XY magnetism, Kitaev exchange, and long-range frustration in the $J_{\text{eff}} = 1/2$ honeycomb cobaltates

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The quest for Kitaev quantum spin liquids has led to great interest in honeycomb quantum magnets with strong spin-orbit coupling. It has been recently proposed that even Mott insulators with 3d transition metal ions, having nominally weak spin-orbit coupling, can realize such exotic physics. Motivated by this, we study the rhombohedral honeycomb cobaltates CoTiO$_3$, BaCo$_2$(PO$_4$)$_2$, and BaCo$_2$(AsO$_4$)$_2$, using ab initio density functional theory, which takes into account realistic crystal field distortions and chemical information, in conjunction with exact diagonalization numerics. We show that these Co$^{2+}$ magnets host $J_{\text{eff}} = 1/2$ local moments with highly anisotropic $g$-factors, and we extract their full spin Hamiltonians including longer-range and anisotropic exchange couplings. For CoTiO$_3$, we find a nearest-neighbor easy-plane ferromagnetic $XXX$ model with additional bond-dependent anisotropies and interlayer exchange, which supports three-dimensional (3D) Dirac nodal line magnons. In contrast, for BaCo$_2$(PO$_4$)$_2$ and BaCo$_2$(AsO$_4$)$_2$, we find a strongly suppressed interlayer coupling, and significant frustration from additional third-neighbor antiferromagnetic exchange mediated by P/As. Such bond-anisotropic $J_1$-$J_3$ spin models can support collinear zig-zag or coplanar spiral ground states. We discuss their dynamical spin correlations which reveal a gapped Goldstone mode, and argue that the effective parameters of the pseudospin-1/2 models in these two materials may be strongly renormalized by coupling to a low energy spin-exciton. Our results call for re-examining proposals for realizing Kitaev spin liquids in the honeycomb cobaltates.

I. INTRODUCTION

A significant effort has been invested in exploring material realizations of Kitaev’s honeycomb quantum spin liquid (QSL) model and its anyon excitations [1–5]. The initial work in this direction focussed mainly on the iridate honeycomb magnets which have strong spin-orbit coupling (SOC) [6–12]. At this point, the most promising candidate appears to be α-RuCl$_3$ [13–23], where intermediate in-plane Zeeman fields appear to lead to a plateau in the thermal Hall conductivity $\kappa_{xy}$ [24], and quantum oscillations in the diagonal thermal conductivity $\kappa_{xx}$ [25], which have been proposed as potential signatures of emergent Majorana fermion excitations in an insulating quantum magnet. At the same time, there is debate on the precise magnetic Hamiltonian for α-RuCl$_3$ [26, 27] as well as the existence of a field induced QSL [28, 29] in its phase diagram. A search for such exotic physics in a wider range of quantum materials is thus highly desirable.

This quest has led to great interest in honeycomb cobaltates, where the Co$^{2+}$ ion in an octahedral crystal field environment has total spin $S = 3/2$ moment and an effective total orbital angular momentum $L = 1$, which are locked by spin-orbit coupling, leading to a $J_{\text{eff}} = 1/2$ pseudospin doublet ground state [30–32]. These materials were proposed to host to dominant Kitaev exchange between neighboring pseudospins, rendering them candidates for quantum spin liquids [30–33]. While this is an exciting proposal, SOC is much weaker for 3d transition metal ions as compared with the 5d-iridates or 4d-ruthenates. As a result, trigonal distortions of the local crystal field environment, inevitable in any layered honeycomb material, may be expected to have a considerable impact on the nature of exchange interactions and the low energy fate of magnetism in these materials.

To critically examine this issue, we explore several rhombohedral $d^7$ cobaltates — CoTiO$_3$, BaCo$_2$(PO$_4$)$_2$, and BaCo$_2$(AsO$_4$)$_2$ — which are formed from stacked honeycomb Co$^{2+}$ layers as shown in Fig. 1. In particular, we ask: does a realistic theory of the $d^7$ cobaltates, using a combination of $ab$ initio density functional theory (DFT) and exact diagonalization numerics, favor the realization of Kitaev spin liquids in these materials?

To address this issue, we use non-spin-polarized DFT calculation to extract the non-interacting part of the Hamiltonian, namely the hopping interactions and crystal field splitting, and then solve the many-body problem of the Co multiplet structure by including Coulomb interactions and spin-orbit coupling in an exact diagonalization for a single Co ion. Finally we consider the lowest two $d^7$ states as the pseudospin-1/2 basis, to derive superexchange interactions by utilizing the multiplet structure and incorporating hoppings within second-order perturbation theory. Our approach thus combines the material specific theory DFT with the many-body calculation to handle the multiplet structure, which we use to shed light on magnetism in the $d^7$ cobaltates.

A quick summary of our key results are as follows. Our $ab$ initio computations reveal that although all three

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compounds host the stacked honeycomb Co$^{2+}$ layers, the difference in the geometry and chemical composition of the spacer layers between the Co$^{2+}$ layers greatly influences the resulting electronic structure of the three compounds. In CoTiO$_3$, strong Co-Ti covalency leads to a more 3D electronic structure, while the delicate Co-As/P covalency and large separation between the Co$^{2+}$ layers leads to weakly coupled 2D layers but with longer-range hoppings in the electronic structure of BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$. We use these DFT inputs to carry out an exact diagonalization study incorporating correlation effects, which has been shown to work well in other Mott insulators with SOC [22, 34]. Our exact diagonalization numerics reveal that the Co$^{2+}$ ion has strongly anisotropic $g$-factors, consistent with experimental data [35–37]. For CoTiO$_3$, our computations reveal a dominant nearest-neighbor XXZ easy-plane ferromagnetic coupling, with additional anisotropic compass-type exchange interactions and interlayer couplings. Such a spin Hamiltonian supports 3D Dirac spin models can significantly frustrate from third-neighbor antiferromagnetic exchange. Such $J_1$-$J_3$ honeycomb lattice spin models can support collinear zig-zag or coplanar spiral ground states [12, 38, 39]. We present results on their dynamical spin structure factor which reveals a gapped Goldstone mode [12, 38, 39]. We discuss next.

II. CRYSTAL STRUCTURE

All three compounds CoTiO$_3$, BaCo$_2$(AsO$_4$)$_2$, and BaCo$_2$(PO$_4$)$_2$ crystallize in the rhombohedral $R\overline{3}$ space group. While the basic structural motif of all three compounds consist of stacked honeycomb cobaltate layers formed by edge shared CoO$_6$ octahedra, the out of plane stacking involving spacer layers between honeycomb planes are distinctly different between CoTiO$_3$, and BaCo$_2$(AsO$_4$)$_2$ or BaCo$_2$(PO$_4$)$_2$. The left and middle panels of Fig. 1 show the crystal structures of CoTiO$_3$ and BaCo$_2$(AsO$_4$)$_2$, respectively; the crystal structure of BaCo$_2$(PO$_4$)$_2$ being very similar to that of BaCo$_2$(AsO$_4$)$_2$, is not shown. In case of CoTiO$_3$, the cobalt layers are separated by Ti layers, where octahedrally coordinated Ti$^{4+}$ ions face share with CoO$_6$ octahedra along the hexagonal $c$-axis, with the Ti ion on top of Co ion, vertically displaced by 2.67Å. In case of BaCo$_2$(AsO$_4$)$_2$, on the other hand, the Co layers are separated by bilayers of AsO$_4$ tetrahedra, one pointing up and another pointing down, and separated by large Ba$^{2+}$ ions. This difference in spacer layer thickness between CoTiO$_3$ and the Ba compounds, makes the $c$-axis lattice constant of BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(AsO$_4$)$_2$ significantly different from CoTiO$_3$, being 13.92Å for CoTiO$_3$, 23.49Å for BaCo$_2$(AsO$_4$)$_2$, and 23.22Å for BaCo$_2$(PO$_4$)$_2$. However, their inplane lattice constants are rather similar: 5.06Å for CoTiO$_3$, 5.00Å for BaCo$_2$(AsO$_4$)$_2$, and 4.86Å for BaCo$_2$(PO$_4$)$_2$. This gives rise to a more 2D character of the Co network in Ba compounds, while CoTiO$_3$ has more 3D character. Furthermore, as opposed to face-shared geometry of Co-Ti network, the AsO$_4$ tetrahedra corner share with CoO$_6$ octahedra, the As ion being displaced from Co ion by 1.67Å along the in-plane directions and 1.41Å along the vertical direction. This creates O-As-O bridges both from top and bottom between long ranged in-plane Co neighbors, this feature being absent for CoTiO$_3$ compound. These structural details have important implications for the electronic structure and low-energy Hamiltonian of the three compounds which we discuss next.

