Possible quantum paraelectric state in Kitaev spin liquid candidate \( \text{H}_3\text{LiIr}_2\text{O}_6 \)

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A new quantum spin liquid (QSL) candidate \( \text{H}_3\text{LiIr}_2\text{O}_6 \) was synthesized recently and was found not to show any magnetic order or phase transition down to low temperatures. In this work, we study the quantum dynamics of the hydrogen ions, i.e., protons, in this material by combining first-principles calculations and theoretical analysis. We show that each proton and its adjacent oxygen ions form an electric dipole. The dipole interactions and the proton tunneling are captured by a transverse-field Ising model with a quantum disordered paraelectric ground state. The dipole excitations have an energy gap \( \Delta_d \approx 60 \text{ meV} \), and can be probed by the infrared optical spectroscopy and the dielectric response. We argue that the electric dipole fluctuations renormalize the magnetic interactions in \( \text{H}_3\text{LiIr}_2\text{O}_6 \) and lead to a Kitaev QSL state.

spin liquid, Kitaev material, quantum paraelectricity, first-principles calculations

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1 Introduction

Quantum spin liquids (QSLs) are paramagnetic ground states of Mott insulators without any long-range magnetic orders or lattice symmetry breaking, which can be induced by (geometrical) frustration [1] and strong charge fluctuations [2]. The QSLs are characterized by fractionalized spinons and emergent gauge flux excitations [3, 4]. They were proposed to be the parent states of high-\( T_c \) superconductors [5, 6] and may be used for quantum computation [7, 8].

The Kitaev model on the honeycomb lattice [8] is a prototype of QSL. The Hamiltonian hosts the bond-dependent Ising-type interactions:

\[
H_K = K \sum_{\langle ij \rangle} S_i^\gamma S_j^\gamma,
\]

where \( \gamma = x, y, z \) labels the three types of nearest-neighbor bonds (Figure 1(b)). The Kitaev model is exactly solvable with a QSL ground state [8]. Its excitations can be represented by Majorana fermions and emergent \( Z_2 \) gauge fluxes.

It was soon realized [9] that the Kitaev interaction naturally arises in several transition metal compounds, e.g., \( \text{Na}_2\text{IrO}_3 \), \( \alpha\)-\( \text{Li}_2\text{IrO}_3 \), and \( \alpha\)-\( \text{RuCl}_3 \) [10]. In these quasi-two dimensional materials, the edge-sharing \( \text{IrO}_6 \) (\( \text{RuCl}_6 \)) octahedra form a honeycomb lattice in the \( ab \) plane. The strong spin-orbit coupling on the cations lifts the degeneracy of the...
The anion-mediated electron hopping projected in this subband is strongly suppressed due to the destructive interference of the two Ir-O-Ir hopping paths [9]. The leading-order magnetic interaction involves the Hund coupling on the cations and has exactly the form of the Kitaev term [9].

However, all these Kitaev QSL candidates turn out to have long-range magnetic orders at low temperatures [11-16]. This can be accounted for by the nonnegligible Heisenberg interactions up to third nearest neighbors [17]:

$$H_J = J_1 \sum_{\langle ij \rangle} S_i \cdot S_j + J_2 \sum_{\langle \langle ij \rangle \rangle} S_i \cdot S_j + J_3 \sum_{\langle \langle \langle ij \rangle \rangle \rangle} S_i \cdot S_j,$$

and/or other spin-anisotropic interactions [18].

A new Kitaev candidate material, $\text{H}_3\text{LiIr}_2\text{O}_6$, was synthesized recently by substituting hydrogen for the inter-IrO$_3$-layer lithium ions in $\alpha$-Li$_2$IrO$_3$ [19]. The nuclear magnetic resonance and thermodynamic measurements did not find any magnetic order or spin glassiness down to 50 mK despite a large Curie-Weiss temperature $\theta_{\text{CW}} = -105$ K, thus suggesting a QSL state.

