Coulomb Correlations in 4d and 5d Oxides from First Principles - or How Spin-Orbit Materials choose their Effective Orbital Degeneracies

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Abstract

The interplay of spin-orbit interactions and Coulomb correlations has become a hot topic in condensed matter theory. Here, we review recent advances in dynamical mean-field theory-based electronic structure calculations for iridates and rhodates. We stress the notion of the effective degeneracy of the compounds, which introduces an additional axis into the conventional picture of a phase diagram based on filling and on the ratio of interactions to bandwidth.

1 Introduction

Electronic Coulomb correlations are at the heart of a variety of exotic properties in compounds with partially filled 3d or 4f shells. Prominent examples are found among the 3d transition metal oxides, where unconventional transport behaviors, ordering phenomena or unusual spectroscopic properties are observed [1]. It was argued early on that the comparably weak spatial extension of 3d orbitals leads to large electronic Coulomb interactions, competing with kinetic contributions. Depending on crystal fields, hybridisation, Hund’s exchange, and band filling, this interplay can lead to renormalised metallic behavior such as in simple oxides like SrVO$_3$ [2, 3] or iron pnictide compounds [4–9] or induce Mott insulating behavior like in YTiO$_3$ [10] or V$_2$O$_3$ [11–14]. According to common belief until recently, such effects would be less dramatic in 4d and even less in 5d compounds, due to the substantially more extended radial wave functions of those shells, as shown in Fig. 1. The discovery of Mott insulating behavior in Sr$_2$IrO$_4$ therefore triggered a little revolution in the field [15, 16]. In 5d oxides, spin-orbit coupling acts

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on an energy scale comparable to the other scales of the system (Coulomb interactions, bandwidths, ligand fields ...), and the electronic state is the result of a complex interplay of Coulomb correlations, spin-orbit splitting and crystal field effects (for recent reviews see [17, 18]). But, as pointed out already earlier [19, 20], also in 4d compounds spin-orbit interactions can influence the electronic properties substantially. In Sr$_2$RhO$_4$, for example, the experimentally observed Fermi surface can only be reconciled with experiments when spin-orbit coupling and electronic Coulomb correlations are taken into account [19–22]. Here, we give a review of recent efforts to describe correlated spin-orbit physics from first principles, in a combined density functional and dynamical mean-field theory framework [21].

2 Spin-orbit materials – an incomplete literature review

The term spin-orbit material refers to systems where spin-orbit coupling (SOC) and its interplay with other elements of the electronic structure – crystal or ligand fields, Coulomb correlations, magnetism, ... – is essential in determining the physical properties. In many such materials, the physics is largely determined by the geometrical aspects of the crystalline structure, and the electronic properties can be understood by analysing the one-particle band structure. In particular, strong enough spin-orbit coupling can cause band inversions, possibly leading to non-trivial topological effects. The quest for topological materials is nowadays a hot topic of condensed matter physics, and several excellent reviews exist in the literature [23–25].

The scope of the present review is however a different one. Here, we focus on materials, where the interplay of spin-orbit interactions and Coulomb correlations is crucial, and the band picture is at best useful as a starting point for further many-body calculations. Early examples are found among the layered tantalum chalcogenides: TaS$_2$ [26–28] is Mott insulating thanks to the presence of a lone narrow band resulting from the combined effect of SOC and a charge-density wave instability. The corresponding selenide, TaSe$_2$ [29] displays a surface Mott metal-insulator
transition. Nevertheless, the true power of the interplay of spin-orbit interactions was fully appreciated only after the discovery of \( \text{Sr}_2\text{IrO}_4 \): the insulating behavior – despite of moderate Coulomb interactions usually present in 5d compounds – was even more intriguing, as the electronic and crystal structures are otherwise seemingly simple. The interplay of Coulomb correlations and spin-orbit coupling was indeed shown to be essential to drive the system insulating, leading to a state dubbed “spin-orbit Mott insulator” \([15, 16]\). A flurry of further spin-orbit materials have by now been characterized, or known compounds have been reinvestigated in the light of new insights. Iridium-based materials, where several families of compounds have been studied systematically, still hold a privileged position. Tab. 1 summarizes the structural, transport and magnetic properties of a selection of iridates. It is interesting to note that the large majority among them display insulating phases. The \( \text{Ir}^{4+} (5d^5) \) state does not allow for a band insulating state without symmetry breaking, and magnetic order is an obvious candidate for helping in opening the gap. Nevertheless, few compounds have been unambiguously characterized as Slater insulators.

Slightly more recently, attention focussed yet onto another class of 5d materials, namely osmium-based compounds. In this class fall for example ferroelectric \( \text{LiOsO}_3 \) \([30]\) as well as the prototypical Slater insulator \( \text{NaOsO}_3 \) \([31–36]\) where the loss of magnetic order with increasing temperature is accompanied by a closure of the insulating gap. It has been realised, however, that SOC can also have notable effects in 4d compounds, with prominent examples among ruthenium- and rhodium-based materials, where most interesting consequences for magnetic excitations have been discussed \([37]\). Tab. 2 gives an overview of the properties of a selection of osmates, ruthanates and rhodates. In the following discussion, we will restrict ourselves to the prototypical correlated iridate \( \text{Sr}_2\text{IrO}_4 \) and its 4d analog, \( \text{Sr}_2\text{RhO}_4 \).

### 2.1 Correlated spin-orbit insulators: the example of \( \text{Sr}_2\text{IrO}_4 \)

The 5d transition metal oxide (TMO) \( \text{Sr}_2\text{IrO}_4 \) has a tetragonal crystal structure, the symmetry of which is lowered from the \( \text{K}_2\text{NiF}_4 \)-type, well-known in \( \text{Sr}_2\text{RuO}_4 \) or \( \text{La}_2\text{CuO}_4 \), by an 11° rotation of its IrO\(_6\) octahedra around the c-axis \([136]\). Each Ir atom accommodates 5 electrons and the standard picture neglecting spin-orbit interactions would give a "t\(_{2g}\)" ground state. However, this compound exhibits insulating behavior up to the highest measured temperatures, with a strongly temperature-dependent gap. The optical gap at room temperature is about 0.26 eV \([137]\). Below \( T_N = 240 \text{K} \), a canted-antiferromagnetic (AF) order sets in, with an effective local moment of 0.5 \( \mu_B \)/Ir, and a saturation moment of 0.14 \( \mu_B \)/Ir \([138]\). This phase has triggered much experimental and theoretical work \([139–142]\), highlighting in particular the importance of the SOC.

Here, we focus on the paramagnetic phase, above 240 K, which is most interesting due to the persistance of the insulating nature despite the absence of magnetic order, as shown by transport measurements \([15]\), by scanning tunneling microscopy and spectroscopy experiments \([143]\), by angle-resolved spectroscopy \([16, 144]\), time-resolved spectroscopy \([145, 146]\) or optical conductivity \([137]\).