III. ELECTRONIC STRUCTURE

To characterize the valences, spin states, and orbital contributions of various ions, we first carry out the spin-polarized DFT calculations within the framework of generalized gradient approximation (GGA) [42]. See Supplementary Materials (SM) [43] for calculation details [44–46]. The magnetic moment of Co site is found to be around 2.60$\mu_B$ confirming the high spin $d^7$ configuration of Co ions. Interestingly for CoTiO$_3$, large fraction of the missing moment is found to be at Ti and O sites of 0.12$\mu_B$ and 0.10$\mu_B$, respectively, despite the nominally nonmagnetic configuration of Ti$^{4+}$ and O$^{2-}$, indicating strong Co-O, and Ti-O covalency. For the Ba compounds, a similar magnitude of missing moment
(\sim 0.10 \mu_B) is found at O sites. Furthermore, a non-negligible moment of \sim 0.05 \mu_B is also found at the nominally valenced As\textsuperscript{5+}/P\textsuperscript{5+} sites, indicating the subtle role of As/P in describing the electronic structure of the Ba compounds. Repeating the calculations within the GGA+SOC approach uncovers a substantial orbital moment of 0.16-0.17 \mu_B at the Co site highlighting importance of SOC in these compounds.

In order to check the effect of missing correlation effect beyond GGA, GGA with supplemented Hubbard $U$ correction \cite{47} within the framework of GGA+$U$ and GGA+SOC+$U$ was carried out with choice of $U = 3$ eV and $J_H = 0.7$ eV \cite{48, 49}. We find that the resulting magnetic moments remain qualitatively unchanged; however, inclusion of a supplemented Hubbard $U$ correction strongly impacts the electronic structure. Crucially, an insulating solution is only obtained upon addition of $U$ correction, while GGA and GGA+SOC solutions are metallic. The magnetic moments calculated within GGA, GGA+SOC and GGA+SOC+$U$ as well as density of states calculated within three scheme of calculations are given in the SM \cite{43}.

Since our goal is to use the DFT calculations to derive a low-energy Hamiltonian to be used as an input for a model Hamiltonian study, we henceforth focus on the non-spin-polarized electronic structure of these compounds. Fig. 2 shows the density of states of CoTiO\textsubscript{3} and BaCo\textsubscript{2}(AsO\textsubscript{4})\textsubscript{2} compounds projected to different orbital characters; the electronic structure of BaCo\textsubscript{2}(PO\textsubscript{4})\textsubscript{2} is very similar to BaCo\textsubscript{2}(PO\textsubscript{4})\textsubscript{2} and is thus not shown. In an ideal octahedral environment the Co $d$ states are split into three-fold degenerate $t_{2g}$ and two-fold degenerate $e_g$ states. However, the CoO\textsubscript{6} octahedra in the studied compounds are not perfect, rather they are trigonally distorted with the Co atom moved along [111] direction from the centre of the octahedra, leading to three short and three long Co-O bonds. As shown in the insets of Fig. 2, this further splits the $d$ levels into two-fold degenerate $e_g^o$, non-degenerate $a_{1g}$, and two-fold degenerate $e_g^\pi$ levels. The octahedral splitting is found to be about $\sim 1$ eV, while trigonal splitting is found to be $\sim 0.1$ eV and thus larger than the nominal SOC on Co. Within the non-spin-polarized scheme of calculations, the Co $t_{2g}$ are fully occupied while the Co $e_g$ states are partially filled. As seen from the density of states near the Fermi level, there is significant contribution of O $p$ states along with the Co $d$ states, indicating strong Co-O covalency; this was also manifest in the presence of substantial magnetic moment at the otherwise non-magnetic O sites. In CoTiO\textsubscript{3}, we also notice a significant presence of Ti-$d$ character near the Fermi level, which we deem responsible for the 3D nature of the density of states. While the density of states of BaCo\textsubscript{2}(AsO\textsubscript{4})\textsubscript{2} bears an overall resemblance to that of CoTiO\textsubscript{3}, the details are markedly different. Near the Fermi level, we find the appearance of pseudogap like features seen in the inset of the bottom panel of Fig. 2, which arises due to intricate interplay of long-ranged in plane Co-Co interactions mediated by As; this feature is absent in CoTiO\textsubscript{3}. While the contribution of As states near the Fermi level is small compared to Ti, it is still non-negligible as highlighted in the zoomed-in plot of the density of states in the second inset of the bottom panel of Fig. 2. As discussed below, we believe this overlap with As states drives the overlap of further neighbor Wannier orbitals in the Ba compounds and leads to strong third-neighbor exchange.
IV. LOW-ENERGY DFT HAMILTONIAN

In an attempt to derive Co $d$-only low energy Hamiltonian out of DFT calculations, we resort to the energy selective N-th order muffin-tin orbital (NMTO) based downfolding technique [50]. Starting from a self-consistent DFT calculation in linear muffin-tin orbital basis, NMTO-downfolding calculation arrives at a low-energy Co $d$-only Hamiltonian by integrating out degrees that are not of interest like O-$p$, Ti-$d$, As and Ba states. This procedure constructs the ab-initio derived effective Co Wannier functions, the head parts of which are shaped according to Co $d$ symmetries, while the tail parts are shaped according to the integrated out degrees of freedom which are mixed in with Co $d$ characters. The construction of these effective Wannier functions depends on the choice of basis. We chose the octahedral local coordinate system with $z$-axis of the local coordinate system pointed along one of short Co-O bond, and the local $y$-axis pointed closest to neighboring Co-O bond. With this choice, the local $z$-axis on nearest neighbor edge-shared Co pairs point in opposite directions, with the center of inversion at the middle of the vector connecting the Co-Co pair. Fig. 3 shows a representative example of the effective Co $d_{x^2-y^2}$ Wannier function as given by NMTO-downfolded calculations for CoTiO$_3$ and BaCo$_2$(AsO$_4$)$_2$, which exhibits $pd\sigma$ antibonds formed between Co and O, which appear as pronounced tails shaped according to $O\,p$ symmetry. In the case of CoTiO$_3$, a significant weight of the tail also sits at the out-of-plane Ti site, as we find from other Wannier orbitals (not shown). What is remarkable in case of Ba compound is that one of the lobes of the O-tail bends towards As sites due to overlap of Co-O and As-O covalency at the corner-shared O site of CoO$_6$ octahedra and AsO$_4$ tetrahedra. This As-covalency driven bending of the tails promotes the long-ranged third neighbor in-plane Co-Co interaction, which plays an important role in the spin model for BaCo$_2$(AsO$_4$)$_2$; we find similar features in BaCo$_2$(PO$_4$)$_2$.

The low-energy tight-binding Hamiltonian, in the basis of NMTO-downfolded effective Co $d$ Wannier functions, encodes the effect of local distortion of CoO$_6$ octahedra, as well as the effect of spacer chemistry and geometry. The full local crystal field matrix and the hopping matrices for various neighbors are given in the SM [43]. This information is next used to build model Hamiltonians for these cobaltates.

V. EXACT DIAGONALIZATION RESULTS: SINGLE ION PROPERTIES

From our DFT calculations, we extract a local crystal field Hamiltonian $H_{CF}$ describing the d-orbital manifold of the Co$^{2+}$ ion in a distorted octahedral crystal field environment which only has a residual $C_3$ symmetry. We supplement this Hamiltonian with SOC and interactions, so that the on-site Hamiltonian takes the form

$$H_{loc} = \xi H_{CF} + H_{SOC} + H_{int}. \quad (1)$$

Here, $H_{SOC}$ is the single-particle SOC term, explicitly given by

$$H_{SOC} = \lambda \sum_{\ell\ell'} \sum_{s,s'} c^\dagger_{\ell s} L_{\ell\ell'}^{m} c_{\ell' s'} \sigma_{ss'}^m, \quad (2)$$

where $(\ell, \ell')$ are orbital labels corresponding to $\{(yz, xz, xy), (x^2-y^2, 3z^2-r^2)\}$, $m$ labels the vector component of the orbital $L$ or spin $\sigma$ angular momentum, with $s, s'$ being spin component labels. $H_{int}$ is the spherically symmetric Kanamori Hamiltonian encoding interactions between the electrons:

$$H_{int} = U \sum_{\ell} n_{\ell\uparrow} n_{\ell\downarrow} + U' \sum_{\ell\neq\ell'} n_{\ell\uparrow} n_{\ell'\downarrow}$$

$$- J_H \sum_{\ell \neq \ell'} S_{\ell \uparrow} \cdot S_{\ell' \downarrow} + J_H \sum_{\ell \neq \ell'} c^\dagger_{\ell s\uparrow} c_{\ell' s\downarrow} c^\dagger_{\ell' s\downarrow} c_{\ell s\uparrow} \cdot (3)$$

