2$ ground state, it is necessary to quantify the relevant microscopic interactions. Moreover, it is important to correctly describe their effects. Thus, in this work we used \textit{ab initio} wave function based methods to analyze in detail the formation of the $\tilde{j} = 1/2$ ground state, by studying the local electronic structure of the $5d^5$ Ir$^{4+}$ ion in a number of compounds displaying four different types of lattice structures. The possibility to explicitly calculate the correlated electronic structure either with or without the
spin-orbit interactions makes it possible to disentangle the effect of electronic correlations and spin-orbit effects.

We first established through scalar-relativistic calculations that longer-range crystal anisotropy, i.e., low-symmetry fields related to ionic sites beyond the NN oxygen cage, strongly influence the energies of the Ir $d$ levels. In particular, for the square-lattice $Ae_2$IrO$_4$ ($Ae = Ba,Sr$) compounds, we found opposite signs for the Ir $t_{2g}$ level splittings even though both materials display positive tetragonal distortions with elongated apical Ir-O bonds. The Ir $t_{2g}$-level splitting in Sr$_2$IrO$_4$ is large and negative ($-0.15$ eV), whereas in Ba$_2$IrO$_4$ it is positive and significantly smaller (0.065 eV), although the latter system displays much stronger tetragonal distortions. We showed that this $d$-level inversion in Sr$_2$IrO$_4$ and the surprisingly small splitting in Ba$_2$IrO$_4$ has to do with the way the positive ionic charge is distributed between the Ir-O and Ae-O layers. The relativistic spin-orbit coupling nevertheless gives rise to a ground state that is close to the effective total-angular-momentum $\tilde{j} = \frac{1}{2}$ state, with a very small admixture of $\tilde{j} = \frac{3}{2}$ character in the range of only 1%. The computed excitation energies into the $\tilde{j} \simeq \frac{3}{2}$ states at $\sim 0.65$ eV in both Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ matches well with the available RIXS data [40, 113, 202]. However, the difference in the order of the $t_{2g}$ levels gives rise to a different order of the excited $\tilde{j} = 3/2, m_j = \pm 3/2$ and $\tilde{j} = 3/2, m_j = \pm 1/2$ components in the two compounds.

For the honeycomb-lattice Na$_2$IrO$_3$, the crystal field anisotropy due to the 2D layered structure as well as trigonal distortions of the oxygen cage results in Ir $t_{2g}$ splittings of 0.11 eV. In the isostructural sister compound Li$_2$IrO$_3$, the highly distorted IrO$_6$ octahedron gives rise to a splitting as high as 0.34 eV of the Ir $t_{2g}$ levels. The spin-orbit interactions in the former compound results in an almost pure $\tilde{j} = 1/2$ ground state with less than a percent admixture of $\tilde{j} = 3/2$ character, whereas in Li$_2$IrO$_3$ the admixture of $\tilde{j} = 3/2$ terms in the ground state wave function is as large as 10%. An interesting finding in these trigonally distorted systems is that the coupling of $t_{2g}^5$ and $t_{2g}^4 e_g^1$ states due to off-diagonal spin-orbit matrix elements is important. Although the Ir $e_g$ levels are separated from the $t_{2g}$ manifold by 2.5 – 2.8 eV, we found it necessary to include those high-lying states to obtain a good agreement among the calculated and experimentally (RIXS) measured spin-orbit $\tilde{j} \simeq 3/2$ excitations. For the monoclinic crystal structures of Sr$_3$CuIrO$_6$ and Na$_4$Ir$_3$O$_8$, with Ir $t_{2g}$ splittings as large as the spin-orbit interaction strength ($\sim 0.5$ eV), we found the ground state to contain $\sim 15\%$ $\tilde{j} = 3/2$ character. Nevertheless, the average $\tilde{j} \simeq 1/2 \rightarrow \tilde{j} \simeq 3/2$ excitations are around 0.6 eV as for the other iridates.

Having understood the composition of the spin-orbit entangled ground state wave functions in various iridates, we then moved on to address the origin of unusually large ground state expectation values of the spin-orbit coupling operator $\langle \mathcal{Z} \rangle = \langle \mathbf{L} \cdot \mathbf{S} \rangle$, extracted from XAS experiments. The latter is related to the ratio of the white-line intensities at the $L_2$ and $L_3$ x-ray absorption edges, also referred to as branching ratios. We found that the coupling of
the $^2T_{2g}$ ($t_{2g}^5$) states with the high-lying $^4A$, $^4E$, $^4T$, and $^2A$, $^2E$, $^2T$ states arising from the $t_{2g}^4e_g^1$ and $t_{2g}^3e_g^2$ configurations, due to off-diagonal spin-orbit matrix elements, gives rise to values larger than one that is expected for a “pure” $j = 1/2$ state. Although the values obtained from our calculations were slightly smaller than those extracted from XAS measurements, they reproduce the experimental trend, e.g., with a larger $\langle Z \rangle$ for Ba$_2$IrO$_4$ than for Sr$_2$IrO$_4$. We also estimated the effective spin-orbit interaction strength that couples the $t_{2g}^5$ and $t_{2g}^4e_g^1$ states. This value is expected to be smaller than the spin-orbit coupling within the $t_{2g}^5$ states due to the significantly larger $\sigma$-overlap of the Ir $e_g$ orbitals compared to the $\pi$ overlap of the Ir $t_{2g}$ orbitals with the neighboring ligand $2p$ orbitals.

We then proceeded to analyze the magnetic exchange interactions between the Ir$^{4+}$ $j = 1/2$ pseudospin moments in two of the most studied 214 (Ba$_2$IrO$_4$ and Sr$_2$IrO$_4$) and 213 (Na$_2$IrO$_3$ and Li$_2$IrO$_3$) iridate families, by evaluating the sign and the magnitude of both isotropic and anisotropic NN exchange couplings. The $j = 1/2$ pseudospins are fundamentally different from pure $S = 1/2$ spins as they encompass both spin and orbital angular momentum components. Because of the entanglement of spin and orbital degrees of freedom, the magnetic exchange interactions between such pseudospin moments were predicted to depend strongly on the geometry of the underlying lattice. In Ba$_2$IrO$_4$, the point-group symmetry of the two NN IrO$_6$ octahedra ([Ir$_2$O$_{11}$] unit) is $D_{2h}$ and the Ir-O-Ir bond angle is 180°. As a result, only two diagonal elements of the symmetric anisotropic tensor are non-zero. However, the magnetic energy spectrum obtained from our quantum chemistry calculations indicate uniaxial anisotropy. By mapping the calculated magnetic spectrum onto the appropriate effective spin Hamiltonian, we extracted the isotropic interaction $J \approx 65$ meV, in excellent agreement with estimates based on RIXS measurements for 214 iridates [40] and an effective anisotropy as large as 3.5 meV. The latter is an order of magnitude larger than what is found in, e.g., 3$d$ cuprates. Given the uniaxial structure of the exchange coupling tensor, the relevant in-plane (pseudo)spin model is of a compass-Heisenberg type in Ba$_2$IrO$_4$. Yet, to understand the experimentally determined AF ordering pattern with spins along the $\langle 110 \rangle$ direction [227], interlayer interactions must also be included in the effective Hamiltonian. We showed that a semiclassical phase diagram obtained for an extended Hamiltonian that includes additional anisotropic interlayer interactions does contain a large region where the spins are aligned as observed in experiments.

The lack of inversion symmetry due to the staggered rotation of IrO$_6$ octahedra in Sr$_2$IrO$_4$ gives rise to an additional non-zero parameter $D_z$, the $z$ component (perpendicular to the IrO plane) of the antisymmetric DM interaction. As a result, the $ab$ initio magnetic spectrum of two Ir ions alone is insufficient to uniquely extract all the parameters in the effective spin Hamiltonian. Nevertheless, using the insights from model Hamiltonian calculations based on superexchange theory [28] and the expressions between the isotropic and anisotropic interaction parameters derived using our quantum chemistry data, the extracted $J = 56$ meV
and $D_z \simeq J/4$ values are in excellent agreement with estimates deduced from RIXS experiments \cite{10, 40}. Moreover, our analysis also provides estimates for the symmetric anisotropic interactions, although they are an order of magnitude smaller than the $J$ and $D_z$. The singlet-“triplet” (average energy of the split triplet states) splitting that is computed for strained thin films of Sr$_2$IrO$_4$ correctly reproduces the trend observed for the zone-boundary magnon energies in RIXS measurements. We concluded that strain in Sr$_2$IrO$_4$ mainly affects the Ir-O bond lengths rather than the Ir-O-Ir bond angles.

Finally, we addressed the nature of magnetic interactions in $A_2$IrO$_3$ ($A=$Li,Na) compounds. Due to their layered honeycomb-lattice structure and the peculiar superexchange mechanism between $j = 1/2$ pseudospins via edge-shared oxygens in [Ir$_2$O$_{10}$] units, these compounds have been put forward to host bond-dependent anisotropic exchange interactions similar to the Kitaev-honeycomb model. The latter supports topological phases with relevance in, e.g., quantum computation. A careful symmetry analysis of the [Ir$_2$O$_{10}$] units in $A_2$IrO$_3$ compounds indicates that in the Kitaev-type reference frame \cite{10, 111}, even for 90° Ir-O-Ir bond angles, the off-diagonal $xy$ anisotropic couplings are non-zero. Hence, the spin Hamiltonian for these compounds goes beyond the plain Kitaev-Heisenberg model. For Na$_2$IrO$_3$, our \textit{ab initio} quantum chemistry calculations nevertheless predict that the largest energy scale is the Kitaev interaction, 10 to 20 meV, while the NN Heisenberg superexchange and the off-diagonal $xy$ coupling are significantly weaker. Additionally, our results establish that the Kitaev term is FM. The latter issue, the sign of the Kitaev type interaction, has been intensively debated. Exact diagonalization calculations on 24-site clusters using the NN exchange parameters found by QC calculations result in the experimentally observed zig-zag magnetic ground state for realistic values of the second and third neighbor interactions. An important conclusion we draw is that all NN couplings are highly sensitive to subtle distortions involving the O ions.

