


Strong Effect of Hydrogen Order on Magnetic Kitaev Interactions in $\text{H}_3\text{LiIr}_2\text{O}_6$

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Very recently a quantum liquid was reported to form in $\text{H}_3\text{LiIr}_2\text{O}_6$, an iridate proposed to be a close realization of the Kitaev honeycomb model. To test this assertion we perform detailed quantum chemistry calculations to determine the magnetic interactions between Ir moments. We find that weakly bond dependent ferromagnetic Kitaev exchange dominates over other couplings, but still is substantially lower than in Na_2IrO_3 . This reduction is caused by the peculiar position of the interlayer species: removing hydrogen cations next to a Ir_2O_2 plaquette increases the Kitaev exchange by more than a factor of 3 on the corresponding Ir—Ir link. Consequently, any lack of hydrogen order will have a drastic effect on the magnetic interactions and strongly promote spin disordering.

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Introduction.—Quantum spin liquids (QSLs) are states of matter that cannot be described by the broken symmetries associated with conventional magnetic ground states [1]. Whereas there is a rich variety of mathematical models that exhibit QSL behavior, finding materials in which a QSL state is realized is an intensely pursued goal in present day experimental condensed-matter physics [2–4]. Of particular interest is the Kitaev Hamiltonian on the honeycomb lattice [5], which is a mathematically well-understood two-dimensional model exhibiting various topological QSL states. Its remarkable properties include protection of quantum information and the emergence of Majorana fermions [5,6].

The search to realize the Kitaev model of effective spin-1/2 sites on the honeycomb lattice was mainly centered until recently on honeycomb iridate materials [7,8] of the type $A_2\text{IrO}_3$, where A is either Na or Li. Also of interest is ruthenium trichloride, RuCl_3 [9], for which Raman and neutron scattering measurements suggest that this $4d^5$ halide honeycomb system is close to the Kitaev limit [10–12]. However, in all these compounds long-range magnetic order develops at low temperatures, for all known different crystallographic phases [13–17]; computational investigations suggest that the QSL regime is preempted by sizable residual Heisenberg couplings, nearest-neighbor (NN) or of longer-range nature [18–21]. Very recently, however, it was reported that a Kitaev QSL state of pseudospin-1/2 moments forms in the honeycomb iridate $\text{H}_3\text{LiIr}_2\text{O}_6$. In particular, this material does not display magnetic ordering down to 0.05 K, in spite of magnetic interaction energies in the range of 100 K [22].

Here we present results of quantum chemistry electronic-structure computations for the NN magnetic interactions between Ir moments and compare these to other

honeycomb iridates. This is done for the crystal structure recently proposed on the basis of x-ray diffraction data [22] and also for atomic positions optimized by density-functional calculations. We find that the Kitaev exchange K is ~ 10 meV, substantially smaller than in Na_2IrO_3 [23], but in contrast only weakly bond dependent [20] and, most importantly, the residual NN Heisenberg J is significantly weaker relative to K . The *ab initio* calculations show that the smaller absolute K values are related to the peculiar position of the interlayer species, with a single H site neighboring each O ion [22]. Exact-diagonalization (ED) computations using the quantum chemistry NN couplings augmented with longer-range Heisenberg interactions show the presence of a QSL state, which is, however, very susceptible to the formation of long-range order for only weak longer-range exchange, a situation that is reminiscent of the $A_2\text{IrO}_3$ (hyper)honeycomb materials. In this context, the presence of hydrogen vacancies and stacking faults is very interesting: removing H cations coordinating the bridging ligands on a Ir_2O_2 plaquette increases the Kitaev exchange by more than a factor of 3 for the corresponding Ir—Ir link. This suggests that the tendency toward the formation of long-range magnetic order in $\text{H}_3\text{LiIr}_2\text{O}_6$ is very strongly counteracted by H-ion disorder.

Basic (electronic) structure.—The spin-orbit-driven Mott insulator $\text{H}_3\text{LiIr}_2\text{O}_6$ displays a layered structure in which IrO_6 octahedra form a planar honeycomblike network by sharing O—O edges (see Fig. 1). Within this honeycomb lattice, one Li ion is present at the center of each hexagon. As compared to the related iridate $\alpha\text{-Li}_2\text{IrO}_3$, the Li ions sandwiched between two honeycomb planes are replaced by H species in this recently discovered system. For the stacking pattern proposed in Ref. [22], interlayer connectivity is realized through linear O—H—O links. The

