Magnetic Couplings in Edge-Sharing $d^7$ Compounds

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High-spin $d^7$ Co(II) compounds have recently been identified as possible platforms for realizing highly anisotropic and bond-dependent couplings featured in quantum-compass models such as the celebrated Kitaev model. In order to evaluate this potential, we consider all symmetry-allowed contributions to the magnetic exchange for ideal edge-sharing bonds. Though a combination of ab-initio and cluster many-body calculations we conclude that bond-dependent couplings are generally suppressed in favor of Heisenberg exchange for realistic materials. Consequences for several prominent materials including Na$_2$Co$_2$TeO$_6$ and BaCo$_2$(AsO$_4$)$_2$ are discussed.

I. INTRODUCTION

Pursuit of strongly anisotropic $d$-block magnets has been motivated by the possibility of material realization of so-called quantum compass models, such as Kitaev's celebrated honeycomb model. In these materials, competition between different bond-dependent magnetic interactions produces an extensive classical degeneracy conducive to quantum spin liquid ground states. Realizing these conditions in real materials requires precise tuning and suppression of the usual isotropic magnetic exchange. This can be accomplished, in principle, in edge-sharing compounds with $d^5$ filling and strong spin-orbital coupling. Remarkably, for ideal considerations, the specific spin-orbital composition of the local moments suppresses all couplings except those bond-dependent Ising interactions. While this bonding geometry might support all couplings except those bond-dependent Ising couplings precisely prescribed by Kitaev's model. This revelation led to a flurry of studies in $d^5$ Ir(IV) compounds such as $A_2$IrO$_3$ (A = Na, Li) and the $4d^5$ Ru(III) compound $\alpha$-RuCl$_3$. These studies have revealed clear evidence of a field-induced anisotropic couplings in these compounds, leading to a variety of anomalous behaviors from the breakdown of conventional magnon excitations to the possibility of a field-induced spin-liquid. However, while Kitaev couplings are thought to be the largest interaction, other couplings of similar magnitude always lift the classical degeneracy leading to magnetic order at zero-field.

In this context, the seminal work of Liu et al. and Sano et al. renewed hope for realizing Kitaev's spin liquid, by showing that the magnetic exchange in high-spin $3d^5$ Co(II) ions may also produce dominant Kitaev interactions for ideal considerations. In particular, these studies assumed the dominant hopping between metals occurs via metal-ligand hybridization, which suppresses other couplings. While this condition is satisfied for $5d^5$ Ir(IV) compounds such as $A_2$IrO$_3$, the presence of significant direct metal-metal hopping in $4d^5$ $\alpha$-RuCl$_3$ is the primary source of non-Kitaev interactions. It is not clear that these assumptions are satisfied in $3d$ systems.

The possibility of strong bond-dependent Kitaev interactions also challenges the conventional view that Co(II) compounds typically have bond-independent XXZ anisotropy largely driven by the effects of local crystal field distortions on the $j_{1/2}$ doublets. For example, CoNb$_2$O$_6$ (CNO) is considered to be a prototypical 1D Ising ferromagnet, and has been studied in the context of transverse-field Ising criticality. The structure consists of zigzag chains of edge-sharing CoO$_6$ octahedra, which can be considered as alternating X- and Y-bonds per Fig. 1(a). While this bonding geometry might be expected to produce large bond-dependent couplings, the dominant nearest neighbor interaction is known to have an Ising form $S^a_i S^a_j$ with a common $\alpha$-axis for all bonds. Recent studies have highlighted the importance of small deviations, but it is nonetheless evident that the Kitaev coupling is not dominant.

More recently, the pursuit of 2D honeycomb materials with large bond-dependent couplings has drawn attention to Na$_3$Co$_2$SbO$_6$ (NCSO), and Na$_2$Co$_2$TeO$_6$ (NCTO). Both materials show zigzag antiferromagnetic order. This ground state is natural for strong bond-dependent couplings, although longer-range Heisenberg $J_2$ and $J_3$ may also be invoked. Indeed, analysis of inelastic neutron scattering has led to a wide variety of proposed models for the couplings, which span the entire range from dominant Heisenberg to dominant Kitaev. Overall, the relative role of nearest neighbor bond-dependent coupling vs. longer range Heisenberg exchange remains unclear.

Two more honeycomb materials of recent interest are BaCo$_2$(AsO$_4$)$_2$ (BCAO) and BaCo$_2$(PO$_4$)$_2$ (BCPO). Of these, BCPO displays only short-range incommensurate correlations, suggesting strong frustration. BCAO orders in a state intermediary between zigzag antiferromagnetic and ferromagnetic states with unconventional magnon dispersion, which has been discussed as an incommensurate helimagnet or double stripe zigzag. Under applied field in-plane, BCAO undergoes a series of phase transitions between magnetization plateaus, and was proposed to host a field-induced spin-liquid. However, this was recently called into question due to the appearance of sharp magnon modes in each of the phases. As with NCTO, the relative role of different couplings is a subject of much discussion; the first $ab$-initio studies favored a nearly XXZ model, in contrast with the assumption of large Kiteav interactions.

All of these findings call for a reinvestigation of the magnetic couplings in edge-sharing Co(II) materials. In
this work, we find, in contrast to the assumptions of the initial theoretical analysis, that ligand-mediated hopping is not large in these compounds. For this reason the character of the magnetic couplings is significantly altered from the expected Kitaev form. In particular, ferromagnetic Heisenberg $J$ typically dominates, while the myriad of smaller anisotropic couplings may appear depending on the specific details of the hopping and crystal field distortions.

The paper is organized as follows: We first review the single-ion ground state, and the effect of crystal field distortions on the spin-orbital composition of the single-ion ground state, and the effect of crystal field distortions. We then analyze the full set of relevant symmetry-allowed hoppings in edge-sharing bonds. On the basis of these hoppings, we then compute the resulting magnetic Heisenberg Hamiltonian that satisfies the expected Kitaev form. In particular, ferromagnetic tendencies belonging to different orbital occupancies and saturations are all related to the three Slater parameters $U$, $J$, and $t$. The initial theoretical analysis, that ligand-mediated hopping are, for example:

$$U_{i2g} = F_0 + \frac{4}{49} (F_2 + F_4)$$

$$J_{i2g} = \frac{3}{49} F_2 + \frac{20}{441} F_4$$

We take the approximate ratio $F_4/F_2 = 5/8$, following Ref. 55. The full parameterization is described in Ref. 56. The full parameterization is described in Ref. 52.

