Electronic excitations in $\gamma$-Li$_2$IrO$_3$

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We investigate the electronic properties of the three-dimensional stripy-honeycomb $\gamma$-Li$_2$IrO$_3$ via relativistic density functional theory calculations as well as exact diagonalization of finite clusters and explore the details of the optical conductivity. Our analysis of this quantity reveals the microscopic origin of the experimentally observed (i) optical transitions and (ii) anisotropic behavior along the various polarization directions. In particular we find that the optical excitations are overall dominated by transitions between $j_{\text{eff}} = 1/2$ and $3/2$ states and the weight of transitions between $j_{\text{eff}} = 1/2$ states at low frequencies can be correlated to deviations from a pure Kitaev description. We furthermore reanalyze within this approach the electronic excitations in the known two-dimensional honeycomb systems $\alpha$-Li$_2$IrO$_3$ and Na$_2$IrO$_3$ and discuss the results in comparison to $\gamma$-Li$_2$IrO$_3$.

I. INTRODUCTION

The two-dimensional honeycomb iridates Na$_2$IrO$_3$ and $\alpha$-Li$_2$IrO$_3$ have been suggested as candidate materials for the realization of bond-dependent anisotropic interactions as described by the Kitaev model\cite{Kitaev2006}. The appropriate description of the electronic structure of these materials is currently being discussed. In the limit of strong spin-orbit coupling (SOC) and electron-electron interactions, the low-energy degrees of freedom are predicted to be localized spin-orbital doublet $j_{\text{eff}} = 1/2$ states\cite{Jiang2010}. These localized moments are thought to persist despite relatively weak correlations in the 5$d$ Ir orbitals due to an effective bandwidth reduction via SOC. That is, once SOC is included, the highest occupied $j_{\text{eff}} = 1/2$ bands become very narrow, enhancing the role of correlations. A complementary perspective was also given from the limit of weak correlations. In this case, the electronic properties of these systems can be described in terms of a recently proposed quasimolecular orbital (QMO) basis\cite{Li2011, Li2013}. When SOC is included in this picture, a (pseudo)gap was found at the Fermi energy for Na$_2$IrO$_3$, suggesting the material is relatively close to a band insulating state in the weak correlation limit\cite{Li2011}. Thus even weak correlations may be sufficient to induce an insulating state. Overall, a correct understanding of the electronic structure is important for evaluating the relevance of localized spin-Hamiltonians such as the (extended) Heisenberg-Kitaev models currently under discussion for these materials. It is generally agreed that long-range second and/or third neighbour interactions are required to understand the magnetic properties in the 2D honeycomb Na$_2$IrO$_3$ and $\alpha$-Li$_2$IrO$_3$\cite{Jiang2013}, suggesting relatively delocalized moments.

Three-dimensional generalizations of the honeycomb lattices were also recently synthesized: the hyperhoneycomb $\beta$-Li$_2$IrO$_3$\cite{Liu2015, Qi2015} and the stripyhoneycomb $\gamma$-Li$_2$IrO$_3$\cite{Li2015, Li2016} (Fig. 1). These materials are expected to display 3D Kitaev physics and to potentially support spin quantum liquid states analogous to the 2D cases\cite{Xu2013, Xu2016}. Resonant magnetic x-ray diffraction experiments found that $\gamma$-Li$_2$IrO$_3$ hosts, at low temperatures, a non-coplanar counter-rotating long range spiral magnetic order with incommensurate ordering wavevector $\mathbf{q} = (0.57, 0.0)$ along the orthorhombic $\alpha$-axes\cite{Jiang2016}. Various investigations of the combined Kitaev-Heisenberg spin Hamiltonian suggest that Kitaev interactions must dominate over the Heisenberg terms in order to produce the observed complex spin spirals\cite{Jiang2016, Liu2016}, although long-range antisymmetric interactions cannot be ignored\cite{Jiang2016}.

In order to gain microscopic insight on the electronic properties of $\gamma$-Li$_2$IrO$_3$ in comparison to its 2D counterparts, we consider the electronic structure and optical conductivity of each material within density functional theory (DFT) and the exact diagonalization (ED) method. Optical conductivity measurements for $\gamma$-Li$_2$IrO$_3$\cite{Jiang2016} show anisotropic behavior between polarizations along the $a$ and $b$ axes, but both polarizations show a broad peak structure at 1.5 eV, similar to that of Na$_2$IrO$_3$. However, the observed optical conductivity was significantly reduced in magnitude for $\gamma$-Li$_2$IrO$_3$ compared to Na$_2$IrO$_3$. This difference was initially attributed...
TABLE I: Nearest neighbour distances (in Å) and Ir-O-Ir angles for the different bond types, determined in the experimental γ-Li₂IrO₃ structure (see Fig. 1 (b) for bond notation).

| Bond Type | Distance   | Angle   |
|-----------|------------|---------|
| Ir-Ir     | 2.976      |         |
| Ir-O1     | 1.992.14   | 1.97    |
| Ir-O2     | 2.012.01   | 1.97    |
| Ir-O1-Ir  | 92.0°      | 97.40°  |
| Ir-O2-Ir  | 95.52°     | 97.40°  |

II. ELECTRONIC PROPERTIES OF γ-Li₂IrO₃

A. Crystal Structure

The experimental structure of γ-Li₂IrO₃[1313] (see Fig. 1 (a)-(b)) has two hexagonal chains oriented in the directions a ± b linked along the c-direction. There are three kinds of Z bonds in γ-Li₂IrO₃: the Zc bond bridges two chains of hexagons while the Za and Zb bonds complete each Ir hexagon in the layered structure. The cartesian coordinates x, y, z for the orbitals are displayed in Fig. 1 (b). The unit cell has two nonequivalent Ir atoms and a total of eight Ir: Ir(1) atoms are linked by Za and Zb bonds, while Ir(2) atoms are linked by Zc bonds. Xa, Ya, Xb and Yb link Ir(1) and Ir(2) sites. Details of the crystal structure are given in Table I.