In this work, we study $\text{H}_3\text{LiIr}_2\text{O}_6$ with first-principles calculations and theoretical analysis, focusing on the role of the substitute hydrogen ions. We find that each hydrogen ion, i.e., proton, together with two adjacent oxygen ions, forms a uniaxial electric dipole almost perpendicular to the $ab$ plane. The electric dipole-dipole interaction is described by the Ising model on the ABC-stacking triangular lattice. The quantum tunneling of the proton flips the electric dipole and corresponds to a strong transverse field term in the Ising model, and leads to a quantum disordered paraelectric ground state with first-principles calculations and pay particular attention to the impact of the substitute hydrogen ions.

The first-principles calculations are performed with the projector augmented wave (PAW) method [20, 21] and the generalized gradient approximation (GGA) to the exchange-correlation functional [22], which are implemented in the Vienna $\text{ab initio}$ Simulation Package (VASP) [23, 24]. The spin-orbit coupling and the onsite Coulomb interaction on the iridium atoms are included in the noncollinear magnetic calculations. The details of the implementation of first-principles calculations are presented in the Supporting information online.

We first adopt the experimental crystal structure of $\text{H}_3\text{LiIr}_2\text{O}_6$ without stacking faults refined with a monoclinic structure and the $C2/m$ space group [25]. The precise positions of the protons were not determined by the X-ray diffraction, therefore, their positions are fully relaxed and optimized in first-principles calculations until the force on each atom is smaller than 0.01 eV/Å.

The relaxed crystal structure that preserves the $C2/m$ symmetry is shown in Figure 1. The hydrogen ions deviate from the original lithium positions in $\alpha$-Li$_2$IrO$_3$ and bridge the two nearest oxygen ions in the two adjacent IrO$_3$ layers, and form an ABC-stacking triangular lattice. The $O$–H–$O$ bonds are almost perpendicular to the $ab$ plane.

The total energy is further lowered if the proton is shifted away from the O–H–O bond center towards either one of the oxygen ions, which breaks the $C2/m$ symmetry, while its displacement in the $ab$ plane increases the energy significantly. By varying the height of one proton while fixing other protons at the O–H–O bond centers in a supercell in the first-principles calculations, we find that the proton is trapped in a double-well potential $V(z)$ (Figure 2(b)). The potential minima are at ±0.22 Å away from the O–H–O bond center. We note that there are two types of O–H–O bonds formed by O(2)–H(1)–O(2) and O(1)–H(2)–O(1) with the bond lengths 2.54 and 2.46 Å, respectively. The proton energy potentials and the electric dipole moments of them are different. The results presented in Figure 2 correspond to the O(2)–H(1)–O(2) bonds. The results of the O(1)–H(2)–O(1) bonds are pre-
sented in the Supporting information online.

The proton at one of the energy minima forms a uniaxial electric dipole with the oxygen ions. The net dipole moment is calculated by integrating the dipole moment density over a cylinder surrounding the O–H–O bond, \( p_0 = 0.06 \sim 0.11 \text{ e}\cdot\text{Å} \) (the uncertainty comes from different choices of the cylinder height).

3 Electric dipole-dipole interactions

We treat these uniaxial electric dipoles as Ising variables, \( \sigma_i^z = \pm 1 \). In order to capture the dipole-dipole interactions in the crystal, we obtain the total energies of various dipole configurations from the first-principles calculations (Figure 3) and fit the Ising model on the ABC-stacking triangular lattice:

\[
H_D = \sum_{ij} D_{ij} \sigma_i^z \sigma_j^z,
\]