Resonant Inelastic X-ray spectroscopy (RIXS) experiments \([15]\) have early on proposed a picture in terms of \( j_{\text{eff}}=1/2 \) and \( j_{\text{eff}}=3/2 \) states:
<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal Structure</th>
<th>Transport Property</th>
<th>Magnetic Ordering</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaIrO₃</td>
<td>post-perovskite</td>
<td>Ins. gap: 0.34 eV</td>
<td>AFM</td>
<td>[38–40]</td>
</tr>
<tr>
<td>NaIrO₃</td>
<td>post-perovskite</td>
<td>Ins. –</td>
<td>None</td>
<td>[41, 42]</td>
</tr>
<tr>
<td>Ba₂IrO₆</td>
<td>monoclinic C2/m</td>
<td>Ins. gap: 0.65 eV</td>
<td>FM</td>
<td>[43–45]</td>
</tr>
<tr>
<td>Sr₂IrO₆</td>
<td>monoclinic C2/m</td>
<td>Metal</td>
<td>None</td>
<td>[46–49]</td>
</tr>
<tr>
<td>α-Na₂IrO₃</td>
<td>honeycomb monoclinic C2/c</td>
<td>Ins. gap: 0.35 eV</td>
<td>zig-zag AFM</td>
<td>[50–55]</td>
</tr>
<tr>
<td>α-Li₂IrO₃</td>
<td>honeycomb monoclinic C2/c</td>
<td>Ins. –</td>
<td>spiral AFM</td>
<td>[56, 57]</td>
</tr>
<tr>
<td>β-Li₂IrO₃</td>
<td>hyperhoneycomb Fdddl</td>
<td>Ins. –</td>
<td>unconventional AFM</td>
<td>[58, 59]</td>
</tr>
<tr>
<td>γ-Li₂IrO₃</td>
<td>striphoneycomb Ccmm</td>
<td>Ins. –</td>
<td>none</td>
<td>[60]</td>
</tr>
<tr>
<td>Ba₂IrO₄</td>
<td>K₂NiF₄-type T₄/mmm</td>
<td>Ins. gap: 0.14 eV</td>
<td>AFM</td>
<td>[61–64]</td>
</tr>
<tr>
<td>Sr₂IrO₃</td>
<td>distorted K₂NiF₄-type T₄/m/m</td>
<td>Ins. gap: 0.25 eV</td>
<td>AFM</td>
<td>[15, 16, 21]</td>
</tr>
<tr>
<td>Cu₂IrO₄</td>
<td>hexagonal P63m</td>
<td>Ins. –</td>
<td>AFM</td>
<td>[65–67]</td>
</tr>
<tr>
<td>Y₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>Ins. –</td>
<td>AIO</td>
<td>[70, 71]</td>
</tr>
<tr>
<td>Pr₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>Metal</td>
<td>None</td>
<td>[72]</td>
</tr>
<tr>
<td>Nd₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>MIT T = 36 K</td>
<td>AIO</td>
<td>[70, 72]</td>
</tr>
<tr>
<td>Sm₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>MIT T = 117 K</td>
<td>AIO</td>
<td>[70, 72]</td>
</tr>
<tr>
<td>Eu₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>MIT T = 120 K</td>
<td>AIO</td>
<td>[70, 73, 75]</td>
</tr>
<tr>
<td>Gd₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>Ins. –</td>
<td>AIO</td>
<td>[70]</td>
</tr>
<tr>
<td>Tb₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>Ins. –</td>
<td>AIO</td>
<td>[70, 76]</td>
</tr>
<tr>
<td>Dy₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>Ins. –</td>
<td>AIO</td>
<td>[70]</td>
</tr>
<tr>
<td>Ho₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>Ins. –</td>
<td>AIO</td>
<td>[70]</td>
</tr>
<tr>
<td>Er₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>Ins. –</td>
<td>AIO</td>
<td>[70]</td>
</tr>
<tr>
<td>Yb₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>Ins. –</td>
<td>AIO</td>
<td>[77]</td>
</tr>
<tr>
<td>Lu₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>Ins. –</td>
<td>AIO</td>
<td>[78]</td>
</tr>
<tr>
<td>Big₂Ir₂O₇</td>
<td>pyrochlore Fd3m</td>
<td>Metal</td>
<td>None</td>
<td>[79, 80]</td>
</tr>
<tr>
<td>Sr₂Ir₂O₇</td>
<td>monoclinic C2/c</td>
<td>Ins. gap: 0.1 eV</td>
<td>AFM</td>
<td>[46, 81–85]</td>
</tr>
<tr>
<td>Na₂Ir₄O₆</td>
<td>hyperkagome P4₁32</td>
<td>Ins. –</td>
<td>AFM</td>
<td>[86–88]</td>
</tr>
<tr>
<td>CaIr₂O₃</td>
<td>hexagonal P-63m</td>
<td>Ins. –</td>
<td>AFM</td>
<td>[88–89]</td>
</tr>
<tr>
<td>La₂ZrIrO₆</td>
<td>double-perovskite P2₁/n</td>
<td>Ins. –</td>
<td>FM</td>
<td>[90]</td>
</tr>
<tr>
<td>La₂MgIrO₆</td>
<td>double-perovskite P2₁/n</td>
<td>Ins. gap: 0.16 eV</td>
<td>AFM</td>
<td>[90, 91]</td>
</tr>
<tr>
<td>Pr₂MgIrO₆</td>
<td>double-perovskite P2₁/n</td>
<td>Ins. gap: 0.2 eV</td>
<td>AFM</td>
<td>[91, 92]</td>
</tr>
<tr>
<td>Nd₂MgIrO₆</td>
<td>double-perovskite P2₁/n</td>
<td>Ins. –</td>
<td>AFM</td>
<td>[92]</td>
</tr>
<tr>
<td>Sm₂MgIrO₆</td>
<td>double-perovskite P2₁/n</td>
<td>Ins. –</td>
<td>AFM</td>
<td>[92]</td>
</tr>
<tr>
<td>Eu₂MgIrO₆</td>
<td>double-perovskite P2₁/n</td>
<td>Ins. –</td>
<td>AFM</td>
<td>[92]</td>
</tr>
<tr>
<td>Gd₂MgIrO₆</td>
<td>double-perovskite P2₁/n</td>
<td>Ins. –</td>
<td>AFM</td>
<td>[92]</td>
</tr>
<tr>
<td>Sr₂CdIrO₆</td>
<td>double-perovskite P2₁/n</td>
<td>Ins. gap: 0.3 eV</td>
<td>AFM</td>
<td>[83–85]</td>
</tr>
<tr>
<td>Ba₂YIrO₆</td>
<td>double perovskite Fm3m</td>
<td>Ins. gap: 0.221 eV</td>
<td>None</td>
<td>[96]</td>
</tr>
<tr>
<td>Ba₃Ir₂Ti₂O₉</td>
<td>hexagonal P₆₃m.mc</td>
<td>Ins. –</td>
<td>None</td>
<td>[97, 98]</td>
</tr>
<tr>
<td>Ba₃Sr₂Ir₂O₉</td>
<td>hexagonal P₆₃/m/mc</td>
<td>Ins. –</td>
<td>None</td>
<td>[99]</td>
</tr>
<tr>
<td>Ba₃YIr₂O₃</td>
<td>hexagonal P₆₃/m/mc</td>
<td>Ins. –</td>
<td>FM</td>
<td>[99]</td>
</tr>
<tr>
<td>Ba₃ZnIr₂O₉</td>
<td>hexagonal P₆₃/m/mc</td>
<td>Ins. –</td>
<td>None</td>
<td>[100]</td>
</tr>
</tbody>
</table>

Table 1: Main structural, transport and magnetic properties of Ir-based spin-orbit materials. In the third column, Ins. refers to insulator and MIT to metal-insulator transition. The notations AFM, FM and AIO refer to a antiferromagnetic, ferromagnetic and all-in-all-out magnetic ordering respectively.

\[
\left| j_{eff} = \frac{1}{2}, m_{j_{eff}} = \pm \frac{1}{2} \right\rangle = \frac{1}{\sqrt{3}} \left( |d_{yz}, \downarrow \rangle + i |d_{xz}, \downarrow \rangle \right) + \frac{1}{\sqrt{3}} |d_{xy}, \uparrow \rangle
\]

\[
\left| j_{eff} = \frac{1}{2}, m_{j_{eff}} = \mp \frac{1}{2} \right\rangle = \frac{1}{\sqrt{3}} \left( |d_{yz}, \uparrow \rangle - i |d_{xz}, \uparrow \rangle \right) - \frac{1}{\sqrt{3}} |d_{xy}, \downarrow \rangle
\]

\[
\left| j_{eff} = \frac{3}{2}, m_{j_{eff}} = \pm \frac{1}{2} \right\rangle = -\frac{1}{\sqrt{6}} \left( |d_{yz}, \downarrow \rangle + i |d_{xz}, \downarrow \rangle \right) + \sqrt{\frac{2}{3}} |d_{xy}, \uparrow \rangle
\]

\[
\left| j_{eff} = \frac{3}{2}, m_{j_{eff}} = \mp \frac{1}{2} \right\rangle = \frac{1}{\sqrt{6}} \left( |d_{yz}, \uparrow \rangle - i |d_{xz}, \uparrow \rangle \right) + \sqrt{\frac{2}{3}} |d_{xy}, \downarrow \rangle
\]

\[
\left| j_{eff} = \frac{3}{2}, m_{j_{eff}} = \mp \frac{1}{2} \right\rangle = -\frac{1}{\sqrt{6}} \left( |d_{yz}, \uparrow \rangle + i |d_{xz}, \uparrow \rangle \right) + \sqrt{\frac{2}{3}} |d_{xy}, \downarrow \rangle
\]

\[
\left| j_{eff} = \frac{3}{2}, m_{j_{eff}} = -\frac{1}{2} \right\rangle = \frac{1}{\sqrt{2}} \left( |d_{yz}, \uparrow \rangle + i |d_{xz}, \uparrow \rangle \right)
\]

\[
\left| j_{eff} = \frac{3}{2}, m_{j_{eff}} = -\frac{1}{2} \right\rangle = -\frac{1}{\sqrt{2}} \left( |d_{yz}, \downarrow \rangle - i |d_{xz}, \downarrow \rangle \right)
\]

Since the quartet of states lies lower in energy than the doublet and the splitting between the \( j_{eff}=3/2 \) and \( j_{eff}=1/2 \) is large, neglecting any band dispersion would result in a configuration...
Table 2: Main structural, transport and magnetic properties of Ru, Rh and Os-based spin-orbit materials. In the third column, Ins. refers to insulator and MIT to metal-insulator transition. The notations AFM, FM and AIAO refer to an antiferromagnetic, ferromagnetic and all-in-all-out magnetic ordering respectively.

with one electron in the $j_{\text{eff}}=1/2$ state. The DFT band structure displays a dispersion of width comparable to this splitting, leaving the question \textit{a priori} open again. However, the bandwidth is narrowed due to structural distortions [21], and electronic correlations can then become effective and eventually drive the compound insulating.

Since the discovery of this mechanism, other Ir-based compounds (cf. Tab. 1) have been classified as spin-orbit Mott insulators (Na$_2$IrO$_3$, pyrochlores, etc...). Recent theoretical studies predict also some fluoride material [147] to be in this class. The one-orbital nature of insulating Sr$_2$IrO$_4$ has contributed to intense activities attempting to dope the compound, with the hope of inducing a superconducting state as in the cuprates. Doping-induced metal-insulator transitions and the properties of the metallic phases have therefore become a hot topic, with studies of various compounds, e.g. Sr$_2$IrO$_4$[144, 148], (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ [149], Ca$_{1-x}$Sr$_x$IrO$_3$ [150], Ca$_{1-x}$Ru$_x$IrO$_3$ [151], Sr$_2$Ir$_{1-x}$Rh$_x$O$_4$ [152, 153], Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$ [154], Sr$_2$La$_{11-x}$Ir$_4$O$_{24}$ [155].

2.2 Correlated spin-orbit metals: the example of Sr$_2$RhO$_4$

It is natural that also in metallic 4d or 5d transition metal compounds, SOC can have notable consequences. An example of a “spin-orbit correlated metal” is the end member SrIrO$_3$ of the Ir-based Ruddlesden-Popper Sr$_{n+1}$Ir$_n$O$_{3n+1}$ series [46] but also many Ru-, Rh- or Os-based transition metal oxides (TMOs) belong to this class (cf. Tab. 1 and 2). In these compounds, correlations are important enough to renormalize the Fermi surface – albeit in a strongly spin-orbit coupling-dependent way. The respective roles of both effects have been worked out in some details for several compounds, among which SrIrO$_3$ [46–48], Sr$_2$RuO$_4$/Ca$_2$RuO$_4$ [108, 109, 156]
We will focus our attention in the following on Sr$_2$RhO$_4$ motivated by its structural proximity and isoelectronic nature to Sr$_2$IrO$_4$. Indeed, this TMO is the 4d counterpart of Sr$_2$IrO$_4$, both concerning structure and filling. Understanding its Fermi surface requires to include both SOC and correlations [21]. It is composed of three pockets (cf. Fig. 8): a circular hole-like $\alpha$-pocket around $\Gamma$, a lens-shaped electron pocket $\beta_M$ and a square-shaped electron pocket $\beta_X$ with a mass enhancement of 3.0, 2.6 and 2.2 respectively [120].

In this review, we will put Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$ in parallel, shedding light on the spectral properties of these compounds and elaborating on the notion of a reduced effective (spin-orbital) degeneracy that is crucial for their properties.