B. Density Functional Theory Calculations

We performed linearized augmented plane-wave (LAPW) calculations[23] with the generalized gradient approximation (GGA)[24]. We chose the basis-size controlling parameter RK_max = 8 and a mesh of 432 k points in the first Brillouin zone (FBZ) of the primitive unit cell. Relativistic effects were taken into account within the second variational approximation. A U_eff = 2.4 eV as implemented in GGA+SO+U[25] was employed in order to keep consistency with previous calculations[10].

The hopping parameters between Ir 5d orbitals in γ-Li₂IrO₃ were computed via the Wannier function projection method[26][27][28] and we employed the optics code package[29] within LAPW to calculate the optical conductivity. The density of states and optical properties were computed with 10 x 10 x 10 k points in the full Brillouin zone while the hopping parameters were evaluated using 12 x 12 x 12 k points.

The non-relativistic GGA density of states (DOS) for γ-Li₂IrO₃ is displayed in Fig. 2 (a) - (c). The Iridium 5d states are split into eg (2.2 eV to 3.6 eV) and t₂g (-1.6 eV to 0.2 eV) states (Fig. 2 (b)) due to the octahedral crystal field of IrO₆ with the Fermi level lying within the t₂g manifold. The t₂g band is further split into lower dₓᵧ and higher dₓz, dᵧz (Fig. 2 (c)), arising from an additional weak trigonal field. By using the projection method described in Ref.[9] we obtained the hopping parameters from the GGA bandstructure. Table I displays the crystal field splitting compared with Na₂IrO₃.

Full hopping integral tables are given in Appendix A. In terms of the t₂g d-orbital basis:

\[ \mathbf{c}_i = (c_{i,xz,↑}, c_{i,xz,↓}, c_{i,yz,↑}, c_{i,yz,↓}, c_{i,xz,↑}, c_{i,xz,↓}, c_{i,yz,↑}, c_{i,yz,↓}) \]

the crystal field terms can be written:

\[ \mathcal{H}_{CF} = - \sum_i \mathbf{c}_i \{ \mathbf{E}_i \otimes I_{2 \times 2} \} \mathbf{c}_i \]

where I₂ₓ₂ is the 2 x 2 identity matrix (for the spin variables); the crystal field tensor E_i is constrained by local 2-fold symmetry at each Ir site to be:

\[ \mathbf{E}_i = \begin{pmatrix} 0 & \Delta_1 & \Delta_2 \\ \Delta_1 & 0 & \Delta_2 \\ \Delta_2 & \Delta_2 & \Delta_3 \end{pmatrix} \]

The t₂g crystal fields Δ₁, Δ₂ denote the on-site hopping between dₓz and dᵧz orbitals, and between dₓy and dᵧz/xy.
orbitals, respectively (Table II). \( \Delta_1 \) is the on-site energy of \( d_{xy} \) minus that of \( d_{xz} \) and \( d_{yz} \). \( \Delta_3 \) is larger in magnitude than in Na\( _2 \)IrO\( _3 \) (27.2 meV)\( ^{21} \). This means that in the 3D \( \gamma \)-Li\( _2 \)IrO\( _3 \) structure, the \( t_{2g} \) crystal field is of the same order of magnitude as the spin-orbit coupling \( \lambda \sim 400 \) meV and this likely has significant effects on the local magnetic interactions.

Table III shows the nearest neighbour hopping parameters where \( t_{1\parallel} \), \( t_{1O} \) and \( t_{1\sigma} \) are defined as in Ref. 20 (labelled \( t_1 \), \( t_2 \), and \( t_3 \) in Ref. 20): \( t_{1O} \) (\( t_2 \)) refers to effective Ir–Ir hopping through the bridging oxygens, \( t_{1\parallel} \) (\( t_3 \)) refer to \( \sigma \) - and \( \delta \)-type direct metal-metal hopping, respectively. A full table of hopping integrals in the \( t_{2g} \) basis are given in the Appendix. There are three significant differences in the nearest neighbour hoppings of the 3D \( \gamma \)-Li\( _2 \)IrO\( _3 \) (see Table III) when compared with Na\( _2 \)IrO\( _3 \): i) the direct metal-metal hopping \( t_3 \) (\( d_{xy} \to d_{xy} \)) along the \( Z_A \) and \( Z_B \) bonds (Fig. 1(b)) is larger than the oxygen-assisted hopping \( t_2 \) (\( d_{xz} \to d_{yz} \), \( d_{yz} \to d_{xz} \)) due to the nearly 90° Ir-O-Ir angle (Table I). ii) the \( t_2 \) in the \( X_A \) (\( Y_A \)), \( X_B \) (\( Y_B \)) bonds have opposite signs, as a result of different local environments (see Appendix). The different sign arises because such bonds are related to one another by crystallographic 2-fold rotations. Finally, iii) the absence of inversion symmetry for the majority of nearest neighbour bonds allows for some asymmetry in the \( t_2 \) hopping, e.g. for the \( X_A \) bond, \( d_{xy} \to d_{xz} \) and \( d_{xz} \to d_{xy} \) hoppings are unequal. For this reason, a finite Dzyaloshinskii-Moriya (DM) interaction is both allowed and expected to appear for the majority of first-neighbour bonds: \( X_A \), \( Y_A \), \( Y_B \), and \( Z_C \). This result is in contrast to Na\( _2 \)IrO\( _3 \) and \( \alpha \)-Li\( _2 \)IrO\( _3 \), for which a weaker DM interaction only exists for the second nearest neighbour bond\( ^{20} \). Since these antisymmetric interactions are likely to strongly stabilize the observed incommensurate magnetic order\( ^{12} \), one may question the completeness of previous interaction models for \( \gamma \)-Li\( _2 \)IrO\( _3 \) including only symmetric exchange interaction\( ^{13,14} \).

