Title: Microscopic aspects of insulating rare-earth pyrochlore magnets

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Abstract: In this tutorial, we will review the microscopic aspects of rare-earth magnets relevant for quantum spin ice. We first discuss the single-ion properties of the variety of rare-earth atoms that appear in quantum spin ice candidate materials. Second, we consider the origin of the two-ion exchange interactions, including electric and magnetic multipolar interactions, super-exchange and virtual crystal field mediated interactions. We provide a detailed microscopic basis for the super-exchange interaction and discuss the implications of its multipolar structure for models of rare-earth materials. Finally, we introduce the generic symmetry allowed anisotropic exchange model for rare-earth pyrochlore magnets.

Tutorial on:

Microscopic aspects of insulating rare-earth pyrochlore magnets

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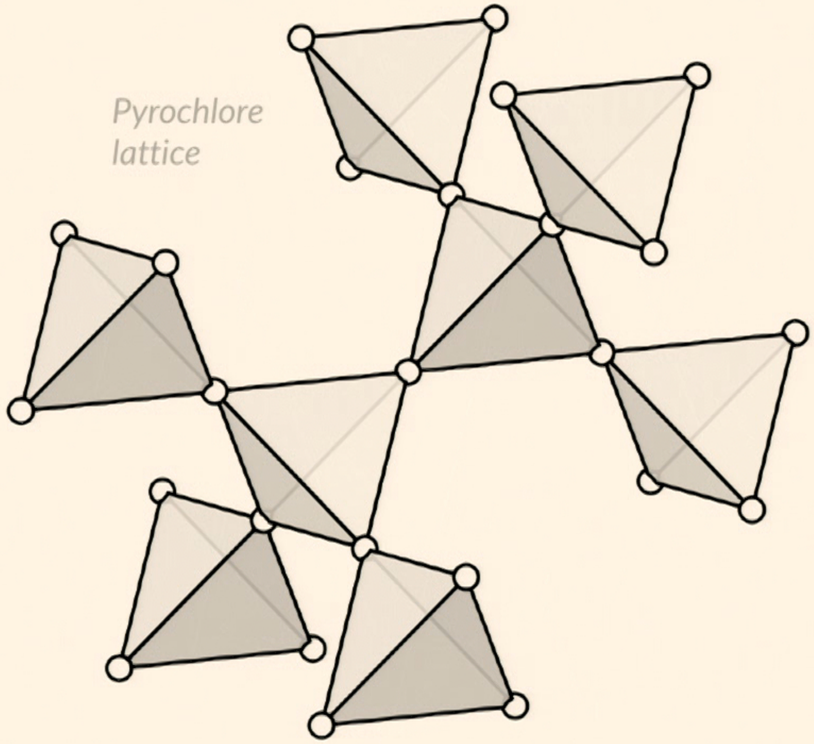
International workshop on quantum spin ice (Perimeter Institute, June 7th, 2017)

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
- Strong insulators



Rare-earths?

Why rare-earths?

- Lathanide series: **partially filled** $4f^n$ shell (n = 1, …, 13)

Magnetic trivalent rare-earths

La-Ce-Pr-Nd-Pm-Sm-Eu-Gd-Tb-Dy-Ho-Er-Tm-Yb-Lu

Non-magnetic *Radioactive* *Non-magnetic* *Non-magnetic*

- Chemically **versatile**
- Clean **separation of energy scales** (*mostly*)

Coulomb >> Spin-Orbit >> Crystal field >> Exchange

O(10 eV) *O(1 eV)* *O(100 meV)* *O(0.1-1 meV)*

- Well-defined local degrees of freedom (contrast: transition metals)