where \( D_{ij} \) denotes both the intralayer interactions \( D_{1,2,3} \) and the interlayer interactions \( D'_{1,2,3} \) up to the third nearest neighbors defined in Figure 3. This method was adopted to study the electric dipole-dipole interactions in the hexaferrite \( \text{BaFe}_{12}\text{O}_{19} \) [26]. The least-square fitting yields \( D_1 = 1.7 \text{ meV}, D_2 = -0.5 \text{ meV}, D_3 = -0.3 \text{ meV}, D'_1 = -0.2 \text{ meV}, D'_2 = 1.0 \text{ meV}, \) and \( D'_3 = 0.1 \text{ meV} \). The details are presented in the Supporting information online. The comparison of the first-principles total energies and the fitted model energies is shown in Figure 3. On the other hand, the intralayer nearest-neighbor interaction can be estimated from the dipole-dipole interaction at a distance \( r = 3.15 \text{ Å}, D_1 \approx p_0^2 / 4\pi \varepsilon_0 r^3 = 1.7-5.6 \text{ meV} \), which is roughly consistent with the result of fitting.

4 Proton tunneling and quantum paraelectricity

The Ising model of the dipole-dipole interactions may suggest an antiferroelectric order at the ground state; however, we will show this is not the case because of the quantum tunneling of the protons. The proton tunneling between the energy minima flips the electric dipole, and thus acts as a transverse field in the Ising model:

\[
H_h = -h_z \sum_i \sigma_i^z.
\]

\( h_z \) can be calculated from the difference of the bonding and the antibonding state energies, \( \varepsilon_b \) and \( \varepsilon_{ab} \), in the double-well potential \( V(z) \). By numerically solving the 1D Schrödinger equation:

\[
\frac{\hbar^2}{2m_p} \psi''(z) + V(z) \psi(z) = E \psi(z),
\]

where \( m_p \) is the proton mass, we find \( h_z = (\varepsilon_{ab} - \varepsilon_b) / 2 = 36.7 \text{ meV} \). The wavefunctions of the bonding and the antibonding states are shown in Figure 2.

The proton tunneling term dominates over the dipole interactions, \( h_z \gg |D_{ij}| \), therefore the ground state of the electric dipoles is a quantum disordered paraelectric state and the \( C2/m \) symmetry is thus dynamically restored. This leads to the following predictions to experiments. First, these electric dipoles contribute a sizable uniaxial dielectric response to the electric field perpendicular to the \( ab \) plane in a large temper-
nature range. The temperature-dependence of the electric susceptibility $\chi_e(T)$ can be derived by the mean field theory of the transverse-field Ising model, and the result is the Barrett formula [27]:

$$\chi_e(T) = \frac{M}{T_1 \coth(T_1/2T) - T_0},$$

where $T_1 = 2\hbar/|k| B \approx 870$ K marks the crossover from the high-$T$ Curie-Weiss behavior to the low-$T$ plateau, $\chi_e(T \to 0) = M/(T_1/2 - T_0)$, and $T_0 = -k_B^{-1} \sum J_{ij} \approx -130$ K is the effective antiferroelectric interaction strength. The overall amplitude $M = \rho_0 p_0^2 / \epsilon_0 k_B$ depends on the electric dipole moment $p_0$ and the dipole density $\rho_0$.

Second, the electric dipole excitations correspond to an optical phonon mode. Its spectrum is derived by a single-mode approximation on the paraelectric ground state and is shown in Figure 4. There is a dipole excitation gap $\Delta_{dip} \approx 60$ meV. These dipole excitations may be probed by the infrared optical spectroscopy.

5 Discussion: impact on the magnetic interactions

The magnetic interactions can be extracted from the total energies of various magnetic moment configurations when both the atom positions and the magnetic moment configurations are prescribed in the first-principles calculations. The details are presented in the Supporting Information online. The protons are placed at the O–H–O bond centers preserving the $C2/m$ symmetry. The following (extended) Kitaev-Heisenberg model is fitted to the calculated total energies of various magnetic configurations:

$$H_{KH} = H_K + H_J + \Gamma \sum_{(ij)\neq\gamma} (S_i^x S_j^x S_\gamma^y + S_i^y S_j^y S_\gamma^x) + \Gamma \sum_{(ij)\neq\gamma} (S_i^z S_j^z + S_i^\alpha S_j^\alpha S_\gamma^\beta + S_i^\beta S_j^\beta S_\gamma^\alpha),$$

