Spin-orbit coupling of the t_{2g} orbitals

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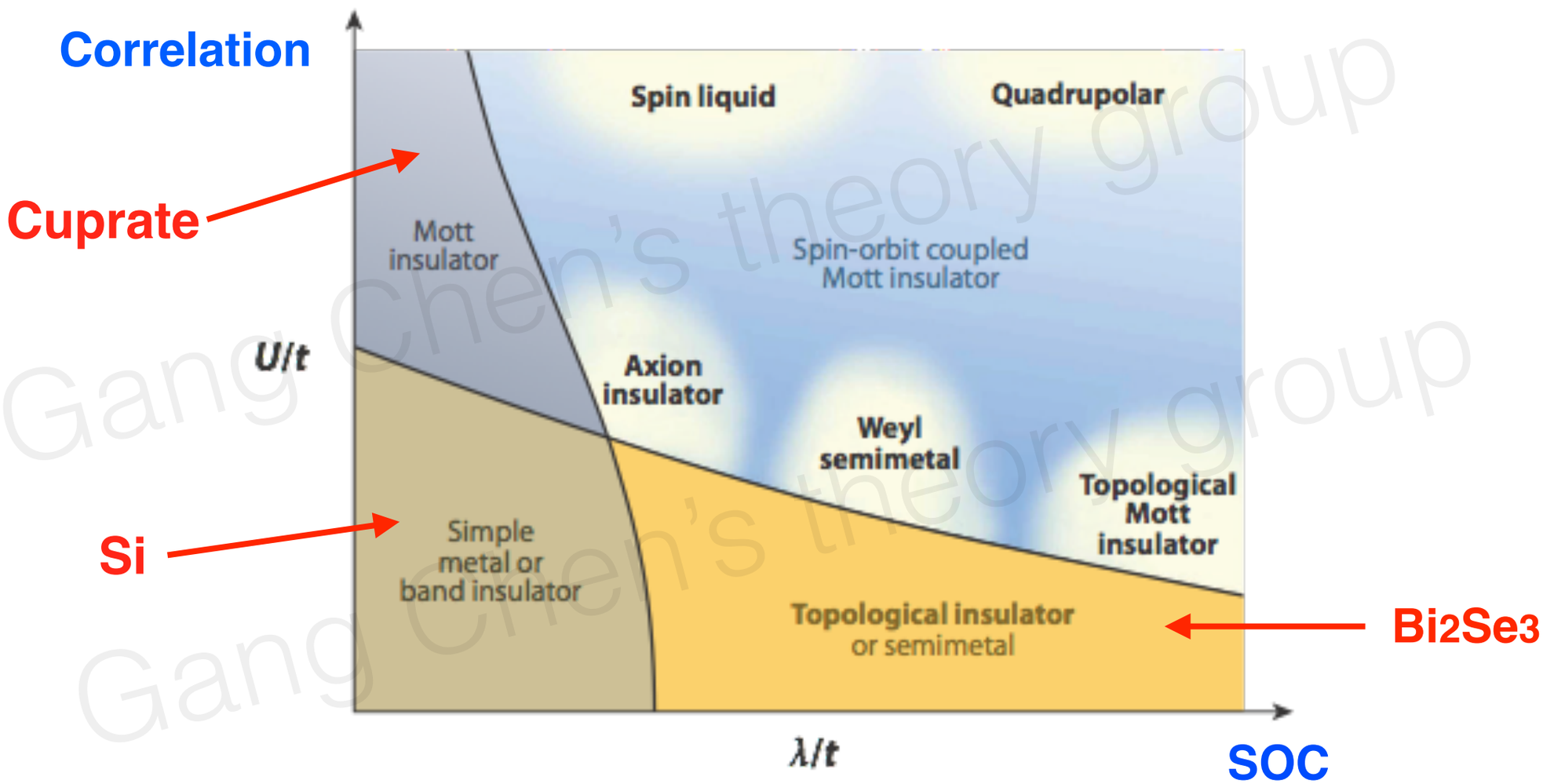
Outline

- General overview: spin-orbit coupling and correlation
- Iridates: spin-orbit coupling and $J_{eff} = 1/2$
- Beyond iridates: multipolar order, exciton magnetism, etc
- Summary

1. General overview: the interplay between spin-orbit coupling and correlation

Extended Hubbard model and generic phase diagram

$$H = \sum_{i,j;\alpha\beta} t_{ij,\alpha\beta}\, c^{\dagger}_{i\alpha} c_{j\beta} + \text{h.c.} + \lambda \sum_i \boldsymbol{L}_i \cdot \boldsymbol{S}_i + U \sum_{i,\alpha} n_{i\alpha}(n_{i\alpha} - 1)\,,$$



"Spin-orbit coupled" Mott insulator is a relatively unexplored region.

