Supplementary Information for "Van Vleck Excitonic Magnetism in Ruthenium Pyrochlores"

This Supplementary Information provides the technical details supporting the results presented in the main text. In particular, we derive the effective spin–orbital Hamiltonian from the multi-orbital Hubbard model, present additional details of the mean-field analysis and Raman response, and provide analytical derivations and numerical results used throughout the manuscript.

A Hopping matrices from Slater–Koster parameters

Here we give the explicit Slater–Koster construction underlying Methods. We use the notation introduced there: $|d_i^G\rangle$ denotes the five-orbital basis centered on site i but expressed in the global cubic frame, $|d_i\rangle$ denotes the corresponding basis in the local octahedral frame, and $\mathcal{R}_{LG}^i$ rotates the global basis into the local basis. For a bond ij, $\mathcal{T}_{ij}^G(l,m,n)$ denotes the Slater–Koster hopping matrix in the global five-orbital basis, with (l,m,n) the direction cosines of the bond from j to i.

A.1 Orbital hopping on the representative Z bond

The local t_{2g} hopping matrix is obtained by rotating the global Slater–Koster matrix into the local frames at the two sites and projecting to the t_{2g} subspace,

$$\mathcal{T}_{ij}^{t_{2g}} = \left[\mathcal{R}_{LG}^i\, \mathcal{T}_{ij}^G(l,m,n)\, \left(\mathcal{R}_{LG}^j\right)^\dagger\right]_{t_{2g}}. \tag{A1}$$

For the representative Z bond connecting sites 1 and 4, the direction cosines on the two tetrahedra are

$$(l,m,n)_{14}^A = \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right), \qquad (l,m,n)_{14}^B = \left(-\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0\right). \tag{A2}$$

Here the superscripts A and B label the two tetrahedra sharing the bond, and the sign difference reflects the opposite orientation of the same bond in the two local tetrahedral environments. Thus,

$$\begin{aligned}
\mathcal{T}_{14,A}^{t_{2g}} &= \left[\mathcal{R}_{LG}^1\, \mathcal{T}_{14,A}^G \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right) \left(\mathcal{R}_{LG}^4\right)^\dagger\right]_{t_{2g}}, \\
\mathcal{T}_{14,B}^{t_{2g}} &= \left[\mathcal{R}_{LG}^1\, \mathcal{T}_{14,B}^G \left(-\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0\right) \left(\mathcal{R}_{LG}^4\right)^\dagger\right]_{t_{2g}}, \\
\mathcal{T}_{41,A}^{t_{2g}} &= \left[\mathcal{R}_{LG}^4\, \mathcal{T}_{41,A}^G \left(-\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0\right) \left(\mathcal{R}_{LG}^1\right)^\dagger\right]_{t_{2g}}, \\
\mathcal{T}_{41,B}^{t_{2g}} &= \left[\mathcal{R}_{LG}^4\, \mathcal{T}_{41,B}^G \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right) \left(\mathcal{R}_{LG}^1\right)^\dagger\right]_{t_{2g}}.
\end{aligned} \tag{A3}$$

Evaluating these expressions gives

$$\mathcal{T}_{14,A}^{t_{2g}} = \mathcal{T}_{14,B}^{t_{2g}} = \begin{pmatrix} t_1 & t_2 & t_4 \\ t_2 & t_1 & t_4 \\ -t_4 & -t_4 & t_3 \end{pmatrix}, \qquad \mathcal{T}_{41,A}^{t_{2g}} = \mathcal{T}_{41,B}^{t_{2g}} = \begin{pmatrix} t_1 & t_2 & -t_4 \\ t_2 & t_1 & -t_4 \\ t_4 & t_4 & t_3 \end{pmatrix}. \tag{A4}$$

The equality of the A- and B-tetrahedron hopping matrices shows that inversion symmetry is preserved in the local basis.