Free-ion

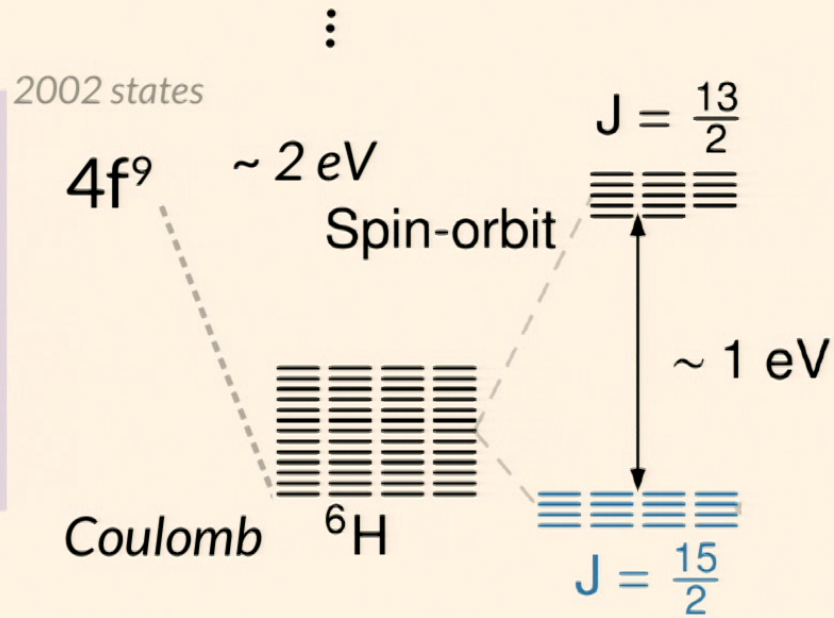
- Many 4f electrons in most cases – many states
- Only **free-ion ground state** is relevant

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



Free-ion (cont.)

- Many degrees of freedom in J-manifold
- Has **much more than dipoles**

Multipole operator — |Q| <= K

$$\langle J, M|\, O_{KQ}(\mathbf{J})\, |J, M'\rangle \propto \langle J, M; K, Q|J, M'\rangle,$$

Imparts Q units of angular momentum to state — *Clebsch-Gordan coefficient*

- K = multipole's **rank** (K^{th} order polynomial in J)
  - *Maximum rank of 2J*

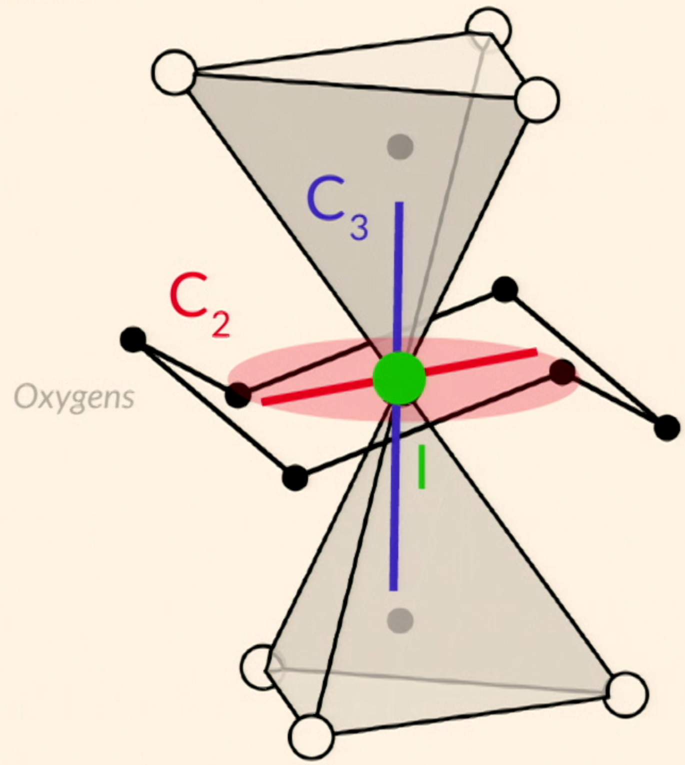
Examples:

- Rank-2 ~ $J_zJ_y + J_yJ_z$, $J_x^2 - J_y^2$, … (quadrupoles)
- Rank-3 ~ $J_xJ_yJ_z$, J_z^3, … (octupoles)
- Rank-6 ~ $(J_+)^6 + (J_-)^6$, … (no name)

Crystalline electric field

- J-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 from 2J+1 to **singlet or doublet**

Form of CEF interaction?



