Fingerprints of quantum spin ice in Raman scattering

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We develop a theory of the dynamical response of a minimal model of quantum spin ice (QSI) by means of inelastic light scattering. In particular, we are interested in the Raman response of the fractionalized U(1) spin liquid realized in the XXZ QSI. We show that the low-energy Raman intensity is dominated by spinon and gauge fluctuations. We find that the Raman response in the QSI state of that model appears only in the T_{2g} polarization channel. We show that the Raman intensity profile displays a broad continuum from the spinons and coupled spinon and gauge fluctuations, and a low-energy peak arising entirely from gauge fluctuations. Both features originate from the exotic interaction between photon and the fractionalized excitations of QSI. Our theoretical results suggest that inelastic Raman scattering can in principle serve as a promising experimental probe of the nature of a U(1) spin liquid in QSI.

Quantum spin liquids (QSLs) have proven to be one of the most fascinating and challenging subjects in modern condensed matter physics.1–5 They are known to host a remarkable set of emergent phenomena, including long-range entanglement, topological ground state degeneracy and a number of unusual fractionalized excitations such as fermionic or bosonic spinons as well as emergent gauge excitations. In recent years, there has been significant progress both in the theoretical understanding of such phenomena and in identifying realistic microscopic models that may host QSL phases. Notable examples include the spin-1/2 Heisenberg antiferromagnet on the kagome lattice,6–10 the family of exactly solvable Kitaev-type models,11–13 and quantum spin ice.14–24

Direct experimental observation and characterization of QSLs is challenging. Unlike states with spontaneously broken symmetry, the topological order characteristic of QSLs13 cannot be captured by a local order parameter and thus cannot be directly detected by local measurements. Identifying QSLs thus requires finding experimental probes that provide information beyond the measurement of local order parameters. One of the most promising avenues in this direction is the characterization of the excitations of QSL candidates. The fractionalized excitations of a QSI can be probed by conventional methods such as inelastic neutron scattering,25 Raman scattering26–30 or resonant X-ray scattering (RIXS),31–33 all offering signatures that enable their detection. Due to their fractionalized nature, these kinds of scattering probes necessarily create multi-particle excitations in the system. The appearance of such multi-particle continua in their dynamical response is a hallmark of QSL behavior.34–39 These continua are in stark contrast with the excitation spectra of conventionally ordered phases, where sharp single-particle excitations are expected. Given the field currently still lacks the experimental methods to probe the topological order of QSLs, it is therefore important to have both a qualitative and a quantitative understanding of these multi-particle continua and how they manifest themselves in various experimental scattering probes and in QSL candidates.

In this paper, we study such a dynamical response in a model QSL, quantum spin ice (QSI). Defined on the pyrochlore lattice, a network of corner-sharing tetrahedra (see Fig.1), this QSL emerges naturally from the classical spin ice limit.3,40 In this limit, there are a macroscopic number of ground states characterized by the so-called “ice rule”; each tetrahedron must be in a two-in/two-out state.40 Excitations about this manifold have three spins up and one down (or vice-versa) and can be separated at no energy cost.31 As first shown by Hermele et al.,14 adding transverse exchange induces quantum tunneling between different ice states. A sufficiently weak tunneling stabilizes a QSL ground state with an emergent U(1) gauge field and bosonic spinon excitations.14,16–19–21 Much effort has been put forth to understand the nature of the QSI phase as well as its static and dynamic properties.14,17–21,42–46

These theoretical studies have sparked intense experimental activity aiming to find a concrete realization of QSI. The wide range of rare-earth pyrochlore materials4,47 have provided an ample playground for this search. Potential candidates for hosting a QSI phase currently include Tb2Ti2O7, Yb2Ti2O7, the Pr2M2O7 family (M = Zr, Sn, Hf) as well as the canonical classical spin ices Dy2Ti2O7 and Ho2Ti2O7 (see Ref. [4] for a survey). However, the physics of these materials is complex; for many, it is even unclear how close they are to the classical spin ice limit. Identifying experimental probes that are sensitive to both the gauge and spinon excitations that manifest in QSI would thus be useful for a better characterization of these QSI candidates. Perhaps more importantly, it would deepen our general understanding of the dynamical response of QSLs and their various excitations.

In this article, we propose that inelastic Raman scattering may be of particular interest for QSI systems. In a loose sense, we are inspired by rather recent works on Raman scattering from Kitaev QSLs.26–30 Using photons as a probe, the Raman response can in principle offer insights in the excitation spectrum of a QSI that may not be accessible through usual methods such as inelastic neutron scattering. We derive the Raman vertex for relevant rare-earth pyrochlore materials using the traditional framework of an effective Hamiltonian for the interaction of light with spin degrees of freedom.26,48–50 Applying these results to an effective theory of QSI, we show how the gapped and deconfined spinons as well as emergent gapless gauge modes appear in the Raman spectrum. Intriguingly, we
find that real light can scatter from the emergent “light” of QSI$^{17}$ and produce a measurable response. In addition, the spin excitations themselves have a direct signature in the Raman spectrum.

The structure of the paper is as follows: in Sections I, II and III, we set our notations and review the basic concepts of QSI and its elementary excitations.$^{14,17–19,21}$ In Section IV, we briefly review the Loudon-Fleury theory of the Raman scattering in Mott insulators that we need for our study. Armed with this, we then derive the relevant Raman operator involving the super-exchange processes between pseudo-spins that represent the magnetic degrees of freedom. By studying the polarization dependence of the Raman response, we explicitly show that the response occurs only in the $T_{2g}$ polarization channel. In Section V, we compute the Raman response for the XXZ QSI. In particular, we first separate three contributions to the Raman response – from pure spin excitations, from gauge fluctuations and from their hybridization – and then present the numerical results for the total Raman intensity in the $T_{2g}$ channel. Some discussion and a conclusion are given in Secs. VI and VII.

I. SPIN HAMILTONIAN

Before delving into the details of the Raman process, we first review the relevant anisotropic exchange models for the pertinent pyrochlore materials. In the current materials of interest which may realize QSI, the magnetic degrees of freedom originate from rare-earth ions.$^{4}$ Although we are not per se confining ourselves to the details of the rare-earth ions that form the majority of the QSI materials, it is useful to set the stage and make some general observations about the spin Hamiltonian so far considered in the theoretical and experimental investigations of QSI systems.

In the rare-earth ions, the atomic interactions dominate; the free-ion ground state is determined by following Hund’s rules, first minimizing the Coulomb energy, followed by the spin-orbit energy. These free-ion states have well defined total angular momentum, $J$, and (approximately) well-defined total orbital and spin angular momenta. In a crystalline environment, due to the electric fields from the surrounding ions, the remaining $2J + 1$ degeneracy of this manifold is partially lifted. When $J$ is a half-odd-integer, only Kramers’ degeneracy remains and there is a series of doublets for the relevant $D_{3d}$ site symmetry$^{47}$. With respect to this symmetry, these can transform either like spin-1/2 objects, “pseudo-spin” doublet (as in Yb$_2$Ti$_2$O$_7$ or Er$_2$Ti$_2$O$_7$), or like a more exotic “dipolar-octupolar” doublet$^{51}$ (as in Dy$_2$Ti$_2$O$_7$ and Nd$_2$Zr$_2$O$_7$). For integer $J$, Kramers’ theorem does not apply and singlet states are possible. However, the $D_{3d}$ site symmetry can allow a non-magnetic doublet, a so-called non-Kramers doublet (as, for example in Ho$_2$Ti$_2$O$_7$ or Tb$_2$Ti$_2$O$_7$). If well separated from the other crystal field levels, each of these kinds of crystal field doublets behaves like an effective spin-1/2 degree of freedom. For this reason we will refer to all of these states as a “spin” regardless of whether they are pseudo-spin-1/2, dipolar-octupolar or non-Kramers type.

To describe these doublets, we introduce the spin operators $S_{i}$, defined in the local basis at each site.$^{15}$ For the dipolar-octupolar and non-Kramers doublet, only $S_{i}^z$ contributes to the magnetic dipole moment with $\mu = -g_{\mu B}S^z$, where $\vec{z}$ is the local [111] direction. For the pseudo-spin-1/2 case, both the $\vec{z}$ component and the components perpendicular to $\vec{z}$ contribute to the dipole moment. Since these three types of doublets transform quite differently under the lattice symmetries,$^{20,51}$ the allowed exchange interactions are generally distinct. The most general nearest-neighbor anisotropic exchange model on the pyrochlore lattice can be written as$^{18,19}$

$$H_{ex} = \sum_{ij} \left[ J_{zz} S_{i}^z S_{j}^z - J_{x} (S_{i}^+ S_{j}^- + S_{i}^- S_{j}^+) + J_{zz} (\gamma_{ij} S_{i}^z S_{j}^z + S_{i}^+ S_{j}^- + h.c.) \right],$$

(1)

where the matrices $\gamma_{ij} = -\gamma_{ji}$ and $\gamma_{ij}$ are defined in Appendix A. For the case of a pseudo-spin-1/2 doublet, all of these couplings are allowed. For a non-Kramers doublet, one has $J_{zz} = 0$ whereas for a dipolar-octupolar doublet, the phases are absent, i.e. $\gamma_{ij} = 1$ and $\gamma_{ij} = 1.51$. Microscopically, these kinds of short-range anisotropic interactions can be generated by various super-exchange mechanisms.$^{16,22}$ If $J_{zz} > 0$ and $J_{x} = J_{zz} = 0$, one recovers classical spin ice$^{52}$.

