# Tutorial:
# **Quantum Pyrochlore Magnets**

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*YFQM online meeting, October 10th, 2022*

# Three Questions

1. What are the spins?

   *What's possible for single-ion physics?*

2. How do they interact?

   *What kind of exchange interactions do we have?*

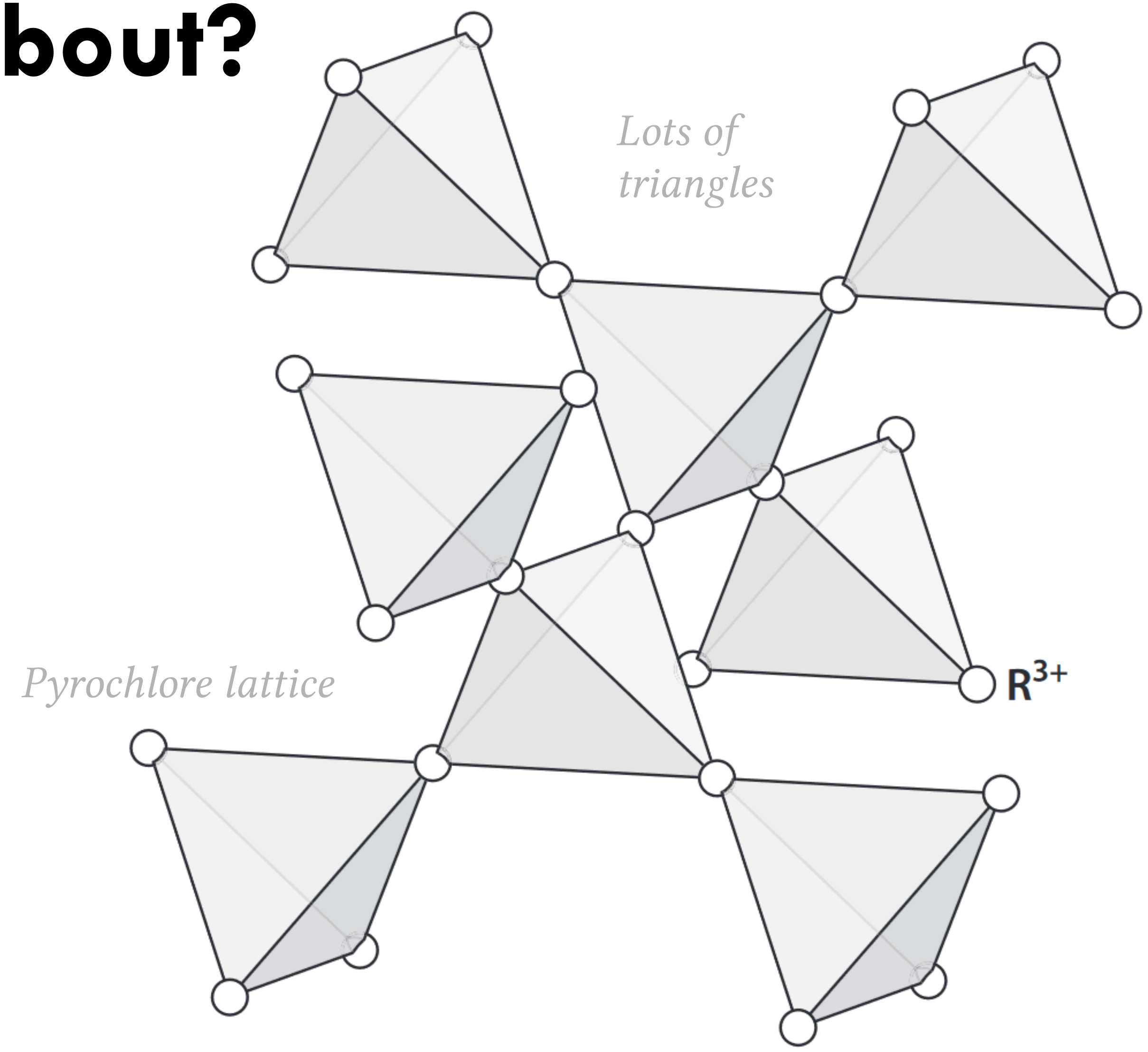
3. Where to look for interesting *quantum* phases?

   *Where do ordered phases breakdown?*

# What are we talking about?

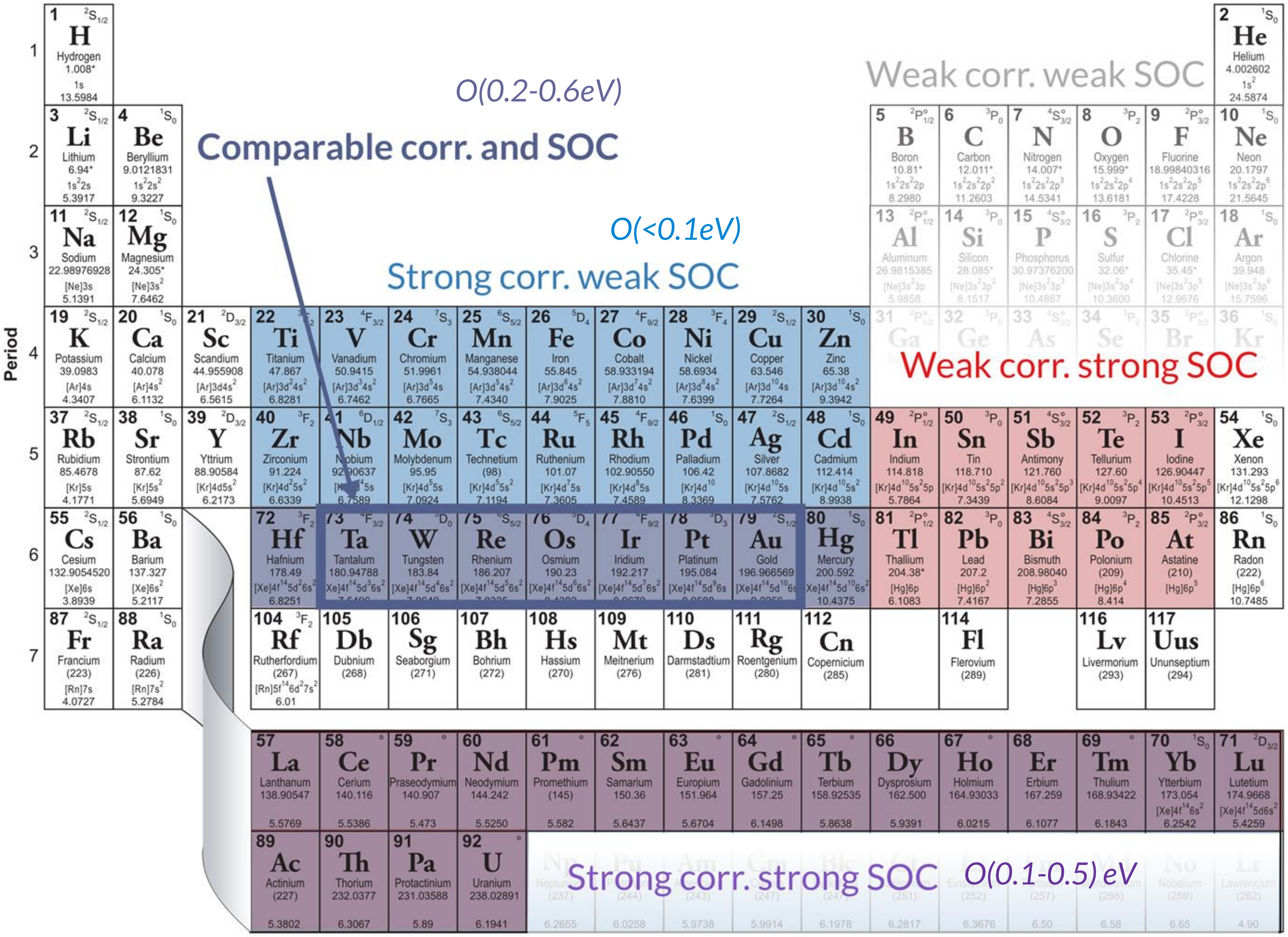
- Corner-sharing tetrahedra
- Canonical 3D **frustrated** lattice
- Materials:
  - $R_2M_2O_7$ *Pyrochlore oxides*
  - $AR_2X_4$ *Spinels*
  - ...
- R = Rare-earth, M = Transition Metal
- Strong insulators

*Will focus on this case*




**Atomic Physics?**

# Spin-orbit coupling




**Increases** with $Z$

(does **not** scale as $Z^4$; screening)

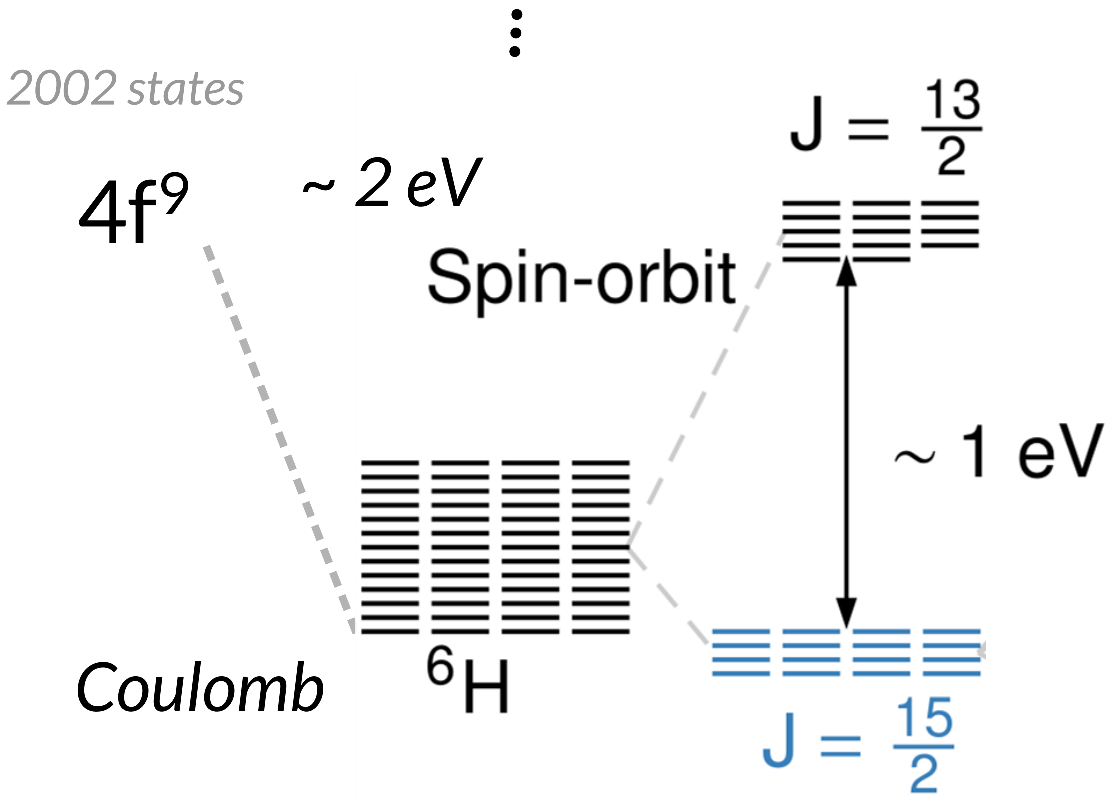
# Free-ion Physics

- For 4f electrons: in most cases many atomic states
- Only **free-ion ground state** is relevant