For the crystal-field Hamiltonian, we consider an ideal trigonal distortion within $D_{3d}$ site symmetry. The Hamiltonian can be written:

$$\mathcal{H}_{\text{CFS}} = \sum_{i} c_{i,\sigma}^\dagger D c_{i,\sigma}$$

where:

$$c_{i,\sigma}^\dagger = \left( c_{i,yz,\sigma}^\dagger c_{i,xz,\sigma}^\dagger c_{i,y,\sigma}^\dagger c_{i,x,\sigma}^\dagger c_{i,z^2,\sigma}^\dagger c_{i,x^2-y^2,\sigma}^\dagger \right)$$

In terms of the global $(xyz)$ coordinates defined in Fig. 1(a), the CFS matrix can be written:

$$D = \begin{pmatrix}
0 & \Delta_2 & \Delta_2 & 0 & 0 \\
\Delta_2 & 0 & \Delta_2 & 0 & 0 \\
\Delta_2 & \Delta_2 & 0 & 0 & 0 \\
0 & 0 & 0 & \Delta_1 & 0 \\
0 & 0 & 0 & 0 & \Delta_1
\end{pmatrix}$$

where $\Delta_1$ is the $t_{2g}-e_g$ splitting, and $\Delta_2$ is the trigonal term. Generally, $\Delta_2 > 0$ corresponds to trigonal elongation, as shown in Fig. 1(b), although the actual sign is further influenced by the details of the ligand environments and longer ranged Coulomb potentials. Without SOC, the $t_{2g}$ levels are split into a doubly degenerate $e$ pair and a singly degenerate $a$ level, with $E_a - E_e = 3\Delta_2$. As discussed below, the trigonal splitting has a strong impact on the nature of the local moments.

For the “high-spin” $d^7$ case, the ground state has nominal configuration $(t_{2g})^5(e_g)^2$, with three unpaired electrons ($S = 3/2$), as shown in Fig. 1(b). In the absence of trigonal splitting ($\Delta_2 = 0$), there is a three-fold orbital degeneracy associated with the $t_{2g}$ levels, leading to an effective orbital momentum $L_{\text{eff}} = 1$. Spin-orbit coupling $\mathcal{H}_{\text{SOC}} = \lambda \mathbf{L} \cdot \mathbf{S}$ splits the resulting multiplets into $J_{\text{eff}} = 1/2$, 3/2, and 5/2 states. The $j_{1/2}$ doublet is always the ground state, and furnishes the effective spin-orbital moment relevant at low energies. The resulting $J_{\text{eff}}$ multiplets are composed of many configurations belonging to different orbital occupancies and spin values. However, third row metals typically satisfy $J_{\text{eff}}, \Delta_1 \gg \lambda, \Delta_2$, such that configurations belonging precisely to the $(t_{2g})^5(e_g)^2$, $S = 3/2$ manifold carry the dominant weight. When projected into this manifold, the ground state doublet can be written in terms of $|m_L, m_S>$

![FIG. 1. (a) Three types of edge-sharing bonds, with definition of global $(xyz)$ coordinates. (b) Energy level diagram showing the splitting of the local electronic levels in the absence of spin-orbit coupling.]

where the coefficients \( c_n \) vary with \( \Delta_2, \lambda \). The pure \( L, S \) multiplets \( |m_L, m_S\rangle \) can be conveniently expressed in terms of the single-particle levels with precise orbital momentum:

\[
|e_{a,\sigma}\rangle = |d_{z^2,\sigma}\rangle 
|e_{b,\sigma}\rangle = |d_{x^2-y^2,\sigma}\rangle 
|t_{+,\sigma}\rangle = -\frac{1}{\sqrt{2}}(|d_{yz,\sigma}\rangle + i|d_{xz,\sigma}\rangle) 
|t_{0,\sigma}\rangle = |d_{xy,\sigma}\rangle 
|t_{-,\sigma}\rangle = \frac{1}{\sqrt{2}}(|d_{yz,\sigma}\rangle - i|d_{xz,\sigma}\rangle) 
\]

This leads to:

\[
\left| -\frac{3}{2} \right\rangle = |e_{a,\uparrow} e_{b,\uparrow} t_{+,-} t_{0,\uparrow} t_{-,\downarrow} t_{-,\downarrow} \rangle 
\left| 0, \frac{1}{2} \right\rangle = \frac{1}{\sqrt{3}} \left| e_{a,\uparrow} e_{b,\uparrow} t_{+,-} t_{+,\downarrow} t_{0,\downarrow} t_{-,\downarrow} \rangle 
+ \frac{1}{\sqrt{3}} \left| e_{a,\uparrow} e_{b,\uparrow} t_{+,\downarrow} t_{+,\downarrow} t_{0,\downarrow} t_{-,\downarrow} \rangle 
+ \frac{1}{\sqrt{3}} \left| e_{a,\downarrow} e_{b,\downarrow} t_{+,\downarrow} t_{+,\downarrow} t_{0,\downarrow} t_{-,\downarrow} \rangle 
\right| 1, -\frac{1}{2} \right\rangle = \frac{1}{\sqrt{3}} \left| e_{a,\uparrow} e_{b,\uparrow} t_{+,-} t_{+,\downarrow} t_{0,\downarrow} t_{-,\downarrow} \rangle 
+ \frac{1}{\sqrt{3}} \left| e_{a,\downarrow} e_{b,\downarrow} t_{+,\downarrow} t_{+,\downarrow} t_{0,\downarrow} t_{-,\downarrow} \rangle 
+ \frac{1}{\sqrt{3}} \left| e_{a,\downarrow} e_{b,\downarrow} t_{+,\downarrow} t_{+,\downarrow} t_{0,\downarrow} t_{-,\downarrow} \rangle 
\right|
\]