A.2 Direct hopping amplitudes

We now express t_1, t_2, t_3, t_4 in terms of the Slater–Koster parameters. For this purpose, we work in the global five-orbital basis $|d_i^G\rangle = \left(d_{i,YZ}^G, d_{i,XZ}^G, d_{i,XY}^G, d_{i,X^2-Y^2}^G, d_{i,3Z^2-R^2}^G\right)^T$. For the representative Z

bond, the corresponding global hopping matrix is

$$\mathcal{T}_{14}^{G}=\begin{pmatrix} \frac{3}{4}(dd\sigma)+\frac{1}{4}(dd\delta) & 0 & -\frac{\sqrt{3}}{4}(dd\sigma)+\frac{\sqrt{3}}{4}(dd\delta) & 0 & 0 \\ 0 & dd\pi & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{4}(dd\sigma)+\frac{\sqrt{3}}{4}(dd\delta) & 0 & \frac{1}{4}(dd\sigma)+\frac{3}{4}(dd\delta) & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}(dd\pi)+\frac{1}{2}(dd\delta) & \frac{1}{2}(dd\pi)-\frac{1}{2}(dd\delta) \\ 0 & 0 & 0 & \frac{1}{2}(dd\pi)-\frac{1}{2}(dd\delta) & \frac{1}{2}(dd\pi)+\frac{1}{2}(dd\delta) \end{pmatrix} \tag{A5}$$

Projecting this matrix onto the local t_{2g} orbitals gives the hopping matrix in Eq. (A4), with

$$\begin{aligned} t_1 &= \frac{1}{4}\left[\big((dd\delta)+4(dd\pi)+3(dd\sigma)\big)\cos 2\varphi+(dd\delta)-2(dd\pi)-3(dd\sigma)\right]\cos^2\varphi, \\ t_2 &= \frac{1}{8}\left[-\big((dd\delta)+3(dd\sigma)\big)\sin^2 2\varphi-4(dd\delta)\cos^2\varphi+4(dd\pi)\left(\sin^2\varphi+\cos^2 2\varphi\right)\right], \\ t_3 &= \frac{1}{32}\left[\big((dd\delta)+4(dd\pi)+3(dd\sigma)\big)\cos 4\varphi+12\big((dd\sigma)-(dd\delta)\big)\cos 2\varphi+19(dd\delta)-4(dd\pi)+9(dd\sigma)\right], \\ t_4 &= \frac{1}{8\sqrt{2}}\left[3(dd\delta)-3(dd\sigma)-\big((dd\delta)+4(dd\pi)+3(dd\sigma)\big)\cos 2\varphi\right]\sin 2\varphi. \end{aligned} \tag{A6}$$

For ideal octahedra, $\varphi=\arctan(2\sqrt{2})$, and Eq. (A6) gives

$$\mathcal{T}_{14}^{t_{2g}}=\frac{1}{162}\times \begin{pmatrix} (dd\delta)-23(dd\pi)-24(dd\sigma) & -17(dd\delta)+121(dd\pi)-24(dd\sigma) & 34(dd\delta)+28(dd\pi)-6(dd\sigma) \\ -17(dd\delta)+121(dd\pi)-24(dd\sigma) & (dd\delta)-23(dd\pi)-24(dd\sigma) & 34(dd\delta)+28(dd\pi)-6(dd\sigma) \\ -34(dd\delta)-28(dd\pi)+6(dd\sigma) & -34(dd\delta)-28(dd\pi)+6(dd\sigma) & \frac{289}{2}(dd\delta)-16(dd\pi)+\frac{3}{2}(dd\sigma) \end{pmatrix}. \tag{A7}$$

A.3 Oxygen-mediated hopping amplitudes

Next we consider the oxygen-mediated hopping. For the oxygen shared by two neighboring octahedra, we fix it along the global (X,Y,Z) cubic coordinate. For convenience, we can align the Z-axis on the oxygen to z_1 and z_4 separately when we consider Slater-Koster parameters for the hopping between the oxygen ion and the Ru ion, which are given in Table A1. We can also find how p_X, p_Y, p_Z are expressed in the local reference frames of the Ru ions, p_{x_1}, p_{y_1}, p_{z_1} on Ru_1 and p_{x_4}, p_{y_4}, p_{z_4} on Ru_4, respectively:

$$\begin{aligned} p_X &= \cos^2\frac{\varphi}{2}p_{x_1}+\frac{\cos\varphi-1}{2}p_{y_1}-\frac{\sin\varphi}{\sqrt{2}}p_{z_1}, \\ p_Y &= \frac{\cos\varphi-1}{2}p_{x_1}+\cos^2\frac{\varphi}{2}p_{y_1}-\frac{\sin\varphi}{\sqrt{2}}p_{z_1}, \\ p_Z &= \frac{\sin\varphi}{\sqrt{2}}p_{x_1}+\frac{\sin\varphi}{\sqrt{2}}p_{y_1}+\cos\varphi p_{z_1}, \end{aligned} \tag{A8}$$