### 2.3 Spin-orbit coupling and cubic symmetry: the $j_{\text{eff}}$ picture

Necessary conditions for realising a $j_{\text{eff}}$ picture are (1) a strong spin-orbit coupling constant and (2) an important cubic crystal field. These conditions are often met in crystalline structures where IrO$_6$ octahedra are present (cf. Tab. 1). Similar compounds based on Ru, Rh and Os also show such $j_{\text{eff}}$ states (cf. Tab 2). However, not all Ir-based structures belong to this case: we note that neither epitaxial thin films of IrO$_2$ [157] nor the correlated metal IrO$_2$ in its rutile structure [158, 159] exhibit such $j_{\text{eff}}=1/2$ state. We will now turn to a more precise description of that picture.

The spin-orbit interaction is one of the relativistic corrections to the Schrödinger-Pauli equation arising when taking the non-relativistic limit of Dirac’s equation. It introduces a coupling between the spin $S$ and the motion – or more precisely the orbital momentum $L$ in the atomic case – of the electron. In a solid described within an independent-particle picture, spin-orbit coupling has the following general form:

$$H_{SO} = \frac{\hbar}{4m_0^2c^2} \sigma \cdot [\nabla V(r) \times \mathbf{p}] \quad (3)$$

where $m_0$ is the electron mass, $V(r)$ is the effective Kohn-Sham potential and $\sigma_{i=x,y,z}$ denote the Pauli-spin matrices. Assuming that the potential close to the nucleus has spherical symmetry the mean value of the spin-orbit interaction on the atomic state $(n, \ell)$ takes the more common form:

$$H_{SO} = \zeta_{SO}(n\ell) \mathbf{1} \cdot \mathbf{s} \quad \text{with} \quad \zeta_{SO}(n\ell) = \frac{\hbar^2}{2m_0^2c^2} \left\langle \frac{1}{r} \frac{dV}{dr} \right\rangle_{(n, \ell)} \quad (4)$$

where $\mathbf{S} = \frac{1}{2}\sigma$, $\mathbf{L} = \mathbf{r} \times \mathbf{p} = \hbar \mathbf{1}$ and $\langle \ldots \rangle_{(n, \ell)}$ denotes the mean value of the radial quantity in the state $(n, \ell)$. Tab. 3 gives some values of the spin-orbit constant $\zeta_{SO}$ for 3$d$, 4$d$ and 5$d$ atoms. The SOC increases with the atomic number, explaining why spin-orbit materials are mostly found in 5$d$ and 4$d$ TMOs.

Due to the effect of SOC, a multiplet splitting arises in the $d$-orbitals. Fig. 2 shows the multiplet splitting of $d$-orbitals due to the spin-orbit coupling as a function of the strength of a cubic crystal field $\Delta = 10Dq$.

In spherical symmetry the fine structure is composed of a six-fold $J = 5/2$ multiplet (in red) and a $J = 3/2$ quartet of lower energy (in blue), following "Landé’s interval rule". The presence
Figure 2: Orbital diagrams for the $d$-shell of an atom as a function of a cubic crystal field $\Delta$ and spin-orbit coupling $\zeta_{SO}$, paramagnetic case. Starting from the $d$-shell in spherical symmetry, the cubic crystal field splits them into $e_g$ and $t_{2g}$, while the SOC creates a 6-fold $J = 5/2$ multiplet and a $J = 3/2$ quartet of lower energy. When both parameters are at stake, one gets a new multiplet structure where $J$ remains a good quantum number but not $J_z$. The initial $J = 5/2$ multiplet splits into a quartet and a doublet of lower energy, while the quartet $J = 3/2$ undergoes some redefinition inside its submanifold. The energetic splitting and the nature of the spin-orbitals depend on the ratio between $\Delta / \zeta_{SO}$. An exception is the doublet which is already of the form of the $j_{eff} = 1/2$. In the limit where $\Delta >> \zeta_{SO}$, as is the case in the compounds of our interest, one gets the celebrated splitting into $e_{g}$, $j_{eff} = 1/2$ and $j_{eff} = 3/2$. 
of a cubic crystal field splits further the six-fold multiplet. Indeed, the spin-orbit interaction in the cubic basis \(e_g\) and \(t_{2g}\) in \(J = 5/2\) states (in red) with an energy

\[
\varepsilon_{\frac{5}{2}^+} = \frac{1}{4} (2\Delta - \zeta_{SO}) + \frac{1}{4} \sqrt{(2\Delta + \zeta_{SO})^2 + 24\zeta_{SO}^2}
\]

- a doublet of \(J = 5/2\) states (in yellow) of energy

\[
\varepsilon_{\frac{5}{2}^-} = +\frac{5}{2} \zeta_{SO}
\]

- a quartet of \(J = 3/2\) states (in light blue) with an energy

\[
\varepsilon_{\frac{3}{2}^-} = \frac{1}{4} (2\Delta - \zeta_{SO}) - \frac{1}{4} \sqrt{(2\Delta + \zeta_{SO})^2 + 24\zeta_{SO}^2}
\]

In the limit of strong crystal field \((\Delta >> \zeta_{SO})\), the \(J = 5/2\) doublet (in yellow) remains invariant while the higher-energy quartet will tend to the usual \(e_g\) states and the lower-energy \(J = 3/2\) quartet will be composed of \(t_{2g}\) states only, with an energy of \(-\zeta_{SO}/2\).

Since the SOC-matrix restricted to the \(t_{2g}\) subspace is exactly the opposite of the SOC-matrix of the \(p\)-states of a free atom, one usually labels these latter states by a \(j_{\text{eff}}\) quantum number in analogy with the \(p_1\) and \(p_2\) multiplets, leading to the expressions given in Eq. (1) and (2). We point out that the \(j_{\text{eff}}=1/2\) doublet arises from the interplay of both cubic symmetry and SOC, whatever the strength of the crystal field. The corresponding eigenstates can indeed be written:

\[
\begin{align*}
\begin{pmatrix} 1/2, +1/2 \end{pmatrix} & = +\frac{1}{\sqrt{3}} \left( |d_{yz}, \downarrow \rangle + i |d_{xz}, \downarrow \rangle \right) + \frac{1}{\sqrt{3}} |d_{xy}, \uparrow \rangle = \frac{i}{\sqrt{6}} \left( \sqrt{5} \begin{pmatrix} 5/2 \ 3/2 \end{pmatrix} - \begin{pmatrix} 5/2 \ -5/2 \end{pmatrix} \right) \\
\begin{pmatrix} 1/2, -1/2 \end{pmatrix} & = +\frac{1}{\sqrt{3}} \left( |d_{yz}, \uparrow \rangle - i |d_{xz}, \uparrow \rangle \right) - \frac{1}{\sqrt{3}} |d_{xy}, \downarrow \rangle = \frac{i}{\sqrt{6}} \left( \sqrt{5} \begin{pmatrix} 5/2 \ 3/2 \end{pmatrix} - \begin{pmatrix} 5/2 \ -5/2 \end{pmatrix} \right)
\end{align*}
\]
(where the right-hand side is written using the $J, m_J$ quantum numbers). This may explain the robustness of this doublet in spin-orbit compounds [163]. However, the splitting between the $j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2$ multiplets follows the inverse Landé interval rule (with the $j_{\text{eff}}=1/2$ above the $j_{\text{eff}}=3/2$ states) only in the strong crystal field limit.

3 Interplay of spin-orbit interaction and Coulomb correlations from first principles

3.1 DFT+DMFT calculations with spin-orbit coupling

Combined density functional theory (DFT) and dynamical mean-field theory (DMFT), as pioneered in [164, 165] (for a review, see [166, 167]), has made correlated electron systems accessible to first principles calculations. Over the years, various classes of systems ranging from transition metals [168–171], their oxides [11, 172–177], sulphides [178, 179], pnictides [4, 9, 180, 181], rare earths [182–184] and their compounds [185–188], including heavy fermions [189, 190], actinides [191, 192] and their compounds [193, 194] to organics [195], correlated semiconductors [196, 197], and correlated surfaces and interfaces [198–200] have been studied with great success. Besides intensive methodological developments (see e.g. [2, 3, 201–205]), recent research activities continue to extend to new materials classes. In this context, also 4d and 5d oxides have come into focus [21, 22, 62]. In this section, we review the technical aspects related to combined DFT+DMFT calculations in the presence of spin-orbit interactions. Since the applications we later focus on are 4d and 5d oxides in their paramagnetic phases, we restrict the discussion to this case.

In DMFT, a local approximation is made to the many-body self-energy which can then be calculated from an effective atom problem, subject to a self-consistency condition (see Fig. 3). The notion of locality is understood in the sense of many-body theory as a site-diagonal form, with respect to atomic sites after representing the Hamiltonian in an atom-centered Wannier-type basis $|w_{\alpha \ell m \sigma}^\nu \rangle$, where the index $\alpha$ labels the atom in the unit-cell, $(\ell, m)$ the angular momentum quantum numbers of the atomic orbital and $\sigma$ the spin degree of freedom. Different choices are possible for the construction of the atom-centered orbitals, and the work reviewed here is based on the construction of projected atomic orbitals subject to a subsequent orthonormalisation procedure [180].

The DMFT self-consistency cycle links the local effective atom problem to the electronic structure of the solid, via the transformation matrix from the Kohn-Sham states $|\psi_{k\nu}^\sigma \rangle$, labelled by their momentum $\mathbf{k}$ their band index $\nu$ and their spin $\sigma$, to the resulting Wannier-like local orbitals $|w_{\alpha \ell m \sigma}^\nu \rangle$. These key quantities are called projectors and denoted $P_{\alpha \ell m \sigma, \nu}^{\nu \sigma}(\mathbf{k})$.

