Ab initio analysis of the tight-binding parameters and magnetic interactions in Na$_2$IrO$_3$

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By means of density functional theory (DFT) calculations (with and without inclusion of spin-orbit (SO) coupling) we present a detailed study of the electronic structure and corresponding microscopic Hamiltonian parameters of Na$_2$IrO$_3$. In particular, we address the following aspects: (i) We investigate the role of the various structural distortions and show that the electronic structure of Na$_2$IrO$_3$ is exceptionally sensitive to structural details. (ii) We discuss both limiting descriptions for Na$_2$IrO$_3$; quasi-molecular orbitals (small SO limit, itinerant) versus relativistic orbitals (large SO limit, localized) and show that the description of Na$_2$IrO$_3$ lies in an intermediate regime. (iii) We investigate whether the nearest neighbor Kitaev-Heisenberg model is sufficient to describe the electronic structure and magnetism in Na$_2$IrO$_3$. In particular, we verify the recent suggestion of an antiferromagnetic Kitaev interaction and show that it is not consistent with actual or even plausible electronic parameters. Finally, (iv) we discuss correlation effects in Na$_2$IrO$_3$. We conclude that while the Kitaev-Heisenberg Hamiltonian is the most general expression of the quadratic spin-spin interaction in the presence of spin-orbit coupling (neglecting single-site anisotropy), the itinerant character of the electrons in Na$_2$IrO$_3$ makes other terms beyond this model (including, but not limited to 2nd and 3rd neighbor interactions) essential.

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I. INTRODUCTION

The electronic and magnetic behavior of layered 5$d$ transition metal oxides has been a subject of intensive discussion in the last years. Particularly exciting has been the suggestion by the authors of Ref. 2 that hexagonal iridates such as Na$_2$IrO$_3$ are a realization of the nearest neighbor Kitaev-Heisenberg (nnKH) model:

$$H_{ij}^{(n)} = 2K S_i^+ S_j^- + JS_i^- S_j^-$$

This proposal is based on the premise that spin-orbit (SO) coupling is the most important energy scale for the description of these systems so that Ir 5$d$ $t_{2g}$ orbitals are written in terms of $j_{eff} = 1/2$ and $j_{eff} = 3/2$ relativistic orbitals, with the Kramers doublet $j_{eff} = 1/2$ represented by the operator $S = 1/2$. The combination of Kitaev and Heisenberg terms leads to a complex phase diagram with various magnetic and spin-liquid phases. Obviously, some of these properties can only manifest themselves when the Kitaev term dominates or is at least comparable to the Heisenberg term. Also, other possible contributions, such as magnetic anisotropy, ring exchange or biquadratic exchange, to mention a few, may alter the phase diagram and the properties of the model considerably. Most importantly, while the Kitaev-Heisenberg expression is the most general fully-symmetric expression for anisotropic pairwise magnetic interactions in the second order in spin in the presence of SO coupling (just as the Heisenberg exchange represents the same in the isotropic non-relativistic case), it is not necessarily short ranged in the presence of considerable itinerancy.

So far, essentially all analyses of the nnKH model for Na$_2$IrO$_3$ have been performed in the localized limit, where an assembly of weakly interacting relativistic atomic orbitals is assumed to be a good starting approximation. On the other hand, first principles calculations suggest considerable delocalization of electrons over individual Ir hexagons building quasi-molecular orbitals (QMOs). The associated “itinerant” energy scale (the band width) is $\approx 1.5$ eV, to be compared to the single-site spin-orbit splitting scale $3/2(\lambda) \approx 0.7$ eV and the Hubbard and Hund’s rule correlation energy scale of $U - J_H \approx 0.5 - 1$ eV. This makes the entire premise of the nnKH model questionable. At the same time, it has also been pointed out that the nnKH model with the addition of the 2nd and 3rd neighbors Heisenberg interaction is easier to reconcile with the experimental data. Such relatively long-range exchange interaction is another hallmark of considerable itinerancy (here and below, when we speak of itinerancy, we imply mostly delocalization over Ir$_6$ rings, but not necessarily over the entire crystal).

In the present work we revisit and discuss the validity of both limiting descriptions for Na$_2$IrO$_3$; itinerant (QMO picture) versus localized ($j_{eff} = 1/2$ Kramers doublet). To this end, we perform a thorough analysis of the electronic properties of Na$_2$IrO$_3$ within non-relativistic and relativistic density functional theory (DFT) and derive, using projection on Wannier functions, the relevant hopping parameters and show that QMOs are naturally obtained as linear combinations of Ir $t_{2g}$ Wannier functions. We discuss the relation between the quasi-molecular orbital and the relativistic orbital, $j_{eff}$, representations and show that the behavior of Na$_2$IrO$_3$ lies in...
between a fully localized and fully itinerant description. Finally, the parametrization of the electronic bandstructure allows us to provide realistic estimates for the model parameters in the localized $nnKH$ model. We thus investigate whether we are close to a regime where the Kitaev interaction plays a decisive role or not.

Quite unexpectedly, we find that Na$_2$IrO$_3$ is an example of a material where minor details of the crystal structure can dramatically affect the electronic structure, and simple guessing of the band structure parameters, or estimating them from simplified crystallographic models (so far all model calculations for this compound were utilizing one or the other approach) can be exceptionally misleading. In fact some of the models energetically discussed in the community, while of undeniable theoretical appeal, are not even qualitatively close to the actual parameter range in Na$_2$IrO$_3$.

While this particular compound is very intriguing and has been enjoying extraordinary popularity lately, we want to emphasize that this strong dependence of the electronic properties on details of the crystal structure is an important result, whose relevance goes beyond specifically Na$_2$IrO$_3$ and is likely true for many other materials based on honeycomb transition-metal layers.

The paper is organized as follows. In Section II we review the crystal structure and magnetic properties of Na$_2$IrO$_3$. In Section III we provide details of the DFT calculations and the projector method. In Section IV we present the results of the electronic structure analysis without inclusion of spin-orbit coupling and analyze the role of the structural distortions in Na$_2$IrO$_3$. In Section V we investigate the role of spin-orbit coupling and discuss the relation between the QMOs and the relativistic orbitals ($j_{\text{eff}}$). In this context, we discuss whether the existing experimental situation can distinguish between the DFT description (with the resulting itinerancy) and localized ($j_{\text{eff}} = 1/2$) models. We proceed with an analysis of the single-site magnetic anisotropy in Na$_2$IrO$_3$ and find it to be relevant (pure $j_{\text{eff}} = 1/2$ states do not have any single-site anisotropy). In Section VI we provide ab initio-derived estimates for the parameters appearing in the Kitaev and Heisenberg terms in Na$_2$IrO$_3$ and discuss the validity of the $nnKH$ model by considering the experimentally observed magnetic order and attempts to explain it from a local point of view. Finally in Section VII we present our conclusions.

II. CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF Na$_2$IrO$_3$

Na$_2$IrO$_3$ crystallizes in the monoclinic space group C$2/m$ (No. 12) and consists of Ir honeycomb layers (Fig. 1(b)) stacked along the monoclinic c axis (Fig. 1(a)) with an in-plane offset along a. Na ions occupy both the interlayer positions and 1/3 of the in-plane positions at the centers of Ir hexagons. This structure can be visualized as proceeding from NaIrO$_2$ with a CdI$_2$ structure with triangular IrO$_2$ layers. In these layers 1/3 of the in-plane iridium atoms are substituted by extra Na, i.e., its formula can be written as Na(Na$_{1/3}$Ir$_{2/3}$)O$_2$, which, multiplied by 3/2, gives the usual formula of Na$_2$IrO$_3$.

An idealized crystal structure of this kind corresponds to having all nearest neighbor (NN) Ir-Ir and NN Ir-O distances equal and Ir-O-Ir angles of 90 degrees. The experimental structure of Na$_2$IrO$_3$ departs from the idealized case and shows a few distortions: (i) orthorhombic distortion that introduces inequality among NN Ir-Ir distances and among NN Ir-O distances, (ii) IrO$_6$ octahedra rotations that place O atoms on the faces of a cube containing an Ir hexagon (see Fig. 2 of Ref. [5]) and (iii) trigonal distortion which is a compression of the IrO$_6$ octahedra in the c-direction that induces a departure from 90 degrees of the Ir-O-Ir angles. In Section VII we will discuss the effect of these distortions on the electronic structure of Na$_2$IrO$_3$. 

![Crystal structure of Na$_2$IrO$_3$. (a) Projection on the ac plane and (b) projection on the ab plane.](image)

FIG. 1: Crystal structure of Na$_2$IrO$_3$. (a) Projection on the ac plane and (b) projection on the ab plane.
employ the Perdew-Burke-Ernzerhof generalized gradient VI.

In Section V, we will discuss this proposition correctly includes all the terms contributing to NN Ir-Ir of a stripe order by the nnKH model, which is much smaller than \( \Theta_{\text{CW}} \). The magnetic pattern observed experimentally corresponds to a zigzag ordering, in contrast to the prediction of a tight-binding (TB) model where the TB Ir 5d electrons as will be discussed in Section V.

The magnetic pattern observed experimentally corresponds to a zigzag ordering, in contrast to the prediction of a stripe order by the nnKH model as will be discussed in Section V. Recently, Chaloupka et al. argued that such a zigzag ordering can be also obtained by the nnKH model, when one correctly includes all the terms contributing to NN Ir-Ir exchange. In Section V, we will discuss this proposition in more detail.

III. METHOD

In this work we perform DFT calculations using the linearized augmented plane wave (LAPW) method as implemented in the full-potential code WIEN2k\(^{12}\). We employ the Perdew-Burke-Ernzerhof generalized gradient approximation\(^{13}\) to the DFT exchange-correlation functional and set the basis-size controlling parameter \( R_K \) to 7. We consider a mesh of 500 \( k \)-points in the first Brillouin zone. Relativistic effects are treated within the second variational approach. Convergence with respect to relevant parameters (the \( k \)-point mesh, the \( R_K \) and the second variational energy cutoff, etc.) has been carefully checked.

