Topical Review

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 coupling and Coulomb correlations has become a hot topic in condensed matter theory and is especially important in 4d and 5d transition metal oxides, like iridates or rhodates. Here, we review recent advances in dynamical mean-field theory (DMFT)-based electronic structure calculations for treating such compounds, introducing all necessary implementation details. We also discuss the evaluation of Hubbard interactions in spin–orbit materials. As an example, we perform DMFT calculations on insulating strontium iridate (Sr₂IrO₄) and its 4d metallic counterpart, strontium rhodate (Sr₂RhO₄). While a Mott-insulating state is obtained for Sr₂IrO₄ in its paramagnetic phase, the spectral properties and Fermi surfaces obtained for Sr₂RhO₄ show excellent agreement with available experimental data. Finally, we discuss the electronic structure of these two compounds by introducing the notion of effective spin–orbital degeneracy as the key quantity that determines the correlation strength. We stress that effective spin–orbital degeneracy introduces an additional axis into the conventional picture of a phase diagram based on filling and on the ratio of interactions to bandwidth, analogous to the degeneracy-controlled Mott transition in d¹ perovskites.

Keywords: dynamical mean-field theory, electronic structure, iridates, rhodates, spin–orbit coupling

(Some figures may appear in colour only in the online journal)
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 renormalized metallic behavior such as in simple oxides like SrVO₃ [2, 3] or iridate compounds [4–9] or induce Mott insulating behavior like in YTiO₃ [10] or V₂O₃ [11–14]. According to common belief held until recently, such effects would be less dramatic in 4d, and even less so in 5d compounds, due to the substantially more extended radial wave functions of those shells, as shown in figure 1. The discovery of Mott insulating behavior in Sr₂IrO₄ therefore triggered a little revolution in the field [15, 16]. In 5d oxides, spin–orbit coupling acts 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 earlier [19, 20], spin–orbit interactions can also influence the electronic properties substantially in 4d compounds. In Sr₂RhO₄, 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: TaS₂ [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, TaSe₂, [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 Sr₂IrO₄: the insulating behavior—despite 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 in driving the system insulation, 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 the new insights. Iridium-based materials, where several families of compounds have been studied systematically, still hold a privileged position. Table 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 Ir⁴⁺ (5d⁵) state does not allow for a band insulating state without symmetry breaking, and magnetic order is an obvious candidate for helping to open the gap. Nevertheless, few compounds have been unambiguously characterized as Slater insulators.

Slightly more recently, attention focused on yet another class of 5d materials, namely osmium-based compounds. In this class fall, for example, ferroelectric LiOsO₃ [30], as well as the prototypical Slater insulator NaOsO₃ [31–36], where the loss of magnetic order with increasing temperature is accompanied by a closure of the insulating gap. It has been realized, 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]. Table 2 gives an overview of the properties of a selection of...
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 AIAO refer to an antiferromagnetic, ferromagnetic and all-in-all-out magnetic ordering, respectively.

| Compound                  | Crystal struct. | Transport property | Magnetic ordering | Reference |
|---------------------------|-----------------|--------------------|-------------------|-----------|
| CaIrO3                   | Post-perovskite  | Cmcm               | Ins. gap: 0.34 eV | AFM       | \(T_K = 115\) K \([38-40]\) |
| NaIrO3                   | Post-perovskite  | Cmcm               | Ins.              | None      | \(T_K = 115\) K \([41, 42]\) |
| BaIrO3                   | Monoclinic      | C2/m               | Ins. gap: 0.05 eV | FM        | \(T_C = 180\) K \([43-45]\) |
| SrIrO3                   | Monoclinic      | C2/c               | Metal             | None      | \(T_K = 38\) K \([46-49]\) |
| \(\alpha\)-Na2IrO3        | Honeycomb       | C2/c               | Ins. gap: 0.35 eV | Zig-zag AFM | \(T_K = 15\) K \([50-55]\) |
| \(\alpha\)-Li2IrO3        | Honeycomb       | C2/c               | Ins.              | Spiral AFM | \(T_K = 15\) K \([56, 57]\) |
| \(\beta\)-Li2IrO3         | Hyperhoneycomb  | Fddd               | Ins.              | Unconventional AFM | \(T_K = 38\) K \([58, 59]\) |
| \(\gamma\)-Li2IrO3        | Stripyhoneycomb | Cccm               | Ins.              | Unconventional AFM | \(T_K = 38\) K \([60]\) |
| Ba3IrO4                  | K2NiF4-type     | I4mm               | Ins. gap: 0.14 eV | AFM       | \(T_K = 240\) K \([61-64]\) |
| Sr3IrO4                  | Distorted K2NiF4-type | P4 1/acd         | Ins. gap: 0.25 eV | Canted AFM | \(T_K = 240\) K \([15, 16, 21]\) |
| CaIrO4                   | Hexagonal       | R3c                | Ins.              | AFM       | \(T_K = 13.95\) K \([65-67]\) |
| Y2IrO7                   | Pyrochlore      | Fd\(\bar{3}\)m   | Ins.              | AIAO      | \(T = 155\) K \([68, 69]\) |
| Pr2IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | Metal              |          | \(T = 141\) K \([70]\) |
| Nd3IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | MIT \(T = 36\) K | AIAO      | \(T = 140\) K \([76]\) |
| Sm3IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | MIT \(T = 171\) K | AIAO      | \(T = 141\) K \([77]\) |
| Eu3IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | MIT \(T = 120\) K | AIAO      | \(T = 130\) K \([78]\) |
| Gd3IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | Ins.              | AIAO      | \(T = 130\) K \([79]\) |
| Tb3IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | Ins.              | AIAO      | \(T = 130\) K \([80]\) |
| Dy3IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | Ins.              | AIAO      | \(T = 130\) K \([81]\) |
| Ho3IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | Ins.              | AIAO      | \(T = 130\) K \([82]\) |
| Er3IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | Ins.              | AIAO      | \(T = 130\) K \([83]\) |
| Yb3IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | Ins.              | AIAO      | \(T = 130\) K \([84]\) |
| Lu3IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | Ins.              | AIAO      | \(T = 130\) K \([85]\) |
| Bi3IrO7                  | Pyrochlore      | Fd\(\bar{3}\)m   | Metal             | None      | \(T = 285\) K \([86-88]\) |
| Sr3Ir2O7                 | Monoclinic      | C2/c               | Ins. gap: 0.1 eV  | AFM       | \(T_K = 6\) K \([89-91]\) |
| Na3Ir2O4                 | Hyperkagome     | P4\(\bar{1}\)2\(\bar{1}\) | Ins.              | AFM       | \(T_K = 7.8\) K \([92, 93, 94]\) |
| Ca3Ir2O12                | Hexagonal       | P \(-\bar{6}\)m | Ins.              | AFM       | \(T_K = 7.8\) K \([95-99]\) |
| La2ZnIr6O8               | Double-perovskite | \(P2_1/\bar{1}\)n | Ins.              | FM        | \(T_K = 7.5\) K \([100]\) |
| La2MgIr6O6               | Double-perovskite | \(P2_1/\bar{1}\)n | Ins. gap: 0.16 eV | AFM       | \(T_K = 12\) K \([101, 102]\) |
| Pr2MgIr6O6               | Double-perovskite | \(P2_1/\bar{1}\)n | Ins. gap: 0.2 eV  | AFM       | \(T_K = 14\) K \([102, 103]\) |
| Nd2MgIr6O6               | Double-perovskite | \(P2_1/\bar{1}\)n | Ins.              | AFM       | \(T_K = 12\) K \([104]\) |
| Sm2MgIr6O6               | Double-perovskite | \(P2_1/\bar{1}\)n | Ins.              | AFM       | \(T_K = 12\) K \([105]\) |
| Eu2MgIr6O6               | Double-perovskite | \(P2_1/\bar{1}\)n | Ins.              | AFM       | \(T_K = 12\) K \([106]\) |
| Gd2MgIr6O6               | Double-perovskite | \(P2_1/\bar{1}\)n | Ins.              | None      | \(T = 15\) K \([107]\) |
| Sr2CeIr6O6               | Double-perovskite | \(P2_1/\bar{1}\)n | Ins. gap: 0.3 eV  | AFM       | \(T_K = 21\) K \([108-110]\) |
| Ba2YIr6O6                | Double-perovskite | \(Pm\bar{3}m\)    | Ins. gap: 0.221 eV | None      | \(T = 4\) K \([111]\) |
| Ba2ScIr6O6               | Hexagonal       | \(P6_3/mmc\)     | Ins.              | None      | \(T = 4\) K \([112]\) |
| Ba2YbIr6O6               | Hexagonal       | \(P6_3/mmc\)     | Ins.              | None      | \(T = 4\) K \([113]\) |
| Ba2ZnIr6O6               | Hexagonal       | \(P6_3/mmc\)     | Ins.              | None      | \(T = 4\) K \([114]\) |