Unlike the 2D Na\( _2 \)IrO\( _3 \), the 3D \( \gamma \)-Li\( _2 \)IrO\( _3 \) does not allow a clear description of the DFT electronic structure in terms of QMOs. Indeed, there is no pseudogap at the Fermi energy at the GGA+SO level (Fig. 2(d)), in contrast with Na\( _2 \)IrO\( _3 \). As in the \( P\overline{3} \)\( 1 \)\( 2 \) structure of \( \alpha \)-RuCl\( _3 \), the oxygen assisted hopping \( t_{1O} \), which is crucial for the formation of the QMOs, is smaller than \( t_{1\sigma} \)\( ^{21} \). In addition, since not all local Ir 5d orbitals can be attributed to a single hexagon, the QMO basis is incomplete. We therefore choose to work with the \( j_{\text{eff}} \) basis. Fig. 2(d) shows the projection of the GGA+SO DOS onto the \( j_{\text{eff}} \) basis. At the Fermi level, the DOS is dominantly \( j_{\text{eff}} = 1/2 \) with a small contribution from \( j_{\text{eff}} = 3/2 \).

According to experiment, the magnetic ground state in \( \gamma \)-Li\( _2 \)IrO\( _3 \) is spin spiral\( ^{13} \) and the magnetic structure shows that the zigzag chains in the \( a \) direction are connected along the \( c \) direction (see Fig. 1(c)). In order to perform spin-polarized DFT calculations in the magnetically ordered state, we employed a collinear zigzag magnetic configuration with spin polarization along the \( c \) direction as an approximate representation of the ordered configuration\( ^{13} \). Calculations with the spin polarization along \( a \) are shown in Appendix B for comparison. Inclusion of \( U \) within the GGA+SO+U approach in the zigzag magnetic configuration (Fig. 1(c)) opens a gap of 242 meV (Fig. 3) which is smaller than the experimentally measured value of 0.5 eV\( ^{21} \). We note that the size of the gap is influenced by the choice of \( U \). We however decided here to use the same \( U \) parameter as for previous calculations for Na\( _2 \)IrO\( _3 \) and \( \alpha \)-Li\( _2 \)IrO\( _3 \) in order to allow a better comparison below. The magnetic moment converged to 0.58 \( \mu_B \) for \( j_{\text{eff}} = 1/2 \) and 0.44 \( \mu_B \) for \( j_{\text{eff}} = 3/2 \).

### C. Exact Diagonalization of Finite Clusters

While the GGA+SO+U calculations are able to describe many significant aspects of the electronic structure of \( \gamma \)-Li\( _2 \)IrO\( _3 \) they do not fully capture effects originating from correlations beyond GGA+SO+U, which are expected to be relevant when analyzing electronic excitations. Therefore, we consider here a complementary approach to DFT, namely exact diagonalization of the fully interacting Hamiltonian on finite clusters\( ^{32} \) and compare with DFT results.

We have employed four-site clusters shown in the inset of Fig. 5 and obtained the exact eigenstates of the Ir

| Crystal field | Na\( _2 \)IrO\( _3 \)\( ^{20} \) | \( \gamma \)-Li\( _2 \)IrO\( _3 \) |
|--------------|----------------|----------------|
| Parameter    | Ir(1)          | Ir(2)          |
| \( \Delta_1 \) | -22.9          | -24.4          |
| \( |\Delta_2| \) | 27.6           | 4.2            |
| \( \Delta_3 \) | -27.2          | -213.5         |

| \( \gamma \)-Li\( _2 \)IrO\( _3 \) | \( X_A \), \( Y_A \) | \( Y_B \), \( X_B \) | \( Z_A \), \( Z_B \) | \( Z_C \) |
|-------------------------------|----------------|----------------|----------------|----------------|
| \( t_{1\parallel} \) (\( t_1 \)) | 91.4           | 91.4           | 91.8           | 77.4           |
| \( t_{1O} \) (\( t_2 \)) | -262.5         | 262.5          | 132.8          | 294.1          |
| \( t_{1\sigma} \) (\( t_3 \)) | -240.5         | 240.5          | 132.8          | 294.1          |

| \( \alpha \)-RuCl\( _3 \) | \( \gamma \)-Li\( _2 \)IrO\( _3 \) | \( X_A \), \( Y_A \) | \( Y_B \), \( X_B \) | \( Z_A \), \( Z_B \) | \( Z_C \) |
|--------------------------|----------------------------|----------------|----------------|----------------|----------------|
| \( t_{1\parallel} \) (\( t_1 \)) | 91.4                       | 91.4           | 91.8           | 77.4           |
| \( t_{1O} \) (\( t_2 \)) | -262.5                     | 262.5          | 132.8          | 294.1          |
| \( t_{1\sigma} \) (\( t_3 \)) | -240.5                     | 240.5          | 132.8          | 294.1          |
spin-orbit coupling (SOC) is described by:

\[ \mathcal{H}_{\text{inter}} = \mathcal{H}_{\text{hop}} + \mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{SO}} + \mathcal{H}_U \]

including the kinetic hopping term \( \mathcal{H}_{\text{hop}} \), the crystal field splitting \( \mathcal{H}_{\text{CF}} \), spin-orbit coupling \( \mathcal{H}_{\text{SO}} \), and Coulomb interaction \( \mathcal{H}_U \). In terms of the \( t_{2g} \) basis introduced above, spin-orbit coupling (SOC) is described by:

\[ \mathcal{H}_{\text{SO}} = \frac{\lambda}{2} \sum_i \mathbf{c}_i^\dagger \begin{pmatrix} 0 & -i \sigma_z & i \sigma_y \\ i \sigma_z & 0 & -i \sigma_x \\ -i \sigma_y & i \sigma_x & 0 \end{pmatrix} \mathbf{c}_i \]

where \( \sigma \mu, \mu = \{x, y, z\} \) are Pauli matrices. The Coulomb terms are:

\[ \mathcal{H}_U = U \sum_{i,a} n_{i,a,\uparrow} n_{i,a,\downarrow} + (U' - J_H) \sum_{i,a < b,\sigma} n_{i,a,\sigma} n_{i,b,\sigma} \]

\[ + U' \sum_{i,a \neq b} n_{i,a,\uparrow} n_{i,b,\downarrow} - J_H \sum_{i,a \neq b} c_{i,a,\uparrow} c_{i,a,\downarrow} c_{i,b,\downarrow} c_{i,b,\uparrow} \]

\[ + J_H \sum_{i,a \neq b} c_{i,a,\downarrow} c_{i,a,\uparrow} c_{i,b,\downarrow} c_{i,b,\uparrow} \]

where \( c_{i,a} \) creates a hole in orbital \( a \in \{d_{xy}, d_{xz}, d_{yz}\} \) at site \( i \); \( J_H \) gives the strength of Hund’s coupling, \( U \) is the intraorbital Coulomb repulsion, and \( U' = U - 2J_H \) is the interorbital repulsion. For 5\text{d} Ir\text{V}+, we take \( U = 1.7 \text{ eV}, J_H = 0.3 \text{ eV} \). For the four-site clusters, we retain all hoppings including second neighbour.