Introducing a finite $J_{zz}$ or $J_{x}$ with $J_{zz} \gg J_{x}$, $J_{zz} \gg J_{x}$ induces quantum tunneling between the ice states$^{14,19}$ and stabilizes a QSI ground state.$^{33}$ While in Dy$2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ one expects $J_{zz}$ and $J_{x}$ to be negligible$^{22}$ in other materials such as Yb$_2$Ti$_2$O$_7$, Er$_2$Ti$_2$O$_7$ or Tb$_2$Ti$_2$O$_7$, experiments strongly suggest these couplings are significant.$^{18,24–26}$ Since we are interested in the spin ice limit, we will restrict ourselves to cases where $J_{zz}$ is dominant and is antiferromagnetic ($J_{zz} > 0$). In the remainder

![FIG. 1. The pyrochlore lattice relevant for QSI materials. The centers of blue and yellow tetrahedra, labeled by $x$, form the (A) and (B) sublattices of the diamond lattice, correspondingly. $µ = 0, 1, 2, 3$ label the bonds of the diamond lattice. The spins, $S_{i}$, reside on the pyrochlore sites located on the middle of the bond $µ$. The dashed lines illustrate the electron hopping paths involved in the super-exchange processes that generate the Raman vertex.](image-url)
of the paper, we thus work with the dimensionless ratios
\[ j_\pm = \frac{J_{\pm x}}{J_{zz}}, \quad j_{x\pm} = \frac{J_{x\pm}}{J_{zz}}, \quad j_{xx} = \frac{J_{xx}}{J_{zz}}, \]  
which we assume to be small.

II. QUANTUM SPIN ICE

We now review the slave-particle description of QSI, using the formulation introduced in Ref. [21]. In the following, we use the notation of Refs. [19,21] and label the pyrochlore sites by a combined index \((x, \mu)\), in which \(x\) denotes a diamond lattice site belonging to sublattice \((A)\) and \(\mu = 0, 1, 2, 3\) are the four nearest neighbors of the diamond site, as shown in Fig. 1. The spin at the center of the bond \((x, x + \mu)\) is then labeled as \(S_{x\mu}\), with \(\mu\) being the vector connecting the two neighboring diamond sites in Fig. 1.

The slave-particle formulation we will use is built on extending the original Hilbert space to track the spin ice charge \(Q_x\) of the diamond lattice sites independently of the spins of the pyrochlore sites. In terms of the spins, the charges are defined as
\[ Q_x = \left\{ \begin{array}{ll}
\pm \sum_x S_x^z, & x \in \langle A \rangle, \\
-\sum_x S_x^z, & x \in \langle B \rangle.
\end{array} \right. \]  
(3)

The charge operator \(Q_x\) characterizes violations of the ice rules: \(Q_x = 0\) being satisfied for a two-in/two-out state, while tetrahedra with three-in/one-out or three-out/one-in have \(Q_x = \pm 1\) and those with all-in/all-out have \(Q_x = \pm 2\).

We study the exchange Hamiltonian, Eq. (1), in an enlarged Hilbert space containing both the charge and the spin degrees of freedom separately. We construct this by first introducing a new Hilbert space for the charge operator \(Q_x\) that is now taken as distinct from the spins. Second, we enlarge the range of allowed charges from strictly 0, \(\pm 1\), and \(\pm 2\) to include all integers. Explicitly, if we define the physical Hilbert space as \(\mathcal{H}_{\text{phys}} = \bigotimes_{x, \mu} \mathcal{H}_{1/2}\), where \(\mathcal{H}_{1/2}\) is the spin Hilbert space, then the extended space is
\[ \mathcal{H}_{\text{ext}} = \left( \bigotimes_{x, \mu} \mathcal{H}_{1/2} \right) \otimes \left( \bigotimes_x \mathcal{H}_{\text{(2)}} \right) \equiv \mathcal{H}_1 \otimes \mathcal{H}_Q, \]  
(4)

and where \(\mathcal{H}_{\text{(2)}}\) is the Hilbert space of an \(O(2)\) rotor, defined at each diamond site and spanned by an infinite set of basis states that satisfies \(Q_x |q_x\rangle = q_x |q_x\rangle\), where \(q_x\) is an integer. We define the physical subspace as the one in which the \(Q_x\) operators satisfy the constraint of Eq. (3).

In this extended space, one then introduces a phase \(\theta_x\), conjugate to the charge operators \(Q_x\). These two operators satisfy the canonical commutation relations
\[ [\theta_x, Q_x'] = i \delta_{xx'} \]  
(5)

The quantization of \(Q_x\) implies the periodicity of \(\theta_x\). The operators \(Q_x\) and \(\theta_x\) allow us to introduce a spinon operator, \(\psi_x\), which is the basic element in a slave particle description of spin ice. To be precise, we define the raising and lowering operators \(\psi_x^\dagger = e^{i\theta_x} \) and \(\psi_x = e^{-i\theta_x} \), satisfying
\[ [\psi_x^\dagger, Q_x'] = -\delta_{xx'}, \]  
(6a)
\[ [\psi_x, Q_x'] = +\delta_{xx'}. \]  
(6b)

which thus increase or decrease the charge quantum number at diamond lattice site \(x\). We then interpret \(Q_x\) as the spinon number operator in the quantum theory, with \(\psi_x^\dagger\) and \(\psi_x\) being spinon creation and annihilation operators, which live in the Hilbert space \(\mathcal{H}_Q\).

For the \(\mathcal{H}_s\) part of the extended Hilbert space, we define new auxiliary spin-1/2 operators, \(s_{x,\mu}\). The original physical spin-1/2 operators \(S_{x,\mu}\) can be expressed in terms of the \(s_{x,\mu}\), \(\psi_x^\dagger\), and \(\psi_x\) operators as
\[ S_{x,\mu} = \psi_x^\dagger s_{x,\mu}^\dagger \psi_x, \]  
(7a)
\[ S_{x,\mu}^{-} = \psi_x^\dagger s_{x,\mu} \psi_x, \]  
(7b)
\[ S_{x,\mu}^{\pm} = s_{x,\mu}^\dagger \psi_x \mp i\delta_{\mu} s_{x,\mu} \psi_x. \]  
(7c)

These combinations of operators are chosen such that the canonical commutation relations of the original spin-1/2 operators, \(S_{x,\mu}\), are preserved, and the physical constraint defined by Eq. (3) is also respected. If we were able to enforce these constraints exactly, Eqs. (3-7) would then constitute an exact reformulation of the original spin-1/2 problem of Eq. (1). While such an exact description is not feasible, this set of variables have nevertheless proven to be a useful starting point for describing the QSI phases of the anisotropic exchange model given in Eq. (1).

The enlargement of the Hilbert space implies a large degree of redundancy in this description. In particular, note that the mapping defined by Eq. (7) is invariant under the U(1) transformation
\[ \psi_x \rightarrow e^{i\alpha} \psi_x, \quad s_{x,\mu}^\dagger \rightarrow e^{i\delta_{\mu} \alpha} s_{x,\mu}^\dagger, \quad s_{x,\mu}^{-} \rightarrow e^{i\delta_{\mu} \alpha} s_{x,\mu}^{-}, \]  
(8)

for an arbitrary local phase factor \(\alpha\). This gauge redundancy can be made explicit by recasting the \(s_{x,\mu}\) operators in terms of an emergent gauge field, \(A_{x,\mu}\), and an emergent electric field, \(E_{x,\mu}\), via
\[ s_{x,\mu}^\dagger = |s_{x,\mu}^\dagger| e^{iA_{x,\mu}}, \quad s_{x,\mu}^{-} = E_{x,\mu}. \]  
(9)

To simplify the problem, we replace the transverse components of the spin operator by their average value, with \(|s_{x,\mu}^\dagger| \approx |s_{x,\mu}^{-}|\), and only keep the phase of \(s_{x,\mu}^{-}\) as dynamical variable. It is easy to check that the electric field and the gauge field satisfy the commutation relation
\[ [A_{x,\mu}, E_{x',\nu}] = i \delta_{xx'} \delta_{\mu
u}. \]  
(10)

By construction, these fields are compact given the redundancy built into the definition of \(A_{x,\mu}\) and the periodicity of \(\theta_x\). This kind of mapping of an auxiliary spin-1/2 system to a gauge theory has been explored in many contexts; we refer the reader to the literature for further details.

Having performed this reformulation of the original spin degrees of freedom, we now rewrite \(H_{\text{ex}}\) in terms of these new variables. One finds
We have broken this Hamiltonian into three parts, two of which are new: \( H_\theta \) which describes the kinetic energy of the bosonic spinons \( \psi_x \) and their “charging” energy \( \sim Q_x^2 \), and \( H_{\phi A} \) which describes a minimal coupling between the spinons and the emergent U(1) gauge field.