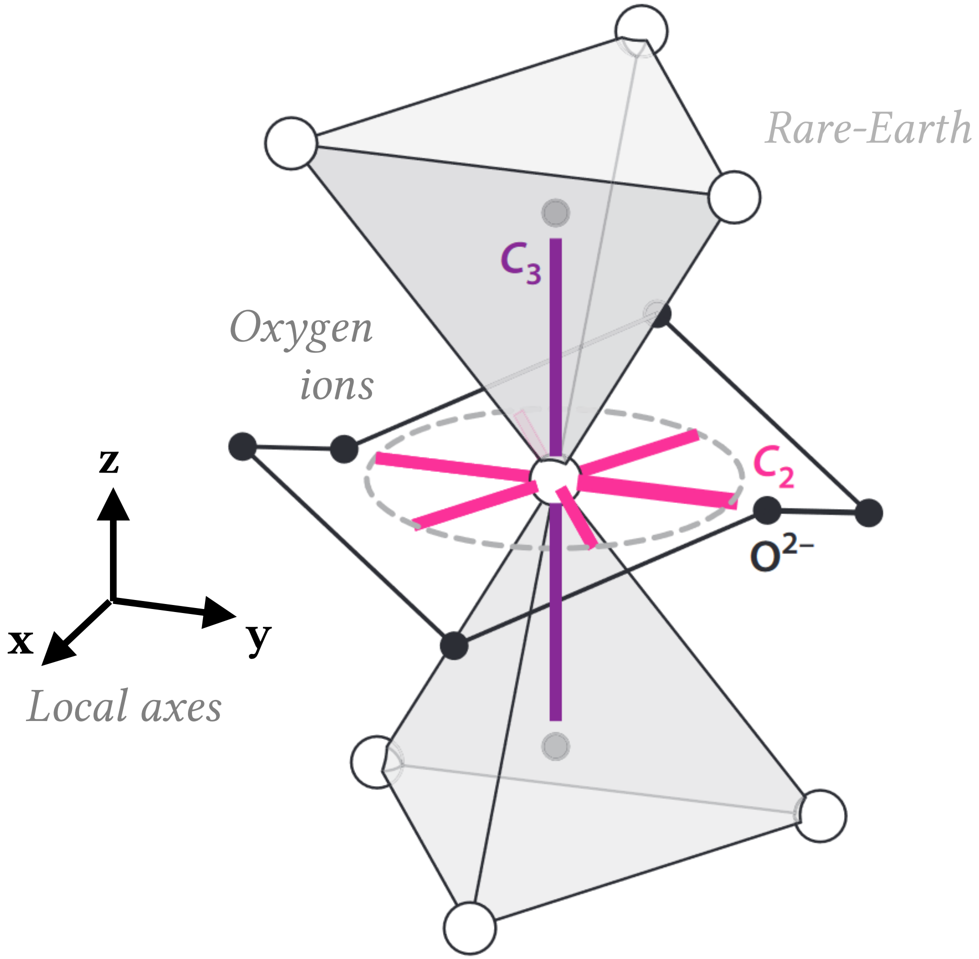
**Hund's rules:**
1. Maximize S
2. Maximize L
3. Maximize J (n<7)
   Minimize J (n>7)

- For *4f* series:
  - 5/2 <= J <= 8, 0 <= L <= 6

**Example:** $Dy^{3+}$, $4f^9$
L=5, S=5/2 ⟶ J=15/2



# Crystalline Electric Field




*Local environment for RE in $R_2M_2O_7$*

- Atomic manifold split by electric fields from surrounding ions
- Local symmetry: $D_{3d}$
  - $C_3$ axis (local **z**)
  - $C_2$ axis (local **y**)
  - Inversion
- Reduces degeneracy (e.g. from $2J+1$) to **singlet or doublet**

**Form of CEF ground state?**

# Crystalline Electric Field (cont.)

- Classify states by **local symmetry**: label by irreducible representations of (site-symmetry group) $D_{3d}$

- **Kramers** (*odd* number of electrons)
  - $\Gamma_4$ irrep. ⟶ **pseudo-spin doublet** — Case #1
  - $\Gamma_{5,6}$ irrep. ⟶ **dipolar-octupolar doublet** — Case #3

- **non-Kramers** (*even* number of electrons)
  - $A_{1g}$ or $A_{2g}$ irrep. ⟶ **singlet** (non-magnetic)
  - $E_g$ irrep. ⟶ **non-Kramers doublet** — Case #2

# Case #1: Pseudo-Spin Kramers Doublet ($\Gamma_4$)

- Simplest case, doublet **protected by time-reversal**

*Doublet states*

$$|\pm\rangle = \alpha\,|\pm 1/2\rangle + \beta\,|\mp 5/2\rangle + \cdots$$

*Differ by multiples of 3 in $J_z$*

- Effective spin operators ($S_x$, $S_y$, $S_z$) **all** represent **magnetic dipoles**

*Effective spin-1/2 operators*

- **Two** g-factors generically:

*Local axes*

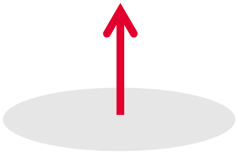
$$\boldsymbol{\mu}_i \equiv \mu_B[g_\pm(\hat{\mathbf{x}}_i S_i^x + \hat{\mathbf{y}}_i S_i^y) + g_z \hat{\mathbf{z}}_i S_i^z],$$

*Magnetic dipole moment*

- **Transforms in same way as spin-1/2** under spatial symmetries of pyrochlore lattice

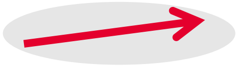
$\langle S_z \rangle \neq 0$

- Time-reversal odd
- Breaks $C_2$



$\langle S_\pm \rangle \neq 0$

- Time-reversal odd
- Breaks $C_2$, $C_3$



# Case #2: Non-Kramers Doublet ($E_g$)

- **Not** protected by time-reversal

$$|\pm\rangle = \alpha\,|\pm 4\rangle + \beta\,|\pm 1\rangle + \cdots$$

*Doublet states*

- **Strongly anisotropic**
  - $S_z$ transforms as **magnetic dipole** along local z
  - $S_x$, $S_y$ transform as **electric quadrupoles**
- Magnetic probes couple **only** to $S_z$ directly

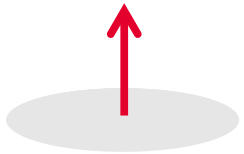
$$\boldsymbol{\mu}_i = \mu_B g_z S_i^z \hat{\mathbf{z}}_i$$

*Single g-factor*

- Sensitive to non-magnetic disorder, couples directly to elastic degrees of freedom, …

$$\langle S_z \rangle \neq 0$$

- Time-reversal odd
- Breaks $C_2$



$$\langle S_\pm \rangle \neq 0$$

- Time-reversal ***even***
- Breaks $C_2$, $C_3$

*~xz, yz orbital*

# Case #3: Dipolar-Octupolar Doublet ($\Gamma_{5,6}$)

- State unrelated under spatial symmetry, connected **only by time-reversal**

*At least 3 to flip*

$$|\pm\rangle = \alpha\,|\pm 3/2\rangle + \beta\,|\mp 9/2\rangle + \cdots$$

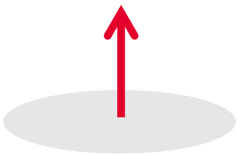
- Canonical basis choice: magnetic moment proportional to $S_z$

$$\boldsymbol{\mu}_i = \mu_B g_z S_i^z \hat{\mathbf{z}}_i$$ *(By construction)*

- **Strongly anisotropic**
  - *Both* $S_x$ and $S_z$ transform like magnetic dipoles **along the local z axis**
  - $S_y$ transforms like magnetic octupole – invariant under *all* $D_{3d}$ symmetries

$\langle S_z\rangle, \langle S_x\rangle \neq 0$

- Time-reversal odd
- Breaks $C_2$



$\langle S_y\rangle \neq 0$

- **Only** breaks time-reversal!