Here, $U, U'$, and $J_H$ represent intra-orbital Hubbard, inter-orbital Hubbard, and Hund’s couplings, respectively, and the spin operator in orbital $\ell$ is

$$S_{\ell m} = \frac{1}{2} c^\dagger_{\ell s\uparrow} \sigma_{ss'}^m c_{\ell s\downarrow}. \quad (4)$$

We assume $U' = U - 2J_H$ as appropriate for a spherically symmetric Coulomb interaction [52]. Finally, in this single-ion Hamiltonian Eq. 1, we have incorporated a scaling factor $\xi$ multiplying the $H_{CF}$ obtained from our DFT calculations, as a crude way to account for the “double-counting” of interactions. We refer here to the fact that $ab\,\text{initio}$ calculations partially account for inter-orbital repulsion and changes in the corresponding orbital occupancies and energies at mean field level, while such a renormalization of crystal field levels will also occur from the full set of Kanamori interactions in Eq. 3. An intrinsic issue of any realistic many-body approach is the so-called double-counting of interaction terms. How to
choose the double-counting potential in a manner that is both physically sound and consistent is unknown. Various different schemes of double-counting have been proposed in literature, as it is an ill-posed question to make connection between DFT based on electronic densities, and a Hubbard-like many-body model based on localized atomic orbitals. The double counting schemes like around mean-field [53] or fully localized limit, [54] or self-interaction correction [55] used in DFT+U approach may provide different results. An alternative approach is to use double-counting correction as an adjustable parameter, $\xi$, which we have used, to give the best comparison with experiment (see discussions later).

Below, we set $\lambda = 80\text{meV}$ for Co$^{2+}$ [56], and choose the scaling factor $\xi = 0.65$. Based on an exploration of how the different exchange couplings vary with interactions (discussed below), we fix the interaction strengths to $U = 3.25\text{eV}$ and $J_H = 0.7\text{eV}$ [57]. We find that this set of parameters leads to reasonable results for the single ion g-factors, as well as the low energy single ion excitations and spin-wave modes observed in CoTiO$_3$ using inelastic neutron scattering experiments [36, 37]. We have found that the exchange Hamiltonians we derive in later sections are not substantially impacted by the precise value of $\xi$.

### A. Kramers doublet ground state

As discussed in Ref [30, 31], the 3$d^7$ Co$^{2+}$ ion in an octahedral crystal field environment is predominantly in the high-spin $S = 3/2$ ($t_{2g}e^2_g$) configuration. Combining this with the total effective orbital angular momentum $L = 1$, of a single hole in the $t_{2g}$ orbitals, the SOC term with $\lambda > 0$ stabilizes a $J_{\text{eff}} = 1/2$ pseudospin degree of freedom. Indeed, our exact diagonalization of the Hamiltonian leads to a Kramers doublet ground state for a wide range of parameter values, indicating that such a pseudospin-1/2 picture remains valid for all three cobaltates even in the presence of realistic distortions.

### B. Single-ion excitations

Inelastic neutron scattering experiments on CoTiO$_3$ reveal magnetic excitations above the $J_{\text{eff}} = 1/2$ doublet at energies $\{29(2), 58(7), \ldots, 132(3)\}\text{meV}$, where "..." indicates a broad continuum of significant scattering intensity in the 60-120 meV range where individual sharp peaks cannot be resolved [36, 37]. Choosing the scaling factor $\xi = 0.65$ in $H_{\text{loc}}$, we find that these low-lying many-body crystal field excitations above the $J_{\text{eff}} = 1/2$ doublet ground state in CoTiO$_3$ are at energies $\{22, 63, 104, 111, 132\}\text{meV}$, with the underlined excitations energy levels being in reasonably good agreement with the experimentally observed peaks. We contrast these results with the corresponding values when the scale factor is set to $\xi = 1$, which leads to excitation energies $\{15, 84, 118, 130, 152\}\text{meV}$ quite unlike the data.

Using this scaling factor $\xi = 0.65$ for BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$, we find the excited states at excitation energies which are respectively at $\{14, 85, 120, 134, 158\}$ and $\{16, 77, 112, 126, 151\}$. These could be explored in future experiments. We note that similar spin exciton states have also been measured in certain pyrochlore cobaltates [58].

### C. g-factors

Table I lists the g-factors associated with this pseudospin degree of freedom which we obtain from the ground state expectation value $2(\langle L + 2S \rangle)$ in the presence of a weak Zeeman field $\vec{B}$. By choosing $\vec{B}$ to point perpendicular or parallel to the $C_3$ axis (i.e., $c$-axis), we extract $g_\perp$ and $g_\parallel$ respectively. In contrast to the isotropic g-factors obtained for the iridate $d^9$ Mott insulators, all the cobaltates studied here show highly anisotropic g-factors, in agreement with recent experiments [35, 41]. Such anisotropic g-factors have also been measured in certain pyrochlore cobaltates [58]. To the best of our knowledge, g-factors for BaCo$_2$(PO$_4$)$_2$ have not been measured; our estimates may be compared with future experiments.

| Material             | $g_\perp$ | $g_\parallel$ |
|----------------------|-----------|----------------|
| CoTiO$_3$            | 5.0       | 3.2            |
| BaCo$_2$(AsO$_4$)$_2$| 5.0       | 2.7            |
| BaCo$_2$(PO$_4$)$_2$ | 5.0       | 3.0            |

TABLE I. Computed g-factors corresponding to directions perpendicular (in-plane) or parallel (out-of-plane) to the $C_3$ axis ($c$-axis) for honeycomb cobaltates studied in this paper.

### VI. PERTURBATION THEORY FOR INTER-SITE EXCHANGE

In order to obtain the exchange interactions between pseudospins on a pair of sites, we use the single-ion energy levels and eigenfunctions and incorporate inter-site hopping to second order in perturbation theory. We outline this below, together with a brief discussion about the dependence on the various exchange couplings on interaction parameters such as $U$ and $J_H$, with further details given in the SM [43].

#### A. Two-site perturbation theory

The interactions between the pseudospins can be obtained via second order perturbation theory, using hopping integrals extracted from the above DFT calculations. The calculation schematically proceeds as follows.
(i) We solve the single site problem for occupancies $d^6$, $d^7$, and $d^8$, to obtain the full set of energy levels and many-body wavefunctions including SOC. In doing this, we apply a weak field along the global Z-axis ($C_3$ axis perpendicular to the honeycomb planes) in order to define our pseudospin $|\uparrow\rangle$, $|\downarrow\rangle$ basis states (see Fig. 4, reproduced from [6]). (ii) We extract spin-independent hopping matrices $T^{(ij)}$ from DFT, whose elements $T^{(ij)}_{\ell\ell'}$ describe an electron in orbital $\ell$ at site $i$ hopping to an orbital $\ell'$ at site $j$, so that the $(ij)$ kinetic energy is

$$\hat{T}_{ij} = \sum_{\ell\ell'\alpha}(T^{(ij)}_{\ell\ell'} c_{j\ell'\alpha}^\dagger c_{i\ell\alpha} + T^{(ij)}_{\ell'\ell} c_{i\ell\alpha}^\dagger c_{j\ell'\alpha}) \tag{5}$$

(iii) We focus on initial and final states where each of the two sites live in a ground doublet which we denote as $|b\rangle$, $|b'\rangle$. These kets span a 4-dimensional Hilbert space, formed by the direct product of doublet levels at each site. The operator $\hat{T}_{ij}$ connects these states to intermediate many-body levels ($d^6$, $d^7$) or ($d^8$, $d^9$) which we denote as $|e\rangle$. (iv) From second order perturbation theory, we obtain the effective Hamiltonian as

$$\hat{H}^{(2)}_{\text{eff}} = \sum_{\ell} \frac{\langle b' | \hat{T}_{ij} | e \rangle \langle e | \hat{T}_{ij} | b \rangle}{E_b - E_{e}} \tag{6}$$

where $E_{e}$ and $E_b = E_{b'}$ refer to the energies of the intermediate and initial/final ground states, respectively. $\hat{H}^{(2)}_{\text{eff}}$ is a 4x4 matrix, describing the interactions between the doublet manifolds on the two sites. (v) Finally, from this 4x4 Hamiltonian, the exchange matrix $J$ is extracted by writing $\hat{H}^{(2)}_{\text{eff}}$ above as a pseudospin exchange term

$$J^{ij} = \sum_{\alpha\beta} S^j_\alpha J^{ij}_{\alpha\beta} S^j_\beta \tag{7}$$

where $\alpha$ and $\beta$ are the components of the spin vectors, and the $S_\alpha$ are pseudospin-1/2 operators.