Witczak-Krempa, Gang Chen, YB Kim, Balents (Annu. Rev. CMP 2014)

Why do we care about this? **First it is real !**

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Heavy elements have stronger spin-orbit couplings.
For 4d, 5d, 4f, 5f electrons, even for 3d electrons (when the orbitals are degenerate), SOC needs to be seriously considered.

Candidate materials as “spin-orbit coupled” Mott insulator

Table 1 Emergent quantum phases in correlated spin-orbit coupled materials[a]

Phase	Symmetry	Correlation	Properties	Proposed materials
Topological insulator	TRS	W-I	Bulk gap, TME, protected surface states	Many
Axion insulator	P	I	Magnetic insulator, TME, no protected surface states	$R_2Ir_2O_7$, $A_2Os_2O_7$
Weyl semimetal	TRS or P (not both)	W-I	Dirac-like bulk states, surface Fermi arcs, anomalous Hall effect	$R_2Ir_2O_7$, $HgCr_2Se_4$, . . .
LAB semimetal	Cubic + TRS	W-I	Non-Fermi liquid	$R_2Ir_2O_7$
Chern insulator	Broken TRS	I	Bulk gap, QHE	$Sr[Ir/Ti]O_3$, $R_2[B/B']_2O_7$
Fractional Chern insulator	Broken TRS	I-S	Bulk gap, FQHE	$Sr[Ir/Ti]O_3$
Quantum spin liquid	Any	S	Several possible phases, charge gap, fractional excitations	$(Na,Li)_2IrO_3$, Ba_2YMoO_6
Multipolar order	Various	S	Suppressed or zero magnetic moments, exotic order parameters	$A_2BB'O_6$

First order question: Why do some of they form Mott insulators?
Strong correlation physics can appear in 4d/5d systems

Witczak-Krempa, Gang Chen, YB Kim, Balents (Annu. Rev. CMP 2014)

Why do we care about this?
It may give novel phases!

The phase diagram already lists some of the new phases, e.g. axion insulator, Weyl semimetal, topological Mott insulator, spin liquid, etc

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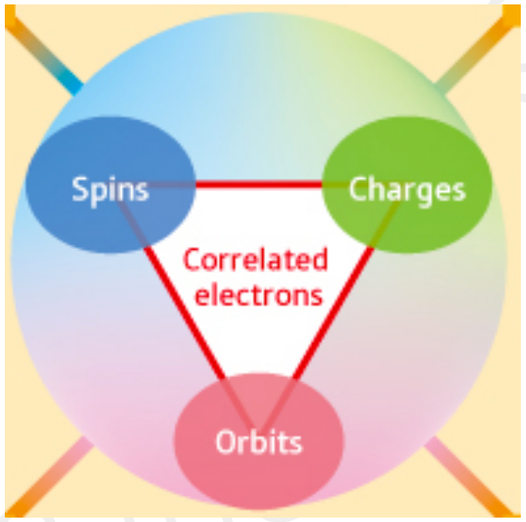