A. Calculation of hopping integrals

In order to be able to discuss various Ir-Ir 5d processes, we parameterize our non-relativistic DFT results in terms of a tight-binding (TB) model where the TB Ir 5d hopping parameters are obtained through the Wannier function projection formalism proposed in Ref.\(^{15}\) and generalized to molecular Wannier functions in Ref.\(^{16}\). We first construct Wannier function projectors \( P^\alpha_{mm}(k) \) for the three \( t_{2g} \) Ir 5d orbitals and calculate the TB Hamiltonian \( H^{\text{TB}}(k) \) (in matrix form) via

\[
H^{\text{TB}}(k) = P(k)D(k)P^\dagger(k),
\]

where \( D(k) \) is a diagonal matrix of Ir 5d \( t_{2g} \) Bloch eigenvalues and the matrix \( P(k) \) is formed by the projectors \( P^\alpha_{mm}(k) \). Here, \( \alpha, \beta, m, \) and \( \nu \) run over equivalent Ir atoms in the unit cell, Ir \( t_{2g} \) orbitals, and Bloch bands, respectively. \( \text{Na}_2\text{IrO}_3 \) has two Ir per unit cell and only the six Ir \( t_{2g} \) bands near the Fermi level \( E_F \) are considered in the construction of projectors.

We calculate the hopping integral \( t_{\alpha\alpha\beta\gamma}^{mm'}(\mathbf{R},\mathbf{R}') \) between orbital \( m \) on Ir atom \( \alpha \) in the unit cell at a distance \( \mathbf{R} \) from a reference unit cell and orbital \( m' \) on Ir atom \( \alpha' \) in the unit cell at a distance \( \mathbf{R}' \) from a reference unit cell by integrating \( H^{\text{TB}}(k) \) over \( N_k \) \( k \)-vectors in the first Brillouin zone:

\[
t_{\alpha\alpha\beta\gamma}^{mm'}(\mathbf{R},\mathbf{R}') = \frac{1}{N_k} \sum_{\mathbf{k}} H^{\text{TB}}_{mm',\alpha\alpha',\beta\gamma}(\mathbf{k}) e^{-i\mathbf{k} \cdot (\mathbf{R}-\mathbf{R}')}.
\]

where \( H^{\text{TB}}_{am,\alpha'm',\beta\gamma}(\mathbf{k}) \) are the matrix elements of \( H^{\text{TB}}(k) \). Correspondingly, the diagonal matrix elements \( t_{\alpha\alpha}^{mm} \) give the on-site energies.

B. Construction of quasi-molecular projectors

As was argued in Ref.\(^5\), the most natural description of the electronic structure of Na2IrO3 is in terms of quasi-molecular (QMO) orbitals localized on a hexagon. The strongest Ir-Ir hopping is between \( 5d \) \( t_{2g} \) orbitals of neighboring iridium ions via common oxygens. In this case, an electron on a given Ir \( t_{2g} \) orbital propagates around an Ir hexagon with the peculiarity than only a certain \( t_{2g} \) orbital at each Ir participates in the hopping, e.g. Ir1(xy)-Ir2(zx)-Ir3(yz)-Ir4(xy)-Ir5(xz)-Ir6(yz) (see Fig. 2 of Ref.\(^5\)). These QMOs are analogous to the molecular orbitals of the benzene molecule \( C_6H_6 \) except for the fact that in benzene the same \( p \)-orbital on each carbon ion participates in the formation of the molecular orbital while in \( \text{Na}_2\text{IrO}_3 \), as described above, different \( t_{2g} \) orbitals are involved in one QMO and the three \( t_{2g} \) orbitals on one Ir ion contribute to three different neighboring QMOs. We elaborate the details of the construction of the QMOs in what follows.

QMO projectors \( P_{M\mu}(k) \) are obtained as linear combinations of Ir \( t_{2g} \) projectors \( P_{M\mu}(k) \):

\[
P_{M\mu}(k) = \sum_M U_{M,M} T_M(k) P_{M\mu}(k).
\]

where in the Ir \( t_{2g} \) projectors \( P_{M\mu}(k) \), the index \( M \) combines now the atomic index \( \alpha \) and orbital index \( m \), i.e. \( M \) and orbital index \( m \), i.e. \( M \)
runs over all \( t_{2g} \) orbitals of all equivalent Ir atoms. With QMOs ordered as \( M = A_{1g}, E_{2u}, E_{1g}, B_{1u}, E_{1g}, E_{2u} \) and Ir \( t_{2g} \) orbitals ordered as \( M = xy^1, xz^1, yz^1, xy^2, xz^2, yz^2 \) (the upper index labels Ir atoms), \( U \) is given by \( \omega = \exp(i\pi/3) \)

\[
U = \begin{pmatrix}
1 & 1 & 1 & 1 & 1 & 1 \\
1 & \omega^4 & \omega^2 & -1 & \omega & \omega^5 \\
1 & \omega^2 & \omega^4 & 1 & \omega^2 & \omega^4 \\
1 & 1 & 1 & -1 & -1 & -1 \\
1 & \omega & \omega^2 & 1 & \omega^4 & \omega^2 \\
1 & \omega^2 & \omega & 1 & \omega^5 & \omega
\end{pmatrix},
\]

and \( T_M(k) \) are the Bloch factors, accounting for the fact that the 6 sites forming a QMO belong to several different unit cells. Actual values for these factors depend on the manner in which a particular band structure code selects the unit cell (see the Appendix for the WIEN2k settings).

IV. NON-RELATIVISTIC ELECTRONIC STRUCTURE

In this Section we analyze and discuss the Ir-Ir 5d \( t_{2g} \) tight-binding parameters for Na\(_2\)IrO\(_3\) up to second nearest neighbors. As mentioned in Section III three structural distortions are present in Na\(_2\)IrO\(_3\): orthorhombic distortion, IrO\(_6\) octahedra rotation and trigonal distortion. Besides, the stacking of the honeycomb planes inherently violates the rhombohedral symmetry even if each plane is ideal. The formation of QMOs relies on the dominance of intrahexagon hopping \(^{18}\) and therefore is sensitive to structural details. Therefore it is important to understand the role of structural distortions in establishing electron hopping paths. This motivates us to study electronic properties of a number of artificially idealized Na\(_2\)IrO\(_3\) unit cells where structural distortions of different types are systematically eliminated \(^{20}\). Such a procedure has proven very useful \(^{21}\) in understanding the behavior of Sr\(_2\)IrO\(_4\).

We consider four different crystal structures: (i) the experimental crystal structure \(^{5}\), \( S_{\text{exp}} \), (ii) an artificially idealized Na\(_2\)IrO\(_3\) unit cell, \( S_1 \), where the orthorhombic distortion has been removed from the experimental crystal structure, (iii) an artificially idealized Na\(_2\)IrO\(_3\) unit cell, \( S_2 \), where the IrO\(_6\) octahedra rotations have been removed from \( S_1 \), and (iv) an artificially idealized Na\(_2\)IrO\(_3\) unit cell, \( S_3 \), where the trigonal distortion has been removed from \( S_2 \). Table I shows a comparison of total (non-magnetic) DFT energies for the various structures. As it is to be expected, the experimental structure is the energetically most stable case. Tight-binding hopping parameters between Ir \( t_{2g} \) orbitals up to second nearest neighbors calculated for the four structures are given in Table II and schematically represented in Fig. 3. We consider the following rationale for labeling of the hopping parameters Eq. (4). In the experimental structure of Na\(_2\)IrO\(_3\) there are two first NN Ir-Ir distances and two second NN Ir-Ir distances due to the fact that the Ir\(_6\) hexagons are not perfect. We denote the corresponding \( \text{Ir} \ t_{2g} \) hopping parameters as \( t_1 \) and \( t_2 \) for the first NN and, respectively, \( t_2 \) and \( t_2 \) for the second NN hoppings. Further, we have various possible hoppings between equal and different \( t_{2g} \) orbitals. Regarding first NN, we denote \( t_{10} \) and \( t_{10} \) the hoppings between unlike \( t_{2g} \) orbitals via O \( p \) states (Fig. 3(a)). \( t_{10} \) and \( t_{10} \) denote NN direct hoppings of \( \sigma \)-type. \( t_{11} \) and \( t_{11} \) denote NN hoppings between like orbitals lying in parallel planes. In the ideal structure such hoppings consist of linear combinations with equal weight of \( d\bar{\pi} \) and \( d\sigma \) bonds. \( t_{1\perp} \) and \( t_{1\perp} \) denote NN hoppings between unlike orbitals lying in perpendicular planes (see Figs. 3(b) and (c)).

Regarding the second NN hopping parameters, \( t_{20} \) and \( t_{20} \) denote hoppings between unlike orbitals via O \( p \) and Na \( s \) states (Fig. 3(e)). \( t_{2a} \) and \( t_{2b} \) (\( t_{2a} \) and \( t_{2b} \)) denote hoppings between like orbitals as shown in Fig. 3(d) and \( t_{2c} \), \( t_{2d} \) and \( t_{2e} \) (\( t_{2c} \), \( t_{2d} \) and \( t_{2e} \)) denote hoppings between unlike orbitals (Fig. 3(e)).

A. Experimental crystal structure

Previous electronic structure calculations \(^{5}\) have identified the dominant hopping integrals for Na\(_2\)IrO\(_3\) to be \( t_{10} \) and \( t_{20} \) (as well as \( t_{10} \) and \( t_{20} \)); further on, if not explicitly stated otherwise, we refer to both equivalent \( t_1 \) (\( t_2 \)) and \( t_1 \) (\( t_2 \)) when writing \( t_1 (t_2) \). In Table I column \( S_{\text{exp}} \) we present the complete list of hopping parameters up to the second nearest neighbors. A TB model based only on these hopping integrals provides already a reasonable description of Na\(_2\)IrO\(_3\) Ir \( t_{2g} \) states near the Fermi level \( E_F \) [Fig. 3(a)].

