Supplementary material for "Generic spin model for the honeycomb iridates beyond the Kitaev limit"

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I. TIGHT-BINDING MODEL FOR EDGE-SHARING OCTAHEDRA

Consider a single $xy(z)$ type bond, placing the Ir^{4+} ions at the origin and along $\hat{y}-\hat{x}$ as shown in Fig. 1. The remaining bonds can generated using lattice symmetries. We denote the corresponding t_{2g} electron operators as $d_1^\dagger = (d_{1,yz}^\dagger\ d_{1,zx}^\dagger\ d_{1,xy}^\dagger)$ and $d_2^\dagger = (d_{2,yz}^\dagger\ d_{2,zx}^\dagger\ d_{2,xy}^\dagger)$. The bond Hamiltonian can be seen to be

$$T + T^\dagger = d_1^\dagger T_{12} d_2 + d_2^\dagger T_{21} d_1 \tag{1}$$

where $T_{21} = T_{12}^\dagger$. Due to inversion about the bond center and time-reversal, in the t_{2g} basis we have that $T_{12} = T_{12}^\dagger = T_{12}^*$ so T_{12} is real and symmetric.

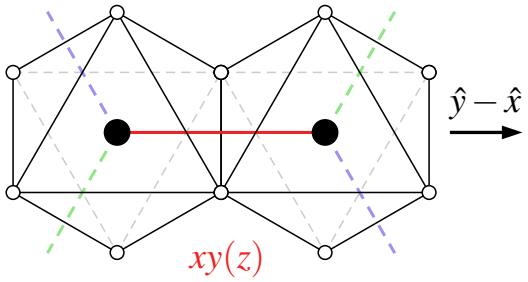

FIG. 1: The $xy(z)$ bond on which we will compute the effective Hamiltonian

When only the two Ir^{4+} ions and the octahedra of O^{2-} ions are included the form of T_{12} is constrained by symmetry. These symmetries are inversion through the bond center, as well as C_2 axes through the [110], [1$\bar{1}$0] and [001] axes, giving the form

$$T_{12} = \begin{pmatrix} t_1 & t_2 & 0 \\ t_2 & t_1 & 0 \\ 0 & 0 & t_3 \end{pmatrix} \tag{2}$$

with the three independent real parameters t_1, t_2 and t_3. The actual bond symmetry in the crystal can be lower, for example due to trigonal distortion. Within the t_{2g} manifold this can introduce additional $xz-xy$ and $yz-xy$ hoppings such as

$$T_{12} = \begin{pmatrix} t_1 & t_2 & t_4 \\ t_2 & t_1 & t_4 \\ t_4 & t_4 & t_3 \end{pmatrix} \tag{3}$$

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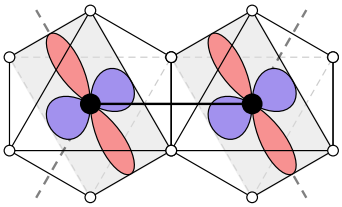
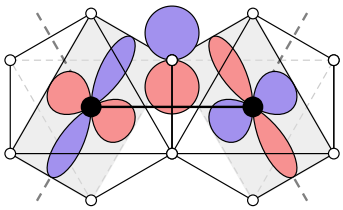
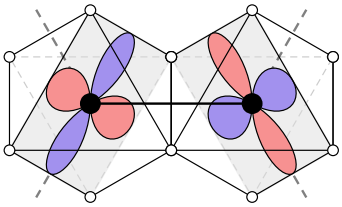


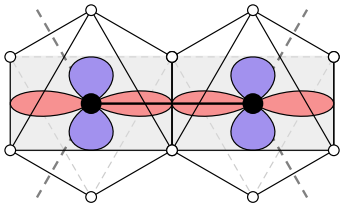
(a) Ir-Ir overlap for t_1



(b) Ir-O-Ir overlap for t_2



(c) Ir-Ir overlap for t_2



(d) Ir-Ir overlap for t_3

FIG. 2: Schematic visual representation of the types orbital overlap contributing to the hoppings t_1, t_2 and t_3 in Eq. 4a for the $xy(z)$ bond.