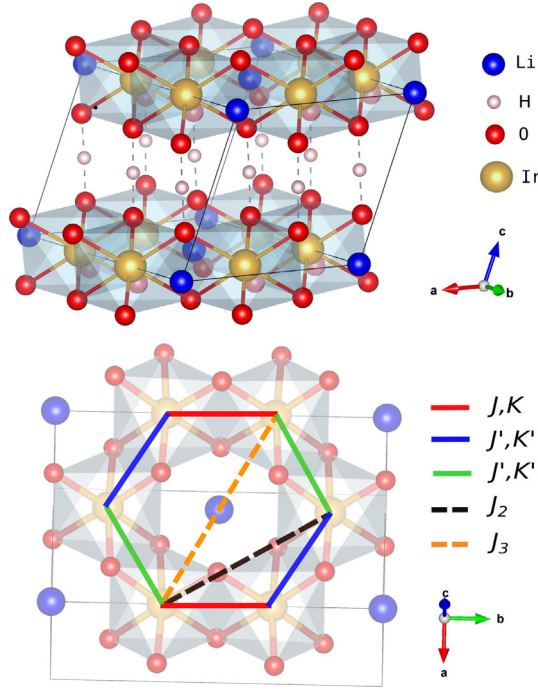


FIG. 1. Layered honeycomb network of IrO_6 octahedra in $\text{H}_3\text{LiIr}_2\text{O}_6$. For the stacking pattern proposed in Ref. [22], interlayer connectivity is realized through linear O—H—O links (top); the different types of magnetic couplings on a given hexagonal ring are also shown (bottom).

octahedral ligand field splits the Ir $5d$ levels into e_g and t_{2g} states, with the latter lying at significantly lower energy [24]. Given the large t_{2g} - e_g splitting, the leading ground-state configuration is Ir t_{2g}^5 , which yields an effective picture of one hole in the t_{2g} sector. In the presence of strong spin-orbit coupling, this can be mapped onto a set of fully occupied $j_{\text{eff}} = 3/2$ and magnetically active $j_{\text{eff}} = 1/2$ states [7,25,26]. Deviations from a perfect cubic environment may lead to some degree of admixture of these $j_{\text{eff}} = 1/2$ and $j_{\text{eff}} = 3/2$ components.

Similar to the parent compound $\alpha\text{-Li}_2\text{IrO}_3$, two structurally different types of Ir—Ir links are present in this system [22], which we denote as $B1$ and $B2$. For each of these links, the unit of two NN octahedra displays C_{2h} point-group symmetry, which then implies a generalized bilinear Hamiltonian of the following form for a pair of pseudospins $\tilde{\mathbf{S}}_i$ and $\tilde{\mathbf{S}}_j$:

$$\mathcal{H}_{ij}^{(\gamma)} = J\tilde{\mathbf{S}}_i \cdot \tilde{\mathbf{S}}_j + K\tilde{S}_i^\gamma\tilde{S}_j^\gamma + \sum_{\alpha \neq \beta} \Gamma_{\alpha\beta}(\tilde{S}_i^\alpha\tilde{S}_j^\beta + \tilde{S}_i^\beta\tilde{S}_j^\alpha), \quad (1)$$

where the $\Gamma_{\alpha\beta}$ coefficients refer to the off-diagonal components of the 3×3 symmetric-anisotropy exchange matrix, with $\alpha, \beta \in \{x, y, z\}$ [20]. An antisymmetric Dzyaloshinskii-Moriya coupling is not allowed, given the inversion center for each block of two NN octahedra.

A local Kitaev reference frame is used here, such that for each Ir—Ir link the z axis is perpendicular to the Ir_2O_2 plaquette.

Calculation of magnetic interactions.—To derive magnetic exchange couplings between two NN Ir sites, quantum chemistry calculations were performed on embedded clusters having two edge-sharing octahedra as the central region. To describe the finite charge distribution in the immediate neighborhood, the four adjacent IrO_6 octahedra were also included in the calculations, while the farther solid-state surroundings were modeled by large arrays of point charges fitted to reproduce the ionic Madelung potential in the cluster region. In the first step, complete-active-space self-consistent-field (CASSCF) computations [27] using an active space of six t_{2g} orbitals (belonging to two NN Ir sites) and ten electrons were carried out for an average of the lowest nine singlet and nine triplet states, essentially of t_{2g}^5 - t_{2g}^5 character. By construction, t_{2g}^4 - t_{2g}^6 configuration state functions describing intersite $5d$ - $5d$ hopping contribute, however, with finite weight to the CASSCF wave functions. Single and double excitations from the Ir $5d$ (t_{2g}) and bridging-ligand $2p$ valence shells were accounted for in the subsequent multireference configuration-interaction (MRCI) calculations [28,29]. To obtain localized orbitals and select for the MRCI treatment only $5d$ and $2p$ orbitals on the Ir_2O_2 plaquette, we used a Pipek-Mezey algorithm [30]. A similar computational strategy was successfully adopted in earlier quantum chemistry studies [20,31–34].