The 5d transition metal oxide (TMO) Sr3IrO4 has a tetragonal crystal structure, the symmetry of which is lowered from the K2NiF4-type, well-known in Sr3RuO4 or La2CuO4, by an 11° rotation of its IrO6 octahedra around the c-axis \([136]\). Each Ir atom accommodates 5 electrons and the standard picture neglecting spin–orbit interactions would give a \(3\gamma\) 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 \(T_K = 240\) 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 persistence 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] proposed a picture early on in terms of $J_{\text{eff}} = 1/2$ states and $J_{\text{eff}} = 3/2$ states:

$$J_{\text{eff}} = \frac{3}{2}, m_{\text{J}} = +\frac{3}{2} = -\frac{1}{\sqrt{6}} (|d_{yz, \downarrow}\rangle + i|d_{xz, \downarrow}\rangle) + \sqrt{\frac{2}{3}} |d_{xy, \uparrow}\rangle,$$

$$J_{\text{eff}} = \frac{3}{2}, m_{\text{J}} = -\frac{3}{2} = +\frac{1}{\sqrt{6}} (|d_{yz, \uparrow}\rangle - i|d_{xz, \uparrow}\rangle) + \sqrt{\frac{2}{3}} |d_{xy, \downarrow}\rangle,$$

$$J_{\text{eff}} = \frac{3}{2}, m_{\text{J}} = +\frac{1}{2} = \frac{1}{\sqrt{3}} |d_{xy, \uparrow}\rangle,$$

$$J_{\text{eff}} = \frac{3}{2}, m_{\text{J}} = -\frac{1}{2} = -\frac{1}{\sqrt{3}} |d_{xy, \downarrow}\rangle.$$

Since the quartet of states lies lower in energy than the doublet and the splitting between the $J_{\text{eff}} = 3/2$ and $J_{\text{eff}} = 1/2$ is large, neglecting any band dispersion would result in a configuration 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 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 (see table 1) have been classified as spin–orbit Mott insulators (Na$_2$IrO$_3$, pyrochlores, etc...). Recent theoretical studies also predict some fluoride material [147] to be in this class. The one-orbital nature of insulating Sr$_3$IrO$_4$ has contributed to intense activities attempting to dope the compound.

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.