We will discuss two possibilities relevant for $Na_2IrO_3$and Li_2IrO_3: direct overlap between the d orbitals and hopping mediated through the O^{2-} ions.

$$t_1 = \frac{1}{2}\left(t_{dd\pi} + t_{dd\delta}\right) \tag{4a}$$

$$t_2 = \frac{1}{2}\left(t_{dd\pi} - t_{dd\delta}\right) + \frac{t_{pd\pi}^2}{\Delta_{pd}} \tag{4b}$$

$$t_3 = \frac{1}{4}\left(3t_{dd\sigma} + t_{dd\delta}\right) \tag{4c}$$

The three parameters $t_{dd\sigma}$, $t_{dd\pi}$ and $t_{dd\delta}$ are the usual Slater-Koster parameters for direct d-orbital overlap, with one expecting $|t_{dd\sigma}| > |t_{dd\pi}| > |t_{dd\delta}|$. The oxygen mediated hopping is through the $t_{pd\pi}$ overlap with Δ_{pd} being the chemical potential difference between the Ir^{4+} and O^{2-} ions. A visual representation of these overlaps is shown in Fig. 2.

II. STRONG COUPLING EXPANSIONS

To derive the effective Hamiltonian for the $j_{\text{eff}} = 1/2$ states we consider two forms of strong coupling expansion. The first is the conventional case, where we take $U, J_H \gg \lambda \gg t$. We consider the Kanamori Hamiltonian for the two atoms

$$H_1 + H_2 = \frac{U - 3J_H}{2}\left[(N_1 - 5)^2 + (N_2 - 5)^2\right] - 2J_H(S_1^2 + S_2^2) - \frac{J_H}{2}(L_1^2 + L_2^2) \tag{5}$$

where U is the (screened) Coulomb interaction, J_H is Hund's coupling, N is the total density operator, L is the total (effective) angular momentum operator and S is the total spin operator.

Treating $T + T^\dagger$ as a perturbation to $H_1 + H_2$, an effective Hamiltonian within the $j_{\text{eff}} = 1/2$ subspace can be determined

$$H_{\text{eff}} \sim -\sum_{\alpha\beta}\sum_{n\neq 0}\left[\frac{\langle\alpha|T^\dagger|n\rangle\langle n|T|\beta\rangle}{E_n - E_0} + \frac{\langle\alpha|T|n\rangle\langle n|T^\dagger|\beta\rangle}{E_n - E_0}\right]|\alpha\rangle\langle\beta| \tag{6}$$

where α,β run over $j_{\text{eff}} = 1/2$ states, $\left|+\frac{1}{2},+\frac{1}{2}\right\rangle$, $\left|+\frac{1}{2}-\frac{1}{2}\right\rangle$, $\left|-\frac{1}{2}+\frac{1}{2}\right\rangle$ and $\left|-\frac{1}{2},-\frac{1}{2}\right\rangle$. The excited states of $H_1 + H_2$ are denoted by $|n\rangle$ with energies E_n greater than the ground state energy E_0. By symmetry, the resulting spin Hamiltonian takes the form

$$H_{\text{eff}} \sim J\vec{S}_1\cdot\vec{S}_2 + KS_1^zS_2^z + \Gamma\left(S_1^xS_2^y + S_1^yS_2^x\right) + \Gamma'\left(S_1^xS_2^z + S_1^zS_2^x + S_1^yS_2^z + S_1^zS_2^y\right) \tag{7}$$

Carrying out the expansion one arrives at the following expressions for the exchange constants