The main advantage of projector-based implementations of DFT+DMFT (see e.g. [180, 207, 208]) is that not only the DFT-based part of the calculations but also the determination of the local Green’s function, used within the DMFT self-consistency condition, can be performed in any convenient basis set, and notably in the one used in the respective DFT code. Since the transformation of the DFT Hamiltonian matrix in that basis into the Kohn-Sham eigenset $|\psi_{k\nu}^\sigma \rangle$ is known, it is sufficient to further determine the projections of the Kohn-Sham eigenstates onto
Figure 3: Projector-based implementation of DFT+DMFT for calculations including spin-orbit coupling in the Kohn-Sham equations. Once the Kohn-Sham eigenstates $|\psi_{k\nu}\rangle$ are known, their projections $P_{j,\nu}^{\alpha,m_j}(k)$ to the correlated Wannier-like orbitals $|w_{j}^{\alpha,m_j}\rangle$ are calculated. One can then build an effective local many-body atomic problem, subject to a self-consistency condition, which is solved using an impurity solver: this defines the DMFT loop (see Section 3.1). The interaction parameters can also be evaluated consistently using the projectors $P_{j,\nu}^{\alpha,m_j}(k)$ (see [206] and Section 3.3). After convergence of the DMFT cycle, the chemical potential is updated and the spectral function can be evaluated using partial projectors $\Theta_{j,\nu,i}^{\alpha,m_j}(k)$ (see Appendix A).
the local orbitals $|w_{\ell m}^{\alpha,\sigma}\rangle$ used in the DMFT impurity problem. This is precisely the role of the projectors.

In [21], this construction was generalised to the case when spin is not a good quantum number any more, and implemented within the framework of the DFT+DMFT implementation of Ref. [180]. Nowadays, it is available within the TRIQS/DFTTools package [209] that links the Wien2k code [210] to DMFT. We give here the main lines of this generalisation of the projector-based DFT+DMFT formalism.

When taking into account SOC, the Kohn-Sham eigenstates $|\psi_{k\nu}\rangle$ are built out of both spin-up and spin-down states – in a similar fashion as the previously introduced $j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2$ atomic states. Nevertheless, we can still write them in the following Bloch form:

$$
\psi_{k\nu}(r) = \left[ u_{k\nu}^\uparrow(r) + u_{k\nu}^\downarrow(r) \right] e^{i k r} = \phi_{k\nu}^\uparrow(r) + \phi_{k\nu}^\downarrow(r),
$$

where the index $\nu$ now runs over both spin and band indices. The state $|\phi_{k\nu}^\sigma\rangle$ denotes the projection of the Kohn-Sham state onto its spin-$\sigma$ contribution and is not an eigenstate of the Hamiltonian.

Using this decomposition, we can define the new projectors:

$$
P_{\ell m,\nu}^{\alpha,\sigma}(k) = \langle w_{\ell m}^{\alpha,\sigma}|\psi_{k\nu}\rangle = \langle w_{\ell m}^{\alpha,\sigma}|\phi_{k\nu}^\sigma\rangle
$$

We define them in the standard complex basis, but allow for a basis transformation to quantum numbers $j, m_j$ (like $j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2$) afterwards by means of a unitary matrix transformation in the correlated $\ell$-space:

$$
P_{j,\nu}^{m_j,\ell m}(k) = \sum_{m,\sigma} S_{j,\ell m}^{m_j,\sigma} \langle w_{\ell m}^{\alpha,\sigma}|\psi_{k\nu}\rangle = \sum_{m,\sigma} S_{j,\ell m}^{m_j,\sigma} P_{\ell m,\nu}^{\alpha,\sigma}(k)
$$

The main difference with the usual implementation where spin is a good quantum number is that there are now two projectors associated to each band index $\nu$: $P_{\ell m,\nu}^{\alpha,\sigma}(k)$ with $\sigma = \uparrow, \downarrow$.

Using the decomposition (6) in the formulation of the self-consistency condition relating the lattice Green’s function of the solid to the impurity model, the (inverse) Green’s function of the solid is given by:

$$
[G^{-1}(k, i\omega_n)]_{\nu\nu'} = (i\omega_n + \mu - \varepsilon_k^\nu)\delta_{\nu\nu'} - \Sigma_{\nu\nu'}(k, i\omega_n),
$$

where $\varepsilon_k^\nu$ are the ($\nu$-dependent only) Kohn-Sham eigenvalues and $\Sigma_{\nu\nu'}(k, i\omega_n)$ is the approximation to the self-energy obtained by the solution of the DMFT impurity problem. It is obtained by ”mapping” the impurity self-energy to the local self-energy of the lattice and ”upfolding” it as:

$$
\Sigma_{\nu\nu'}(k, i\omega_n) = \sum_{\alpha,j,j'} \sum_{m_j,m_{j'}} \left[ P_{j',\nu'}^{\alpha,m_{j'}}(k) \right] ^* \left[ \Delta \Sigma_{\text{loc}}^{\alpha}(i\omega_n) \right]_{jj'}^{m_j m_{j'}} P_{j,\nu}^{\alpha,m_j}(k).
$$

with

$$
\left[ \Delta \Sigma_{\text{loc}}^{\alpha}(i\omega_n) \right]_{jj'}^{m_j m_{j'}} = \left[ \Sigma_{\text{imp}}(i\omega_n) \right]_{jj'}^{m_j m_{j'}} - \left[ \Sigma_{\text{dc}} \right]_{jj'}^{m_j m_{j'}}
$$
Here, $\Sigma_{\text{imp}}(i\omega_n)$ is the impurity self-energy, expressed in the local orbitals, and $\Sigma_{\text{dc}}$ is the double-counting correction. Consequently, the equations of the DMFT loop (see Figure 3) are formally the same as in the case without SOC but the computations now involve matrices which are double in size.

The local Green’s function is obtained by projecting the lattice Green’s function to the set of correlated orbitals and summing over the full Brillouin zone,

$$[G_{\text{loc}}^{\alpha}(i\omega_n)]_{jj'}^{m_jm_{j'}} = \sum_{k\nu\nu'} P_{j,\nu}^{\alpha,m_j}(k) G_{\nu\nu'}(k,i\omega_n) [P_{j',\nu'}^{\alpha,m_{j'}}(k)]^*.$$  \hspace{1cm} (12)

In practice, the summation over momenta is done in the irreducible Brillouin zone only, supplemented by a standard symmetrization procedure, using Shubnikov magnetic point groups [211, 212].

The DMFT equations are solved iteratively: starting from an initial local Green’s function $G_{\text{loc}}^{\alpha}(i\omega_n)$ (obtained from the “pure” Kohn-Sham lattice Green’s function using Eq. (12)), the Green’s function $G_{\nu}(i\omega_n)$ of the effective environment in the impurity model is constructed. The impurity model is solved, allowing to evaluate the local self-energy of the solid (cf. Eq. 10) and a new lattice Green’s function $G(k,i\omega_n)$. The latter can then be projected again onto the correlated subset and the cycle is repeated until convergence is reached.

### 3.2 Computation of the Wannier projectors within the augmented plane wave framework

The present implementation is within a full-potential linearized augmented plane wave (FLAPW) framework, as realised in the Wien2k package [210]. With respect to the existing DFT+DMFT implementation [180] in this context, the main changes concern the projection technique for building the correlated orbitals: as discussed above, one has to take care of the fact that spin is no longer a good quantum number, leading to the more general construction of localized “spin-orbitals”. The necessary modifications in the construction of the projectors are reviewed in the following.

As in the case without SOC, we still use the Kohn-Sham states within a chosen energy window $W$ to form the Wannier-like functions that are treated as correlated orbitals, and the construction of the Wannier projectors is done in two steps. First, auxiliary Wannier projectors $\tilde{P}_{\ell m,\nu}^{\alpha,\sigma}$ are calculated – separately for each $|\phi_{\nu k}\rangle$ term – from the following expression:

$$\tilde{P}_{\ell m,\nu}^{\alpha,\sigma}(k) = \langle u_{\ell m}^{\alpha,\sigma}(E_1\ell) Y_m^{\nu}\psi_{k\nu}\rangle$$

$$= A_{\ell m}^{\nu}(k,\sigma) + \sum_{n,LO=1}^{N_{LO}} \epsilon_{n,LO}^{\nu,\sigma} C_{\ell m,\nu,\ell m'}^{\alpha,\sigma} O_{\ell m,\ell m'}^{\alpha,\sigma}.$$  \hspace{1cm} (13)

A description of the augmented plane wave (APW) basis can be found in Ref. [180]. We use the same notations e.g. for the coefficients $A_{\ell m}^{\nu}(k,\sigma)$ and the overlap matrix $O_{\ell m,\ell m'}^{\alpha,\sigma}$ as introduced there.

One performs an orthonormalisation step in order to get the Wannier projectors $P_{\ell m,\nu}^{\alpha,\sigma}(k)$. The
overlap matrix \( [O(k)]_{\alpha,\alpha'}^{\sigma,\sigma'}^{(m\sigma),(m'\sigma')} \) between the correlated \( \ell \) orbitals is defined by:

\[
[O(k)]_{\alpha,\alpha'}^{\sigma,\sigma'}^{(m\sigma),(m'\sigma')} = \sum_{\nu=\nu_{\min}(k)}^{\nu_{\max}(k)} \tilde{P}^{\alpha,\sigma}_{\ell m,\nu}(k) \tilde{P}^{\alpha',\sigma'}_{\ell m',\nu}(k),
\]

leading to the final projectors:

\[
P^{\alpha,\sigma}_{\ell m,\nu}(k) = \sum_{\alpha',m',\sigma'} \left\{ [O(k)]^{-1/2} \right\}_{\alpha,\alpha'}^{\sigma,\sigma'}^{(m\sigma),(m'\sigma')} \tilde{P}^{\alpha',\sigma'}_{\ell m',\nu}(k),
\]

which are then further transformed into a \( j, m_j \) basis as described above (cf. Eq. (8)).

### 3.3 Effective local Coulomb interactions from first principles

Hubbard interactions \( U \) – obtained as the static (\( \omega = 0 \)) limit of the onsite matrix element \( \langle |W_{\text{partial}}| \rangle \) within the “constrained random phase approximation” (cRPA) – have by now been obtained for a variety of systems, ranging from transition metals [213] to oxides [206, 214–217], pnictides [181, 218–220], f-electron elements [221] and compounds [188], to surface systems [222], and several implementations within different electronic structure codes and basis sets have been done, e.g. within linearized muffin tin orbitals [213, 223], maximally localized Wannier functions [214, 219, 224] (as elaborated in [225]), or localised orbitals constructed from projected atomic orbitals [206]. The implementation into the framework of the Wien2k package [206] made it possible that Hubbard \( U \)’s be calculated for the same orbitals as the ones used in subsequent DFT+DMFT calculations, and, to our knowledge, Ref. [21] was indeed the first work using in this way consistently calculated Hubbard interactions in a DFT+DMFT calculation. Systematic calculations investigating the basis set dependence for a series of correlated transition metal oxides revealed furthermore interesting trends, depending on the choice of the low-energy subspace. In contrast to common belief until then, Hubbard interactions increase for example with the principal quantum number when low-energy effective models encompassing only the \( t_{2g} \) orbitals are employed. These trends can be rationalised by two counteracting mechanisms, the increasing extension of the orbitals with increasing principal quantum number and the less efficient screening by oxygen states [206]. We will come back to this point below, in the context of the cRPA calculations for our target compounds.