# Aside: Multipolar Content of Spin

- Can project multipole into CEF ground doublet

*Projection into ground doublet*

$$PO_{KQ}(\mathbf{J})P = \sum_{\mu} C^{\mu}_{KQ} S_{\mu}$$

*Akin to multipolar "g" factors*

- **Any** multipole can contribute to effective spin so long as symmetries match
  - Pseudo-spin: dipole, octupole, … (odd ranks) ~ $A_{2g}$, $E_g$
  - Dipolar-Octupolar:

~ $A_{2g}$ $S_x$, $S_z$ : dipole, octupole, … (odd ranks)

~ $A_{1g}$ $S_y$ : octupole, … (odd ranks)

  - Non-Kramers:

~ $A_{2g}$ $S_z \longrightarrow$ dipole, octupole, … (odd ranks)

~ $E_g$ $S_x$, $S_y \longrightarrow$ quadrupole, hexadecapole … (even ranks)

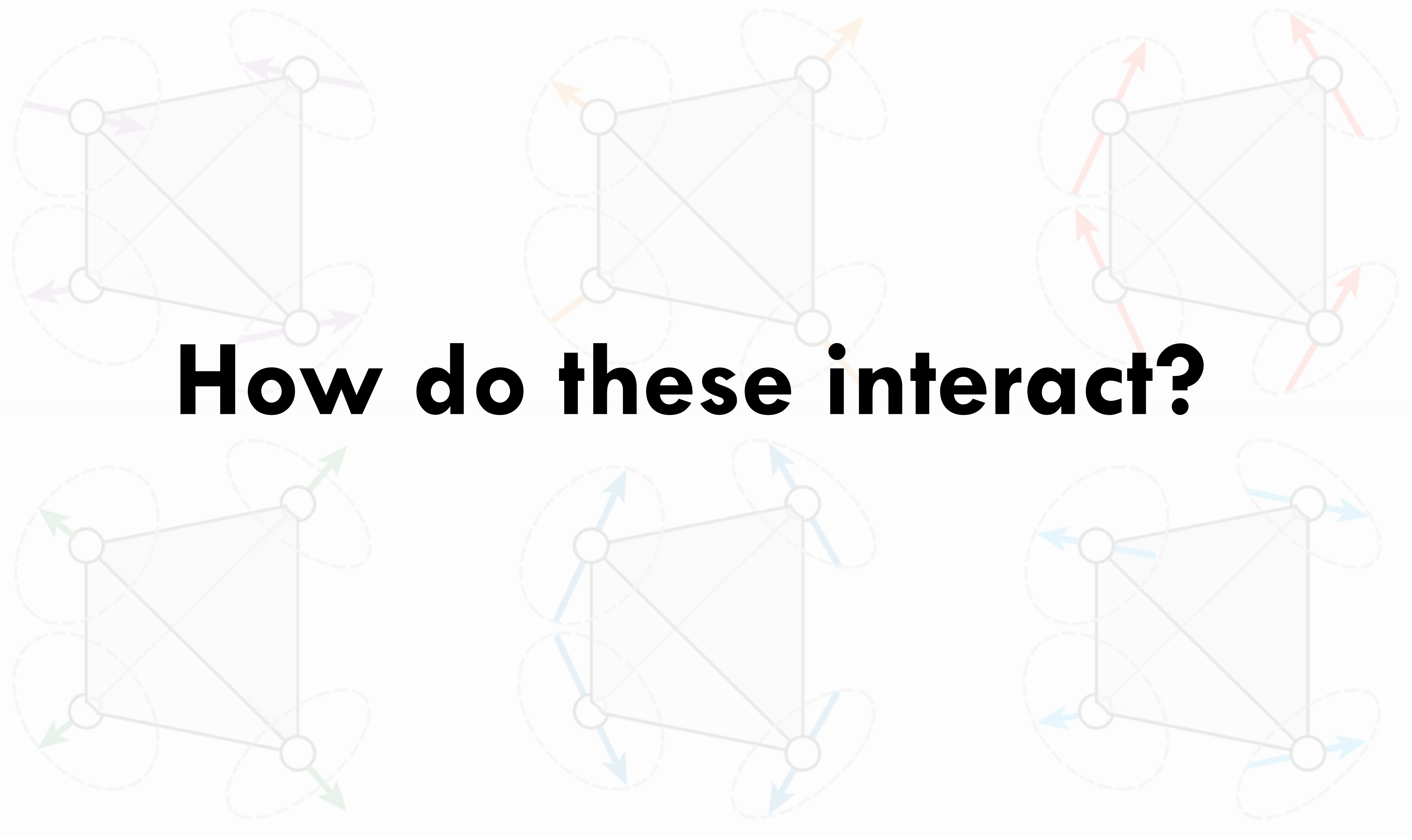
*"Singlet" $A_{1g}$ , $A_{2g}$ even rank multipoles project to nothing*

# Summary of Single-Ion Physics

- Three **doublet** types under $D_{3d}$ symmetry:
  pseudo-spin, dipolar-octupolar, non-Kramers

| Irrep. | $g_z$ | $g_\pm$ | Time. rev. | $C_3$ | $C_2$ | States | Examples |
|---|---|---|---|---|---|---|---|
| $\Gamma_4$ | $\neq 0$ | $\neq 0$ | $\mathbf{S} \to -\mathbf{S}$ | $S^z \to S^z$<br>$S^\pm \to e^{\pm\frac{2\pi i}{3}} S^\pm$ | $S^z \to -S^z$<br>$S^\pm \to S^\mp$ | $\left\|\pm\frac{1}{2}\right\rangle, \left\|\pm\frac{5}{2}\right\rangle, \cdots$ | $Er_2Ti_2O_7$,<br>$Yb_2Ti_2O_7$ |
| $\Gamma_5 \oplus \Gamma_6$ | $\neq 0$ | $0$ | $\mathbf{S} \to -\mathbf{S}$ | $\mathbf{S} \to \mathbf{S}$ | $S^z \to -S^z$<br>$S^\pm \to S^\mp$ | $\left\|\pm\frac{3}{2}\right\rangle, \left\|\pm\frac{9}{2}\right\rangle, \cdots$ | $Dy_2Ti_2O_7$ |
| $E_g$ | $\neq 0$ | $0$ | $S^z \to -S^z$<br>$S^\pm \to S^\mp$ | $S^z \to S^z$<br>$S^\pm \to e^{\pm\frac{2\pi i}{3}} S^\pm$ | $S^z \to -S^z$<br>$S^\pm \to S^\mp$ | $\|\pm 1\rangle, \|\pm 4\rangle, \|\mp 5\rangle, \cdots$ | $Ho_2Ti_2O_7$,<br>$Tb_2Ti_2O_7$ |

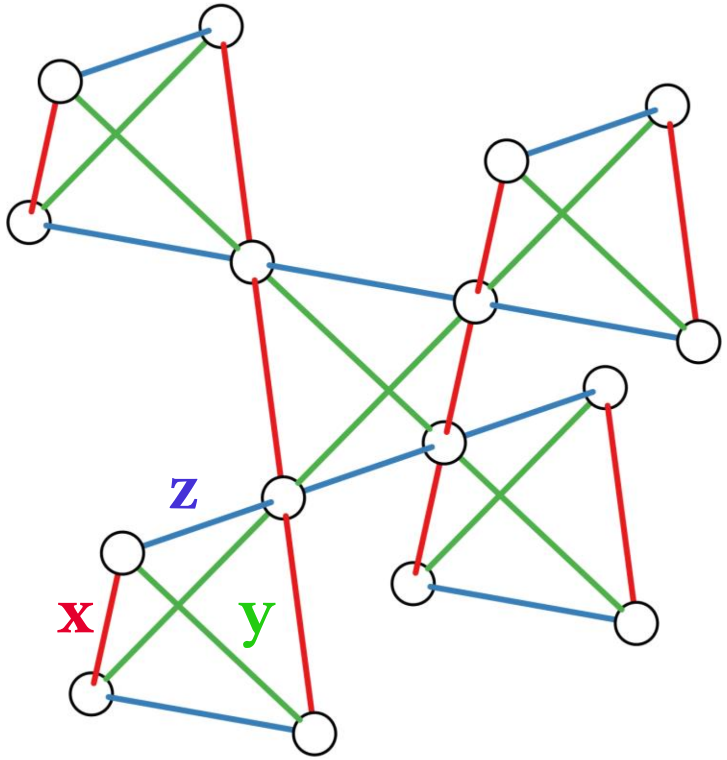
**Interactions?**



# How do these interact?

# Two-ion physics

- How do these doublets **interact**?
- Consider neighbours
- Strongly constrained by symmetry of lattice

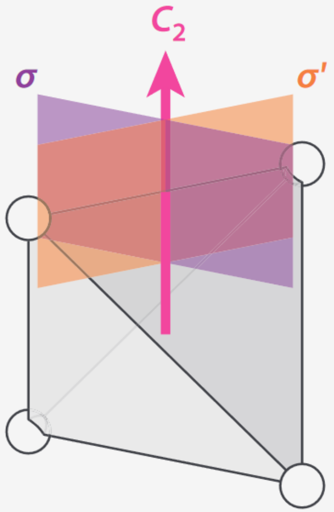



*Three types of bond*

**Symmetry of bond:**

- $C_2$ axis
- Reflection σ
- Reflection σ'

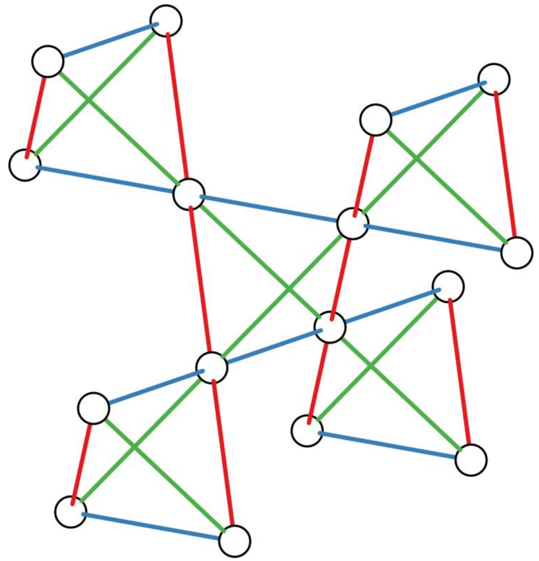
*Nearest neighbour bond*




- Connect other bonds using $C_3$ :

$$x \longrightarrow y \longrightarrow z$$

# Anisotropic exchange model



- Symmetry constrained model takes the form:

*XXZ model*

$$\sum_{\langle ij\rangle} \left[ J_{zz} S_i^z S_j^z - J_{\pm}\left(S_i^+ S_j^- + S_i^- S_j^+\right) + J_{\pm\pm}\left(\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^-\right) \right.$$