and

$$\begin{aligned} p_X &= \cos^2\frac{\varphi}{2}p_{x_4}+\frac{\cos\varphi-1}{2}p_{y_4}+\frac{\sin\varphi}{\sqrt{2}}p_{z_4}, \\ p_Y &= \frac{\cos\varphi-1}{2}p_{x_4}+\cos^2\frac{\varphi}{2}p_{y_4}+\frac{\sin\varphi}{\sqrt{2}}p_{z_4}, \\ p_Z &= -\frac{\sin\varphi}{\sqrt{2}}p_{x_4}-\frac{\sin\varphi}{\sqrt{2}}p_{y_4}+\cos\varphi p_{z_4}. \end{aligned} \tag{A9}$$

This gives us the hopping amplitudes between the global p orbitals on the shared oxygen ion and the local t_{2g} orbitals on two Ru ions in Table A1. Suppose the charge transfer energy from d orbital to p orbital is Δ_{pd}, and we can obtain the effective hopping amplitudes between two Ru ions through the shared oxygen as

$$\begin{pmatrix} \frac{pd\pi^2}{\Delta_{pd}}\cos^2\varphi & -\frac{pd\pi^2}{\Delta_{pd}}\sin^2\varphi & 0 \\ -\frac{pd\pi^2}{\Delta_{pd}}\sin^2\varphi & \frac{pd\pi^2}{\Delta_{pd}}\cos^2\varphi & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{A10}$$

We can absorb these hopping amplitudes into t_1 and t_2. In the ideal pyrochlore lattice, we have

	$d_{y_1z_1}(d_{y_4z_4})$	$d_{x_1z_1}(d_{x_4z_4})$	$d_{x_1y_1}(d_{x_4y_4})$
$p_{x_1}(p_{x_4})$	0	$pd\pi$	0
$p_{y_1}(p_{y_4})$	$pd\pi$	0	0
$p_{z_1}(p_{z_4})$	0	0	0

Table A1: The Slater-Koster parameters for hopping between p orbitals to t_{2g} orbitals ($l = 0$, $m = 0$, $n = 1$)

B Details of basis transformations

For completeness, we summarize the local single-ion basis conventions used in the numerical implementation. All states in this section are defined with respect to the local octahedral frame of a given Ru site; the site index is suppressed for notational simplicity. For one hole in the local t_{2g} shell, or equivalently for a d^5 configuration, we use three related bases:
the orbital basis

$$|O\rangle = \{|X_\uparrow\rangle, |X_\downarrow\rangle, |Y_\uparrow\rangle, |Y_\downarrow\rangle, |Z_\uparrow\rangle, |Z_\downarrow\rangle\}, \tag{B1}$$

where $|X\rangle = d_{yz}$, $|Y\rangle = d_{xz}$, and $|Z\rangle = d_{xy}$;
the LS basis

$$|LS\rangle = \left\{|1,\frac{1}{2}\rangle, |1,-\frac{1}{2}\rangle, |0,\frac{1}{2}\rangle, |0,-\frac{1}{2}\rangle, |-1,\frac{1}{2}\rangle, |-1,-\frac{1}{2}\rangle\right\}; \tag{B2}$$

and the total-angular-momentum basis

$$|J\rangle = \left\{|\frac{3}{2},\frac{3}{2}\rangle, |\frac{3}{2},\frac{1}{2}\rangle, |\frac{3}{2},-\frac{1}{2}\rangle, |\frac{3}{2},-\frac{3}{2}\rangle, |\frac{1}{2},\frac{1}{2}\rangle, |\frac{1}{2},-\frac{1}{2}\rangle\right\}. \tag{B3}$$