$$\begin{aligned}
J &= \frac{4}{27}\left[\frac{6t_1(t_1+2t_3) - 9t_4^2}{U-3J_H} + \frac{9t_4^2 + 2(t_1-t_3)^2}{U-J_H} + \frac{(2t_1+t_3)^2}{U+2J_H}\right] && \text{(8a)}\\
&\approx \frac{4}{9U}\left[(2t_1+t_3)^2 + \frac{2J_H}{U}\left[2t_1(t_1+2t_3) - 3t_4^2\right]\right] + O\left(\frac{J_H^2}{U^2}\right)\\
K &= \frac{8J_H}{9}\left[\frac{(t_1-t_3)^2 - 3(t_2^2-t_4^2)}{(U-3J_H)(U-J_H)}\right] \approx \frac{8}{9U}\left(\frac{J_H}{U}\right)\left[(t_1-t_3)^2 - 3(t_2^2-t_4^2)\right] + O\left(\frac{J_H^2}{U^2}\right) && \text{(8b)}\\
\Gamma &= \frac{8J_H}{9}\left[\frac{3t_4^2 + 2t_2(t_1-t_3)}{(U-3J_H)(U-J_H)}\right] \approx \frac{8}{9U}\left(\frac{J_H}{U}\right)\left[3t_4^2 + 2t_2(t_1-t_3)\right] + O\left(\frac{J_H^2}{U^2}\right) && \text{(8c)}\\
\Gamma' &= -\frac{8J_H}{9}\left[\frac{t_4(t_1-t_3-3t_2)}{(U-3J_H)(U-J_H)}\right] \approx -\frac{8}{9U}\left(\frac{J_H}{U}\right)[t_4(t_1-t_3-3t_2)] + O\left(\frac{J_H^2}{U^2}\right) && \text{(8d)}
\end{aligned}$$

The full nearest neighbour spin model can be obtained using lattice symmetries to generate the remaining bonds. The expressions given in Eqs. 3-5 of the main text can be obtained from Eq. 8 by setting $t_4 = 0$.

A similar calculation can be carried out taking the limit $U, \lambda \gg J_H \gg t$. Here the atomic Hamiltonian includes only the Coulomb interaction U and spin-orbit coupling λ. The contributions proportional to J_H can then be included in the eigenstates and energies using (degenerate)

perturbation theory, and H_{eff} evaluated as above. This gives expressions

$$J = \frac{4}{27}\left[\frac{(2t_1+t_3)^2(4J_H+3U)}{U^2} - \frac{8J_H\left(9t_4^2+2(t_1-t_3)^2\right)}{(2U+3\lambda)^2}\right] \tag{9a}$$

$$K = \frac{32J_H}{9}\left[\frac{(t_1-t_3)^2-3(t_2^2-t_4^2)}{(2U+3\lambda)^2}\right] \tag{9b}$$

$$\Gamma = \frac{32J_H}{9}\left[\frac{3t_4^2+2t_2(t_1-t_3)}{(2U+3\lambda)^2}\right] \tag{9c}$$

$$\Gamma' = -\frac{32J_H}{9}\left[\frac{t_4(t_1-t_3-3t_2)}{(2U+3\lambda)^2}\right] \tag{9d}$$

up to corrections of order $O(J_H^2/\lambda^2)$ and $O(J_H^2/U^2)$. Note that the dependence of these exchanges on the hoppings is nearly identical in both perturbation theories.

III. DERIVATION OF Γ TERM

To unambiguously show the existence of the Γ term in the strong-coupling Hamiltonian, we derive the expression for Γ explicitly. We will work in $U, J_H \gg \lambda \gg t$ limit to connect with the equations shown in the main text. The coefficient Γ can then be determined from the matrix element

$$\Gamma = 2i\left\langle -\tfrac{1}{2}, -\tfrac{1}{2}\,|H_{\text{eff}}|\,+\tfrac{1}{2}+\tfrac{1}{2}\right\rangle \tag{10}$$

where H_{eff} is the two-site effective Hamiltonian for a $xy(z)$ bond. To simplify notation we use the particle-hole mapping $d^5 \to d^1$, mapping the Hamiltonian of Eq. 5 to

$$H_0 = H_1 + H_2 = \frac{U-3J_H}{2}\left[(N_1-1)^2+(N_2-1)^2\right] - 2J_H\left(S_1^2+S_2^2\right) - \frac{J_H}{2}\left(L_1^2+L_2^2\right) \tag{11}$$