Local environment for $R_2M_2O_7$

Crystalline electric field (cont.)

- Effective Stevens' operator form

$$\mathcal{V}(\mathbf{J}) = B_{20}O_{20}(\mathbf{J}) + B_{40}O_{40}(\mathbf{J}) + B_{43}O_{43}(\mathbf{J}) + B_{60}O_{60}(\mathbf{J}) + B_{63}O_{63}(\mathbf{J}) + B_{66}O_{66}(\mathbf{J})$$

- Six parameters B_{kq} strongly material dependent
- Typical energy splittings **~ 10 meV – 100 meV** (~ 1 meV in exceptional cases)

Essentially zero in spin-only cases with L=0

Kinds of CEF ground states?

Crystalline electric field (cont.)

- Classify states by **local symmetry**: label by irreducible representations of D_{3d}

Kramers (*odd* number of electrons)

- Γ_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 doublet (Γ_4)

- Simplest case, **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

$$S^{\pm} = |\pm\rangle\langle\mp| \qquad S^{z} = \frac{|+\rangle\langle+| - |-\rangle\langle-|}{2}$$

Effective spin-1/2 operators

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

- **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

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

- **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

  Single g-factor
  $$\boldsymbol{\mu}_i = \mu_B g_z S_i^z \hat{\mathbf{z}}_i$$

- Sensitive to non-magnetic disorder
- Can couple 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 prop. 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 effective 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} $S_z \rightarrow$ dipole, octupole, … (odd ranks)
    - ~ E_g S_x, $S_y \rightarrow$ quadrupole, hexadecapole … (even ranks)

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

Single-ion summary

- Three **doublet** types under D_{3d} symmetry:

  pseudo-spin, dipolar-octupolar, non-Kramers

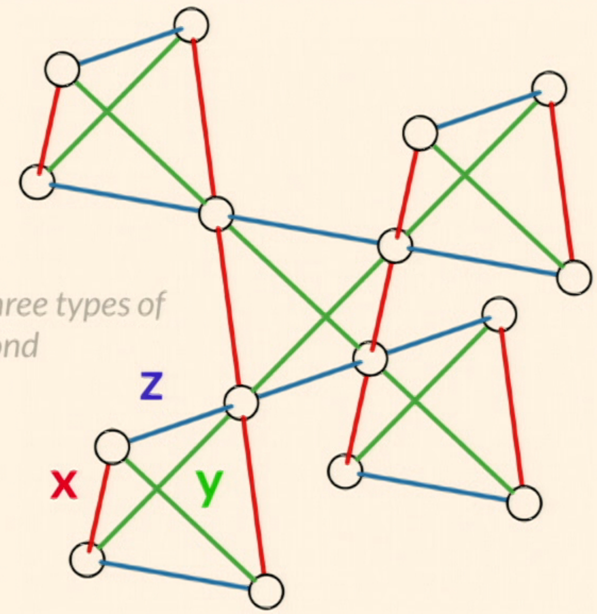
Irrep.	g_z	$g_\pm$	Time. rev.	C_3	C_2	States	Examples
Γ_4	$\neq 0$	$\neq 0$	$\mathbf{S} \to -\mathbf{S}$	$S^z \to S^z$ $S^\pm \to e^{\pm\frac{2\pi i}{3}} S^\pm$	$S^z \to -S^z$ $S^\pm \to S^\mp$	$\lvert\pm\frac{1}{2}\rangle, \lvert\pm\frac{5}{2}\rangle, \cdots$	$Er_2Ti_2O_7$, $Yb_2Ti_2O_7$
$\Gamma_5 \oplus \Gamma_6$	$\neq 0$	0	$\mathbf{S} \to -\mathbf{S}$	$\mathbf{S} \to \mathbf{S}$	$S^z \to -S^z$ $S^\pm \to S^\mp$	$\lvert\pm\frac{3}{2}\rangle, \lvert\pm\frac{9}{2}\rangle, \cdots$	$Dy_2Ti_2O_7$
E_g	$\neq 0$	0	$S^z \to -S^z$ $S^\pm \to S^\mp$	$S^z \to S^z$ $S^\pm \to e^{\pm\frac{2\pi i}{3}} S^\pm$	$S^z \to -S^z$ $S^\pm \to S^\mp$	$\lvert\pm 1\rangle, \lvert\pm 4\rangle, \lvert\mp 5\rangle, \cdots$	$Ho_2Ti_2O_7$, $Tb_2Ti_2O_7$