*Bond dependent phases*

$$\left. + J_{z\pm}\left(\zeta_{ij}\left[S_i^z S_j^+ + S_i^+ S_j^z\right] + \zeta_{ij}^*\left[S_i^z S_j^- + S_i^- S_j^z\right]\right)\right]$$

*Zero for non-Kramers*

*Bond dependent phases*

*Three or four independent exchange parameters*

**Cases:** $\zeta_{ij} = -\gamma_{ij}^*$

- Pseudo-spin: $\gamma_x = 1, \gamma_y = e^{2\pi i/3}, \gamma_z = e^{-2\pi i/3}$
- Non-Kramers: $\gamma_x = 1, \gamma_y = e^{2\pi i/3}, \gamma_z = e^{-2\pi i/3}$ $J_{z\pm} = 0$
- Dipolar-Octupolar: $\gamma_{ij} = 1$

**Origin of exchange?**

# Origin of Exchange interactions?

- Lots of ways to generate exchange interactions
  - **Magneto- and electro-statics** *Rare-Earths*
  - *Direct exchange* *Transition Metals*
  - **Super-exchange (ligand-mediated)** *Transition Metals, Rare-earths*
  - Exchange via higher orbitals (5d, 6s)
  - Exchange via inter-shell interactions
  - Magneto-elastic couplings
  - Virtual crystal field interactions
- Many competing mechanisms, small energy scales, hard to estimate

**Complicated …**

# Special Cases?

- General (*pseudo-*) *spin-1/2* model can take the form

*Heisenberg – Align or Anti-align*

*In **weak** SOC limit $J >> D >> \Gamma$*

*$\Gamma$ is a symmetric 3x3 matrix*

$$\sum_{ij}\left[J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j + \mathbf{D}_{ij}\cdot(\mathbf{S}_i\times\mathbf{S}_j) + \mathbf{S}_i\cdot(\mathbf{\Gamma}_{ij}\cdot\mathbf{S}_j)\right]$$

*Dzyaloshinskii-Moriya (DM) interaction*

*Symmetric anisotropy (pseudo-dipolar, Ising, etc)*

- **Transition metal with weak SOC**: Expect leading terms to be Heisenberg + D.M.
- **Spin-Only Moment ($Fe^{3+}$, $Gd^{3+}$, $Eu^{2+}$, …) :** Expect Heisenberg dominant (& possibly dipolar interactions)
- **Large ΔJ in CEF doublet:** Ising-like interactions

**"Standard" limits:**

*Heisenberg* $J\sum_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j$

*XY* $J\sum_{\langle ij\rangle}\left(S_i^xS_j^x + S_i^yS_j^y\right)$

*Ising* $J\sum_{\langle ij\rangle}S_i^zS_j^z$

**Strong SOC? No prescribed form!**

I. Dzyaloshinskii, J. Phys. Chem. of Solids **4**, 241 (1958), T. Moriya, Phys. Rev. **120**, 91 (1960)

# Summary of Two-Ion Physics

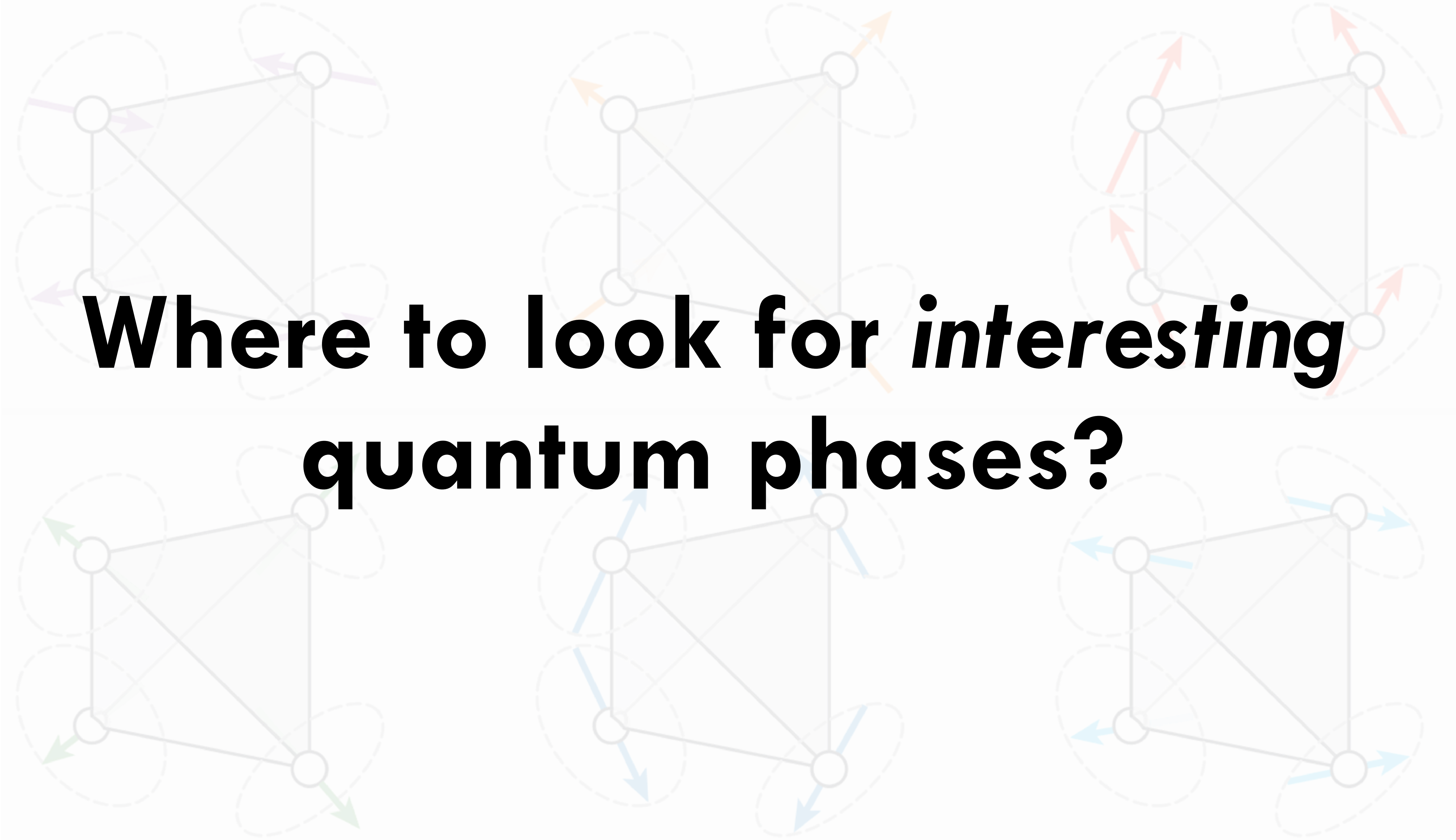
| | Irrep. | $g_z$ | $g_\pm$ | Time. rev. | $C_3$ | $C_2$ | States | Examples |
|---|---|---|---|---|---|---|---|---|
| Pseudo-spin | $\Gamma_4$ | $\neq 0$ | $\neq 0$ | $\mathbf{S} \to -\mathbf{S}$ | $S^z \to S^z$<br>$S^\pm \to e^{\pm\frac{2\pi i}{3}} S^\pm$ | $S^z \to -S^z$<br>$S^\pm \to S^\mp$ | $\lvert\pm\frac{1}{2}\rangle, \lvert\pm\frac{5}{2}\rangle, \cdots$ | $Er_2Ti_2O_7$,<br>$Yb_2Ti_2O_7$ |
| Dipolar-octupolar | $\Gamma_5 \oplus \Gamma_6$ | $\neq 0$ | $0$ | $\mathbf{S} \to -\mathbf{S}$ | $\mathbf{S} \to \mathbf{S}$ | $S^z \to -S^z$<br>$S^\pm \to S^\mp$ | $\lvert\pm\frac{3}{2}\rangle, \lvert\pm\frac{9}{2}\rangle, \cdots$ | $Dy_2Ti_2O_7$ |
| Non-Kramers | $E_g$ | $\neq 0$ | $0$ | $S^z \to -S^z$<br>$S^\pm \to S^\mp$ | $S^z \to S^z$<br>$S^\pm \to e^{\pm\frac{2\pi i}{3}} S^\pm$ | $S^z \to -S^z$<br>$S^\pm \to S^\mp$ | $\lvert\pm 1\rangle, \lvert\pm 4\rangle, \lvert\mp 5\rangle, \cdots$ | $Ho_2Ti_2O_7$,<br>$Tb_2Ti_2O_7$ |

$$\sum_{\langle ij \rangle} \Big[ J_{zz} S_i^z S_j^z - J_\pm \left( S_i^+ S_j^- + S_i^- S_j^+ \right) + J_{\pm\pm} \left( \gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^- \right)$$

$$+ J_{z\pm} \left( \zeta_{ij} \left[ S_i^z S_j^+ + S_i^+ S_j^z \right] + \zeta_{ij}^* \left[ S_i^z S_j^- + S_i^- S_j^z \right] \right) \Big]$$

$$\zeta_{ij} = -\gamma_{ij}^*$$

| | |
|---|---|
| $\gamma_x = 1, \gamma_y = e^{2\pi i/3}, \gamma_z = e^{-2\pi i/3}$ | $\gamma_{ij} = 1$ |
| $\gamma_x = 1, \gamma_y = e^{2\pi i/3}, \gamma_z = e^{-2\pi i/3}$ | $J_{z\pm} = 0$ |