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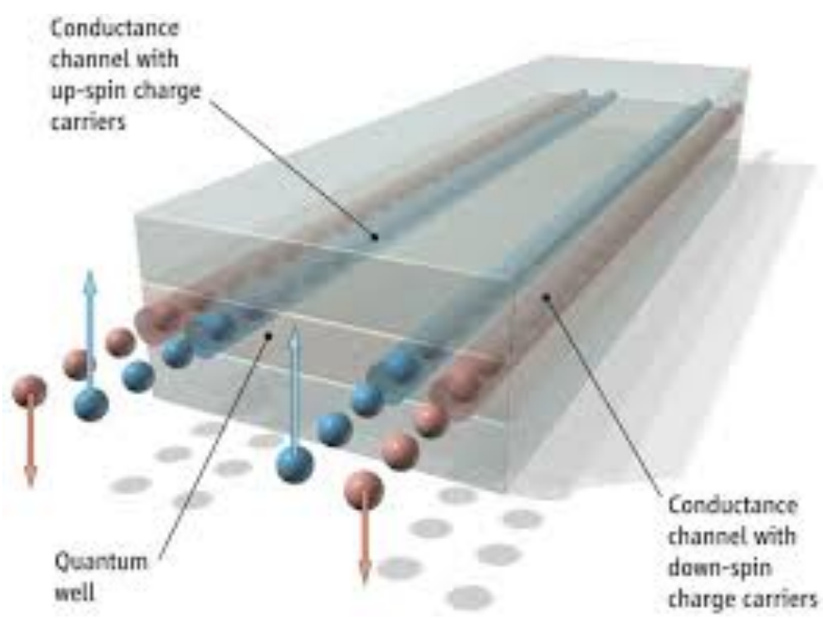
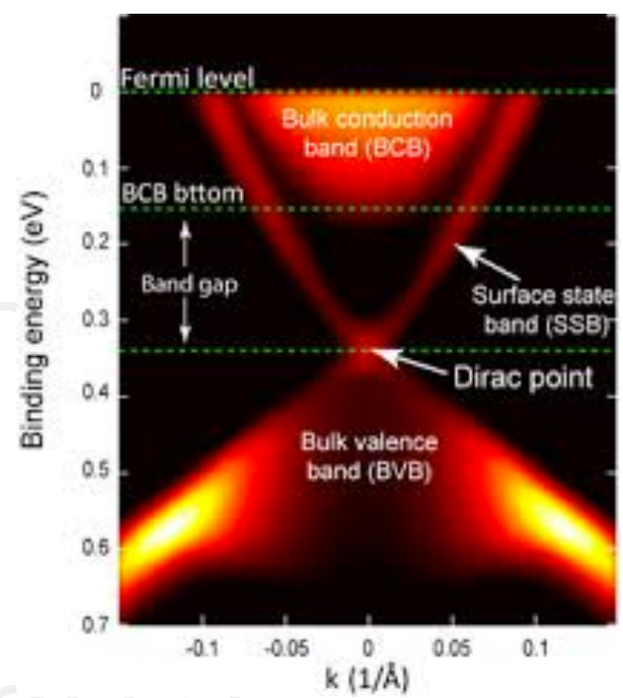
topology **correlation**

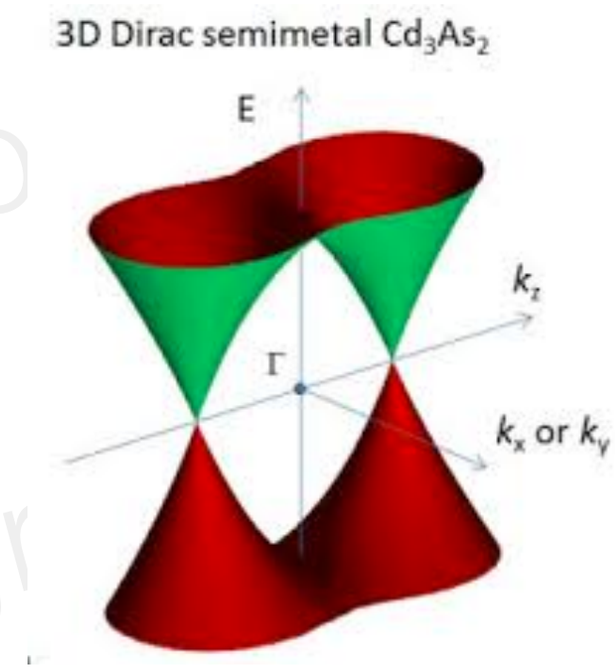
Topological insulator does not require correlation. **An important theoretical question** is to understand correlation physics in topological matters.

This is not only an academic problem, but also relevant for **many experimental systems**.