The time-reversed partners can be similarly obtained. For \( \Delta_2 = 0 \), the coefficients are \( c_1 = 1/\sqrt{2}, c_2 = 1/\sqrt{3}, c_3 = 1/\sqrt{6} \). In this same limit, the multiplet energies satisfy:

\[
E_{3/2} - E_{1/2} = \frac{1}{2} \lambda 
E_{5/2} - E_{1/2} = \frac{4}{3} \lambda 
\]

With \( \lambda_{CO} \approx 60 \text{ meV} \), the \( j_{1/2} \to j_{3/2} \) excitation is expected to appear in the range of \( \sim 30 \text{ meV} \), as has been seen experimentally in numerous compounds.\(^{22,13,27,55}\)

### B. Local Effects of Trigonal Distortion

For finite \( \Delta_2 \), the composition of the doublet is significantly altered. Here, we review similar discussions in Ref.\(^{20,25}\) and Fig. 2. In Fig. 2, we show the evolution of the local spectrum as a function of \( \Delta_2/\lambda \), as well as the coefficients \( c_n \) and \( g \)-tensor for the lowest doublet.

In the limit of large trigonal elongation \( \Delta_2 > 0 \), the unpaired hole in the \( t_{2g} \) levels occupies the singly degenerate \( a \) level, thus quenching the orbital moment completely. This corresponds to \( c_2 \to 1 \) and \( c_1, c_3 \to 0 \). The energetic splitting between the lowest two doublets becomes small, thus restoring the fourfold degeneracy of the nearly pure \( S = 3/2 \) moment. The \( m_s = \pm 1/2 \) states lie slightly below the \( m_s = \pm 3/2 \) states, due to residual easy-plane single-ion anisotropy. As such, the \( g \)-tensor for the lowest doublet satisfies \( g_\perp > g_|| \), where \( g_|| \) refers to the component along the trigonal axis. However, a model incorporating only the lowest doublet remains valid only as long as the single-ion anisotropy remains large compared to...
the intersite magnetic exchange (roughly, if \( \Delta_2 < \lambda/2 \)).

For the opposite case of trigonal compression \( \Delta_2 < 0 \),
the unpaired hole in the \( t_{2g} \) levels occupies the doubly
degenerate \( e \) levels, thus retaining some orbital degeneracy
consistent with \( L_{\text{eff}} = 1/2 \). This corresponds to \( c_1 \to 1 \),
\( c_2, c_3 \to 0 \). The effect of SOC is then to split the \( S = 3/2 \),
\( L_{\text{eff}} = 1/2 \) manifold into four doublets. Since the
lowest doublet corresponds to pure \( m_s = \pm 3/2 \),
this may be considered as strong easy-axis single-ion anisotropy.
Consistently, the \( g \)-tensor satisfies \( g_\parallel \gg g_\perp \) in this limit. The
gap between the lowest doublets converges to \( \lambda/3 \sim 20 \)
meV, which should typically exceed the intersite magnetic
interaction. For this reason, a model incorporating
only the lowest doublet may remain valid for large
\( \Delta_2 < 0 \).

III. EDGE-SHARING BOND HOPPINGS

A. General Form

The effective \( d-d \) hopping between metal sites is
described by:

\[
\mathcal{H}_{\text{hop}} = \sum_{i,j,\sigma} t_{ij} \hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma}
\] (20)

For an ideal edge-sharing bond, \( C_{2v} \) symmetry restricts
the form of the hopping matrices. In terms of the global
\((x, y, z)\) coordinates defined in Fig. 3, the matrices are
constrained to take the following form, for the \( Z \)-bond:

\[
\mathcal{T}_Z = \begin{pmatrix}
t_1 & t_2 & 0 & 0 & 0 \\
t_2 & t_1 & 0 & 0 & 0 \\
0 & t_3 & t_6 & 0 & 0 \\
0 & 0 & t_4 & 0 & 0 \\
0 & 0 & 0 & t_5 & 0
\end{pmatrix}
\] (21)

Of these, \( t_1, t_3, t_4, \) and \( t_5 \) are primarily direct hopping
between metal atoms, as shown in Fig. 3. Only \( t_2 \) and \( t_6 \)
have significant contributions from both direct hopping
and hybridization with the ligands.

B. Survey of Materials

There are two main factors affecting the balance of
direct vs. ligand-assisted hopping: (i) the degree of
hybridization with the ligands, and (ii) the Co-Co bond
lengths. In general, metal-ligand hybridization is
typically lower in third row metal compounds than their \( 4d \)
and \( 5d \) counterparts, particularly for \( t_{2g} \) orbitals.
It is precisely this effect that reduces \( t_{2g} - t_{eg} \) splitting \( \Delta_1 \)
for \( 3d \) metals, which is required for stability of the high-
spin state in Co \( 3d^7 \) compounds. For this reason, ligand-
assisted hopping is expected to be suppressed overall.

Real materials span a wide range Co-Co distances in
edge-sharing Co(II) compounds, e.g. from \( \sim 2.9 \text{ Å} \) in
BaCo\(_2\)(AsO\(_4\))\(_2\) to \( \sim 3.9 \text{ Å} \) in Co\(_4\)(AsO\(_4\))\(_8\). While we leave

complete discussion of individual materials for later work,
it is useful to establish realistic ranges of hoppings. In
order to do so, we employed fully relativistic density func-
tional theory calculations performed with FPLO at the
GGA (PBE) level. Hopping integrals were extracted by
formulating Wannier orbitals via projection onto atomic
\( d \)-orbitals and/or \( p \)-orbitals.

In order to get a general idea of the of the bond-length
dependence, we first considered hypothetical cubic CoO
\((\text{NaCl type; } Fm\bar{3}m)\) structures with a symmetrically
stretched unit cells. Hoppings for the 5-band \( 3d \)-only
fitting are shown in Fig. 4a. This construction maintains
90° Co-O-Co bond angles, which deviates slightly
from real materials, but nonetheless provides insight.
In particular, we find in the entire range of Co-Co bond
lengths, that direct hopping is the largest, leading to
\( |t_3| > |t_2|, |t_6| \). This trend is also true for estimates of
real materials. In particular, we show in Fig. 3a) results
for several prominent materials based on literature
structures: CoNb\(_2\)O\(_6\) (Ref. 61), BaCo\(_2\)(AsO\(_4\))\(_2\) (Ref. 59),
Na\(_3\)Co\(_2\)SbO\(_6\) (Ref. 42), and Na\(_2\)Co\(_2\)TeO\(_6\) (Ref. 43).