For \( \gamma\text{-Li}_2\text{IrO}_3 \), there are four translationally inequivalent clusters constructed from bonds \( (X_A, Y_A, Z_A), (X_B, Y_B, Z_B), (X_A, Y_A, Z_C), \) and \( (X_B, Y_B, Z_C) \). Of these, the first two are related to one another by 2-fold rotation and the last two are also related by 2-fold rotation. The results presented correspond to an average over these four clusters. In each four-site cluster, we consider states with a total of four holes in the \( t_{2g} \) orbitals; each Ir site contains six relativistic orbitals including two \( j_{\text{eff}} = 1/2 \) and four \( j_{\text{eff}} = 3/2 \) levels. As in Ref. [22], the many-body basis states for the cluster can be divided into several subspaces based on the occupancy of the various orbitals and sites. Basis states with site occupancy \( d^0 - d^0 - d^0 - d^0 \) are included in subspaces \( S_1 - S_3 \), states with site occupancy \( d^1 - d^0 - d^0 - d^0 \) belong to subspaces \( S_4 - S_6 \), and \( S_5 \) contains all higher excitations. We show representative diagrams of the lowest energy subspace \( S_1 \) and one particle excitation \( S_2 \), and \( S_5 \) in Fig. 4. Subspace \( S_1 \) contains all states with \( (j_{3/2})^4 (j_{1/2})^4 \) occupancy at every site, which represent a significant contribution to the ground state and low-lying magnon-like spin excitations.

From these configurations, promotion of a single electron via onsite \( j_{1/2} \rightarrow j_{1/2} \) generates subspace \( S_2 \), containing all states with a single spin-orbital exciton; the characteristic excitation energy for such states is given by \( \Delta E_2 \sim 3\lambda/2 \sim 0.6 \text{ eV} \). All states with multiple excitons are grouped into subspace \( S_3 \), and represent \( n \)-particle excitations from the ground state, with energies \( \Delta E_3 \sim 3n\lambda/2 \sim 1.2, 1.8, ... \text{ eV} \).

Starting from \( S_1 \), promotion of an electron via intersite \( j_{1/2} \rightarrow j_{1/2} \) yields subspace \( S_4 \), containing states with

FIG. 3: (Color online) Ir 5\text{d} \( t_{2g} \) band structure and relativistic DOS for \( \gamma\text{-Li}_2\text{IrO}_3 \) in zigzag magnetic order, obtained with GGA+SO+U (\( U_{\text{eff}} = U-J_H = 2.4 \text{ eV} \)).

FIG. 4: (Color online) Schematic diagrams of lowest energy subspace \( S_1 \) and one particle excitations \( S_2, S_3, \) and \( S_5 \). Solid circles indicate electrons while empty circles are holes. \( S_1 \) are all the states with \( (j_{3/2})^4 (j_{1/2})^4 \). \( S_2 \) are the states obtained from \( S_1 \) by promoting an electron \( j_{3/2} \rightarrow j_{1/2} \) on the same site. \( S_4 \) are the states obtained from \( S_1 \) by promoting an intersite \( j_{1/2} \rightarrow j_{1/2} \) transition, and \( S_5 \) are the states with promotion of an electron \( j_{3/2} \rightarrow j_{1/2} \).
characteristic energy $\Delta E_4 \sim A^{-1}$, where \( A = - \frac{1}{3} \left\{ \frac{J_H + 3(U + 3\lambda)}{6J_H^2 - U(U + 3\lambda) + J_H(U + 4\lambda)} \right\} \) \( (7) \)

Taking \( U = 1.7 \) eV, \( J_H = 0.3 \) eV, and \( \lambda = 0.4 \) eV suggests \( \Delta E_4 \sim 1.1 \) eV.

Starting from \( S_1 \), promotion of an electron via intersite \( j_{3/2} \to j_{1/2} \) yields subspace \( S_5 \), containing states with characteristic energy \( \Delta E_5 \sim C^{-1} \sim 1.6 \) eV, where \( ^{20} \)

\[
\begin{align*}
C &= \frac{6}{8} \left\{ \frac{1}{2U - 6J_H + 3\lambda} + \frac{5}{9} \frac{3U - 7J_H + 9\lambda}{J_H} \right\} \\
\eta &= \frac{J_H}{6J_H^2 - J_H(8U + 17\lambda) + (2U + 3\lambda)(U + 3\lambda)}
\end{align*}
\( \tag{8} \)

Subspace \( S_6 \) contains two-particle excited states for which the \( d^4 \) site contains occupancies \( (j_{3/2})^2(j_{1/2})^2 \), while subspace \( S_7 \) contains all other excitations with occupancy of \( d^4 - d^0 = d^5 - d^6 \). Single particle excitations most relevant for the optical conductivity in the next section are contained in \( S_1, S_4, S_5 \). The effect of intersite hopping (and Hund’s coupling) is to mix states from different subspaces, but the characteristic energies remain valid.