We first note a very good agreement between the \( t_{10} \) (~75 meV) and \( t_{20} \) (~75 meV) values obtained with our WIEN2k-based projection method and with the FPLO code \(^{13}\) as was used in Ref. 5. These leading Ir \( t_{2g} \) hoppings strongly tend to confine the electron’s motion to a single Ir hexagon and, as a result, the electronic structure of Na\(_2\)IrO\(_3\) near the Fermi level is dominated by the formation of well separated and relatively weakly dispersive QMOs \(^{5}\). On an Ir hexagon, as shown above, each Ir atom participates with one of its \( t_{2g} \) orbitals (see Fig. 2 of Ref. 5). These orbitals combine to form six QMOs according to the unitary transformation Eq. (5). In support of this picture, Fig. 3(a) shows the density of states of Na\(_2\)IrO\(_3\) projected onto the six QMOs (singlets \( A_{1g} \) and \( B_{1u} \) and doublets \( E_{2u} \) and \( E_{1g} \)), where states
FIG. 3: Schematic representation of Ir-Ir $t_{2g}$ hopping paths up to second nearest neighbor in Na$_2$IrO$_3$.

with certain predominant QMO character are clearly separated in energy from one another. The near-degeneracy of $A_{1g}$ and $E_{2u}$ states around $E_F$ is rather accidental resulting from the $t_{1O}/t_{2O} \sim -3.6$ ratio (see Table II and Ref. 5). The real-space representations of the QMO Wannier functions onto which the Na$_2$IrO$_3$ DOS is being projected are shown in Fig. 6. The QMO Wannier functions were constructed as described in Section II by explicitly accounting for the location of each Ir $t_{2g}$ orbital in the crystal.

Other NN and second NN hopping processes involving intraorbital and interorbital hoppings (see Table II) allow an electron to jump from one QMO to another and hence are responsible for the band dispersion. Many of those hoppings are of the same order of magnitude (although mostly by at least an order of magnitude smaller) than $t_{2O}$, like, for example, $t_{1\parallel}$ and $t_{1\parallel}$. For the “$z$” bond such hoppings will be between $xz$ and $xz$ or $yz$ and $yz$ orbitals (see Fig. 3 (b)). These hoppings are equal to 47.7, 30.0, and 33.1 meV, depending on the NN bond (see Table II). In fact, such appreciable variations in magnitude, which violate the $D_{6h}$ symmetry of an ideal Ir hexagon, are ubiquitous among the hoppings that connect neighboring QMOs. Some of them even change sign, as, for instance $t_{1\sigma}$ and $t_{1\sigma}$. This feature results from the orthorhombic stacking, distortions within the Ir$_2$Na planes, and rotations of IrO$_6$ octahedra.

B. Structure $S_1$ obtained by removing the orthorhombic distortion

We now consider an idealized Na$_2$IrO$_3$ structure without the orthorhombic distortion of Ir hexagons; this structure, which we call $S_1$, as well as other structures in this Section, is tabulated in the Appendix. In the structure $S_1$: (i) all intralayer Ir-Ir bonds are of the same length, i.e., the $D_{6h}$ symmetry of an Ir hexagon is restored, (ii) all NN Ir-O bonds are of the same length, (iii) all Ir-O-Ir bond angles are equal to $98.7^\circ$, and (iv) the oxygens lie on the faces of a cube drawn around an Ir hexagon (see Fig. 2 of Ref. 5). The 3D crystal structure, though, remains orthorhombic in this approximation, due to the presence of multiple Ir layers. This explains small residual variations among the nominally equivalent TB model parameters (Table II column $S_1$): E.g., comparing parameters labeled with and without overbar; also, onsite energies like the $xy$ on-site energy is slightly lower than the $xz/yz$ on-site energy. However, these variations of $t_{2g}$ orbital on-site energies, as well as of equivalent hopping integrals, are now noticeably smaller than in the experimental Na$_2$IrO$_3$ structure.
only that considers calculated using DFT (black solid lines) and a TB model 0

FIG. 4: Na$_2$IrO$_3$ bandstructures near the Fermi level $E_F = 0$ calculated using DFT (black solid lines) and a TB model that considers only up to NNN hopping processes between Ir $t_{2g}$ orbitals (dashed lines). The data are obtained with (a) experimental crystal structure and idealized structures (b) $S_1$, (c) $S_2$, and (d) $S_3$.

TABLE II: Nearest neighbor (NN) and second NN hopping integrals in meV between Ir $t_{2g}$ orbitals for the experimental structure and three idealized structures $S_1$, $S_2$, $S_3$ of Na$_2$IrO$_3$ (see text and Appendix for a description of the structures and parameter labeling). The NN = 0 data are Ir $t_{2g}$ on-site energies and interorbital energies and interorbital hoppings; the NN = 1 and NN = $\bar{1}$ (NN = 2 and NN = $\bar{2}$) data are hoppings over nonequivalent (due to orthorhombic distortion) NN (second NN) Ir bonds.

| NN   | $S_{exp}$ | $S_1$ | $S_2$ | $S_3$ |
|------|-----------|-------|-------|-------|
| 0    | $xy \rightarrow xy$ | -448.8 -422.9 -422.8 -601.1 |
|      | $xz \rightarrow xz$ | -421.5 -421.8 -421.2 -601.1 |
|      | $yz \rightarrow yz$ | -421.5 -421.8 -421.2 -601.1 |
|      | $xy \rightarrow xz$, $xy \rightarrow yz$ | -27.8 -26.4 -21.2 -13.5 |
|      | $xz \rightarrow yz$ | -23.1 -25.2 -18.8 -14.7 |
| 1    | $xy \rightarrow xy$ ($t_{1\bar{1}}$) | 47.7 34.1 27.8 120.8 |
|      | $xy \rightarrow xz$, $xy \rightarrow yz$ ($t_{1\bar{O}}$) | 269.6 268.5 231.7 209.7 |
|      | $xy \rightarrow xz$, $xy \rightarrow yz$ ($t_{1L}$) | -25.6 -16.6 43.7 -5.3 |
|      | $xz \rightarrow xz$, $yz \rightarrow yz$ ($t_{1\bar{1}}$) | 30.0 33.2 17.2 118.9 |
|      | $xz \rightarrow xz$, $yz \rightarrow yz$ ($t_{1\bar{O}}$) | -20.7 3.5 -66.5 -381.6 |
|      | $xz \rightarrow yz$ ($t_{1L}$) | -21.4 -16.4 41.7 -4.9 |
| 2    | $xy \rightarrow xy$ ($t_{2\bar{1}}$) | 25.4 0.2 -65.5 -382.8 |
|      | $xy \rightarrow xz$, $xy \rightarrow yz$ ($t_{2\bar{O}}$) | -11.9 -17.6 46.9 -5.3 |
|      | $xz \rightarrow xz$, $yz \rightarrow yz$ ($t_{1\bar{L}}$) | 33.1 33.9 21.2 120.5 |
|      | $xz \rightarrow yz$ ($t_{1\bar{O}}$) | 264.4 264.8 228.7 211.7 |
|      | $x \rightarrow y$ ($t_{2a}$) | -3.5 -2.6 -18.9 2.0 |
|      | $xy \rightarrow xz$, $xy \rightarrow yz$ ($t_{2\bar{O}}$) | -75.8 -77.4 -94.7 -82.1 |
|      | $xy \rightarrow xz$, $xy \rightarrow yz$ ($t_{2c}$) | -36.5 -35.3 -52.1 -38.5 |
|      | $xy \rightarrow xz$, $xy \rightarrow yz$ ($t_{2a}$) | 12.5 10.1 1.7 6.9 |
|      | $xy \rightarrow xz$, $xy \rightarrow yz$ ($t_{2\bar{O}}$) | -21.4 -19.2 -7.3 1.9 |
|      | $xz \rightarrow xz$, $yz \rightarrow yz$ ($t_{2\bar{a}}$) | -0.6 -3.1 -16.6 1.4 |
|      | $xz \rightarrow xz$, $yz \rightarrow yz$ ($t_{2\bar{O}}$) | -1.5 -1.6 -1.0 5.7 |
|      | $xz \rightarrow yz$ ($t_{2c}$) | 18.6 -19.0 -7.1 2.4 |
|      | $xz \rightarrow yz$ ($t_{2\bar{a}}$) | 10.2 10.2 2.4 6.6 |
| 3    | $xy \rightarrow xy$ ($t_{3\bar{1}}$) | -1.4 -1.4 -1.2 5.7 |
|      | $xy \rightarrow xz$, $xy \rightarrow yz$ ($t_{3\bar{a}}$) | -1.9 -19.2 -8.4 2.1 |
|      | $xy \rightarrow xz$, $xy \rightarrow yz$ ($t_{3\bar{O}}$) | 9.3 10.2 0.7 7.5 |
|      | $xz \rightarrow xz$, $yz \rightarrow yz$ ($t_{3\bar{a}}$) | -1.4 -3.0 -17.7 1.5 |
|      | $xz \rightarrow yz$ ($t_{3\bar{O}}$) | -77.0 -78.0 -95.2 -81.9 |
|      | $xz \rightarrow yz$ ($t_{3\bar{c}}$) | -30.4 -35.1 -51.6 -38.9 |

We conclude that removal of the orthorhombic distortion restores (to a certain degree) the degeneracy of the Ir $t_{2g}$ orbitals, but does not change the hierarchy of hopping integrals. In the structure $S_1$, the $t_{1\bar{O}}$ and $t_{2\bar{O}}$ values are close to the respective values in the experimental Na$_2$IrO$_3$ structure and, as a consequence, the overall structure of the $t_{2g}$ bands is only slightly changed [Figs. 4 (b) and 5 (b)].