For each case, the cubic projection coordinates were
defined to be orthogonal but minimize the difference
with the corresponding Co-O bond vectors in the (dis-
torted) octahedra. From these results, it is evident that

FIG. 3. Summary of symmetry allowed hoppings for ideal Z-
bonds with \( C_{2v} \) symmetry. \( t_1, t_3, t_4, \) and \( t_5 \) arise from direct
metal-metal hopping, while \( t_2 \) and \( t_6 \) have contributions from
both direct and ligand-assisted processes. The global \((xyz)\)
and local \((\hat{e}_1 \hat{e}_2 \hat{e}_3)\) coordinates are shown.
the physical region corresponds to large $t_3$ and subdominant $t_6$. By contrast, $t_2$ is suppressed, such that $|t_2| \sim |t_1|, |t_4|, |t_5| \lesssim 0.05$ eV. A similar situation was recently proposed for Na$_2$BaCo(PO$_4$)$_2$. For materials with Co-Co bond lengths $\sim 3.0$ Å, direct hopping almost certainly dominates. This differs from the previous theoretical works predicting large Kitaev couplings which considered ligand-mediated hopping $t_2$ and $t_6$ to be the largest. This discrepancy calls for a reexamination of the magnetic couplings.

Finally, in Fig. 4(b), we show Slater-Koster hoppings extracted from the CoO calculations by fitting with an 8-band ($3d + 2p$) model including explicitly the O orbitals. These are relevant for considering some exchange processes (see below). In terms of these, the $d$-only hoppings are given approximately by:

$$t_2 \approx -\frac{1}{2} t_{pd}^\sigma + \frac{(t_{pd}^\delta)^2}{\Delta_{pd}}$$

$$t_3 \approx t_{dd}^\sigma$$

$$t_6 \approx \frac{\sqrt{3}}{4} t_{dd}^\sigma - \frac{t_{pd}^\sigma t_{pd}^\delta}{\Delta_{pd}}$$

where $\Delta_{pd} = 4.5$ eV is the charge-transfer energy from Co $d$ to O $p$ orbitals. For $t_2$ and $t_6$, the contributions from ligand-assisted hopping is positive, while the direct hopping contribution is negative.

### IV. MAGNETIC COUPLINGS

#### A. General Form

For ideal edge-sharing bonds with $C_{2v}$ symmetry, the magnetic couplings may be written in the familiar form:

$$
\mathcal{H}_{ij} = J S_i \cdot S_j + K S_i^\sigma S_j^\sigma + \Gamma \left( S_i^\sigma S_j^\delta + S_i^\delta S_j^\sigma \right) + \Gamma' \left( S_i^\sigma S_j^\sigma + S_i^\delta S_j^\delta + S_i^\sigma S_j^\delta + S_i^\delta S_j^\sigma \right)
$$

where $(\alpha, \beta, \gamma) = (x, y, z)$ for the Z-bonds, $(y, z, x)$ for the X-bonds, and $(z, x, y)$ for the Y-bonds, in terms of the global $xyz$ coordinates. In order to estimate the couplings in the following sections, we exactly diagonalize the full $d$-only Hamiltonian $\mathcal{H}_U + \mathcal{H}_{CF}$ and $\mathcal{H}_{SOC} + \mathcal{H}_{hop}$ for two neighboring sites. The couplings are extracted by projecting onto the ideal $j_1/2$ doublets defined in eq’n (8).

This procedure is analogous to Ref. 24 and is guaranteed to yield couplings that converge to the results of perturbation theory with respect to $\mathcal{H}_{hop}$. As discussed in Ref. 19 there are several different electronic processes that contribute to the magnetic couplings at low orders in the full $p + d$ model. These can be grouped into two categories: (i) those involving excited states with up to one hole occupying the ligand orbitals, and (ii) those involving multiple excited ligand holes simultaneously. The majority of these processes are captured, in principle, in the downfolded $d$-only hopping model, assuming suitably renormalized hopping and on-site Coulomb terms. We assume that the hopping integrals extracted from DFT incorporate this renormalization already. However, our approach does not capture the subset of processes in category (ii) in which two holes meet on a ligand in different $p$-orbitals, and interact via Hund’s coupling. Such processes effectively renormalize the nearest neighbor Coulomb terms when downfolded, which we have not considered explicitly. We therefore estimate the effects of the additional contributions. From Ref. 19 there is a correction to both $J$ and $K$ given approximately by:

$$\delta J \approx -\frac{\gamma}{\Delta_{pd}^2} \left( \frac{5}{2}(t_{pd}^\sigma)^4 + \frac{3}{2}(t_{pd}^\sigma)^2(t_{pd}^\delta)^2 + (t_{pd}^\delta)^4 \right)$$

$$\delta K \approx -\frac{\gamma}{\Delta_{pd}^2} \left( \frac{1}{2}(t_{pd}^\sigma)^2(t_{pd}^\delta)^2 - \frac{1}{2}(t_{pd}^\delta)^4 \right)$$

$$\gamma = \frac{40J_H}{81(\Delta_{pd} + U_p/2)^2}$$

where $J_H$ is the Hund’s coupling at the ligand, $U_p$ is the excess Coulomb repulsion at the ligand, $\Delta_{pd} \approx 4.5$ eV is the charge-transfer gap. We take the same approximations as Ref. 19 ($U_p = 0.7 U_{1/2g}$, $J_H = 0.3 U_p$), and consider $t_{pd}^\sigma \approx 1$ eV, $t_{pd}^\delta \approx -0.5$ eV, according to Fig. 4(b). From this, we estimate the correction to the Kitaev coupling to be negligible $\delta K \approx 0.1$ meV, while the corrections to the Heisenberg coupling may be typically

![FIG. 4. Evolution of the relevant hoppings as a function of Co-Co distance. Solid lines correspond to hypothetical stretched cubic CoO (see text). Points correspond to real materials; BCAO = BaCo$_2$(AsO$_4$)$_2$, NCTO = Na$_2$Co$_2$TeO$_4$, NCSO = Na$_3$Co$_2$SbO$_6$, CNO = CoNb$_2$O$_6$. (a) Hoppings in the $d$-only scheme. (b) Hoppings in the $p + d$ scheme.](image-url)
in the range $\delta J \sim -2$ to $-6$ meV. The remaining contributions to the exchange are investigated in the next sections.