where $(\alpha, \beta, \gamma)$ is the cyclic permutation of $(x, y, z)$. The fitted parameters are listed in Table 1. The Curie-Weiss temperature of this model is $\theta_{CW} = -K - 3J_2 - 6J_3 = -104$ K. The results of the closely related materials $\text{Na}_2\text{IrO}_3$ and $\alpha$-Li$_2$IrO$_3$ derived from first-principles calculations [28] and nonperturbative exact diagonalization [29] are also listed in Table 1 for comparison.

It is instructive to compare the magnetic interaction parameters of $\text{H}_3\text{LiIr}_2\text{O}_6$ and $\text{Na}_2\text{IrO}_3$. In both materials, the spin-anisotropic $\Gamma$ and $\Gamma'$ terms as well as the $J_2$ term are relatively small, which suggests a minimal model incorporating only the $K$-$J_1$-$J_3$ terms [29], which is not applicable to $\alpha$-Li$_2$IrO$_3$ due to a large $\Gamma$ term. The phase diagram of this model is obtained by exact diagonalization on small lattice clusters (Figure 5) [29]. Both $J_1$ and $J_3$ terms can destabilize the Kitaev QSL phase and lead to magnetic ordered states. In particular, a sizable $J_3$ term favors the zigzag order, which is consistent with the experiments on $\text{Na}_2\text{IrO}_3$ [11-13]. Both ratios $J_1/|K|$ and $J_3/|K|$ in $\text{H}_3\text{LiIr}_2\text{O}_6$ are significantly reduced upon the hydrogen substitution, thus its ground state is closer to the Kitaev QSL phase. Nevertheless, the fitted $K$-$J_1$-$J_3$ model of $\text{H}_3\text{LiIr}_2\text{O}_6$ remains in the zigzag ordered phase.

We argue that the proton fluctuations may further push the effective magnetic interaction parameters of $\text{H}_3\text{LiIr}_2\text{O}_6$ into the Kitaev QSL phase. Recall that the oxygen-mediated nearest-neighbor electron hopping in the Slater-Koster approximation exactly vanishes in the pseudospin $J_{\text{eff}} = 1/2$ subspace due to the destructive interference of the two Ir-O-Ir hopping paths [9]. This exact cancellation is absent when the fluctuations of the nearby protons set in and the two hopping paths are not equivalent. When the proton gets closer to one of the oxygen ions, the onsite energy of a hole at this oxygen ion is increased, $E_p \rightarrow E_p + \delta E_p$, thus the hopping amplitude along this path is reduced, $t \rightarrow t - \delta t$, with $\delta t/t \approx \delta E_p / E_p$, and the two hopping paths do not cancel out completely. For example, on a $z$-bond, the remnant hopping term is

$$\delta H_z = -\frac{1}{3} \delta \theta (\sigma_z^+ + \sigma_z^-) \sum_{\alpha} i a d^\dagger_{\alpha z} d_{\alpha z} + \text{h.c.},$$

where $d^\dagger_{\alpha z}$ is the creation operator of the pseudospin $J_{\text{eff}} = 1/2$.

| Material          | $K$   | $J_1$ | $J_2$ | $J_3$ | $\Gamma$ | $\Gamma'$ |
|-------------------|-------|-------|-------|-------|----------|----------|
| $\text{H}_3\text{LiIr}_2\text{O}_6$ | -21.6 | 6.3   | 0.4   | 3.5   | -0.2     | -1.6     |
| $\text{Na}_2\text{IrO}_3$ [28] | -19.1 | 7.2   | -1.6  | 7.8   | 1.5      | -3.5     |
| $\text{Na}_2\text{IrO}_3$ [29] | -16.8 | 0.5   | 0.2   | 6.7   | 1.4      | -2.1     |
| $\alpha$-Li$_2$IrO$_3$ [29] | -6.8  | -2.7  | 0.4   | 6.0   | 8.9      | -0.6     |