| Compound | Crystal struct. | Transport property | Magnetic ordering | Reference |
|----------|-----------------|--------------------|------------------|-----------|
| BaRuO$_3$ | Cubic perovskite, $Pm\bar{3}m$ | Metal | FM | $T_c = 410$ K [31–36] |
| CaRuO$_3$ | Perovskite, $Pnma$ | Metal | None | [125] |
| SrRuO$_3$ | Perovskite, $Pnma$ | Metal | FM | $T_c = 160$ K [104, 106, 107] |
| Sr$_2$Ru$_4$O$_7$ | $K_2NiF_2$-type | $I4/mmm$ | Metal | None | [109] |
| Ca$_2$Ru$_4$O$_7$ | Distorted $K_2NiF_2$-type | $P6_3/mcc$ | MIT | $T = 357$ K | AFM | $T = 110$ K [108, 110–112] |
| Sr$_4$Ru$_6$O$_{10}$ | Hexagonal | $P3_1m$ | Ins. | AFM | $T_N = 565$ K [113, 114] |
| Sr$_2$Ru$_4$O$_9$ | Orthorhombic | $BBcb$ | Metal | None | [106, 115] |
| Sr$_2$Ru$_4$O$_{10}$ | Orthorhombic | $Pham$ | Metal | FM | $T_c = 105$ K [106, 116, 117] |
| Li$_3$Rh$_2$O$_7$ | Honeycomb | $C2/m$ | Ins. | gap: 0.08 eV | None | [118, 119] |
| Sr$_2$RhO$_3$ | Distorted $K_2NiF_2$-type | $I4/acd$ | Metal | None | [21, 120, 121] |
| Sr$_2$RhO$_3$ | Hexagonal | $R3c$ | Ins. | gap: 0.1 eV | AFM | $T_N = -K$ [122] |
| Sr$_2$RhO$_4$ | Hexagonal | $P3c1$ | Ins. | AFM | $T_N = 23$ K [66, 123] |
| Li$_3$Rh$_2$O$_7$ | Honeycomb | $C2/m$ | Ins. | gap: 0.08 eV | None | [118, 119] |
| Ba$_2$NaOsO$_6$ | Double-perovskite | $Fm\bar{3}m$ | MIT | $T = 226$ K | AFM | $T = 410$ K [31–36] |
| Ba$_2$LiOsO$_6$ | Double-perovskite | $Fm\bar{3}m$ | Ins. | FM | $T_c = 6.8$ K [130–132] |
| Ba$_2$CaOsO$_6$ | Double-perovskite | $Fm\bar{3}m$ | Ins. | AFM | $T_N = 8$ K [131] |
| Ba$_2$YO$_3$ | Double-perovskite | $Fm\bar{3}m$ | Ins. | FM | $T_c = 50$ K [133, 134] |
| Ba$_2$OsO$_3$ | Hexagonal | $Pnma$ | Metal | None | [125] |
| Sr$_2$OsO$_4$ | Perovskite | $Pnma$ | Metal | None | [125] |
| BaOsO$_3$ | Six-layer hexagonal 6H | $Pn\bar{3}m$ | Metal | None | [124, 125] |
| Ba$_2$OsO$_3$ | Double-perovskite | $Fm\bar{3}m$ | Ins. | AFM | $T_N = 565$ K [113, 114] |
| Ba$_2$OsO$_3$ | Double-perovskite | $Fm\bar{3}m$ | Ins. | AFM | $T_N = 23 K$ [66, 123] |

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 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$_{1-n}$Rh$_n$O$_4$ [152, 153], Sr$_2$Ir$_{1-n}$Ru$_n$O$_4$ [154], Sr$_2$La$_{1-n}$Ir$_n$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 (see tables 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 detail for several compounds, among which are SrIrO$_3$ [46–48], Sr$_2$RuO$_4$/Ca$_2$RuO$_4$ [108, 109, 156] and Sr$_2$RhO$_4$ [19–21].

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$_4$, which is Sr$_{11}$Ir$_1$O$_{21}$ where IrO$_6$ octahedra are present (see table 1). Similar conditions where IrO$_6$ octahedra are present (see table 1). Similar compounds based on Ru, Rh and Os also show such $j_{\text{eff}}$ states (see table 2). However, not all Ir-based compounds 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 a $j_{\text{eff}} = 1/2$ 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:

\[
H_{\text{SO}} = \frac{\hbar}{4mc^2} \sigma \cdot [\nabla \mathbf{V}(\mathbf{r}) \times \mathbf{p}],
\]

where $m_0$ is the electron mass, $\mathbf{V}(\mathbf{r})$ is the effective Kohn–Sham potential and $\sigma_{x,y,z}$ 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:

\[
H_{\text{SO}} = \zeta_{\text{SO}}(n\ell) \mathbf{L} \cdot \mathbf{s}, \quad \zeta_{\text{SO}}(n\ell) = \frac{\hbar^2}{2mc^2} \int \frac{1}{r} \mathbf{dV} \bigg|_{(n,\ell)},
\]

where $\mathbf{s} = \frac{1}{2} \sigma \cdot \mathbf{L} = \mathbf{r} \times \mathbf{p} = \hbar \mathbf{l}$ and $(...)_n\ell$ denotes the mean value of the radial quantity in the state $(n, \ell)$. Table 3 gives some values of the spin–orbit constant $\zeta_{\text{SO}}$ 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. Figure 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 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 green and light green, respectively, in figure 2) can be reduced to two five-dimensional submatrices:

\[
\begin{pmatrix}
0 & -i & i \\ i & 0 & -i \\ -i & 1 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\sqrt{3} & i \sqrt{3} & 0 & 0 \\ i \sqrt{3} & 0 & 0 & 0 \\ -1 & i & 2i & 0 \\
\end{pmatrix}
\begin{pmatrix}
0 & i & i \\ -i & 0 & i \\ -i & 1 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\sqrt{3} & 1 & 0 & 0 \\ 1 & \sqrt{3} & 0 & 0 \\ i & 1 & 2i & 0 \\
\end{pmatrix}
\]

in the bases $\{d_{xz}, d_{yz}, d_{xy}, d_{x^2-y^2}, d_{z^2}, d_{x^2+y^2}\}$ and $\{d_{xz}, d_{yz}, d_{xy}, d_{x^2-y^2}, d_{z^2}, d_{x^2+y^2}\}$, respectively. After diagonalization, the total angular momentum $J$ remains a good
quantum number, contrary to $j_m J_z$ and one gets the following fine structure:

- A first quartet of $J = 5/2$ states (in red) with an energy $\varepsilon_{5/2}^+ = \frac{1}{4}(2\Delta - \zeta_{SO}) + \frac{1}{4}(2\Delta + \zeta_{SO})^2 + 2\zeta_{SO}^2 / 2$.
- A doublet of $J = 5/2$ states (in yellow) of energy $\varepsilon_{5/2}^- = + 2\zeta_{SO}^2 / 2$.
- A quartet of $J = 3/2$ states (in light blue) with an energy $\varepsilon_{3/2} = \frac{1}{4}(2\Delta - \zeta_{SO}) - \frac{1}{4}(2\Delta + \zeta_{SO})^2 + 2\zeta_{SO}^2 / 2$.

In the limit of strong crystal field ($\Delta \gg \zeta_{SO}$), 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 $-\zeta_{SO}^2 / 2$.