For instance, along a $C$-type nearest-neighbor bond (see left panel in Fig.4), the exchange matrix $J[C]$ is defined as

$$J[C] = \begin{pmatrix} J^{XY} + D & E & G \\ E & J^{XY} - D & F \\ G & F & J^Z \end{pmatrix} \tag{8}$$

with antisymmetric terms, e.g. Dzyaloshinskii-Moriya (DM) exchange couplings, being forbidden by inversion symmetry about the bond center. We can extract the corresponding exchange matrices $J[A]$ and $J[B]$ on the $A$-type and $B$-type bonds simply by a $\pm2\pi/3$ rotations of the above exchange matrix about the $C_3$ axis. More generally, the exchange matrices on generic bonds would allow DM terms, but we find that these are negligible, even for bonds where there is no center of inversion (e.g. second-neighbor bonds 2 and 2').

In Appendix A, we present results for the exchange matrices in terms of the ideal local octahedral basis in which the famous Kitaev-$\Gamma$ type Hamiltonians are usually formulated (also shown in the left panel in Fig.4). However, we note that in all the cobaltates we have examined, the pseudospin Hamiltonian is simplest in the above global basis, i.e. with the fewest number of nonzero entries in the exchange matrices.

B. Dependence of Exchanges on Interaction Parameters

The exchange interactions are sensitive to the interaction parameters $U, J_H$ in Equation (3). To illustrate
this, Fig. 5 shows the dependence of the first-neighbor XY exchange $J_{XY}^1$ on the Hubbard repulsion $U$ for all three cobaltates, while the inset displays the variation of the non-negligible third-neighbor exchange $-J_{XY}^3 / J_{XY}^1$ in BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$. The SM includes additional plots for the $J_H$ dependence of these couplings, as well as the $(U, J_H)$ dependence of bond-dependent anisotropies and further neighbor interactions.

Based on Fig. 5, and similar plots, we find that a reasonable choice of $U = 3.25$ eV and $J_H = 0.7$ eV [48, 49] leads to exchange couplings for CoTiO$_3$ which are in excellent agreement with inelastic neutron scattering experiments. For BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$, however, the spin ground state is extremely sensitive to the third-neighbor exchange over a range of $J_{XY}^3$. This suggests that some degree of fine-tuning might be needed to explain their precise magnetic ordering. Indeed, experiments on BaCo$_2$(PO$_4$)$_2$ have even argued for the coexistence of orderings with different wavevectors in the same sample [40]. In addition to this issue, we find a much larger overall scale of the exchange couplings in these two materials when compared with experimental reports - we later discuss a possible reason for this significant discrepancy.

### VII. SPIN HAMILTONIANS, ORDERED STATES, SPIN DYNAMICS

#### A. CoTiO$_3$

We find that the spin model in CoTiO$_3$ is best described as a nearest-neighbor ferromagnetic easy-plane XXZ model with significant compass-type anisotropies in the honeycomb plane, along with a weaker antiferromagnetic coupling between honeycomb layers. The full set of significant exchange coupling values are listed in Table II. This complete set of spin interactions favors an ordered ground state where the moments have XY ferromagnetic order within each honeycomb layer, but are antiferromagnetically stacked from one layer to the next. The interlayer exchanges are mediated by the significant overlap of the Co Wannier orbitals with the spacer Ti ions. The first-neighbor exchange coupling and its strong anisotropy, as well as the weaker interlayer couplings, are in very good agreement with those inferred from neutron scattering studies of the material [36, 37]. The scale of the compass anisotropy terms are consistent with those conjectured in previous work [37].

Fig. 6 shows the linear spin wave dispersion, obtained with our computed exchange interactions, along specific cuts in momentum space. The left panel reveals a Goldstone mode at the zone center - this is an artefact of linear spin wave theory, since the significant anisotropic “compass”-type exchange couplings $D$ and $E$ break the $U(1)$ symmetry of the pure XXZ model. Order by disorder physics, beyond linear spin-wave theory, is expected to pin the ordered moment and gap the Goldstone mode [37]. The right panel shows the computed Dirac node which has been observed in inelastic neutron scattering experiments; we find that this node is shifted away from the Brillouin zone corner which is at $(2/3, 3/2, 1/2)$ (dotted line in the right panel of Figure 6). This is in accordance with predictions that there are 3D Dirac nodal lines which should wind, like a triple helix, around the $(2/3, 2/3, L)$ axis in momentum space. This displacement of the Dirac nodal lines is enabled by the anisotropic $D$ and $E$ exchange couplings, and might lead to a suppression of the magnon density of states, as seen in recent experiments [37].

#### B. BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$

The Barium compounds are much more two-dimensional compared to CoTiO$_3$, with extremely small inter-layer couplings $\lesssim 0.1$ meV. The source of this layer decoupling is the large inter-plane distances discussed in Section II. In addition, the less buckled nature of the honeycomb planes and the Wannier orbital overlap with As/P appears to promote larger in-plane hoppings amplitudes. As a result, we find that the computed exchange interactions between $j = 1/2$ pseudospins in these compounds are significantly enhanced compared with CoTiO$_3$.

Tables III and IV show values for the exchange parameters for the BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$ respectively. The first-neighbor interaction leads to an easy-plane XXZ model, but with subdominant anisotropies.
which is qualitatively similar to CoTiO$_3$. However, in contrast to CoTiO$_3$ we find strong frustration coming from significant third-neighbor antiferromagnetic exchange; this leads to antiferromagnetic $XY$ ground states in the Barium compounds.

The classical phase diagram of the $J_1$-$J_3$ model [38, 39] features a tiny sliver $(0.25 \lesssim -J_3/J_1 \lesssim 0.4)$ of an incommensurate coplanar spiral phase sandwiched between the more robust ferromagnetic and zig-zag ordered phases; see Appendix B for a phase diagram reproduced from Ref. [39]. Based on our exploration of how the exchange couplings vary with the interaction parameters in Eq. 3 (see Figure 5), we find that the ratio $J_3/J_1$ lies close to this window. We thus deduce that the ground states of these materials could be extremely sensitive to small variations in material parameters.

Using SpinW [59], we have computed the magnetic order and dynamical spin correlations corresponding to the exchange values in Table III. We find that this parameter set supports collinear zig-zag magnetic order as shown in Fig. 7 (left panel), with moment directions as shown for the ordering wavevector along $X$. The wavevector $(H, K)$ for this order corresponds to $Q_0 = (1/2, 0)$; reinstating the lattice units, this translates to $Q_0 \approx (0.628, 0) \text{Å}^{-1}$. The dynamical spin correlations corresponding to this order show significant intensity at a band of excitations around an energy transfer $\hbar \omega \sim J_{XY}^3$. In addition, the Goldstone mode expected at $Q_0$ for a simple $XXZ$ model is gapped out by the anisotropy terms in the Hamiltonian, with a gap $\sim 0.3 J_{XY}^1$. Below the scale of this Goldstone gap, we expect that the magnetic specific heat should be exponentially suppressed. Similar results follow for the exchange parameter set from Table IV.

On the other hand, experiments on BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$ do not find a zig-zag ordered ground state. While early experiments on BaCo$_2$(AsO$_4$) [60] reported results consistent with a coplanar spiral (helical) ground state with a wavevector $Q_0 \approx (0.27, 0)$, or equivalently $(0.34, 0) \text{Å}^{-1}$, recent work [41] has instead suggested a collinear order with this wavevector. For BaCo$_2$(PO$_4$), recent experiments [40] have argued for short-range ordering involving both zig-zag and spiral states. Overall, these experiments suggest a slightly smaller third-neighbor coupling, which would favor a smaller wavevector compared with the zig-zag ordered ground state, reflecting the extreme sensitivity of the magnetic ground state to small changes in the frustration. This, in turn, might arise from small differences in the microscopic Kanamori interactions. To illustrate this, we have computed the magnetic ground state and dynamical spin correlations by rescaling all third-neighbor hoppings by a factor $\approx 0.8$, which leads to a renormalized $J_3^{XY}/J_1^{XY} = -0.3$. In this case, we find that the magnetic ground state has the experimentally reported ordering

### Table III

| BaCo$_2$(AsO$_4$)$_2$ | Bond-1 | Bond-3 |
|----------------------|--------|--------|
| $J_{XY}$             | $-14.5 \text{ meV}$ | $7.1 \text{ meV}$ |
| $J^Z$                | $-3.8 \text{ meV}$ | $2.3 \text{ meV}$ |
| $D$                  | $1.5 \text{ meV}$ | $\sim 0$ |
| $E$                  | $-1.7 \text{ meV}$ | $\sim 0$ |

### Table IV

| BaCo$_2$(PO$_4$)$_2$ | Bond-1 | Bond-3 |
|----------------------|--------|--------|
| $J_{XY}$             | $-17.3 \text{ meV}$ | $6.9 \text{ meV}$ |
| $J^Z$                | $-5.0 \text{ meV}$ | $2.4 \text{ meV}$ |
| $D$                  | $-2.7 \text{ meV}$ | $\sim 0$ |
| $E$                  | $0.2 \text{ meV}$ | $\sim 0$ |

FIG. 7. Left panel: Zig-zag ordered phase with $Q_0 = (1/2, 0) \approx (0.628, 0) \text{Å}^{-1}$. Right panel: Powder averaged dynamical structure factor of the zig-zag ordered phase for the parameter set from Table III.