For the sister honeycomb compound Li$_2$IrO$_3$, our calculations show that the structural inequivalence between the two types of Ir-Ir links has a striking influence on the effective spin Hamiltonian. So much so that the isotropic interaction $J$ for one set of Ir-Ir links is weakly antiferromagnetic and for another set strongly ferromagnetic. We demonstrated that this change of sign in the isotropic interaction follows a general trend of $J$ as a function of Ir-O-Ir bond-angle and Ir-O distances. The strong ferromagnetic coupling of $J \simeq 19$ on one set of bonds gives rise to the formation of triplet dimers on a triangular lattice. The magnetic phase diagram we obtained by semiclassical analysis of this effective triplet-dimer model as a function of second and third neighbor exchange interactions compare well with that of exact cluster diagonalization calculations on the original honeycomb lattice. For the realistic values of second and third neighbor isotropic interactions in honeycomb iridates, we find Li$_2$IrO$_3$ to have an incommensurate magnetic order. The inelastic neutron scattering experiments indeed suggest an incommensurate order \cite{265}.
Appendix A

Spin-orbit interaction

A.1 Classical derivation

An electron with spin $S$ is accompanied by magnetic moment $\mu = -g\mu_BS$, where $g \approx 2$ is the $g$ factor of the electron. In the electron’s rest frame the nucleus with a charge $Ze$ moves around the electron leading to a magnetic field $\mathbf{B} = (-\mathbf{v}) \times \mathbf{E}/c$ where $\mathbf{v}$ is the velocity of electron orbiting the nucleus and $\mathbf{E} = -\nabla V(r) = -\frac{r}{r} \frac{dV}{dr}$ is the electric field at the electron due to the nucleus [6]. The electron spin couples with this magnetic field and the Hamiltonian is given by

$$H_{SO} = -\mu \cdot B = -\frac{eh}{m_0c^2} S \cdot \mathbf{v} \times \mathbf{r} \frac{1}{r} \frac{dV}{dr} = -\frac{eh^2}{m^2c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S}. \quad (A.1)$$

Although this classical reasoning led to almost correct result, it is twice larger than that obtained from relativistic Dirac equation. This relativistic correction called as Thomas precession is half of Eq. A.1. Inserting the Coulomb potential $Ze/r$, one obtains

$$H_{SO} = \lambda \mathbf{L} \cdot \mathbf{S}, \quad \lambda = \frac{\hbar^2 Z e^2}{2m^2c^2 r^3}. \quad (A.2)$$

For electronic states with quantum numbers $n$ and $l$ one has [276]

$$\langle 1/r^3 \rangle = \frac{Z^3}{a^3n^3l(l+1/2)(l+1)}, \quad (A.3)$$

giving rise to the SO splitting

$$E_{SO} = \langle H_{SO} \rangle = \frac{Z^4 e^2\hbar^2}{2m^2c^2 l(l+1/2)(l+1)a^3n^3} \frac{\langle \mathbf{L} \cdot \mathbf{S} \rangle}{\langle \mathbf{L} \cdot \mathbf{S} \rangle} \quad (A.4)$$
where \( a \) is the Bohr radius\(^1\).

In the presence of SO coupling, \( S \) and \( L \) are no longer separately conserved. The rotational invariance merely guarantees the conservation of the total angular momentum \( J = L + S \) and \( L \cdot S = \frac{1}{2}(J^2 - L^2 - S^2) \). Hence the eigenvalues of \( L \cdot S \) are

\[
\langle L \cdot S \rangle = \frac{1}{2} \left[ j(j+1) - l(l+1) - s(s+1) \right].
\] (A.5)

Combining Eq. A.4 and A.5 one obtains the SO splitting

\[
E_{SO} = \frac{Z^4 e^2 \hbar^2}{4m^2 c^2} \left\{ \begin{array}{c} j(j+1) - l(l+1) - s(s+1) \\ l(l+1/2)(l+1)a^3 n^3 \end{array} \right\}.
\] (A.6)

### A.2 T-P equivalence

The matrix elements of orbital angular momentum \( l \) for a single electron in the five fold degenerate \( d \)-orbitals in the basis of the \( t_{2g} \) (Eq. 2.1) and \( e_g \) (Eq. 2.2) states, and that of a single electron in atomic \( p \)-orbitals are written as [91]

\[
l^d_x = \begin{pmatrix}
0 & 0 & 0 & -\sqrt{3}i & -i \\
0 & 0 & i & 0 & 0 \\
0 & -i & 0 & 0 & 0 \\
\sqrt{3}i & 0 & 0 & 0 & 0 \\
i & 0 & 0 & 0 & 0
\end{pmatrix},
\]

\[
l^p_x = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & -i \\
0 & i & 0
\end{pmatrix}
\] (A.7)

\[
l^d_y = \begin{pmatrix}
0 & 0 & -i & 0 & 0 \\
0 & 0 & 0 & \sqrt{3}i & -i \\
i & 0 & 0 & 0 & 0 \\
0 & -\sqrt{3}i & 0 & 0 & 0 \\
0 & i & 0 & 0 & 0
\end{pmatrix},
\]

\[
l^p_y = \begin{pmatrix}
0 & 0 & i \\
0 & 0 & 0 \\
-i & 0 & 0
\end{pmatrix}
\] (A.8)

\(^1\)\( L \) and \( S \) are dimensionless in the whole analysis.
The zero matrix elements of $l$ in the $e_g$ states indicate that the orbital angular momentum is completely quenched in these states resulting in no first order spin-orbit interaction among the $e_g$ states. In the $t_{2g}$ states the orbital angular momentum is not quenched. Comparing the matrix elements of $l$ in $t_{2g}$ states with those in $p$ states in free atoms, one can map the former $l = 2$ $t$-states onto the latter $p$-states with $l = 1$ with the relation

$$l(t_{2g}) = -l(p).$$  \hspace{1cm} (A.10)

This relation is called the $T - P$ equivalence, according to which the orbital angular momentum in $t_{2g}$ states is partially quenched from $l = 2$ to $l = 1$. When the cubic crystal field splitting is large, one can neglect the off-diagonal elements between $t_{2g}$ and $e_g$ manifolds and the $T - P$ equivalence can be conveniently used.

\section*{A.3 Spin-orbit eigenstates}

Using A.7, A.8 and A.9 and the matrices for spin operators

\begin{equation}
\begin{aligned}
\hat{s}_x &= \begin{pmatrix}
\frac{1}{2} & -\frac{1}{2} \\
\frac{1}{2} & \frac{1}{2}
\end{pmatrix}, & \hat{s}_y &= \begin{pmatrix}
\frac{1}{2} & -i \frac{1}{2} \\
i \frac{1}{2} & \frac{1}{2}
\end{pmatrix}, & \hat{s}_z &= \begin{pmatrix}
\frac{1}{2} & -\frac{1}{2} \\
\frac{1}{2} & \frac{1}{2}
\end{pmatrix},
\end{aligned}
\end{equation}

the matrix elements of the spin-orbit interaction in the $t_{2g}$ space can be obtained as

$$\mathcal{H}_{\text{SO}} = \lambda (l_x \hat{s}_x + l_y \hat{s}_y + l_z \hat{s}_z)$$
Spin-orbit interaction

<table>
<thead>
<tr>
<th>$d_{yz}, \frac{1}{2}$</th>
<th>$d_{xz}, -\frac{1}{2}$</th>
<th>$d_{zx}, \frac{1}{2}$</th>
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</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>$i$</td>
<td>0</td>
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<td>$-1$</td>
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<td>$0$</td>
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<td>1</td>
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<tr>
<td>$-1$</td>
<td>0</td>
<td>$-i$</td>
<td>0</td>
<td>0</td>
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</tr>
</tbody>
</table>

\[ \frac{\lambda}{2} \left( \begin{array}{ccc} 0 & i & -1 \\ -i & 0 & i \\ -1 & -i & 0 \end{array} \right) \] (A.12)

which can be written in a block diagonal form with two three-dimensional matrices

\[ \frac{\lambda}{2} \left( \begin{array}{ccc} 0 & -i & 1 \\ i & 0 & -i \\ 1 & i & 0 \end{array} \right) \] (A.13)