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 $j_{eff}$ quantum number in analogy with the $p_1$ and $p_2$ multiplets, leading to the expressions given in equations (1) and (2). We point out that the $J_{eff} = 1/2$ 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:

$$\frac{1}{4} (5 \frac{5}{2} - \frac{3}{2}) = \frac{2 \zeta_{SO}^2}{2}$$

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 $J_{eff} = 1/2$ and $J_{eff} = 3/2$ multiplets follows the inverse Landé interval rule (with the $J_{eff} = 1/2$ above the $J_{eff} = 3/2$ 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...
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[168–171], their oxides [11, 172–177], sulphides [178, 179], pnictides [4, 9, 180, 181], rare earths [182–184] and their compounds [185–187], including heavy fermions [188, 189], actinides [190, 191] and their compounds [192, 193] to organics [194], correlated semiconductors [195, 196], and correlated surfaces and interfaces [197–199] have been studied with great success. Besides intensive methodological developments (see e.g. [2, 3, 167, 200–203]), recent research activities continue to extend to new classes of materials. In this context, 4d and 5d oxides have also 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, 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 $P_{j,m}^{\alpha}(k)$ (see [204] 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 $\Theta_{j,m}^{\alpha}(k)$ (see appendix).

Figure 3. Projector-based implementation of DFT + DMFT for calculations including spin–orbit coupling in the Kohn–Sham equations. Once the Kohn–Sham eigenstates $|\psi_{\nu}\rangle$ are known, their projections $P_{j,m}^{\alpha}(k)$ to the correlated Wannier-like orbitals $|w_{j,m}\rangle$ 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 $P_{j,m}^{\alpha}(k)$ (see [204] 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 $\Theta_{j,m}^{\alpha}(k)$ (see appendix).
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 $|\psi_{\alpha\nu}^k\rangle$, labelled by their momentum $k$ their band index $\nu$ and their spin $\sigma$, to the resulting Wannier-like local orbitals $|w_{\alpha\nu}^{\text{loc}}\rangle$. These key quantities are called projectors and denoted $P_{\alpha\nu\nu'}^{\text{loc}}(k)$.

The main advantage of projector-based implementations of DFT+DMFT (see e.g. [180, 205, 206]) 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 $|\psi_{\alpha\nu}^k\rangle$ is known, it is sufficient to further determine the projections of the Kohn–Sham eigenstates onto the local orbitals $|w_{\alpha\nu}^{\text{loc}}\rangle$ used in the DMFT impurity problem. This is precisely the role of the projectors.

In [21], this construction was generalized to the case when spin is not a good quantum number anymore, and implemented within the framework of the DFT+DMFT implementation of [180]. Nowadays, it is available within the TRIQS/DFTTools package [207] that links the Wien2k code [208] to DMFT. We give here the main lines of this generalization of the projector-based DFT+DMFT formalism.

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

$$\psi_{\nu\alpha}(r) = \left[u_{\nu\alpha}^+(r) + u_{\nu\alpha}^-(r)\right] e^{i k \cdot r}, \quad (7)$$

where the index $\nu$ now runs over both spin and band indices. The state $|\phi_{\nu\alpha}^k\rangle$ 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:

$$P_{\alpha\nu\nu'}^{\text{loc}}(k) = \langle \psi_{\alpha\nu}^k | \psi_{\nu'\alpha}^k \rangle = \langle \psi_{\alpha\nu}^k | \phi_{\nu'\alpha}^k \rangle. \quad (8)$$

We define them in the standard complex phase basis, allowing for a basis transformation to quantum numbers $j, m$ (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:

$$P_{\nu\nu'}^{\text{loc}}(k) = \sum_{m, \sigma} S_{\nu\nu'}^{\text{loc},m}(w_{\nu\nu'}^{\text{loc}} | \psi_{\nu\alpha}^k) = \sum_{m, \sigma} S_{\nu\nu'}^{\text{loc},m}(w_{\nu\nu'}^{\text{loc}} | \psi_{\nu\alpha}^k). \quad (9)$$

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

Using the decomposition (7) 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:

$$[G^{-1}(k, i\omega_n)]_{\nu\nu'} = (i\omega_n + \mu - \varepsilon_{\nu\nu'}^{\text{imp}}) \delta_{\nu\nu'} - \Sigma_{\nu\nu}(k, i\omega_n), \quad (10)$$

where $\varepsilon_{\nu\nu'}^{\text{imp}}$ 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:

$$\Sigma_{\nu\nu}(k, i\omega_n) = \sum_{m, \nu'} [P_{\nu\nu'}^{m,\text{loc}}(k)]' \left[ \Delta \Sigma_{\text{loc}}^{\nu}(i\omega_n) \right]_{\nu\nu'}^{m,\text{loc}} P_{\nu\nu'}^{m,\text{loc}}(k), \quad (11)$$

with

$$[\Delta \Sigma_{\text{loc}}^{\nu}(i\omega_n)]_{\nu\nu'}^{m,\text{loc}} = [\Sigma_{\text{imp}}^{\nu}(i\omega_n)]_{\nu\nu'}^{m,\text{loc}} - [\Sigma_{\text{loc}}^{\nu}(i\omega_n)]_{\nu\nu'}^{m,\text{loc}}. \quad (12)$$

Here, $\Sigma_{\text{imp}}^{\nu}(i\omega_n)$ is the impurity self-energy, expressed in the local orbitals, and $\Sigma_{\text{loc}}^{\nu}$ 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,

$$[G^{\nu\nu}_{\text{loc}}(i\omega_n)]_{\nu\nu'}^{m,\text{loc}} = \sum_{k, \nu'} P_{\nu\nu'}^{m,\text{loc}}(k) G_{\nu\nu}(k, i\omega_n) [P_{\nu\nu'}^{m,\text{loc}}(k)]'. \quad (13)$$

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 [209, 210].