In order to show this, we project the exact cluster eigenstates \( \phi_m \) on different subspaces:

\[
\Gamma_m^i = \sum_{s \in S_i} |\langle \phi_m | s \rangle|^2
\] \( \tag{10} \)

and take the spectral weight (SW) of the projected excitation spectra \( P_i \)\( ^{33} \)

\[
P_i (\omega) = \sum_m \Gamma_m^i \delta (\omega - E_m)
\] \( \tag{11} \)

\( P_1 \) to \( P_7 \) are shown in Fig. 5. As expected, the ground state and low-lying magnon-like spin excitations \( \omega \sim 0 \) eV have the dominant \( S_1 \) character (large \( P_1 \)), while intersite hopping perturbatively mixes in some \( S_2, S_4 \), \( S_5 \) character. Indeed, from the localized picture, it is the intersite \( j_{3/2} \to j_{1/2} \) mixing that is the origin of the anisotropic Kitaev exchange couplings.

Regarding the higher excitations: centered at \( \omega = \Delta E_2 \sim 0.6 \) eV are the single exciton-like states, with dominant \( S_2 \) character. These states weakly mix with the single-particle \( S_4 \) and \( S_5 \) and multi-particle \( S_6 \) and \( S_7 \) excitations via intersite hopping. As expected, excitations with dominant \( S_4 \) character (i.e. \( j_{1/2} \to j_{1/2} \)) are centered around \( \omega = \Delta E_4 \sim 1.1 \) eV, and excitations with dominant \( S_5 \) character (i.e. \( j_{3/2} \to j_{1/2} \)) are centered around \( \omega = \Delta E_5 \sim 1.6 \) eV. The widths of these bands are approximately 1 eV and 2 eV, respectively, which is consistent with the GGA+SO+U results above.

It is worth noting that the total spectral weight \( \int P_i d\omega \) is much larger for \( S_5 \) than \( S_4 \), such that \( j_{3/2} \to j_{1/2} \) excitations dominate the projected excitation spectra. Similar results were obtained in Ref. \( ^{22} \) in the analysis of the excitation spectrum of Na$_2$IrO$_3$.

\section{III. Optical Conductivity}

We employ two methods to compute the optical conductivity. The interband contribution to the real part of the optical conductivity in the DFT calculations is approximated by \( ^{29,30} \)

\[
\sigma_{\mu\nu}(\omega) \propto \frac{1}{\omega} \sum_{c,v} \int d\mathbf{k} \langle c_{\mathbf{k}} | p^\mu | v_{\mathbf{k}} \rangle \langle v_{\mathbf{k}} | p^\nu | c_{\mathbf{k}} \rangle \times \delta (\varepsilon_{c_{\mathbf{k}}} - \varepsilon_{v_{\mathbf{k}}} - \omega)
\] \( \tag{12} \)

where \( \mu \) and \( \nu \) correspond to the cartesian axes \( x', y', z' \), which is chosen as the direction of \( a, b, c \) in this system. \( \omega \) indicates the energy of the incident photon, and \( p \) is the momentum operator. The states \( |c_{\mathbf{k}}\rangle \) in \( \mathbf{k} \) space with energy \( \varepsilon_{c_{\mathbf{k}}} \) belong to occupied single-particle states, while \( |v_{\mathbf{k}}\rangle \), \( \varepsilon_{v_{\mathbf{k}}} \) describe unoccupied states.

For the exact diagonalization calculations, we calculate the real part of the optical conductivity at finite temperature using \( ^{33} \)

\[
\sigma_{\mu\nu}(\omega) \propto \frac{\pi(1 - e^{-\omega/(k_B T)})}{\omega V} \sum_{n,m} B_{nm} \delta(\omega + E_n - E_m)
\] \( \tag{13} \)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{(Color online) The investigated four-site cluster (insert) and spectral weight (SW) of projected excitations spectra for $\gamma$-Li$_2$IrO$_3$. $P_1$ includes all states with \((j_{3/2})^4(j_{1/2})^1 (S_1)\), $P_2$ and $P_3$ include the states with an exciton on one site ($S_2$) or on more sites ($S_4$), respectively. $P_4$ includes states from $S_1$ with promotion of an electron $j_{1/2} \to j_{1/2}$ to another site ($S_1$), and $P_5$ includes states with promotion of an electron $j_{3/2} \to j_{1/2}$ to another site ($S_5$). $P_6$ is for states that contain two-particle excited states for which the $d^4$ site contains occupations $(j_{1/2})^2(j_{1/2})^2 (S_6)$, while $P_7$ includes all other excitations with occupancy of $d^4 - d^0 = d^5 - d^6$ ($S_7$), $\Delta E_2 \sim 0.6$ eV, $\Delta E_4 \sim 1.1$ eV, $\Delta E_5 \sim 1.6$ eV are the excitation energies for $P_2$, $P_4$ and $P_5$ respectively.}
\label{fig5}
\end{figure}
The current operator 
\[ j_\mu = \frac{ie}{\hbar} \sum_{\alpha,b,\sigma,\sigma'} (c_{i,a,\sigma,j,b,\sigma'}^\dagger - c_{j,b,\sigma',\alpha,i,a,\sigma}^\dagger) t_{i,j}^{\alpha,b,\sigma,\sigma'} (16) \]

where \( t_{i,j}^{\alpha,b,\sigma,\sigma'} \) are the hopping parameters between the \( t_{2g} \) orbitals and \( r_{ij}^{\mu} \) is the \( \mu \) component of the vector from site \( j \) to site \( i \). Note that the expression of the optical conductivity considered in Eq. (12) is defined at zero temperature and in \( k \) space while in Eq. (13) we consider the definition in real space and at finite temperature \( k_B T = 30 \text{ meV} \) (room temperature). We observe that the finite temperature modifies the zero temperature results only slightly. The optical conductivity is normalized by the sum-rule that the energy integral of the optical conductivity considered in Eq. (12) is defined at zero temperature and in \( k \) space while in Eq. (13) we consider the definition in real space and at finite temperature \( k_B T = 30 \text{ meV} \) (room temperature). We observe that the finite temperature modifies the zero temperature results only slightly. The optical conductivity is normalized by the sum-rule that the energy integral of the optical conductivity in both ED and DFT methods is proportional to the effective density of electrons.

