Strongly frustrated triangular spin lattice emerging from triplet dimer formation in honeycomb Li$_2$IrO$_3$

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Iridium oxides with a honeycomb lattice have been identified as platforms for the much anticipated Kitaev topological spin liquid: the spin-orbit entangled states of Ir$^{4+}$ in principle generate precisely the required type of anisotropic exchange. However, other magnetic couplings can drive the system away from the spin-liquid phase. With this in mind, here we disentangle the different magnetic interactions in Li$_2$IrO$_3$, a honeycomb iridate with two crystallographically inequivalent sets of adjacent Ir sites. Our ab initio many-body calculations show that, while both Heisenberg and Kitaev nearest-neighbour couplings are present, on one set of Ir–Ir bonds the former dominates, resulting in the formation of spin-triplet dimers. The triplet dimers frame a strongly frustrated triangular lattice and by exact cluster diagonalization we show that they remain protected in a wide region of the phase diagram.
As early as in the 1970s it was suggested that quantum spins in a solid can, instead of ordering in a certain pattern, form a fluid type of ground state—a quantum spin liquid\textsuperscript{12}. Theory predicts a remarkable set of collective phenomena to occur in spin liquids\textsuperscript{3}. In the honeycomb lattice Kitaev spin model\textsuperscript{4}, for instance, a spin-liquid state that has different topological phases with elementary excitations displaying Majorana statistics has been anticipated. This has been argued to be relevant for arguments in topological quantum computing\textsuperscript{5,9}.

The essential feature of the Kitaev model is that there is a different type of spin coupling for each of the three magnetic bonds originating from a given $S = 1/2$ spin site, $K_S^S S_l^S$, $K_S^S S_j^S$ and $K_S^S S_j^S$, where $j$, $k$ and $l$ are $S = 1/2$ nearest neighbours (NN's) of the reference site $i$ and $K$ is the Kitaev coupling strength. However, finding materials in which the Kitaev spin model and the spin-liquid ground state are realized has proven to be very challenging\textsuperscript{5}. In this respect the strongly spin-orbit coupled honeycomb iridates have recently been brought to the fore\textsuperscript{10,11}. The compounds have the chemical formula $A_2IrO_3$, with $A = Na$ or $Li$, and contain $Ir^{4+}$ ions in the centre of oxygen octahedra that form a planar hexagonal network. Each $Ir^{4+}$ ion has five electrons in the $5d$ shell which the crystal field splits into a $t_2g$ and an $e_g$ manifold. Since the crystal field splitting is large, the lowest-energy electron configuration is $t_{2g}^5$. This is equivalent to the $t_{2g}$ shell containing a single hole with spin $S = 1/2$. However, the $t_{2g}$ state additionally bears a finite effective angular momentum $L_{eff} = 1$. The strong spin-orbit coupling for $5d$ electrons therefore splits up the $t_{2g}$ manifold into an effective total angular momentum $\mathcal{J} = [L_{eff} + S] = 3/2$ quartet and a $\mathcal{J} = [L_{eff} - S] = 1/2$ doublet. As for the hole the latter is lowest in energy, an effective spin $\mathcal{J} = 1/2$ doublet (often referred to as a pseudospin $\tilde{S}$) defines to first approximation the local ground state of the $Ir^{4+}$ ion.

Whereas the formation of such a local $\mathcal{J} = 1/2$ doublet is well-known for $Ir^{4+}$ ions inside an undistorted oxygen octahedron\textsuperscript{12}, the remarkable insight of refs 10,11 is that when two such octahedra share an edge, the magnetic superexchange interactions between the $\mathcal{J} = 1/2$ sites are in principle precisely of Kitaev type. This observation has made the $A_2IrO_3$ honeycomb iridates prime candidate materials in the search for Kitaev spin-liquid ground states.

Experimentally, however, both $Na_2IrO_3$ and $Li_2IrO_3$ have been found to order magnetically below 15 K (refs 13,14). While inelastic neutron scattering\textsuperscript{15}, X-ray diffraction\textsuperscript{16} and resonant inelastic X-ray scattering experiments\textsuperscript{17} indicate an antiferromagnetic (AF) zigzag ordering pattern in $Na_2IrO_3$, the nature of the magnetic order of $Li_2IrO_3$ is to date unknown\textsuperscript{13,14}. The questions that arise are therefore, (i) which magnetic instability preempts the formation of the spin-liquid state, and (ii) how close does the system remains to that state.