FIG. 8. Left panel: Spiral ordered phase with $Q_0 = (0.34, 0) \text{Å}$. Right panel: Powder averaged dynamical structure factor of the zig-zag ordered phase for the parameter set from Table III but with all third-neighbor couplings rescaled such that $J_3^{XY}/J_1^{XY} = -0.3$. 

In addition, the Goldstone mode expected at $Q_0$ for a simple $XXZ$ model is gapped out by the anisotropy terms in the Hamiltonian, with a gap $\sim 0.3 J_{XY}^1$. Below the scale of this Goldstone gap, we expect that the magnetic specific heat should be exponentially suppressed. Similar results follow for the exchange parameter set from Table IV.

On the other hand, experiments on BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$ do not find a zig-zag ordered ground state. While early experiments on BaCo$_2$(AsO$_4$) [60] reported results consistent with a coplanar spiral (helical) ground state with a wavevector $Q_0 \approx (0.27, 0)$, or equivalently $(0.34, 0) \text{Å}^{-1}$, recent work [41] has instead suggested a collinear order with this wavevector. For BaCo$_2$(PO$_4$), recent experiments [40] have argued for short-range ordering involving both zig-zag and spiral states. Overall, these experiments suggest a slightly smaller third-neighbor coupling, which would favor a smaller wavevector compared with the zig-zag ordered ground state, reflecting the extreme sensitivity of the magnetic ground state to small changes in the frustration. This, in turn, might arise from small differences in the microscopic Kanamori interactions. To illustrate this, we have computed the magnetic ground state and dynamical spin correlations by rescaling all third-neighbor hoppings by a factor $\approx 0.8$, which leads to a renormalized $J_3^{XY}/J_1^{XY} = -0.3$. In this case, we find that the magnetic ground state has the experimentally reported ordering

### Table III

| BaCo$_2$(AsO$_4$)$_2$ | Bond-1 | Bond-3 |
|----------------------|--------|--------|
| $J_{XY}$             | $-14.5 \text{ meV}$ | $7.1 \text{ meV}$ |
| $J^Z$                | $-3.8 \text{ meV}$ | $2.3 \text{ meV}$ |
| $D$                  | $1.5 \text{ meV}$ | $\sim 0$ |
| $E$                  | $-1.7 \text{ meV}$ | $\sim 0$ |

### Table IV

| BaCo$_2$(PO$_4$)$_2$ | Bond-1 | Bond-3 |
|----------------------|--------|--------|
| $J_{XY}$             | $-17.3 \text{ meV}$ | $6.9 \text{ meV}$ |
| $J^Z$                | $-5.0 \text{ meV}$ | $2.4 \text{ meV}$ |
| $D$                  | $-2.7 \text{ meV}$ | $\sim 0$ |
| $E$                  | $0.2 \text{ meV}$ | $\sim 0$ |
wavevector, with the spin order as shown in Fig. 8 (left panel). The corresponding dynamical spin correlations are shown in Fig. 8 (right panel). As expected, the Goldstone mode continues to be gapped due to the anisotropic exchange terms. Indeed, inelastic neutron scattering experiments on BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$ find evidence for spin gapped excitations, qualitatively consistent with our results [40, 41].

It is possible that the collinear order reported in [41] could reflect the impact of strong quantum fluctuations on the competition between spiral and collinear ground states. Such competition has been extensively investigated in spatially anisotropic triangular antiferromagnets [61]; we defer a full quantum analysis of our model to a future publication.

Specific heat measurements on BaCo$_2$(AsO$_4$)$_2$ have reported a $\sim T^2$ specific heat at the lowest temperature $T < 2K$ [41, 62], which was attributed to 2D magnetic fluctuations. However, our calculations suggest that the specific heat should be suppressed below a spin gap scale $\sim 0.3J_{1}^{XY}$; we thus conclude that the experimentally observed specific heat may be of non-magnetic origin. Alternatively, it might reflect the impact of disorder which has not been taken into account in our work.

One key discrepancy between our calculations and the experimental results on BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$ is in the overall scale of the magnetic exchange. The exchange couplings we find are about 3–4 times larger than those reported in the experimental literature. We have explored varying $U$, $J_H$ and the crystal field matrix in order to resolve this discrepancy while maintaining a reasonable ratio of $J_3^{XY}/J_1^{XY}$, but without any success. We therefore propose the following tentative explanation to reconcile this problem. We have seen that the Co$^{2+}$ ion supports a lowest energy single-ion excitation, i.e. a spin exciton, at an energy $\sim 20-30$ meV. In CoTiO$_3$, the exchange interactions between the $J_{eff}=1/2$ pseudospins is much smaller than this spin-exciton gap, justifying the restriction to a pseudospin-1/2 model. By contrast, the magnetic exchange interactions in BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$ are comparable to the spin-exciton gap. This suggests that the spin dynamics and Curie-Weiss temperatures might both be strongly impacted by coupling between the low energy magnon and the spin exciton. Level repulsion between these states could then lead to an effectively smaller magnon bandwidth for the $J_{eff}=1/2$ spins. The theory of this magnon-exciton coupling will be discussed elsewhere.

Our viewpoint taken in this paper is that we can focus on a Co-only model with site-local interactions, although Fig. 3 shows that the Wannier orbitals do have oxygen character. To what extent is this a reasonable assumption? Partial justification for retaining only an effective Co interacting model stems from the recognition that compounds in the transition metal oxide series go from being Mott-Hubbard insulators to charge-transfer insulators as we go from Ti to Cu, with the cuprates being well-known charge transfer insulators. Recent work suggests that nickelates, such as NdNiO$_2$, lie at the borderline [63]. Based on this, the cobaltates, are perhaps better viewed as Mott-Hubbard insulators where focussing on excitations on the Co d-levels is a good starting point, and indeed we do seem to find excellent agreement with experiments on CoTiO$_3$ following this approach. Nevertheless, in light of the above discrepancies, a more quantitative treatment of the two-site exchange interaction incorporating oxygen orbitals, in addition to the Co ions, might be important to consider in future studies of BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$.

**VIII. DISCUSSION**

We have explored the magnetism of the honeycomb cobaltates CoTiO$_3$, BaCo$_2$(AsO$_4$)$_2$, and BaCo$_2$(PO$_4$)$_2$ which crystallize in the rhombohedral structure with $R3$ space group. The Co$^{2+}$ ions in the $d^7$ configuration have been proposed as possible candidate materials for realizing strong Kitaev interactions and Kitaev quantum spin liquids. Based on our combined DFT and exact diagonalization study, we find that the magnetism in these cobaltates is strongly perturbed by the trigonal distortion, and that they are better described as XXZ quantum magnets with subdominant but nevertheless important anisotropy terms. Our results for CoTiO$_3$ are in excellent agreement with neutron scattering experiments [36, 37]. The bond-anisotropic exchanges we have uncovered can gap the Goldstone modes in these magnets, and lead to a helical winding of the Dirac magnon nodal line in CoTiO$_3$. In BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$, we have found microscopic evidence for strong third-neighbor antiferromagnetic exchange, which can drive possibly quite distinct quantum spin liquid phases proximate to zig-zag or spiral ordered phases. Indeed, the reported collinear order [41] and small magnetic field to drive saturation [35] point to the importance of strong quantum fluctuations in these two materials. In addition, we have presented arguments that the low-energy spin excitations in the B compounds may involve strongly coupled magnons and spin excitons. While such magnon-exciton coupling has been explored within phenomenological models for CoTiO$_3$ [37] and Fe$_2$ [64], it would be worth revisiting those ideas in light of our work in order to provide a quantitative understanding of BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$, and their magnetic field driven phase diagram [35, 65, 66]. Carefully integrating out the high energy exciton may lead to an enhancement of the Kitaev exchange interaction for the $J_{eff}=1/2$ pseudospins; we are presently exploring this possibility.

While we have explored a limited set of all the honeycomb cobaltates, i.e. the rhombohedral cases, most other candidate cobaltates have even lower symmetry. For instance, Na$_2$Co$_2$SbO$_6$ [67–72], Ag$_3$Co$_2$SbO$_6$ [73], Li$_3$Co$_2$SbO$_6$ [74, 75], and CoPS$_3$ [76] crystallize in the monoclinic $C2/m$ space group, while Co$_4$Nb$_2$O$_9$ and Co$_4$Ta$_2$O$_9$ [77–80] crystallize in the $P3c1$ space group.
We thus suspect that they may support even more complex magnetic exchange interactions. In addition, the zig-zag magnetic order observed in many of these compounds may again stem from a significant third-neighbor coupling as was initially proposed also for the iridates [12] and also recognized to be important for the cobaltates [30].