The spin-orbit computations were performed in terms of the low-lying nine singlet and nine triplet states. The resulting lowest four *ab initio* spin-orbit eigenstates were then mapped onto the eigenvectors of the effective spin Hamiltonian Eq. (1). The other 32 spin-orbit states in this manifold involve $j_{\text{eff}} \approx 3/2$ to $j_{\text{eff}} \approx 1/2$ excitations and lie at significantly higher energy [20,24]. The mapping of the *ab initio* data onto the effective spin Hamiltonian is carried out following the procedure described in Refs. [31,33,35]. All quantum chemistry computations were performed using the quantum chemistry package MOLPRO [36].

Effective magnetic couplings obtained by such a procedure are listed for the experimental structural data provided by Kitagawa *et al.* [22] in Table I. On both types of Ir—Ir links the Kitaev K is ferromagnetic, with $K \approx -12$ meV. The bond “asymmetry” is only 5% and residual Heisenberg interactions are weak; the ratio $|K/J|$ is $|K/J| > 6$, which puts the system relatively close to the “pure” Kitaev limit. The additional exchange anisotropies Γ can even exceed J in magnitude but being frustrating they do not act towards long-range magnetic order.

To test the stability of the lattice and the effect that small variations of the atomic positions might have on the magnetic coupling constants, we also performed structure-optimization calculations in the frame of density-functional theory (DFT). We employed the Perdew-Burke-Ernzerhof

TABLE I. Nearest-neighbor magnetic couplings (meV) for the two different bonds, $B1$ and $B2$, in $\text{H}_3\text{LiIr}_2\text{O}_6$; results of spin-orbit MRCI calculations. The structural data provided in Ref. [22] were used for this set of calculations.

Bond	$\angle\text{Ir-O-Ir}$	K	J	Γ_{xy}	$\Gamma_{yz} = -\Gamma_{zx}$
$B2$ (3.10 Å)	99.8°	-12.0	1.8	-0.2	-3.2
$B1$ (3.05 Å)	99.0°	-12.6	1.5	-1.8	-0.7

(PBE) variant [37] of the generalized gradient approximation (GGA) with scalar relativistic corrections as implemented in the FPLO code [38,39]; the lattice parameters were fixed to the values derived from x-ray diffraction measurements [22]. The DFT relaxed structure corresponds to forces < 1 meV/Å for each atom. The most significant difference between the two sets of atomic positions concerns the location of the ligands relative to the Ir sites, which then affects, somewhat, the Ir–O bond lengths and Ir–O–Ir angles. For the computationally optimized geometry we also find slight deviations from linear arrangement for one of the O–H–O links, consistent with the space group symmetry [22]. The Ir–Ir distance changes only marginally, $\leq 0.3\%$ (see Supplemental Material for details [40]). As shown in Table II, the Kitaev interactions are slightly smaller but still dominant in the relaxed structure as well. Also in this case $|K/J| > 6$ but the differences between the two types of Ir–Ir links are somewhat larger. Interestingly, in earlier quantum chemistry calculations for idealized lattice configurations of Li_2IrO_3 and Na_2IrO_3 where all distortions beyond trigonal compression were neglected, it has been found that J tends to zero for Ir–O–Ir bond angles of approximately 98° [21]. Even if the Ir–O–Ir bond angles are reduced from 99°–100° [22] to somewhat lower values in the computationally optimized lattice, we still obtain nevertheless finite J values by MRCI.

In addition to intersite couplings, we also calculated the Ir $5d^5$ g factors, by spin-orbit MRCI computations having a single IrO_6 octahedron as reference unit. The active space in the reference CASSCF calculation includes in this case all $5d$ Ir orbitals. The g factors obtained for the $C2/m$ structure of Ref. [22] are at the MRCI level $g_{\alpha\alpha} = 1.83$, $g_{\beta\beta} = 1.98$, and $g_{\gamma\gamma} = 2.30$, where $g_{\gamma\gamma}$ corresponds to an axis perpendicular to the Ir honeycomb plane and $g_{\beta\beta}$ corresponds to the crystallographic b axis, parallel to the

TABLE II. Nearest-neighbor magnetic couplings (meV) for the two different bonds $B1$ and $B2$ in $\text{H}_3\text{LiIr}_2\text{O}_6$; results of spin-orbit MRCI calculations. The structural data used for this set of calculations were obtained by DFT lattice optimization.