Topological insulator and semimetal: known examples



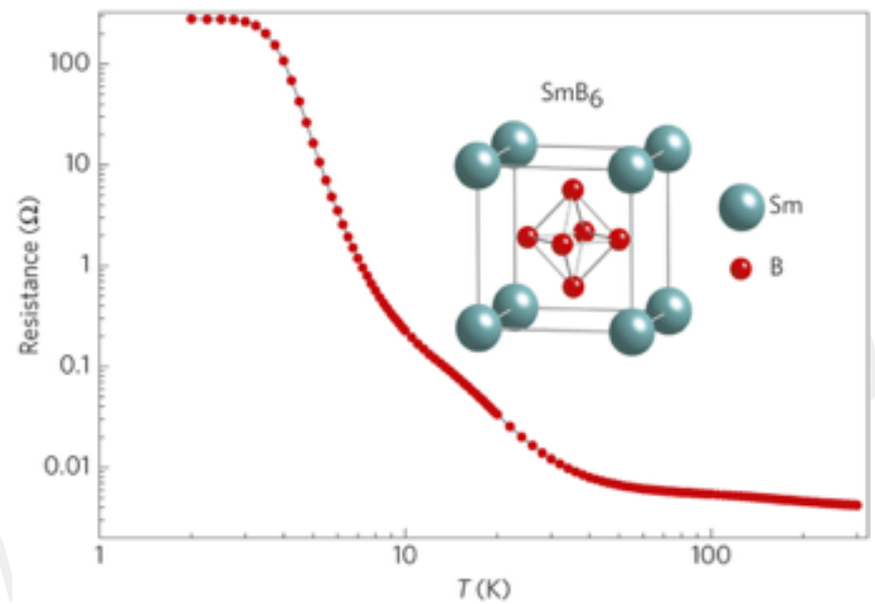




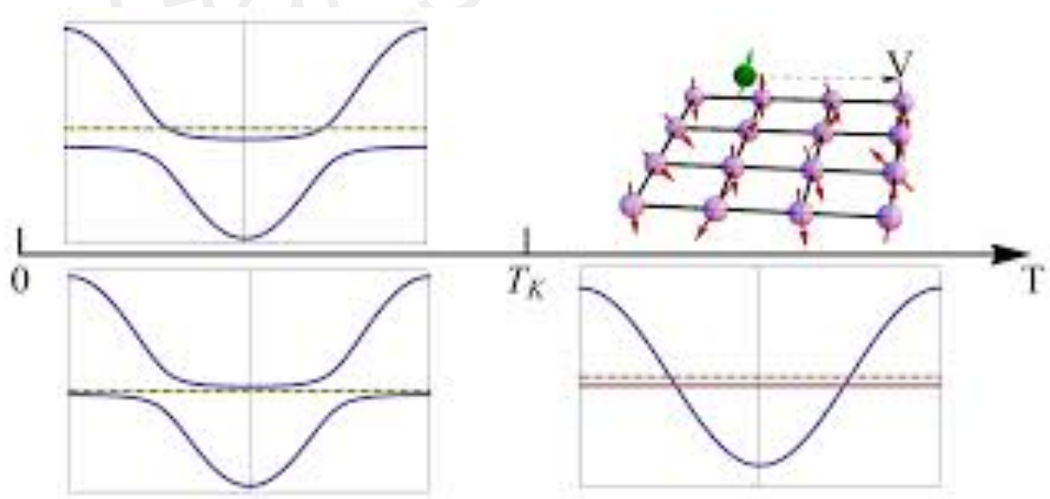
Topological insulator (HgTe/CdTe, Bi_2Se_3, etc) and topological semimetal (Cd_2As_3, Na_3Bi, etc): because only s and p orbitals are involved, they are weakly correlated.

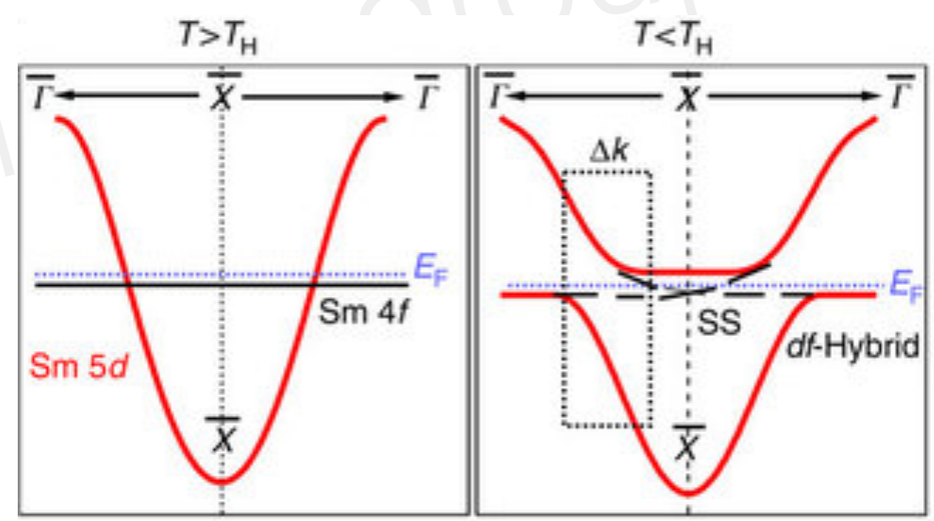
Topological Kondo insulator
a **trivial** interplay between topology and correlation