The eigenvalues of the above matrices are:

\[ \left( -\frac{\lambda}{2}, -\frac{\lambda}{2}, \lambda \right), \quad \left( -\frac{\lambda}{2}, -\frac{\lambda}{2}, \lambda \right) \] (A.14)

respectively, and the corresponding eigenfunctions are

\[ |\phi_1\rangle = \frac{1}{\sqrt{2}} \left( |d_{yz}, \frac{1}{2}\rangle + i |d_{xz}, \frac{1}{2}\rangle \right) \]
\[ |\phi_2\rangle = \frac{1}{\sqrt{6}} \left( - |d_{yz}, \frac{1}{2}\rangle + i |d_{xz}, \frac{1}{2}\rangle - 2 |d_{xy}, -\frac{1}{2}\rangle \right) \] (A.15)
\[ |\phi_3\rangle = \frac{1}{\sqrt{3}} \left( |d_{yz}, \frac{1}{2}\rangle - i |d_{xz}, \frac{1}{2}\rangle - |d_{xy}, -\frac{1}{2}\rangle \right) \]
\[ |\phi_4\rangle = \frac{1}{\sqrt{2}} \left( - |d_{yz}, -\frac{1}{2}\rangle + i |d_{xz}, -\frac{1}{2}\rangle \right) \]
\[ |\phi_5\rangle = \frac{1}{\sqrt{6}} \left( |d_{yz}, -\frac{1}{2}\rangle + i |d_{xz}, -\frac{1}{2}\rangle - 2 |d_{xy}, \frac{1}{2}\rangle \right) \] (A.16)
\[ |\phi_6\rangle = \frac{1}{\sqrt{3}} \left( |d_{yz}, -\frac{1}{2}\rangle + i |d_{xz}, -\frac{1}{2}\rangle + |d_{xy}, \frac{1}{2}\rangle \right) . \]

The eigenfunctions A.15 and A.17 are related by time-reversal symmetry

\[ T\hat{X}(t)T^{-1} = \hat{X}(-t) \quad \text{and} \quad T\hat{L}(t)T^{-1} = -\hat{L}(-t), \] (A.17)

where $T$ is the time-reversal operator, $\hat{X}(t)$ and $\hat{L}(t)$ are position and angular momentum
operators respectively.

The effective orbital angular momentum states, $|l, m_l\rangle$, are given by [97]

$$
|1, 1\rangle = \frac{1}{\sqrt{2}}(|d_{yz}\rangle + i|d_{xz}\rangle)
$$

$$
|1, 0\rangle = d_{xy}
$$

$$
|1, -1\rangle = \frac{1}{\sqrt{2}}(|d_{yz}\rangle + i|d_{xz}\rangle).
$$

Now including the spin degrees of freedom, the above can be written in the matrix form as

$$
|m_l, m_s\rangle =
\begin{bmatrix}
|1, \frac{1}{2}\rangle \\
|1, -\frac{1}{2}\rangle \\
|0, \frac{1}{2}\rangle \\
|0, -\frac{1}{2}\rangle \\
|1, \frac{1}{2}\rangle \\
|1, -\frac{1}{2}\rangle \\
\end{bmatrix}
\begin{bmatrix}
\frac{1}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} & 0 & 0 & 0 \\
0 & \frac{1}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 1 \\
\frac{1}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} & 0 & 0 & 0 \\
0 & \frac{1}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} & 0 & 0 \\
\end{bmatrix}
\begin{bmatrix}
|d_{yz}, \frac{1}{2}\rangle \\
|d_{yz}, -\frac{1}{2}\rangle \\
|d_{xz}, \frac{1}{2}\rangle \\
|d_{xz}, -\frac{1}{2}\rangle \\
|d_{xy}, \frac{1}{2}\rangle \\
|d_{xy}, -\frac{1}{2}\rangle \\
\end{bmatrix}.
$$

(A.18)

We use Clebsch-Gordan coefficients for adding angular momentum, $J = J_1 + J_2$. For $J_1 = l = 1$ and $J_2 = S = 1/2$, we have

$$
|J, M_J\rangle \langle M_{J1}, M_{J2}| =
\begin{bmatrix}
|1, \frac{1}{2}\rangle & |1, \frac{1}{2}\rangle & |1, \frac{1}{2}\rangle & |1, \frac{1}{2}\rangle & |1, \frac{1}{2}\rangle & |-1, -\frac{1}{2}\rangle \\
|\frac{3}{2}, \frac{3}{2}\rangle & 1 & 0 & 0 & 0 & 0 \\
|\frac{3}{2}, -\frac{1}{2}\rangle & 0 & \frac{\sqrt{3}}{3} & \sqrt{\frac{2}{3}} & 0 & 0 \\
|\frac{1}{2}, \frac{1}{2}\rangle & 0 & \sqrt{\frac{2}{3}} & - \frac{1}{\sqrt{3}} & 0 & 0 \\
|\frac{1}{2}, -\frac{1}{2}\rangle & 0 & 0 & \frac{\sqrt{3}}{3} & - \sqrt{\frac{2}{3}} & 0 \\
|\frac{3}{2}, -\frac{3}{2}\rangle & 0 & 0 & 0 & \sqrt{\frac{2}{3}} & - \frac{1}{\sqrt{3}} \\
\end{bmatrix}
$$

(A.19)

The total angular momentum states $|j, m_j\rangle$ obtained in the basis $|m_l, m_s\rangle$ are

$$
|\frac{1}{2}, \frac{1}{2}\rangle = \sqrt{\frac{2}{3}} |1, \frac{1}{2}\rangle - \sqrt{\frac{1}{3}} |0, \frac{1}{2}\rangle
$$

$$
|\frac{1}{2}, -\frac{1}{2}\rangle = -\sqrt{\frac{2}{3}} |1, -\frac{1}{2}\rangle + \sqrt{\frac{1}{3}} |0, -\frac{1}{2}\rangle
$$
\[\begin{align*}
\frac{3}{2}, \frac{1}{2} & = \sqrt{\frac{1}{3}} \left| \frac{1}{2}, -\frac{1}{2} \right| + \sqrt{\frac{2}{3}} \left| 0, \frac{1}{2} \right| \\
\frac{3}{2}, -\frac{1}{2} & = -\sqrt{\frac{1}{3}} \left| -1, \frac{1}{2} \right| + \sqrt{\frac{2}{3}} \left| 0, -\frac{1}{2} \right| \\
\frac{3}{2}, 0 & = \left| \frac{1}{2} \right| \\
\frac{3}{2}, -\frac{3}{2} & = \left| -1, -\frac{1}{2} \right|
\end{align*}\] (A.21)

From Eq. A.19 and Eq. A.21 one the \(j,m_j\) states can be written in the cartesian \(d\)-orbital basis as

\[\begin{align*}
\frac{1}{2}, \frac{1}{2} & = \frac{1}{\sqrt{3}} \left( d_{yz}, -\frac{1}{2} + i d_{zx}, -\frac{1}{2} + d_{xy}, \frac{1}{2} \right) \\
\frac{1}{2}, -\frac{1}{2} & = \frac{1}{\sqrt{3}} \left( d_{yz}, \frac{1}{2} - i d_{zx}, \frac{1}{2} - d_{xy}, -\frac{1}{2} \right) \\
\frac{3}{2}, \frac{1}{2} & = \frac{1}{\sqrt{6}} \left( d_{yz}, -\frac{1}{2} + i d_{zx}, -\frac{1}{2} - 2 d_{xy}, \frac{1}{2} \right) \\
\frac{3}{2}, -\frac{1}{2} & = \frac{1}{\sqrt{6}} \left( -d_{yz}, \frac{1}{2} + i d_{zx}, \frac{1}{2} - 2 d_{xy}, -\frac{1}{2} \right) \\
\frac{3}{2}, 0 & = \frac{1}{\sqrt{2}} \left( d_{yz}, \frac{1}{2} + i d_{zx}, \frac{1}{2} \right) \\
\frac{3}{2}, -\frac{3}{2} & = \frac{1}{\sqrt{2}} \left( -d_{yz}, -\frac{1}{2} + i d_{zx}, -\frac{1}{2} \right).
\] (A.22)

One can see that the eigenfunctions A.15 and A.17 are nothing but total angular momentum \(|j,m_j\rangle\) states given in Eq. A.22.

**A.4 Spin-orbit matrix elements for \(d^5\) electronic configuration**

The spin-orbit matrix elements in the units of spin-orbit strength \(\lambda = \zeta\) between terms \(2T_{2g}\) of \(t_{2g}^5\), \(4T_{1g}\) and \(4T_{2g}\) of \(t_{2g}^4e_g^1\) and \(6A_{1g}\) of \(t_{2g}^3e_g^2\) are given in Table A.1 (also see Appendix 2 Table A36 in Ref. [92]). Here, the total angular momentum \(J\) states are reduced into the irreducible representations of \(O_h\) group as \(J = 1/2 \rightarrow E', J = 3/2 \rightarrow U', J = 5/2 \rightarrow U' + E''\) (also see Appendix 2, Table A14 in Ref. [92]). For matrix elements between several other higher lying states, see Ref. [228].
A.5 Spin-orbit mixing of the $t_{2g}$ and $e_g$ subspaces

For a single electron in the crystal field split $d$ orbitals ($t_{2g}$ and $e_g$), the residual SO Hamiltonian, $H_{SO}$, the couples $^2T_{2g} (t_{2g}^1e_g^0)$ and the $2E_g (t_{2g}^0e_g^1)$ states is given by [91]

$$H_{SO} = \frac{\lambda}{2} \times \begin{pmatrix} d_z \\ d_{yz} \\ d_{zx} \\ d_{xy} \end{pmatrix},$$

\[ \begin{pmatrix} 1 \\ \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\ 0 & -\sqrt{3}i & 0 & -i \\ -\sqrt{3}i & 0 & -i & 0 \\ 0 & \sqrt{3} & 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix} = \frac{\sqrt{3}i}{2} \lambda \begin{pmatrix} 1 \\ \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{3}{2} & -\frac{3}{2} \\ \frac{3}{2} & \frac{3}{2} \end{pmatrix} \begin{pmatrix} 1 \\ \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix} = \frac{\sqrt{3}i}{2} \lambda \begin{pmatrix} 1 \\ \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{3}{2} & -\frac{3}{2} \\ \frac{3}{2} & \frac{3}{2} \end{pmatrix} \begin{pmatrix} 1 \\ \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix}.$$
Exchange interactions