The orbital angular-momentum states are related to the t_{2g} orbital basis by

$$|0\rangle = |Z\rangle, \tag{B4a}$$

$$|1\rangle = -\frac{1}{\sqrt{2}}(|X\rangle + i|Y\rangle), \tag{B4b}$$

$$|-1\rangle = \frac{1}{\sqrt{2}}(|X\rangle - i|Y\rangle). \tag{B4c}$$

In matrix form, the transformation from the angular-momentum basis $\{|1\rangle, |0\rangle, |-1\rangle\}$ to the local orbital basis $\{|X\rangle, |Y\rangle, |Z\rangle\}$ is

$$U_{L\to O} = \begin{pmatrix} -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} & 0 & -\frac{i}{\sqrt{2}} \\ 0 & 1 & 0 \end{pmatrix}. \tag{B5}$$

The LS basis is obtained by taking the tensor product of the orbital angular-momentum basis with the spin basis $\{|\uparrow\rangle, |\downarrow\rangle\}$. Since $U_{L\to O}$ acts only on the orbital part, the transformation in the full spin–orbital basis is

$$U_{LS\to O} = U_{L\to O} \otimes \mathbb{1}_2. \tag{B6}$$

The transformation from the LS basis to the total-angular-momentum basis is fixed by Clebsch-Gordan coefficients:

$$\begin{pmatrix} |\frac{3}{2},\frac{3}{2}\rangle \\ |\frac{3}{2},\frac{1}{2}\rangle \\ |\frac{3}{2},-\frac{1}{2}\rangle \\ |\frac{3}{2},-\frac{3}{2}\rangle \\ |\frac{1}{2},\frac{1}{2}\rangle \\ |\frac{1}{2},-\frac{1}{2}\rangle \end{pmatrix} = U_{LS\to J} \begin{pmatrix} |1,\frac{1}{2}\rangle \\ |1,-\frac{1}{2}\rangle \\ |0,\frac{1}{2}\rangle \\ |0,-\frac{1}{2}\rangle \\ |-1,\frac{1}{2}\rangle \\ |-1,-\frac{1}{2}\rangle \end{pmatrix}, \tag{B7}$$

with

$$U_{LS\to J}=\begin{pmatrix}1 & 0 & 0 & 0 & 0 & 0\\ 0 & \frac{1}{\sqrt{3}} & \sqrt{\frac{2}{3}} & 0 & 0 & 0\\ 0 & 0 & 0 & \sqrt{\frac{2}{3}} & \frac{1}{\sqrt{3}} & 0\\ 0 & 0 & 0 & 0 & 0 & 1\\ 0 & \sqrt{\frac{2}{3}} & -\frac{1}{\sqrt{3}} & 0 & 0 & 0\\ 0 & 0 & 0 & \frac{1}{\sqrt{3}} & -\sqrt{\frac{2}{3}} & 0\end{pmatrix}. \tag{B8}$$

These conventions fix the phases used in constructing the local spin–orbit states and the numerical projection matrices.

C Symmetry-related bond Hamiltonians

In Methods, the projected exchange Hamiltonian is constructed explicitly for the representative Z bond connecting sites 1 and 4. Here we describe how the remaining nearest-neighbor bond Hamiltonians are generated from this representative bond by symmetry.

Starting from the projected Hamiltonian $\mathcal{H}_{14}^{Z}$ on the representative Z bond, the Hamiltonians on the symmetry-related bonds are obtained by applying rotations of the tetrahedral point group T_d. These rotations map one local bond environment to another. Since the singlet is invariant, their only nontrivial action in the low-energy Hilbert space is to permute the Cartesian triplet components.

For example, a C_3 rotation about the [111] axis maps the local environment of the representative Z bond $(1,4)$ to that of the X bond $(1,2)$. We denote the basis after this rotation by $|\widetilde{\tau}_\alpha\rangle$ and choose the convention

$$|\tau_\alpha\rangle = P_{111}\,|\widetilde{\tau}_\alpha\rangle\,. \tag{C1}$$

With this convention, the projected Hamiltonian in the rotated basis is related to the representative Z-bond Hamiltonian by

$$\begin{aligned}&\langle\widetilde{\tau}_{1\alpha}\widetilde{\tau}_{2\beta}|\,\mathcal{H}_{12}^{X}\,|\widetilde{\tau}_{1\gamma}\widetilde{\tau}_{2\delta}\rangle\\ &\quad=\langle\tau_{1\alpha}\tau_{2\beta}|\,(P_{111}\otimes P_{111})\,\mathcal{H}_{14}^{Z}\,\left(P_{111}^{-1}\otimes P_{111}^{-1}\right)|\tau_{1\gamma}\tau_{2\delta}\rangle\,.\end{aligned} \tag{C2}$$

Equivalently, at the matrix level,

$$\mathcal{H}_{12}^{X}=(P_{111}\otimes P_{111})\,\mathcal{H}_{14}^{Z}\,\left(P_{111}^{-1}\otimes P_{111}^{-1}\right), \tag{C3}$$

with the site labels relabeled from $(1,4)$ to $(1,2)$.