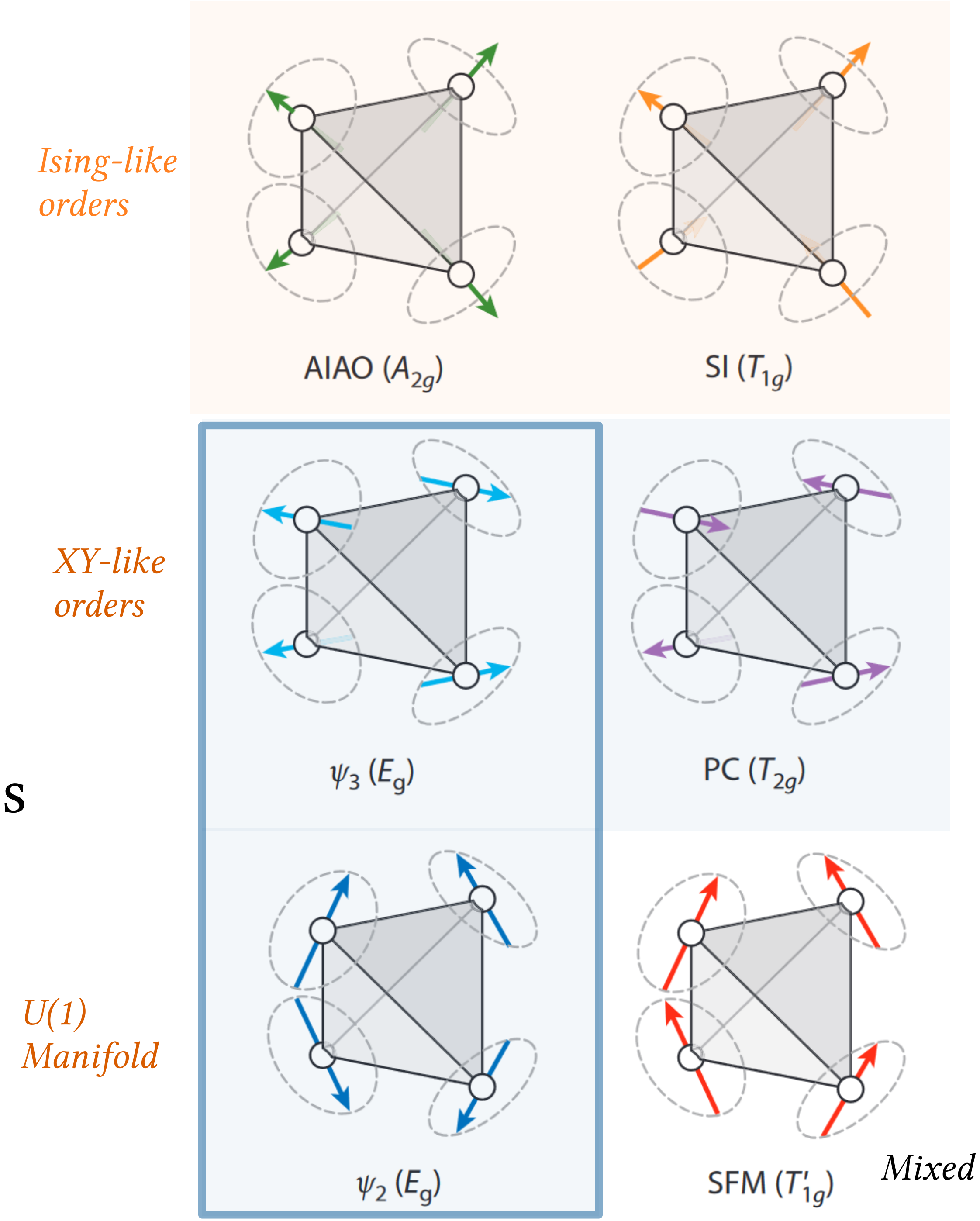
# Where to look for *interesting* quantum phases?

# Classical Phases

- To find *interesting* regions, identify “boring” ones first:
- Start from *classical* limit

$$\boldsymbol{S}_i \approx \langle \boldsymbol{S}_i \rangle$$

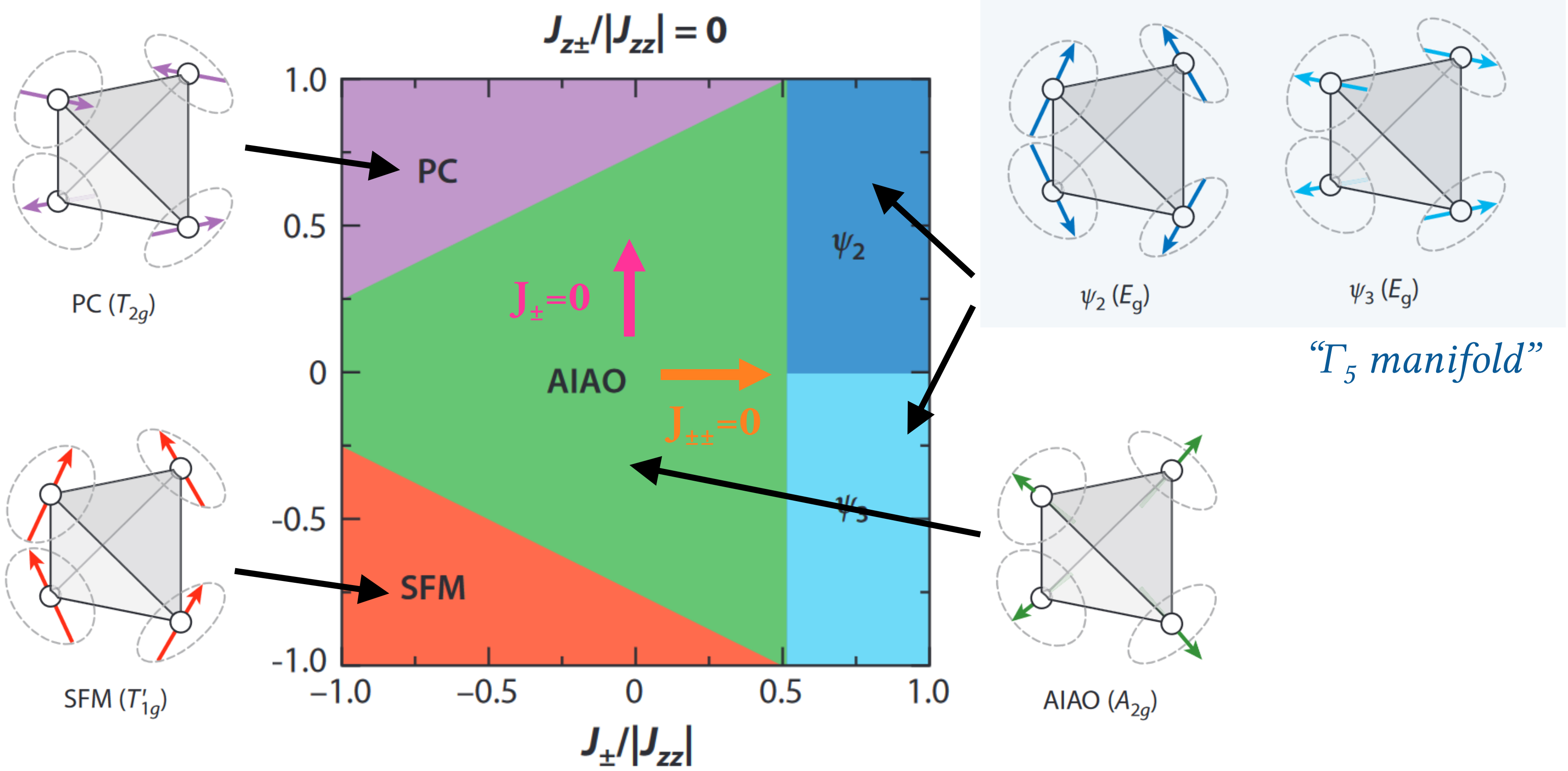
- Energy minimization finds only orders within the unit cell (**Q=0**)
- *Six* classes of order




e.g. Yan et al, Phys. Rev. B **95** 094422 (2017)