The spinon part, \( H_\theta \), defines a quantum rotor model and is
where we have introduced the sublattice label $\lambda = \langle A \rangle, \langle B \rangle$ and defined the vertex
\[
\tilde{f}_{\mu}^{\nu}(k) \equiv 2 \cos \left[ k \cdot (\mu - \nu) \right].
\]
To approximately solve this rotor model, we use the “exclusive boson” representation introduced in Ref. [21]
\[
\psi_x = \frac{d_x + b_x^\dagger}{(1 + d_x^2 d_x + b_x b_x)^{1/2}},
\]
\[
Q_x = d_x^2 d_x - b_x^\dagger b_x.
\]
Here $b_x$ and $d_x$ are bosonic operators constrained to satisfy $b_x d_x \equiv b_x^\dagger d_x^\dagger \equiv 0$ for all the basis states. Under the approximation that the density of bosons is small, and thus dropping all four-boson terms, the Hamiltonian $H_\psi$ is simplified significantly into a quadratic form. This can then be diagonalized with the help of a Bogoliubov transformation, giving
\[
H_\psi = \sum_{k,l} E_k \left( \tilde{d}_{k,l}^\dagger \tilde{d}_{k,l} + \tilde{b}_{k,l}^\dagger \tilde{b}_{k,l} \right) + \text{const.}
\]
where $\tilde{b}_{k,l}, \tilde{d}_{k,l}$ are the Bogoliubov quasi-particles and the dispersion relation $E_k$ is given by
\[
E_k = \frac{1}{2} \left[ 1 - 2 \tilde{j}_s \sum_{\alpha \neq \beta} \cos \left( \frac{k_\alpha}{2} \right) \cos \left( \frac{k_\beta}{2} \right) \right]^{1/2},
\]
where $\alpha, \beta = x, y, z$ are the three global cubic directions. Explicit expressions for the relationship between the spinons $\psi_{k,l}$ and the bosons $\tilde{b}_{k,l}, \tilde{d}_{k,l}$ are given in Ref. [21]. The Green’s function for the spinon field$^{21}$ is then given by
\[
\tilde{G}_\phi(\omega, k) = \int dt e^{i\omega t} \left[ -i(T \psi_{k}(t)\psi_{k}^\dagger(0)) \right],
\]
\[
= \frac{1}{2E_k} \left[ \frac{1}{\omega - E_k + i\delta} - \frac{1}{\omega + E_k - i\delta} \right],
\]
where $T$ implements time-ordering and $\delta = 0^+$.

Next, we discuss the dynamics of the gauge Hamiltonian, $H_g$. This can be done using standard methods$^{21}$ once the condition $A_{x,\mu} \ll 1$ has been imposed. Explicitly, one has
\[
H_g \sim \frac{U}{2} \sum_{x \in \langle A \rangle, \mu} E_x^\dagger \mu + \frac{g}{2} \sum_{\mu \in \langle \mu \rangle} \left( \sum_{x \in \langle A \rangle} A_{x,\mu} \right)^2.
\]
To diagonalize $H_g$, a linear transformation is defined as
\[
A_{\mu,\nu} = \sum_{y=0,1} \eta_{\mu\nu}(p)a_{\gamma,\nu}^\dagger, \quad E_{\mu,\nu} = \sum_{y=0,1} \eta_{\mu\nu}(p)e_{\gamma,\nu},
\]
where $\eta_{\mu\nu}(p)$ is a matrix satisfying
\[
\sum_{\gamma} \eta_{\mu\nu}(p)\eta_{\nu\gamma}(p) = \delta_{\mu\nu}.
\]
The two operators, $\hat{a}_{\gamma,\nu}$ and $\hat{e}_{\gamma,\nu}$, satisfy the canonical commutation relation $[\hat{a}_{\gamma,\nu}, \hat{e}_{\gamma,\nu}^\dagger] = i\delta_{\mu\nu}$. This way, the a-excitons act like positions and e-excitons act like momenta in a quantum harmonic oscillator. This unitary transformation diagonalizes $H_g$, resulting in
\[
H_g = \sum_{p} \left( \frac{U}{2} \hat{e}_{\gamma,\nu}^\dagger \hat{e}_{\gamma,\nu} + \frac{e_p^2}{2U} \hat{a}_{\gamma,\nu} \hat{a}_{\gamma,\nu}^\dagger \right),
\]
where we see that $\hat{a}_{\gamma,\nu}$ and $\hat{e}_{\gamma,\nu}$ are transverse modes ($\gamma = 0, 1$) describing the gauge fluctuations and dynamics of electric fluxes, respectively. The photon dispersion is defined as
\[
e_p^2 = 4Ug \left[ 3 - \frac{1}{2} \sum_{\alpha \neq \beta} \cos \left( \frac{p_\alpha}{2} \right) \cos \left( \frac{p_\beta}{2} \right) \right]
\approx c^2 |p|^2 + O(|p|^4),
\]
where $c = (Ug)^{1/2}$. This speed of emergent light, $c \approx 0.3g$, has been estimated in simulations of the effective ring-exchange model$^{17}$ and motivated the value of $U$ given in Eq. (15). The Green’s functions for these $a$- and $e$-operators can also be easily worked out. One arrives at
\[
G_{\Lambda}(\omega, p) = \int dt e^{i\omega t} \left[ -i(T \hat{a}_{\gamma,\nu}(t)\hat{a}_{\gamma,\nu}^\dagger(0)) \right],
\]
\[
= \frac{U}{\omega^2 - e_p^2 + i\delta},
\]
\[
G_{E}(\omega, p) = \int dt e^{i\omega t} \left[ -i(T \hat{e}_{\gamma,\nu}(t)\hat{e}_{\gamma,\nu}^\dagger(0)) \right],
\]
\[
= \frac{e_p^2}{U(\omega^2 - e_p^2 + i\delta)},
\]
where $\delta = 0^+$. Finally, we have the interaction between the spinons and gauge field encapsulated in $H_{\phi A}$. This interaction can be rewritten in momentum space as
\[ H_{\phi A} = -\frac{J}{N} \sum_{\mu < \nu} \sum_{x \in (A)} i \left[ (\psi^\dagger_{i,\mu} \psi_{i,\mu} + \psi^\dagger_{i,\mu} \psi_{i,\mu}) (A_{x,\mu} - A_{x+\mu,\nu}) \right] + (\psi^\dagger_{i,\mu} \psi_{i,\mu} + \psi^\dagger_{i,\mu} \psi_{i,\mu}) (A_{x,\nu} - A_{x,\mu}) \].

(29)

where \( N \) is the number of unit cells and we have defined the vertex

\[ f_{\mu\rho\lambda}(k, p) = \frac{i}{\sqrt{N}} \sum_{\mu < \nu} \sum_{x \in (A)} f_{\mu\rho\lambda}(k, p) \psi_{i,\mu}^\dagger \psi_{i,\mu} A_{\rho,\lambda}. \]

This part, \( H_{\phi A} \), describes an interaction between the spinons \( \psi \) and the gauge field \( A \), similar to the interaction in regular quantum electrodynamics, coupling \( A \) to the “current” of the spinons. At this point, we thus have a theory of spinons interacting with a U(1) gauge field.

IV. MICROSCOPIC ORIGIN OF THE RAMAN VERTEX

We now investigate the mechanism of light scattering from the excitations of a QSI phase. Light can interact with matter in various ways. It is well known that, in general, the strongest coupling does not come from the direct coupling of the magnetic field of the light with the magnetic moments, but rather through the coupling of its electric field to the electric dipole moments of the scattering medium.48,59 The basic processes leading to the Raman response in Mott insulators are similar to those leading to exchange interactions, except that the virtual electron hopping is assisted by photons. Consequently, in the simplest approximation, the operator describing Raman processes is generically expected to be proportional to the spin-exchange couplings, weighted by polarization-dependent factors that determine the ability of the photons to control the magnitude of an electron hopping along certain bonds.26,27,48–50,60–62

To describe the coupling of light to electrons on a lattice, one can, in a first approximation, perform a Peierls substitution,63 attaching a “Wilson line” operator to the electron hopping term to preserve gauge invariance.

\[ e^{i \theta_{\mu} c_{\mu} \cdot \mu} \rightarrow e^{i \theta_{\mu} c_{\mu} \cdot \mu} \exp \left[ i \frac{e}{\hbar c} \int_{r_j}^{r_k} d\mathbf{r} \cdot \mathbf{A}(\mathbf{r}) \right]. \]

(31)

Here we use \( \mathbf{A} \) to denote the vector potential of the radiation field, not to be confused with the emergent U(1) gauge field in QSI, which we have denoted as \( A \). Intuitively, the photon couples to the electric dipole formed by charge transfer between different lattice sites. Thus, in order to get the correct Raman vertex, we must know the microscopic electron hopping mechanism at play in the material.

In the case of QSI, the super-exchange interactions between neighboring spins are expected to be mediated by the oxygen atoms that surround each rare-earth ion,6,22 as illustrated in Fig. 1. The microscopic derivation of Eq. (1) starts from separating the total microscopic Hamiltonian into an on-site part,

\[ H_0, \text{ and the hopping between rare-earth } f \text{ electrons and oxygen } p \text{ electrons, } V_0 \]

\[ H = H_0 + V_0. \]

(32)

All other hoppings are assumed to be small and thus neglected.22 The \( V_0 \) term is given by

\[ V_0 = \sum_{x \in (A)} \sum_{\mu < \nu} \sum_{\alpha} \left( \frac{1}{2} \mu_{\mu,\alpha} \rho f_{\mu,\alpha} + f_{\mu,\alpha} \rho f_{\mu,\alpha} \right), \]

(33)

where \( f_{\mu,\alpha} \) denotes the hopping amplitude, \( f_{\mu,\alpha} \) and \( \rho_{x,\alpha} \) represent the electron annihilation operators on the rare-earth and oxygen ions, respectively. Here we only include the high-symmetry oxygens, those which lie in the centers of the rare-earth tetrahedra, as they are closer to the rare-earth ions than the low symmetry oxygens.27 The on-site part \( H_0 \) contains the atomic interactions of the rare-earth ion, including Coulomb, spin-orbit, and crystal field contributions. We do not need the detailed properties of \( H_0 \), save for that its ground state is a doublet, as discussed in Sec. I, and that the energy to add or remove an electron, denoted roughly as \( \sim U_f \), is large relative to the hoppings, \( t \).