Table 1 The magnetic interaction parameters (in meV) of $\text{H}_3\text{LiIr}_2\text{O}_6$ derived from first-principles calculations with the hydrogen ions placed at the O–H–O bond centers. The results of Na$_2$IrO$_3$ and $\alpha$-Li$_2$IrO$_3$ reported in refs. [28] and [29] are included for comparison. The parameters cited from ref. [29] are averaged over the three bond directions.
electron on the iridium ion, and $\sigma_1^z$ and $\sigma_2^z$ are the configurations of the two dipoles close to the two oxygen ions, respectively. Treating it as a perturbation gives the following correction to the effective magnetic interactions:

$$\delta H_{KH} = \delta J \sum_{\langle ij \rangle \neq \gamma} (2S_i^z S_j^z - S_i \cdot S_j), \quad (9)$$

where $\delta J = 8d(\gamma^2/9(U + 2h))$ and $U$ is the onsite repulsion on the iridium ions. Therefore, the proton fluctuations renormalize the magnetic interaction parameters, $|K| \rightarrow |K| - 2\delta J$, and $J_1 \rightarrow J_1 - \delta J$. The ratio $J_1/|K|$ is nevertheless reduced because $J_1/|K| < 0.5$. By considering the oxygen-mediated long-range hopping paths, we may similarly argue that $J_3$ is also reduced by the proton fluctuations. Therefore, the proton/electric dipole fluctuations may further push the magnetic interactions towards the Kitaev QSL phase.

6 Summary and outlook

We have studied the physical consequences of the hydrogen substitution in the Kitaev QSL candidate $\mathrm{H}_2\mathrm{LiIr}_2\mathrm{O}_6$. We find that each proton is trapped in a double-well potential and forms an electric dipole with two adjacent oxygen ions. Incorporating the dipole interactions and the proton tunneling, the low-energy dynamics of these dipoles is captured by a transverse-field Ising model. The strong proton tunneling leads to a quantum disordered paraelectric ground state. The dipole excitations may be probed with the dielectric response and the infrared optical spectroscopy. The dipole fluctuations renormalize the effective magnetic interactions and may push the magnetic ground state of $\mathrm{H}_2\mathrm{LiIr}_2\mathrm{O}_6$ into the Kitaev QSL phase. Similar study of the role of the hydrogen ions in $\mathrm{H}_2\mathrm{LiIr}_2\mathrm{O}_6$ was also presented in two independent works published recently [30, 31]. Evidence of the proposed quantum paraelectricity has been obtained in recent experiments with dielectric spectroscopy [32].

The electric dipoles formed by displaced ions are ubiquitous in materials. Our approach to the quantum dynamics of the electric dipoles can be applied to other materials. Moreover, the interplay of the electric dipoles and the spin and orbit degrees of freedom may provide a new route towards quantum paraelectric states, QSLs and other exotic quantum states of matter [33-36].

In this work, we have not analyzed the unusual thermodynamic behaviors of $\mathrm{H}_2\mathrm{LiIr}_2\mathrm{O}_6$ found in the experiments [19]. In a recent theoretical work accounting for this behavior [37] was based on the assumption that a single layer of $\mathrm{H}_2\mathrm{LiIr}_2\mathrm{O}_6$ would be in the Kitaev QSL phase. On the other hand, it was also proposed that the low-energy excitations could be attributed to a random singlet phase [38], which is qualitative consistent with the recent experimental evidence of slowing-down dynamics in the dielectric response at low temperature [32]. The effect of quenched disorder on the thermodynamic and magnetic properties in $\mathrm{H}_2\mathrm{LiIr}_2\mathrm{O}_6$ and other related materials is worth further studying.

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Supporting Information

The supporting information is available online at phys.scichina.com and link.springer.com. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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