As a test case, we have carried out a preliminary study of the exchange couplings in Na$_2$Co$_2$SbO$_6$. We find that its spin Hamiltonian is consistent with nearly decoupled 2D honeycomb layers. However, the $3 \times 3$ matrix of in-plane exchange couplings does not appear to be simple (i.e., sparse) in either the local octahedral basis or a global spin basis; indeed all couplings permitted by symmetry appear to be relevant. Our preliminary calculations yield, in the local octahedral basis, a nearest-neighbor ferromagnetic Heisenberg coupling $J_1 \sim -3$ meV, a comparable antiferromagnetic Kitaev exchange $K \sim 2.5$ meV, an off-diagonal symmetric exchange $\Gamma \sim 2.5$ meV, and a frustrating antiferromagnetic third-neighbor Heisenberg exchange $J_3 \sim 2.5$ meV, together with additional bond-anisotropic terms $\Gamma'_1, \Gamma'_2$. The significant $J_3$ appears to be mediated by the Sb ion in the honeycomb plane. This spin Hamiltonian favors a zig-zag ground state with a gapped Goldstone mode, in qualitative agreement with neutron diffraction and inelastic scattering experiments [81, 82]. Our estimated exchange couplings are roughly in the same ballpark as those extracted from careful spin-wave fits to the inelastic neutron scattering data [81, 82], but differ in detail (e.g., the sign of $\Gamma$). Clearly, given the absence of $C_3$ symmetry in this monoclinic crystal, a more careful study is needed to reliably extract the exchange interactions and model the spin-wave spectrum. Nevertheless, our preliminary calculations appear to confirm that the spin model is far more complex in this lower symmetry magnet, suggesting that this material also does not realize a simple Kitaev-exchange dominated spin model. The presence of multiple competing interactions could still lead to nearby quantum spin liquid phases whose existence and nature remain open issues.

In other cobaltates, such as the recently studied Na$_2$Co$_2$TeO$_6$ [83] which crystallizes in the P6$_3$22 space group and exhibits zig-zag magnetic order, randomness in the Na$^+$ arrangement might promote disorder-enabled spin liquid signatures. However, this randomness stymies a full ab initio based study of the exchange interactions. Progress may be made by exploring a suitable periodic arrangement of Na$^+$ ions in a supercell; we defer this to a future investigation.

In summary, we argue that the honeycomb cobaltates can realize a rich set of magnetic Hamiltonians with frustration and anisotropic bond-dependent interactions, and may potentially host interesting quantum spin liquids driven by further-neighbor interactions and disorder. Realizing the Kitaev quantum spin liquid in this class of materials may require further fine-tuning of the chemistry and crystal fields in order to promote the Kitaev coupling over other competing exchange interactions.

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Appendix A: Exchange couplings in local Kitaev basis

In this Appendix, we discuss the basis rotation and the rewriting of the exchange couplings in the Kitaev basis. The spins written in the global basis (Sα) can be transformed into the local $\tilde{x}\tilde{y}\tilde{z}$ basis ($\tilde{S}_\alpha$) via a transformation $\tilde{S}_\alpha = U_{\alpha\beta}S_\beta$, where $U$ is given by the matrix

$$U = \begin{pmatrix}
1/\sqrt{6} & 1/\sqrt{2} & 1/\sqrt{3} \\
-\sqrt{2/3} & 0 & 1/\sqrt{3} \\
1/\sqrt{6} & -1/\sqrt{2} & 1/\sqrt{3}
\end{pmatrix}$$  \hspace{1cm} (A1)

Thus, the local exchange matrix $J_{\text{loc}}$ is obtained via

$$J_{\text{loc}} = UJU^T$$  \hspace{1cm} (A2)

where $J$ is the exchange matrix in the global basis. Along the same C bond (referred to in the local basis as the z bond), the Heisenberg ($J$), Kitaev ($K$), Diagonal ($\eta$) and off-diagonal ($\Gamma$, $\Gamma'$, $\Gamma''$) anisotropy couplings are defined as

$$J_{\text{loc}}^{(z)} = \begin{pmatrix}
J + \eta & \Gamma & \Gamma' \\
\Gamma & J - \eta & \Gamma'' \\
\Gamma' & \Gamma'' & J + K
\end{pmatrix}$$  \hspace{1cm} (A3)

Below we present the couplings in this local basis for the materials considered. It should be noted that many couplings have comparable values, which does not allow for as simple a description as the XXZ model in the global basis which is presented in the main text.
Appendix B: $J_1$-$J_2$-$J_3$ Phase Diagram

The figure below shows the classical $J_1$-$J_2$-$J_3$ phase diagram explored in [39]. In this work, we find that the relevant part of the phase diagram is the $y$-axis, specifically where $J_3/J_1 < 0$. Experiments on the Barium compounds appear to stabilize the shaded "Spiral 2" phase (characterized by a nonzero angle between spins on different sublattices. While the aforementioned study does not consider off-diagonal anisotropy terms ($D$ and $E$), we find that including them retains the general structure of the phase diagram. The narrowness of this spiral phase emphasizes the sensitivity of the magnetic order to the microscopics of the systems considered.
SUPPLEMENTARY MATERIAL

XY magnetism, Kitaev exchange, and long-range frustration in the $J_{\text{eff}} = 1/2$ honeycomb cobaltates

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I. DFT CALCULATION DETAILS

We carried out theoretical calculations within the framework of first-principles density functional theory (DFT) taking into account the structural as well as chemical information completely.

Our DFT based calculations were executed with the choices of different basis sets as, (i) the plane-wave based basis as implemented in the Vienna ab-initio Simulation Package (VASP) [1] with projector-augmented wave (PAW) potential [2] and (ii) the muffin-tin orbital (MTO) based linear muffin-tin orbital (LMTO) method [3], and the $N^{th}$ order MTO method namely, NMTO method [4], as implemented in the STUTTGART code. The consistency of results between two different basis sets have been confirmed in terms density of states, band structure and magnetic moments. The exchange correlation functional was chosen as the generalized gradient approximation (GGA) implemented following the Perdew-Burke-Ernzerhof (PBE) prescription [5].

For the plane wave calculation, energy cutoff of 600 eV and MonkhorstPack k-points mesh of $6 \times 6 \times 2$ for the unit cell of CoTiO$_3$ and BaCo$_2$(AsO$_4$)$_2$ were found to provide good convergence of the total energy in self-consistent field calculations. The effect of spin-orbit coupling (SOC) was included within GGA+SOC implementation of VASP and the effect of missing correlation effect beyond GGA at the Co site was considered within the GGA+SOC+U framework [6] with the choice of $U = 3$ eV and Hund’s coupling $J_H = 0.7$ eV [7, 8].

For construction of low energy Hamiltonian, we used the $N^{th}$ order muffin-tin orbital method, which relies on a self-consistent potential generated by the linear MTO (LMTO) method. The low-energy tight-binding Hamiltonian, defined in the effective Co Wannier basis, provides information about the crystal-field splitting at the Co site along with the effective hopping interactions between the Co sites. The muffin-tin radii of different atomic sites used in LMTO calculations were chosen as $1.52 \, \text{Å}$ for Co, $1.27 \, \text{Å}$ for Ti, $0.98 \, \text{Å}$ for O atoms in CoTiO$_3$; $2.44 \, \text{Å}$ for Ba, $1.52 \, \text{Å}$ for Co, $1.09 \, \text{Å}$ for As and $0.82/0.89 \, \text{Å}$ for the O atoms in BaCo$_2$(AsO$_4$)$_2$. For BaCo$_2$(PO$_4$)$_2$, the atomic radii are chosen to be $2.43 \, \text{Å}$ for Ba, $1.58 \, \text{Å}$ for Co, $0.97 \, \text{Å}$ for P and $0.74/0.83 \, \text{Å}$ for the O atoms.

II. GGA, GGA+SOC, GGA+SOC+U MAGNETIC MOMENTS AND ELECTRONIC STRUCTURE

|   | CoTiO$_3$ | BaCo$_2$(AsO$_4$)$_2$ |
|---|---|---|
| GGA | Co | 2.55 | Ba | 2.58 |
| GGA+SOC | Ti | 0.11 | Co | 0.00 |
| GGA+SOC+U | O | 0.10 | As | 0.02 |
|     | (0.17) | (0.00) | (0.00) | (0.15) |
|     | (0.00) | (0.00) | (0.00) | (0.00) |

TABLE I. The magnetic moments (in $\mu_B$) at different atomic sites of CoTiO$_3$ and BaCo$_2$(AsO$_4$)$_2$, as calculated within GGA, GGA+SOC and GGA+SOC+U. The numbers in the bracket refer to orbital moments.
FIG. 1. Density of states of CoTiO$_3$ (left panels) and BaCo$_2$(AsO$_4$)$_2$ (right panels), as calculated within GGA (top), GGA+SOC (middle) and GGA+SOC+U (bottom). The GGA+SOC+U shows the clear appearance of an insulating gap.