C. Structure $S_2$ obtained by removing the IrO$_6$ octahedra rotations

In the structure $S_1$ that we designed in the previous Section, two types of distortions are still present: (i) trigonal squeezing of IrO$_6$ octahedra along the (111) direc-
tion perpendicular to Ir hexagon planes and (ii) IrO$_6$ octahedra rotations that place O atoms on the cube’s faces. We now consider structure $S_2$, where the IrO$_6$ octahedra rotations are removed from $S_1$. In this structure, the Na-O and Ir-O bond lengths are the same (in the experimental structure, the former is considerably longer). This feature enhances the second NN hopping processes through Na $s$ states, such as $t_{2o}$, $t_{2o}$, $t_{2c}$ (and the equivalent overbar hoppings) as shown in Table II column $S_2$. At the same time, the NN O-assisted hopping $t_{1o}$ gets reduced and the $t_{1o}/t_{2o}$ ratio decreases to $\sim -2.4$, resulting in a larger separation of the lowest ($B_{1u}$) band from the rest of $t_{2g}$ bands [Fig. 4 (c)]. Formation of QMOs still takes place in structure $S_2$ [Fig. 5(c)], but the QMO bands are more dispersive compared to the experimental or $S_1$ structures, due to increased interhexagon NN hopping integrals $t_{1o}$, $t_{1\perp}$ (and equivalent $t_{1\sigma}$, $t_{1\perp\sigma}$): thus, one observes broadening of the $A_{1g}$ band and redistribution of weight away from the $E_{2u}$ doublet.

D. Structure $S_3$, obtained by removing the trigonal distortion

We finally consider a most idealized Na$_2$IrO$_3$ structure $S_3$ without the trigonal distortion, i.e., with 90° Ir-O-Ir bond angles. Importantly, one can only remove this distortion, while keeping the Ir-O bond length the same, if...
the Ir-Ir bonds are shortened. Because of that, the hierarchy of hopping integrals changes drastically (Table I column $S_3$). The dominant hopping is now the direct NN hopping between like orbitals $t_{1\sigma}$ (and the equivalent $t_{1\rho}$) reaching $\sim -380$ meV, while the O-assisted hopping $t_{1O}$ ($t_{1O}$) has been reduced to $\sim 210$ meV. Accordingly, the large interhexagon interaction destroys the QMO picture, as illustrated by the strongly dispersive $t_{2g}$ manifold in Fig. 4(d) and the delocalization of individual QMO characters over the whole DOS range in Fig. 5(d).

We also observe that the main reason for the trigonal squeezing is the geometrical effect of optimizing simultaneously the Ir-Ir and Ir-O bonds. As a result, even though the on-site $t_{2g}$ orbitals split into an $a_{1g}$ singlet and an $e_g$ doublet, this is not a strong effect and not the driving force for the squeeze, as it is often assumed in the spirit of localized limit and the Jahn-Teller effect.

Summarizing these results, in the $S_3$ structure, the NN direct hopping increases by an order of magnitude compared to the experimental Na$_2$IrO$_3$ structure and the NN O-assisted hopping get suppressed. Therefore we conclude that structural distortions of all types in Na$_2$IrO$_3$ act constructively to enhance the intra-hexagon effective hopping parameters (such as $t_{1O}$ and $t_{2O}$) and suppress the inter-hexagon ones (such as NN direct hopping) favoring the formation of QMOs.

V. SPIN-ORBIT COUPLING

We proceed now with the analysis of the electronic structure of Na$_2$IrO$_3$ in the presence of spin-orbit (SO) coupling. Previous relativistic DFT calculations showed that Na$_2$IrO$_3$ states near the Fermi level experience strong relativistic splitting with pronounced concentration of $j_{\text{eff}} = \frac{3}{2}$ character in the upper two bands. However, the Na$_2$IrO$_3$ relativistic states seem to preserve their QMO identity as well (see Fig. S6 (b) of Ref. 5). In order to understand such duality, we set up a TB model for the Ir $t_{2g}$ orbitals that includes also local SO interaction terms. With this TB+SO model, we are able not only to confirm the relativistic DFT results by calculating DOS but also to access the composition of individual states and trace their evolution as a function of the spin-orbit coupling $\lambda$.

A. TB+SO model

We start with a TB model that perfectly describes the non-relativistic DFT Ir $t_{2g}$ bands of Na$_2$IrO$_3$. It includes three hundred and twenty one hopping integrals between up to 50 nearest neighbors. We then double the dimension of the TB Hamiltonian matrix to introduce spin dependence and add local SO coupling terms $\langle \lambda \textbf{L} \cdot \textbf{S} \rangle$ that mix spin-$\uparrow$ and spin-$\downarrow$ subspaces:

$$
\begin{pmatrix}
xy & xz & yz & x\uparrow & y\uparrow & z\uparrow & x\downarrow & y\downarrow & z\downarrow \\
xy & 0 & 0 & 0 & 0 & -\lambda^2 & 0 & 0 & 0 \\
xz & 0 & 0 & -\lambda^2 & 0 & -\lambda^2 & 0 & 0 & 0 \\
yz & 0 & -\lambda^2 & 0 & -\lambda^2 & 0 & 0 & 0 & 0 \\
x\downarrow & 0 & -\lambda^2 & 0 & -\lambda^2 & 0 & 0 & 0 & 0 \\
x\uparrow & \lambda^2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
y\uparrow & \lambda^2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
y\downarrow & \lambda^2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
z\uparrow & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
z\downarrow & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
$$

Importantly, even though SO coupling is a local on-site interaction, it couples neighboring quasi-molecular orbitals and therefore is $\textbf{k}$-vector dependent in the QMO basis.

Having thus set up the TB model, we vary the SO coupling strength $\lambda$ until the best matching with the DFT relativistic bands is achieved, which is found to correspond to $\lambda = 0.44$ eV (Fig. 7).

Since our purpose is to reconcile the QMO and relativistic orbital (RO) pictures, we analyze the $\textbf{L} \cdot \textbf{S}$ matrix elements between spin-$\uparrow$ and spin-$\downarrow$ QMOs to see how SO coupling mixes QMO characters. They can be easily obtained by applying the unitary transformation $U_T(\textbf{k})$ [Eq. (5)] to the $\textbf{L} \cdot \textbf{S}$ matrix in the $t_{2g}$ basis:

$$
H_{QMO}^{SO}(\textbf{k}) = U_T(\textbf{k})H_{t_{2g}}^{SO}T(\textbf{k})U^T.
$$

This equation explicitly illustrates how $\textbf{k}$-vector dependence enters the SO matrix elements in the QMO basis. Concise expressions can be derived if one notes that QMOs can be represented by their “winding number” $n$ which defines a phase change $\Delta \phi = \frac{2\pi n}{3}$ of $t_{2g}$ orbitals around a hexagon. In this notation, QMOs $A_{1g}, E_{2g}, E_{1g}, B_{1u}, E_{1g}, E_{2u}$ correspond to, respectively, $n = 0, 1, 2, 3, 4, 5$ winding numbers. The $\textbf{L} \cdot \textbf{S}$ matrix
elements in the QMO basis are given then by

\[
H_{n'n_\uparrow}^{SO} = \frac{\lambda}{2} e^{i\frac{\pi}{2}(n' - n)} \cos \frac{(n' - n)\pi}{2} \cos(k_x + k_y)
\]

\[
\times \left( e^{i\frac{\pi}{3}n_x} - e^{-i\frac{\pi}{3}(n' - n)x} \right) + \frac{\lambda}{2} e^{i\frac{\pi}{2}(n' - n)} \sin \frac{(n' - n)\pi}{2} \sin(k_x + k_y)
\]

\[
\times \left( e^{-i\frac{\pi}{3}n_x} + e^{-i\frac{\pi}{3}(n' - n)x} \right)
\]

(8)

and

\[
H_{n'n_\downarrow}^{SO} = 2e^{i\frac{\pi}{2}(n' - n)} \left( e^{i\frac{\pi}{3}n_x} \cos \frac{(n' - n)\pi}{2} + k_y \right)
\]

\[
- e^{-i\frac{\pi}{3}n_x} \cos \frac{(n' - n)\pi}{2} - k_y \right) + ie^{i\frac{\pi}{3}n_x} \cos \frac{(n' - n)\pi}{2} - k_x \right)
\]

\[
- ie^{-i\frac{\pi}{3}n_x} \cos \frac{(n' - n)\pi}{2} + k_x \right).
\]

(9)

We list numerical values of the matrix elements for two representative \(k\)-vectors: \(k = (0, 0, 0)\) (point \(\Gamma\)) (first two tables) and \(k = (\frac{\pi}{T}, 0, 0)\) (last two tables).

| \(n = 5\) | \(n = 0\) | \(n = 1\) | \(n = 2\) | \(n = 3\) | \(n = 4\) |
| \(E_{2u} \uparrow\) | \(A_{1g} \uparrow\) | \(E_{2u} \downarrow\) | \(E_{1g} \uparrow\) | \(B_{1u} \downarrow\) | \(E_{1g} \downarrow\) |
| --- | --- | --- | --- | --- | --- |
| \(E_{2u} \uparrow\) | \(C_1\) | 0 | 0 | 0 | -\(C_1\) |
| \(A_{1g} \uparrow\) | 0 | 0 | 0 | \(-C_1\) | 0 | \(C_1\) |
| \(E_{2u} \uparrow\) | 0 | 0 | -\(C_1\) | 0 | 0 | \(C_1\) |
| \(E_{1g} \uparrow\) | 0 | -\(C_1\) | 0 | \(C_1\) | 0 | 0 |
| \(B_{1u} \uparrow\) | -\(C_1\) | 0 | 0 | 0 | 0 | -\(C_1\) |
| \(E_{1g} \uparrow\) | 0 | 0 | 0 | 0 | 0 | -\(C_1\) |