To answer these fundamental questions it is essential to quantify the relative strengths of the NN magnetic interactions in $Li_2IrO_3$, which are already known to be not only of Kitaev, but also of Heisenberg type. The observed zigzag order in its counterpart system $Na_2IrO_3$ has indeed been rationalized on the basis of ferromagnetic (FM) Heisenberg $J$ and AF Kitaev $K$ couplings\textsuperscript{15–20}, but also interpreted in terms of an AF $J$ and FM $K$ (refs 13,15,21,22). Recent ab initio many-body calculations favour the latter scenario, with a relatively large FM Kitaev exchange and significantly weaker AF NN Heisenberg interactions in this material\textsuperscript{23}. This scenario is also supported by investigations of model Hamiltonians derived by downfolding schemes based on density functional theory calculations\textsuperscript{24}. Besides the NN terms, strongly frustrating longer range exchange couplings involving the second ($J_{2b}$) and third ($J_{3b}$) iridium coordination shells were also shown to be relevant\textsuperscript{13,15,20}, resulting in very rich magnetic phase diagrams\textsuperscript{13,23,25}.

On the basis of the similarity in crystal structure, one might naively expect that the magnetic interactions in $A = Li$ are similar to the ones in $A = Na$. Here we show that this is not at all the case. The strengths of the NN interactions $J$ and $K$ turn out to crucially depend on the Ir-O–Ir bond angles and distances. Employing ab initio wave-function quantum chemistry methods, we find in particular that in contrast to $Na_2IrO_3$ (ref. 23) the Heisenberg coupling $J$ in $Li_2IrO_3$ even has opposite signs for the two crystallographically inequivalent sets of adjacent Ir sites. This behaviour follows a general trend of $J$ and $K$ as functions of bond angles and interatomic distances that we have established through a larger, additional set of quantum chemistry calculations. The latter show that the NN Heisenberg $J$ has a parabolic dependence on the Ir-O–Ir bond angle and at around 98° changes sign. This explains why in $Na_2IrO_3$ with Ir–O–Ir angles in the range of 98–100° (ref. 15), all $J$s are positive, while in $Li_2IrO_3$, which has significantly smaller bond angles $\sim 95°$ (ref. 26), the FM interaction to the NN Heisenberg exchange is much stronger. The large FM coupling $J \simeq -19$ meV on one set of Ir–Ir links in $Li_2IrO_3$ gives rise to an effective picture of triplet dimers composing a triangular lattice. To determine the magnetic phase diagram as a function of the strength of the second and third neighbour exchange interactions ($J_2$ and $J_3$) we use for this effective triplet-dimer model a semiclassical approach, which we further confront to the magnetic phase diagram for the original honeycomb Hamiltonian calculated by exact cluster diagonalization. This comparison shows that indeed the triplet dimers act as rigid objects in a wide range of the $J_2$–$J_3$ parameter space. We localize $Li_2IrO_3$ in a parameter range where the phase diagram has incommensurate magnetic order, the nature of which goes beyond the standard flat helix modulation scenario, owing to the Kitaev exchange anisotropy.

### Results

#### Heisenberg–Kitaev Hamiltonian.

The experimental data reported in ref. 26 indicate $C_{1h}$ point-group symmetry for one set of NN IrO$_2$ octahedra, denoted as B1 in Fig. 1, and slight distortions of the Ir$_2$O$_2$ plaquettes that lower the symmetry to $C_i$. For the other type of adjacent octahedra, labelled B2 and B3. The most general, symmetry allowed form of the effective spin Hamiltonian for a pair of NN Ir $d^5$ sites, as discussed in Methods and Supplementary Note 1, is then

$$\mathcal{H}_{(j \in k)} = J_0 \tilde{S}_j \cdot \tilde{S}_k + K_0 \tilde{S}_j^{\text{t}} \tilde{S}_k^{\text{t}} + \sum_{\alpha \neq \beta} \Gamma_{\alpha \beta} \left( \tilde{S}_j^{\text{g} \alpha} \tilde{S}_k^{\text{g} \beta} + \text{h.c.} \right).$$