For \( \gamma\text{-Li}_2\text{IrO}_3 \), the orthorhombic symmetry of the space group allows the optical conductivity tensor to be defined in terms of the three independent components \( \sigma_a, \sigma_b, \sigma_c \) \( (\sigma_a = \sigma_{z'z'}, \sigma_b = \sigma_{yy'}, \sigma_c = \sigma_{z'z'}) \):

\[
\begin{pmatrix}
J_a \\
J_b \\
J_c
\end{pmatrix} =
\begin{pmatrix}
\sigma_a & 0 & 0 \\
0 & \sigma_b & 0 \\
0 & 0 & \sigma_c
\end{pmatrix}
\begin{pmatrix}
E_a \\
E_b \\
E_c
\end{pmatrix} .
\]

(17)

In Fig. 6 we compare the DFT (GGA+U+SO), ED and experimental optical conductivity tensor components for \( \gamma\text{-Li}_2\text{IrO}_3 \). Both DFT and ED capture correctly the anisotropy \( \sigma_a < \sigma_b < \sigma_c \), which is due to the structural orientation of the planes shown in the inset of Fig. 6(b). Given that interplane hopping is very weak, the in-plane component of \( \sigma(\omega) \) dominates. The magnitude of \( \sigma(\omega) \) for polarization along each axis is therefore related to the projection of that axis on to the Ir planes. For light polarized along the \( c \)-axis, the response is solely due to in-plane processes, while polarization along the \( a \)- or \( b \)-axes measures only a fraction of the in-plane response. This observation explains the reduction of the measured \( \sigma(\omega) \) \( (\sigma_a, \sigma_b) \) for \( \gamma\text{-Li}_2\text{IrO}_3 \) discussed in Ref. [21] when compared with the in-plane measurements of \( \text{Na}_2\text{IrO}_3 \).

While ED calculations show a dominant peak around \( \omega = 1.6 \text{ eV} \) for all polarizations, consistent with the experimental data, the DFT results suggest also significant spectral weight at lower frequencies. The origin of this anomalous spectral weight can be found in Fig. 7. For
the DFT calculations, we show the decomposition of $\sigma(\omega)$ into intraband $j_{1/2} \rightarrow j_{1/2}$ and interband $j_{3/2} \rightarrow j_{1/2}$ excitations. For the ED calculations, we plot the projection of $\sigma(\omega)$ onto the $S_1 \rightarrow S_2$ (i.e., spin-orbital excitons), $S_4 \rightarrow S_1$ (i.e., $j_{1/2} \rightarrow j_{1/2}$), and $S_1 \rightarrow S_5$ (i.e., $j_{3/2} \rightarrow j_{1/2}$) excitations. Although direct $S_1 \rightarrow S_2$ excitations are optically forbidden, the spin-orbital excitonic states $S_2$ also make a weak contribution to $\sigma(\omega)$ in the mid-energy range due to weak higher order effects. These contributions are also shown. Both the DFT and ED calculations suggest that the peak around 1.6 eV is due primarily to interband $j_{3/2} \rightarrow j_{1/2}$ contributions. The anomalous low-frequency ($\omega < 1$ eV) spectral weight in the DFT arises primarily from $j_{1/2} \rightarrow j_{1/2}$ excitations between the upper and lower Hubbard bands, the intensity of which are dramatically suppressed in the ED results. This difference can be traced back to two main effects:

(i) From a localized perspective, we can consider the ground state for two sites as having an electronic configuration $S_1$: site 1 = $(j_{3/2})^4(j_{1/2})^1$, site 2 = $(j_{3/2})^4(j_{1/2})^1$. Intersite $j_{1/2} \rightarrow j_{1/2}$ transitions yield local configurations like $S_4$: $(j_{3/2})^4(j_{1/2})^0 - (j_{3/2})^3(j_{1/2})^2$, which have a low spin degeneracy as a result of the filled or empty $j_{1/2}$ states. Intersite $j_{3/2} \rightarrow j_{1/2}$ excitations yield local configurations like $S_5$: $(j_{3/2})^3(j_{1/2})^1 - (j_{3/2})^4(j_{1/2})^2$, which have a larger spin-degeneracy due to the partially filled $j_{3/2}$ and $j_{1/2}$ states. Overall, the ratio of the total spectral weight associated with these transitions should be $\int P_1(\omega) : \int P_2(\omega) = 1 : 8$, as shown in Fig. 8. In contrast, the DFT calculations take an effective single-particle momentum space perspective, in which the $j_{3/2}$ band is fully occupied, and the $j_{1/2}$ band is half-occupied. The spectral weight associated with $j_{1/2} \rightarrow j_{1/2}$ and $j_{3/2} \rightarrow j_{1/2}$ transitions is therefore 1 : 4, which overestimates the contributions of the former in DFT calculations compared to the localized view. In other words, DFT does not correctly capture the spin-multiplicity associated with the localized states.

(ii) In a localized picture, the current operator depends on the intersite hopping matrix elements via Eq. (16). It is therefore useful to rewrite the nearest neighbour hopping integrals in the relativistic basis. For example, for the $Z$-bonds, these are:

$$t_{ij}(j_{1/2} \rightarrow j_{1/2}) \propto (2t_1 + t_3)$$

(18)

$$t_{ij}(j_{3/2}; m_{\pm 1/2} \rightarrow j_{1/2}) \propto (t_3 - t_1)$$

(19)

$$t_{ij}(j_{3/2}; m_{\pm 3/2} \rightarrow j_{1/2}) \propto t_2$$

(20)

Via the current operator Eqs. (15)-(16), the optical conductivity associated with each transition scales with $\sigma(\omega) \propto (t_{ij})^2$. Typically, in the corner-sharing iridates such as $\gamma$-Li$_2$IrO$_3$, $t_1$ and $t_3$ have opposite sign (and may be quite small), which suppresses the $(j_{1/2} \rightarrow j_{1/2})$ hopping, reducing the influence of such excitations on the optical conductivity. This effect is partially captured in DFT, as can be seen from comparing the relative widths of the $j_{1/2}$ and $j_{3/2}$ bands in Fig. 8. However, DFT likely overestimates the degree of $j_{1/2} - j_{3/2}$ mixing which leads, effectively, to larger optical matrix elements between low-energy states.