trivial != interesting



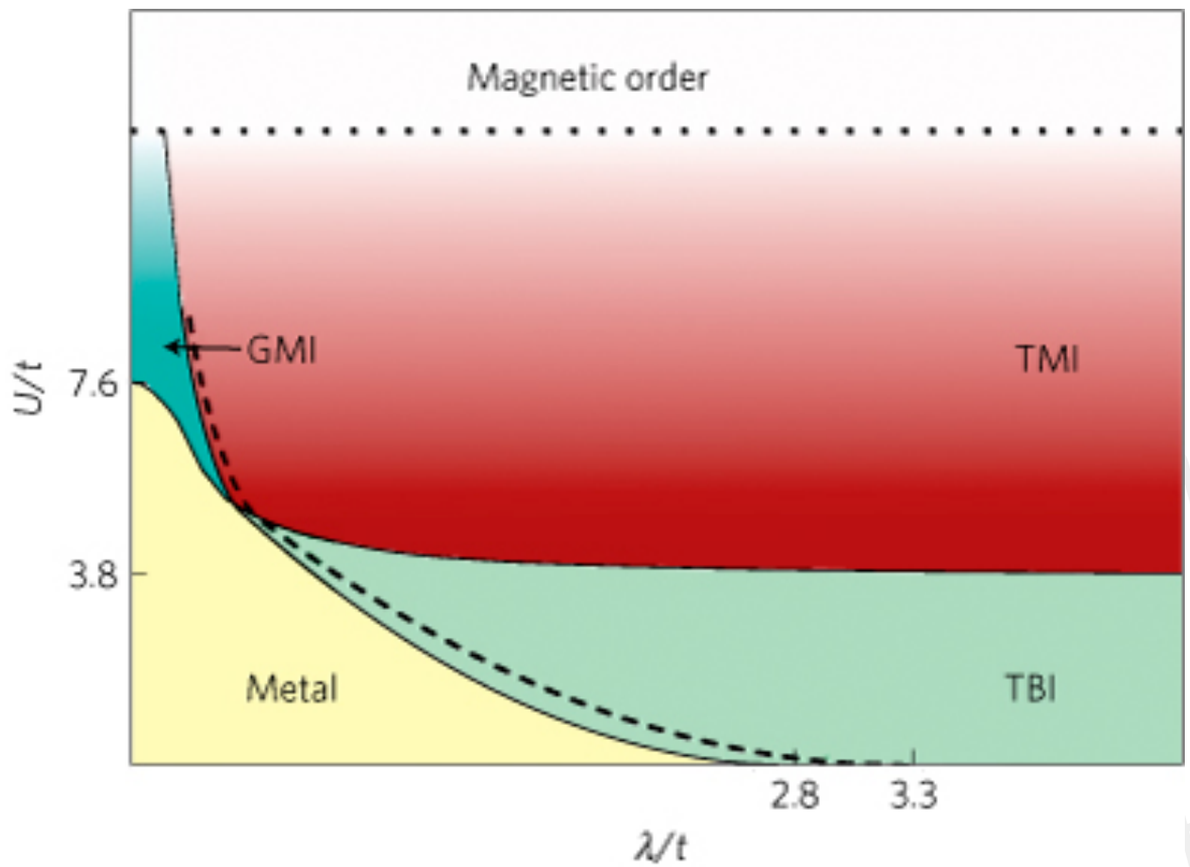
Neupane, etc,
Nature Comm. 2013

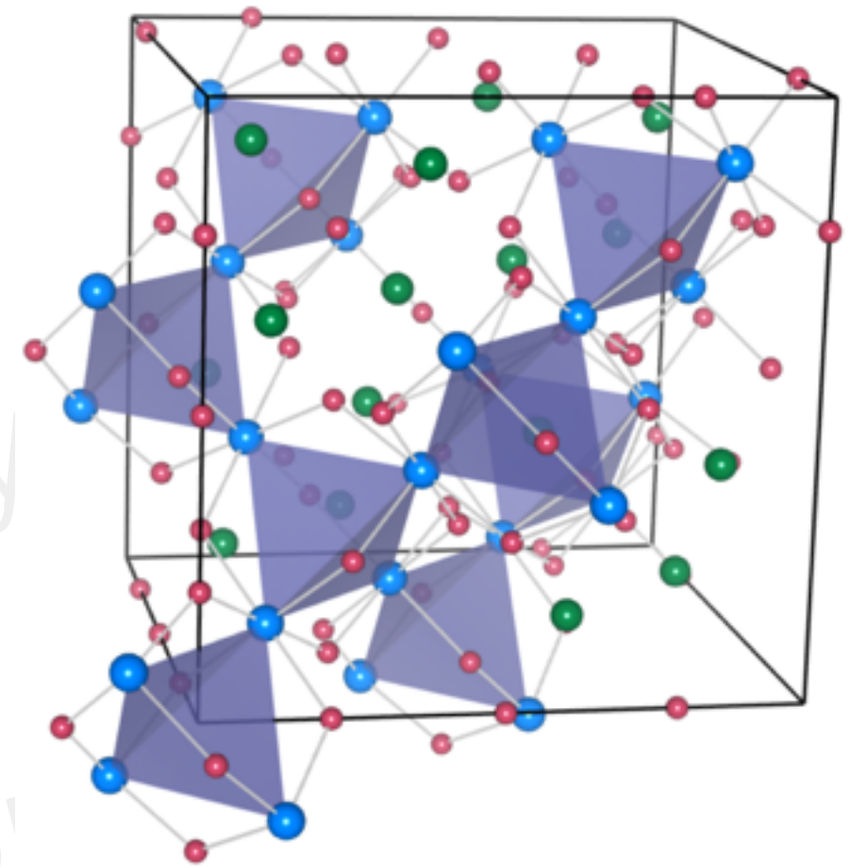




Topological Kondo insulator arises from strong correlation, but is still understood within **the same framework** as topological band insulator.

Topological Mott insulator: a **non-trivial** example





$R_2Ir_2O_7$

When topological band insulator becomes Mott insulating, where did the topologicalness go? Anything inherits the band structure topology?

electron = charge + spin

c_sigma = b*f_sigma

Pesin, Balents Nature Phys, 2010

We are interested in non-trivial interplay between topology (SOC) and correlation.