The $b$ index refers to the type of Ir–Ir link ($b \in \{B1,B2,B3\}$). Whereas the Hamiltonians $\mathcal{H}_{(j)}$ on the Ir–Ir links B2 and B3 are related by symmetry, the bond B1 is distinct from a symmetry point of view. Further, $\tilde{S}_j$ and $\tilde{S}_k$ denote pseudospin-1/2 operators, $J_0$ is the isotropic Heisenberg interaction and $K_0$ the Kitaev coupling. The latter plus the off-diagonal coefficients $\Gamma_{\alpha \beta}$ define the symmetric anisotopic exchange tensor. It is shown below that these $\Gamma_{\alpha \beta}$ elements are not at all negligible, as assumed in the plain Kitaev–Heisenberg Hamiltonian.

In equation (1), $\alpha$ and $\beta$ stand for components in the local, Kitaev bond reference frame ($x_0$, $y_0$, $z_0$). The $z_0$ axis is perpendicular to the Ir$_2$O$_2$ plaquette (Methods section, Supplementary Note 2 and Supplementary Fig. 1). In the following, we denote $J_{1b} = J$, $J_{2b} = J_{3b} = f$, $K_{B1} = K$, $K_{B2} = K_{B3} = K$ and similarly for the $\Gamma_{\alpha \beta}$ elements.

#### NN exchange interactions.

To make reliable predictions for the signs and strengths of the exchange coupling parameters we rely...
Since two of the triplet terms may interact, the most compact way to express the eigenstates of the effective Hamiltonian in equation (1) is then \( \Psi^b_1 = \Phi_{5b}^{Sb} \cos \theta_b + i \Phi_{5b}^{Fb} \sin \theta_b \), \( \Psi^b_2 = i \Phi_{5b}^{Sb} \sin \theta_b + \Phi_{5b}^{Fb} \cos \theta_b \), \( \Psi^b_3 = \Phi_{5b}^s \) and \( \Psi^b_4 = \Phi_{5b}^f \). The angle \( \theta_b \) parametrizes the amount of \( \Phi_{5b}^{Sb} - \Phi_{5b}^{Fb} \) mixing, related to finite off-diagonal \( \Gamma_{4b} \) couplings. This degree of admixture is determined by analysis of the full quantum chemistry spin-orbit wave functions. The effective parameters provided in Table 1 are obtained for each type of Ir–Ir link by using the \( E_0^b, E_1^b, E_2^b, E_3^b \) MRCI relative energies and the \( \Phi_{5b}^s - \Phi_{5b}^f \) mixing coefficients (see Methods and Supplementary Note 1). For a comparison of the effective parameters derived from CASSCF and MRCI relative energies, see Supplementary Tables 1 and 2.

For the B1 links in \( \text{Li}_2\text{IrO}_3 \) (Li213) we find that both \( J \) and \( K \) are FM, in contrast to \( \text{Na}_2\text{IrO}_3 \) (Na213) where \( J \) is AF for all pairs of Ir NN.\(^{23}\) Insights into this difference between the Li and Na iridates are provided by the curves plotted in Fig. 2, displaying the dependence of the NN \( J \) on the amount of trigonal distortion for simplified structural models of both Li213 and Na213. The trigonal compression of the O octahedra translates into Ir–O–Ir bond angles > 90°. Additional distortions giving rise to unequal Ir–O bond lengths, see the footnotes in Table 1, were not considered in these idealized lattice configurations. Interestingly, we find that for 90° bond angle—the case for which most of the superexchange models are constructed\(^{10,11,18,22}\)—both \( J \) and \( K \) are very small, \( \leq 1 \) meV.