(10)

| \(n = 5\) | \(n = 0\) | \(n = 1\) | \(n = 2\) | \(n = 3\) | \(n = 4\) |
| \(E_{2u} \downarrow\) | \(A_{1g} \downarrow\) | \(E_{2u} \downarrow\) | \(E_{1g} \downarrow\) | \(B_{1u} \downarrow\) | \(E_{1g} \downarrow\) |
| --- | --- | --- | --- | --- | --- |
| \(E_{2u} \uparrow\) | \(C_2\) | 0 | 0 | 0 | \(C_4\) |
| \(A_{1g} \uparrow\) | 0 | 0 | 0 | -\(C_3\) | 0 | -\(C_4\) |
| \(E_{2u} \uparrow\) | 0 | 0 | -\(C_2\) | 0 | \(C_3\) | 0 |
| \(E_{1g} \uparrow\) | 0 | \(C_4\) | 0 | \(C_2\) | 0 | 0 |
| \(B_{1u} \uparrow\) | -\(C_3\) | 0 | -\(C_4\) | 0 | 0 | 0 |
| \(E_{1g} \uparrow\) | 0 | \(C_3\) | 0 | 0 | 0 | -\(C_2\) |

(11)

| \(n = 5\) | \(n = 0\) | \(n = 1\) | \(n = 2\) | \(n = 3\) | \(n = 4\) |
| \(E_{2u} \uparrow\) | \(A_{1g} \uparrow\) | \(E_{2u} \uparrow\) | \(E_{1g} \uparrow\) | \(B_{1u} \uparrow\) | \(E_{1g} \uparrow\) |
| --- | --- | --- | --- | --- | --- |
| \(E_{2u} \uparrow\) | \(-\frac{1}{3}\) | 0 | \(-\frac{1}{3}\) | 0 | \(-\frac{1}{3}\) |
| \(A_{1g} \uparrow\) | 0 | \(-\frac{1}{3}\) | \(-\frac{1}{3}\) | 0 | \(-\frac{1}{3}\) |
| \(E_{2u} \uparrow\) | \(-\frac{1}{3}\) | 0 | \(-\frac{1}{3}\) | \(-\frac{1}{3}\) | 0 |
| \(E_{1g} \uparrow\) | 0 | 0 | \(-\frac{1}{3}\) | 0 | \(-\frac{1}{3}\) |
| \(B_{1u} \uparrow\) | -\(\frac{1}{3}\) | \(-\frac{1}{3}\) | \(-\frac{1}{3}\) | 0 | \(-\frac{1}{3}\) |
| \(E_{1g} \uparrow\) | 0 | \(-\frac{1}{3}\) | 0 | \(-\frac{1}{3}\) | \(-\frac{1}{3}\) |

(12)

with \(C_1 = \frac{\lambda}{12}, C_2 = \frac{\lambda}{12} (1 + i), C_3 = 0.105663 \lambda (1 + i), C_4 = 0.394337 \lambda (1 + i), C_5 = \frac{\lambda}{12} + \frac{\lambda}{24} i, C_6 = \frac{\lambda}{12} + \frac{\lambda}{24} i, C_7 = \frac{\lambda}{12} + \frac{\lambda}{24} i.

Several comments are in place here. First, spin-orbit coupling mixes QMOs at all \(k\)-vectors. Even at the \(\Gamma\) point, \(i.e.,\) on the same hexagon, the three upper QMOs (\(A_{1g}\) and two \(E_{2u}\)) are SO coupled to the three lower QMOs (\(B_{1u}\) and two \(E_{1g}\)), which explains sizable shifts of the relativistic bands compared to the non-relativistic ones at this \(k\)-vector. Additionally, SO coupling induces splitting of the degenerate \(E_{2u}\) and \(E_{1g}\) states at all \(k\)-vectors. Another striking feature of the calculated \(\mathbf{\lambda L} \cdot \mathbf{S}\) matrix is that its \(A_{1g}, E_{2u}\) (upper triplet) and \(B_{1u}, E_{1g}\) (lower triplet) blocks are identical. This means that if not for the accidental near-degeneracy of the \(A_{1g}\) and \(E_{2u}\) states (which magnifies the SO induced energy shifts) the upper and the lower triplets would have been equally affected by the SO coupling.

B. Quasimolecular orbital basis versus relativistic basis

The main difficulty in describing the Na\(_2\)IrO\(_3\) bandstructure is that it interpolates between eigenstates of two Hamiltonians: the itinerant TB Hamiltonian of (primarily) intrahexagon electron hopping that preserves the \(s_z\) spin subspace and the local spin-orbit (SO) interaction \(\mathbf{\lambda L} \cdot \mathbf{S}\) Hamiltonian that couples different spin subspaces. The eigenstates of the TB Hamiltonian are quasimolecular orbitals (QMOs), while the eigenstates of the SO interaction (in the \(t_{2g}\) subspace) are relativistic orbitals (ROs) \(|j_{\text{eff}}, j_{z\text{eff}}\rangle\) characterized by an effective total angular momentum \(j_{\text{eff}}\) and its z-projection \(j_{z\text{eff}}\): 

\[
|\frac{1}{2}, \frac{1}{2}\rangle = \frac{1}{\sqrt{3}} |xz \uparrow\rangle + \frac{i}{\sqrt{3}} |xz \downarrow\rangle + \frac{1}{\sqrt{3}} |yz \downarrow\rangle,
\]

\[
|\frac{1}{2}, -\frac{1}{2}\rangle = \frac{i}{\sqrt{3}} |xz \uparrow\rangle - \frac{1}{\sqrt{3}} |yz \uparrow\rangle + \frac{1}{\sqrt{3}} |xy \downarrow\rangle,
\]

\[
|\frac{3}{2}, \frac{3}{2}\rangle = \frac{i}{\sqrt{2}} |xz \uparrow\rangle + \frac{1}{\sqrt{2}} |yz \uparrow\rangle,
\]

\[
|\frac{3}{2}, -\frac{1}{2}\rangle = -\sqrt{\frac{2}{3}} |xy \uparrow\rangle + \frac{i}{\sqrt{6}} |xz \downarrow\rangle + \frac{1}{\sqrt{6}} |yz \downarrow\rangle,
\]

\[
|\frac{3}{2}, \frac{1}{2}\rangle = -\sqrt{\frac{2}{3}} |xy \uparrow\rangle + \frac{i}{\sqrt{3}} |xz \downarrow\rangle + \frac{1}{\sqrt{3}} |yz \downarrow\rangle,
\]

(14)
This basis can be explained as follows; three $t_{2g}$ orbitals (total degeneracy, including spins, is 6) are split into a lower-lying quartet $j_{\text{eff}} = 3/2$ and an upper-lying $j_{\text{eff}} = 1/2$ doublet, and the 5$d$-electrons of Ir$^{4+}$ fully occupy the lower quartet leaving the upper $j_{\text{eff}} = 1/2$ doublet half-filled. This makes this situation similar to a non-degenerate Hubbard model ($S=1/2$ doublet on a site), with the important difference that in the Hubbard model the hopping matrix elements preserve the $s_z$ spin subspace, while here the states of the $j_{\text{eff}} = 1/2$ doublet are spin-orbit mixed states, leading to a strong anisotropy of hoppings and their dependence on spin (or rather total moment) direction. This may bring about anisotropic exchange, e.g., the Kitaev exchange on a honeycomb lattice.

By gradually increasing an effective spin-orbit coupling strength $\lambda_{\text{eff}}$,

$$\lambda_{\text{eff}} = \frac{\lambda^2}{(t_{1O})^2} + \lambda^2, \quad t_{1O} = 0.270 \text{ eV}, \quad (15)$$

from 0 to 1, one can trace a smooth evolution of the TB+SO model eigenvalues from, respectively, the non-relativistic (QMO) limit to the fully relativistic (RO) limit (see Fig. 8 (a) for the data at the $\Gamma$ point). An SO coupling parameter of $\lambda = 0.44$ eV for Na$_2$IrO$_3$ corresponds to $\lambda_{\text{eff}} = 0.73$, which is marked by a vertical dotted line in Fig. 8.

The RO basis is an attractive starting point to describe the low-energy physics of Na$_2$IrO$_3$ as it allows to truncate the Hamiltonian to only $j_{\text{eff}} = 1/2$ states that dominate near the Fermi energy and map Na$_2$IrO$_3$ onto the Kitaev-Heisenberg model. Although this approach might seem reasonable given the noticeable separation of the $j_{\text{eff}} = 1/2$ and $j_{\text{eff}} = 3/2$ characters in the DOS of Na$_2$IrO$_3$ (cf. Fig. 2 (b) of Ref. 22), we argue that the itinerant terms are too strong to be neglected (which should not be surprising since $\lambda = 0.44$ eV $< W \approx 4t_{1O} = 1$ eV) and that, consequently, the QMO basis is as well (or as poorly) justified to work with as the RO basis.

To support this statement, let us concentrate on the TB+SO model states at the $\Gamma$ point. Fig. 8 (a) shows the evolution of the model eigenvalues as a function of $\lambda_{\text{eff}}$ (Eq. 15). In the non-relativistic limit ($\lambda_{\text{eff}} = 0$), the states are almost purely (with slight deviation due to orthorhombic distortion) QMOs, ordered as $B_{1u}, E_{1g}, E_{2g}$ with increasing energy. At the same time, at each state the $j_{\text{eff}} = 1/2$ contribution is 1/3 and the $j_{\text{eff}} = 3/2$ contribution is, correspondingly, 2/3 (for one of the two Ir atoms). Note that, since the model distinguishes spin-up and spin-down states each level is doubly degenerate.