B.1 Coulomb and exchange integrals

The Coulomb interaction is written as

\[
H_C = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \int d^3r_1 d^3r_2 \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} \tag{B.1}
\]

where the density operator \( \rho(r) = -e \sum_\sigma \Psi_\sigma^\dagger(r)\Psi_\sigma(r) \) with \( \sigma = \uparrow, \downarrow \) and \( \Psi_\sigma(r) \) as the field operator. This field operator satisfies the anti-commutation relations, implying the Pauli exclusion principle. Substituting for \( \rho(r) \) we get

\[
H_C = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \int d^3r_1 d^3r_2 \sum_{\sigma_1,\sigma_2} \Psi_{\sigma_1}^\dagger(r_1)\Psi_{\sigma_2}^\dagger(r_2) \frac{e^2}{|r_1 - r_2|} \Psi_{\sigma_1}(r_1)\Psi_{\sigma_2}(r_2) \tag{B.2}
\]

Expanding \( \Psi \) in an orthonormal basis of single-electron wave functions \( \phi_{Rm} \) (\( R \) is the ionic position and \( m \) is the orbital quantum number) and also spinors \( \chi_\sigma \), then

\[
\Psi_\sigma(r) = \sum_{Rm} a_{Rm\sigma} \phi_{Rm}(r)\chi_\sigma \tag{B.3}
\]

where \( a_{Rm\sigma} \) is the Fermionic annihilation operator. The Coulomb interaction in general can be written as

\[
H_C = \frac{1}{2} \sum_{R_1m_1} \cdots \sum_{R_4m_4} \left( \phi_{R_1m_1}^\dagger \phi_{R_2m_2} \left| \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|} \right| \phi_{R_3m_3} \phi_{R_4m_4} \right) \\
\times \sum_{\sigma_1,\sigma_2} a_{R_1m_1\sigma_1}^\dagger a_{R_2m_2\sigma_2}^\dagger a_{R_3m_3\sigma_2} a_{R_4m_4\sigma_1} \tag{B.4}
\]

This is based on the course notes in "Theory of Magnetism" by Carsten Timm (Winter semester 2010 TU Dresden).

\(^1\)In second-quantization notation.
The on-site Coulomb interaction can be obtained by making \( \mathbf{R}_1 = \mathbf{R}_2 = \mathbf{R}_3 = \mathbf{R}_4 \) and considering \( m_1 = m_4 \) and \( m_2 = m_3 \). This gives

\[
H_C \approx \frac{1}{2} \sum_{\mathbf{R}} \sum_{m_1 m_2} \sum_{\sigma_1 \sigma_2} \left\{ K_{m_1 m_2} a_{\mathbf{R}_m 1}^\dagger a_{\mathbf{R}_{m_2} 1} a_{\mathbf{R}_m 2}^\dagger a_{\mathbf{R}_{m_2} 2} \right\} + J_{m_1 m_2} a_{\mathbf{R}_m 1}^\dagger a_{\mathbf{R}_{m_2} 1} a_{\mathbf{R}_m 2} a_{\mathbf{R}_{m_2} 2}, \quad \text{with} \tag{B.5}
\]

\[
K_{m_1 m_2} = \left\langle \phi_{\mathbf{R}_{m_1}}, \phi_{\mathbf{R}_{m_2}} \left| \frac{e^2}{4 \pi \varepsilon_0 |\mathbf{R}_1 - \mathbf{R}_2|} \right| \phi_{\mathbf{R}_{m_2}}, \phi_{\mathbf{R}_{m_1}} \right\rangle \tag{B.6}
\]

\[
J_{m_1 m_2} = \left\langle \phi_{\mathbf{R}_{m_1}}, \phi_{\mathbf{R}_{m_2}} \left| \frac{e^2}{4 \pi \varepsilon_0 |\mathbf{R}_1 - \mathbf{R}_2|} \right| \phi_{\mathbf{R}_{m_1}}, \phi_{\mathbf{R}_{m_2}} \right\rangle \tag{B.7}
\]

are the direct Coulomb and exchange integrals respectively. The latter is called exchange because \( \phi_{\mathbf{R}_{m_1}} \) and \( \phi_{\mathbf{R}_{m_2}} \) are exchanged in the factor compared to the direct integrals. Eq. B.5 can be written as

\[
H_C \approx \frac{1}{2} \sum_{\mathbf{R}} \sum_{m_1 m_2} \sum_{\sigma_1 \sigma_2} \left\{ K_{m_1 m_2} a_{\mathbf{R}_m 1}^\dagger a_{\mathbf{R}_{m_2} 1} a_{\mathbf{R}_m 2}^\dagger a_{\mathbf{R}_{m_2} 2} - J_{m_1 m_2} a_{\mathbf{R}_m 1}^\dagger a_{\mathbf{R}_{m_2} 1} a_{\mathbf{R}_m 2} a_{\mathbf{R}_{m_2} 2} \right\}. \tag{B.8}
\]

Defining the number operator \( n_{\mathbf{R} m} \) and spin operators \( s_{\mathbf{R} m}^\alpha \) as

\[
n_{\mathbf{R} m} = \sum_{\sigma \sigma'} a_{\mathbf{R}_{m \sigma}} a_{\mathbf{R}_{m \sigma}^\dagger}, \tag{B.9}
\]

\[
s_{\mathbf{R} m}^\alpha = \sum_{\sigma \sigma'} a_{\mathbf{R}_{m \sigma}} (\sigma_{\sigma \sigma'}^\alpha) / 2 a_{\mathbf{R}_{m \sigma'}}, \tag{B.10}
\]

where \( \sigma_{\sigma \sigma'}^\alpha, \alpha = x, y, z \) are the Pauli matrices, one can show that

\[
\sum_{\sigma_1 \sigma_2} a_{\mathbf{R}_{m_1 1}}^\dagger a_{\mathbf{R}_{m_1 2}} a_{\mathbf{R}_{m_2 1}}^\dagger a_{\mathbf{R}_{m_2 2}} a_{\mathbf{R}_{m_1 1}} = \frac{1}{2} n_{\mathbf{R}_{m_1}} n_{\mathbf{R}_{m_2}} + 2 s_{\mathbf{R}_{m_1}}^+ s_{\mathbf{R}_{m_2}}^- + s_{\mathbf{R}_{m_1}}^- s_{\mathbf{R}_{m_2}}^+ + s_{\mathbf{R}_{m_1}}^+ s_{\mathbf{R}_{m_2}}^+ - s_{\mathbf{R}_{m_1}}^- s_{\mathbf{R}_{m_2}}^- \tag{B.11}
\]

obtaining

\[
H_C \approx \frac{1}{2} \sum_{\mathbf{R}} \sum_{m_1 m_2} \left\{ \left( K_{m_1 m_2} - \frac{1}{2} J_{m_1 m_2} \right) n_{\mathbf{R}_{m_1}} n_{\mathbf{R}_{m_2}} - 2 J_{m_1 m_2} s_{\mathbf{R}_{m_1}} \cdot s_{\mathbf{R}_{m_2}} \right\}. \tag{B.12}
\]

The first term in the on-site Coulomb interaction and for a single orbital boils down to \( H_C = \sum_{\mathbf{R}} U a_{\mathbf{R}_1}^\dagger a_{\mathbf{R}_2} a_{\mathbf{R}_3} a_{\mathbf{R}_4} \), with \( U > 0 \) the famous Hubbard \( U \)-term. The second term in Eq. B.12

\footnote{In general, all \( m_i \) can be different and give a non-zero integral, however, only non-zero first order contribution is obtained when the creation and annihilation operator are paired for each orbital.}
is the spin-spin interaction with $J_{m_1m_2} > 0$ that prefers the parallel alignment of spins, which is the Hund’s first rule. Note that this term is purely quantum-mechanical in origin.

### B.1.1 Inter-ion exchange

The inter-ion exchange interaction can be obtained by setting $R_1 = R_4$ and $R_2 = R_3$ in Eq. B.4 and considering only one non-degenerate orbital $m$, in complete analogy to the on-site Coulomb interaction we obtain

$$H_C \simeq \frac{1}{2} \sum_{R_iR_2} \left\{ \left( K_{12} - \frac{1}{2} J_{12} \right) n_1 n_2 - 2 J_{m_1m_2} \mathbf{s}_1 \cdot \mathbf{s}_2 \right\}$$

where

$$K_{12} = \int d^3r_1 d^3r_2 |\phi_{R_1}(r_1)|^2 \frac{e^2}{4\pi \varepsilon_0 |r_1 - r_2|} |\phi_{R_2}(r_2)|^2$$

$$= \left\langle \phi_{R_1}, \phi_{R_2} \left| \frac{e^2}{4\pi \varepsilon_0 |r_1 - r_2|} \phi_{R_2}, \phi_{R_1} \right\rangle \right.$$  \hspace{1cm} (B.14)

$$J_{12} = \int d^3r_1 d^3r_2 \phi_{R_1}^*(r_1) \phi_{R_2}^*(r_2) \frac{e^2}{4\pi \varepsilon_0 |r_1 - r_2|} \phi_{R_1}(r_2) \phi_{R_2}(r_1)$$

$$= \left\langle \phi_{R_1}, \phi_{R_2} \left| \frac{e^2}{4\pi \varepsilon_0 |r_1 - r_2|} \phi_{R_1}, \phi_{R_2} \right\rangle \right.$$  \hspace{1cm} (B.15)

For an ionic crystal, the charge $-en_i$ fluctuations are minimal and for $n_i = 1$ the exchange interaction becomes

$$H_{exc} = - \sum_{R_iR_2} J_{12} \mathbf{s}_1 \cdot \mathbf{s}_2$$

(B.16)

This direct exchange between orthogonal orbitals always lead to a ferromagnetic exchange interaction. This is because the electrons with parallel spins cannot occupy the same orbital and therefore avoid the strong intra-orbital Coulomb repulsion.