Overall, we conclude that the ED calculations, based on DFT hopping integrals, provides the best description of the optical conductivity.

IV. COMPARISON TO Na$_2$IrO$_3$ AND $\alpha$-Li$_2$IrO$_3$

Despite differences in crystal architecture, the experimental optical conductivity of $\gamma$-Li$_2$IrO$_3$ and Na$_2$IrO$_3$ share a very similar profile that we will analyze in what follows. As stated in the previous section, $\sigma(\omega)$ should be dominated by intersite $j_{3/2} \rightarrow j_{1/2}$ excitations, at $\omega \sim C^{-1} \sim 1.6$ eV, as observed. The soft shoulder observed at lower energies results from a combination of low spectral weight from intersite $j_{1/2} \rightarrow j_{1/2}$ excitations centered at $\omega \sim C^{-1} \sim 1.1$ eV, and weak mixing with optically forbidden local $j_{3/2} \rightarrow j_{1/2}$ excitons near $\omega \sim 0.6$ eV. These assignments are consistent with the fitting of $\sigma(\omega)$ in Ref. [15] for Na$_2$IrO$_3$, which suggested peaks in the vicinity of 0.72, 1.32, and 1.66 eV. However, the “band gap” reported to be 0.32 eV is likely to be significantly contaminated by low-lying excitonic states, and may therefore not represent the natural charge gap of the material. The origin of the peaks for Na$_2$IrO$_3$ in the relativistic basis are shown in Fig. 9 for both calculations.

In Fig. 8 we display the theoretical DFT and ED results for the in-plane $\sigma_\parallel$ component for Na$_2$IrO$_3$, $\alpha$-Li$_2$IrO$_3$ and $\gamma$-Li$_2$IrO$_3$. For $\alpha$-Li$_2$IrO$_3$, we employed the recently obtained single crystal structure [16]. Hopping integrals and crystal field parameters for the revised structure are given in the Appendix. It should be noted that the results obtained for $\alpha$-Li$_2$IrO$_3$ in this work therefore differ slightly from the results in Ref. [10] which employed instead previously available structures obtained from pow-
The desirable Kitaev limit \( K_1 \gg J_1, \Gamma_1 \) is obtained only for \( t_2 \gg t_1, t_3 \), and will therefore be most closely approached by materials with the low spectral weight near \( \omega \sim 1.1 \) eV. This identifies \( \text{Na}_2\text{IrO}_3 \) as the closest material to the Kitaev limit from all three investigated here, in agreement with Ref. [20].

V. SUMMARY

We have investigated the electronic structure, hopping parameters and optical excitation spectrum of the three-dimensional \( \gamma\text{-Li}_2\text{IrO}_3 \). Due to the lower symmetry of the local Ir-O-Ir environment, the hopping integrals display significant deviations from the ideal case, suggesting e.g. large metal-metal hoppings and departures from inversion symmetric values. This situation likely leads to highly complex magnetic interactions in this system and manifests in certain signatures in the optical conductivity.

We computed the optical conductivity by two methods; (i) relativistic DFT calculations within GGA+SO+U and (ii) exact diagonalization of the full interacting Hamiltonian on finite clusters where the hopping integrals were obtained from DFT. Both methods reproduce the main peak of the in-plane component of the optical conductivity \( \sigma_c \). However, GGA+SO+U seems to overestimate the contribution of the \( j_{1/2} \rightarrow j_{1/2} \) transition at low energies in \( \sigma_a \) and \( \sigma_b \). The ED results, in contrast, validate the model parameters \( (U, J_H, \lambda) \) and suggest that the high-lying excitations appear to be well captured within a localized picture in \( \gamma\text{-Li}_2\text{IrO}_3 \). The comparison with the optical conductivity analysis of \( \text{Na}_2\text{IrO}_3 \) shows that the peak near 1.5 eV in both \( \text{Na}_2\text{IrO}_3 \) and \( \gamma\text{-Li}_2\text{IrO}_3 \) can be identified in terms of intersite \( j_{3/2} \rightarrow j_{1/2} \) excitations. The comparison of \( \sigma(\omega) \) for the various materials suggests that the relative spectral weight of the transitions provide insight into the magnitudes of various hopping integrals, and therefore the local magnetic interactions.

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FIG. 9: (Color online) Optical conductivity component \( \sigma_c \) for \( \text{Na}_2\text{IrO}_3 \) and different \( d-d \) transitions in the relativistic basis calculated (a) with DFT within GGA+U+SO and (b) with the ED method. Comparison with experimental results from Ref. [36] and Ref. [35] is also shown. \( \sigma_c \) of \( \text{Na}_2\text{IrO}_3 \) corresponds to the \( \sigma_{zz} \) component in Ref. [10].

\[
\begin{align*}
J_1 &= \frac{4A}{9}(2t_1 + t_3)^2 - \frac{8B}{9} \left[ 2(t_1 - t_3)^2 \right] \quad (21) \\
K_1 &= \frac{8B}{3} \left\{ (t_1 - t_3)^2 - 3t_2^2 \right\} \quad (22) \\
\Gamma_1 &= \frac{8B}{3} \left\{ 2t_2(t_1 - t_3) \right\} \quad (23)
\end{align*}
\]

where \( B \) is a constant similar to \( A \) and \( C \):

\[
B = \frac{4}{3} \left\{ \frac{(3J_H - U - 3\lambda)}{(6J_H - 2U - 3\lambda)^2} \right\} \quad (24)
\]
Appendix A: Hopping parameters for the nonmagnetic nonrelativistic system

Table IV and Table V show all onsite and nearest neighbor hopping parameters in $\gamma$-Li$_2$IrO$_3$. As noted above, the $t_{1O}$ in the $X_A$ ($Y_A$, $X_B$ ($Y_B$) bonds have opposite signs, as a result of different local environments. The negative value corresponds to type 1 bonds in Fig. 10 while the positive values are type 2 bonds in Fig. 10.