Interactions?

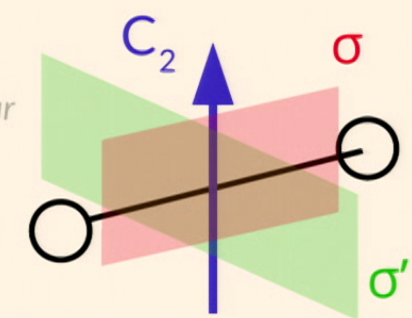
Two-ion physics

- How do these doublets **interact**?
- Consider neighbours
- Strongly constrained by symmetry of lattice
- **Symmetry of bond:**
  - C_2 axis
  - Reflection σ
  - Reflection σ′
- Connect other bonds using C_3 rotations: **x** → **y** → **z**

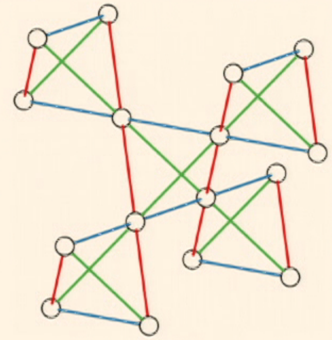
Three types of bond



Nearest neighbour bond



Anisotropic exchange model



- Model takes the form:

XXZ model

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

Bond dependent phases

Zero for non-Kramers

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

Bond dependent phases

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: $\gamma_{ij} = 1$

Quantum spin ice when $J_{zz} > 0$ is **dominant**

Origin of exchange?

Microscopics : Plan

Electronic

$$-\sum_{\langle ij\rangle}\sum_{mm'}\sum_{\sigma}\left(t_{ij}^{mm'} f_{im\sigma}^{\dagger} f_{jm'\sigma} + \text{h.c.}\right) + \sum_{i} H_{\text{ion}}(i)$$

Coulomb, SOC >> CEF, Exchange

$$f_{m\sigma}^{\dagger} f_{m'\sigma'} \to O_{KQ}(\mathbf{J})$$

Project

"Free ion"

$$\sum_{ij}\sum_{KQ}\sum_{K'Q'} \mathcal{M}_{ij}^{KQ,K'Q'} O_{KQ}(\mathbf{J}_i) O_{K'Q'}(\mathbf{J}_j) + \sum_{i} \mathcal{V}(\mathbf{J}_i)$$

CEF >> Exchange

$$O_{KQ}(\mathbf{J}) \to S_{\mu}$$

Project

Effective spin-1/2

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

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

Multipolar interactions

- *All* these multipoles **interact**
- General multipolar Hamiltonian

if K ~ J then non-classical even for large-J

Two-ion interactions *Single-ion interactions*

$$\sum_{ij} \sum_{KQ} \sum_{K'Q'} \mathcal{M}_{ij}^{KQ,K'Q'} O_{KQ}(\mathbf{J}_i) O_{K'Q'}(\mathbf{J}_j) + \sum_i \mathcal{V}(\mathbf{J}_i)$$

Crystal field potential

- *In principle*, rank goes up to 2J → **tens to hundreds** of symmetry allowed couplings for large J

Question: Mechanisms to generate? Any generic, robust features?