In Fig. 2, while \( |K| \) monotonously increases with the Ir–O–Ir bond angle, \( J \) displays a parabolic behaviour and with a minimum at ~ 94°. Indeed on the basis of simplified superexchange models one expects \( J \) to be minimal at around a bond angle close to 90°. However, from superexchange models it is at the same time expected that \( K \) is substantial for such bond angles. The difference between the \textit{ab initio} results for 90° Ir–O–Ir angles and the predictions of simplified superexchange models originates from assuming in the latter perfectly degenerate Ir 5d and O 2p orbitals and from the subsequent cancellation of particular intersite \( d-p-d \) exchange paths. The quantum chemistry calculations show that the Ir 5d levels are not degenerate (nor the O 2p functions at a given site); the symmetry lowering at the Ir/O sites and this degeneracy lifting is related to the strongly anisotropic, layered crystal structure. For the actual honeycomb lattice with trigonal distortions of oxygen cages, one should develop a superexchange theory using the trigonal 5d orbital basis, as well as the correspondingly oriented oxygen orbitals. This produces a more general anisotropy than the Kitaev one. This is the essential reason we find at 90° for Na213 (Ir–Ir average distances of 3.133 Å): \( J = 0.32, K = -0.43, \Gamma_{xy} = 2.6, \Gamma_{zx} = -1.3, \Gamma_{yz} = 1.3 \) and for Li213 (Ir–Ir average distances of 2.980 Å): \( J = 0.40, K = -1.60, \Gamma_{xy} = 5.4, \Gamma_{zx} = -2.8, \Gamma_{yz} = 2.8 \) meV. For both materials \( K \) actually turns out to be the smallest of the anisotropic exchange constants at 90°. The small value of \( K \) may give the impression that only a weak uniaxial anisotropy is active (Supplementary Table 3). However, if one diagonalizes the full \( \Gamma \) matrix to obtain its principal axes (which in general are distinct from any crystallographic directions) and corresponding anisotropies, one finds sizable anisotropic exchange constants as large as few meV.

Our investigation also shows that the large \( FM \) \( J \) value obtained for the B1 Ir–Ir links in Li213 is the superposition of three different effects (Fig. 2): (i) an Ir–O–Ir bond angle smaller than the value of \( \approx 98° \) where \( J \) changes sign which in contrast to Na213 takes us into the FM regime, (ii) the shift to lower values of the minimum of the nearly parabolic \( J \) curve in Li213 as compared with Na213 and further (iii) the additional distortions giving rise to three different sets of Ir–O bond lengths for each...
IrO₆ octahedron. The latter are significantly stronger in Li₂IrO₃, remove the degeneracy of the Ir 2g levels and make that the NN B₁ J is even lower than the minimum of the parabola displayed in Fig. 2. It is also interesting that the off-diagonal Γ₁xx and Γ₂xx couplings on B₁ have about the same strength with the Kitaev exchange interaction terms. While the explicit expressions of these terms are given in Methods, the essential features of the model are as follows. First, among the few different contributions to Γ₁, there is an effective coupling of the form \( K / (T_{1}^{2}) \). Since \( K < 0 \), this term selects the two triplet components with \( T_{1} = \pm 1 \) and therefore acts as an easy-axis anisotropy. Second, there are two different types of effective exchange couplings between NN triplets, see Fig. 1d. This asymmetry reflects the constitutive difference between bonds B₁ and B₂/B₃. Finally, there is also an effective longer range exchange driven by the \( J_{3} \) interaction in the original hexagonal model.

According to our \textit{ab initio} results, the on-site anisotropy splitting is \( K / 2 \approx 3 \text{ meV} \), about twice the ordering temperature in Li₂IrO₃. Naively, this may suggest a truncation of the local Hilbert space such that it includes only the \( T_{1} = \pm 1 \) components, which would lead to an effective doublet instead of a triplet description. However, such a truncation would not properly account for transverse spin fluctuations driven by intersite exchange (which may even exceed the on-site splitting, depending on the values of \( J_{2} \) and \( J_{3} \)) or for the coupling to the \( T_{1} = 0 \) component via off-diagonal terms in \( Γ₁ \). Lacking \textit{a priori} a clear separation of energy scales, one is thus left with a description in terms of \( T = 1 \) triplets.