The permutation matrices used in the construction are

$$P_{111}=\begin{pmatrix}1 & 0 & 0 & 0\\ 0 & 0 & 0 & -1\\ 0 & 1 & 0 & 0\\ 0 & 0 & -1 & 0\end{pmatrix},\qquad P_{1\bar{1}\bar{1}}=\begin{pmatrix}1 & 0 & 0 & 0\\ 0 & 0 & 0 & 1\\ 0 & -1 & 0 & 0\\ 0 & 0 & -1 & 0\end{pmatrix}. \tag{C4}$$

In each matrix, the upper-left entry acts on the singlet, which is invariant, while the lower 3×3 block acts on the Cartesian triplet components.

One convenient sequence of symmetry operations generating the six nearest-neighbor bond Hamiltonians on a tetrahedron is

$$\begin{aligned}&\mathcal{H}_{14}^{Z}\xrightarrow{C_3[111]}\mathcal{H}_{12}^{X}\xrightarrow{C_3[111]}\mathcal{H}_{13}^{Y},\\ &\mathcal{H}_{12}^{X}\xrightarrow{C_3[1\bar{1}\bar{1}]}\mathcal{H}_{42}^{Y}\xrightarrow{C_3[1\bar{1}\bar{1}]}\mathcal{H}_{32}^{Z},\\ &\mathcal{H}_{14}^{Z}\xrightarrow{C_3[1\bar{1}\bar{1}]}\mathcal{H}_{43}^{X}.\end{aligned} \tag{C5}$$

For example, the first relation in Eq. (C5) is implemented by Eq. (C3). Similarly, the transformation $\mathcal{H}_{12}^{X}\xrightarrow{C_3[1\bar{1}\bar{1}]}\mathcal{H}_{42}^{Y}$ is implemented using $P_{1\bar{1}\bar{1}}$,

$$\mathcal{H}_{42}^{Y}=(P_{1\bar{1}\bar{1}}\otimes P_{1\bar{1}\bar{1}})\,\mathcal{H}_{12}^{X}\,\left(P_{1\bar{1}\bar{1}}^{-1}\otimes P_{1\bar{1}\bar{1}}^{-1}\right), \tag{C6}$$

and the remaining relations are obtained analogously. Together, the six matrices

$$\{\mathcal{H}_{14}^{Z}, \mathcal{H}_{12}^{X}, \mathcal{H}_{13}^{Y}, \mathcal{H}_{32}^{Z}, \mathcal{H}_{43}^{X}, \mathcal{H}_{42}^{Y}\} \tag{C7}$$

form the nearest-neighbor building blocks used to assemble the full exchange Hamiltonian on the pyrochlore lattice.

D. Harmonic Approximation of the Quartic Hamiltonian

To analyze the instability toward triplon condensation and the onset of magnetic ordering, we study small fluctuations around the singlet-condensed phase, where the triplon operators describe low-density triplet excitations above the nonmagnetic singlet background. The local constraint,

$$n_s + \sum_{\alpha=x,y,z} n_{T^\alpha} = 1, \tag{D1}$$

is enforced within a Gutzwiller approximation by replacing the singlet operators according to

$$s, s^\dagger \to \sqrt{1 - \sum_\alpha T^{\alpha\dagger} T^\alpha}. \tag{D2}$$

Expanding around the singlet-condensed state and retaining terms up to quadratic order in the triplon operators yields the harmonic triplon Hamiltonian.