Bond	$\angle\text{Ir-O-Ir}$	K	J	Γ_{xy}	$\Gamma_{yz} = -\Gamma_{zx}$
$B2$ (3.10 Å)	98.6°	-8.8	0.8	-0.4	-2.7
$B1$ (3.05 Å)	96.4°	-6.6	0.9	-2.2	-0.9

shorter Ir–Ir bonds. The anisotropy displayed by these components is moderate, far from the highly anisotropic structure found in the honeycomb Kitaev-Heisenberg system RuCl_3 [33,46,47]. Also different from RuCl_3 is the fact that $g_{\gamma\gamma} > g_{\alpha\alpha}, g_{\beta\beta}$ in $\text{H}_3\text{LiIr}_2\text{O}_6$. Test calculations in which the positive H NNs above and below the reference IrO_6 octahedron (six adjacent H sites in total) are simply removed and their charge redistributed within the embedding matrix lead, however, to values featuring the pattern found in RuCl_3 , with $g_{\gamma\gamma} < g_{\alpha\alpha}, g_{\beta\beta}$, suggesting that through polarization of the ligand p orbitals the interlayer cations may significantly affect the structure of the $\bar{\mathbf{g}}$ tensor. Effects of similar nature were found in square-lattice iridates [31].

Phase diagram and longer-range interactions.—From the values and bond asymmetry of the NN magnetic interactions, $\text{H}_3\text{LiIr}_2\text{O}_6$ appears to be closer to a pure Kitaev model than any other $A_2\text{IrO}_3$ iridate ($A = \text{Li}, \text{Na}$) considered so far. It is known, however, that in the $A_2\text{IrO}_3$ systems it is not the residual NN couplings that cause, at low temperatures, the experimentally observed zigzag ordered state, but the longer-range magnetic interactions that are present as well, even if the latter can be weak and of the order of 1 meV [15,20,33,48]. To test the situation for $\text{H}_3\text{LiIr}_2\text{O}_6$, we computed a generic phase diagram by using the NN quantum chemistry coupling parameters from Table I plus farther-neighbor isotropic Heisenberg J 's, second-neighbor (J_2) and third-neighbor (J_3). These calculations were performed as ED for a 24-site cluster with periodic boundary conditions, in analogy to earlier studies [8,20,21,33]. The phase boundaries were obtained from the maximum positions in the second derivative of the ground-state energy. For a given set of J_2 and J_3 parameters, the dominant order was determined according to the wave number $\mathbf{Q} = \mathbf{Q}_{\max}$ providing a maximum value of the static structure factor $S(\mathbf{Q})$. The QSL state is characterized by a rapid decay of the spin-spin correlations; a gapless excitation is found here. More details on this analysis are available in the Supplemental Material [40]. The resulting phase diagram for variable J_2 and J_3 is shown in Fig. 2. Four ordered commensurate (FM, Néel, stripy, zigzag) phases, an incommensurately ordered (IC), and a QSL phase are identified. Representative spin configurations for the ordered phases are also displayed in the figure.

We find that the QSL phase is quickly destabilized by farther-neighbor interactions of Heisenberg type. If in $\text{H}_3\text{LiIr}_2\text{O}_6$ the values for J_2, J_3 are similar to the ones in the $A_2\text{IrO}_3$ family, long-range magnetic order of zigzag type is expected for the NN effective couplings computed on the basis of the crystal structure proposed by Kitagawa *et al.* [22]. A possibility for QSL ground state remains only when $J_2 + J_3 \lesssim 1.2$ meV. If such is indeed realized in $\text{H}_3\text{LiIr}_2\text{O}_6$, the question arises why the farther-neighbor magnetic interactions in this material are so much smaller than estimates made for the $A_2\text{IrO}_3$ systems.