### B. General Hopping Dependence

In the following, we focus on the contributions to the magnetic exchange from (downfolded) $d$-$d$ hopping. We first consider the case $\Delta_2 = 0$. With the choice, $\Gamma' = 0$ strictly. Up to second order in hopping, the couplings may be written:

$$J = t \cdot M_J(t^T + \delta J)$$

$$K = t \cdot M_K(t^T + \delta K)$$

$$\Gamma = t \cdot M_{\Gamma}(t^T)$$

where:

$$t = (t_1, t_2, t_3, t_4, t_5, t_6)$$

and $M$ is a function of $F_n, \lambda, \Delta_n$. We use $\Delta_1 = 1.1$ eV and $\lambda = 0.06$ eV, which is consistent with estimates from DFT in the previous sections and $U_{t2g} = 3.25$ eV, and $J_{t2g} = 0.7$ eV, following Ref.\textsuperscript{52}. To estimate $M$ for these parameters, we computed the magnetic couplings for a grid of hoppings $-0.05 < t_6 < +0.05$ and fit the resulting couplings. This provides an estimate of the couplings in the perturbative regime:

$$M_J = \begin{pmatrix}
    t_1 & t_2 & t_3 & t_4 & t_5 & t_6 \\
    t_1 & 128 & 0 & -119 & -9 & 35 & 0 \\
    t_2 & 0 & -108 & 0 & 0 & 0 & 86 \\
    t_3 & 0 & 0 & -8 & -2 & 5 & 0 \\
    t_4 & 0 & 0 & 0 & -4 & 0 & 0 \\
    t_5 & 0 & 0 & 0 & 0 & 1 & 0 \\
    t_6 & 0 & 0 & 0 & 0 & 0 & -147
\end{pmatrix}$$

$$M_K = \begin{pmatrix}
    t_1 & t_2 & t_3 & t_4 & t_5 & t_6 \\
    t_1 & 0 & -34 & 0 & 0 & 0 & 49 \\
    t_2 & 0 & -116 & -2 & 1 & 0 \\
    t_3 & 0 & 0 & 0 & 0 & -31 & 0 \\
    t_4 & 0 & 0 & 0 & 0 & -67 & 0 \\
    t_5 & 0 & 0 & 0 & 0 & 0 & 0 \\
    t_6 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}$$

in units of 1/eV. Recall, for real materials we generally anticipate $|t_3| > |t_6| > |t_1| \sim |t_2| \sim |t_4| \sim |t_5|$. Furthermore, $t_1 > 0$, $t_3 < 0$, $t_4 < 0$, $t_6 > 0$. These results highlight several key aspects:

**Heisenberg $J$:** For $J$, there are various contributions of different sign. Those arising from hopping between $t_{2g}$ orbitals $(t_1, t_2, t_3, t_4)$ are exclusively ferromagnetic. Processes involving hopping between $e_g$ orbitals $(t_4, t_5)$ are exclusively antiferromagnetic. The terms related to $e_g$-$t_{2g}$ hopping tend to be antiferromagnetic $\propto t_4^2$ and $t_2t_6$ given that $ab$-\textit{initio} tends to yield $t_2 < 0$ and $t_6 > 0$.

**Kitaev $K$:** There are also different contributions to $K$ of varying sign. Hopping between $e_g$ orbitals $(t_4, t_5)$ makes little contribution to the anisotropic couplings overall. The sign of the contribution from $t_{2g}$-$e_g$ hopping depends on the balance of transfer integrals: terms $\propto t_2^2$ are ferromagnetic, while terms $\propto t_4^2$ and $t_1t_3$ are antiferromagnetic. Contributions related to $t_{2g}$-$e_g$ hopping may take both signs: terms $\propto t_6^2$ are ferromagnetic, while terms $\propto t_2t_6$ depend on the sign of $t_2$.

**Off-diagonal $\Gamma$:** For the off-diagonal couplings, the primary contribution arises at order $t_2t_3$, and as a result
sign($\Gamma$) $\approx$ $-$sign($t_2t_3$). There are no contributions that are diagonal with respect to the hopping pairs. A similar result appears in Ref. [19].

The appearance of hopping combinations such as $t_2t_6$, which do not conserve $t_{2g}$ and $e_g$ occupancy, may appear surprising at first. If the ground state doublets have approximate configuration $(t_{2g})^5(e_g)^2$, one might expect terms mixing the occupancy to be forbidden at low orders, because they do not connect ground states. However, in reality, neither occupancy is preserved by either spin-orbit coupling or the full Coulomb terms, which are treated exactly (not perturbatively) in this approach.

For general parameters, we expect all three couplings to be finite. The computed hopping-dependence of $K, J, \Gamma$ are shown in Fig. $5$ for the choice $t_1 = |t_3|/4, t_4 = t_5 = -|t_3|/4, t_6 = +0.1$ eV, which is compatible with the ab-initio estimates. With this choice, we interpolate between the limits of dominant ligand vs. direct hopping.

In the hypothetical regime of pure ligand-mediated hopping ($t_2$ and $t_6$), we find $\Gamma = 0$, while contributions from $d$-$d$ hopping satisfy $J > 0$ is antiferromagnetic and $K < 0$ is ferromagnetic. These findings verify perturbation theory for this limit [19,22]. The Kitaev coupling is the largest, with values $|K/J| \sim 1-10$ depending on the precise balance of hoppings. If we consider also the ferromagnetic correction $\delta J \sim -2$ to $-6$ meV discussed in the previous section, the overall sign of $J$ should reverse, and the magnitude may be suppressed, such that dominant Kitaev coupling is possible with some tuning.