The quartic superexchange Hamiltonian obtained from the second order perturbation theory is

$$\mathcal{H}_{\text{eff}}^{(4)} = \sum_{\phi,\phi'} |\phi\rangle \langle\phi|\mathcal{H}_{\text{eff}}|\phi'\rangle \langle\phi'| = \sum_{\langle ij\rangle,\alpha\alpha'\beta\beta'} J_{ij}^{\alpha\alpha'\beta\beta'} \tau_{i\alpha}^\dagger \tau_{j\alpha'}^\dagger \tau_{i\beta} \tau_{j\beta'} + h.c., \tag{D3}$$

where $J_{ij}^{\alpha\alpha'\beta\beta'}$ (with $\alpha, \alpha', \beta, \beta' = 0, x, y, z$) are the effective interaction amplitudes in the two-site singlet-triplet basis $|\phi\rangle = |\tau_{i\alpha}\rangle \otimes |\tau_{j\alpha'}\rangle$.

After substituting the Gutzwiller expansion for the singlet operators and retaining terms up to quadratic order in the triplon fields, only quartic operator structures containing at least two singlet operators contribute within the harmonic approximation. Among the 16 possible quartic terms appearing in Eq. (D3), the following seven generate constant, onsite, hopping, or pairing contributions:

1. $s_i^\dagger s_j^\dagger s_i s_j \sim 1 - \sum_\alpha (T_{i\alpha}^\dagger T_{i\alpha} + T_{j\alpha}^\dagger T_{j\alpha}) + \mathcal{O}(T^\dagger T)^2$
2. $s_i^\dagger s_j^\dagger T_{i\alpha} T_{j\alpha'} \sim T_{i\alpha} T_{j\alpha'} + \mathcal{O}(TT)^2$
3. $s_i^\dagger T_{j\alpha}^\dagger s_i T_{j\alpha'} \sim T_{j\alpha}^\dagger T_{j\alpha'} + \mathcal{O}(T^\dagger T)^2$
4. $s_i^\dagger T_{j\alpha}^\dagger T_{i\alpha'} s_j \sim T_{j\alpha}^\dagger T_{i\alpha'} + \mathcal{O}(T^\dagger T)^2$
5. $T_{i\alpha}^\dagger s_j^\dagger T_{i\alpha'} s_j \sim T_{i\alpha}^\dagger T_{i\alpha'} + \mathcal{O}(T^\dagger T)^2$
6. $T_{i\alpha}^\dagger s_j^\dagger s_i T_{j\alpha'} \sim T_{i\alpha}^\dagger T_{j\alpha'} + \mathcal{O}(T^\dagger T)^2$
7. $T_{i\alpha}^\dagger T_{j\alpha'}^\dagger s_i s_j \sim T_{i\alpha}^\dagger T_{j\alpha'}^\dagger + \mathcal{O}(T^\dagger T^\dagger)^2$

Thus, the quartic Hamiltonian reduces to a quadratic form containing normal and anomalous triplon terms,

$$\mathcal{H}_{\text{eff}}^{(2)} = \sum_{\langle ij\rangle,\alpha\alpha'} \left[A_{ij}^{\alpha\alpha'} T_{i\alpha}^\dagger T_{j\alpha'} + \frac{1}{2} \left(B_{ij}^{\alpha\alpha'} T_{i\alpha}^\dagger T_{j\alpha'}^\dagger + \text{h.c.} \right) \right], \tag{D4}$$

where $A_{ij}^{\alpha\alpha'}$ and $B_{ij}^{\alpha\alpha'}$ are obtained from the corresponding coefficients of the full quartic Hamiltonian.

Since the harmonic Hamiltonian is quadratic in the triplon operators and preserves lattice translational symmetry, it is convenient to work in momentum space, where different crystal momenta decouple. The

resulting bosonic Bogoliubov-de Gennes Hamiltonian, which determines the triplon dispersion and allows one to identify possible instabilities of the singlet phase toward triplon condensation, can be written as

$$\mathcal{H}^{(2)}_{\text{eff}} = \sum_{\mathbf{k}} \Psi^\dagger_{\mathbf{k}} \begin{pmatrix} \mathcal{A}_{\mathbf{k}} & \mathcal{B}_{\mathbf{k}} \\ \mathcal{B}^\dagger_{\mathbf{k}} & \mathcal{A}^T_{-\mathbf{k}} \end{pmatrix} \Psi_{\mathbf{k}}, \tag{D5}$$

where

$$\Psi_{\mathbf{k}} = \begin{pmatrix} \mathbf{T}_{\mathbf{k}} \\ \mathbf{T}^\dagger_{-\mathbf{k}} \end{pmatrix}, \quad \mathbf{T}_{\mathbf{k}} = \left(T_{1x,\mathbf{k}}, T_{1y,\mathbf{k}}, T_{1z,\mathbf{k}}, \ldots, T_{4x,\mathbf{k}}, T_{4y,\mathbf{k}}, T_{4z,\mathbf{k}}\right)^T. \tag{D6}$$