We now include the interaction with the electromagnetic (EM) field. As mentioned in Eq. (31), this coupling brings about a modification, \( V_0 \rightarrow V \), given by

\[ V = \sum_{x \in (A)} \sum_{\mu < \nu} \sum_{\alpha} \left( \frac{1}{2} \mu_{\mu,\alpha} \rho f_{\mu,\alpha} e^{i \frac{e}{\hbar c} \int_{r_j}^{r_k} d\mathbf{r} \cdot \mathbf{A}(\mathbf{r})} \right)

\[ + \frac{1}{2} \mu_{\mu,\alpha} \rho f_{\mu,\alpha} e^{i \frac{e}{\hbar c} \int_{r_j}^{r_k} d\mathbf{r} \cdot \mathbf{A}(\mathbf{r})} + \text{h.c.}. \]

(34)

To proceed, we make the assumption that the photon field is relatively weak, so that interaction with light does not affect the electronic structure of the material. We also assume that \( \frac{e}{\hbar c} \mathbf{A} \cdot \mathbf{\mu} \) is reasonably small so that we can expand \( V \) using a Taylor expansion as

\[ V = V_0 + V_1 + \cdots. \]

(35)

Knowing that the wavelength of the incoming and outgoing EM waves are much larger than the lattice constant of the material, we can further make the replacement

\[ \frac{ie}{\hbar c} \int_{x+\mathbf{r}}^{x} d\mathbf{r} \cdot \mathbf{A}(\mathbf{r}) \sim -\frac{ie}{2\hbar c} (\mathbf{\mu} \cdot \mathbf{A}_x). \]

(36)
Under these approximations we have that

\[
V_1 = \left( \frac{ie}{2\hbar c} \right) \sum_{\mu<\nu} \sum_{\mu\neq\rho} (A_{k_x} \cdot \mu) t_{\mu,\rho,\alpha}^\dagger p_{\alpha,\mu} x_{\mu,\alpha} + t_{\mu,\rho,\alpha}^\dagger f_{\alpha,\mu} x_{\mu,\alpha} - t_{\mu,\rho,\alpha}^\dagger p_{\alpha,\mu} x_{\mu,\alpha} - t_{\mu,\rho,\alpha}^\dagger f_{\alpha,\mu} x_{\mu,\alpha},
\]

This differs from \(V_0\) in that it attaches to each electron hopping term a factor \(\pm \mathbf{A} \cdot \mu\) coming from the EM field. In addition to this modification of the electron hopping, we also must now include the energy of the EM field itself, which we denote as \(H_y\).

Our goal is to derive an effective Hamiltonian, treating \(V\) as a perturbation, for the low-energy states of \(H_0 + H_y\). For our purposes this low-energy subspace contains all of the relevant EM states and only the ground states of \(H_0\). Now, from standard degenerate perturbation theory, \(^{64}\) this effective Hamiltonian can be written

\[
H_{\text{eff}} = \mathcal{P}H_0 + PH_y + PH_y V + PVVRVP + \mathcal{P}VRVRVP + \cdots, \tag{37}
\]

in which \(P\) projects into the ground state manifold of \(H_0\) and \(R\) is the resolvent

\[
R = \frac{1 - \mathcal{P}}{E_0 - H_0 - H_y + i\delta} = \frac{1 - \mathcal{P}}{E_0 - H_0 + i\delta} \tag{38}
\]

where \(E_0\) is the ground state energy of \(H_0\) and \(\delta = 0^+\). Here, we have made the approximation that the energy of the light, encoded in \(H_y\), is insignificant relative to the atomic energy scales of \(H_0\). We return to this effects of this approximation in Sec. VI B. The presence of the projection operator, \(P\), implies that only even order perturbations have non-zero contribution. To get the non-resonant Raman vertex, we neglect higher order terms and keep only \(V_1\) as perturbation.

We now proceed to compute the effective Hamiltonian in the low-energy subspace relevant for the rare-earth ion, similar to what is done in calculations of super-exchange.\(^{16,22}\) Due to the structure of the super-exchange processes, the anisotropic exchange Hamiltonian shown in Eq. (1) appears at fourth order in \(V_0\), with \(H_{\text{ex}} = PV_0 RV_0 RV_0 P\). It can be shown that the Raman interaction also comes in at fourth order in perturbation theory. To describe the scattering of light, we keep only the leading \(O(\mathbf{A}^2)\) parts of \(H_{\text{eff}}\), that is those having two factors of \(V_0\) and two factors of \(V_1\).\(^{65}\) While second-order processes, \(H_R^{(2)}\), that can contribute single-spin operators to the Raman operator do exist (see Appendix B), they vanish when only the high-symmetry oxygens are considered. We will return to this point this is Sec. VI B. To separate out the Raman part, we then can write

\[
H_R^{(4)} = PVVRVP - H_{\text{ex}},
\]

where \(H_{\text{ex}} = P(V_0 + V_1)R(V_0 + V_1)R(V_0 + V_1)P - H_{\text{ex}} \approx PV_0 RV_0 RV_0 P + \mathcal{P}V_0 RV_0 RV_0 P + \cdots + PV_0 RV_0 RV_0 RV_0 P.
\]

There are six terms that give a Raman contribution at fourth order in \(V\), with the two \(V_1\) terms corresponding one incoming photon and one outgoing photon. Analyzing these terms carefully, we find that the Raman couplings can be derived by attaching photon factors, \(\sim \pm \mathbf{A} \cdot \mu\), to two of the four hoppings in each super-exchange process.

In light of this, we can write down \(H_R^{(4)}\) explicitly. We first write \(A_{k_x}\) in terms of photon operators, splitting it into two parts\(^{26,49}\)

\[
A_{k_x} \approx g_{\hat{k},\hat{x}} a_{k_x,\hat{x}} e^{ik \cdot x} + g_{f_{K_x,\hat{x}}} f_{k_x,\hat{x}} e^{ik \cdot x} \equiv A_i + A_f. \tag{39}
\]

Here, \(a_{k_x,\hat{x}}\) and \(a_{k_x,\hat{x}}^\dagger\) represent the real photons, not to be confused with the emergent excitations that exist in QSI. The vectors \(\hat{k}\) and \(\hat{x}\) denote the polarization vectors of the incoming and outgoing photons, respectively. The \(g_{\hat{k},\hat{x}}\) and \(g_f\) are constant prefactors depending on the incoming/outgoing photon frequencies. We will omit them in what follows. Further, since the photon wave-vector is small relative to the inverse lattice spacing, we can safely replace \(e^{ik \cdot x} \sim e^{ik \cdot x} - 1\), keeping only the polarization vectors \(\hat{k}\) and \(\hat{x}\).

For a hopping process involving bonds \(\mu\) and \(\nu\), the incoming and outgoing EM operator \(A_i\) and \(A_f\) can couple to \(\pm \mu\) and \(\pm \nu\). There are 12 possibilities in total for choosing two out of four bonds to couple with \(A_i\) and \(A_f\) (see Fig. 1). The overall prefactor is then found to be

\[
(A_i \cdot (\pm \mu))(A_f \cdot (\mp \mu)) + (A_i \cdot (\pm \mu))(A_f \cdot (\pm \nu)) + (A_i \cdot (\pm \nu))(A_f \cdot (\mp \nu)) + (A_i \cdot (\pm \nu))(A_f \cdot (\pm \nu)) - (A_i \cdot (\pm \mu))(A_f \cdot (\pm \mu)) + (A_i \cdot (\pm \nu))(A_f \cdot (\pm \nu)).
\]

Since the Raman vertex and the effective Hamiltonian have similar mathematical form, we can easily express the Raman vertex in terms of spin operators.\(^{26,49}\) The final result for the Raman part of the effective Hamiltonian is given by

\[
H_R^{(4)} \sim \sum_{\mu<\nu} [(A_i \cdot \mu)(A_f \cdot \mu) + (A_i \cdot \nu)(A_f \cdot \nu)] R_{\mu\nu}, \tag{40}
\]

where the operator \(R_{\mu\nu}\) is defined as
We next outline how to compute the Raman response in the

\[ \mathbb{R}_{\mu
u} = \sum_{x \in \Lambda} \left[ J_x \left( S^z_{x\mu} S^z_{x\nu} + S^z_{x\mu} \bar{S}^z_{x\nu} + h.c. \right) - J_{\pm} \left( S^z_{x\mu} \bar{S}^z_{x\nu} + S^z_{x\mu} S^z_{x\nu} + h.c. \right) \right] \]

where \( J \) is the exchange integral and \( \bar{S}^z \) is the Raman operator given in Eq. (46) and \( E_n, |n\rangle \) are the energies and eigenstates of the system. Also, since we are interested in the Raman response at zero-temperature we only have intensity for positive \( \Omega \). It is convenient to compute the 

\[ F(\Omega) = \int dt e^{i\Omega t} \left[ -i(\epsilon^\mu \mathcal{R}(t) \mathcal{R}(0)) \right] , \]

where \( \mathbb{R} \) is the Raman operator given in Eq. (46) and \( E_n, |n\rangle \) are the energies and eigenstates of the system. Also, since we are interested in the Raman response at zero-temperature we only have intensity for positive \( \Omega \). It is convenient to compute the

\[ I(\Omega) \equiv \sum_n |\langle n|\mathcal{R}(0)\rangle|^2 \delta(\Omega - E_n - E_\delta) \]

\[ J(\Omega) = \frac{1}{\pi} \Theta(\Omega) \text{Im} F(\Omega) , \]

\[ D_{\mu\nu\mu'\nu'}(t) = -i(\epsilon^\mu \mathcal{R}_{\mu
u}(t) \mathcal{R}_{\mu'\nu'}(0)) \]

\[ I_{\mu\nu\mu'\nu'}(\Omega) = \frac{1}{\pi} \Theta(\Omega) \text{Im} \int dt e^{i\Omega t} D_{\mu\nu\mu'\nu'}(t) . \]
For example, in terms of this generalized intensity the response in the $T_{2g}$ channel is given by
\[ I_{T_{2g}}(\Omega) \equiv I_{01,01}(\Omega) - I_{01,23}(\Omega) - I_{23,01}(\Omega) + I_{23,23}(\Omega). \] (53)

Since the QSI state is fully symmetric, the intensity in each of the $T_{2g}$ channels will be identical. We thus use a common notation $I_{T_{2g}} = I_{T_{2g}}^f = I_{T_{2g}}^g \equiv I_{T_{2g}}$.