By contrast, for the physically relevant region of large $t_3$ and finite values of all hoppings, we anticipate that ferromagnetic $J < 0$ is the dominant coupling, particularly due to contributions $\propto t_1t_3$ and the correction $\delta J$. In fact, $\delta J$ (which is just the regular ferromagnetic exchange for $90^\circ$ bond) is the largest contribution. All possible combinations of signs of $K$ and $\Gamma$ are possible depending on the balance of hoppings, but their magnitude is suppressed relative to $J$. For very short Co-Co bond lengths, where the direct hopping contribution to $t_2$ is the largest ($t_2 < 0$), the tendency is for $K, \Gamma < 0$. For longer bond lengths, where ligand-mediated contributions are the largest ($t_2 > 0$), then $K, \Gamma > 0$.

**C. Effect of Trigonal Distortion**

We next consider the effects of trigonal distortion. Given the relatively small value of the atomic SOC constant $\lambda_{Co} \approx 60$ meV, small distortions may be relevant for Co(II) compounds. This make clarifying the size and sign of $\Delta_2$ important for modelling such materials. Following Ref. [23], the alterations to the nature of the local moments are expected to induce significant uniaxial anisotropy along the trigonal axis. While the $K, J, \Gamma, \Gamma'$ notation is convenient for discussing the couplings in the limit $\Delta_2 \to 0$, the axial anisotropy is more apparent in alternative local XXZ coordinates shown in Fig. $3$. In particular, for each bond we define local coordinates: $\hat{e}_3$ is parallel to the bond and $\hat{e}_3 = (\hat{x} + \hat{y} + \hat{z})/\sqrt{3}$ is along the global trigonal axis. Thus, the couplings may be written [20] via:

$$ H_{ij} = J_{xy} \left( S_i^1 S_j^1 + S_i^2 S_j^2 \right) + J_z S_i^3 S_j^3 + 2J_{\pm\pm} \left( S_i^1 S_j^1 - S_i^2 S_j^2 \right) + J_{\pm\mp} \left( S_i^3 S_j^3 + S_i^2 S_j^2 \right) $$

where the superscript numbers refer to the local directions. The two parameterizations may be related [27] via:

$$ J_{xy} = J + \frac{1}{3} (K - \Gamma - 2\Gamma') $$

$$ J_z = J + \frac{1}{3} (K + 2\Gamma + 4\Gamma') $$

$$ J_{\pm\pm} = -\frac{1}{6} (K + 2\Gamma - 2\Gamma') $$

$$ J_{\pm\mp} = -\frac{\sqrt{2}}{3} (K - \Gamma + \Gamma') $$

A similar parameterization was also suggested in Ref. [20] and [21]. In general, for $\Delta_2 < 0$, as the moments become more axial, components of the exchange along the $\hat{e}_3$ direction are expected to be enhanced compared to the $\hat{e}_1$ and $\hat{e}_2$ direction. As a result $J_{xy}$ and $J_{\pm\pm}$ should be suppressed relative to $J_z$ and $J_{\pm\mp}$. Trigonal elongation $\Delta_2 > 0$ should have the opposite effect. As the moments become more planar, $J_{xy}$ and $J_{\pm\pm}$ should be relatively enhanced.
Following Ref. 21 and 25, the ferromagnetic corrections to \( J \) resulting from ligand exchange processes are rendered anisotropic, with:

\[
\delta J_{xy} \approx u_{xy}^2 \delta J_0 \tag{41}
\]

\[
\delta J_z \approx u_z^2 \delta J_0 \tag{42}
\]

\[
u_{xy} = \frac{3}{5} \left( 2 \sqrt{3} c_1 c_3 + 2 c_2^2 \right) \tag{43}
\]

\[
u_{z} = \frac{3}{5} \left( 1 + 2 (c_1^2 - c_3^2) \right) \tag{44}
\]

with \( c_i \) given in Fig. 2(b) and \( \delta J_0 \) defined according to eqn 26. In the \( J, K, \Gamma, \Gamma' \) parameterisation, these corrections correspond to:

\[
\delta J = \frac{1}{3} \left( u_z^2 + 2 u_{xy}^2 \right) \delta J_0 \tag{45}
\]

\[
\delta \Gamma = \delta \Gamma' = \frac{1}{3} \left( u_z^2 - u_{xy}^2 \right) \delta J_0 \tag{46}
\]

As with the undistorted case, the corrections to the anisotropic couplings \( J_{\pm \pm} \) and \( J_{\pm \mp} \) are predicted to be small. The evolution of the ferromagnetic corrections with distortion are shown in Fig. 6. For \( \Delta_2 < 0 \), the ratio \( \delta J_z / \delta J_{xy} > 1 \) is, in principle, unbounded (and should increase continuously with trigonal distortion). For \( \Delta_2 > 0 \) the degree of anisotropy is restricted, because the distortion-induced effects are bounded \( 1/4 \lesssim J_z / J_{xy} < 1 \). The lower bound is reached for large \( \Delta_2 \), where the orbital moment is quenched, thus restoring the full degeneracy of the \( S = 3/2 \) states. However, a low-energy model including only the lowest doublet would no longer be sufficient, so this limit does not represent a physically sensible model. In terms of global coordinates, the trigonal distortion primarily introduces off-diagonal couplings, where \( \Delta_2 < 0 \) tends to be associated with \( \delta \Gamma, \delta \Gamma' < 0 \), and vice versa.