**Simplest limit:**

$J_{zz}<0$ and $J_{z\pm}=0$

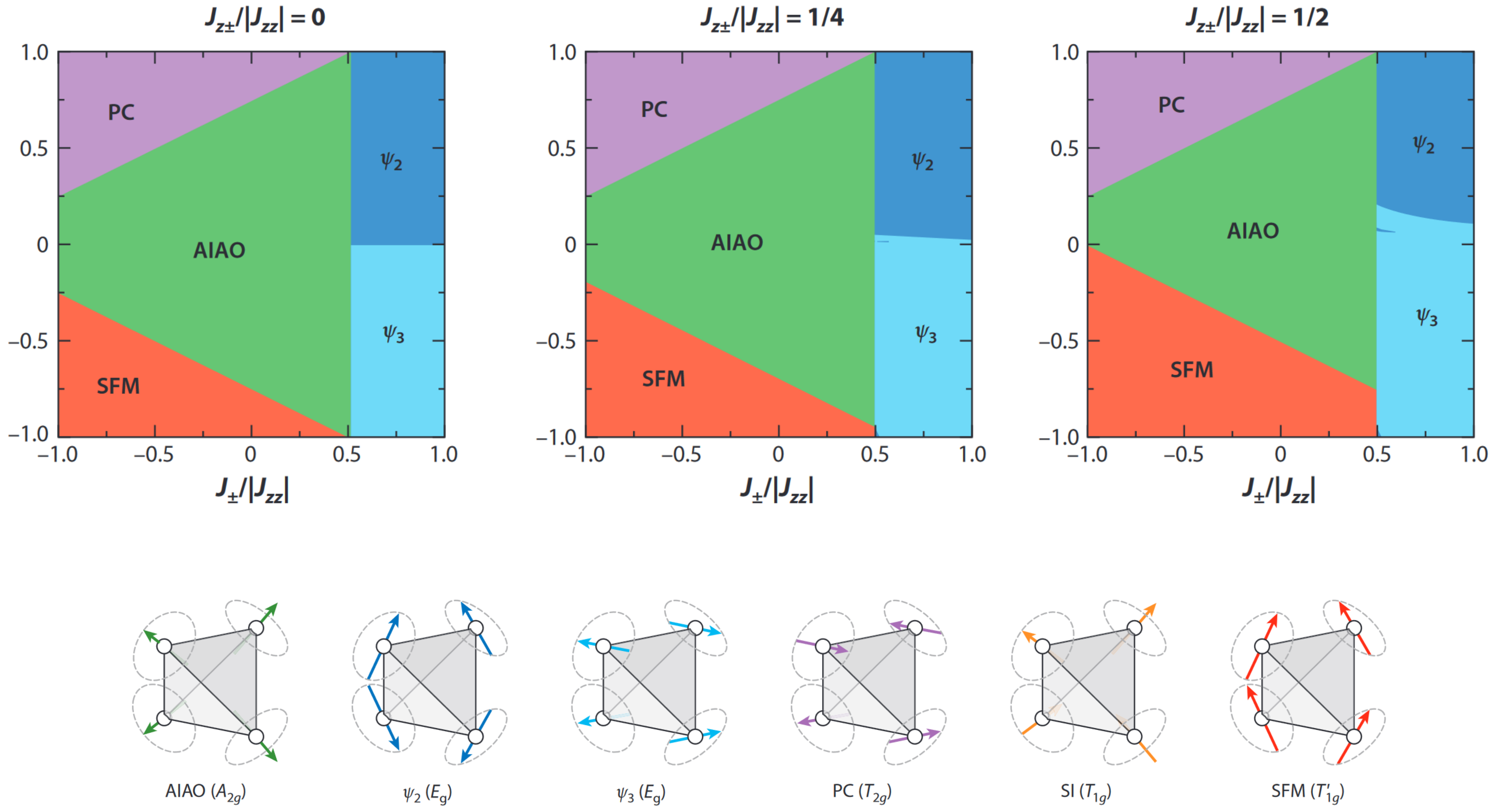



*Negative*

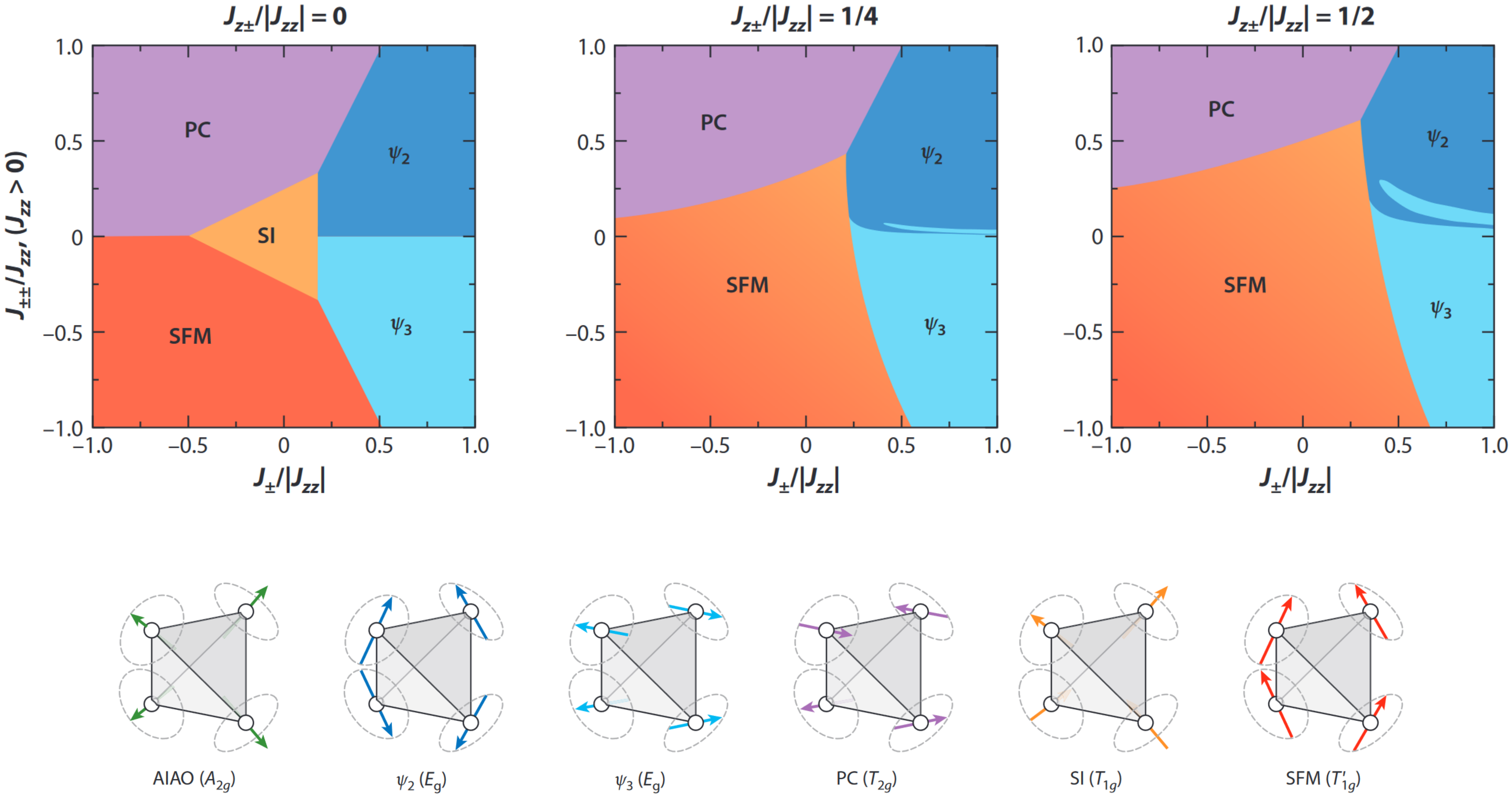
$$\sum_{\langle ij\rangle}\left[J_{zz}S_i^zS_j^z - J_{\pm}\left(S_i^+S_j^- + S_i^-S_j^+\right) + J_{\pm\pm}\left(\gamma_{ij}S_i^+S_j^+ + \gamma_{ij}^*S_i^-S_j^-\right)\right.$$

$$\left. + J_{z\pm}\left(\zeta_{ij}\left[S_i^zS_j^+ + S_i^+S_j^z\right] + \zeta_{ij}^*\left[S_i^zS_j^- + S_i^-S_j^z\right]\right)\right]$$

*Setting $J_{z\pm}=0$ is required in the non-Kramers case*

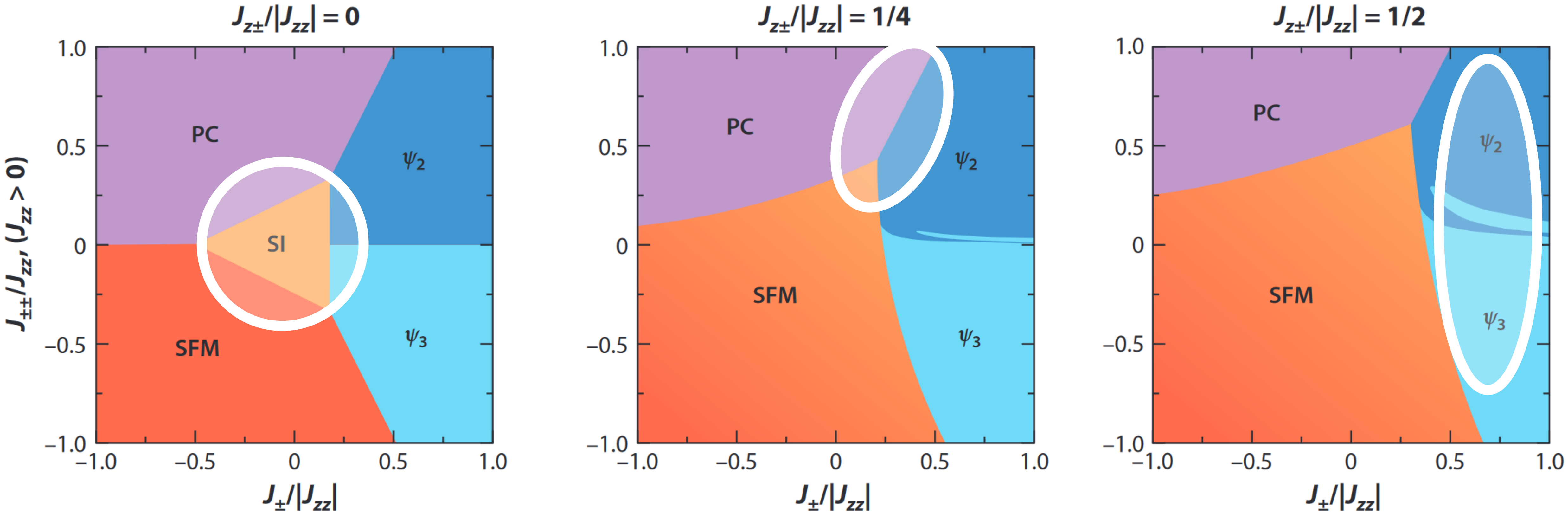


$J_{z\pm}/|J_{zz}| = 0$
$J_{z\pm}/|J_{zz}| = 1/4$
$J_{z\pm}/|J_{zz}| = 1/2$
PC
AIAO
SFM
$\psi_2$
$\psi_3$
1.0
0.5
0
−0.5
−1.0
$J_{\pm}/|J_{zz}|$
AIAO ($A_{2g}$)
$\psi_2$ ($E_g$)
$\psi_3$ ($E_g$)
PC ($T_{2g}$)
SI ($T_{1g}$)
SFM ($T'_{1g}$)



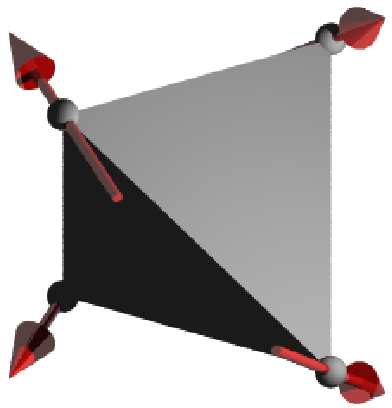
Jz±/|Jzz| = 0
Jz±/|Jzz| = 1/4
Jz±/|Jzz| = 1/2
J±±/Jzz, (Jzz > 0)
J±/|Jzz|
PC
SI
SFM
ψ2
ψ3
1.0
0.5
0
−0.5
−1.0
AIAO (A2g)
ψ2 (Eg)
ψ3 (Eg)
PC (T2g)
SI (T1g)
SFM (T′1g)