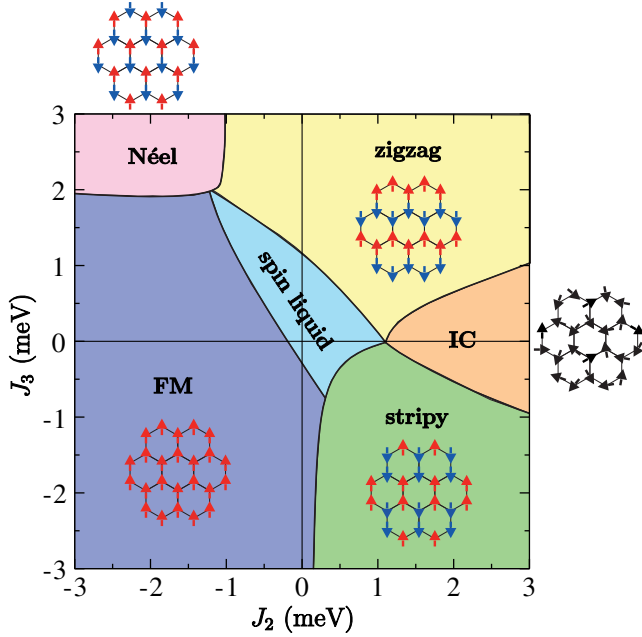


FIG. 2. Phase diagram obtained by ED for the effective spin model (1). The *ab initio* NN interactions listed in Table I and variable second- and third-neighbor isotropic couplings J_2 and J_3 were used. Schematic spin configurations are also shown.

Position of H cations and effect on in-plane interactions.—One peculiar prediction on the quantum chemistry computational side is an enhancement of the Kitaev interaction for large values of the Ir—O—Ir bond angles [21]. The latter are 90° for cubic edge-sharing octahedra but in most honeycomb compounds become significantly larger due to trigonal compression of the oxygen cages. The largest Ir—O—Ir bond angles so far have been actually reported for $\text{H}_3\text{LiIr}_2\text{O}_6$. However, given the earlier estimates for K for angles in the range of 98° – 100° [20,21], the K values listed in Tables I and II look surprisingly small.

Comparing the presently known honeycomb iridate compounds, one notable structural difference concerns the precise position of the interlayer ionic species: in Na_2IrO_3 and $\alpha\text{-Li}_2\text{IrO}_3$, for example, the stacking of honeycomb layers is such that each interlayer Na or Li site has six O nearest neighbors; on the other hand, in the H-containing material the available crystallographic data suggest linear interlayer O—H—O paths with only two O NNs for each H [22]. In a simple ionic picture of $\text{H}_3\text{LiIr}_2\text{O}_6$, the positive H ion next to a given O ligand generates an axial Coulomb potential that may in principle affect the shape of the O $2p$ orbitals, thus influencing the in-plane Ir—Ir superexchange. Obviously, the latter involves the O $2p$ states. To test this scenario, we carried out a numerical experiment in which two H cations, in particular, those H nuclei directly coordinating the bridging O ligands on a given Ir_2O_2 plaquette, were removed from the atomic fragment treated by quantum chemistry methods

TABLE III. NN magnetic couplings (meV) for bonds $B1$, $B2$ in $\text{H}_3\text{LiIr}_2\text{O}_6$, using structural data from Ref. [22]; results of spin-orbit MRCI calculations where the two H ions next to the O ligands of a Ir_2O_2 plaquette were removed and their formal ionic charge redistributed within the embedding.

Bond	K	J	Γ_{xy}	$\Gamma_{yz} = -\Gamma_{zx}$
$B2$ (3.10 Å)	-38.1	5.9	5.0	-11.1
$B1$ (3.05 Å)	-40.0	4.6	7.9	-14.0

but their associated ionic charge was redistributed within the embedding background. Remarkably, we find in this case an enhancement by a factor of ~ 3 of the Kitaev interactions, up to huge values of 40 meV, see Table III. The other effective magnetic couplings between NN Ir sites are also enhanced. The larger J values, in particular, indicate that both direct exchange ($5d$ - $5d$) and O-mediated superexchange processes contribute to the isotropic coupling constant. To additionally check how appropriate an ionic representation of the symmetric linear O—H—O links is, we also derived effective coupling parameters for embedded clusters in which the H NNs of the bridging O sites (one H cation next to each of the bridging ligands) were represented as $1+$ point charges. The results obtained for this material model show only minor differences as compared to the case in which basis functions are used for the H species (see Supplemental Material [40]), indicating that an ionic picture constitutes a rather good approximation for linear O—H—O links and median H positions. In other words, the strong reduction of the in-plane effective couplings for stacking implying linear O—H—O groups is mainly related to the destructive effect of the H-cation Coulomb potential on the Ir—O—Ir superexchange. Such anisotropic, axial fields are not present when the ligands have several interlayer adjacent sites as in $\alpha\text{-Li}_2\text{IrO}_3$ and Na_2IrO_3 .