Of course, we are not just looking for topological matter, more generally looking for new phases of matter that arises from strong correlation and strong SOC.

One place to potentially observe interesting interplay between topology or SOC and correlation is in **iridate materials and other heavy element compounds.**

2. Iridates: spin-orbit coupling and $J_{eff} = 1/2$

The forest of iridates (in time order)

$Na_4Ir_3O_8$: hyperkagome quantum spin liquid

Na_2IrO_3: alpha-Li_2IrO_3, beta-Li_2IrO_3 “Kitaev materials”

$R_2Ir_2O_7$: topological insulator, Weyl semimetal, ABL semimetal

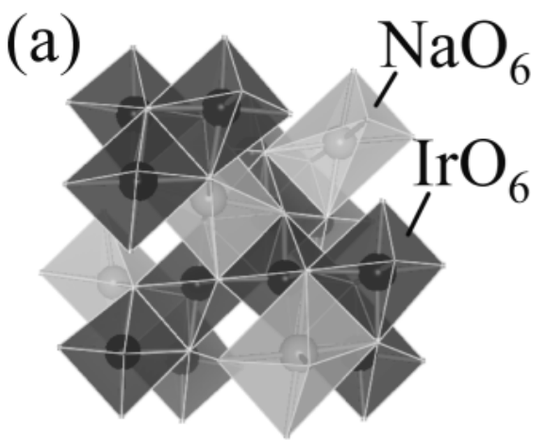
A_2IrO_4: candidate for high-Tc superconductor, isostructure with A_2CuO_4