With the QMO splitting obviously prevailing for zero SO coupling, we now want to quantify the QMO character rectification upon increasing $\lambda_{\text{eff}}$ by calculating the QMO and RO weights on two selected states: the lowest ($B_{1u}$) and the uppermost ($E_{2u}$). The $B_{1u}$ state [Fig. 8 (b)] is a simpler case as it is non-degenerate (apart from spin) and quite well separated from the rest of the QMOs so that the SO effects here should be less important. Changing $\lambda_{\text{eff}}$ from 0 to 0.73 (Na$_2$IrO$_3$ value), the $j_{\text{eff}} = 3/2$ weight on this state increases from 0.6667 to 0.8320, whereas the $B_{1u}$ weight is only slightly reduced from 0.9932 to 0.9567. This indicates that the highest relativistic state at the $\Gamma$ point in Na$_2$IrO$_3$ is better described by a QMO $B_{1u}$ than by one of the $j_{\text{eff}} = 3/2$ ROs. In fact, this turns out to hold for the whole lowest relativistic band (cf. the $j_{\text{eff}} = 3/2$ and QMO-projected Na$_2$IrO$_3$ DOS in, respectively, Fig. 2 (b) of Ref. 22 and Fig. S6 (b) of Ref. 5).

The uppermost state is one of the $E_{2u}$ doublet states. It is near-degenerate with $A_{1g}$ and the other $E_{2u}$, and, therefore, the SO effects are here particularly strong. At

FIG. 8: Properties of the TB+SO model of Na$_2$IrO$_3$ at the $\Gamma$ point as a function of effective SO coupling $\lambda_{\text{eff}}$ defined in Eq. 15. The vertical dotted line marks the realistic $\lambda_{\text{eff}} = 0.73$ value for Na$_2$IrO$_3$. (a) The eigenvalues of the TB+SO model at $\Gamma$. Eigenenergies have been scaled by $\sqrt{1-\lambda_{\text{eff}}}$ to keep them within the $[-1.5, 0.2]$ eV range. (b) The $j_{\text{eff}} = 3/2$ (solid line) and $B_{1u}$ (dashed line) weights on the lowest state. (c) The $j_{\text{eff}} = 1/2$ (solid line) and total $E_{2u}$ (dashed line) weights on the uppermost state. Inset shows individual contributions from the two $E_{2u}$ QMOs.
the Γ point, though, it can only couple to itself or to the other $E_{2u}$ [see Eqs. (10) and (11)], depending on which linear combination of these degenerate states is considered. Upon switching $\lambda_{\text{eff}}$ on, the $j_{\text{eff}} = \frac{1}{2}$ weight on this upper states rapidly grows from 0.3333 to $\sim 0.6$ in the range $0 < \lambda_{\text{eff}} < 0.05$, and then gradually increases to 0.8295 at $\lambda_{\text{eff}} = 0.73$ [Fig. 8 (c)]. At the same time, the weight of one of the $E_{2u}$ states (we may call it $E'_{2u}$) is reduced from 1.0 to 0.53730 [see inset of Fig. 8 (c)]. However, the total weight of two $E_{2u}$ states is barely changed: at $\lambda_{\text{eff}} = 0.73$ it equals 0.9617. This means that the uppermost relativistic state at the Γ point in Na$_2$IrO$_3$ is very well described by a linear combination of two $E_{2u}$ states (which is also a QMO) with, in general, $\lambda_{\text{eff}}$-dependent individual contributions.

The $B_{1u}$ and $E_{2u}$ states (at $\lambda = 0$) seem to simultaneously bear both RO and QMO features up to very strong SO coupling, with the QMO character dominating for $\lambda_{\text{eff}} < 0.9$. This can also be illustrated by inspecting the composition of, e.g., the lowest energy band state as shown in Table III. At zero SO coupling, the doubly degenerate lower state corresponds to (almost) pure $B_{1u}$ $\uparrow$ and $B_{1u}$ $\downarrow$ QMO states. At $\lambda_{\text{eff}} = 0.73$, the structure of this state is strikingly similar to the $B_{1u}$ states, with only slight admixtures of the $xz$ and $yz$ orbitals of opposite spin. Even at very high $\lambda_{\text{eff}}$, when the RO $J_{\text{eff}} = \frac{1}{2}$ weight is close to 1, the states retain the $B_{1u}$ $\uparrow$ and $B_{1u}$ $\downarrow$ QMO features.

The features shown in this Section, not unexpectedly, characterize Na$_2$IrO$_3$ as intermediate between the non-relativistic (pure quasi-molecular orbital) and fully relativistic (pure RO) cases.

Moreover, these results show that, in the RO representation, the upper band states are not pure $J_{\text{eff}} = \frac{1}{2}$ states but there is some significant mixing of $J_{\text{eff}} = \frac{3}{2}$ states. In fact, for the upper band states, the projections onto $J_{\text{eff}} = \frac{1}{2}$ and $J_{\text{eff}} = \frac{3}{2}$ are, respectively, 0.64 and 0.21 with $2(0.64^2 + 2 \times 0.21^2) = 1$, while in the non-relativistic case these projections are both equal to $\sqrt{1/6} = 0.41$. Note that looking at the weights may be misleading. Indeed this state appears to be $2 \times 0.64^2 = 82\%$ pure $j_{\text{eff}} = 1/2$ state [Fig. 8 (bottom)], but its projection on the $j_{\text{eff}} = 3/2$ state is only twice smaller than in the non-relativistic case. In other words, the hopping between the upper Kramers doublets, initially not considered in Ref. [2], is only reduced by about a factor of two compared to the non-relativistic case. One but possibly not the only consequence of this fact is that the contribution of the Kitaev term in the analysis below may be overestimated, probably by as much as a factor of two.

C. Comparison with experiment: branching ratio

An argument frequently used to justify the assumption of pure ROs in Na$_2$IrO$_3$ is that it is experimentally supported. However, the experimental evidence is inconclusive. It is first assumed that the electronic states are pure ROs and then it is shown that this assumption does not contradict the experiment, yet the experiments, upon a closer look, do not falsify the DFT picture, either. A typical and, by far, the most often used quantity to discuss the nature of the states in iridates is the branching ratio (BR) extracted from X-ray absorption spectroscopy (XAS) experiments. In XAS, essentially, $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ is measured. This expectation value is of course zero without spin-orbit coupling. A detailed and very insightful analysis can be found, for instance, in Refs. [26,29]. In particular, it is shown that, for a related iridate, the main contribution to $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ (1.4 out of 2.1) doesn’t come from the $t_{2g}$ orbitals, which define the $J_{\text{eff}} = 1/2$ states, but from the admixture of the $e_g$ orbitals. In our calculations – shown below – we observe the same behavior.

We apply our TB+SO model to calculate $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ for Na$_2$IrO$_3$ where $\mathbf{L}$ and $\mathbf{S}$ are, respectively, the total orbital and spin angular momenta of Ir 5$d$ electrons. $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ is related to the experimentally accessible branching ratio as

$$BR = \frac{(2 - r)}{(1 + r)}, \quad r = \frac{\langle \mathbf{L} \cdot \mathbf{S} \rangle}{n_h},$$  \hspace{1cm} (16)$$

with $n_h = 5$ being the average number of $5d$ Ir holes.

In recent XAS measurement, BR = 5.5 – 5.7, translating to $\langle \mathbf{L} \cdot \mathbf{S} \rangle = -2.7 \hbar^2$, was obtained for Na$_2$IrO$_3$ and interpreted as a sign of strong spin-orbit coupling.

When applying the TB+SO model that we constructed for Na$_2$IrO$_3$ in Section V A, the calculated $\langle \mathbf{L} \cdot \mathbf{S} \rangle = -0.73 \hbar^2$ (as compared to $-1 \hbar^2$ in the limit $\lambda_{\text{eff}} = 1$). This value is several times smaller than the experimental value. This is, however, not unexpected given the significant contribution of the Ir $e_g$ empty states to $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ (cf. Ref. [26]), which are not considered in the TB+SO model discussed in the previous Section. In order to make a meaningful comparison with experiment, we extend our TB+SO model to include (in the same spirit) also the Ir $e_g$ states. $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ within such a model is $-1.91 \hbar^2$. This is about 30% less than the experimental value reported by Clancy et al.\([32]\). This result is indeed in good agreement with experiment, given the large fluctuations in experimental values. For instance, Ref. [32] reported $\langle \mathbf{L} \cdot \mathbf{S} \rangle = -3.1 \hbar^2$ for Sr$_2$IrO$_4$ while Ref. [26] reported $-2.1 \hbar^2$ (about 30% difference) for the same compound. This example gives a sense of possible fluctuations between results of different experimental groups, and therefore our theoretical $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ value for Na$_2$IrO$_3$ might be even closer to the true result.

The main conclusion from these calculations is that with the TB+SO model based on all five Ir 5$d$ orbitals we are able to reasonably reproduce the large experimentally measured $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ value in Na$_2$IrO$_3$, which validates our approach. As our analysis shows, the large $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ does not necessarily mean an ideal separation of $j_{\text{eff}} = \frac{3}{2}$ and $j_{\text{eff}} = \frac{1}{2}$ RO states, but rather the effect of $e_g$ states also contributing in the process. Due to the peculiar electron hopping hierarchy in Na$_2$IrO$_3$, QMOs might be a better
basis.

In conclusion, the XAS experiments only tell us that the upper Kramers doublet has a considerable contribution coming from $j_{\text{eff}} = 1/2$, but not that it is a pure RO state.

### D. Comparison with experiment: RIXS

Another experiment sometimes quoted as supporting the fully relativistic $j_{\text{eff}} = \frac{3}{2}$ picture is resonant inelastic x-ray scattering (RIXS). In this experiment a joint density of electronic states (JDOS) is probed, somewhat similar to that in the infrared absorption but with different matrix elements. The authors of Ref. 33 observed several peaks in JDOS, of which the lowest peak at $\sim 0.42$ eV was interpreted as transitions across the Mott-Hubbard gap, consistent with a 30% smaller optical absorption threshold. The next two peaks are close to each other at 0.72 and 0.83 eV and were ascribed to transitions from the $j_{\text{eff}} = 3/2$ quartet into the upper $j_{\text{eff}} = 1/2$ doublet. The splitting of 110 meV was ascribed to the trigonal splitting. Altogether, this interpretation suggests an SO coupling $\lambda \sim \frac{3}{2} (0.72 + 0.83 - 0.42) \approx 0.39$ eV, a very reasonable number, if slightly too small.