### B.2 Superexchange interaction within Hubbard Model

The charge fluctuations result from the hybridization between orbitals of different ions, allowing the electrons to tunnel or hop one ion to another. This leads to kinetic exchange interaction which can be well understood by the Hubbard model. Neglecting the inter-site Coulomb repulsion, and considering the case of a single relevant orbital per site, the Hubbard Hamiltonian can be written as

$$H = - \sum_{RR'\sigma} t(R - R') a_{R's}^\dagger a_{R\sigma} + U \sum_{R} a_{R\uparrow}^\dagger a_{R\uparrow} a_{R\downarrow}^\dagger a_{R\downarrow} \right.$$  \hspace{1cm} (B.17)
where the first term describes the kinetic energy due to hopping of the electron with \( t \) as hopping parameter and the second is the local Coulomb repulsion \( (U > 0) \). Consider a system having only two atoms at site 1 and 2,

\[
H = -\sum_\sigma t \left( a_{1\sigma}^\dagger a_{2\sigma} + a_{2\sigma}^\dagger a_{1\sigma} \right) - \mu \sum_\sigma \left( a_{1\sigma}^\dagger a_{1\sigma} + a_{2\sigma}^\dagger a_{2\sigma} \right) + U \sum_{i=1}^2 a_i^\dagger a_i^\dagger a_i a_i
\]

There are six possible states: \( \{ |\uparrow\downarrow, 0\rangle, |0, \uparrow\downarrow\rangle, |\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle, |\uparrow, \uparrow\rangle, |\downarrow, \downarrow\rangle \} \) in whose space \( \mu \) term is a constant and hence one ends with a Hamiltonian matrix of size \( 6 \times 6 \) with matrix elements

\[
\begin{pmatrix}
U & 0 & t & -t & 0 & 0 \\
0 & U & t & -t & 0 & 0 \\
t & t & 0 & 0 & 0 & 0 \\
-t & -t & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]

Simplifying \( H \) by transforming from \( |\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle \) onto \( (|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle)/\sqrt{2}, (|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle)/\sqrt{2} \) gives

\[
H' = \begin{pmatrix}
U & 0 & \sqrt{2}t & 0 & 0 & 0 \\
0 & U & \sqrt{2}t & 0 & 0 & 0 \\
\sqrt{2}t & \sqrt{2}t & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]

with eigenvalues

\[
U \to |\uparrow\downarrow, 0\rangle \\
\frac{U + \sqrt{U^2 + 16t^2}}{2} \to |\downarrow\uparrow, 0\rangle \\
\frac{U - \sqrt{U^2 + 16t^2}}{2} \to (|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle)/\sqrt{2} \\
0 \to (|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle)/\sqrt{2}, |\uparrow, \uparrow\rangle, |\downarrow, \downarrow\rangle
\]

the corresponding eigenfunctions are given on the right.

In the case of \( U >> t \), the case of ionic insulators, the first two have very large energies
$U$ and $\cong U + \frac{4t^2}{U}$, the third has an energy $\cong -\frac{4t^2}{U} < 0$. So for $U/|t| \to \infty$ the spin singlet eigenstate $(|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle)/\sqrt{2}$ is the ground state, with the spin-triplet states at 0. With finite $U$ the ground state mixes with the states with double occupancy. The singlet state being lower in energy implies an antiferromagnetic interaction which results form the lowering of the kinetic energy for antiparallel spins.

To compare the above 2-site Hubbard model for the case $U \gg t$ with an interacting pair of spins $s_1 = s_2 = 1/2$, we have

$$H_{eff} = -Js_1 \cdot s_2 = -\frac{J}{2}[S \cdot S - s_1 \cdot s_1 - s_2 \cdot s_2]$$

with $S = s_1 + s_2$

$$= -\frac{J}{2}[S(S + 1) - \frac{3}{4} - \frac{3}{4}] = \text{const} \begin{cases} +0 & \text{for } S = 0, \\ -J & \text{for } S = 1. \end{cases} \quad (B.22)$$

Comparing Eq. B.21 and B.22 one finds

$$J = -\frac{4t^2}{U} \text{ for } U \gg t \quad (B.23)$$

### B.3 Goodengouh-Kanamori-Anderson rules

Goodenough-Kanamori-Anderson rules are a system of semiempirical rules that were developed over a period of years by Goodenough [38], Kanamori [39] and Anderson [105]. These rules in general explain the main features of the superexchange interactions. They taking into account the occupation of the various $d$-levels as dictated by ligand field theory. These rules are summarized in the following. For a detailed analysis see Ref. [277].

- When two cations have lobes of singly occupied TM $d$ orbitals that point toward each other, giving large overlap and hopping integrals, the exchange is strong and antiferromagnetic ($J > 0$). This is the usual case, for $120^\circ$–$180^\circ$ TM-O-TM bonds.

- When two cations have an overlap integral between singly occupied TM $d$ orbitals which is zero by symmetry, the exchange is ferromagnetic and relatively weak. This is the case for $\approx 90^\circ$ TM-O-TM bonds.

- When two cations have an overlap between singly occupied TM $d$ orbitals and empty or doubly occupied orbitals of the same type, the exchange is also ferromagnetic, and relatively weak.
Appendix C

Two-site spin-orbit wave functions, symmetry analysis

C.1 Ba$_2$IrO$_4$: $D_{2h}$ symmetry

For two Ir ions, $a$ and $b$, with corner-shared octahedra, the overall symmetry of the cluster is $D_{2h}$ (see Fig. 6.3 in Chap. 6). In the reference frame with Ir-Ir link along the X axis, the origin of the XYZ coordinate system at the midpoint of the Ir-Ir link and Z axis perpendicular to the Ir-O-Ir plane, the Kramers doublet wave functions $f_{rs}$, where $r = a, b$ and $\vec{S} = \frac{1}{2}, -\frac{1}{2}$ are given as [10]

\[
\begin{align*}
    f_{r, \frac{1}{2}} &= \sin \theta \begin{pmatrix} xy \frac{1}{2} \end{pmatrix}_r + \cos \theta \left( \begin{pmatrix} yz, -\frac{1}{2} \end{pmatrix}_r + i \begin{pmatrix} zx, -\frac{1}{2} \end{pmatrix}_r \right) \\
    f_{r, -\frac{1}{2}} &= \sin \theta \begin{pmatrix} xy, -\frac{1}{2} \end{pmatrix}_r - \cos \theta \left( \begin{pmatrix} yz, \frac{1}{2} \end{pmatrix}_r + i \begin{pmatrix} zx, \frac{1}{2} \end{pmatrix}_r \right)
\end{align*}
\]  

(C.1)

The eight symmetry element of $D_{2h}$ point-group, namely

\[
\begin{align*}
    E &\rightarrow \text{identity}, \\
    I &\rightarrow \text{inversion}, \\
    C_2(x), C_2(y), C_2(z) &\rightarrow 180^\circ \text{rotation}, \\
    \sigma(xy), \sigma(yz), \sigma(zx) &\rightarrow \text{mirrorreflection}
\end{align*}
\]

acts simultaneously on the orbital and spin spaces that form a pseudospin doublet Eq. C.1. It should be noted that the rotations and mirror planes are related by the inversion symmetry $I$ as

\[
C_2(x)\sigma(yz) = I, \quad C_2(y)\sigma(zx) = I, \quad C_2(z)\sigma(xy) = I.
\]

(C.3)
At \( r = 0 \), the rotations act on the Kramers doublets as Pauli matrices in the pseudospin space, i.e., \( C_2(x) = -i\sigma_z, C_2(y) = -i\sigma_y \) and \( C_2(z) = -i\sigma_z \). Hence

\[
C_2(x)f_{0, -1/2} = -if_{0, -1/2}, \quad C_2(x)f_{0, 1/2} = -if_{0, 1/2} \\
C_2(y)f_{0, 1/2} = f_{0, -1/2}, \quad C_2(y)f_{0, -1/2} = -f_{0, 1/2} \\
C_2(z)f_{0, 1/2} = if_{0, -1/2}, \quad C_2(z)f_{0, -1/2} = -if_{0, 1/2}.
\]

(C.4)

From the relations in C.3 it can be seen that the mirror reflection is opposite to the corresponding rotation,

\[
\sigma(xy)f_{0, 1/2} = if_{0, 1/2}, \quad \sigma(xy)f_{0, -1/2} = if_{0, -1/2} \\
\sigma(yz)f_{0, 1/2} = f_{0, -1/2}, \quad \sigma(yz)f_{0, -1/2} = -f_{0, 1/2} \\
\sigma(zx)f_{0, 1/2} = -if_{0, -1/2}, \quad \sigma(zx)f_{0, -1/2} = if_{0, 1/2}.
\]

(C.5)

Now at \( r = a, b \), the \( f_{r(a,b),s} \) undergo an additional transformation of interchange of \( a \) and \( b \) with rotation operations \( C_2(y), C_2(z) \) and mirror \( \sigma(yz) \).