The matrices $\mathcal{A}_{\mathbf{k}}$ and $\mathcal{B}_{\mathbf{k}}$ are 12×12 matrices describing normal hopping and anomalous pairing processes between triplons on the four pyrochlore sublattices.

The normal block $\mathcal{A}_{\mathbf{k}}$ has the general sublattice structure

$$\mathcal{A}_{\mathbf{k}} = \begin{pmatrix} A_{11} & A^X_{12} & A^Y_{13} & A^Z_{14} \\ A^X_{21} & A_{22} & A^Z_{23} & A^Y_{24} \\ A^Y_{31} & A^Z_{32} & A_{33} & A^X_{34} \\ A^Z_{41} & A^Y_{42} & A^X_{43} & A_{44} \end{pmatrix}, \tag{D7}$$

where each entry is itself a 3×3 matrix in the triplon flavor space. The subscripts denote the pyrochlore sublattices, the superscripts label the corresponding bond type, and the $\mathbf{k}$ dependence of all entries is implicit.

As an illustrative example, consider the contribution from the representative Z bond connecting sites $(1,4)$. In momentum space, the corresponding matrix elements generate normal triplon terms of the form

$$\mathcal{H}^Z_{14,\mathbf{k}} = \mathcal{H}^{(2)}_{\text{eff}} + \mathcal{H}_{\text{SOC},1} + \mathcal{H}_{\text{SOC},4} = \begin{pmatrix} \left(\mathcal{H}^Z_{14,\mathbf{k}}\right)_{\text{onsite}/4} & \left(\mathcal{H}^Z_{14,\mathbf{k}}\right)_{4\leftarrow 1} \\ \left(\mathcal{H}^Z_{14,\mathbf{k}}\right)_{1\leftarrow 4} & \left(\mathcal{H}^Z_{14,\mathbf{k}}\right)_{\text{onsite}/1} \end{pmatrix}$$

$$= \left(\begin{array}{c|ccc|ccc} & |s_1T_{4x}\rangle & |s_1T_{4y}\rangle & |s_1T_{4z}\rangle & |T_{1x}s_4\rangle & |T_{1y}s_4\rangle & |T_{1z}s_4\rangle \\ \hline \langle s_1T_{4x}| & \ddots & & & \ddots & & \\ \langle s_1T_{4y}| & & \boxed{\#T^\dagger_{4\alpha,\mathbf{k}}T_{4\alpha',\mathbf{k}}} & & & \boxed{\#T^\dagger_{4\alpha,\mathbf{k}}T_{1\alpha',\mathbf{k}}} & \\ \langle s_1T_{4z}| & & & \ddots & & & \ddots \\ \hline \langle T_{1x}s_4| & \ddots & & & \ddots & & \\ \langle T_{1y}s_4| & & \boxed{\#T^\dagger_{1\alpha,\mathbf{k}}T_{4\alpha',\mathbf{k}}} & & & \boxed{\#T^\dagger_{1\alpha,\mathbf{k}}T_{1\alpha',\mathbf{k}}} & \\ \langle T_{1z}s_4| & & & \ddots & & & \ddots \end{array}\right). \tag{D8}$$

The diagonal blocks generate onsite contributions of the form $T^\dagger_{i\alpha,\mathbf{k}}T_{i\alpha',\mathbf{k}}$, while the off-diagonal blocks describe intersite hopping processes $T^\dagger_{i\alpha,\mathbf{k}}T_{j\alpha',\mathbf{k}}$. Each block is a matrix in the triplon flavor space $\alpha = x,y,z$.