Table VI and Table VII show all onsite and nearest neighbor hopping parameters in $\alpha$-Li$_2$IrO$_3$.

TABLE IV: Hopping parameters for the on-site terms (meV) in $\gamma$-Li$_2$IrO$_3$. A is for hexagon including $X_A$, $Y_A$, $Z_A$ bonds while B is for hexagon including $X_B$, $Y_B$, $Z_B$.

| Ir(1)  | $xy \rightarrow xy$ | -592.6 | $xz \rightarrow xz$ | -379.1 | $yz \rightarrow yz$ | -379.1 |
|--------|---------------------|--------|---------------------|--------|---------------------|--------|
| Ir(2)  | $xy \rightarrow xy$ | -651.3 | $xz \rightarrow xz$ | -540.4 | $yz \rightarrow yz$ | -540.4 |
| Ir(1)  | $xy \rightarrow xz$ | 4.2 (A), -4.2 (B) | $xy \rightarrow yz$ | 4.2 (A), -4.2 (B) |
| Ir(2)  | $xy \rightarrow xz$ | 37.4 (A), -37.4 (B) | $xy \rightarrow yz$ | 37.4 (A), -37.4 (B) |

TABLE V: Nearest neighbor tight-binding hopping matrix elements (meV) for $\gamma$-Li$_2$IrO$_3$.

| $\gamma$-Li$_2$IrO$_3$ | $X_A$ | $X_B$ | $Y_A$ | $Y_B$ | $Z_A$ | $Z_B$ | $Z_C$ |
|------------------------|-------|-------|-------|-------|-------|-------|-------|
| $xy \rightarrow xy$   | 91.4  | 91.4  | 91.4  | -319.7 | -319.7 | -17.1 |
| $xz \rightarrow xz$   | 69.2  | -168.3 | -168.3 | 91.8  | 91.8  | 77.4  |
| $yz \rightarrow yz$   | -168.3 | -168.3 | 69.2  | 69.2  | 91.8  | 91.8  | 77.4  |
| $xy \rightarrow xz$   | -262.5 | 262.5  | 4.2   | -4.2  | 63.9  | -63.9 | -18.7 |
| $xz \rightarrow xz$   | -240.5 | 240.6  | 76.5  | -76.5 | 63.9  | -63.9 | 18.7  |
| $xy \rightarrow yz$   | 4.2   | -4.2   | -262.5 | 262.5  | 63.9  | -63.9 | -18.7 |
| $xz \rightarrow xz$   | 76.5  | -76.5  | -240.5 | 240.6  | 63.9  | -63.9 | 18.7  |
| $yz \rightarrow xz$   | -60.2 | -60.2  | -10.6 | -10.6 | 132.8 | 132.8 | 294.1 |
| $yz \rightarrow xz$   | 10.6  | -10.6  | -60.2 | -60.2 | 132.8 | 132.8 | 294.1 |

TABLE VI: Hopping parameters for the on-site terms (meV) for $\alpha$-Li$_2$IrO$_3$ for the recently available single-crystal structure from Ref. [37].

| $\alpha$-Li$_2$IrO$_3$ | X     | Y     | Z     |
|------------------------|-------|-------|-------|
| $xy \rightarrow xy$   | 70.2  | 70.2  | -139.3 |
| $xz \rightarrow xz$   | 83.6  | -124.0 | 77.7  |
| $yz \rightarrow yz$   | -124.0 | 83.6  | 77.7  |
| $xy \rightarrow xz$   | 239.0 | -34.9 | -30.7 |
| $xz \rightarrow xz$   | 239.0 | -34.9 | -30.7 |
| $xy \rightarrow yz$   | -34.9 | 239.0 | -30.7 |
| $yz \rightarrow xz$   | -34.9 | 239.0 | -30.7 |
| $xy \rightarrow yz$   | -38.6 | -38.6 | 285.5 |
| $yz \rightarrow xz$   | -38.6 | -38.6 | 285.5 |

TABLE VII: Nearest neighbor tight-binding hopping matrix elements (meV) for $\alpha$-Li$_2$IrO$_3$ for the recently available single-crystal structure from Ref. [37].

| $\alpha$-Li$_2$IrO$_3$ | X     | Y     | Z     |
|------------------------|-------|-------|-------|
| $xy \rightarrow xy$   | 91.4  | 91.4  | 91.4  |
| $xz \rightarrow xz$   | 69.2  | -168.3 | -168.3 |
| $yz \rightarrow yz$   | -168.3 | -168.3 | 69.2  |
| $xy \rightarrow xz$   | -262.5 | 262.5  | 4.2   |
| $xz \rightarrow xz$   | -240.5 | 240.6  | 76.5  |
| $xy \rightarrow yz$   | 4.2   | -4.2   | -262.5 |
| $xz \rightarrow xz$   | 76.5  | -76.5  | -240.5 |
| $yz \rightarrow xz$   | -60.2 | -60.2  | -10.6 |
| $yz \rightarrow xz$   | 10.6  | -10.6  | -60.2 |

Appendix B: Optical conductivity with spin polarized to a direction

In order to compare the dependence of the optical conductivity along various spin directions in the zigzag magnetic configuration, we show the results for spins along $a$ and $c$ direction in Fig. 11. The results show that the $\sigma_c$ component doesn’t depend significantly on the spin polarized direction, while $\sigma_a$ and $\sigma_b$ are more sensitive to it.

FIG. 10: (Color online) Local octahedral environment of (a) type 1 and (b) type 2 in $\gamma$-Li$_2$IrO$_3$. ($n_1$, $n_2$, $n_3$) correspond to ($y,z,x$) and ($z,x,y$) for X and Y bonds, respectively.
FIG. 11: (Color online) Optical conductivity tensor components with spin polarization (a) along $c$ and (b) along $a$ in the zigzag configuration.

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