In momentum space, the effective model takes the form

\[
\mathcal{H}_{\text{eff}} = \sum_{\beta \neq \kappa} T_{\beta} \cdot \sum_{\mathbf{R}} \chi_{\beta}^{\mathbf{R}}(\mathbf{k}) \cdot T_{\kappa}^{\mathbf{R}}. \tag{3}
\]

where \( T_{\kappa} = \frac{i}{N} \sum_{\mathbf{R}} e^{i \mathbf{R} \cdot \mathbf{R}} T_{\mathbf{R}} \). N is the number of B₁ bonds and \( \chi(\mathbf{k}) \) is a symmetric \( 3 \times 3 \) matrix (Supplementary Note 3). Since \( T = 1 \), the classical limit is expected to yield a accurate overall description of the phase diagram. The minimum eigenvalue \( \epsilon_{\mathbf{Q}} \) of \( \Lambda(\mathbf{k}) \) over the Brillouin zone provides a lower bound for the classical ground-state energy \( \epsilon_{\mathbf{Q}}(\mathbf{k}) \). As shown in Fig. 3a, there exist five different regions for \( |J_{2,3}| \leq 6 \text{ meV} \), three with commensurate (FM, diagonal zigzag and stripy) and two with incommensurate (IC) \( Q \) (we call them ICX and ICy, with \( Q = (q, 0) \) and \( (0, q) \), respectively). In all commensurate regions, the state \( T_{\kappa} = e^{i \mathbf{R} \cdot \mathbf{Q}} T_{\mathbf{R}} \).

\( b = B₁ \) and \( b = B₂/B₃ \) effective interaction terms. While the explicit expressions of these terms are given in Methods, the essential features of the model are as follows. First, among the few different contributions to \( Γ₁ \), there is an effective coupling of the form \( K / (T_{1}^{2}) \). Since \( K < 0 \), this term selects the two triplet components with \( T_{1} = \pm 1 \) and therefore acts as an easy-axis anisotropy. Second, there are two different types of effective exchange couplings between NN triplets, see Fig. 1d. This asymmetry reflects the constitutive difference between bonds B₁ and B₂/B₃. Finally, there is also an effective longer range exchange driven by the \( J_{3} \) interaction in the original hexagonal model.

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(where $v_Q$ is the eigenvector associated with $\lambda_Q$) saturates the above lower energy bound and in addition satisfies the spin length constraint $[T_{kk}] = 1$ for all $R$. We note in particular that compared to the more symmetric case of Na213 (ref. 23), only the diagonal-zigzag configurations are favoured in Li213, with FM correlations along the two diagonal directions of the lattice. The third, horizontal zigzag configuration is penalized by the strong FM Heisenberg coupling on the B1 links. Correspondingly, we expect Bragg peaks only at two out of the three $\mathbf{M}$ points of the Brillouin zone, namely $Q = (\pi, \pm \hat{a})$ (see $S(Q)$ in Fig. 3c and Supplementary Fig. 3). Turning to the incommensurate regions ICx and ICy, the minimum eigenvalue $\lambda_Q$ is nondegenerate, which implies that one cannot form a flat helical modulation that saturates the low energy bound and satisfies the spin length constraint for all $R$. Especially for ICx that is the most likely candidate for Li213 (see below), this opens the possibility for nontrivial nonplanar modulations of the magnetization.

**Exact diagonalization calculations.** To establish the effect of quantum fluctuations and further test the triplet-dimer picture, we additionally carried out exact diagonalization calculations on 24-site clusters for the original honeycomb spin-1/2 model including the effect of $J_2$ and $J_3$. Periodic boundary conditions were applied, as in previous studies. We calculated the static spin-structure factor $S(Q) = \sum_{ij} (\langle S_i \cdot S_j \rangle \exp[iQ \cdot (r_i - r_j)])$ as a function of $J_2$ and $J_3$ while fixing the NN magnetic couplings to the ones in Table 1. For a given set of $J_2$ and $J_3$ values, the dominant order is determined according to the wave number $Q = Q_{\text{max}}$ providing a maximum of $S(Q)$. The resulting phase diagram is given in Fig. 3b. For each phase, the real-space spin configuration and the reciprocal-space Bragg peak positions are shown. In the absence of $J_2$ and $J_3$, the system is in a spin-liquid phase characterized by a structureless $S(Q)$ (Fig. 3c) that is adiabatically connected to the Kitaev liquid phase for $-K \gg J$ (ref. 10). By switching on $J_2$ and $J_3$, we recover most of the classical phases of the effective spin-1 model, including the ICx phase, albeit with a smaller stability region due to finite-size effects. That the 24-site cluster correlations do not show the ICy phase may well be an intrinsic effect, given that the classical ICy region is very narrow. We also find an AF Neél state region,
which is now shifted to larger $J_3$'s as compared with Na213 (ref. 23), due to the large negative $J_1$ on B1 bonds.