The anomalous block $\mathcal{B}_{\mathbf{k}}$ is constructed in the same way from pair-creation terms of the form $T^\dagger_{i\alpha,\mathbf{k}}T^\dagger_{j\alpha',-\mathbf{k}}$. These terms originate from matrix elements connecting the singlet-singlet state to two-triplon states, $|T^\alpha_i T^{\alpha'}_j\rangle\langle s_i s_j|$, in the quartic Hamiltonian. Since there are no onsite pair-creation terms of the form $T^\dagger_{i\alpha,\mathbf{k}}T^\dagger_{i\alpha',-\mathbf{k}}$, the diagonal sublattice blocks vanish. Thus,

$$\mathcal{B}_{\mathbf{k}} = \begin{pmatrix} \mathbf{0} & B^X_{12} & B^Y_{13} & B^Z_{14} \\ B^X_{21} & \mathbf{0} & B^Z_{23} & B^Y_{24} \\ B^Y_{31} & B^Z_{32} & \mathbf{0} & B^X_{34} \\ B^Z_{41} & B^Y_{42} & B^X_{43} & \mathbf{0} \end{pmatrix}, \tag{D9}$$

where each entry is again a 3×3 matrix in triplon flavor space, and the $\mathbf{k}$ dependence is implicit.

Once we construct the quadratic Hamiltonian, it is diagonalized in momentum space via the Fourier transform

$$\mathbf{T}^\dagger_{\mu,\mathbf{k}} = \frac{1}{\sqrt{N}}\sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}}\,\mathbf{T}^\dagger_{\mu,\mathbf{r}}, \quad \mathbf{T}_{\mu,\mathbf{k}} = \frac{1}{\sqrt{N}}\sum_{\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{r}}\,\mathbf{T}_{\mu,\mathbf{r}}, \tag{D10}$$

where μ is the sublattice index. The quadratic Hamiltonian can be expressed in the triplon basis $\Gamma_{\mathbf{k}} = (\mathbf{T}_{1,\mathbf{k}}, \mathbf{T}_{2,\mathbf{k}}, \mathbf{T}_{3,\mathbf{k}}, \mathbf{T}_{4,\mathbf{k}}, \mathbf{T}^{\dagger}_{1,-\mathbf{k}}, \mathbf{T}^{\dagger}_{2,-\mathbf{k}}, \mathbf{T}^{\dagger}_{3,-\mathbf{k}}, \mathbf{T}^{\dagger}_{4,-\mathbf{k}})^T$ where each triplon comes in three flavors $\mathbf{T}_{\mu,\mathbf{k}} = (T^x_{\mu,\mathbf{k}}, T^y_{\mu,\mathbf{k}}, T^z_{\mu,\mathbf{k}})$. Thus, in the harmonic approximation, the Hamiltonian can be expressed in matrix form as

$$\mathcal{H}^{(2)} = \sum_{\mathbf{k}} \Gamma^{\dagger}_{\mathbf{k}} H_{\mathbf{k}} \Gamma_{\mathbf{k}} \tag{D11}$$

$H_{\mathbf{k}}$ can be diagonalized by a bosonic Bogoliubov transformation $\Gamma_{\mathbf{k}} = \mathcal{S}_{\mathbf{k}} \tilde{\Gamma}_{\mathbf{k}}$ such that the bosonic commutation is enforced by the metric tensor $g \equiv \mathrm{diag}(\mathbb{1}, -\mathbb{1})$ through $\mathcal{S}^{\dagger}_{\mathbf{k}} g \mathcal{S}_{\mathbf{k}} = g$. Thus, the diagonalized Hamiltonian

$$\mathcal{H}^{(2)} = \sum_{\mathbf{k}} \sum_{\mu=1}^{12} \omega_{\mu,\mathbf{k}} \left(\tilde{T}^{\dagger}_{\mu,\mathbf{k}} \tilde{T}_{\mu,\mathbf{k}} + \frac{1}{2} \right) \tag{D12}$$

gives 12 physical bands characterized by bosonic modes, $\tilde{\Gamma}_{\mathbf{k}} = (\tilde{T}_{1,\mathbf{k}}, \tilde{T}_{2,\mathbf{k}}, \tilde{T}_{3,\mathbf{k}} \ldots, \tilde{T}_{12,\mathbf{k}}, \tilde{T}^{\dagger}_{1,-\mathbf{k}}, \ldots, \tilde{T}^{\dagger}_{12,-\mathbf{k}})^T$, each with frequency $\omega_{\mu,\mathbf{k}}$.