# Interesting “Quantum” Regions




***Quantum Spin Ice*** ***Pinch “lines”?*** ***Order-by-Disorder***

# Order by Disorder

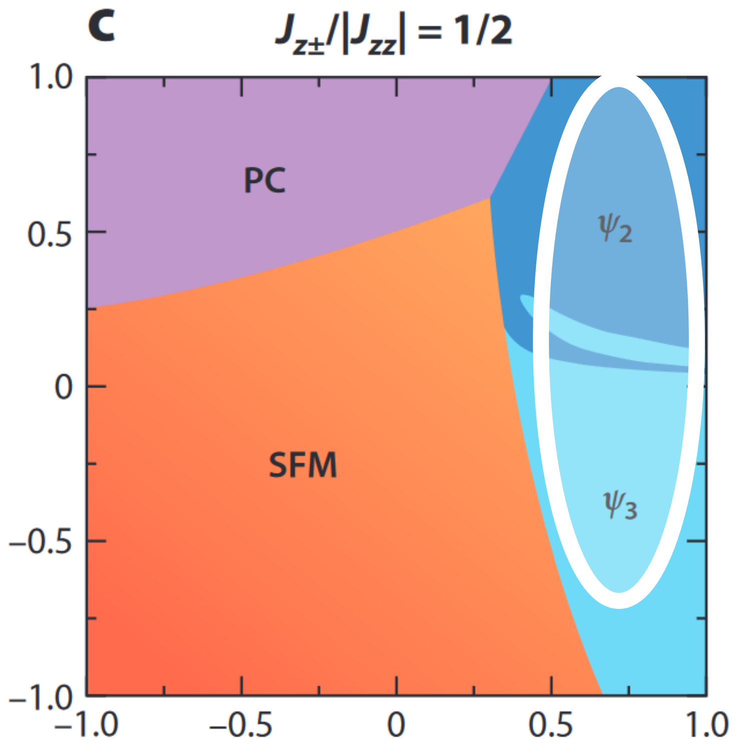


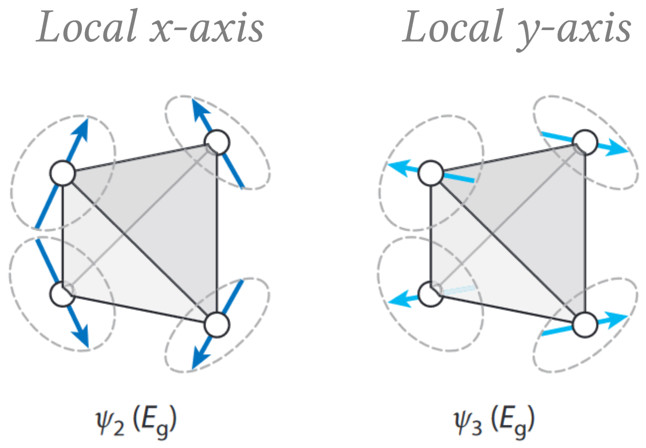
State with minimum energy isn't unique

- Classical energy *doesn't distinguish* between $\psi_2$ and $\psi_3$ states

**U(1) degeneracy:** Rotating these states about local z-axes does not change energy

- *Not a symmetry of the Hamiltonian – "accidental"*

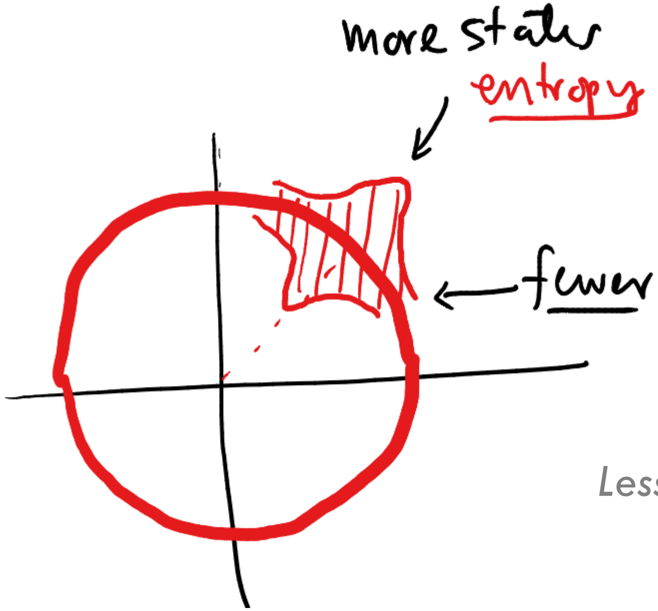


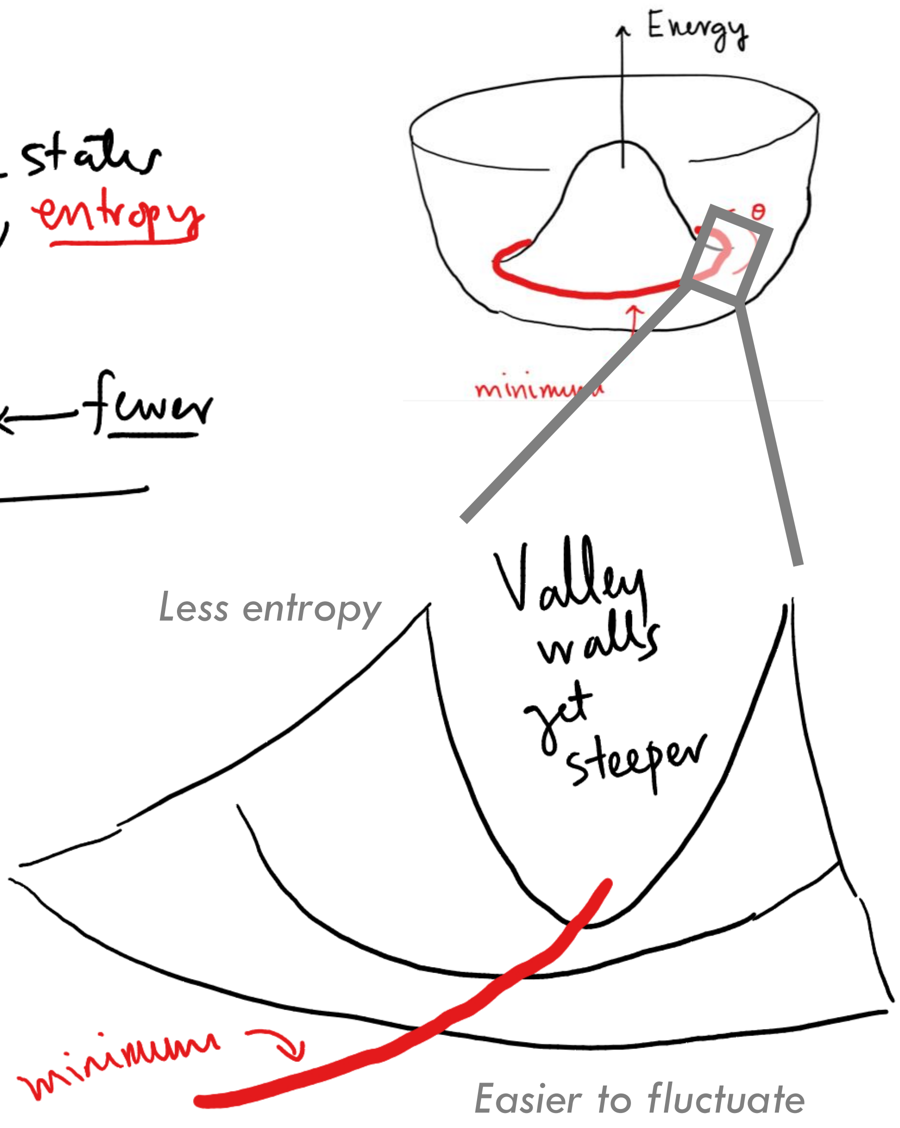

Champion et al, Phys. Rev. B. **68** 020401(R) (2003)

# Ground State Selection

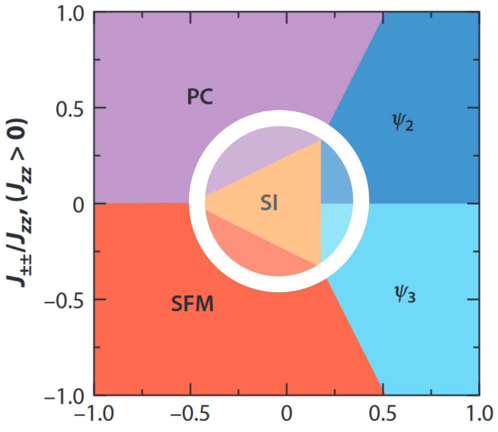
- Fluctuations *around* the ground states can be different
- **Quantum zero point fluctuations** select a ground state




- **Realized in $Er_2Ti_2O_7$:** $\psi_2$ ground state is selected by quantum fluctuations




*Savary et al., Phys. Rev. Lett.* ***109*** *167201 (2012), Zhitomirsky et al, Phys. Rev. Lett.* ***109*** *077204 (2012)*