This analysis, even though it looks reasonable on the first glance, has serious shortcomings. First, the deduced trigonal splitting is nearly twice as large as the actual trigonal splitting. In fact, the trigonal splitting is decided by the electrostatic field of the ligands, and in addition one-electron hoppings; both are very well accounted for by the DFT calculations, which give $\Delta_T = 75$ meV. Second, even a $\Delta_T = 110$ meV cannot produce well separated peaks in JDOS, given that the Ir-Ir hopping is $t_{\text{Ir-Ir}} = 270$ meV. Third, even if one completely neglects the Ir-Ir hopping in order to extract $\lambda$ and $\Delta_T$ one has to diagonalize the full Hamiltonian including both factors and then fit the resulting eigenvalues to the observed peaks. After doing that, one gets $\lambda = 0.5$ eV and $\Delta_T = 180$ meV. Although the previous numbers are a rough estimate since they depend on the direction of the Ir spins as well as on $U$ (here we considered $U = 0$), the latter number is more than twice the actual trigonal splitting. This argument shows that an interpretation of RIXS in terms of infinitely narrow bands split by the trigonal field may not be completely correct.

We find, on the other hand, that this experiment is consistent with DFT band structure. To demonstrate that, we have performed DFT calculations for the magnetic zigzag phase. We note that the results do not depend qualitatively on the choice of the pattern and the magnetization direction. In order to account for the missing correlation effects and adjust the direct gap to be consistent with infrared measurement, we applied a rigid shift of 200 meV between the occupied and empty bands (“scissor operator”). This exercise gives a JDOS which has a broad feature, consisting of (i) a peak at 0.42 and a shoulder 0.48 eV (compared to 0.42 eV in the experiment) corresponding to the transition between the top QMOs and (ii) a peak at 0.77 eV and a shoulder at 0.81 eV corresponding to transitions from the lower QMOs. While the experiment finds two peaks at 0.72 and 0.83 eV, one should keep in mind that the matrix elements, omitted in our calculation, can easily suppress or enhance a shoulder, making it disappear (at 0.48 eV) or become a separate peak (at 0.81 eV). Therefore we conclude that the agreement between experiment and our calculations, simplified as they are, is reasonably good.

### Table III: Expansion coefficients of the lowest doubly degenerate energy states of the TB+SO model in the $t_2g$ basis (The upper index of the $t_2g$ orbitals labels Ir atoms in the unit cell). The coefficients are given for three $\lambda (\lambda_{\text{eff}})$ values. The $B_{1u}$ and $j_{\text{eff}} = \frac{3}{2}$ weights of the various states are given at the bottom of the table.

| $\lambda = 0 (\lambda_{\text{eff}} = 0)$ | $\lambda = 0.44 \text{ eV} (\lambda_{\text{eff}} = 0.73)$ | $\lambda = 2.66 \text{ eV} (\lambda_{\text{eff}} = 0.99)$ |
|----------------------------------------|----------------------------------------|----------------------------------------|
| Shifted $u$ weight | 0.6667 | 0.8320 | 0.9816 |
| $B_{1u}$ weight | 0.9932 | 0.9567 | 0.7824 |
VI. MAGNETISM

We proceed now with the discussion of the magnetic behavior of Na$_2$IrO$_3$. Neutron diffraction experiments reported long-range antiferromagnetic order at low temperatures in a zigzag pattern$^3$ This ordering was confirmed by relativistic spin-polarized DFT calculations$^3$ where we showed that it is the itinerancy of the system that stabilizes the zigzag configuration. Such a pattern was also predicted from the localized mnKH model$^Ω$ (Eq. [1]). In the following we will provide ab initio-derived estimates for the Kitaev and Heisenberg terms and will show that in the physically reasonable parameter range this model unfortunately fails to reproduce the experimentally observed magnetic order.

A. Nearest neighbor Kitaev-Heisenberg model

One term neglected in the conventional Kitaev-Heisenberg model treatment is the single-site magnetocrystalline anisotropy. Localized electrons with the spin 1/2 do not have any anisotropy, no matter how strong the spin-orbit coupling is. However, if hopping is considered, electrons can have a preferred spin direction, which in the language of the nnKH Hamiltonian is considered, electrons can have a preferred spin direction. In the physically reasonable parameter range this model unfortunately fails to reproduce the experimentally observed magnetic order.

Chaloupka et al.$^Ω$ discuss four relevant processes contributing to the exchange interactions in Na$_2$IrO$_3$: (1) Direct hopping $t_{1σ}$ between nearest neighbor Ir $t_{2g}$ orbitals contributing with a term $I_1 = \frac{(\frac{2}{3}t_{1σ})^2}{U}$ to the Heisenberg term, where $U$ is the Coulomb repulsion between $t_{2g}$ electrons.

(2) Interorbital nearest neighbor Ir $t_{2g}$ hopping via intermediate oxygens $t_1$, with $t_1 = t_{pdσ}t_{pδσ}/\Delta$, where $\Delta$ is the charge-transfer energy (the difference between the O $p$ and Ir $d$ levels) contributing with a term $I_2 = \frac{2}{9}J_1\frac{U}{\Delta}$ both to the Kitaev and Heisenberg terms, but with the opposite signs. Here $\bar{U}$ is the excitation energy associated with the $t_{2g}-e_g$ hopping i.e. it also includes crystal field splitting, $U = U + 10Dq$. $J_H$ is the Hund’s rule coupling between $t_{2g}$ and $e_g$ electrons.

(3) Oxygen-assisted hopping between two nearest neighbor Ir $t_{2g}$ orbitals $t_{1O}$ contributing with a term $I_3 = \frac{8}{9}\bar{U}J_1\frac{U}{\Delta}$ to the Kitaev term, where $J_H$ is the Hund’s rule coupling between $t_{2g}$ electrons, and, we remind, $t_{1O} = t_{2pδσ}/\Delta$.

(4) Oxygen-2p – Iridium-5d charge transfer contributing with a term $J_1 = \frac{8\bar{U}}{9}\left(\frac{1}{\Delta+U_p-3J_p} + \frac{1}{3(2\Delta+U_p-J_p)} + \frac{2}{3(2\Delta+J_p+2J_p)} - \frac{1}{\Delta}\right)$, where $U_p$ and $J_p$ are, respectively, the Hubbard repulsion and the Hund’s rule parameter for oxygen. This expression was derived by G. Khaliliullah$^{[24]}$ and is worth some additional discussion. The first three terms correspond to processes where two holes of the same or of opposite spins meet at an oxygen atom. Neglecting $J_p$, one gets simply $\frac{8\bar{U}}{9}\frac{1}{\Delta+U_p}$, which reflects the fact that if the Ir atoms have opposite spins one can create an intermediate state with two holes on the same oxygen orbital, which lowers the total energy. The last term appears due to ring exchange, with an intermediate state where two holes are located on different oxygens. This process is only allowed when the ground state is FM, and only if the ground state hole is in an $a_{1g}$ or $j_{eff} = 1/2$ state, but not for pure $t_{2g}$ orbitals. However, contrary to a common misconception, $J_p$ is large, between 1.2 and 1.6 eV. We have estimated $U_p$ and $J_p$, using the technique described in Ref. [37] and obtained
U_p = 2.7 and J_p = 1.6 eV, consistent with earlier DFT estimates. For non-relativistic orbitals it is comparatively straightforward to account for the Hund’s rule coupling on O, but for relativistic orbitals it becomes more tedious.

If we expand I_4 in both U_p and J_p, then I_4 \approx \frac{8t_{\sigma\sigma}^2}{9} U_p - J_p. \quad \text{(17)}

This expression shows that U_p alone contributes ferromagnetically to the Heisenberg term and antiferromagnetically to the Kitaev term and may shift the various phases in the nnKH model. Together with J_p, though, for the values suggested above the effect of U_p and J_p largely cancels and I_4 appears to be unimportant (note though that if J_p is entirely neglected, as in Ref. 4, this proposition becomes more questionable).

Summarizing the above terms into a single expression, Eq. (1) can be written as:

\[ H^{(1)}_{ij} = \frac{(2I_2 - I_3 + 2I_4) S_i \cdot S_j + (I_1 - I_2 - I_4) S_i \cdot S_j}{2K} \]

This model has a zigzag magnetic ground state if the Kitaev term is antiferromagnetic (AFM) and the Heisenberg term is ferromagnetic (FM), with K > 0, J < 0 and \(-26 \lesssim J/K \lesssim -0.3\). In Table IV we provide the parameter values relevant for Na_2IrO_3, as obtained from our DFT results. Note that the t_1 parameter was assumed to be 2t_1O in Ref. 4, while in the calculations (DFT calculations are usually very reliable in this respect) t_1/t_1O is 1.4. However, using the ratio of 2 hardly changes any conclusions.

We present our results in Figures 9 and 10. In Fig. 9 we show the calculated values of K and J as a function of two variables: the x axis is the Hubbard U associated with the upper Kramers doublet, and the y axis is the energy \( \tilde{U} \), associated with exciting an individual electron from the upper t_{2g} to an average e_g state. The Hubbard U for 5d electrons is, generally speaking, 1.5 to 2 eV. However, in this case it is additionally screened by the e_g electrons, and also reduced by hybridization (cf. Na_3CoO_2 and Fe pnictides). Experimental estimates of the Hubbard U defined as the energy cost for exciting electrons across the insulating gap (which is the definition relevant to superexchange) yield 0.3-0.5 eV. Additionally, LDA+U calculations with U \sim 2 eV yield an exciton gap of the same order. We conclude that the realistic range of this parameter is 0.5-2 eV, with the smaller values more likely.

For the second parameter, \( \tilde{U} \), DFT calculations give \sim 2.5 eV. This should be considered as a lower bound since DFT tends to slightly overestimate the orbital overlap and crystal fields, and misses the effects of the t_{2g} - e_g Hubbard interaction. One can thus limit the physically admissible range in the region 2.5 eV \lesssim \tilde{U} \lesssim 3 eV.