Hence for the even and odd superpositions of the Kramers doublets in Eq. C.1

\[
\psi_s^\pm(r) = \frac{1}{\sqrt{2}} \left[ f_{as}(r) \pm f_{bs}(r) \right],
\]

(C.6)

the symmetry operations can be followed from expressions in C.4 and C.5. For two particles 1 and 2 occupying the sites \( a \) and \( b \), there are six antisymmetric product functions:

\[
\psi_{1, -1/2}^{+, +}(1, 2), \quad \psi_{1, -1/2}^{+, -}(1, 2), \quad \psi_{1, -1/2}^{-, +}(1, 2),
\]

\[
\psi_{1, -1/2}^{-, -}(1, 2), \quad \psi_{1, 1/2}^{+, -}(1, 2), \quad \psi_{1, 1/2}^{-, +}(1, 2),
\]

(C.7)

each written as the Slater determinant of the single particle spin wave function \( \psi_s^\pm \), for instance,

\[
\psi_{1, -1/2}^{++, +}(1, 2) = |\psi_{1, 1/2}^{+}(1)\psi_{1, -1/2}^{+}(2)|.
\]

(C.8)

One then finds the following combinations

\[
\Psi_S = \psi_{1, -1/2}^{+, +}(1, 2), \quad \Psi_1 = \psi_{1, -1/2}^{+, -}(1, 2),
\]

\[
\Psi_2 = \psi_{1, 1/2}^{+, -}(1, 2), \quad \Psi_3 = \psi_{1, 1/2}^{-, +}(1, 2),
\]

\[
\Psi_4 = \psi_{1, -1/2}^{-, -}(1, 2), \quad \Psi_5 = \psi_{1, -1/2}^{-, -}(1, 2).
\]

(C.9)

to transform according to the different irreducible representations (irrep.) of \( D_{2h} \) point group.
The above assignment is obtained by calculating the characters for each of those states in C.9, and comparing the results with the $D_{2h}$ point-group to find the irrep. The numbers in the brackets in the above relations are the list of characters in the sequence of operations $(E, I, C_2(x), C_2(y), C_2(z), \sigma(xy), \sigma(yz), \sigma(zx))$ respectively.

The states $\Psi_S, \Psi_4$ and $\Psi_5$ are pseudospin singlet states and $\Psi_1, \Psi_2$ and $\Psi_3$ are the pseudospin triplets. From a two-site Hubbard model with onsite correlations $U$ (see App. B.2), we can conclude that the singlet states $\Psi_4$ and $\Psi_5$ are separated from $\Psi_S$ by an energy scale $U$. Thus the states $\Psi_S$ and $\Psi_{1,2,3}$ correspond to the single and the three triplet states of the magnetic spectrum respectively.

### C.1.1 Dipole moment transition matrix elements for Ba$_2$IrO$_4$

The dipole moment (DM) transition matrix elements calculated between the lowest four states corresponding to the magnetic Hamiltonian computed for Ba$_2$IrO$_4$ are given below.

\begin{equation}
\begin{array}{cccc}
\text{DM}_x & 1 & 2 & 3 & 4 \\
1 & 0 & 0 & 0 & 0 \\
2 & 0 & 0 & 0 & 0 \\
3 & 0 & 0 & 0 & 0 \\
4 & 0 & 0 & 0 & 0 \\
\end{array}, \quad
\begin{array}{cccc}
\text{DM}_y & 1 & 2 & 3 & 4 \\
1 & 0 & 0 & 1.09 & 0 \\
2 & 0 & 0 & 0 & 0 \\
3 & 0 & 0 & 0 & 0 \\
4 & 0 & 0 & 0 & 0 \\
\end{array}, \quad
\begin{array}{cccc}
\text{DM}_z & 1 & 2 & 3 & 4 \\
1 & 0 & 0 & 0 & 1.22 \\
2 & 0 & 0 & 0 & 0 \\
3 & 0 & 0 & 0 & 0 \\
4 & 0 & 0 & 0 & 0 \\
\end{array}.
\end{equation}

\begin{equation}
\begin{array}{cccc}
\text{DM}_{x'} & 1 & 2 & 3 & 4 \\
1 & 0 & 0 & 0 & 0 \\
2 & 0 & 0 & 0 & 0 \\
3 & 0 & 0 & 0 & 0 \\
4 & 0 & 0 & 0 & 0 \\
\end{array}, \quad
\begin{array}{cccc}
\text{DM}_{y'} & 1 & 2 & 3 & 4 \\
1 & 0 & 0 & 0 & 0 \\
2 & 0 & 0 & 0 & 0 \\
3 & 0 & 0 & 0 & 0 \\
4 & 0 & 0 & 0 & 0 \\
\end{array}, \quad
\begin{array}{cccc}
\text{DM}_{z'} & 1 & 2 & 3 & 4 \\
1 & 0 & 0 & 0 & 0 \\
2 & 0 & 0 & 0 & 0 \\
3 & 0 & 0 & 0 & 0 \\
4 & 0 & 0 & 0 & 0 \\
\end{array}.
\end{equation}

The states are numbered from 1 – 4 on the right and top of the matrices. Each of the elements in the above matrices should be multiplied by $10^{-3}$. It can be seen that only $\text{DM}_y$ and $\text{DM}_z$ have non-zero elements between states 1 and 3, and 1 and 4 respectively. For $D_{2h}$ point-group symmetry, $\text{DM}_y$ and $\text{DM}_z$ belong to the irreps. $B_{2u}$ and $B_{1u}$ respectively [243]. Because the product of the irrep. of the states with non-zero elements should belong to the same irrep. as the respective DM, the symmetries of states can be easily identified.


C.2 \(A_2\text{IrO}_3\): \(C_{2h}\) symmetry

In the case of \(C_{2h}\) point-group symmetry, we use the symmetry reduction \(D_{2h} \rightarrow C_{2h}\) tables [243] to arrive at the following correspondence, \(A_{1g} \rightarrow A_g\), \(A_{1u} \rightarrow A_u\), \(B_{2u} \rightarrow B_u\) and \(B_{1u} \rightarrow B_u'\). Thus the two-site wave functions in the \(C_{2h}\) case belong to the irrep.

\[ \Psi_S \rightarrow A_g, \quad \Psi_1 \rightarrow B_u', \quad \Psi_2 \rightarrow B_u, \quad \Psi_3 \rightarrow A_u. \]  

(C.12)

The \(B_u'\) is the second (repeating) irrep. equivalent to \(B_u\), meaning that \(\Psi_1\) and \(\Psi_2\) are in general mixed due to the lowered symmetry.

C.2.1 Dipole moment transition matrix elements for \(\text{Na}_2\text{IrO}_3\)

The dipole moment transition matrix elements obtained from the QC calculations among the lowest four states corresponding to the magnetic Hamiltonian of \(\text{Na}_2\text{IrO}_3\) are give below (see Table 7.3 in Chap. 7). For the B1 links (\(\times 10^{-4}\)):

For B2 links (\(C_i\) symmetry, \(\times 10^{-4}\)):

C.2.2 Dipole moment transition matrix elements for \(\text{Li}_2\text{IrO}_3\)

In the case of \(\text{Li}_2\text{IrO}_3\), the DM matrix elements obtained from QC calculations are as follows. See Table 7.5 in Chap. 7. For B1 links having \(C_{2h}\) symmetry, (\(\times 10^{-3}\)):

\[
\begin{array}{cccccc}
\text{DM}_x & 1 & 2 & 3 & 4 & \\
\ h & 0 & 0 & 1.6 & 0 & \\
2 & 0 & 0 & 0 & 0 & \\
3 & 1.6 & 0 & 0 & -7.1 & \\
4 & 0 & 0 & -7.1 & 0 & \\
\end{array}
\begin{array}{cccccc}
\text{DM}_y & 1 & 2 & 3 & 4 & \\
\ h & 0 & 0 & 0 & 0 & \\
2 & 0 & 0 & 2.9 & 0 & \\
3 & 0 & 2.9 & 0 & 0 & \\
4 & 0 & 0 & 0 & 0 & \\
\end{array}
\begin{array}{cccccc}
\text{DM}_z & 1 & 2 & 3 & 4 & \\
\ h & 0 & 0 & 0 & 0 & \\
2 & 0 & 0 & 0 & 0 & \\
3 & 0 & 2.9 & 0 & 0 & \\
4 & 0 & 0 & 0 & 0 & \\
\end{array}
\]
The energies of the states \{1,2,3,4\} are \{0,3.2,7.7,24.8\} for the B1 links.