Exchange interactions

- Lots of ways to generate exchange interactions
  - Magneto- and electro-statics
  - Direct exchange
  - Super-exchange (ligand-mediated)
  - 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

Electro- and magneto-statics

- Atomic multipoles carry **magnetic** (*odd* rank) and **electric** (*even* rank) **multipole moments**
- Only two significant:
  - Magnetic dipole-dipole (MDD)

Long-range

Between 0.1-10K or so

$$\frac{g_L^2\mu_B^2\mu_0}{4\pi}\sum_{i<j}\left[\frac{\mathbf{J}_i\cdot\mathbf{J}_j}{|\mathbf{r}_{ij}|^3}-\frac{3(\mathbf{J}_i\cdot\hat{\mathbf{r}}_{ij})(\mathbf{J}_j\cdot\hat{\mathbf{r}}_{ij})}{|\mathbf{r}_{ij}|^3}\right]$$

  - Electric quadupole-quadrupole (EQQ)

Effectively short-range ~ $1/r^5$

$$\mathscr{Q}\sum_{\langle ij\rangle}\hat{\mathbf{r}}_{ij}^{\intercal}\left(\frac{1}{3}\mathrm{tr}\left[\mathbf{Q}_i\mathbf{Q}_j\right]-\frac{10}{3}\mathbf{Q}_i\mathbf{Q}_j+\frac{35}{6}\mathbf{Q}_i\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}^{\intercal}\mathbf{Q}_j\right)\hat{\mathbf{r}}_{ij}$$

Can be of order ~ 1K

Quadrupole matrix

Only relevant at low energy for non-Kramers

Super-exchange

- Generate exchange through ligand mediated processes
- Complicated in rare-earths
  - **Large orbital contributions** to states
  - Large and varied set of **virtual atomic states** in process