To aid in the interpretation of these results, we divide the Raman operators and the intensities into several parts that represent qualitatively distinct physical processes. As for the $H_{\text{QSI}}$, Eq. (16) Hamiltonian, we can write the Raman operator in terms of the spinon and gauge-fields. We thus write the generalized Raman operator, $R_{\mu\nu}$, as a sum of several contributions
\[ R_{\mu\nu} \equiv R_{\mu\nu}^g + R_{\mu\nu}^A + R_{\mu\nu}^E. \] (54)

There are three parts here: the scattering from spinons, $R^g$, the scattering from a combination of spinon and gauge excitations, $R^A$, and the scattering from the emergent light itself, $R^E$. In computing the Raman operator, we consider only the leading terms of the exponential of the gauge field, as we did in Eq. (16). These parts are closely related to the decomposition of $H_{\text{QSI}}$ [Eq. (16)] into $H_g$ and $H_{\text{KA}}$.

We begin with the terms of the Raman operator in Eq. (41) proportional to $J_{\alpha}$ which can be written as spinon-only and spinon-gauge interactions. These terms can be expressed analogously to $H_g$ and $H_{\text{KA}}$ [see Eqs. (17) and (29)] as
\[
R_{\mu\nu}^g = -\frac{J_g}{\hbar} \sum_{k,l} f_{\mu\nu}(k)\psi_{k,l}^{\dagger}\psi_{k,l},
\]
\[
R_{\mu\nu}^A = -\frac{J_A}{\hbar N} \sum_{k,p,\rho} f_{\mu\nu,\alpha}(k, p)\psi_{k+p,\rho}^{\dagger}\psi_{k,\rho} A_{\alpha,\rho},
\]
\[
R_{\mu\nu}^E \equiv R_{\mu\nu}^{E_{\chi}}[E_{\chi}E_{\chi} + E_{\chi}E_{\chi+\mu-\nu}],
\]
\[
= \sum_{k} f_{E_{\chi}}^{\mu\nu}(k)E_{k}\cdot E_{-k},
\] (55c)

where the vertex $f_{\mu\nu}(k)$ is defined in Eq. (18) and the vertex $f_{\mu\nu,\alpha}(k, p)$ is defined in Eq. (30).

Next we consider the terms of the Raman operator [Eq. (41)] that are proportional to $J_{zz}$. These terms can be written using the electric field operators $E_{\chi}$ as
\[ R_{\mu\nu}^E \equiv \sum_{x,\chi} \left[ E_{\chi x}E_{x \chi} + E_{\chi x}E_{x+\mu-\nu,\chi} \right], \]
\[ = \sum_{k} f_{E_{\chi}}^{\mu\nu}(k)E_{k}\cdot E_{-k}, \] (55c)

where we have defined the vertex
\[ f_{E_{\chi}}^{\mu\nu}(k) \equiv 1 + e^{-i(kq_{\chi-\nu})}. \] (56)

Note that, in contrast to the $J_{\alpha}$ parts of the Hamiltonian, since the Raman operator contains $\sim \sum_{x} S_{x/2}^{z}S_{x/2}^{z}$, not summed over $\mu, \nu$, one cannot easily represent this operator in terms of the charges $Q_x$.

At leading order, these three parts do not mix since they create distinct sets of excitations. We now calculate the intensity for each of these different mechanisms.

## A. Spinon-only contribution

This process involves the light scattering from a pair of spinons. Since the incoming light carries (essentially) zero momentum, this pair of particles must also have zero total momentum. The spinon-only part of the response tensor is given by
\[ D_{\mu\nu,\mu'-\nu'}^{\phi}(t) \equiv -i\langle T R_{\mu\nu}(t) R_{\mu'-\nu'}^{\phi} \rangle, \]
\[ = -i\frac{J_g^2}{\hbar} \sum_{k, k', \lambda} \int_{-\infty}^{\infty} dt \left( T \psi_{k}(t)\psi_{k'}(t)\psi_{k,\lambda}^{\dagger}\psi_{k',\lambda}^{\dagger} \right), \]
\[ \times \langle T \psi_{k}(t)\psi_{k'}(t)\psi_{k,\lambda}^{\dagger}\psi_{k',\lambda}^{\dagger} \rangle, \] (58)

where $R^{\phi}_{\mu\nu}$ is defined in Eq. (17) and $f_{\mu\nu}(k)$ in Eq. (18). Using Eq. (22), we can write the response tensor as
\[ D_{\mu\nu,\mu'-\nu'}^{\phi}(t) = 2i\frac{J_g^2}{\hbar} \sum_{k} f_{\mu\nu}(k) f_{\mu'-\nu'}(k) G_{\phi}(k, t)G_{\phi}(k, t), \]
\[ \equiv R_{\mu\nu}^{\phi}(k) f_{\mu'-\nu'}(k) \equiv 4 \cos[k \cdot (\mu - \nu)] \cos[k \cdot (\mu' - \nu')]. \] (60)

The intensity tensor for the spinon-only contribution is thus given by
\[ I_{\mu\nu,\mu'-\nu'}^{\phi}(\Omega) \equiv \frac{1}{\pi} \Theta(\Omega) \text{Im} \int dt e^{i\Omega t} D_{\mu\nu,\mu'-\nu'}^{\phi}(t), \]
\[ = 4 \int_{-\infty}^{\infty} dt e^{i\Omega t} \left( \sum_{k} f_{\mu\nu}(k) f_{\mu'-\nu'}(k) \right) \frac{\delta(\Omega - 2E_k)}{4E_k^2}, \] (61)

where the Green’s function integrals are computed using conventional techniques. To obtain the response in the $T_{2g}$ channel we use Eq. (53) and get
\[ I_{T_{2g}}^{\phi}(\Omega) = \int_{-\infty}^{\infty} dt e^{i\Omega t} \left( \sum_{k} \frac{8}{E_k^2} \sin^{2}\left(\frac{k_{z}}{2}\right) \sin^{2}\left(\frac{k_{z}}{2}\right) \delta(\Omega - 2E_k) \right), \]
\[ = \frac{8}{E_k^2} \left\{ \int_{-\infty}^{\infty} dt e^{i\Omega t} \left( \sum_{k} \frac{8}{3} \sin^{2}\left(\frac{k_{z}}{2}\right) \sin^{2}\left(\frac{k_{z}}{2}\right) \delta(\Omega - 2E_k) \right) \right\}. \] (62)

In the last step we have symmetrized the vertex to emphasize that this intensity is valid for each of the $R_{T_{2g}}$ Raman operators.

## B. Spinon-gauge contribution

Next we consider the spinon-gauge contribution. Here, in addition to exciting a spinon-pair, the light also excites an emergent photon. Due to the accompanying emergent photon, the spinon-pair can have arbitrary total momentum. To evaluate the intensity, we consider the response tensor
\[ D_{\mu\nu,\mu'-\nu'}^{A}(t) = -i\langle T R_{\mu\nu}(t) R_{\mu'-\nu'}^{A}(0) \rangle, \]
\[ \equiv \sum_{x,\chi} \left[ E_{\chi x}E_{x \chi} + E_{\chi x}E_{x+\mu-\nu,\chi} \right], \] (63)
where $R^{A}_{\mu\nu}(t)$ is defined in Eq. (29). Next step in computing $D^{A}_{\mu'\nu'}(t)$ is the evaluation of

$$-i\langle T \psi_{k+p,t}^\dagger(t)\psi_{k,t}(t)\psi_{k'p',t}^\dagger(t)\psi_{k'p',t}\rangle.$$ 

There is one relevant contraction, which yields

$$-\delta_{p,-p'}\delta_{k,k'}\delta_{k+k'}\delta_{\nu,\nu'}\delta_{\mu',\mu}G_{\psi}(k,t)G_{\psi}(k+p,t)G_{A}(p,t),$$

where $G_{\psi}(k,t)$ and $G_{A}(p,t)$ are the Green’s function of the spinon and gauge-field, respectively, as defined in Eqs. (22) and (28a). The response tensor $F^{A}_{\mu'\nu'}(t)$ is then given by

$$F^{A}_{\mu'\nu'}(t) = \frac{-i}{N} \sum_{kp} \Phi_{\mu'\nu'}(k,p)G_{\psi}(k,t)G_{\psi}(k+p,t)G_{A}(p,t),$$

where we have defined the vertex

$$\Phi_{\mu'\nu'}(k,p) = \sum_{lp} [f^{A}_{\mu\nu,p}(k,p)]^* f^{A}_{\mu'\nu',p}(k,p).$$