For B2 links having \(C_i\) symmetry, \((\times 10^{-4})\):

\[
\begin{pmatrix}
1 & 0 & 0 & 4.1 \\
2 & 0 & 0 & 0 \\
3 & 4.1 & 0 & 0 \\
4 & 0 & 0 & -5.6 \\
\end{pmatrix},
\]

\[
\begin{pmatrix}
1 & 0 & 0 & -3.5 \\
2 & 0 & 0 & -3.6 \\
3 & -3.5 & -3.6 & 0 \\
4 & 0 & 0 & -9.9 \\
\end{pmatrix},
\]

\[
\begin{pmatrix}
1 & 0 & 0 & 3.7 \\
2 & 0 & 0 & 0.3 \\
3 & 3.7 & 0.3 & 0 \\
4 & 0 & 0 & 3.9 \\
\end{pmatrix}
\]

The energies of the states \{1,2,3,4\} are \{0,3.7,7.1,8.4\} for the B2 links.

### C.3 \(C_{2v}\) symmetry

For \(C_{2v}\) point-group symmetry, symmetry reduction from \(D_{2h} \rightarrow C_{2v}\) leads to the following correspondence \([243]\), \(A_{1g} \rightarrow A_1, A_{1u} \rightarrow A_2, B_{2u} \rightarrow A'_1\) and \(B_{1u} \rightarrow B_2\). Hence we have

\[
\Psi_S \rightarrow A_1, \quad \Psi_1 \rightarrow A'_1, \quad \Psi_2 \rightarrow B_2, \quad \Psi_3 \rightarrow A_2.
\]  
(C.13)

The \(A'_1\) is the repeating irreducible representation equivalent to \(A_1\), meaning that \(\Psi_S\) and \(\Psi_1\) are in general allowed to mix due to the lowered symmetry.

#### C.3.1 Dipole moment transition matrix elements for \(Sr_2IrO_4\)

For the two-site cluster with \(C_{2v}\) symmetry, \((\times 10^{-3})\):

\[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
2 & 0 & 0 & 0.6 \\
3 & 0 & 0.6 & 0 \\
4 & 0 & 0 & 0 \\
\end{pmatrix},
\]

\[
\begin{pmatrix}
1 & 0 & 0 & 2.2 \\
2 & 0 & 0 & 0.0 \\
3 & 0 & 0.0 & 0 \\
4 & 2.2 & 0 & 0 \\
\end{pmatrix},
\]

\[
\begin{pmatrix}
1 & 0 & 0 & 2.6 \\
2 & 0 & 0 & 0.0 \\
3 & 2.6 & 0 & 0.03 \\
4 & 0 & 0 & 0.03 \\
\end{pmatrix}
\]
Spin-orbit wave functions of the low-lying magnetic states

The MOLPRO output for two-site \((a, b)\) calculations gives 36 SO coupled states \(|\Psi\rangle = \{\psi_0, \psi_1, ..., \psi_{35}\}^{-1}\) in the basis of zeroth-order eigenfunctions \(|\Phi, S, M_S\rangle\). Here \(\Phi = |\phi_0^s\rangle \ldots |\phi_8^s\rangle\) and \(|\phi_0^t\rangle \ldots |\phi_8^t\rangle\)’s are the nine singlet and nine triplet states, respectively, obtained from the MRCI calculations without the inclusion of SOC. \(S\) is the total spin \((s^a + s^b)\) and \(M_S\) is the projection on the \(z\) axis. So we have

\[ |\Psi\rangle = C_{SOC} |\Phi, S, M_S\rangle \tag{D.1} \]

with \(C_{SOC}\) as the complex coefficients of the SOC wave functions.

To obtain \(|\Psi\rangle\) in total angular momentum basis \(|j_a, j_b, m_{ja}, m_{jb}\rangle\), the following procedure is used:

1. First the zeroth-order states \(|\Phi\rangle\) are expressed in \(t_{2g}\) orbital basis \(\{d_{xy}, d_{xz}, d_{yz}\}\). This can be obtained from the wave functions the MOLPRO outputs for each of the MRCI states. Now the basis states are \(|d_i^a, d_j^b, S, M_S\rangle\), \(i\) and \(j\) \(\in \{xy, yz, zx\}\).

2. Using the relations to express the \(t_{2g}\) orbitals in the effective orbital angular momentum states, see A.19, the wave functions can then be rotated into \(|l, m_l\rangle\) basis. Thus we obtain the basis states \(|m_i^a, m_j^b, S, M_S\rangle, m \in \{-1, 0, 1\}\). Further writing the total spin \(|S, M_S\rangle\) into individual spins on \(a\) and \(b\), the spin part of the basis can be written as \(|m_s^a, m_s^b, M_S\rangle, m_s \in \{-1/2, 1/2\}\), giving rise to \(|m_i^a, m_j^b, m_s^a, m_s^b\rangle\) basis.

3. Using the Clebsch-Gordan coefficients, given in A.20, to sum the orbital and spin angular momentum for each of the sites \(a\) and \(b\), \(\Psi\) can be written in total angular momentum basis \(|j_a, j_b, m_{ja}, m_{jb}\rangle\), with \(j_{a,b} \in \{1/2, 3/2\}\) and \(m_{ja,b} \in \{\pm 1/2, \pm 3/2\}\) as

\[ |\Psi\rangle = C^{ij}_{soc} |j_a, j_b, m_j^a, m_j^b\rangle \tag{D.2} \]
Here $C_{SOC}^{jj}$ are the SOC wave function coefficients.

Of the 36 states only the lowest four correspond to the exchange interactions between the $\tilde{j} = 1/2$ moments of the two Ir sites. However, because the $\tilde{j} = 3/2$ quartet states are $\sim 0.6$ eV from the $\tilde{j} = 1/2$ states for each of the Ir sites, the former also participate in the superexchange and hence the wave function of the lowest four states also contains contribution from these $\tilde{j} = 3/2$ basis states. Thus all the 36 basis states coming from $J = j_a + j_b$ values $\in \{0, 1, 2, 1, 2, 1, 3, 2, 1, 0\}$ should be considered. The $|j_a, j_b, m_{ja}, m_{jb}\rangle$ then contains states with total $M_J (m_{ja} + m_{jb})$ taking values $\{-3, -2, -1, 0, 1, 2, 3\}$.

For a system with a point-group symmetry that leads to only isotropic exchange interactions for which the singlet $\Psi_S$ and triplet $\Psi^1_{1-3}$ states belong to different irreps., e.g. $D_{2h}$, one finds the basis states with $M^s_J \in \{-2, 0, 2\}$ contribute to only the singlet $\Psi_S = |\uparrow\downarrow - \downarrow\uparrow\rangle/\sqrt{2}$ and triplet $\Psi^1 = |\uparrow\downarrow \pm \downarrow\uparrow\rangle/\sqrt{2}$ states. Whereas the basis states with $M^t_J \in \{-3, -1, 1, 3\}$ contribute to the other triplet states $\Psi^2_{2,3} = |\uparrow\uparrow \pm \downarrow\downarrow\rangle/\sqrt{2}$ of the magnetic spectrum.

### D.1 Ba$_2$IrO$_4$: $D_{2h}$ symmetry

The [Ir$_2$O$_{11}$] unit used to calculate the magnetic spectrum of Ba$_2$IrO$_4$ has $D_{2h}$ symmetry for which the singlet $\Psi_S$ and the triplet $\Psi^1_{1-3}$ states belong to different irreducible representations (see App. C) and hence are not mixed. Rotating the SO coupled wave functions of the four lowest states $\psi_{1-4}$ computed in the QC calculations to $|j_a, j_b, m_{ja}, m_{jb}\rangle$ basis, the obtained contributions from different basis states are shown in Table D.1. We see $\psi_1$ and $\psi_2$ having contribution only from $M^s_J$ states. Also looking at the energies of these two states, it can be concluded that $\psi_1 = \Psi_S$ and $\psi_2 = \Psi^1_1$.

<table>
<thead>
<tr>
<th>State</th>
<th>Energy (meV)</th>
<th>$M^s_J$ (%)</th>
<th>$M^t_J$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_1$</td>
<td>0.0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>66.7</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>$\psi_3$</td>
<td>66.7</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>$\psi_4$</td>
<td>65.0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

### D.2 Na$_2$IrO$_3$ and Li$_2$IrO$_3$: $C_{2h}$ symmetry

The [Ir$_2$O$_{10}$] unit used to calculate the magnetic spectrum of Na$_2$IrO$_3$ has $C_{2h}$ symmetry. The states $\Psi_S$, $\Psi_1$, $\Psi_2$, $\Psi_3$ in this point-group symmetry transform according to irreps $A_g, B_u, B_u$ and $A_u$, respectively (App. C). Since $\Psi_1$ and $\Psi_2$ belong to $B_u$, they can in principle be mixed. The contributions from different basis states to the four magnetic states obtained from the transformed wave functions are shown in Table D.2.
D.2 Na$_2$IrO$_3$ and Li$_2$IrO$_3$: $C_{2h}$ symmetry

**Table D.2** Contribution from $j$-basis states to the four low lying states corresponding to the magnetic spectrum in Na$_2$IrO$_3$. On the left is for the Ir-Ir link B1 and on the right for the link B2.