Conclusions.—From the calculations and discussion above it is clear that the configuration of hydrogen cations next to a Ir—Ir link very strongly affects the magnetic interaction on that link. Consequently, structural hydrogen disorder will introduce very strong magnetic bond disorder. Any form of hydrogen disorder thereby counteracts the tendency to form long-range ordered states that are driven by longer-range magnetic couplings. Experimental investigations into the role of hydrogen disorder on the formation of a spin-liquid state in this material would therefore be of prime interest to disentangle the effects of NN Kitaev interactions, that drive the formation of a topological spin-liquid state, and the effect of hydrogen disorder which induces strong local spin disorder. In this respect, an experimental study of the magnetic and structural properties of $\text{H}_3\text{LiIr}_2\text{O}_6$ as a function of hydrogen concentration might provide valuable insights.

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- [1] L. Balents, Spin liquids in frustrated magnets, *Nature (London)* **464**, 199 (2010).
- [2] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Spin Liquid State in an Organic Mott Insulator with a Triangular Lattice, *Phys. Rev. Lett.* **91**, 107001 (2003).
- [3] M. Yamashita, N. Nakata, Y. Senshu, M. Nagata, H. M. Yamamoto, R. Kato, T. Shibauchi, and Y. Matsuda, Highly mobile gapless excitations in a two-dimensional candidate quantum spin liquid, *Science* **328**, 1246 (2010).
- [4] T.-H. Han, J. S. Helton, S. Chu, D. G. Nocera, J. A. Rodriguez-Rivera, C. Broholm, and Y. S. Lee, Fractionalized excitations in the spin-liquid state of a kagome-lattice antiferromagnet, *Nature (London)* **492**, 406 (2012).
- [5] A. Kitaev, Anyons in an exactly solved model and beyond, *Ann. Phys. (Amsterdam)* **321**, 2 (2006).
- [6] J. K. Pachos, *Introduction to Topological Quantum Computation* (Cambridge University Press, Cambridge, England, 2012).
- [7] G. Jackeli and G. Khaliullin, Mott Insulators in the Strong Spin-Orbit Coupling Limit: From Heisenberg to a Quantum Compass and Kitaev Models, *Phys. Rev. Lett.* **102**, 017205 (2009).
- [8] J. Chaloupka, G. Jackeli, and G. Khaliullin, Kitaev-Heisenberg Model on a Honeycomb Lattice: Possible Exotic Phases in Iridium Oxides $A_2\text{IrO}_3$, *Phys. Rev. Lett.* **105**, 027204 (2010).
- [9] K. W. Plumb, J. P. Clancy, L. J. Sandilands, V. V. Shankar, Y. F. Hu, K. S. Burch, H.-Y. Kee, and Y.-J. Kim, $\alpha\text{-RuCl}_3$: A spin-orbit assisted Mott insulator on a honeycomb lattice, *Phys. Rev. B* **90**, 041112 (2014).
- [10] L. J. Sandilands, Y. Tian, K. W. Plumb, Y.-J. Kim, and K. S. Burch, Scattering Continuum and Possible Fractionalized Excitations in $\alpha\text{-RuCl}_3$, *Phys. Rev. Lett.* **114**, 147201 (2015).
- [11] A. Banerjee, C. A. Bridges, J.-Q. Yan, A. A. Aczel, L. Li, M. B. Stone, G. E. Granroth, M. D. Lumsden, Y. Yiu, J. Knolle, S. Bhattacharjee, D. L. Kovrizhin, R. Moessner, D. A. Tennant, D. G. Mandrus, and S. E. Nagler, Proximate Kitaev quantum spin liquid behaviour in a honeycomb magnet, *Nat. Mater.* **15**, 733 (2016).
- [12] A. Banerjee, J. Yan, J. Knolle, C. A. Bridges, M. B. Stone, M. D. Lumsden, D. G. Mandrus, D. A. Tennant, R. Moessner, and S. E. Nagler, Neutron scattering in the proximate quantum spin liquid $\alpha\text{-RuCl}_3$, *Science* **356**, 1055 (2017).