To explore the exchange contributions from (down-
folded) d-d hopping, we recomputed the couplings using exact diagonalization with significant distortion $\Delta_2/\lambda = \pm 0.5$ to emphasize the effects. Results are shown in Fig. 7 for the choice $t_1 = |t_3|/4, t_4 = t_5 = -|t_3|/4, t_6 = +0.1$ eV, which is compatible with the ab-initio estimates. In Fig. 7(e,f) and (k,l), we also show the effect of corrections $\delta J$. The results are as follow:

**Trigonal compression:** For $\Delta_2 < 0$, as shown in Fig. 7(a-e), we find all four of the couplings $J, K, \Gamma, \Gamma'$ may be of similar magnitude. This is particularly true in the region of large ligand-assisted hopping. For the physically relevant region of large direct hopping ($t_3 \gg t_2$), we find that $K$ is still relatively suppressed (same as for $\Delta_2 = 0$), but large $\Gamma, \Gamma'$, with $\text{sign}(\Gamma, \Gamma') \sim \text{sign}(J)$ are induced. These results are more easily interpreted in the alternative XXZ parameterization shown in Fig. 7(e). In particular, as the local moments become more axial with larger trigonal distortion, the coupling becomes dominated by a ferromagnetic Ising exchange $J_z$. Overall, the estimated ferromagnetic correction $\delta J_z$ is quite large compared to the regular d-d contributions. For the physically relevant region, we anticipate $J_{xy} = -2$ to 0 meV, $J_z = -3$ to $-10$ meV, $J_{\pm \pm} = -0.5$ to $+0.5$ meV, and $J_{\pm \mp}$ is typically the dominant coupling, with $J_{xy}/J_z \sim 4$, which is the hypothetical limit. Overall, we anticipate $J_{xy} = -2$ to $-10$ meV, $J_z = -0.5$ to $-4$ meV, $J_{\pm \pm} = -2$ to $+1$ meV, and $J_{\pm \mp} = 0$ to $+1$ meV for significant trigonal distortion of $\Delta = \pm \lambda/2$. As a result, we expect such materials to be described mostly by Ising couplings with a common axis for every bond.

**Trigonal elongation:** For $\Delta_2 > 0$, we find that $K$ is less suppressed. The distortions induce off-diagonal couplings following roughly $\text{sign}(\Gamma, \Gamma') \sim -\text{sign}(J)$. In the XXZ parameterization, this corresponds to an enhancement of $J_{xy}$. In the hypothetical ligand-assisted hopping region, we find that $J_z$ may be almost completely suppressed due to different values of the ferromagnetic shifts $\delta J_z$ and $\delta J_{xy}$. While $J_{xy}$ appears to be the largest coupling in this limit, the bond-dependent couplings $J_{\pm \pm}$ and $J_{\pm \mp}$ may also remain significant. For the physically relevant region, we find that $J_{xy}$ is typically the dominant coupling, with $J_{xy}/J_z \sim 4$, which is the hypothetical limit. Overall, we anticipate $J_{xy} = -2$ to $-10$ meV, $J_z = -0.5$ to $-4$ meV, $J_{\pm \pm} = -2$ to $+1$ meV, and $J_{\pm \mp} = 0$ to $+1$ meV for significant trigonal distortion of $\Delta = \pm \lambda/2$.

D. Longer Range Couplings

While we have discussed above that $t_{2g}$-ligand hybridization should generally be small in 3d metal oxides (as reflected by small $t_{pp}^{pd}$), the $e_g$-ligand hybridization may still play a significant role through the large $t_{pd}^{pp}$. This is particularly relevant for third neighbor bonds in honeycomb materials, because it gives rise to a large hopping between $d_{z^2}$ orbitals shown in Fig. 8 at order $(t_{pd}^{pp})^2 t_{sd}^{pp} / \Delta_{pd}^{pp} \sim 0.05$ to 0.1 eV. This is equivalent to a 3rd neighbor hopping $t_5$, which allows the associated coupling to be readily estimated from the matrices $\mathcal{M}$. In particular, we estimate (for $\Delta_2 = 0$):

$$J_3 \approx +0.5 \text{ to } +2.5 \text{ meV} \quad (47)$$

$$K_3 \approx \Gamma_3 \approx 0 \quad (48)$$

This is the only major third neighbor hopping pathway, so there are no additional terms to compete, and a relatively large antiferromagnetic $J_3$ should be expected for all honeycomb materials with partially occupied $e_g$ orbitals.

V. CONCLUSIONS

In this work, we have considered the magnetic couplings in edge-sharing $d^7$ compounds. On this basis, we make several observations:

1. All of the edge-sharing Co(II) oxides considered in this work appear to fall outside the regime of primary focus in previous theoretical studies. In particular, direct hopping likely dominates over ligand-assisted hopping ($t_3 \gg t_2$). In the realistic regime, we find that $K$ is generally suppressed compared to $J$, which calls into question models with dominant $K$ proposed for these materials.

2. Compared to heavy $d^9$ Kitaev materials such as iridates $\text{A}_2\text{IrO}_3$ and $\alpha$-RuCl$_3$, the weak spin-orbit coupling of Co increases the relative importance of local distortions. The presence of the $e_g$ spins also opens additional exchange pathways, whose balance depends sensitively on local parameters such as $J_H, U$, and $\Delta_1$. This makes anticipating the magnetic Hamiltonian somewhat challenging. For oxides, fortuitous fine-tuning may result in a different balance of couplings, but we anticipate that ferromagnetic $J$ (or equivalently $J_z, J_{xy}$) is likely always the largest coupling. The signs and magnitudes of the other couplings $K, \Gamma, \Gamma'$ are influenced by the crystal field splitting and specific details of the hoppings. We find regions with all possible signs and relative magnitudes. Real materials with small trigonal distortions are likely described by $|K/J| \sim 0.2$ to 0.5, and $K \approx \Gamma'$; specifically: $J \sim -8$
to $-2$ meV, $K \sim -2$ to $+2$ meV, and $\Gamma \sim -1$ to $+3$ meV. $\Gamma'$ is likely small unless there are significant departures from ideal symmetry of the bonds. These findings are compatible with the overall scale of those reported in the literature. It is not clear that a uniquely dominant $K$ is possible.