We note that detecting the diagonal-zigzag phase by exact diagonalization calculations requires large-size setups of lattice sites. This is related to the proximity of this phase to the special point $\Gamma = 0$ where the model is highly frustrated. Indeed, in this limit the classical ground-state manifold consists of a one-parameter family of states with two sublattices of spins with arbitrary relative orientation angle. This situation is common in various well-known frustrated models, such as the $J_1$-$J_2$ model on the square lattice$^{35-37}$. The lifting of the accidental degeneracy, either by quantum fluctuations or due to a finite $\Gamma$ (Supplementary Note 4, Supplementary Figs 4 and 5), and the associated locking mechanism between the two sublattices involve a very large length scale$^{38,39}$. This explains why our exact spin–spin correlation profiles provided in Fig. 3d show that the two sublattices are nearly decoupled from each other.

Except for the Néel and the spin-liquid phase, all other phases feature rigid triplets on the B1 bonds. This is shown in Fig. 3d for the diagonal-zigzag phase at $J_2 = J_3 = 3$, where the NN correlation function in the B1 bonds, $(S_0 \cdot S_i) \sim 0.24$, almost saturates to the full spin-triplet value of 1.4. This shows that the effective triplet picture is quite robust.

Comparison to experiment. Our result for rigid triplet degrees of freedom finds support in recent fits of the magnetic susceptibility data, which yield effective moments of 2.22 $\mu_B$ for Li213 (ref. 40), much larger than the value of 1.74 $\mu_B$ expected for an isotropic 1/2 spin system. Triplet dimerization was earlier suggested to occur in the chain-like compound In$_3$VO$_4$ (ref. 41). FM, quintet dimers were also proposed to form in ZnV$_2$O$_4$ (ref. 42).

Turning finally to the nature of the actual magnetic ground state of Li213, we first note that the longer range couplings $J_2$ and $J_3$ are expected to be both AF$^{13,15}$ and to feature values not larger than 5–6 meV (ref. 15) in honeycomb iridates, which suggests that Li213 orders either with a diagonal-zigzag or ICX pattern. Recent magnetic susceptibility and specific heat measurements indeed show indications (ref. 14) that the magnetic ground state of Li213 could be different from AF zigzag, while powder diffraction and inelastic neutron scattering data (R. Coldea, personal communication) show signatures of incommensurate magnetic order. These experimental findings are consistent with the ICX spin configuration. As explained above, the actual nature of this phase goes beyond the standard flat helical modulations because the latter are penalized by the anisotropic exchange terms in the Hamiltonian. It should be noted that the incommensurate type of magnetic order in Li$_2$IrO$_3$ has also been rationalized with model Hamiltonian calculations by including additional long range anisotropic Kitaev couplings on the honeycomb lattice$^{43}$.

Conclusions

To summarize, we have established a microscopic spin model and zero-temperature phase diagram for the layered honeycomb iridate Li$_2$IrO$_3$, one of the proposed realizations of the spin-1/2 Kitaev–Heisenberg model with strongly spin-orbit coupled Ir$^{4+}$ magnetic ions. Ab initio quantum chemistry electronic-structure calculations show that, in contrast to Na$_2$IrO$_3$, the structural inequivalence between the two types of Ir–Ir links has a striking influence on the effective spin Hamiltonian, leading in particular to two very different nearest-neighbour superexchange pathways, one weakly antiferromagnetic ($\approx 1$ meV) and another strongly ferromagnetic ($\approx 19$ meV). The latter gives rise to rigid spin-1 triplets on a triangular lattice that remain well protected in a large parameter regime of the phase diagram, including a diagonal zigzag and an incommensurate ICX phase. In view of these theoretical findings and the experimental observation of an incommensurate magnetic propagation vector in neutron diffraction (R. Coldea, personal communication), we propose that the magnetic ground state of Li$_2$IrO$_3$ lies in the incommensurate ICX phase. SETTLING ITS DETAILED NATURE AND PROPERTIES CALLS FOR FURTHER, DEDICATED EXPERIMENTAL AND THEORETICAL INVESTIGATIONS.