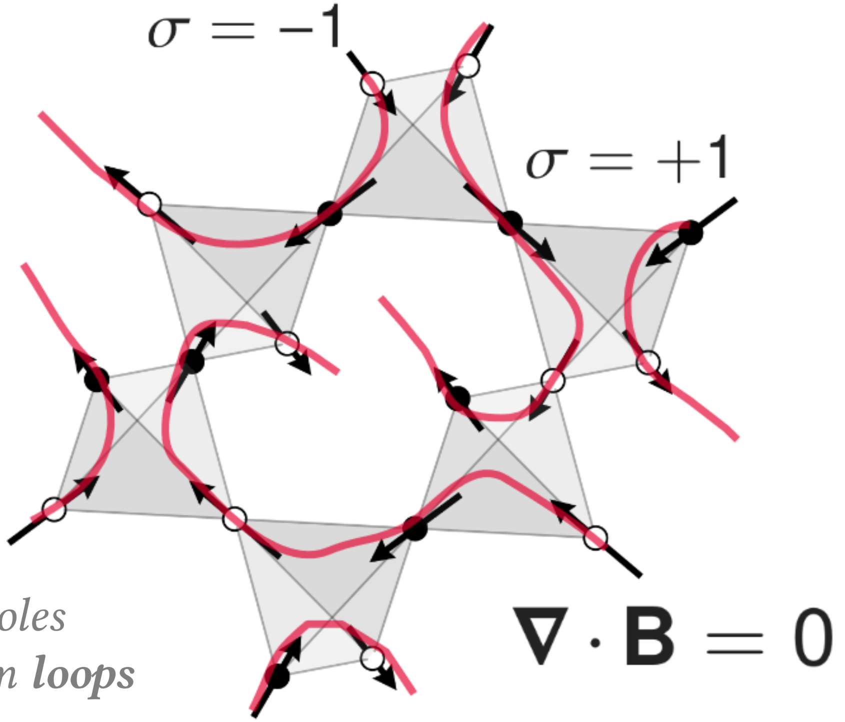



# Classical Spin Ice

- Ising model:

$$J_{zz} \sum_{\langle ij \rangle} S_i^z S_j^z$$

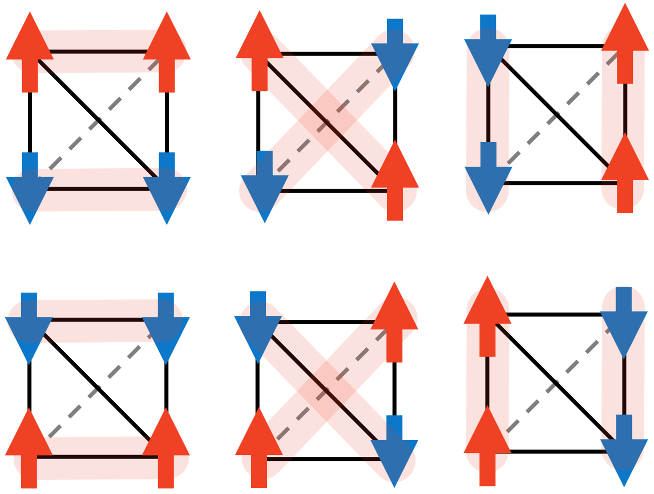
*Positive*



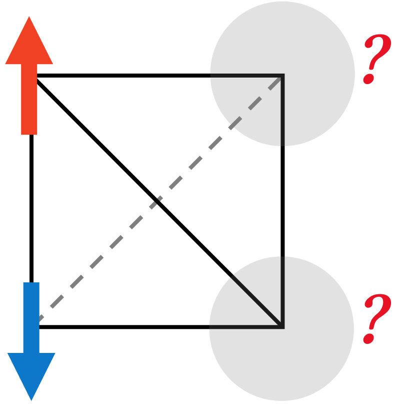

*Dipoles form **loops***

*Corner-sharing tetrahedra*

*"Two in / two out" rule*



*Six ground states per tetrahedron*




*Tetrahedron*

- Extensive ground state degeneracy
- **Classical spin liquid**

# Quantum Spin Ice

- Simplest perturbation:

$$H = J_{zz} \sum_{\langle ij \rangle} S_i^z S_j^z - J_{\pm} \sum_{\langle ij \rangle} \left( S_i^+ S_j^- + \text{h.c.} \right)$$

*Classical spin ice model*

*Term that induces quantum fluctuations*

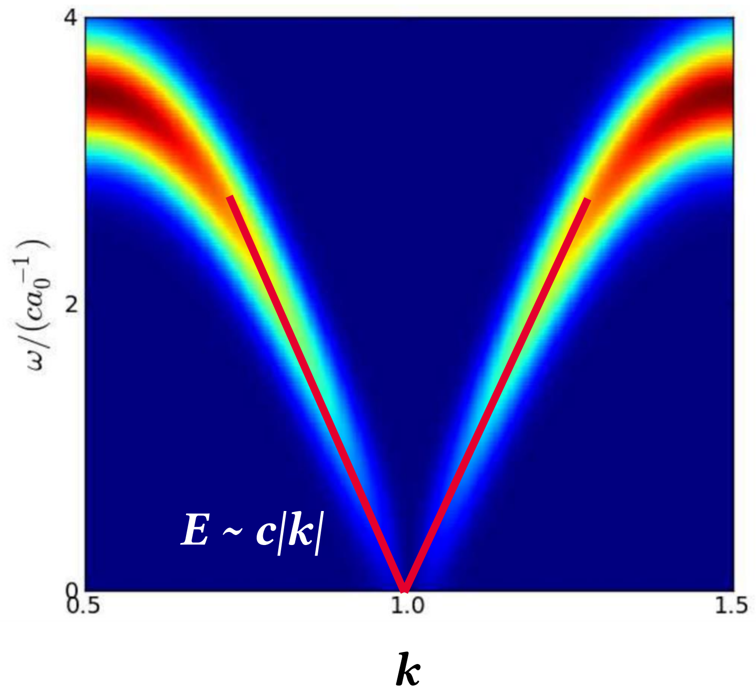
- Effective model:

*Perturbative in quantum part*

$$-\frac{12 J_{\pm}^3}{J_{zz}^2} \sum_{\text{hexagons}} P_{\text{ice}} \left( S_1^+ S_2^- S_3^+ S_4^- S_5^+ S_6^- + \text{h.c.} \right) P_{\text{ice}}$$

*Can map to U(1) lattice gauge theory;* ***solve numerically***

*Emergent photon excitation*



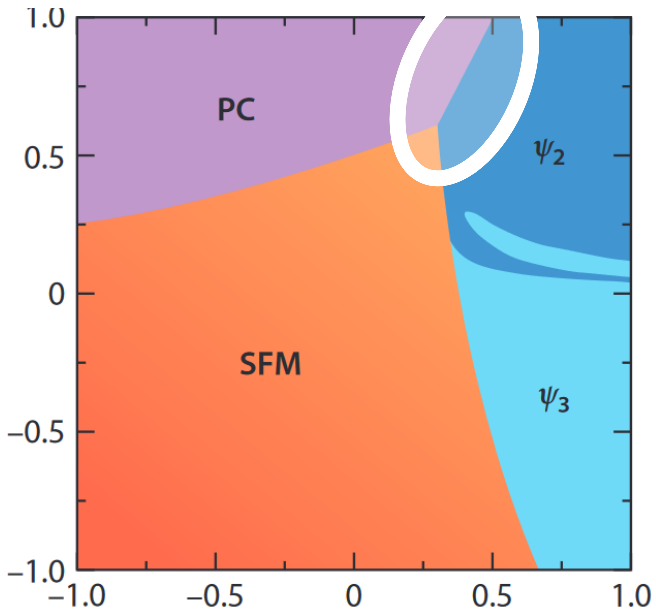

***Classical SI:*** **emergent magnetostatics**

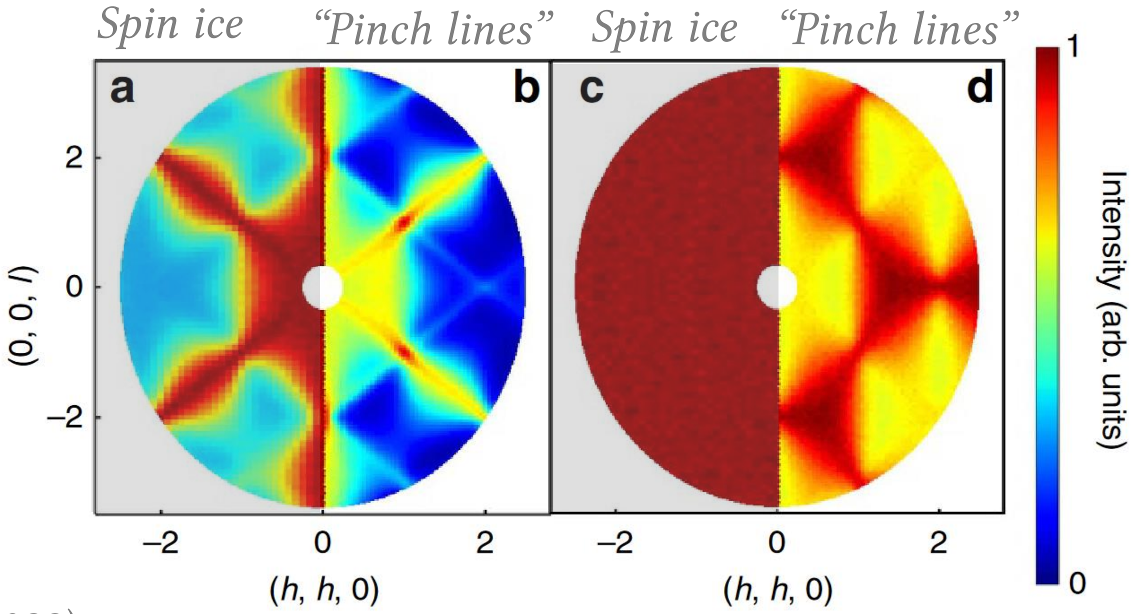
***Quantum SI:*** **emergent electrodynamics**

*Hermele et al., Phys. Rev. B* ***69*** *064404 (2004), Benton et al, Phys. Rev. B* ***86*** *075154 (2012)*

# More exotic spin liquids?

- Interesting physics at *other* places multiple phases meet (*away* from ice limit)
- *Classical models* show new kinds of **classical spin liquids** near the points
- "Higher rank" gauge structures
  - **What happens in the quantum limit?**
- Applications to $Yb_2Ti_2O_7$?




*Benton et al, Nat. Comm. 7 11572 (2016); Scheie et al, arXiv:2202.11085 (2022)*

# Summary

## Quantum Pyrochlores

- Rich variety of degrees of freedom and models
- **Three types of "effective spin"**, each with unique features
- **Up to four anisotropic exchanges**, leading to classical phase diagram with **six (non-colinear) ordered phases**
- *Quantum* effects appear in bulk of phases, at phase boundaries and points where three or more phases meet
  - **Order-by-quantum-disorder**
  - **Quantum spin ice** (classical spin ice limit)
  - Other, *new*, phases along the boundary?

**Thank you for your attention**

Rau & Gingras, Annual Review of Condensed Matter Physics **10**, 357-386 (2019)