- [13] Y. Singh and P. Gegenwart, Antiferromagnetic Mott insulating state in single crystals of the honeycomb lattice material Na_2IrO_3 , *Phys. Rev. B* **82**, 064412 (2010).
- [14] F. Ye, S. Chi, H. Cao, B. C. Chakoumakos, J. A. Fernandez-Baca, R. Custelcean, T. F. Qi, O. B. Korneta, and G. Cao, Direct evidence of a zigzag spin-chain structure in the honeycomb lattice: A neutron and x-ray diffraction investigation of single-crystal Na_2IrO_3 , *Phys. Rev. B* **85**, 180403 (2012).
- [15] S. K. Choi, R. Coldea, A. N. Kolmogorov, T. Lancaster, I. I. Mazin, S. J. Blundell, P. G. Radaelli, Y. Singh, P. Gegenwart, K. R. Choi, S.-W. Cheong, P. J. Baker, C. Stock, and J. Taylor, Spin Waves and Revised Crystal Structure of Honeycomb Iridate Na_2IrO_3 , *Phys. Rev. Lett.* **108**, 127204 (2012).
- [16] T. Takayama, A. Kato, R. Dinnebier, J. Nuss, H. Kono, L. S. I. Veiga, G. Fabbri, D. Haskel, and H. Takagi, Hyperhoneycomb Iridate $\beta\text{-Li}_2\text{IrO}_3$ as a Platform for Kitaev Magnetism, *Phys. Rev. Lett.* **114**, 077202 (2015).
- [17] K. A. Modic, T. E. Smidt, I. Kimchi, N. P. Breznay, A. Biffin, S. Choi, R. D. Johnson, R. Coldea, P. Watkins-Curry, G. T. McCandless, J. Y. Chan, F. Gandara, Z. Islam, A. Vishwanath, A. Shekhter, R. D. McDonald, and J. G. Analytis, Realization of a three-dimensional spin-anisotropic harmonic honeycomb iridate, *Nat. Commun.* **5**, 4203 (2014).
- [18] I. Kimchi and Y.-Z. You, Kitaev-Heisenberg- $J_2 - J_3$ model for the iridates $A_2\text{IrO}_3$, *Phys. Rev. B* **84**, 180407 (2011).
- [19] J. G. Rau, E.-H. Lee, and H.-Y. Kee, Generic Spin Model for the Honeycomb Iridates beyond the Kitaev Limit, *Phys. Rev. Lett.* **112**, 077204 (2014).
- [20] V. M. Katukuri, S. Nishimoto, V. Yushankhai, A. Stoyanova, H. Kandpal, S. Choi, R. Coldea, I. Rousochatzakis, L. Hozoi, and J. van den Brink, Kitaev interactions between $j = 1/2$ moments in honeycomb Na_2IrO_3 are large and ferromagnetic: Insights from *ab initio* quantum chemistry calculations, *New J. Phys.* **16**, 013056 (2014).
- [21] S. Nishimoto, V. M. Katukuri, V. Yushankhai, H. Stoll, U. K. Röfler, L. Hozoi, I. Rousochatzakis, and J. van den Brink, Strongly frustrated triangular spin lattice emerging from triplet dimer formation in honeycomb Li_2IrO_3 , *Nat. Commun.* **7**, 10273 (2016).
- [22] K. Kitagawa, T. Takayama, Y. Matsumoto, A. Kato, R. Takano, Y. Kishimoto, S. Bette, R. Dinnebier, G. Jackeli, and H. Takagi, A spin-orbital-entangled quantum liquid on a honeycomb lattice, *Nature (London)* **554**, 341 (2018).
- [23] In $\alpha\text{-Li}_2\text{IrO}_3$ peculiar structural distortions cause $J > K$ for one set of Ir-Ir links [21].
- [24] H. Gretarsson, J. P. Clancy, X. Liu, J. P. Hill, E. Bozin, Y. Singh, S. Manni, P. Gegenwart, J. Kim, A. H. Said, D. Casa, T. Gog, M. H. Upton, H.-S. Kim, J. Yu, V. M. Katukuri, L. Hozoi, J. van den Brink, and Y.-J. Kim, Crystal-Field Splitting and Correlation Effect on the Electronic Structure of $A_2\text{IrO}_3$, *Phys. Rev. Lett.* **110**, 076402 (2013).
- [25] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970).
- [26] B. J. Kim, H. Jin, S. J. Moon, J.-Y. Kim, B.-G. Park, C. S. Leem, J. Yu, T. W. Noh, C. Kim, S.-J. Oh, J.-H. Park, V. Durairaj, G. Cao, and E. Rotenberg, Novel $J_{\text{eff}} = 1/2$ Mott State Induced by Relativistic Spin-Orbit Coupling in Sr_2IrO_4 , *Phys. Rev. Lett.* **101**, 076402 (2008).
- [27] T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, Chichester, 2000).