Performing the time integral [see Eq. (52)] using standard contour methods, we obtain the intensity tensor in the spinon and gauge-field channel to be

$$I^{A}_{\mu'\nu'}(\Omega) = \frac{-i}{N} \sum_{kp} \Phi_{\mu'\nu'}(k,p) \frac{U}{8E_k E_{k+p} E_p} \times \delta(\Omega - (E_k + E_{k+p} + E_p)).$$

(65)

For the $T_{2\gamma}$ channel, the vertex is given by

$$\Phi_{T_{2\gamma}}(k,p) = 16 \left(1 - \cos k_y \frac{p_y}{2} - \cos k_x \frac{p_x}{2}\right).$$

(66)

The final result for the spinon-gauge contribution to the $T_{2\gamma}$ intensity is then

$$I^{A}_{T_{2\gamma}}(\Omega) = \frac{-i}{N} \sum_{kp} \frac{2U}{E_k E_{k+p} E_p} \delta(\Omega - (E_k + E_{k+p} + E_p)) \times \left(1 - \cos k_y \frac{p_y}{2} - \cos k_x \frac{p_x}{2}\right).$$

We see that if the photon energy scale is small, the intensity is proportional to the density of states of the spinon pairs with arbitrary total momentum. As in the spinon-only case, we rewrite the intensity $I^{A}_{T_{2\gamma}}(\Omega)$ in a manifestly symmetric form as

$$I^{A}_{T_{2\gamma}}(\Omega) = \frac{-i}{N} \sum_{kp} \frac{2U}{E_k E_{k+p} E_p} \delta(\Omega - (E_k + E_{k+p} + E_p)) \times \left(1 - \frac{1}{3} \sum_{a<\beta} \cos k_a \frac{p_a}{2} \cos k_\beta \frac{p_\beta}{2}\right).$$

C. Electric field contribution

Finally, we consider the contribution from the electric field alone. Physically, this process corresponds to the light exciting a pair of emergent photons. As in the case of spinons alone, the pair of emergent photons has zero total momentum. The relevant response tensor is

$$D^{E}_{\mu'\nu'}(t) = -i\langle T R^{E}_{\mu'\nu'}(t) R^{E}_{\mu'\nu'} \rangle$$

$$= \sum_{pp'} f^{E}_{\mu'\nu'}(p) f^{E}_{\nu'\mu'}(p') \delta(\Omega - (E_{p} + E_{p'} + E_{p'} E_{p'})),$$

where $R^{E}_{\mu'\nu'}$ is defined in Eq. (55c). This correlation function has two relevant contractions leading to

$$D^{E}_{\mu'\nu'}(t) = i \sum_{p} [\delta_{\mu\nu} - \delta_{\mu\nu'} - \delta_{\mu'\nu}] [f^{E}_{\mu'\nu'}(p)]^2 G_{E}(p,t)^2,$$

where the Green’s function for the electric field, $G_{E}(k,t)$, is defined in Eq. (28b). Evaluating the time integral [see Eq. (52)] one finds

$$\frac{1}{\pi} \int dt e^{i\Omega t} G_{E}(p,t)^2 = \frac{e_p^2}{4U^2} \left[\delta(\Omega - 2\epsilon_p) + \delta(\Omega - 2\epsilon_p)\right].$$

We thus have the generalized intensity from the electric fields

$$I^{E}_{\mu'\nu'}(\Omega) = \sum_{p} \frac{e_p^2}{4U^2} \left[\delta_{\mu\nu} - \delta_{\mu\nu'} - \delta_{\mu'\nu}] [f^{E}_{\mu'\nu'}(p)]^2 \delta(\Omega - 2\epsilon_p).$$

(68)

The intensity can easily be evaluated for the $T_{2\gamma}$ channel, yielding

$$I^{E}_{T_{2\gamma}}(\Omega) = \sum_{p} \frac{e_p^2}{U^2} \left[1 + \cos \frac{p_y}{2} \cos \frac{p_x}{2}\right] \delta(\Omega - 2\epsilon_p)$$

$$= \sum_{p} \frac{e_p^2}{U^2} \left[1 + \frac{1}{3} \sum_{a<\beta} \cos \frac{p_a}{2} \cos \frac{p_\beta}{2}\right] \delta(\Omega - 2\epsilon_p).$$

This intensity reflects the density of states of a pair of emergent photons with total momentum zero. As in the spinon-only and spinon-gauge cases, we have given the symmetric form for this intensity.
D. Total intensity

The total intensity in the $T_{2g}$ channel is thus given by the following sum:

$$I^T_{T_{2g}}(\Omega) = I^\phi_{T_{2g}}(\Omega) + I^{\phi_A}_{T_{2g}}(\Omega) + I^E_{T_{2g}}(\Omega),$$

where the three different contributions are given by

$$I^\phi_{T_{2g}}(\Omega) = j_s^2 \sum_k \frac{8}{E_k^2} \left[ \frac{1}{3} \sum_{\alpha<\beta} \sin^2 \left( \frac{k_\alpha}{2} \right) \sin^2 \left( \frac{k_\beta}{2} \right) \right] \delta(\Omega - 2E_k),$$

$$I^{\phi_A}_{T_{2g}}(\Omega) = j_s^2 \sum_k \frac{2U}{N} \left[ 1 - \frac{1}{3} \sum_{\alpha<\beta} \cos \left( \frac{k_\alpha + p_\alpha}{2} \right) \cos \left( \frac{k_\beta + p_\beta}{2} \right) \right] \delta(\Omega - (E_k + E_{k+p} + \epsilon_p)), $$

$$I^E_{T_{2g}}(\Omega) = \sum_p \frac{\epsilon_p^2}{U^2} \left[ 1 + \frac{1}{3} \sum_{\alpha<\beta} \cos \left( \frac{p_\alpha}{2} \right) \cos \left( \frac{p_\beta}{2} \right) \right] \delta(\Omega - 2\epsilon_p).$$

E. Numerical results

With the developed formalism in hand, we now numerically evaluate the Raman intensities in the $T_{2g}$ polarization channel. We examine the contribution from each of the different physical processes: namely the spinon-only, spinon-gauge and gauge-only contributions. The single sums found of Eqs. (70a) and (70b) were evaluated on a grid of $384^3$ $k$ points, with the origin shifted by a small amount to resolve any singularities in the vertices at $k = 0$. For the double sum of Eq. (70c), a similar procedure was employed, but $48^3$ points for each momentum proved sufficient to reach convergence. The results for the Raman intensity profiles are presented in Fig. 3. This figure contains the main results of this paper. All intensities are computed assuming $j_s = 0.05$ (taking $\langle s^2 \rangle = 1$ for simplicity) and are normalized to the maximum intensity of the spinon-only Raman response.

First, we consider the Raman intensity from the spinon-only scattering. As expected, this contribution has intensity centered around the classical spinon energy cost $\sim J_z$ with a width proportional to the energy of the tunneling term $J_z$. Since the incoming light can only generate a spinon pair with zero total momentum, this channel does not probe the full two-spinon continuum. Some aspects of the spinon-only response can be better understood by considering the zero-momentum, two-spinon density of states defined as

$$\rho_\phi(\Omega) \propto \sum_k \delta(\Omega - 2E_k),$$

as shown in Fig. 4(a). Here we can see that the onset of the spinon density of states is $\sim \sqrt{\Omega - \Omega_0}$ with $\Omega_0 = \sqrt{1 - 12J_z}$ being twice the gap in the spinon dispersion of Eq. (21). Further, the density of states also has a sharp peak (Van Hove singularity) due to the presence of flat regions in the spinon dispersion. These features – a slow onset at low frequencies and a large intensity near the maximum of the two-spinon band – are characteristic features of the two-spinon Raman response.
The Raman response from coupled spinon and gauge fluctuations also takes the form of a broad continuum in roughly the same range of energies as the two-spinon case. However, the excitation of the emergent gauge photon now allows access to the full two-spinon continuum, as its presence relaxes the constraint on having zero total momentum for the spinon pair. Correspondingly, the Raman response in this channel includes the full two-spinon continuum. While this does not change the maximum or minimum of the two-spinon energies (compared to the zero-momentum case), it does affect the intensity profile at intermediate energies. As in the spinon-only case the spinon-gauge intensity can be better understood by considering the corresponding density of states

\[ \rho_{\delta A}(\Omega) \propto \sum_{kp} \delta(\Omega - (E_k + E_{k+p} + \epsilon_{p})), \]  

(72)
as shown in Fig. 4(b). One important feature is that the width of this broad continuum is slightly larger than that of the pure two-spinon scattering; due to the interaction with the gauge-field, the combined spinon-photon states can reach higher energies than the spinons alone. This can be seen in the bottom right inset of Fig. 3, where the upper edge of the intensity is pushed to higher energies. However, this shift is quite small, being proportional to the emergent photon bandwidth, which scales as \( \sim f_{\epsilon}^2 \). Given this fact, we can effectively ignore the energy of gauge particle in the \( \delta \)-functions in \( I_{\delta A} \). Physically, the photon is thus acting as a “momentum-sink” for the spinon-pair: for essentially zero energy cost one can excite a photon with arbitrary momentum.

Finally, we consider the gauge-field-only response from the emergent electric field. It appears as a strong, sharp peak at the energies corresponding to the emergent photon bandwidth. The energy scale of the emergent photon dispersion relation goes as \( \sim f_{\epsilon}^2 \) and is thus much smaller than the energy scale of the aforementioned features that involve the spinons. The intensity profile of the Raman response in this case follows very closely the zero-momentum, two-photon density of states

\[ \rho_A(\Omega) \propto \sum_p \delta(\Omega - 2\epsilon_{p}), \]  

(73)
which is shown in Fig. 4(c). At low energies, this intensity follows a power-law \( \sim \Omega^2 \) due to the linear photon dispersion.