(3) For systems with significant crystal field distortions, our findings are compatible with the historical description of Co(II) magnetic couplings in terms of XXZ models by M. E. Lines (Ref. 25). This is true particularly because of the importance of ligand exchange processes, which are responsible for ferromagnetic couplings in materials with 90° bond angles in the Goosenough-Kanamori description. We estimate that these are at least as important as processes involving $d$-$d$ hopping. In this case, the considerations discussed in Ref. 21 and 25 become equivalent to the classic results of Lines. For trigonal crystal fields with $\Delta_2 < 0$ (corresponding to $g_1 > g_3$), the Ising anisotropy induced by the crystal field may be very large, such that the couplings are dominated by a ferromagnetic $J_z$ with a common Ising axis for every bond. For positive crystal field $\Delta_2 > 0$ (corresponding to $g_1 < g_3$), XXZ anisotropy is more limited, but may still be large for significant distortions $\Delta_2 \sim \lambda/2$. Such materials are generally more desirable for realising strongly bond-dependent couplings.

(4) Regarding NCSO and NCTO: Some constraints can be placed on the interactions on the basis of the ordered moment directions in the zigzag state. Related discussions appear in Ref. 68. For NCTO, it is generally agreed that the ordered moments lie nearly in the honeycomb plane, oriented along the direction of the ferromagnetic chains. For the zigzag domain with magnetic wavevector parallel to the Z-bond, this is $\delta^Z = (1, 1, -2)/\sqrt{6}$ in cubic coordinates. This orientation is generally expected for $K, \Gamma > 0$, which is compatible with large $t_3$ and small $t_2 > 0$, as we find in ab-initio for NCTO (see Fig. 1). The antiferromagnetic sign of $K$ is driven by a combination of hopping processes $\propto t_{2g6}$, $t_{2g1}$ and $t_{1g3}$. Most of these were not previously considered in the literature. For moments precisely along $\delta^Z$, the magnetic state is left invariant under a 180° rotation around (111) followed by time reversal; it is thus reasonable to assume the couplings bear the same symmetry. This places the constraint on the couplings $\Gamma + \delta \Gamma = K + \Gamma' + \delta \Gamma'$. Experimental estimates for NCSO and NCTO suggest $\Delta_2 \sim +4$ to $+13$ meV, which corresponds to a $\delta \Gamma, \delta \Gamma' \sim 0.2 - 0.5$ meV. With these suggestions, one may then consider the small magnitude of the magnon gap ($\sim 1$ meV) observed in experiment at both the $\Gamma$-point and the ordering wavevector. This would be anomalous for large departures from XXZ-symmetry. It may further be remarked that the field-evolution of the ESR model follow expectations for moderate easy-plane XXZ anisotropy. Taken together, we suggest $J_{xy} = -3.25, J_2 = -2.25, J_\pm = -0.125, J_z = 0$ meV as an appropriate starting point for analysis. These correspond to $J_1 = -3, J_3 = +2.5, K = \Gamma' = +0.25, \Gamma = +0.5$ meV, which are essentially consistent with the model of Ref. 44.

(5) Regarding BCAO: The breadth of experimental data on BCAO, in terms of the progression of field-induced phases and inelastic neutron data provide a number of clues towards the magnetic model. While we leave full elaboration for future study, some comments can be made. A recent reinvestigation of the zero-field structure suggested it might better be described by a double stripe $\uparrow\downarrow\downarrow\uparrow$ analogue of the zigzag antiferromagnet, with moments oriented nearly along the in-plane $\delta^Z$ direction, as with NCTO. This orientation points to $K, \Gamma > 0$. The large discrepancy between in-plane critical fields (0.2, 0.5 T) and the out-of-plane critical field (4T) suggests significant anisotropy. Indeed, the $g$-tensor appears to satisfy $\delta^Z g_z \sim 0.5 g_{xy}$, and within an XXZ model, $J_z \sim 0.4 J_{xy}$. These findings point to significant crystal field effects, with $\Delta_2 \sim 0.2$ to $0.25 \lambda$, i.e. $\Delta_2 \sim 15$ meV, implying significant $\Gamma$ and $\Gamma'$ in the global coordinate scheme. In the XXZ scheme, the nearly in-plane moments suggest small $J_{\pm\pm}$, while an apparently small anisotropy between in-plane field directions may place restrictions on $J_{\pm\pm}$. In contrast, the authors of Ref. 50 have advocated for small $J$, large $K < 0$, and small average off-diagonal coupling $\Gamma = (\Gamma + 2\Gamma')/3$ on the basis of THz spectroscopy experiments. It should be emphasized that these conditions are not mutually compatible: small $J_{\pm\pm}$ and $J_{\pm\pm}$ implies small $K$, and large anisotropy between $J_z$ and $J_y$ implies large $\Gamma + 2\Gamma' > 0$. If we consider BCAO to be in the physical regime of hoppings, our findings tend to contradict the Kitaev-dominant model. We propose a model similar to NCTO: $K$ is small and likely antiferromagnetic, $J < 0$ is the dominant coupling, and $\Gamma, \Gamma' > 0$ reflect a planar XY-anisotropy $|J_{xy}| > |J_z|$. The anomalous aspects of the ground state are then understood as a competition between $J_1, J_2$ and $J_3$, as previously suggested. These suggestions are compatible with the recent ab-initio estimates. From the perspective of chemistry, it is unclear how to access the desirable ligand-assisted hopping regime where Kitaev coupling is largest. It is necessary to increase the metal-ligand hybridization relative to direct hopping between metal atoms. This may typically be achieved by matching the electronegativity of the metals and ligands, such that $\Delta_{pd}$ is small. As a general trend, electronegativity of transition metals increases for heavier atoms, while the opposite is true for $p$-block ligands. The combination of heavy metals with heavy ligands results in the most covalent metal-ligand bonds. However, with increased covalency comes increased $t_{2g}-e_g$ splitting, and heavier metals tend to have reduced Coulomb terms $J_H$. As a result, the high-spin $(t_{2g})^5(e_g)^2$ state is only typically achievable in Co(II) compounds. By contrast, Rh(II) and Ni(III) tend to adopt low-spin $(t_{2g})^6(e_g)^1$ ground states. The most promising avenue then appears to be the combination of Co(II) with heavier ligands. With this in mind, we computed the hopping integrals for the triangular lattice compounds CoCl₂, CoBr₂ and
CoI$_2$ according to crystal structures from Ref. 60 and 70. For these compounds, we still estimate $|t_3/t_2| \sim 4$. Thus, it is not clear that Kitaev-dominant exchange can be achieved without extreme fine tuning.

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