In the following, we review the specificities involved when determining the Hubbard interactions for our target spin-orbit compounds. We hereby use the same notations as in [206].

We start from the standard Hubbard-Kanamori Hamiltonian \( H_{\text{int}} \) which allows us to describe the interactions between \( t_{2g} \) orbitals within a Hamiltonian restricted to the \( t_{2g} \)-space:

\[
H_{\text{int}} = U \sum_{m} n_{m\uparrow} n_{m\downarrow} + U' \sum_{m<n,\sigma} n_{m\sigma} n_{n\bar{\sigma}} + (U' - J) \sum_{m<n,\sigma} n_{m\sigma} n_{n\bar{\sigma}} - J \sum_{m<n,\sigma} \left[ c_{m\sigma}^\dagger c_{m\bar{\sigma}}^\dagger c_{n\bar{\sigma}} c_{n\sigma} + c_{m\sigma} c_{m\bar{\sigma}}^\dagger c_{n\sigma} c_{n\bar{\sigma}} \right]
\]
where $U$ is the intra-orbital Coulomb repulsion term and $U'$ ($= U - 2J$ with cubic symmetry) the interorbital Coulomb interaction which is reduced by Hund’s exchange $J$. ($m$ and $n$ run over the three $t_{2g}$ orbitals and $\sigma$ stands for the spin).

To draw the link between the cRPA calculations and this model Hamiltonian, the terms $U$, $U'$ and $J$ are understood as the Slater-symmetrized effective interactions in the $t_{2g}$ subspace, related to the Slater integrals $F^0$, $F^2$ and $F^4$ as:

$$ U = F^0 + \frac{4}{49}(F^2 + F^4) \quad \text{and} \quad J = \frac{3}{49}F^2 + \frac{20}{441}F^4 $$

(17)

The last relation $U' = F^0 - \frac{2}{49}F^2 - \frac{4}{441}F^4$ is redundant since $U' = U - 2J$.

One now transforms $H_{\text{int}}$ into the $j_{\text{eff}}$ basis using the unitary matrix transformation $S_{j,j',m}^{m,j',\sigma}$. Keeping only density-density terms, $H_{\text{int}}$ becomes:

$$ H_{\text{int}} = \frac{1}{2} \sum_{j,j',m,j',m',j} U_{jj'}^{m,j,m'} n_{j,m} n_{j',m'} $$

(18)

Here, the index $j$ is a shortcut notation for the $j_{\text{eff}} = \{3/2, 1/2 \}$ quantum number and $m_j = \{\pm 3/2, \pm 1/2 \}$. The reduced interaction matrix $U_{jj'}^{m,j,m'}$ has the following form:

$$ U_{jj'}^{m,j,m'} = U_{jj'}^{m,j,m'} = \begin{pmatrix} 0 & U - 2J & U - \frac{4}{3}J \\ U - 2J & 0 & U - \frac{7}{3}J \\ U - \frac{4}{3}J & U - \frac{7}{3}J & 0 \end{pmatrix} $$

(19)

$$ U_{jj'}^{m,j,m'} = U_{jj'}^{m,j,m'} = \begin{pmatrix} U - \frac{4}{3}J & U - \frac{5}{3}J & U - \frac{8}{3}J \\ U - \frac{5}{3}J & U - \frac{7}{3}J & U - \frac{8}{3}J \\ U - \frac{8}{3}J & U - \frac{7}{3}J & U - \frac{5}{3}J \end{pmatrix} $$

(20)

We use the standard convention that $m_j$ denotes $-m_j$, as usually done for spin degree of freedom. The ordering of the orbitals $|j,|m_j| \rangle$ is: $|1/2, 1/2\rangle, |3/2, 1/2\rangle, |3/2, 3/2\rangle, j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2$ blocks are emphasized to ease the reading of the matrices.

3.4 Technicalities of the DMFT calculation

For the solution of the quantum impurity problem we apply the continuous-time quantum Monte Carlo method (CTQMC) in the strong-coupling formulation [226]. We are able to perform calculations at room temperature ($\beta = 1/k_B T = 40$ eV$^{-1}$) with reasonable numerical effort. In our calculations, we use typically around $16 \times 10^6$ Monte Carlo sweeps and 28 $k$-points in the irreducible Brillouin zone.

Since the CTQMC solver computes the Green’s function on the imaginary-time axis, an analytic continuation is needed in order to obtain results on the real-frequency axis. A continuation of the impurity self-energy using a stochastic version of the maximum entropy method [227] yields real and imaginary parts of the retarded self-energy. From those, we calculate the momentum-resolved spectral function $A(k, \omega)$ using partial projectors introduced in Appendix A.

During the calculations we use the Fully Localized Limit (FLL) expression for the double-counting:

$$ \Sigma_{j,j'}^{\text{dc}} = \left[ U(N_e - \frac{1}{2}) - J(\frac{1}{2}N_e - \frac{1}{2}) \right] \delta_{jj'} $$

(21)
Figure 4: Kohn-Sham band structures of Sr$_2$RuO$_4$ (a) Sr$_2$RhO$_4$ (b) and Sr$_2$IrO$_4$ (c) within LDA (and without spin-orbit coupling), artificially assuming that both Sr$_2$RhO$_4$ and Sr$_2$IrO$_4$ crystallize in the same K$_2$NiF$_4$ structure as their Ru-counterpart. For Sr$_2$RuO$_4$, we use the lattice parameters at 300 K given in [230]. The t$_{2g}$-dominated bands are plotted in green ($d_{xy}$) and blue ($d_{xz}$ and $d_{yz}$) while the e$_g$ bands are in red ($d_{x^2-y^2}$) and yellow ($d_{3z^2-r^2}$), the O-2p states in black.

where $j$ and $j'$ run over the $j_{\text{eff}}$ states and $N_e$ is the total occupancy of the orbitals. (Since each orbital is doubly degenerate in $m_j$, $N_e/2$ is used in the term containing $J$). Moreover, we neglect the off-diagonal terms in the local Green’s functions (particularly, we neglect the term between the $j_{\text{eff}}=1/2$ and the $j_{\text{eff}}=3/2$ $|m_j|=1/2$ which we checked to be two orders of magnitude smaller than the diagonal terms, in the chosen basis).

4 Electronic structure of Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$

4.1 Electronic structure of Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$ within DFT-LDA

The Kohn-Sham band structures of Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$ within the local density approximation and in the presence of spin-orbit coupling (LDA+SO) are represented in Fig. 5-(d) and (e). For Sr$_2$IrO$_4$, we use the lattice parameters measured at 295 K in [228], and for Sr$_2$RhO$_4$ those measured at 300 K in [229].

The LDA+SO band structures for Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$ are very similar, as a consequence of both, the structural similarity and the key role of spin-orbit coupling in these compounds. The e$_g$-states ($d_{x^2-y^2}$ in red and $d_{3z^2-r^2}$ in yellow) start at about 1 to 1.5 eV, and are fully separated from the t$_{2g}$-manifold which lies around the Fermi level and overlaps at lower energies with the oxygen 2p-states (black). Given the $t^5_{2g}$ filling and the four-atom unit cell of both compounds, a metallic solution is obtained within LDA for both Sr$_2$RhO$_4$ and Sr$_2$IrO$_4$ – at variance with experiments for Sr$_2$IrO$_4$. Among the $t_{2g}$-manifold (in green), only the four highest-lying bands, highlighted in blue, cross the Fermi level: this is suggestive of the existence of a separated half-filled $j_{\text{eff}}=1/2$ -derived band, which – within a four-atom unit cell – corresponds to a quartet of bands at each k-point. We stress however that the true picture is much more subtle: in
Figure 5: Kohn-Sham band structures within LDA+SO of Sr$_2$RhO$_4$ and Sr$_2$IrO$_4$ assuming that they crystallize without distortions in a K$_2$NiF$_4$ structure (a-b), of Sr$_2$IrO$_4$ in a supercell containing 4 “undistorted” unit-cells (c) and of “real” Sr$_2$RhO$_4$ and Sr$_2$IrO$_4$ (d-e). The reduction of the first Brillouin zone, when the crystal symmetry is lowered, is also shown. The $e_g$ states are in yellow ($d_{3z^2-r^2}$) and red ($d_{x^2-y^2}$). In the $t_{2g}$ manifold, in purple the $j_{\text{eff}}=1/2$ in light blue the $j_{\text{eff}}=3/2$ $m_j = 3/2$ and in green the $j_{\text{eff}}=3/2$ $m_j = 1/2$. In black, the O-2$p$ states.
Comparing Fig 5-(c) and (e) highlights the key role of the structural distortion in Sr$_2$ of each structure. Zones in the unit cells. Each band is now folded four times and we provide a scheme of the two first Brillouin undistorted Fig 5-(c) the LDA+SO band structure of the to a K$_2$NiF$_4$-type crystal structure, like in Sr$_2$RuO$_4$, the well-known LDA band structure of which is plotted in Fig. 4-(a).

The similarity of the three band structures is obvious. Around the Fermi level, one distinguishes the three t$_{2g}$ bands. The $d_{xy}$-band (green) reaches out to lower energies and overlaps with the oxygen 2$p$-states (black). The e$_g$-states ($d_{x^2−y^2}$ in red and $d_{3z^2−r^2}$ yellow), higher in energy, cut the Fermi level in both Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$ due the additional electron remaining in the d-manifold, contrary to Sr$_2$RuO$_4$, which has actually a mere t$_{2g}^4$-filling. The larger extension of the 5$d$ orbitals (cf. Fig 1) explains the wider bandwidth observed for Sr$_2$IrO$_4$ in comparison to Sr$_2$RhO$_4$: the $d_{xy}$ band reaches the value of $-3.5$ eV in $\Gamma$, while it remains above $-3$ eV for the 4$d$ counterparts. Another consequence of this wider extension is the stronger hybridization between the 5$d$ states with the oxygen p-states, which are located 1 eV lower in energy in Sr$_2$IrO$_4$ than in the 4$d$-TMOs.