Since particle-hole conjugation effectively maps $\left|+\tfrac{1}{2}\right\rangle \leftrightarrow \left|-\tfrac{1}{2}\right\rangle$ we see that we are interested in $\left\langle +\tfrac{1}{2}, +\tfrac{1}{2}\,|H_{\text{eff}}|\,-\tfrac{1}{2}-\tfrac{1}{2}\right\rangle = \left\langle -\tfrac{1}{2}, -\tfrac{1}{2}\,|H_{\text{eff}}|\,+\tfrac{1}{2}+\tfrac{1}{2}\right\rangle^*$ in this new basis. The eigenstates of H_1 or H_2 are eigenstates of N, L^2, L_z, S^2 and S_z at each site, which we will denote as sets using terms symbols ${}^{2S+1}L$. Each individual eigenstates will be denoted as $\left|{}^{2S+1}L, M_L, M_S\right\rangle_a$ with the total number N understood from context and $a = 1, 2$ denoting the site index. The ground state is an $N = 1$ six-fold degenerate ${}^2P$ state with energy $-5J_H/2$. Since the perturbation T moves an electron from site 2 to site 1 we need then only consider $N_1 = 2$ and $N_2 = 0$ states. While the $N = 0$ state is a trivial ${}^1S$ state, anti-symmetric $N = 2$ states can be formed by ${}^1S$, ${}^3P$ and ${}^1D$ terms giving three relevant

excitation energies

$$E_2(^1S) + E_0(^1S) - 2E_1(^2P) = U + 2J_H \tag{12a}$$

$$E_2(^3P) + E_0(^1S) - 2E_1(^2P) = U - 3J_H \tag{12b}$$

$$E_2(^1D) + E_0(^1S) - 2E_1(^2P) = U - J_H \tag{12c}$$

where we have denoted the energy of the N-electron term ^{2S+1}L as $E_N(^{2S+1}L)$. The most straightforward way to compute Γ is to first decompose $T\left|+\frac{1}{2}\right\rangle_1\left|+\frac{1}{2}\right\rangle_2$ into eigenstates of $H_1 + H_2$. Break T into two parts $T = T_1 + T_2$ with

$$T_1 = \sum_\sigma \left[t_1 \left(d^\dagger_{1,xz,\sigma} d_{2,xz,\sigma} + d^\dagger_{1,yz,\sigma} d_{2,yz,\sigma} \right) + t_3 \sum_\sigma d^\dagger_{1,xy,\sigma} d_{2,xy,\sigma} \right] \tag{13a}$$

$$T_2 = t_2 \sum_\sigma \left(d^\dagger_{1,xz,\sigma} d_{2,yz,\sigma} + d^\dagger_{1,yz,\sigma} d_{2,xz,\sigma} \right) \tag{13b}$$

Recall the definition of the $j_{\text{eff}} = 1/2$ states as

$$\left|+\tfrac{1}{2}\right\rangle_a = \sqrt{\frac{1}{3}} \left(d^\dagger_{a,yz,\downarrow} + i d^\dagger_{a,xz,\downarrow} + d^\dagger_{a,xy,\uparrow} \right) |0\rangle_a = \left[\sqrt{\frac{2}{3}} d^\dagger_{a,+,\downarrow} - i \sqrt{\frac{1}{3}} d^\dagger_{a,0,\uparrow} \right] |0\rangle_a \tag{14a}$$

$$\left|-\tfrac{1}{2}\right\rangle_a = \sqrt{\frac{1}{3}} \left(d^\dagger_{a,yz,\uparrow} - i d^\dagger_{a,xz,\uparrow} - d^\dagger_{a,xy,\downarrow} \right) |0\rangle_a = \left[\sqrt{\frac{2}{3}} d^\dagger_{a,-,\uparrow} + i \sqrt{\frac{1}{3}} d^\dagger_{a,0,\downarrow} \right] |0\rangle_a \tag{14b}$$

where $a = 1, 2$ and we have defined the $l_{\text{eff}} = 1$ operators

$$d^\dagger_{a,+,\sigma} = \sqrt{\frac{1}{2}} \left(d^\dagger_{a,yz,\sigma} + i d^\dagger_{a,xz,\sigma} \right) \tag{15a}$$

$$d^\dagger_{a,0,\sigma} = i d^\dagger_{a,xy,\sigma} \tag{15b}$$

$$d^\dagger_{a,-,\sigma} = \sqrt{\frac{1}{2}} \left(d^\dagger_{a,yz,\sigma} - i d^\dagger_{a,xz,\sigma} \right) \tag{15c}$$