III. ONSITE MATRICES

The on-site term ($H_{\text{CF}}$) is written in second quantized language as

$$H_{\text{CF}} = \sum_{\ell m} A_{\ell m} \sum_s c_{\ell s}^\dagger c_{ms}$$

where $\ell$ and $m$ are orbital indices, and $s$ refers to the electron spin. Below, we present the $A$ matrices for each of the materials considered in the main text. All the matrices below are written in the orbital basis $\{(yz, xz, xy), (x^2−y^2, 3z^2−1)\}$

A. CoTiO$_3$

$$A_{\text{CTO}} = \begin{pmatrix}
-1.1642 & 0.0312 & -0.0008 & -0.0063 & -0.0039 \\
0.0312 & -0.1429 & -0.0040 & 0.0033 & -0.0044 \\
-0.0008 & -0.004 & -1.0968 & 0.0926 & 0.0103 \\
-0.0063 & 0.0033 & 0.0926 & -0.4133 & 0.4380 \\
-0.0039 & -0.0044 & 0.0103 & 0.4380 & -0.8765
\end{pmatrix}$$

B. BaCo$_2$(AsO$_4$)$_2$

$$A_{\text{BCAO}} = \begin{pmatrix}
-2.9578 & 0.0140 & -0.0005 & 0.0202 & 0.0123 \\
0.0140 & -1.6838 & 0.0124 & 0.0020 & -0.0043 \\
-0.0005 & 0.0124 & -2.8610 & 0.0490 & -0.0495 \\
0.0202 & 0.0020 & 0.0490 & -1.9904 & 0.5312 \\
0.0123 & -0.0043 & -0.04950 & 0.5312 & -2.6055
\end{pmatrix}$$
C. \text{BaCo}_2(\text{PO}_4)_2

\[
A_{\text{BCPO}} = \begin{pmatrix}
-3.5049 & -0.0717 & 0.0008 & 0.0034 & 0.0008 \\
-0.0717 & -2.2912 & 0.0017 & -0.0136 & 0.0249 \\
0.0008 & 0.0017 & -3.4155 & -0.0900 & 0.0157 \\
0.0034 & -0.0136 & -0.0900 & -2.5757 & 0.5051 \\
0.0008 & 0.0249 & 0.0157 & 0.5051 & -3.1866
\end{pmatrix}
\]

\[ (8) \]

IV. HOPPING MATRICES

Below, we list the hopping matrices for the relevant bonds, listing both the connecting vector \( \vec{V} \), as well as the associated hopping matrix \( T \). These should be read in terms of the hopping Hamiltonian (in the same basis as above)

\[
\hat{T}_{i,i+\vec{V}} = \sum_{\ell\ell'\alpha} (T_{\ell\ell'c_{i+\vec{V},\ell\alpha}}^c + T_{\ell'\ell c_{i\alpha}}^c) \]

A. CoTiO$_3$

1. In-plane 1st Nearest Neighbour

\[
\vec{V} = (-0.5, -0.866, 0.205) \quad T = \begin{pmatrix}
-0.0803 & -0.0411 & 0.1233 & -0.0163 & -0.0415 \\
-0.0411 & -0.0588 & 0.0236 & -0.0143 & -0.0433 \\
0.1233 & 0.0236 & -0.0684 & 0.0575 & -0.0073 \\
-0.0163 & -0.0143 & 0.0575 & -0.0333 & -0.0641 \\
-0.0415 & -0.0433 & -0.0073 & -0.0641 & -0.0093
\end{pmatrix}
\]

\[ (5) \]

\[
\vec{V} = (1.0, 0.0, 0.205) \quad T = \begin{pmatrix}
0.0012 & -0.0100 & -0.0026 & -0.0243 & -0.0134 \\
-0.0100 & -0.0427 & 0.0194 & 0.0268 & -0.0026 \\
-0.0026 & 0.0194 & 0.0793 & -0.0515 & -0.0051 \\
-0.0243 & 0.0268 & -0.0515 & -0.1734 & 0.0811 \\
-0.0134 & -0.0026 & -0.0051 & 0.0811 & -0.1146
\end{pmatrix}
\]

\[ (6) \]

\[
\vec{V} = (-0.5, 0.866, 0.205) \quad T = \begin{pmatrix}
-0.0779 & -0.0214 & -0.1259 & -0.0006 & 0.0287 \\
-0.0214 & -0.0991 & -0.0691 & 0.0119 & 0.0123 \\
-0.1259 & -0.0691 & -0.0744 & 0.0405 & -0.0154 \\
-0.0006 & 0.0119 & 0.0405 & -0.0364 & -0.0271 \\
0.0287 & 0.0123 & -0.0154 & -0.0271 & 0.0376
\end{pmatrix}
\]

\[ (7) \]

2. Out-of-plane 1st Nearest Neighbour

\[
\vec{V} = (0.0, 0.0, 1.381) \quad T = \begin{pmatrix}
-0.0015 & 0.0210 & 0.0010 & 0.0082 & 0.0052 \\
0.0210 & 0.0272 & 0.0052 & -0.0049 & 0.0067 \\
0.0010 & 0.0052 & -0.019 & -0.0097 & 0.0033 \\
0.0082 & -0.0049 & -0.0097 & 0.0353 & 0.0086 \\
0.0052 & 0.0067 & 0.0033 & 0.0086 & -0.0142
\end{pmatrix}
\]

\[ (8) \]
3. Out-of-plane 2nd Nearest Neighbour

\[ \vec{V} = (-0.5, -0.866, 1.587) \], \[ T = \begin{pmatrix}
-0.0089 & -0.0308 & -0.0046 & -0.0155 & 0.0042 \\
0.0358 & 0.0038 & 0.0106 & 0.0063 & -0.0129 \\
0.0131 & 0.0124 & 0.0070 & 0.0079 & -0.0065 \\
0.0208 & 0.0234 & -0.0049 & 0.0144 & -0.0140 \\
0.0005 & 0.0276 & -0.0167 & 0.0264 & -0.0216
\end{pmatrix} \] (9)

\[ \vec{V} = (0.5, 0.866, -1.587) \], \[ T = \begin{pmatrix}
-0.0089 & 0.0358 & 0.0131 & 0.0208 & 0.0005 \\
-0.0308 & 0.0038 & 0.0124 & 0.0234 & 0.0276 \\
-0.0046 & 0.0106 & 0.0070 & -0.0049 & -0.0167 \\
-0.0155 & 0.0063 & 0.0079 & 0.0144 & 0.0264 \\
0.0042 & -0.0129 & -0.0065 & -0.0140 & -0.0216
\end{pmatrix} \] (10)

\[ \vec{V} = (1.0, 0.0, 1.587) \], \[ T = \begin{pmatrix}
0.0109 & -0.0542 & 0.0071 & -0.0099 & -0.0169 \\
0.0275 & 0.0071 & 0.0056 & -0.0019 & -0.0022 \\
-0.0295 & 0.0188 & -0.0137 & 0.0062 & 0.0201 \\
-0.0036 & -0.0051 & -0.0085 & 0.0013 & 0.0184 \\
0.0104 & -0.0117 & 0.0016 & 0.0017 & -0.0109
\end{pmatrix} \] (11)

\[ \vec{V} = (-1.0, 0.0, -1.587) \], \[ T = \begin{pmatrix}
0.0109 & 0.0275 & -0.0295 & -0.0036 & 0.0104 \\
-0.0542 & 0.0071 & 0.0188 & -0.0051 & -0.0117 \\
0.0071 & 0.0056 & -0.0137 & -0.0085 & 0.0016 \\
-0.0099 & -0.0019 & 0.0062 & 0.0013 & 0.0017 \\
-0.0169 & -0.0022 & 0.0201 & 0.0184 & -0.0109
\end{pmatrix} \] (12)

\[ \vec{V} = (-0.5, 0.866, 1.587) \], \[ T = \begin{pmatrix}
0.0174 & -0.0180 & 0.0049 & -0.0224 & 0.0102 \\
0.0232 & -0.0098 & 0.0085 & -0.0022 & 0.0031 \\
-0.0146 & -0.0278 & 0.0052 & 0.0079 & -0.0013 \\
0.0534 & 0.0160 & 0.0090 & -0.0153 & 0.0179 \\
0.0093 & -0.0087 & 0.0063 & 0.0024 & -0.0027
\end{pmatrix} \] (13)

\[ \vec{V} = (-0.5, -0.866, -1.587) \], \[ T = \begin{pmatrix}
0.0174 & 0.0232 & -0.0146 & 0.0534 & 0.0093 \\
-0.0180 & -0.0098 & -0.0278 & 0.0160 & -0.0087 \\
0.0049 & 0.0085 & 0.0052 & 0.0090 & 0.0063 \\
-0.0224 & -0.0022 & 0.0079 & -0.0153 & 0.0024 \\
0.0102 & 0.0031 & -0.0013 & 0.0179 & -0.0027
\end{pmatrix} \] (14)