Re-introducing the effects of the spin-orbit coupling in Sr$_2$RhO$_4$ and Sr$_2$IrO$_4$ (but without considering the structural distortions) modifies these Kohn-Sham band structures to those shown in Fig 5-(a) and (b). The t$_{2g}$ bands are the most affected, while the e$_g$ bands are slightly shifted as a consequence of the topological change in the t$_{2g}$ manifold. A detailed study of the character of these band structures confirms the decoupling between $e_g$ and t$_{2g}$ states (see also Refs. [19, 20]).

The cubic crystal field at stake in these compounds is indeed much larger than the energy scale associated to the spin-orbit coupling of about $\zeta_{SO} \approx 0.4$ eV and $\zeta_{SO} \approx 0.2$ eV for Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$ respectively.

The $j_{eff}$ picture is thus justified in both, Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$: the t$_{2g}$ orbitals split into a quartet of $j_{eff}=3/2$ states and a higher lying doublet $j_{eff}=1/2$. Each state is doubly degenerate in $\pm m_j$ – since we observe the system in its paramagnetic phase at room temperature and the crystal structure has a center of inversion. Therefore we still refer to them as the ”$j_{eff}=1/2$ band” and the two ”$j_{eff}=3/2$ bands” in the following. The three $j_{eff}$ bands can easily be identified: the $j_{eff}=1/2$ one (light green) lies above the two $j_{eff}=3/2$ ones ($m_j = 3/2$ in light blue and $m_j = 1/2$ in violet). The three $j_{eff}$ bands are well-separated all along the k-path, and more generally in the whole Brillouin zone. Since the spin-orbit coupling is twice smaller in Sr$_2$RhO$_4$, the splitting between the $j_{eff}$ bands is reduced by a factor of 2, as one can see for instance at $X$ or $\Gamma$.

To draw the link between the ”undistorted” band structures and the realistic ones, we plot in Fig 5-(c) the LDA+SO band structure of the undistorted Sr$_2$IrO$_4$ in a supercell containing four unit cells. Each band is now folded four times and we provide a scheme of the two first Brillouin Zones in the $k_z = 0$ plane to understand the correspondence between the high-symmetry points of each structure.

Comparing Fig 5-(c) and (e) highlights the key role of the structural distortion in Sr$_2$IrO$_4$: an
hybridisation between two neighboring Ir $d_{xy}$ and $d_{x^2-y^2}$ orbitals via the in-plane oxygens is now allowed and pushes the $t_{2g}$ and $e_g$ bands apart. Another consequence of the distortions is the general narrowing of the $j_{\text{eff}}$ bandwidth, which is of crucial importance to drive the compound insulating, as we will see below.

Finally, comparing Fig 5-(c) and (e) gives more insights into the nature of the four highest-lying bands (blue) of Fig 5-(c). While along the $M-X$ direction, each quartet of $j_{\text{eff}}$ bands remain well-separated, $j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2$ overlap in the other direction $\Gamma-M$ and $M-X$. As a result, the $j_{\text{eff}}=3/2$ bands cross the Fermi-level closest to the $\Gamma$-point, while the other crossings are due to the $j_{\text{eff}}=1/2$ bands. The identification of the upper four bands in Sr$_2$IrO$_4$ as ”pure” $j_{\text{eff}}=1/2$ states is thus too simplistic, implying the need for a Hamiltonian containing more than one orbital in a realistic calculation.

The same mechanisms are at stake in Sr$_2$RhO$_4$ even though we do not display the orbital characters here: the four highest-lying bands, highlighted in blue in Fig. 5-(d) exhibit a mixed character of type $j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2$. Moreover, thanks to the distortions which allow the opening of a gap between $t_{2g}$ and $e_g$ bands, the LDA+SO Fermi surface becomes qualitatively similar to the experimental one: as shown in Fig. 8-(a), they both contain three closed contours: a circular hole-like $\alpha$-pocket around $\Gamma$, a lens-shaped electron pocket $\beta_M$ and a square-shaped electron pockets $\beta_X$. However the striking discrepancies in the size of the pockets point out a subtle deficiency of the LDA for Sr$_2$RhO$_4$[19, 20].

4.2 Wannier functions

We have derived the Wannier functions associated to the $j_{\text{eff}}$ manifold for both Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$, using the framework introduced in section 3.1. Because of the mixed character of the four bands that cross the Fermi level in Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$, the local effective atomic problem used in the DMFT cycle must contain the three $j_{\text{eff}}$ orbitals and thus accomodate five electrons. We construct Wannier functions for the $j_{\text{eff}}$ orbitals from the LDA+SO band structure of Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$, using an energy window $[-3.0, 0.5]$ eV for Sr$_2$IrO$_4$ and an energy window $[-2.67; 0.37]$ eV for Sr$_2$RhO$_4$.

Fig. 6 and 7 depict the projection of these Wannier functions on the LDA+SO band structure. The similarities between Fig 6 and Fig 5-(c) are numerous, thus confirming our previous band character analysis. Tab. 5 gives the decomposition of these local Wannier functions on the $t_{2g}$ manifold and their respective occupation.

To obtain deeper insights into the nature of these Wannier orbitals, Tab. 4 gives the coefficients of the local Wannier orbitals obtained from the LDA+SO band structure of ”undistorted” Sr$_2$IrO$_4$ using an energy window $[-3.5, 0.8]$ eV. The results agree well with the standard $j_{\text{eff}}$ picture (cf. Eq. (1) and (2)) in both modulus and phase. Discrepancies are mostly due to the elongation of the IrO$_6$ along the $c$-axis, which introduces an additional tetragonal field between the $t_{2g}$ states. This effect also explains the lifting of the degeneracy of the two $j_{\text{eff}}=3/2$ ($m_j = \pm 1/2$ and $m_j = \pm 3/2$) states and implies the reason why the $j_{\text{eff}}=1/2$ is slightly more than half-filled. Because of the hybridization between the $d_{xy}$ and $d_{x^2-y^2}$ orbitals in the distorted structures, we had to define in practice “effective $j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2$ $|m_j| = 1/2$ states”, which remain
Table 4: Coefficients and occupation of the $j_{\text{eff}}$ Wannier orbitals in "undistorted" Sr$_2$IrO$_4$. The discrepancy between these coefficients and those given in Eq. (1) and (2) are due to the small elongation of the octahedra along the c-axis.

| occupation (LDA+SO) | $|\frac{1}{2}, \pm \frac{1}{2}\rangle$ | $|\frac{3}{2}, \pm \frac{1}{2}\rangle$ | $|\frac{3}{2}, \pm \frac{3}{2}\rangle$ |
|---------------------|----------------------------------|----------------------------------|----------------------------------|
| ±0.6605             | +0.7508                          | 0                                |
| ±0.5309 i           | −0.4670 i −0.7071 i              |                                  |
| +0.5309 i           | ±0.4670 ±0.7071 i                |                                  |

Figure 6: LDA+SO band structure of Sr$_2$IrO$_4$, projected on the $j_{\text{eff}}=1/2$ (left panel), $j_{\text{eff}}=3/2 \ |m_j|=3/2$ (middle), and $j_{\text{eff}}=3/2 \ |m_j|=1/2$ (right panel) spin-orbitals.

Figure 7: LDA+SO band structure of Sr$_2$RhO$_4$, projected on the $j_{\text{eff}}=1/2$ (left panel), $j_{\text{eff}}=3/2 \ |m_j|=3/2$ (middle), and $j_{\text{eff}}=3/2 \ |m_j|=1/2$ (right panel) spin-orbitals.
close to the atomic $j_{\text{eff}}$ picture but take into account a small amount of $d_{x^2-y^2}$ character (cf. Tab. 5). The coefficients have been calculated such that the density matrix of the local atomic problem is closest possible to diagonal form.\(^1\) In addition to the hybridization, the construction of the ”effective $j_{\text{eff}}$” takes also into account the tetragonal crystal field due to the elongation of the octahedra in each crystal structure: this explains the discrepancies with the standard coefficients given in Eq. (1) and (2). We note that the coefficients obtained for the $j_{\text{eff}}=1/2$ state of Sr$_2$IrO$_4$ are equivalent to those obtained in the AF phase in Ref. [139].

Finally, comparing the occupation of the orbitals in Tab. 4 and 5 highlights again the role of the hybridisation between the $d_{xy}$ and $d_{x^2-y^2}$ orbitals which pushes the band $j_{\text{eff}}=3/2 \ |m_j|=1/2$ further below the Fermi level close to $\Gamma$: as a result, the four bands that cross the Fermi level are formed only by the $j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2 \ |m_j|=3/2$ orbitals and the $j_{\text{eff}}=1/2$ tend to be close to half-filling. Similar conclusions were drawn for the AF phase within a Variational Cluster Approximation (VCA) approach in Ref. [140]. Similar conclusions hold for Sr$_2$RhO$_4$.