The DMFT equations are solved iteratively: starting from an initial local Green’s function $G^{\nu\nu}_{\text{loc}}(i\omega_n)$ (obtained from the ‘pure’ Kohn–Sham lattice Green’s function using equation (13)), the Green’s function $G_{\nu\nu}(k, i\omega_n)$ of the effective environment in the impurity model is constructed. The impurity model is solved, allowing the evaluation of the local self-energy of the solid (see equation (11)) 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 realized in the Wien2k package [208]. 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 $\tilde{P}_{\nu\nu'}^{\sigma,\text{loc}}(k)$ are calculated—separately for each $|\phi_{\nu\alpha}^k\rangle$ term—from the following expression:

$$\tilde{P}_{\nu\nu'}^{\sigma,\text{loc}}(k) = \sum_{\mu, \sigma} \left( w_{\nu\nu'}^{\text{loc}} | \phi_{\nu\alpha}^k \right) \left( w_{\mu\sigma}^{\text{loc}} | \phi_{\nu'\alpha}^k \right).$$
\[
\begin{align*}
\tilde{P}^{\alpha\sigma}_{\ell,m}(k) &= (u^{\alpha\sigma}_\ell(E_\ell)Y^\dagger_{1m}\psi_{k\omega}) \\
&= A^{\alpha\sigma}_{\ell,m}(k, \sigma) + \sum_{\sigma_{m'\omega}} c^{\alpha\sigma}_{\ell,m,m'} O^{\alpha\sigma}_{\ell,m,m'}. 
\end{align*}
\]

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

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

\[
[O(k)]_{\ell,m',(m'\sigma')} = \frac{1}{\text{max}(k)} \sum_{p=1}^{\text{max}(k)} P^{\alpha\sigma}_{\ell,m}(k) \bar{P}^{\alpha'\sigma'}_{\ell,m',p}(k),
\]

leading to the final projectors:

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

which are then further transformed into a \(j,m_j\) basis as described above (see equation (9)).

3.3. Effective local Coulomb interactions from first principles

Hubbard interactions \(U\)—obtained as the static (\(\omega = 0\)) limit of the on-site 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 [211] to oxides [204, 212–215], pnictides [181, 186, 216, 217], f-electron elements [218] and compounds [187], to surface systems [219], and several implementations within different electronic structure codes and basis sets have been done, e.g. within linearized muffin tin orbitals [211, 220], maximally localized Wannier functions [212, 216, 221] (as elaborated in [222]), or localized orbitals constructed from projected atomic orbitals [204]. The implementation into the framework of the Wien2k package [204] made it possible for Hubbard \(U\)’s be calculated for the same orbitals as the ones used in subsequent DFT+DMFT calculations, and, to our knowledge, [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 further 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 rationalized by two counteracting mechanisms, the increasing extension of the orbitals with increasing principal quantum number and the less efficient screening by oxygen states [204]. 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 [204].

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:

\[
H_{\text{int}} = \mathcal{U} \sum_m n_m n_m + \mathcal{U}' \sum_{m<n,\sigma} n_m n_n \\
- \mathcal{J} \sum_{m<n,\sigma} [c^\dagger_m \sigma c^\dagger_n \sigma c_{m\sigma} + c_{m\sigma} c_{n\sigma} c_{n\sigma}],
\]

where \(\mathcal{U}\) is the intra-orbital Coulomb repulsion term and \(\mathcal{U}'\) (\(= \mathcal{U} - 2\mathcal{J}\) with cubic symmetry) the inter-orbital Coulomb interaction which is reduced by Hund’s exchange \(\mathcal{J}\). (\(m\) 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 \(\mathcal{U}, \mathcal{U}'\) and \(\mathcal{J}\) are understood as the Slater-symmetrized effective interactions in the \(t_{2g}\) subspace, related to the Slater integrals \(F^1, F^2\) and \(F^3\) as:

\[
\mathcal{U} = F^2 + \frac{4}{49} \left(F^3 + F^4\right) \quad \text{and} \quad \mathcal{J} = \frac{3}{49} F^2 + \frac{20}{441} F^4.
\]

The last relation \(\mathcal{U}' = F^0 - \frac{2}{3} F^2 - \frac{4}{41} F^4\) is redundant since \(\mathcal{U}' = \mathcal{U} - 2 \mathcal{J}\).

One now transforms \(H_{\text{int}}\) into the \(j_m\) basis using the unitary matrix transformation \(S^{\sigma}_{j_m,lm}\). Keeping only density-density terms, \(H_{\text{int}}\) becomes:

\[
H_{\text{int}} = \frac{1}{2} \sum_{j_m j_{m'} f_m f_{m'}} U^{\sigma_{j_m, f_m}}_{j_f, j_{m'}} n_{j_m} n_{j_{m'}}.
\]

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 \(U^{\sigma_{j_m, f_m}}_{j_f, j_{m'}}\) has the following form:

\[
U^{\sigma_{j_m, f_m}}_{j_f, j_{m'}} = U^{\sigma_{j_m, f_m}}_{j_f, j_{m'}} = \begin{pmatrix}
0 & U - 2 \mathcal{J} & U - \frac{5}{3} \mathcal{J} \\
U - 2 \mathcal{J} & 0 & U - \frac{7}{3} \mathcal{J} \\
U - \frac{5}{3} \mathcal{J} & U - \frac{7}{3} \mathcal{J} & 0
\end{pmatrix}
\]

\[
U^{\sigma_{j_m, f_m}}_{j_f, j_{m'}} = U^{\sigma_{j_m, f_m}}_{j_f, j_{m'}} = \begin{pmatrix}
U - \frac{4}{3} \mathcal{J} & U - \frac{8}{3} \mathcal{J} & U - \frac{8}{3} \mathcal{J} \\
U - \frac{8}{3} \mathcal{J} & U - \frac{7}{3} \mathcal{J} & U - \frac{7}{3} \mathcal{J} \\
U - \frac{8}{3} \mathcal{J} & U - \frac{7}{3} \mathcal{J} & U - \mathcal{J}
\end{pmatrix}
\]

We use the standard convention that \(m_j\) denotes \(-m_n\), as is usually done for spin degree of freedom. The ordering of the orbitals \(|j, |m_j|\) is: \(1/2, 1/2\), \(3/2, 1/2\), \(3/2, 3/2\), \(j_{\text{eff}} = 1/2\) 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 [223]. We are able to perform calculations at room temperature (\( \beta = 1/k_B T = 40 \text{ eV}^{-1} \)) with reasonable numerical effort. In our calculations, we typically use around \( 16 \times 10^6 \) Monte Carlo sweeps and 28 \( \mathbf{k} \)-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 [224] yields real and imaginary parts of the retarded self-energy. From those, we calculate the momentum-resolved spectral function \( A(\mathbf{k}, \omega) \) using partial projectors introduced in the appendix.