In this form we can now act each part of T, decomposing into the excited states as we go

$$\begin{aligned} T_1 \left|+\tfrac{1}{2}\right\rangle_1 \left|+\tfrac{1}{2}\right\rangle_2 &= \left(\frac{t_1 - t_3}{3} \right) \left(d^\dagger_{1,yz,\downarrow} + i d^\dagger_{1,xz,\downarrow} \right) d^\dagger_{1,xy,\uparrow} |0\rangle_1 |0\rangle_2 \\ &= -i \left(\frac{t_1 - t_3}{3} \right) \left[|+\downarrow, 0\uparrow\rangle_1 - |0\uparrow, +\downarrow\rangle_1 \right] |0\rangle_2 \\ &= -i \left(\frac{t_1 - t_3}{3} \right) \left[|^3P, +1, 0\rangle_1 - |^1D, +1, 0\rangle_1 \right] |0\rangle_2 \end{aligned} \tag{16a}$$

$$\begin{aligned} T_2 \left|+\tfrac{1}{2}\right\rangle_1 \left|+\tfrac{1}{2}\right\rangle_2 &= \frac{t_2}{3} \left[2 d^\dagger_{1,xz,\downarrow} d^\dagger_{2,yz,\downarrow} + i \left(d^\dagger_{1,yz,\downarrow} - i d^\dagger_{1,xz,\downarrow} \right) d^\dagger_{1,xy,\uparrow} \right] |0\rangle_1 |0\rangle_2 \\ &= \frac{t_2}{3} \left[-2i \left(|+\downarrow, -\downarrow\rangle - |-\downarrow, +\downarrow\rangle \right) + \left(|-\downarrow, 0\uparrow\rangle - |0, \uparrow, -\downarrow\rangle \right) \right] |0\rangle_2 \\ &= \frac{t_2}{3} \left[-2\sqrt{2} i \left| ^3P, 0, -1 \right\rangle - \left| ^3P, -1, 0 \right\rangle - \left| ^1D, -1, 0 \right\rangle \right] |0\rangle_2 \end{aligned} \tag{16b}$$

To compute the matrix element we also need $T\left|-\frac{1}{2}\right\rangle_1\left|-\frac{1}{2}\right\rangle_2$ related to the states shown in Eq. 16 by the action of time-reversal

$$T_1\left|-\tfrac{1}{2}\right\rangle_1\left|-\tfrac{1}{2}\right\rangle_2 = -i\left(\frac{t_1-t_3}{3}\right)\left[|^3P,-1,0\rangle_1 - |^1D,-1,0\rangle_1\right]|0\rangle_2 \tag{17a}$$

$$T_2\left|-\tfrac{1}{2}\right\rangle_1\left|-\tfrac{1}{2}\right\rangle_2 = \frac{t_2}{3}\left[-2\sqrt{2}i\left|^3P,0,+1\right\rangle + \left|^3P,+1,0\right\rangle + \left|^1D,+1,0\right\rangle\right]|0\rangle_2 \tag{17b}$$

where we have used that the $\left|^{2S+1}L,M_L,M_S\right\rangle$ states pick up an additional sign $(-1)^{L+S+M_L+M_S}$ under time-reversal. In this form we can simply read off the matrix elements

$$\begin{aligned}\left\langle -\tfrac{1}{2},-\tfrac{1}{2}\right|H_{\text{eff}}\left|+\tfrac{1}{2},+\tfrac{1}{2}\right\rangle &= 4i\left(\frac{t_2(t_1-t_3)}{9}\right)\left[\frac{1}{U-3J_H}-\frac{1}{U-J_H}\right]\\ &= \frac{8iJ_H}{9}\left[\frac{t_2(t_1-t_3)}{(U-3J_H)(U-J_H)}\right]\end{aligned} \tag{18}$$

Thus

$$\Gamma = \frac{16J_H}{9}\left[\frac{t_2(t_1-t_3)}{(U-3J_H)(U-J_H)}\right] \tag{19}$$

consistent with the expressions in the Eq. 5 of the main text and with Eq. 8c when $t_4 = 0$.