Methods

Embedded-cluster quantum chemistry calculations. All ab initio calculations were carried out with the quantum chemistry package Molpro$^{44}$. Embedded clusters consisting of two NN edge-sharing IrO$_6$ octahedra were considered. To accurately describe the charge distribution at sites in the immediate neighbourhood$^{45,46}$, the four adjacent Ir$^{4+}$ ions and the closest 22 Li$^+$ neighbours were also explicitly included in the actual cluster. The surrounding solid-state matrix was modeled as a fine array of point charges fitted to reproduce the crystal Madelung field in the cluster region. The spin-orbit treatment was carried out according to the procedure described in ref. 47, using spin-orbit pseudopotentials for Ir (Supplementary Note 1).

Even with trigonal distortions of the oxygen cages, the point-group symmetry of a given block of two NN IrO$_6$ octahedra is $C_{2v}$. Since the $C_2$ axis lies along the Ir–Ir bond, the effective magnetic Hamiltonian for two adjacent Ir sites is most conveniently expressed in a local reference system $\{X_0, Y_0, Z_0\}$ with $X_0$ along the Ir–Ir link ($Z_0$ is always perpendicular to the IrO$_6$ plane). It reads

$$H_{ab} = \begin{pmatrix} A_0 & 0 & 0 \\ 0 & B_0 & C_0 \\ 0 & C_0 & -A_0 - B_0 \end{pmatrix} \mathbf{S} \cdot \mathbf{S} \quad \quad (4)$$

where $b = \{B1, B2, B3\}$. The diagonal elements in the second term on the right hand side sum up to 0 to give a traceless symmetric anisotropic exchange tensor. If $X_0$ is $C_2$ axis, only one off-diagonal element is nonzero.

In the local Kitaev reference frame $\{x_0, y_0, z_0\}$, that is rotated from $\{X_0, Y_0, Z_0\}$ by 45$^\circ$ about $z_0$ axis (Supplementary Note 2, Supplementary Fig. 1 and refs 10, 23), the Hamiltonian shown above in equation (4) is transformed to the Hamiltonian in equation (1). For the latter, the effective exchange couplings are obtained for each type of Ir–Ir link as

$$J_b = J_b^{(0)} + \frac{\Delta e_{b}}{\sqrt{N_b}} \quad \text{and} \quad \Delta e_{b} = \frac{\eta_b}{\gamma_b} \left( A_b + B_b \right),$$

where the connection to the quantum chemically computed eigenvalues provided in Table 1 (and Supplementary Tables 1 and 2) is

$$J_b^{(0)} = \frac{1}{3} \left( E_{x}^{(i)} + E_{y}^{(i)} + E_{z}^{(i)} \right) - E_{p}^{(i)},$$

$$A_b = \frac{2}{3} \left( E_{x}^{(i)} + E_{y}^{(i)} \right) - \frac{4}{3} E_{p}^{(i)},$$

$$B_b = -A_b \pm \frac{2 \left( E_{x}^{(i)} - E_{p}^{(i)} \right)}{\sqrt{1 + 4N_b}} \quad \text{and} \quad \eta_b = \eta_b(A_b + 2B_b),$$

$$C_b = \frac{1}{2} \left( E_{x}^{(i)} + E_{y}^{(i)} \right).$$

$E_{x}^{(i)}, E_{y}^{(i)}, E_{z}^{(i)}$ are the ab initio eigenvalues, $\eta_b = \frac{\Delta e_{b}}{\sqrt{N_b}}$ and $\gamma_b = \sin z_0$, where $z_0$ is the mixing parameter.