During the calculations we use the fully localized limit (FLL) expression for the double-counting:

\[
\Sigma^\text{FLL}_{jj'} = \left[ t_{jj'} - \left( \frac{1}{2} \right) N_{c} \right] \delta_{jj'},
\]

where \( j \) and \( j' \) run over the \( J_{\text{eff}} \) states and \( N_{c} \) is the total occupancy of the orbitals. (Since each orbital is doubly degenerate in \( m_{\mu}, N_{c}/2 \) 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 \( J_{\text{eff}} = 3/2 \) which we checked to be two orders of magnitude smaller than the diagonal terms, in the chosen basis).

4. Electronic structure of \( \text{Sr}_2\text{IrO}_4 \) and \( \text{Sr}_2\text{RhO}_4 \)

4.1. Electronic structure of \( \text{Sr}_2\text{IrO}_4 \) and \( \text{Sr}_2\text{RhO}_4 \) within DFT-LDA

The Kohn–Sham band structures of \( \text{Sr}_2\text{IrO}_4 \) and \( \text{Sr}_2\text{RhO}_4 \) within the local density approximation and in the presence of spin–orbit coupling (LDA + SO) are represented in figures 4(d) and (e). For \( \text{Sr}_2\text{IrO}_4 \), we use the lattice parameters measured at 295 K in [225], and for \( \text{Sr}_2\text{RhO}_4 \) those measured at 300 K in [226].

The LDA + SO band structures for \( \text{Sr}_2\text{IrO}_4 \) and \( \text{Sr}_2\text{RhO}_4 \) 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 \( d_{z^2} \) in yellow) start at about 1−1.5 eV, and are fully separated from the \( t_{2g} \)-manifold which lies around the Fermi level and overlaps at lower energies with the oxygen 2\( p \)-states (black). Given the \( t_{2g} \)-filling and the four-atom unit cell of both compounds, a metallic solution is obtained within LDA for both \( \text{Sr}_2\text{RhO}_4 \) and \( \text{Sr}_2\text{IrO}_4 \)—at variance with experiments for \( \text{Sr}_2\text{IrO}_4 \). 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 \( \mathbf{k} \)-point. We stress, however, that the true picture is much more subtle: in fact, \( J_{\text{eff}} = 1/2 \) and \( J_{\text{eff}} = 3/2 \) overlap (see the band structure between the \( \Gamma \) and the \( M \)-point for instance) and the identification of the upper four bands as the \( J_{\text{eff}} = 1/2 \) states is too simplistic. We will come back to this point below.
To get a better understanding of the Kohn–Sham band structures of Sr₂RuO₄ and Sr₂IrO₄, we study artificial compounds where both the structural distortions and the spin–orbit coupling have been switched off. Figures 5(b) and (c) depict the LDA band structure of such ‘idealized undistorted Sr₂RuO₄ and Sr₂IrO₄’. Neglecting the rotation of about 10° of their IrO₆ and RhO₆ octahedra around the c-axis leads to a K₂NiF₄-type crystal structure, like in Sr₂RuO₄, the well-known LDA band structure of which is plotted in figure 5(a).

The similarity of the three band structures is obvious. Around the Fermi level, one distinguishes the three t₂g bands. The d₃z²−r²-band (green) reaches out to lower energies and overlaps with the oxygen 2p-states (black). The eg-states (dₓ²−r² in red and dₓz−y² yellow), higher in energy, cut the Fermi level closest to the 3.5 eV and band reaches the Fermi-level closest to the 3.5 eV for the dxz-dominated bands are plotted in green (dₓz) and blue (dₓ² and dₓ²) while the eg bands are red (dₓz−r²) and yellow (dₓz−r²), and the O-2p states are plotted in black.

To draw the link between the ‘undistorted’ band structures and the realistic ones, we plot in figure 4(c) the LDA + SO band structure of the undistorted Sr₂IrO₄ 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-path, and more generally in the whole Brillouin zone. Since the spin–orbit coupling is half the size in Sr₂RhO₄, the splitting between the jₑff bands is reduced by a factor of 2, as one can see, for instance, at X or Γ.

Re-introducing the effects of the spin–orbit coupling in Sr₂RuO₄ and Sr₂IrO₄ (but without considering the structural distortions) modifies these Kohn–Sham band structures to those shown in figures 4(a) and (b). The t₂g bands are the most affected, while the eg bands are slightly shifted as a consequence of the topological change in the t₂g manifold. A detailed study of the character of these band structures confirms the decoupling between eg and t₂g states (see also [19, 20]). The cubic crystal field at stake in these compounds is indeed much larger than the energy scale associated with the spin–orbit coupling of about ζSO ≈ 0.4 eV and ζSO ≈ 0.2 eV for Sr₂IrO₄ and Sr₂RhO₄ respectively.

The jₑff picture is thus justified in both Sr₂IrO₄ and Sr₂RhO₄: the t₂g orbitals split into a quartet of jₑff = 3/2 states and a higher lying doublet jₑff = 1/2 (see figure 2). Each state is doubly degenerate in ±mj, 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 ‘jₑff = 1/2 band’ and the two ‘jₑff = 3/2 bands’ in the following. The three jₑff bands can easily be identified: the jₑff = 1/2 one (light green) lies above the two jₑff = 3/2 ones (mj = 3/2 in light blue and mj = 1/2 in violet). The three jₑff bands are well-separated all along the k-path, and more generally in the whole Brillouin zone. Since the spin–orbit coupling is half the size in Sr₂RhO₄, the splitting between the jₑff bands is reduced by a factor of 2, as one can see, for instance, at X or Γ.

Finally, comparing figures 4(c) and (e) gives more insight into the nature of the four highest-lying bands (blue) of figure 4(e). Along the M − X direction, each quartet of the jₑff bands remain well-separated, jₑff = 1/2 and jₑff = 3/2 overlap in the other direction Γ − M and M − X. As a result, the jₑff = 3/2 bands cross the Fermi-level closest to the...
Γ-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’ $j_{1/2}$ states is thus too simplistic, implying the need for a Hamiltonian containing more than one orbital in a realistic calculation.

The same mechanisms are important in Sr$_2$RhO$_4$ even though we do not display the orbital characters here: the four highest-lying bands, highlighted in blue in figure 4(d) exhibit a mixed character of type $j_{1/2}$ and $j_{3/2}$.