### 4.3 Effective Hubbard Interactions from cRPA

After defining the $j_{\text{eff}}$ Wannier orbitals, we evaluate the local Coulomb interaction in the effective atomic problem within cRPA [206, 213], as explained in section 3.3. For reasons of computational resources, the cRPA calculations were performed in the case without distortions (without the rotations of the octahedra, hence considering only one formula-unit in a unit-cell) and without SOC. To mimic the effect of the distortions, the $e_g$ states are shifted up to their energetic position in the presence of distortions. We find $U = 2.54$ eV and $J = 0.23$ eV for Sr$_2$IrO$_4$ and $U = 1.94$ eV and $J = 0.23$ eV for Sr$_2$RhO$_4$. These parameters lead to the following local

\(^1\)With the obtained coefficients, the off-diagonal terms remaining in the local Greens functions between the $j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2 \ |m_j|=1/2$ are smaller than 0.05. In practice, the coefficients were chosen real. This can be done in the local problem since only density-density terms were kept for the interaction terms and off-diagonal terms of the density matrix were neglected.
interaction matrices for Sr$_2$IrO$_4$:

$$U_{jj'}^{mjm'j'} = \begin{pmatrix} 0 & 2.08 & 2.21 \\ 2.08 & 0 & 1.93 \\ 2.21 & 1.93 & 0 \end{pmatrix} \quad U_{jj'}^{mjm'j'} = \begin{pmatrix} 2.25 & 1.98 & 1.90 \\ 1.98 & 2.38 & 2.03 \\ 1.90 & 2.03 & 2.31 \end{pmatrix}$$

(22)

and for Sr$_2$RhO$_4$:

$$U_{jj'}^{mjm'j'} = \begin{pmatrix} 0 & 1.48 & 1.66 \\ 1.48 & 0 & 1.29 \\ 1.66 & 1.29 & 0 \end{pmatrix} \quad U_{jj'}^{mjm'j'} = \begin{pmatrix} 1.67 & 1.32 & 1.27 \\ 1.32 & 1.86 & 1.46 \\ 1.27 & 1.46 & 1.71 \end{pmatrix}$$

(23)

where the values are in eV and the ordering of the $|j,|m_j\rangle$ orbitals is: $|1/2,1/2\rangle, |3/2,1/2\rangle, |3/2,3/2\rangle$ and $m_j$ denotes $-m_j$. We remind the reader that $U_{jj'}^{mjm'j'} = U_{jj'}^{mjm'j'}$ and $U_{jj'}^{mjm'j'} = U_{jj'}^{mjm'j'}$. Since we have used "effective $j_{\text{eff}}$" Wannier orbitals instead of the standard definition given in Eq. (1) and (2), some discrepancies with the formulae given in Eq. (19) and in [22] can be observed. Contrary to common belief, the Hubbard interactions are smaller in the 4$d$-counterpart. This might seem counterintuitive at first sight, since the 5$d$-orbitals are more extended than the 4$d$ ones, but finds its explanation in more efficient screening in the 4$d$ material: As shown in Fig. 5-(d) and (e), the hybridization between the Rh-4$d$ states and the O-2$p$ is weaker in Sr$_2$RhO$_4$ than in Sr$_2$IrO$_4$. Correspondingly, the energetic position of the O-2$p$ bands is closer to the Fermi level by about 1 eV, and as a result, the Coulomb interactions are screened more efficiently in Sr$_2$RhO$_4$ than in Sr$_2$IrO$_4$, explaining the observed trend.

### 4.4 Correlated electronic structure of Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$

DFT+DMFT calculations following the procedure described in section 3.1 indeed find an insulating solution for Sr$_2$IrO$_4$ and a correlated metal for Sr$_2$RhO$_4$[21], in agreement with experiment. The difference in these metallic versus insulating nature of Sr$_2$RhO$_4$ and Sr$_2$IrO$_4$ can be traced back to the different spin-orbital polarization in the three $j_{\text{eff}}$ orbitals, which is enhanced by Coulomb correlations.

The occupations of the $j_{\text{eff}}$ Wannier orbitals within LDA+SO and LDA+SO+DMFT are provided in Tab. 5. In Sr$_2$IrO$_4$, one detects a considerable spin-orbital polarisation already at the LDA+SO level: the four $j_{\text{eff}}=3/2$ states are almost filled with $n_{3/2,|1/2|}=1.98$ and $n_{3/2,|3/2|}=1.84$ while the $j_{\text{eff}}=1/2$ states thus slightly exceed half-filling with $n_{1/2}=1.16$ (as in the "ideal undistorted" case). Taking into account Coulomb correlations within DMFT opens a gap of about 0.26 eV [21] and enhances the spin-orbital polarisation, such as to fill the $j_{\text{eff}}=3/2$ states entirely, leading to a half-filled $j_{\text{eff}}=1/2$ state. This is thus the celebrated "$j_{\text{eff}}=1/2$ -picture" [16], which comes out here as a result of the calculations, rather than being an input as in most model Hamiltonian calculations.

A different picture emerges for Sr$_2$RhO$_4$ according to Tab. 5: while the spin-orbital occupations display some polarisation at the LDA+SO level, the smaller SOC – and thus the smaller effective splitting between the $j_{\text{eff}}$ bands – leads to a picture where only the $j_{\text{eff}}=3/2$ $|m_j\rangle = 1/2$ state is entirely filled while both $j_{\text{eff}}=3/2$ $|m_j\rangle = 3/2$ and $j_{\text{eff}}=1/2$ live at the Fermi level. This spin-orbital polarization is enhanced by Coulomb correlations – just as in Sr$_2$IrO$_4$ – but this
enhancement is not enough to fill both $j_{\text{eff}}=3/2$ states entirely and obtain a half-filled $j_{\text{eff}}=1/2$ state. The higher effective degeneracy together with the smaller value of $\mathcal{U}$ eventually leave Sr$_2$RhO$_4$ metallic.

4.5 Spectral properties of Sr$_2$RhO$_4$: theory vs. experiment

We now turn to the calculated spectral function of the spin-orbital correlated metal Sr$_2$RhO$_4$ that we analyse in comparison to experiment.

Fig. 8 depicts the Fermi surface of Sr$_2$RhO$_4$ within LDA+SO (left panel) and LDA+SO+DMFT (right panel) in the $k_z = 0$ plane, to which we superimpose the experimental measurement from Ref. [120]. Tab. 6 gives more quantitative insight to ease the comparison between the different topologies. All three Fermi surfaces, the two theoretical ones and the experimental one, are qualitatively similar with three closed contours: a circular hole-like $\alpha$-pocket around $\Gamma$, a lens-shaped electron pocket $\beta_M$ and a square-shaped electron pockets $\beta_X$. These two structures merge in the undistorted tetragonal zone (dashed blue line in Fig. 8) to a large electron-like

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>DMFT</th>
<th>Exp.</th>
<th>LDA</th>
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<th>Exp.</th>
<th>LDA</th>
<th>DMFT</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FS volume $A$ (% BZ)</td>
<td>18.4</td>
<td>10.1</td>
<td>6.1(4)</td>
<td>4.5</td>
<td>6.2</td>
<td>8.1(5)</td>
<td>10.0</td>
<td>7.6</td>
<td>7.4(4)</td>
</tr>
<tr>
<td>$\hbar v_F$ (eV.Å)</td>
<td>1.252</td>
<td>0.645</td>
<td>0.41(4)</td>
<td>1.260</td>
<td>0.674</td>
<td>0.55(6)</td>
<td>1.260</td>
<td>0.674</td>
<td>0.61(6)</td>
</tr>
<tr>
<td>$m^* (m_e)$</td>
<td>1.70</td>
<td>2.44</td>
<td>3.0(3)</td>
<td>0.83</td>
<td>1.83</td>
<td>2.6(3)</td>
<td>1.24</td>
<td>2.02</td>
<td>2.2(2)</td>
</tr>
</tbody>
</table>

Table 6: Comparison of the Fermi surface (FS) parameters evaluated within LDA+SO, within LDA+SO+DMFT and ARPES [120]. For each $\alpha$, $\beta_X$ and $\beta_M$ pocket, the FS volume $A$ is defined as a percentage of the two-dimensional-BZ volume (using the experimental lattice parameters ($a = 5.45$ Å)). The Fermi velocity $\hbar v_F$ is obtained from the slope of the band dispersion at the Fermi level. The cyclotron mass $m^*/m_e$ is calculated using the same method as described in [120]: $m^* v_F = \hbar \sqrt{A/\pi}$. 
Figure 9: Calculated momentum-resolved spectral function of Sr$_2$RhO$_4$ within LDA+DMFT (a) and its orbital-resolved versions for the $j_{\text{eff}}=1/2$ states (b), the $j_{\text{eff}}=3/2 |m_j| = 3/2$ (c) and the completely-filled $j_{\text{eff}}=3/2 |m_j| = 1/2$ (d). The dashed blue line on panel (a) are the reproduction of the ARPES structure from [121].

Comparing Fig. 8-(a) and (b) highlights the key role of electronic correlations: they decrease the radius of the $\alpha$ pocket from 0.26–0.29 Å$^{-1}$ to 0.21 Å$^{-1}$ and decrease the radius of the large $\beta$ pocket from 0.69–0.72 Å$^{-1}$ to 0.67–0.70 Å$^{-1}$, thus enlarging the $\beta_M$ and $\beta_X$ pockets such that their volume are well-reproduced within LDA+SO+DMFT (cf. Tab 6). As a result, the agreement between LDA+SO+DMFT data and the experimental measurements becomes even quantitatively excellent.

To go further in the analysis, Fig. 9 depicts the momentum-resolved spectral function, as well as its orbital-resolved version. The completely filled $j_{\text{eff}}=3/2 |m_j| = 1/2$ state is visible (panel d), as well as the partially filled character of the $j_{\text{eff}}=3/2 |m_j| = 3/2$ (panel c) and $j_{\text{eff}}=1/2$ states (panel b). A detailed comparison with angle-resolved photoemission data from [121] (blue dashed line on the figure) shows that the band dispersion around the Fermi level is well-reproduced, while some discrepancies are observed for the structures experimentally observed along $\Gamma - X$ and $\Gamma - M$ at lower energy. These features, reminiscent of the $j_{\text{eff}}=3/2 |m_j| = 1/2$ bands, are indeed located about 0.05 eV higher in energy in our calculated spectral function.

From Fig. 9-(b) and (c), one observes that the Fermi level is crossed by the renormalized $j_{\text{eff}}=3/2 |m_j| = 3/2$ band at 0.20 Å$^{-1}$ along $\Gamma - X$ and at 0.21 Å$^{-1}$ along $\Gamma - M$, while the renormalized $j_{\text{eff}}=1/2$ band is responsible for all other crossings. This allows to label the hole-like $\alpha$-pocket as
being of $j_{\text{eff}}=3/2$ $|m_j| = 3/2$ type, whereas the two other pockets $\beta_M$ and $\beta_X$ are mostly of type $j_{\text{eff}}=1/2$. Using the quasiparticle weight of each state ($Z_{3/2} = 0.535$ and $Z_{5/2,|3/2|} = 0.675$), we evaluate the Fermi velocity at each crossing along the path $[\Gamma M X \Gamma]$: we find a huge variation of the values depending on $k$ and give in Tab. 6 their mean value over the Brillouin zone. Finally, using the same method as described in [120], we evaluate the cyclotron mass $m^*/m_e$ based on the approximate formula used there: $m^* \pi F = \hbar \sqrt{A/\pi}$. The DMFT results shown in Tab. 6 show a substantial improvement over DFT when compared to experiments.