<table>
<thead>
<tr>
<th>B1</th>
<th>Energy (meV)</th>
<th>$M^j_s$ (%)</th>
<th>$M^j_t$ (%)</th>
<th>B2</th>
<th>Energy (meV)</th>
<th>$M^j_s$ (%)</th>
<th>$M^j_t$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_1$</td>
<td>0.0</td>
<td>0.12</td>
<td>99.88</td>
<td>$\psi_1$</td>
<td>0.0</td>
<td>0.33</td>
<td>99.67</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>0.5</td>
<td>0.02</td>
<td>99.98</td>
<td>$\psi_2$</td>
<td>1.2</td>
<td>0.04</td>
<td>99.96</td>
</tr>
<tr>
<td>$\psi_3$</td>
<td>5.5</td>
<td>99.98</td>
<td>0.02</td>
<td>$\psi_3$</td>
<td>6.8</td>
<td>99.96</td>
<td>0.04</td>
</tr>
<tr>
<td>$\psi_4$</td>
<td>10.5</td>
<td>99.88</td>
<td>0.12</td>
<td>$\psi_4$</td>
<td>8.2</td>
<td>99.67</td>
<td>0.33</td>
</tr>
</tbody>
</table>

We see that $\psi_1$ and $\psi_4$ are admixed, so they must belong to the $B_u$ irrep. Because $\psi_4$ has a dominant contribution from the $M^j_s$ states, it must be $\Psi_1$ and hence the other state in $B_u$ irrep $\psi_3 = \Psi_2$. However, less than 1% admixture of $\psi_1$ and $\psi_3$ allows us to map the energy spectrum onto a spin Hamiltonian with $D_{2h}$ symmetry (see Sec. 7.3.2). Although the B2 link has only $C_i$ symmetry we see that the mixing of states is again less than a percent.

**Li$_2$IrO$_3$**

The [Ir$_2$O$_{10}$] unit used to calculate the magnetic spectrum of Li$_2$IrO$_3$ also has $C_{2h}$ point-group symmetry. In Table D.3 for the B1 link we see that there is $\sim 27\%$ admixture of the states $\psi_1$ and $\psi_3$ which is allowed in $C_{2h}$ symmetry. This mixing is considerable and hence the energy spectrum is mapped onto appropriate $C_{2h}$ spin Hamiltonian (see Sec. 7.4.1). For the B2 link ($C_i$ symmetry) this admixture is $\sim 10\%$. We neglect the admixtures in the other states as they are smaller than $\sim 3\%$, and still map the energy spectrum obtained from QC calculations onto spin Hamiltonian dictated by $C_{2h}$ symmetry.

**Table D.3** Contribution from $j$-basis states to the ground and the first three excited states which correspond to the magnetic spectrum in Li$_2$IrO$_3$. For Ir-Ir bond B1 and B2.

<table>
<thead>
<tr>
<th>B1</th>
<th>Energy (meV)</th>
<th>$M^j_s$ (%)</th>
<th>$M^j_t$ (%)</th>
<th>B2</th>
<th>Energy (meV)</th>
<th>$M^j_s$ (%)</th>
<th>$M^j_t$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_1$</td>
<td>0.0</td>
<td>26.72</td>
<td>73.28</td>
<td>$\psi_1$</td>
<td>0.0</td>
<td>2.40</td>
<td>97.60</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>3.2</td>
<td>5.60</td>
<td>94.40</td>
<td>$\psi_2$</td>
<td>3.7</td>
<td>10.69</td>
<td>89.31</td>
</tr>
<tr>
<td>$\psi_3$</td>
<td>7.7</td>
<td>73.00</td>
<td>27.00</td>
<td>$\psi_3$</td>
<td>7.1</td>
<td>97.68</td>
<td>2.32</td>
</tr>
<tr>
<td>$\psi_4$</td>
<td>24.8</td>
<td>95.32</td>
<td>4.68</td>
<td>$\psi_4$</td>
<td>8.4</td>
<td>89.28</td>
<td>10.72</td>
</tr>
</tbody>
</table>
Appendix E

**Ba$_2$IrO$_4$ spin waves and bilayer energy minimization**

### E.1 Spin wave dispersions

In the magnetic Brillouin zone, where $\Sigma_q = N/2$, there are two spin wave branches, with dispersions given by [252]

$$\omega_{\pm}(q) = 4J_{av}S\sqrt{(1 \mp B_q)^2 + A_q^2}.$$  \hspace{1cm} (E.1)

In this expression, $S = 1/2$, $J_{av} = J + (\Gamma_\parallel + \Gamma_\perp)/2$,

$$A_q = \frac{1}{4J_{av}} [J_1 \cos(q_xa) + J_2 \cos(q_ya)], \approx B_q = -\frac{1}{4J_{av}} [J_3 \cos(q_xa) + J_4 \cos(q_ya)],$$  \hspace{1cm} (E.2)

and

$$J_1 = 2J + \Gamma_{zz} + \Gamma_\parallel \sin^2 \phi + \Gamma_\perp \cos^2 \phi, \approx J_2 = 2J + \Gamma_{zz} + \Gamma_\parallel \cos^2 \phi + \Gamma_\perp \sin^2 \phi$$

$$J_3 = -\Gamma_{zz} + \Gamma_\parallel \sin^2 \phi + \Gamma_\perp \cos^2 \phi, \approx J_4 = -\Gamma_{zz} + \Gamma_\parallel \cos^2 \phi + \Gamma_\perp \sin^2 \phi.$$  \hspace{1cm} (E.3)

These can be rewritten in terms of the coupling constants $\tilde{J}$ and $\tilde{\Gamma}_\parallel$ entering the Hamiltonian terms in (6.5) by making the replacements $J = \tilde{J} + \frac{1}{3}\tilde{\Gamma}_\parallel$, $\Gamma_\parallel = \frac{2}{3}\tilde{\Gamma}_\parallel$, and $\Gamma_\perp = \Gamma_{zz} = -\frac{1}{3}\tilde{\Gamma}_\parallel$. 
E.2 Energy minimization for a bilayer

The ground-state magnetic energy of the layered system can be written as a sum over bilayer contributions (per spin and per layer):

\[ E(\phi_1, \phi_2) = -\frac{K}{2} [\cos(4\phi_1) + \cos(4\phi_2)] - B \cos[2(\phi_1 - \phi_2)] - A \sin(\phi_1 + \phi_2) \]

\[ = -K \cos(2\phi_+) \cos(2\phi_-) - B \cos(2\phi_-) - A \sin\phi_+, \]

where the angles \( \phi_1 \) and \( \phi_2 \) define orientations (say, with respect to the \( x \) axis) in two adjacent planes and \( \phi_\pm = \phi_1 \pm \phi_2 \). We note that both \( K \) and \( B \) are positive. In the subsequent discussion, the coupling \( A \) is chosen positive as well by taking into account the fact that for \( A < 0 \) the simultaneous change of signs, \( \phi_1 \rightarrow -\phi_1 \) and \( \phi_2 \rightarrow -\phi_2 \), retains the expression for \( E(\phi_1, \phi_2) \) invariant.

Minimizing \( E(\phi_1, \phi_2) \) we find four possible extrema solutions for \( \phi_1 \) and \( \phi_2 \) and the respective energies (\( n \) and \( m \) are integers):

\[ \phi_-^{(1)} = m\pi, \quad \phi_+^{(1)} = \frac{\pi}{2} + 2n\pi, \quad E^{(1)} = K - B - A, \quad (E.4) \]

which is possible if \( B > K \);

\[ \phi_-^{(2)} = m\pi, \quad \phi_+^{(2)} = \arcsin \frac{A}{4K} + 2n\pi, \quad E^{(2)} = -K - B - \frac{A^2}{8K}, \quad (E.5) \]

with the requirement \( A < 4K \);

\[ \phi_-^{(3)} = (2m+1)\frac{\pi}{2}, \quad \phi_+^{(3)} = \frac{\pi}{2} + 2n\pi, \quad E^{(3)} = B - K - A, \quad (E.6) \]

which is possible if \( B < K \);

\[ \sin \phi_+^{(4)} = \sqrt{\frac{1+B/K}{2}}, \quad \cos(2\phi_-^{(4)}) = \frac{A}{4K} \sqrt{\frac{2}{1+B/K}}, \quad E^{(4)} = -A \sqrt{\frac{1+B/K}{2}} \quad (E.7) \]

which may occur in the parameter region \( B < K, A < K \sqrt{\frac{1+B/K}{2}} \).

Comparison of the energies of the four possible ground-state configurations shows that three of them, from (E.4) to (E.6), occur in different domains of the \( A-B \) parameter space. In the region \( B > K \) and \( A > 4K \), the most stable is the configuration (E.4) with \( \phi_1^{(1)} = \frac{\pi}{4} + n\frac{\pi}{2} \) and \( \phi_2^{(1)} = \phi_1^{(1)} - m\pi \), which means that the spins (staggered magnetizations) are along one of \( \langle 110 \rangle \) axes and in two adjacent planes the spin alignment is either collinear or anticollinear. Next, in the region with \( B > K, 0 < A < 4K \), the second configuration (E.5) with \( \phi_1^{(2)} = \frac{1}{2} \arcsin(A/4K) + n\frac{\pi}{2} \) and \( \phi_2^{(1)} = \phi_1^{(1)} - m\pi \) is realized. Here, the collinear/anticollinear
alignment in successive layers still persists. However, the preferred direction is specified by $A/4K$. In the region with $B < K$, $A > 4K$, the third configuration (E.6) with $\phi_1^{(3)} = m\pi/2$ and $\phi_2^{(3)} = \phi_1^{(3)} - \pi/2 - m\pi$ is the most stable, which corresponds to having the magnetization along one of the $\langle 100 \rangle$ axes with two directions in successive layers being rotated by $90^\circ$. Finally, for $B < K$ and $A < 4K$, the fourth solution (E.7) has the highest energy and two of the other configurations, i.e., (E.5) and (E.6), compete to give the phase boundary depicted in Fig. 6.4.
Publication list


Bibliography


Bibliography