B. \textit{BaCo}_2(\textit{AsO}_4)_2

1. In-plane 1st Nearest Neighbour

\[ \vec{V} = (-0.5, -0.866, 0.056) \], \[ T = \begin{pmatrix}
-0.1539 & -0.0133 & 0.1892 & -0.0808 & 0.0095 \\
-0.0133 & -0.0250 & 0.0676 & -0.0087 & 0.0115 \\
0.1892 & 0.0676 & -0.0883 & 0.0240 & -0.0012 \\
-0.0808 & -0.0087 & 0.0240 & 0.0292 & -0.056 \\
0.0095 & 0.0115 & -0.0012 & -0.056 & 0.0176
\end{pmatrix} \] (15)
\[ \vec{V} = (1.0, 0.0, 0.056) \quad T = \begin{pmatrix} 0.0961 & 0.0558 & 0.0009 & 0.0123 & -0.0033 \\ 0.0558 & -0.0240 & -0.0076 & 0.0129 & -0.0221 \\ 0.0009 & -0.0076 & 0.0442 & 0.0052 & -0.0476 \\ 0.0123 & 0.0129 & 0.0052 & -0.1668 & 0.1650 \\ -0.0033 & -0.0221 & -0.0476 & 0.1650 & -0.1699 \end{pmatrix} \] (16)

\[ \vec{V} = (-0.5, 0.866, 0.056) \quad T = \begin{pmatrix} -0.1581 & -0.0391 & -0.1913 & 0.0531 & -0.0147 \\ -0.0391 & -0.0226 & -0.0711 & 0.0043 & -0.0034 \\ -0.1913 & -0.0711 & -0.0849 & 0.0005 & -0.0034 \\ 0.0531 & 0.0043 & 0.0005 & 0.0416 & -0.0649 \\ -0.0147 & -0.0034 & -0.0034 & -0.0649 & 0.0038 \end{pmatrix} \] (17)

2. In-plane 3rd Nearest Neighbour

\[ \vec{V} = (1.0, 1.732, 0.056) \quad T = \begin{pmatrix} -0.0177 & -0.0075 & 0.0255 & -0.0102 & -0.0026 \\ -0.0075 & 0.0013 & 0.0298 & -0.0658 & -0.0377 \\ 0.0255 & 0.0298 & -0.0283 & -0.0060 & -0.0005 \\ -0.0102 & -0.0658 & -0.0060 & 0.0653 & 0.0394 \\ -0.0026 & -0.0377 & -0.0005 & 0.0394 & 0.0251 \end{pmatrix} \] (18)

\[ \vec{V} = (-2.0, 0.0, 0.056) \quad T = \begin{pmatrix} 0.0061 & 0.0137 & -0.0007 & 0.0077 & 0.0000 \\ 0.0137 & 0.1327 & -0.0134 & -0.0042 & 0.0078 \\ -0.0007 & -0.0134 & -0.0027 & -0.0086 & 0.0015 \\ 0.0077 & -0.0042 & -0.0086 & -0.0646 & 0.0149 \\ 0.0000 & 0.0078 & 0.0015 & 0.0149 & -0.0258 \end{pmatrix} \] (19)

\[ \vec{V} = (1.0, -1.732, 0.056) \quad T = \begin{pmatrix} -0.0226 & -0.0107 & -0.0243 & 0.0141 & 0.0094 \\ -0.0107 & 0.0019 & -0.0084 & -0.0242 & 0.0129 & 0.0151 \\ -0.0243 & -0.0084 & -0.0242 & 0.0129 & 0.0856 & 0.0260 \\ 0.0141 & 0.0661 & 0.0129 & 0.0856 & 0.0260 & 0.0051 \end{pmatrix} \] (20)

C. BaCo$_2$(PO$_4$)$_2$

1. In-plane 1st Nearest Neighbour

\[ \vec{V} = (-0.5, -0.866, 0.059) \quad T = \begin{pmatrix} 0.1162 & -0.0458 & 0.0024 & -0.0152 & 0.0031 \\ -0.0458 & -0.0748 & 0.0106 & 0.0078 & -0.0217 \\ 0.0024 & 0.0106 & 0.0363 & 0.0057 & 0.0519 \\ -0.0152 & 0.0078 & 0.0057 & -0.1642 & 0.1553 \\ 0.0031 & -0.0216 & 0.0519 & 0.1553 & -0.2813 \end{pmatrix} \] (21)

\[ \vec{V} = (1.0, 0.0, 0.059) \quad T = \begin{pmatrix} -0.2091 & 0.0040 & -0.2255 & -0.0496 & 0.0435 \\ 0.0040 & -0.0612 & 0.0309 & 0.0033 & -0.0031 \\ -0.2255 & 0.0309 & -0.0987 & 0.0137 & 0.0194 \\ -0.0496 & 0.0033 & 0.0137 & 0.0115 & -0.0874 \\ 0.0435 & -0.0031 & 0.0194 & -0.0874 & -0.0103 \end{pmatrix} \] (22)
\[ \vec{V} = (-0.5, 0.866, 0.059) \ , \ T = \begin{pmatrix} 
-0.1827 & -0.0309 & 0.2215 & 0.0908 & -0.0315 \\
-0.0309 & -0.0711 & -0.0265 & 0.0043 & 0.0059 \\
0.2215 & -0.0265 & -0.1217 & -0.0213 & 0.0096 \\
0.0908 & 0.0043 & -0.0213 & -0.0084 & -0.0761 \\
-0.0315 & 0.0059 & 0.0096 & -0.0761 & 0.0161 
\end{pmatrix} \] (23)

2. In-plane 3rd Nearest Neighbour

\[ \vec{V} = (1.0, 1.732, 0.056) \ , \ T = \begin{pmatrix} 
0.0243 & -0.0360 & -0.0014 & -0.0084 & -0.0044 \\
-0.0360 & 0.1278 & 0.0189 & -0.0055 & 0.0141 \\
-0.0014 & 0.0189 & -0.0197 & 0.0236 & -0.0042 \\
-0.0084 & -0.0055 & 0.0236 & -0.0463 & 0.0087 \\
-0.0044 & 0.0141 & -0.0042 & 0.0087 & -0.0275 
\end{pmatrix} \] (24)

\[ \vec{V} = (-2.0, 0.0, 0.056) \ , \ T = \begin{pmatrix} 
-0.0118 & -0.0024 & -0.0208 & -0.0211 & -0.0054 \\
-0.0024 & 0.0038 & 0.0056 & 0.0639 & 0.0348 \\
-0.0208 & 0.0056 & -0.0276 & -0.0066 & -0.0233 \\
-0.0211 & 0.0639 & -0.0066 & 0.1013 & 0.0172 \\
-0.0054 & 0.0348 & -0.0233 & 0.0172 & -0.0072 
\end{pmatrix} \] (25)

\[ \vec{V} = (1.0, -1.732, 0.056) \ , \ T = \begin{pmatrix} 
-0.0062 & -0.0117 & 0.0222 & 0.0200 & 0.0014 \\
-0.0117 & 0.0059 & -0.0292 & -0.0659 & -0.0358 \\
0.0222 & -0.0292 & -0.0342 & 0.0151 & -0.0116 \\
0.0200 & -0.0659 & 0.0151 & 0.0809 & 0.0298 \\
0.0014 & -0.0358 & -0.0116 & 0.0298 & 0.0121 
\end{pmatrix} \] (26)

V. DEPENDENCE OF EXCHANGES ON INTERACTION PARAMETERS

In this section, we give more examples of the dependence of the exchanges considered in the main text on the interaction parameters. This is done to emphasize the fact that for reasonable values of these parameters, there is a fairly large variance in the exchanges.

A. CoTiO$_3$

![FIG. 2. Variance of 1NN Exchanges with Hund’s Coupling $J_H$](image-url)
B. BaCo$_2$(AsO$_4$)$_2$ and BaCo$_2$(PO$_4$)$_2$

The Barium compounds show similar behaviour, so the results will only be presented for BaCo$_2$(AsO$_4$)$_2$.

FIG. 3. Variance of 1NN Exchanges with Hubbard $U$

FIG. 4. Variance of 3NN Exchanges with Hubbard $U$
FIG. 5. Variance of 1NN Exchanges with Hund’s coupling $J_H$

FIG. 6. Variance of 3NN Exchanges with Hund’s coupling $J_H$

FIG. 7. Variance of the ratio $-\frac{J_{XY}}{3}/\frac{J_{XY}}{1}$ with Hund’s coupling $J_H$
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