5  The effective orbital degeneracy as a key quantity determining the correlation strength

In section 4.4, we have identified the spin-orbital polarization as a key factor to explain the different behavior of Sr$_2$RhO$_4$ and Sr$_2$IrO$_4$.

In Sr$_2$IrO$_4$, Coulomb correlations enhance the spin-orbital polarisation, such as to fill the $j_{\text{eff}}=3/2$ states entirely, leading to a half-filled $j_{\text{eff}}=1/2$ one-band picture, while in Sr$_2$RhO$_4$ the final situation is an effective two-orbital system containing three electrons. This situation is akin to correlation-induced enhancements of orbital polarisation also observed in other transition metal oxides. In the distorted 3d$^1$ perovskites LaTiO$_3$ and YTiO$_3$, for example, it was argued [10] that the interplay of structural distortions and Coulomb correlations leads to a suppression of orbital fluctuations in the $t_{2g}$-manifold, favoring a particular orbital composition selected by crystal and ligand field effects. At the LDA level, 0.45 [0.88] electrons are found in this particular orbital in LaTiO$_3$ [YTiO$_3$], while Coulomb correlations as described by LDA+DMFT lead to an occupation of 0.88 [0.96] electrons.

In these systems, this reduction of effective orbital degeneracy was shown to be key to their insulating nature since the critical interaction strength needed to localise the single electron is thus effectively determined by the one of a single-orbital system, instead of the one of a three-fold degenerate $t_{2g}$-manifold. Within DMFT, the critical Hubbard interaction scales with the square-root of the orbital degeneracy $N$ for the lower critical interaction of the phase coexistence region of the first order Mott transition, while the upper critical interaction varies with $N$ [231].

Localising electrons in a single-orbital system therefore needs a critical interaction roughly smaller by a factor of 3 as compared to the degenerate case. This was demonstrated to be crucial for the difference in behaviors in the series of d$^1$ compounds SrVO$_3$, CaVO$_3$, LaTiO$_3$, YTiO$_3$, where the former are three-fold degenerate metallic systems, whereas the latter realise the single-orbital Mott state.

The situation in the iridates is analogous with the purely formal difference that one is dealing with a one-hole situation instead of one electron. Furthermore, the strong spin-orbit interaction is instrumental for the suppression of the degeneracy, which is the net result of structural distortions, spin-orbit coupling and Coulomb correlations.

This discussion highlights an important aspect of the physics of transition metal oxides, often neglected when considering band filling and interaction strength only: the effective orbital degeneracy is a crucial tuning parameter for electronic behavior, suggesting that the popular
picture distinguishing filling-controlled and bandwidth-controlled Mott transitions [1] should be complemented by a “third axis” and the notion of degeneracy-controlled Mott behavior.

Crystal and ligand fields together with spin-orbit coupling and the Coulomb correlations themselves are the driving forces for establishing a given effective degeneracy. At the level of the calculations, this effective degeneracy is both an outcome of the calculation and a determining factor of the properties of the given compound.

6 Conclusions and Perspectives

The common belief about electronic Coulomb correlations being less important in 4d and 5d compounds as compared to 3d transition metal oxides, was overruled by insights into the role of spin-orbit coupling for the insulating behavior of iridates [16] and for the Fermi surface topology of Sr$_2$RhO$_4$ [19, 20].

Here, we have reviewed recent work on a first principles many-body description of such effects within a dynamical mean-field framework. We have highlighted the notion of the effective degeneracy of the system as a crucial parameter determining the physical properties of a system. The effective degeneracy is the result of a complex interplay of structural distortions spin-orbit coupling and Coulomb correlations. We have stressed the analogy of the $j_{\text{eff}}=1/2$ Mott insulating picture for Sr$_2$IrO$_4$ with the insulating nature of LaTiO$_3$ and YTiO$_3$ in the “degeneracy-controlled Mott transition” series of $d^1$ perovskites (SrVO$_3$, CaVO$_3$, LaTiO$_3$, YTiO$_3$).

In Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$ the difference in degeneracy is itself a consequence of the quantitative aspects of the physics of these two compounds: all three decisive elements – structural distortions, spin-orbit coupling and Hubbard interaction – are smaller in Sr$_2$RhO$_4$ than in Sr$_2$IrO$_4$ and this quantitative difference in the electronic parameters translates into a qualitative difference of the resulting properties.

We have analysed in detail the spectral properties of Sr$_2$RhO$_4$, a spin-orbit correlated 4d metal where the effective degeneracy is reduced by spin-orbit coupling and correlations but not to the point such as to induce a $j_{\text{eff}}=1/2$ Mott insulator. The calculated spectral properties and Fermi surface are in excellent agreement with experimental data. A detailed analysis of the spectral properties of Sr$_2$IrO$_4$ is left for future work.

7 Acknowledgments

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Appendix A: Generalized partial $\Theta$-projectors and spectral function

In order to calculate quantities for a given atom $\alpha$ and a particular orbital (spin) character $j$ ($m_j$) – such as the spectral functions $A_{j,m_j}^{\alpha,\sigma}(k,\omega)$ –, a set of partial projectors called “$\Theta$-projectors” was built. Contrary to the previously introduced Wannier projectors $P_{j,\nu}^{\alpha,m_j}(k)$, their definition is not restricted to the correlated orbitals only. The formalism of these partial projectors was initially introduced in [180] and was extended to the case where spin is not a good quantum number anymore in [21].

Inside the muffin-tin sphere associated to an atom $\alpha$, one can write the spin-$\sigma$ contribution of the eigenstate $\psi_{\kappa\nu}(r)$ as:

$$\phi_{\kappa\nu}^\sigma(r) = \sum_{\ell=0}^{\ell_{\text{max}}} \sum_{m=-\ell}^{+\ell} \left[ A_{\ell m}^{\alpha,\sigma}(k) u_{\ell m,1}^{\alpha,\sigma}(r^\alpha) + B_{\ell m}^{\alpha,\sigma}(k) u_{\ell m,2}^{\alpha,\sigma}(r^\alpha) + C_{\ell m}^{\alpha,\sigma}(k) u_{\ell m,3}^{\alpha,\sigma}(r^\alpha) \right]$$

(24)

where the basis $\{u_{\ell m,i}^{\alpha,\sigma}\}_{i=1,2,3}$ is not orthonormalized as already mentioned in [180]. That is why, to make the calculations easier, one introduces an orthonormal basis set $\{v_{\ell m,j}^{\alpha,\sigma}\}_{j=1,2,3}$ for each atomic orbital $\ell m$. These orbitals are defined from the initial basis $\{u_{\ell m,i}^{\alpha,\sigma}\}_{i=1,2,3}$ as follows:

$$\forall i \quad u_{\ell m,i}^{\alpha,\sigma}(r^\alpha) = \sum_{j=1}^{3} c_{ij} v_{\ell m,j}^{\alpha,\sigma} \quad \text{with} \quad C = \begin{pmatrix} 1 & 0 & \langle u_{\ell m,1}^{\alpha,\sigma} | u_{\ell m,2}^{\alpha,\sigma} \rangle^{1/2} \\ 0 & \langle u_{\ell m,2}^{\alpha,\sigma} | u_{\ell m,1}^{\alpha,\sigma} \rangle & \langle u_{\ell m,2}^{\alpha,\sigma} | u_{\ell m,3}^{\alpha,\sigma} \rangle \\ \langle u_{\ell m,3}^{\alpha,\sigma} | u_{\ell m,1}^{\alpha,\sigma} \rangle & \langle u_{\ell m,3}^{\alpha,\sigma} | u_{\ell m,2}^{\alpha,\sigma} \rangle & 1 \end{pmatrix}.$$  

(25)

We can then rewrite (24) as:

$$\psi_{\kappa\nu}^\sigma(r) = \sum_{\ell=0}^{\ell_{\text{max}}} \sum_{m=-\ell}^{+\ell} \sum_{i=1}^{3} \Theta_{\ell m,i}^{\alpha,\sigma}(k) v_{\ell m,i}^{\alpha,\sigma}(r^\alpha).$$  

(26)

The matrix elements $\Theta_{\ell m,i}^{\alpha,\sigma}(k)$ are the “$\Theta$-projectors”, which are thus defined by:

$$\Theta_{\ell m,i}^{\alpha,\sigma}(k) = \langle v_{\ell m,i}^{\alpha,\sigma} | \phi_{\kappa\nu}^\sigma \rangle = A_{\ell m}^{\alpha,\sigma}(k) c_{1i} + B_{\ell m}^{\alpha,\sigma}(k) c_{2i} + C_{\ell m}^{\alpha,\sigma}(k) c_{3i}.$$  

(27)

Contrary to the implementation of [180], there is now a couple of $\Theta$-projectors associated to each band index $\nu$, $\Theta_{\ell m,i}^{\alpha,\sigma}(k)$ with $\sigma = \uparrow, \downarrow$, since spin is not a good quantum number anymore.

We have introduced here the $\Theta$-projectors in the complex spherical harmonics basis. As for the Wannier projectors, it is of course possible to get the $\Theta$-projectors in any desired $j, m_j$ basis:

$$\Theta_{j,m_j}^{\alpha,\sigma}(k) = \sum_{m,\sigma} S_{j,\ell m}^{m_j,\sigma} \Theta_{\ell m,i}^{\alpha,\sigma}(k)$$  

(28)

Finally, the spectral function $A(k, \omega)$ which is defined by:

$$A(k, \omega) = -\frac{1}{\pi} \text{Im} [G(k, \omega)].$$  

(29)
is obtained for a given atom $\alpha$ with orbital character $(j, m_j)$ through the following formula:

$$A_j^{\alpha,m_j}(k,\omega) = -\frac{1}{\pi} \text{Im} \left[ \sum_{\nu\nu'} \sum_{i=1}^{3} \Theta_{\nu\nu',i}^{\alpha,m_j}(k) G_{\nu\nu'}(k,\omega + i0^+) \left[ \Theta_{\nu',i}^{\alpha,m_j}(k) \right]^* \right]$$  (30)

where the band indices $\nu$, $\nu'$ run over both spin and orbital quantum number.

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