In Figure 10 we show the phase diagram in the space of the two parameters above. Several observations are in place: (1) While there is a zigzag phase in this diagram, it is very far removed from the range of the parameters that can be called physical, 0.5 eV \lesssim U \lesssim 2 eV, 2 eV \lesssim \tilde{U} \lesssim 3 eV (even though in the above estimate we have liberally stretched the admissible range in favor of a zigzag phase). In fact, the zigzag regime appears only when \( \tilde{U} < 0.6U \), i.e. when the Hubbard gap is larger than the e_g - t_{2g} splitting, a rather unlikely proposition. (2) In the physical range of parameters, the ground state is either ferromagnetic or the spin liquid phase. It is rather curious that the very narrow slivers of the phase space in the J, K coordinates are transformed into a very large range in the U, \tilde{U} space.

It is also worth mentioning that in order to explain the experimental data of Refs. 7,8 one needs not only the ground state to be zigzag, but also that K be several times larger than \( |J| \); Chaloupka et al. used K = 10.44 and J = \sim 4.01 meV. This solution cannot be obtained for a given set of U and \( \tilde{U} \) (see Fig. 9). Moreover, a closer look at the expressions in their work reveals that K + J = I_1 - I_3/2, which does not depend on \( \tilde{U} \) and is always negative. Thus the two equalities above cannot be satisfied simultaneously for any choice of parameters, be they physical or not. Moreover, the values of J and K used in Ref. 14 can only be obtained if \( \tilde{U} < 0.2 \) eV, which is clearly an impossible regime.

### B. Long-range exchange

As mentioned above, an alternative interpretation of the experimental results, given in Refs. 7,8 is in terms of sizable 2nd and 3rd neighbor exchange constants, comparable to the nearest neighbor exchange. In this picture the Kitaev term may or may not play a role, but this role is not decisive in establishing the observed magnetic order. Given that the calculated hopping amplitudes (Table I) are clearly dominated by the nearest neighbor terms, standard superexchange cannot explain such long range interactions.

However, it is important to remember that in the opposite, itinerant limit every electron is fully delocalized over a hexagon and, as such, is equally sensitive to the mean field magnetization pattern on the 1st, 2nd or 3rd

| Parameter | Value (eV) | Meaning |
|-----------|------------|---------|
| t_1s      | 0.03       | direct Ir-Ir hopping |
| t_1O      | 0.27       | O assisted Ir-Ir hopping |
| t_1       | 0.38       | Ir t_{2g} - e_g hopping |
| t_{pdπ}   | 0.57^*     | Ir-O π hopping |
| t_{pdσ}   | 1.6^*      | Ir-O σ hopping |
| Δ         | 2.4        | charge transfer energy between the O p and Ir d levels |

In Table IV we provide the parameter values relevant to superexchange. The values marked with * were obtained from t_1, t_1O and Δ.
FIG. 9: (Color online) Variation of (a) Kitaev parameter $K$ and (b) Heisenberg exchange coupling $J$ with onsite Coulomb coupling strength $U$ and Ir $t_{2g}-e_g$ excitation energy $\tilde{U}$. Positive values refer to antiferromagnetic, negative to ferromagnetic values of $K$ and $J$. The other parameters entering the $K$ and $J$ are given in Table IV.

FIG. 10: (Color online) Phase diagram of the Kitaev-Heisenberg model for Na$_2$IrO$_3$ with parameters determined following Ref. 4. The calculated exchange integrals are functions of the Mott-Hubbard gap $U$ and the cubic crystal field splitting $\tilde{U}$. The contours mark isolines of the ratio $K/J$.

nearest neighbors. As discussed in our earlier work\textsuperscript{5}, the zigzag order, as compared to the stripy one, results in a sizable pseudogap at the Fermi level even without a Hubbard $U$. This creates an energy gain that cannot be cast in a form of nearest neighbor interaction, as it depends on the magnetization pattern over an entire hexagon.

We are far from stating that the superexchange Hamiltonian outlined in Ref. 4 is irrelevant and an itinerant description will give the final answer to all questions regarding the magnetism in Na$_2$IrO$_3$. However, relying solely on the localized picture and, correspondingly, on the mnKH model, is, apparently, inadequate.

VII. CONCLUSIONS

In summary, we have performed an extensive investigation of the electronic properties of Na$_2$IrO$_3$ in the framework of non-relativistic and relativistic density functional theory calculations and derived by means of the Wannier function projector method, the corresponding microscopic parameters. We resolved the following open questions: (1) By considering various idealized crystal structures for Na$_2$IrO$_3$ we could disentangle the effect of each of the structural distortions present in this system and concluded that it is the joint effect of these distortions that constructively enhances the intrahexagon effective hopping parameters and suppresses the interhexagon ones favoring the formation of quasi-molecular orbitals. (2) We modelled the relativistic DFT results in terms of a tight-binding model including the spin-orbit coupling term and analyzed the electronic properties of Na$_2$IrO$_3$ in terms of two complementary descriptions, the (itinerant) quasi-molecular basis and the (localized) relativistic $j_{\text{eff}}$ basis. We observed that the behavior of Na$_2$IrO$_3$ lies in between the fully itinerant and the fully localized description and that a quasi-molecular orbital description keeps its character even at large values of the
spin-orbit coupling strength. (3) We showed that XAS and RIXS observations can be well understood within an itinerant description of Na$_2$IrO$_3$ in contrast to other iridates like Sr$_3$CuIrO$_6$ where localization is imposed by the crystallographic arrangement of the IrO$_6$ octahedra.\(^\text{10}\)

(4) Finally, we provided \textit{ab initio}-derived estimates for the parameters appearing in the Kitaev and Heisenberg terms in Na$_2$IrO$_3$ and found that the recently proposed nnKH model (see Section VI), even though it is a very interesting model \textit{per se}, is unfortunately not realistic for Na$_2$IrO$_3$. In conclusion, in order to obtain a full understanding of the behavior of Na$_2$IrO$_3$ all three features; spin-orbit, Coulomb correlations and delocalization of valence electrons over Ir$_6$ hexagons are essential.

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VIII. APPENDIX. IDEALIZED Na$_2$IrO$_3$

CRYSTAL STRUCTURES AS USED IN WIEN2k

A. Experimental structure from Ref.\(^\text{8}\)

| Space group $C\bar{2}/m$ (No. 12) |
|----------------------------------|
| $a = 5.4269$ Å, $b = 6.4104$ Å, $c = 9.3949$ Å, $\gamma = 124.12^\circ$ |
| Atom | $x$ | $y$ | $z$ |
| Na1 | 0.0 | 0.0 | 0.5 |
| Na2 | 0.5 | 0.5 | 0.0 |
| Na3 | 0.5 | 0.5 | 0.3400 |
| Ir | 0.0 | 0.0 | 0.1670 |
| O1 | 0.4590 | 0.2110 | 0.1780 |
| O2 | 0.0070 | 0.7960 | 0.0 |

B. Idealized structure $S_1$

| Space group $C\bar{2}/m$ (No. 12) |
|----------------------------------|
| $a = 5.4501$ Å, $b = 6.4111$ Å, $c = 9.4399$ Å, $\gamma = 125.26^\circ$ |
| Atom | $x$ | $y$ | $z$ |
| Na1 | 0.0 | 0.0 | 0.5 |
| Na2 | 0.5 | 0.5 | 0.0 |
| Na3 | 0.5 | 0.5 | 0.3333 |
| Ir | 0.0 | 0.0 | 0.1667 |
| O1 | 0.4646 | 0.2097 | 0.1785 |
| O2 | 0.0000 | 0.7903 | 0.0 |

Note that due to the necessity of using a monoclinic angle $\gamma$ in WIEN2k, the Ir honeycomb layers in the Na$_2$IrO$_3$ unit cells presented above are parallel to the ac plane. Accordingly, within this convention the vector of the Bloch factors in Eqs. (4) and (7) is given by

$$T_{M=1\ldots6}(k) \equiv (1, e^{-ik_x\tilde{a}}, e^{-ik_z\tilde{c}}, e^{-i(k_x\tilde{c}-k_z\tilde{a})}, e^{ik_x\tilde{c}}, e^{-ik_z\tilde{a}}),$$

(18)

where $\tilde{a}$ and $\tilde{c}$ are the lengths of the two primitive lattice vectors lying in the ac plane. Here, one explicitly accounts for the choice of WIEN2k of the actual positions of the two Ir atoms in the primitive unit cell, which are, e. g., (-0.167,0.0,0.167) and (-0.833,0.0,0.833) in the experimental Na$_2$IrO$_3$ structure.

C. Idealized structure $S_2$

| Space group $C\bar{2}/m$ (No. 12) |
|----------------------------------|
| $a = 5.4501$ Å, $b = 6.4190$ Å, $c = 9.4399$ Å, $\gamma = 124.47^\circ$ |
| Atom | $x$ | $y$ | $z$ |
| Na1 | 0.0 | 0.0 | 0.5 |
| Na2 | 0.5 | 0.5 | 0.0 |
| Na3 | 0.5 | 0.5 | 0.3333 |
| Ir | 0.0 | 0.0 | 0.1667 |
| O1 | 0.4606 | 0.1909 | 0.1667 |
| O2 | 0.0000 | 0.8091 | 0.0 |

D. Idealized structure $S_3$

| Space group $C\bar{2}/m$ (No. 12) |
|----------------------------------|
| $a = 5.0658$ Å, $b = 5.9869$ Å, $c = 8.7743$ Å, $\gamma = 125.26^\circ$ |
| Atom | $x$ | $y$ | $z$ |
| Na1 | 0.0 | 0.0 | 0.5 |
| Na2 | 0.5 | 0.5 | 0.0 |
| Na3 | 0.5 | 0.5 | 0.3333 |
| Ir | 0.0 | 0.0 | 0.1667 |
| O1 | 0.5000 | 0.2443 | 0.1667 |
| O2 | 0.0000 | 0.7557 | 0.0 |

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