Example:
Charge transfer process

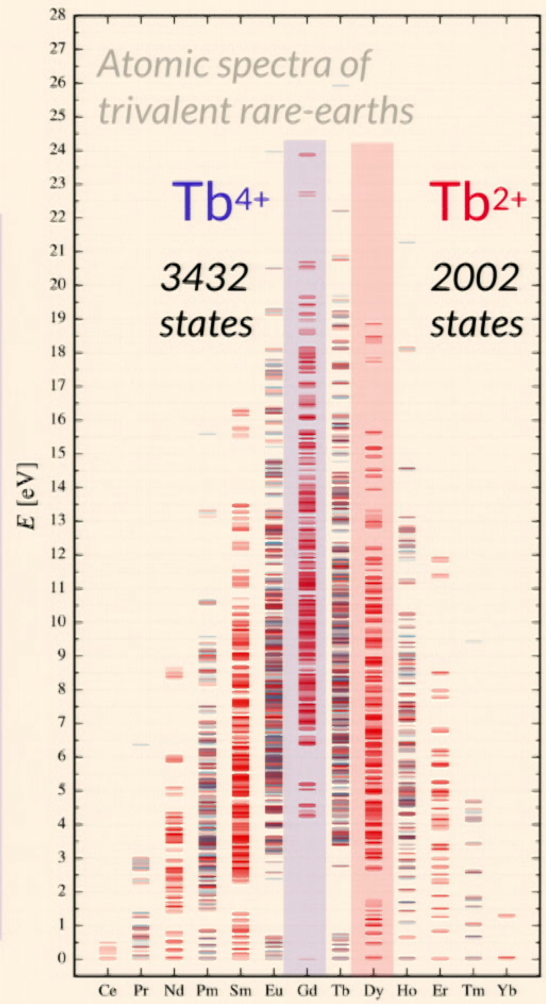
Tb^{3+} - Tb^{3+}

←

Tb^{2+} - Tb^{4+}

→

Tb^{3+} - Tb^{3+}



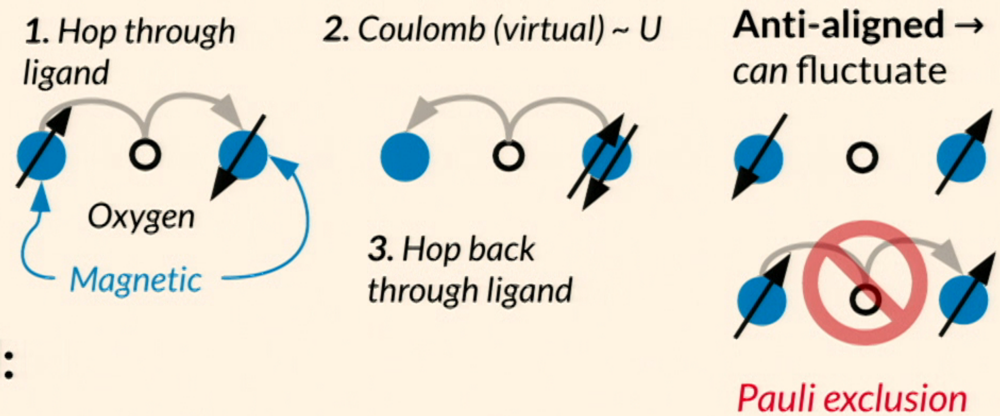
What operators?

Super-exchange (cartoon)

- **Recall:** super-exchange for one-band Hubbard model:

$$-t\sum_{\langle ij\rangle}\left(c^{\dagger}_{i\sigma}c_{j\sigma}+\text{h.c.}\right)+U\sum_{i}n_{i\uparrow}n_{i\downarrow}$$

- **Localized spin-1/2** in Mott limit: U >> t



Effective model:

$$\frac{2t^2}{U}\sum_{\langle ij\rangle}\sum_{\sigma\sigma'}\left(P_1c^{\dagger}_{i\sigma}c_{i\sigma'}P_1\right)\left(P_1c^{\dagger}_{j\sigma'}c_{j\sigma}P_1\right)=\frac{4t^2}{U}\sum_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j$$

Anti-ferromagnetic

Super-exchange (cont.)

- Operators that appear **non-generic**
- Microscopic constraints on multipolar content
- *Roughly*: Must transfer an electron there and back → L=3, S=1/2
- Can only only change angular momentum by at most **seven units**
- Holds even when approximations lifted

Example:
$Dy_2Ti_2O_7$ (J=15/2),
$Ho_2Ti_2O_7$ (J=8)

$$|\pm\rangle_{\mathrm{Dy}} \sim |\pm 15/2\rangle + (\lesssim 10\%)$$
$$|\pm\rangle_{\mathrm{Ho}} \sim |\pm 8\rangle + (\lesssim 10\%)$$

Spin-flip is rank-15, 16
→ **Nearly classical**

Example:
$Yb_2M_2O_7$ (J=7/2)
All operators rank <=7
→ **Always quantum**

Two-ion summary

- High-rank multipolar interactions (*beyond* dipole) are significant
- **But:** generically should expect: rank <= 7 multipoles
  - Can *sometimes* strongly constrain anisotropic model

Key takeaways:

- Single-ion and two-ion physics **not** apriori related
  - Ising moment ≠> Ising interactions
  - XY moment ≠>XY interactions
- Interactions in J-manfiold **not** bilinear
- *Some* constraints on multipolar content

$\mathbf{J}_i \cdot \mathbf{J}_j$

Super-exchange (cont.)

- Integrate out ligands → direct 4f-4f hopping integrals
- Effective (simplified) 4f-electron model:

Coulomb, SOC, ...