The flat dispersion in the photon band structure at the edge of the band (at \( \Omega = 8\epsilon \)) is also apparent high intensity at the highest energies. The larger intensity relative to the spinon features seen in Fig. 3 originates from the lack of a \( \sim f_{\epsilon}^2 \) prefactor in the Raman intensity since this scattering processes is due to the large \( J_{zz} \) interactions, and the narrow support in \( \Omega \).

VI. DISCUSSION

In this section we discuss some of the limitations of the results derived in this work and how they may affect applications to real materials. In particular, we discuss the microscopic origins of the Raman operator, the approximations made in the slave-particle formulation and speculate on the effects of the so far ignored anisotropic \( J_{k\pm} \) and \( J_{zz} \) interactions on the Raman intensity.

A. Slave-particle formulation

In Secs. II and III we introduced a slave-particle formulation for QSI and a framework to enable calculation of the Raman response. There are a number of approximations involved in the slave-particle framework used in this work.

First, in our analysis, we considered only the first order coupling between the spinons and gauge fluctuations, i.e. we kept only the first order terms in the expansion of the exponential \( e^{A} \). This approximation is not necessarily controlled. Indeed this approximation removes completely the gauge monopoles, a set of excitations of the gauge sector with energy comparable to that of the emergent photon. These excitations appear only non-perturbatively in \( A \). A detailed analysis of corrections from the higher orders in the expansion of \( e^{A} \) gauge sector and the possibility of including the gauge monopoles are left for future exploration.

Second, we have computed the response for the XXZ model where only \( j_{\pm} \) is non-zero. The features seen in the intensities are likely to be modified if the Raman response was computed for the complete and more general anisotropic exchange model, Eq. (1). The \( J_{zz} \) terms would bring another spinon-gauge
field interaction vertex, and the $J_{\pm\pm}$ terms would bring a four-spinon interaction vertex. A detailed analysis of these vertices is, technically, significantly more involved, and we therefore leave it for future study. However, believe that the basic qualitative features of the Raman response, the broad intensity continuum and its width would not be changed significantly by the inclusion of these interactions. The detailed features, such as the sharpness of the peak in the spinon-only response, would likely be modified.

Third, one key deficiency in the mean-field theory presented in Sec. II is that the effects of the gauge-field on the spinon are treated in an averaged way. It is unclear whether such an approximation is valid in QSI, given the energy scale of the photon is much lower than the kinetic energy of the spinons. However, recent more exact treatments of the spinon excitations in related contexts, have found that treating the spinon as a (strongly) renormalized free particle, may not be too poor of an approximation.

Finally, we note that the emergent photon-only response is derived entirely from the gauge part of the model, $H_g$. This is essentially equivalent to the lattice gauge theory of Ref. [17] used to describe the physics of QSI when the spinons are not included. This description has proven to be quite accurate in computing the static properties of QSI in this limit, faithfully reproducing the results of direct simulation. We thus expect that our results for the low energy, electric only part of the Raman intensity to be robust, as it is independent of some of these coarser approximations used in the slave-particle formulation.

B. Microscopic considerations

In Sec. IV we derived the Raman operator through degenerate perturbation theory. In doing so we made several approximations that simplify both the calculation and the form of the Raman operator.

First, we comment on the generated polarization channels. Within the approximations used, one obtains an inactive $A_{1g}$ channel and an active $T_{2g}$ channel. The Raman operator, $\mathcal{R}$ [see Eq. (41)]] for each of these channels mimics closely the “parent” exchange model, $H_{\text{ex}}$ [see Eq. (1)], with the different anisotropic interactions appearing in the same ratios as in the exchange Hamiltonian. The appearance of these exchange constants in the Raman operator is predicated on the assumption that one can neglect the photon energies in the relevant denominators in the perturbation theory. When this condition is relaxed, the form of the Raman operator becomes decoupled from that of the exchange Hamiltonian. Indeed, the rich structure of the intermediate states involved in rare-earth superexchange processes will likely affect not only the scale of the interactions, but also the relative importance of the various anisotropic terms. Because of this, we would expect additional polarization channels to be generated and that the inactive $A_{1g}$ would become active. Roughly, such corrections would be proportional to $\omega_i/U_f$ where $\omega_i$ is the incoming light frequency and $U_f$ is a typical rare-earth charge-transfer energy scale.

Second, we note here that our treatment of the Raman intensity only includes contributions from two-ion processes, whereas single-ion processes, for example mediated through the 5d orbitals of the rare-earth site or through the surrounding oxygen ions, have not been included in our calculation. Since the energy cost of single-spin flips and two-spin-flips can be of the same order in QSI materials, these processes might also be important. This can be contrasted with the separation of energy scale in one- and two-magnon processes in conventionally ordered magnets. For Kramers ions, any single-ion Raman operator is necessarily time-reversal odd, and thus must vanish as the frequency of the incoming light becomes small relative to the atomic energy scales, providing some suppression of such contributions. Further, the Raman response will be non-zero only in the $T_{1g}$ channel, as time-reversal odd operators only appear in anti-symmetric channels, which for $O_4$ there is only $T_{1g}$. For non-Kramers ion, the single-ion transverse $S^\pm$ operators can appear in the Raman operator without such suppression. Within the context of our calculations here, such single-ion terms are most easily generated via second-order virtual processes that only involve the surrounding oxygen atoms. For the two axial oxygen ions we have included (see Fig. 1 and Sec. IV), such a contribution vanishes (for details see Appendix B). However, there are six additional, lower symmetry oxygens that we have not considered. If these are included, single-ion terms are generated and they contribute to the Raman response in both the $E_g$ and $T_{2g}$ channels. However, these may be somewhat suppressed given the larger distance to these oxygens. Even given these complications, one should note that these single-ion operators probe the same excitations as the two-ion operators: the $S^\pm$ type terms excite spinon-pairs, while the $S^2$ type terms excite emergent photons. We thus do not expect any qualitative change in the results presented here for the $T_{2g}$ channel when such single-ion terms are included.

VII. CONCLUSIONS

In this paper, we proposed a theory of the Raman scattering in the XXZ limit of the general anisotropic exchange model, which we analyzed using a slave-particle formulation of QSI. We derived the Raman vertex using the traditional framework of an effective Hamiltonian for the interaction of light with spin degrees of freedom. We showed that, at fourth order in perturbation theory, the Raman vertex of Eq. (42) takes a Loudon-Fleury form, generated by photon-assisted superexchange, following the anisotropic exchange model [Eq. (16)] that leads to the QSI behavior. We also showed that the Raman vertex naturally decomposes into two channels corresponding to the irreducible representations $A_{1g}$ and $T_{2g}$ of the lattice point group. Moreover, since the Raman vertex in the $A_{1g}$ channel commutes with the QSI Hamiltonian, the Raman intensity is non-zero only in the $T_{2g}$ polarization channel. Within this framework, we decomposed the Raman intensity into three contributions, from the pure spinon field, coupled spinon and gauge fluctuations and the emergent photon. We showed that the dominant feature of the overall response consists of a broad continuum from the two-spinon spectrum and a sharp narrow peak at low energy originating from the gauge fluctuations of the emergent photon field taken alone. To conclude, we com-
ment below on a few aspects of Raman scattering in general, as well as discuss relevance of these results to real candidate QSI materials.

First, a unique feature of Raman scattering is the ability to probe characteristics of the system that are not directly related to the magnetic moments. For example, the QSI candidates to date have mostly been studied with tools such as neutron scattering. While this approach has proven to be very powerful, there are some limitations when the pseudo-spins are of dipolar-octupolar or non-Kramers character, as they are in Dy$_2$Ti$_2$O$_7$, Ho$_2$Ti$_2$O$_7$, Tb$_2$Ti$_2$O$_7$ and in the Pr$_2$M$_2$O$_7$ family. For these compounds, the transverse components of the pseudo-spin are higher multipoles (quadrupoles or octupoles) and thus are not easily visible in neutron scattering. So while inelastic neutron scattering could observe the photon excitation in such materials (in principle, with sufficient energy resolution), observing the spinon excitations is very difficult. The possibility of seeing the two-spinon continuum at all, irrespective of resolving distinct signatures or features, is from a fundamental perspective a strong asset for Raman scattering as a probe of QSI candidate materials.

Second, from a broader perspective, we would like to comment on the possibility to use Raman scattering as a tool to study the phase transitions between different magnetic phases. In particular, it would be interesting to compare the Raman responses arising from a QSL phase and nearby ordinary magnetically ordered phase appearing at slightly different set of parameters of the same model. For example, aside from exotic phases such as QSI and the conjectured Coulomb ferromagnet, there are also four magnetically ordered phases found in the phase diagram of the anisotropic exchange model. These are the antiferromagnetic $\Gamma_3$ states, a family of splayed ferromagnets, the Palmer-Chalker state and the all-in-all-out (AIAO) order. Even in the simple limit considered here with $J_{xx} = J_{zz} = 0$, there is the nearby $\Gamma_3$ state that is stabilized for $J_{xx} \gtrsim 0.06$. The transition into the state can be captured with the slave-particle description used here and it corresponds to the condensation of the spinons, which is similar to the gauge symmetry breaking in the Higgs’ mechanism. More generally, near the boundary of a QSL and a magnetically ordered phase, one may expect both the conventional excitations of the ordered phases and the unconventional excitations of the QSL to be generically present. The ability to track both the conventional and unconventional excitations across the phase transition through their Raman response could prove useful in the understanding of both phases and the transition itself.