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 figure 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 in the LDA for Sr$_2$RhO$_4$ [19, 20].

4.2. Wannier functions

We have derived the Wannier functions associated with 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 accommodate 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$_4$.

Figures 6 and 7 depict the projection of these Wannier functions on the LDA + SO band structure. The similarities between figures 6 and 4(c) are numerous, thus confirming our previous band character analysis. Table 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, table 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 (see equations (1) and (2)) in both modulus and phase. Discrepancies are mostly due to the elongation of the octahedra along the $c$-axis.

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and are character (see table 5). The coefficients calculated have been such that the density matrix of the local atomic problem is the closest possible to the diagonal form. In addition to the hybridization, the construction of the 'effective' also takes 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 equations (1) and (2). We note that the coefficients obtained for the $\pm U/\pm j$ state of Sr$_2$IrO$_4$ are equivalent to those obtained in the AF phase in [139].

Finally, comparing the occupation of the orbitals in tables 4 and 5 highlights again the role of the hybridisation between the $d_{\alpha\beta}$ and $d_{\bar{\alpha}\bar{\beta}}$ 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 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 interaction matrices for Sr$_2$IrO$_4$:

$$U^m = \begin{pmatrix} 0 & 2.08 & 2.21 \\ 2.08 & 0 & 1.93 \\ 2.21 & 1.93 & 0 \end{pmatrix}$$

and for Sr$_2$RhO$_4$:

$$U^m = \begin{pmatrix} 2.25 & 1.98 & 1.90 \\ 1.98 & 2.38 & 2.03 \\ 1.90 & 2.03 & 2.31 \end{pmatrix}$$

where the values are in eV and the ordering of the $|j, m_j|$ orbitals is: $|1/2, 1/2⟩$, $|3/2, 1/2⟩$, $|3/2, -1/2⟩$, $|3/2, 1/2⟩$ and $m_j$ denotes $-m_j$. We remind the reader that $U^m_{jj'} = U^{m^\prime}_{jj'}$ and $U^{m^\prime}_{jj'} = U^{m^\prime}_{jj'}$. Since we have used 'effective $j_{\text{eff}}$' Wannier orbitals instead of the standard definition given in equations (1) and (2), some discrepancies with the formulae given in equation (20) and in [22] can be observed. Contrary to common belief, the Hubbard interactions are smaller in the 4$d$-TMO than in its 5$d$-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 figures 4(d) and (e), the hybridization between the Rh-4$d$ states and the O-2$p$ orbitals 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.

### 4.3. 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 the cRPA [204, 211], 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 interaction matrices for Sr$_2$IrO$_4$:

$$U^m = \begin{pmatrix} 0 & 2.08 & 2.21 \\ 2.08 & 0 & 1.93 \\ 2.21 & 1.93 & 0 \end{pmatrix}$$

and for Sr$_2$RhO$_4$:

$$U^m = \begin{pmatrix} 2.25 & 1.98 & 1.90 \\ 1.98 & 2.38 & 2.03 \\ 1.90 & 2.03 & 2.31 \end{pmatrix}$$

### 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 the metallic versus insulating
Figure 8. Calculated Fermi surface of Sr$_2$RhO$_4$ in the $k_z = 0$ plane within LDA + SO (left panel) and LDA + SO+DMFT (right panel). Superimposed is the experimentally measured Fermi surface. Adapted with permission from [120]. Copyright 2006 by the American Physical Society.

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 $h\mathbf{v}_F$ 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]: $m^* = \frac{\hbar^2}{e^2}\frac{\mathbf{v}_F}{\pi}$. 

|          | $\alpha$           | $\beta_X$          | $\beta_M$          |
|----------|--------------------|--------------------|--------------------|
| LDA      | Exp.               | LDA                | Exp.               | LDA | Exp.               |
| $FS$ volume $A$ ($\%$ BZ) | 18.4 | 10.1 | 6.1(4) | 4.5 | 6.2 | 8.1(5) | 10.0 | 7.6 | 7.4(4) |
| $h\mathbf{v}_F$ (eV $\cdot$ Å) | 1.252 | 0.645 | 0.41(4) | 1.260 | 0.674 | 0.55(6) | 1.260 | 0.674 | 0.61(6) |
| $m^*$ ($m_e$) | 1.70 | 2.44 | 3.0(3) | 0.83 | 1.83 | 2.6(3) | 1.24 | 2.02 | 2.2(2) |

Table 6 shows that the effective Fermi surface parameters evaluated within LDA + SO, LDA + SO+DMFT and ARPES [120] are in good agreement. The effective Fermi surface parameters are obtained from the slope of the band dispersion at the Fermi level. The cyclotron mass $m^*$ is calculated using the same method as described in [120]. Table 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 figure 8) to a large electron-like pocket $\beta$.

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 analyze in comparison to experiment.

Figure 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, on which we superimpose the experimental measurement from [120]. Table 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 figure 8) to a large electron-like pocket $\beta$.

Comparing figures 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 volumes are well-reproduced within LDA + SO+DMFT (see table 6). As a result, the agreement between LDA + SO + DMFT data and the experimental measurements becomes quantitatively excellent.
Figure 9. Calculated momentum-resolved spectral function of Sr$_2$RhO$_4$ within LDA+DMFT (a) and its orbital-resolved versions for the $k_{\text{eff}} = 1/2$ states (b), the $j_0 = 3/2 |m_j| = 3/2$ (c) and the completely-filled $j_3 = 3/2 |m_j| = 1/2$ (d). The dashed blue line on panel (a) is the reproduction of the ARPES structure from [121].

To go further in the analysis, figure 9 depicts the momentum-resolved spectral function, as well as its orbital-resolved version. The completely filled $j_3 = 3/2 |m_j| = 1/2$ state is visible (panel (d)), as well as the partially filled character of the $j_3 = 3/2 |m_j| = 3/2$ (panel (c)) and $j_0 = 1/2$ 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 $j_3 = 3/2 |m_j| = 1/2$ bands, are indeed about 0.05 eV higher in energy in our calculated spectral function.