Ligand mediated

$$-\sum_{\langle ij\rangle}\sum_{mm'}\sum_{\sigma}\left(t_{ij}^{mm'} f_{im\sigma}^{\dagger} f_{jm'\sigma} + \text{h.c.}\right) + \sum_{i} H_{\text{ion}}(i)$$

  - t = Hopping integrals of f-orbitals
  - H_{ion} = full free-ion interactions (Coulomb, spin-orbit)

- Strong coupling limit, assume one dominant energy scale

Complicated orbital structure

$$\sum_{\langle ij\rangle}\sum_{m_1 m_1'}\sum_{m_2 m_2'}\sum_{\sigma_1\sigma_2} \frac{2t_{ij}^{m_1 m_1'} t_{ij}^{m_2 m_2'}}{U} \left(P_J f_{im_1\sigma_1}^{\dagger} f_{im_2\sigma_2} P_J\right)\left(P_J f_{jm_2'\sigma_2}^{\dagger} f_{jm_1'\sigma_1} P_J\right)$$

Operator in J-manifold at site i

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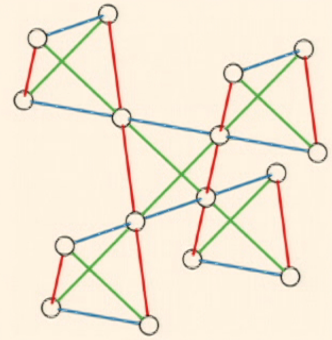

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Bond dependent phases

Zero for non-Kramers

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

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$$\mathbf{J}_i \cdot \mathbf{J}_j$$

- *Some* constraints on multipolar content

Aside: Virtual crystal field interactions

- Assumed separation CEF >> Exchange
  - 1st order perturbation theory (projection)
- **Not always clear**
  - $Tb_2Ti_2O_7$, CEF gap ~ 2 meV
  - $Er_2Ti_2O_7$, CEF gap ~ 4 meV
- Must treat multipolar exchanges as perturbation to CEF and go to 2nd order or higher
  - **All** higher rank interactions contribute!
- Essentially **no constraints** on generated interactions even at 2nd order

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Electronic

$$-\sum_{\langle ij\rangle}\sum_{mm'}\sum_{\sigma}\left(t_{ij}^{mm'} f_{im\sigma}^{\dagger} f_{jm'\sigma} + \text{h.c.}\right) + \sum_{i} H_{\text{ion}}(i)$$

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$$f_{m\sigma}^{\dagger} f_{m'\sigma'} \to O_{KQ}(\mathbf{J})$$

Project

"Free ion"

$$\sum_{ij}\sum_{KQ}\sum_{K'Q'} \mathcal{M}_{ij}^{KQ,K'Q'} O_{KQ}(\mathbf{J}_i) O_{K'Q'}(\mathbf{J}_j) + \sum_{i} \mathcal{V}(\mathbf{J}_i)$$

CEF >> Exchange

$$O_{KQ}(\mathbf{J}) \to S_{\mu}$$

Project

Effective spin-1/2

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

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Summary

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Pseudo-spin	Γ_4	$\neq 0$	$\neq 0$	$\mathbf{S} \to -\mathbf{S}$	$S^z \to S^z$ $S^\pm \to e^{\pm\frac{2\pi i}{3}} S^\pm$	$S^z \to -S^z$ $S^\pm \to S^\mp$	$\|\pm\frac{1}{2}\rangle, \|\pm\frac{5}{2}\rangle, \cdots$	$Er_2Ti_2O_7$, $Yb_2Ti_2O_7$
Dipolar-octupolar	$\Gamma_5 \oplus \Gamma_6$	$\neq 0$	0	$\mathbf{S} \to -\mathbf{S}$	$\mathbf{S} \to \mathbf{S}$	$S^z \to -S^z$ $S^\pm \to S^\mp$	$\|\pm\frac{3}{2}\rangle, \|\pm\frac{9}{2}\rangle, \cdots$	$Dy_2Ti_2O_7$
Non-Kramers	E_g	$\neq 0$	0	$S^z \to -S^z$ $S^\pm \to S^\mp$	$S^z \to S^z$ $S^\pm \to e^{\pm\frac{2\pi i}{3}} S^\pm$	$S^z \to -S^z$ $S^\pm \to S^\mp$	$\|\pm 1\rangle, \|\pm 4\rangle, \|\mp 5\rangle, \cdots$	$Ho_2Ti_2O_7$, $Tb_2Ti_2O_7$

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

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

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

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