One last and yet very important question to address is the possibility to see the Raman responses in experiments on real QSI materials. As far as we know, no magnetic Raman experiments have been done on QSI materials so far. One clear obstacle is the energy scale of exchange interactions in the rare-earth magnets is considerably smaller than one in many transitional metal magnets. For the rare-earth pyrochlore quantum spin ice materials, these coupling constants are typically on the order of 0.1meV. Coupling constants of this magnitude will produce the gross features (scattering from spinons) at energies of order 1-2 cm$^{-1}$, which is, unfortunately, much smaller than the lower limit accessible by current Raman spectroscopy, which typically probes excitations ranging 1-100 meV (10-1000 cm$^{-1}$). However, one possible way to resolve this conundrum might be with Brillouin scattering, which does well for probing energy scales 0.01-1 meV (0.1-10 cm$^{-1}$) and which differs from Raman scattering technique only by the type of spectrometer. However, even with such a setup, the intensity due to scattering from the emergent photon is likely to remain challenging to expose. Further complications can arise in spin ice systems where the spin ice manifold itself is split by dipolar interactions, such as in Dy$_2$Ti$_2$O$_7$ or Ho$_2$Ti$_2$O$_7$. This splitting carries over to the spinon (or classical “monopole”) excitations and thus could mimic the effects of a quantum dispersion in the Raman intensity.

On the other hand, as material science is a fast developing field of research, we believe that new QSI materials with stronger quantum effects may be designed or discovered. One tantalizing possibility could be the discovery of a transition-metal quantum spin ice candidate. If such a system were to exist, a large increase (one or two orders of magnitude) in energy scale relative to the rare-earth materials considered in the present work could possibly render many of the features discussed here at much more experimentally accessible energies. In such a scenario, not only the spinon continuum, but the emergent photon itself could even be visible within experimentally accessible energy ranges.

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Appendix A: The definition of local coordinate space and the $\zeta$ matrix

The definition of the lattice vectors $\mu$ is:

\[
\hat{0} = \frac{\hat{x} + \hat{y} + \hat{z}}{4}, \quad \hat{1} = \frac{\hat{x} - \hat{y} - \hat{z}}{4}, \quad \hat{2} = \frac{\hat{y} - \hat{x} - \hat{z}}{4}, \quad \hat{3} = \frac{\hat{z} - \hat{x} - \hat{y}}{4},
\]

where $\hat{x}, \hat{y}, \hat{z}$ denote the global cubic axes. The local coordinates ($\hat{x}_\mu, \hat{y}_\mu, \hat{z}_\mu$) for the four sites (labeled as $\mu = 0, 1, 2, 3$) of
a certain tetrahedron of the pyrochlore lattice are defined as

\[
\hat{x}_0 = -\frac{2\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}}{\sqrt{6}}, \quad \hat{y}_0 = -\frac{\hat{\mathbf{y}} + \hat{\mathbf{z}}}{\sqrt{2}}, \quad \hat{z}_0 = \frac{\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}}{\sqrt{3}}, \tag{A2a}
\]

\[
\hat{x}_1 = -\frac{2\hat{\mathbf{x}} - \hat{\mathbf{y}} - \hat{\mathbf{z}}}{\sqrt{6}}, \quad \hat{y}_1 = \frac{\hat{\mathbf{y}} - \hat{\mathbf{z}}}{\sqrt{2}}, \quad \hat{z}_1 = \frac{\hat{\mathbf{x}} - \hat{\mathbf{y}} - \hat{\mathbf{z}}}{\sqrt{3}}, \tag{A2b}
\]

\[
\hat{x}_2 = \frac{2\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}}{\sqrt{6}}, \quad \hat{y}_2 = -\frac{\hat{\mathbf{y}} - \hat{\mathbf{z}}}{\sqrt{2}}, \quad \hat{z}_2 = \frac{-\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}}{\sqrt{3}}, \tag{A2c}
\]

\[
\hat{x}_3 = \frac{2\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}}{\sqrt{6}}, \quad \hat{y}_3 = \frac{\hat{\mathbf{y}} + \hat{\mathbf{z}}}{\sqrt{2}}, \quad \hat{z}_3 = \frac{-\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}}{\sqrt{3}}. \tag{A2d}
\]

In Eq. (1), the phase factors \(\gamma\) and \(\zeta\) are defined as

\[
\gamma_{\mu\nu} = \begin{pmatrix}
0 & 1 & \omega & \omega^2 \\
1 & 0 & \omega^2 & 1 \\
\omega & \omega^2 & 0 & 1 \\
\omega^2 & \omega & 1 & 0
\end{pmatrix}, \tag{A3}
\]

where \(\omega = e^{2\pi i/3}\) and \(\zeta_{\mu\nu} = -\gamma^*_{\mu\nu}\).

Appendix B: Second order contributions to the Raman vertex

Here we consider the second order terms, \(\sim PVRVP\), in the perturbative expansion Eq. (37). These processes can only result in operators acting on a single rare-earth ion. Evaluating these terms within the charging approximation\(^\text{16,22}\), one finds

\[
H^{(2)}_R = PV_j RV_j P, \tag{B1}
\]

\[
\sim -\left(\frac{e}{\hbar c}\right)^2 \sum_{\mu\nu} (\hat{\mathbf{e}}_\mu \cdot \hat{\mathbf{e}}_\nu) \sum_{\mathbf{r}_0, \mathbf{r}_1} P f_{\mathbf{r}_1,\mu} f^\dagger_{\mathbf{r}_0,\nu} P, \]

where, loosely, \(U_f\) is an energy scale associated with the cost transferring a hole from an oxygen to the rare-earth ion. As in Sec. IV, we including only hoppings to the high-symmetry oxygens\(^\text{47}\) that sit at the centers of the rare-earth tetrahedra (Wyckoff site 8b). By construction \(H^{(2)}_R\) is symmetric in the polarizations \(\hat{\mathbf{e}}_\mu\) and \(\hat{\mathbf{e}}_\nu\). Since coupling to time-reversal odd operators must be in anti-symmetric channels,\(^\text{71}\) no time-reversal odd operators can be generated by this process. This holds even when the charging approximation is lifted and when energy of the light is included in the resolvents. For Kramers doublets, this implies that \(H^{(2)}_R\) does not contribute to the Raman response. For non-Kramers doublets, this implies operators appearing \(H^{(2)}_R\) must be time-reversal even. We can thus (effectively) consider the operator

\[
P f_{\mathbf{r}_1,\mu} f^\dagger_{\mathbf{r}_0,\nu} P \sim h^0_{\mathbf{r}_0} + h^+_{\mathbf{r}_0} S^-_{\mathbf{r}_1} + h^-_{\mathbf{r}_0} S^+_{\mathbf{r}_1} \tag{B2}
\]

For a given rare-earth site, the two high-symmetry oxygens are along the \(\pm \hat{\mathbf{z}}\) directions. Because of this, within the Slater-Koster (two-center) approximation\(^\text{24}\), one then has that \(t_{\mu\nu}^f\) is diagonal. The diagonal operators \(P f_{\mathbf{r}_1,\mu} f^\dagger_{\mathbf{r}_0,\nu} P\) are then invariant under rotations about the \(\hat{\mathbf{z}}\). Since the \(S^\pm_{\mathbf{r}_1}\) are not invariant under these rotations, this implies that \(h^\pm_{\mathbf{r}_0} = 0\). Note that this argument holds even when the charging approximation is lifted and when energy of the light is included, since the resolvents are invariant under three-fold rotations about \(\hat{\mathbf{z}}\). We thus see that, within our approximations, when only these two high symmetry oxygens\(^\text{47}\) are included there is no second order, or single-ion, contributions to the Raman response.

Note that this argument will not follow when the low-symmetry oxygens\(^\text{47}\) ( Wyckoff site 4f) are included, and thus generically one has \(h^\pm_{\mathbf{r}_0} \neq 0\). In addition, inclusion of additional hoppings in \(t_{\mu\nu}^f\), beyond the Slater-Koster approximation, would render \(t_{\mu\nu}^f\) non-diagonal and thus also give \(h^\pm_{\mathbf{r}_0} \neq 0\). We thus expect that for non-Kramers ions one can have single-ion response from such operators.

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In this case, we pursue a more analytical route. However, given the difficulty and opacity of such calculations, here we perform a more numerical simulation.

Note that the higher order correction, \( V_2 \), would produce at the same order, i.e. \( O(\mathcal{A}^2) \), from the first order perturbative contribution \( PV_2P \). However, since \( V_2 \) still necessarily involves a charge transfer from the ligand to the rare-earth ion one has \( PV_2P \neq 0 \). This would in principle allow validation of these results though direct numerical simulation. However, given the difficulty and opacity of such calculations, here we perform a more analytical route.

Note that a pure \( J_{xx} \) coupling, with \( J_x = J_{zz} = 0 \), would not produce spinon pairs, but two singly-charged spinons and one doubly-charged spinon. Therefore in this case the intensity would appear only near the much higher energy \( 3J_{zz} \).

In this case, the moment operator, \( S_{\perp} \), for a pseudo-spin-1/2 doublet, produces an ordered ferromagnetic state drawn from the ice manifold. To obtain QSI, one can thus only include \( J_{zz} \) in concert with \( J_x \) or \( J_{xx} \). For a dipolar-octupolar doublet, \( J_{zz} \) is entirely innocuous and can be removed by a local redefinition of the doublet states.

In this case, we pursue a more analytical route. However, given the difficulty and opacity of such calculations, here we perform a more numerical simulation. However, given the difficulty and opacity of such calculations, here we perform a more analytical route.