From figures 9(b) and (c), one observes that the Fermi level is crossed by the renormalized $j_3 = 3/2 |m_j| = 3/2$ band at 0.20 Å$^{-1}$ along $\Gamma-X$ and at 0.21 Å$^{-1}$ along $\Gamma-M$, while the renormalized $j_0 = 1/2$ band is responsible for all other crossings. This allows us to label the hole-like $\alpha$-pocket as being of $j_3 = 3/2 |m_j| = 3/2$ type, whereas the two other pockets $j_M$ and $j_\beta$ are mostly of type $j_0 = 1/2$. Using the quasiparticle weight of each state ($Z_{1/2} = 0.535$ and $Z_{3/2, |m_j| = 0.675}$), we evaluate the Fermi velocity at each crossing along the path $[\Gamma MX]$; we find a huge variation in the values depending on $\mathbf{k}$ and give in table 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: $m^* \Phi = h^2 / 4 \pi$ . The DMFT results shown in table 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 in explaining the different behavior of Sr$_2$RhO$_4$ and Sr$_2$IrO$_4$.

In Sr$_2$IrO$_4$, Coulomb correlations enhance the spin–orbital polarization, such as to fill the $j_{\text{eff}} = 3/2$ states entirely, leading to a half-filled $j_0 = 1/2$ 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 polarization 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 localize 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 $N^{[228]}$. 
Localizing electrons in a single-orbital system therefore needs a critical interaction which is smaller by a factor of roughly 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 realize 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 in 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 properties of a system. The calculation of effective degeneracy is the result of a complex interplay of 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 series of d^1 compounds SrVO_3, CaVO_3, LaTiO_3, YTiO_3 [10].

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 Mott insulating picture for Sr_2IrO_4 with the insulating nature of structural distortions, spin–orbit coupling and Coulomb correlations. We have analyzed in detail the spectral properties of Sr_2IrO_4 with the insulating nature of Sr_2RhO_4, a spin difference in the resulting properties. A detailed analysis of the spectral properties of Sr_2IrO_4 is left for future work.

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Appendix. Generalized partial Θ-projectors and spectral function

In order to calculate quantities for a given atom α and a particular orbital (spin) character j (m)—such as the spectral functions $A^{\alpha\beta}_{\alpha\beta}(\omega)$—a set of partial projectors called ‘Θ-projectors’ was built. Contrary to the previously introduced Wannier projectors $P^\alpha_0(\mathbf{k})$, 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 with an atom α, one can write the spin–σ contribution of the eigenstate $\psi_{\alpha}(\mathbf{r})$ as:

$$\phi_{\alpha\sigma}^\ell(\mathbf{r}) = \sum_{\nu=0}^{+\ell} \sum_{m=-\ell}^{\ell} \{ A_{\alpha\sigma}^{\ell\nu}(\mathbf{k}, \sigma) \ u_{\alpha,\nu,1m,1}^{\ell}(\mathbf{r}^\alpha) + B_{\alpha\sigma}^{\ell\nu}(\mathbf{k}, \sigma) \ u_{\alpha,\nu,2m,1}^{\ell}(\mathbf{r}^\alpha) \} + C_{\alpha\sigma}^{\ell\nu}(\mathbf{k}, \sigma) \ u_{\alpha,\nu,3m,1}^{\ell}(\mathbf{r}^\alpha),$$

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

$$\forall i \quad u_{\alpha,\nu,\sigma}^{\ell}(\mathbf{r}^\alpha) = \sum_{j=1}^{3} c_{j} \tilde{u}_{\alpha,\nu,\sigma}^{\ell}(\mathbf{r}^\alpha).$$

$$C = \begin{pmatrix} 1 & 0 & (\tilde{u}_{\alpha,\nu,1m,1}^{\ell})^2 \\ 0 & (\tilde{u}_{\alpha,\nu,1m,2}^{\ell})^2 & 1 \\ (\tilde{u}_{\alpha,\nu,1m,3}^{\ell})^2 & (\tilde{u}_{\alpha,\nu,2m,1}^{\ell})^2 & 1 \end{pmatrix}.$$  

We can then rewrite equation (A.1) as:

$$\psi_{\alpha}(\mathbf{r}) = \sum_{\ell=0}^{\ell_{\text{max}}} \sum_{m=-\ell}^{\ell} \sum_{j=1}^{3} \Theta_{\alpha,\nu,\sigma}^{\ell}(\mathbf{k}) \tilde{u}_{\alpha,\nu,\sigma}^{\ell}(\mathbf{r}^\alpha).$$

The matrix elements $\Theta_{\alpha,\nu,\sigma}^{\ell}(\mathbf{k})$ are the ‘Θ-projectors’, which are thus defined by:

$$\Theta_{\alpha,\nu,\sigma}^{\ell}(\mathbf{k}) = \langle \tilde{u}_{\alpha,\nu,\sigma}^{\ell}(\mathbf{r}) | \varphi_{\alpha}(\mathbf{r}) \rangle = A_{\alpha\sigma}^{\ell\nu}(\mathbf{k}, \sigma) c_{1j} + B_{\alpha\sigma}^{\ell\nu}(\mathbf{k}, \sigma) c_{2j} + C_{\alpha\sigma}^{\ell\nu}(\mathbf{k}, \sigma) c_{3j}.$$  

(A.4)
Contrary to the implementation of [180], there are now a couple of Θ-projectors associated with each band index ν, \( \Theta_{\nu m_\alpha}^{\gamma m_\beta}(k) \) 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:

\[
\Theta_{\nu m_\alpha}^{\gamma m_\beta}(k) = \sum_{m, \sigma} C_{\nu m, \sigma}^{\gamma m, \sigma}(k) . \tag{A.5}
\]

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

\[
A(k, \omega) = -\frac{1}{\pi} \text{Im} \left[ G(k, \omega) \right] , \tag{A.6}
\]

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

\[
A_{\nu m_\alpha}^{\nu m_\beta}(k, \omega) = -\frac{1}{\pi} \text{Im} \left[ \sum_{\omega^\prime} \sum_{\nu^\prime} G_{\nu^\prime \nu}(k, \omega + \omega^\prime) (\Theta_{\nu^\prime m_\alpha}^{\nu m_\beta}(k))^\dagger \right] . \quad \tag{A.7}
\]

where the band indices \( \nu, \nu^\prime \) run over both spin and orbital quantum numbers.

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