- [28] H.-J. Werner and P.J. Knowles, An efficient internally contracted multiconfiguration-reference configuration interaction method, *J. Chem. Phys.* **89**, 5803 (1988).
- [29] P.J. Knowles and H.-J. Werner, Internally contracted multiconfiguration-reference configuration interaction calculations for excited states, *Theor. Chim. Acta* **84**, 95 (1992).
- [30] J. Pipek and P.G. Mezey, A fast intrinsic localization procedure applicable for *ab initio* and semiempirical linear combination of atomic orbital wave functions, *J. Chem. Phys.* **90**, 4916 (1989).
- [31] N. A. Bogdanov, V.M. Katukuri, J. Romhányi, V. Yushankhai, V. Kataev, B. Büchner, J. van den Brink, and L. Hozoi, Orbital reconstruction in nonpolar tetravalent transition-metal oxide layers, *Nat. Commun.* **6**, 7306 (2015).
- [32] V.M. Katukuri, V. Yushankhai, L. Siurakshina, J. van den Brink, L. Hozoi, and I. Rousochatzakis, Mechanism of Basal-Plane Antiferromagnetism in the Spin-Orbit Driven Iridate Ba_2IrO_4 , *Phys. Rev. X* **4**, 021051 (2014).
- [33] R. Yadav, N. A. Bogdanov, V.M. Katukuri, S. Nishimoto, J. van den Brink, and L. Hozoi, Kitaev exchange and field-induced quantum spin-liquid states in honeycomb $\alpha\text{-RuCl}_3$, *Sci. Rep.* **6**, 37925 (2016).
- [34] N. A. Bogdanov, V.M. Katukuri, H. Stoll, J. van den Brink, and L. Hozoi, Post-perovskite CaIrO_3 : A $j = 1/2$ quasi-one-dimensional antiferromagnet, *Phys. Rev. B* **85**, 235147 (2012).
- [35] R. Yadav, M. Pereiro, N. A. Bogdanov, S. Nishimoto, A. Bergman, O. Eriksson, J. van den Brink, and L. Hozoi, Heavy-mass magnetic modes in pyrochlore iridates due to dominant Dzyaloshinskii-Moriya interaction, *Phys. Rev. Mater.* **2**, 074408 (2018).
- [36] H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, Molpro: A general-purpose quantum chemistry program package, *Comput. Mol. Sci.* **2**, 242 (2012).
- [37] J.P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [38] K. Koepnik and H. Eschrig, Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme, *Phys. Rev. B* **59**, 1743 (1999).
- [39] <https://www.fplo.de>.
- [40] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.121.197203> for additional details, which also includes Refs. [41–45].
- [41] T.H. Dunning, Gaussian basis sets for use in correlated molecular calculations. I. the atoms boron through neon and hydrogen, *J. Chem. Phys.* **90**, 1007 (1989).
- [42] D. Figgen, K. A. Peterson, M. Dolg, and H. Stoll, Energy-consistent relativistic pseudopotentials and correlation consistent basis sets for the $5d$ elements Hf – Pt, *J. Chem. Phys.* **130**, 164108 (2009).
- [43] K. Pierloot, B. Dumez, P.-O. Widmark, and B.O. Roos, Density matrix averaged atomic natural orbital (ANO) basis sets for correlated molecular wave functions, *Theor. Chim. Acta* **90**, 87 (1995).
- [44] P. Fuentealba, H. Preuss, H. Stoll, and L. Szentpály, A proper account of core-polarization with pseudopotentials: Single valence-electron alkali compounds, *Chem. Phys. Lett.* **89**, 418 (1982).
- [45] A. Schäfer, H. Horn, and R. Ahlrichs, Fully optimized contracted Gaussian basis sets for atoms Li to Kr, *J. Chem. Phys.* **97**, 2571 (1992).
- [46] Y. Kubota, H. Tanaka, T. Ono, Y. Narumi, and K. Kindo, Successive magnetic phase transitions in $\alpha\text{-RuCl}_3$: XY-like frustrated magnet on the honeycomb lattice, *Phys. Rev. B* **91**, 094422 (2015).
- [47] M. Majumder, M. Schmidt, H. Rosner, A. A. Tsirlin, H. Yasuoka, and M. Baenitz, Anisotropic $\text{Ru}^{3+}4d^5$ magnetism in the $\alpha\text{-RuCl}_3$ honeycomb system: Susceptibility, specific heat, and zero-field NMR, *Phys. Rev. B* **91**, 180401 (2015).
- [48] M. Majumder, R. S. Manna, G. Simutis, J. C. Orain, T. Dey, F. Freund, A. Jesche, R. Khasanov, P. K. Biswas, E. Bykova, N. Dubrovinskaia, L. S. Dubrovinsky, R. Yadav, L. Hozoi, S. Nishimoto, A. A. Tsirlin, and P. Gegenwart, Breakdown of Magnetic Order in the Pressurized Kitaev Iridate $\beta\text{-Li}_2\text{IrO}_3$, *Phys. Rev. Lett.* **120**, 237202 (2018).