Effective spin $T = 1$ description. To find the effective interactions between the B1 triplet dimers, we begin by deriving the equivalent operators in the $T = 1$ manifold for a B1 bond at position $\mathbf{R}$, where $\mathbf{T}_B = \mathbf{S}_B \cdot \mathbf{S}_A$, and $\mathbf{S}_B \cdot \mathbf{S}_C$ are the ionic Ir pseudospins defining the B1 bond. If the projector in the $T = 1$ manifold is tagged as $P_1$, we obtain for the dipolar channel $P_2 \mathbf{S}_B \mathbf{S}_A P_1 = P_1 \mathbf{S}_B \mathbf{S}_C = \frac{1}{2} \mathbf{T}_B$, while for the quadrupolar channel

$$P_T \left[ \mathbf{S}_B \mathbf{S}_A \mathbf{S}_C + \mathbf{S}_D \mathbf{S}_E \mathbf{S}_F - 2 \left( \mathbf{S}_B \cdot \mathbf{S}_A \right) \mathbf{S}_C \right] P_T = \frac{1}{4} \mathbf{Q}_T^{ab} \mathbf{Q}_T^{cd}.$$

$Q_T^{ab} = T_2^{ab} T_2^{cd} - \sqrt{T_1^{ab} T_1^{cd} - \frac{4}{3} T_2^{ab} T_2^{cd}}$ is here the quadrupolar operator for a spin-1/2 degree of freedom and $\xi = 1/2$. Using equivalent operators we then find the first-order effective Hamiltonian $H_{ab} = P_T H_{ab} P_T$ of equation (2). The only non-zero elements of the symmetric on-site tensor $\Gamma_{ij}$ are $\Gamma_{xx} = \frac{1}{6} \xi^2$, $\Gamma_{yy} = \frac{1}{6} \xi^2$, and $\Gamma_{zz} = -\frac{1}{6} \xi^2$, while those of $\Gamma_{ij}^{ab}$ are $\Gamma_{xx}^{ab} = \frac{1}{6} \xi^2 b$, $\Gamma_{xy}^{ab} = \frac{1}{6} \xi^2 b$, $\Gamma_{yx}^{ab} = \frac{1}{6} \xi^2 b$, and $\Gamma_{yy}^{ab} = -\frac{1}{6} \xi^2 b$. Finally, the intersite isotropic exchange interactions are $J_b = (J_1 + J_2)/2$, $J_b \cdot b = J_1 b_z + J_2 b_y$, $h_b \cdot b = h_1 b_z + h_2 b_y$, and $h_b \cdot b = h_1 b_z + h_2 b_y$. We here employed the global coordinate system $\{x, y, z\}$ corresponding to the Kitaev-like frame $\{x_0, y_0, z_0\}$ with $b = B1$ (Supplementary Figure 1), $f, K, A', B'$ and $C'$ are effective coupling constants on the bonds B2 and B3, as also mentioned in the main text. We stress that on the on-site quadrupolar term $T_2^{ab} T_2^{cd}$ scales with $K_2$, while in the classical treatment of the original spin-1/2 model a term would scale with $K_4$. We can trace this back to the value of $\xi = 1/2$ found above, which in the classical treatment is $c_{ab} = 1/4$. This means that the quantum mechanical correlations strongly enhance the effect.
of the ‘on-site’ anisotropy term $K$. The latter favours alignment along the $z$ axis, against the effect of $K'$ which favours alignment within the $xy$ plane. This point is further discussed in Supplementary Note 3 and 4, where we compare the classical treatment of the original spin-1/2 hexagonal model with the effective spin-1 triangular model.

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Acknowledgements

We thank R. Coldea, Y. Singh, N. A. Bogdanov and D. I. Khomskii for insightful discussions. The computations were partially performed at the High Performance Computing Center (ZHIV) at the Technical University Dresden. Partial financial support from the German Research Foundation (HO-4427 and SFB 1143) is gratefully acknowledged.

Author contributions

V.M.K. carried out the ab initio calculations and subsequent mapping of the ab initio data onto the effective spin Hamiltonian, with assistance from L.H., H.S., V.Y. and I.R. S.N. performed the exact diagonalization calculations. I.R. performed the triplet-dimer mapping and analysis, with assistance from S.N. and U.K.R. L.H. and J.v.d.B. designed the project. S.N., V.M.K., L.H., I.R. and J.v.d.B. wrote the paper, with contributions from all co-authors.

Additional information

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Nishimoto, S. et al. Strongly frustrated triangular spin lattice emerging from triplet dimer formation in honeycomb Li$_2$IrO$_3$. Nat. Commun. 7:10273 doi: 10.1038/ncomms10273 (2016).

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