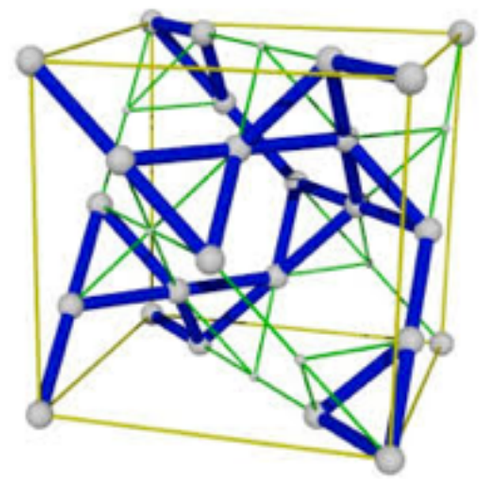
$Sr_3Ir_2O_7$: metamagnetic transition, isostructure with $Sr_3Ru_2O_7$

IrO_2: pyrochlore lattice spin liquid

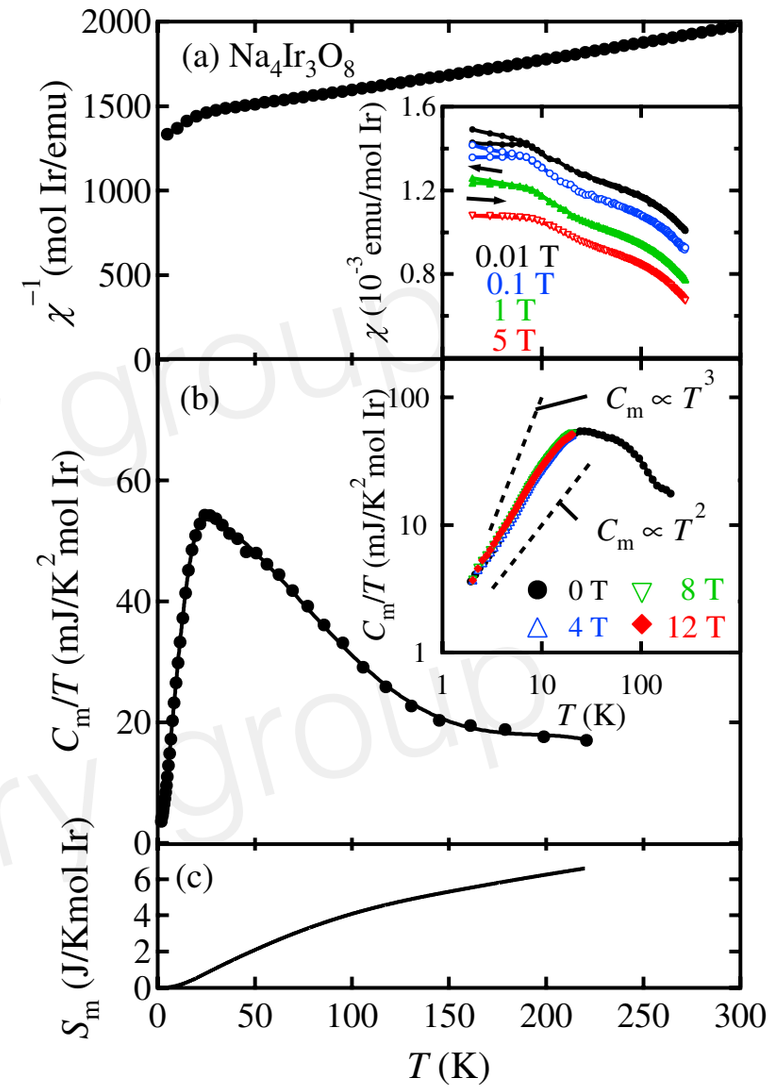
$AIrO_3$ perovskite heterostructure: topological crystalline metal

$Na_4Ir_3O_8$: hyperkagome quantum spin liquid ?





3d printed (balents) hyperkagome

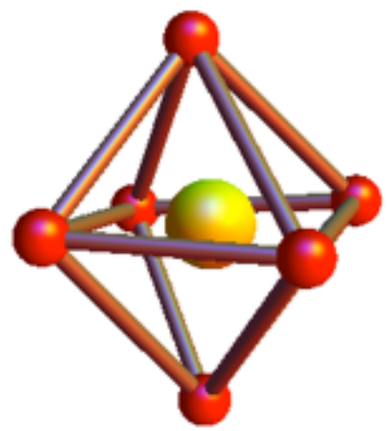


Takagi,etc, PRL, **2007**

$$\chi \sim \text{constant}, \quad C_v/T \sim \text{constant}$$

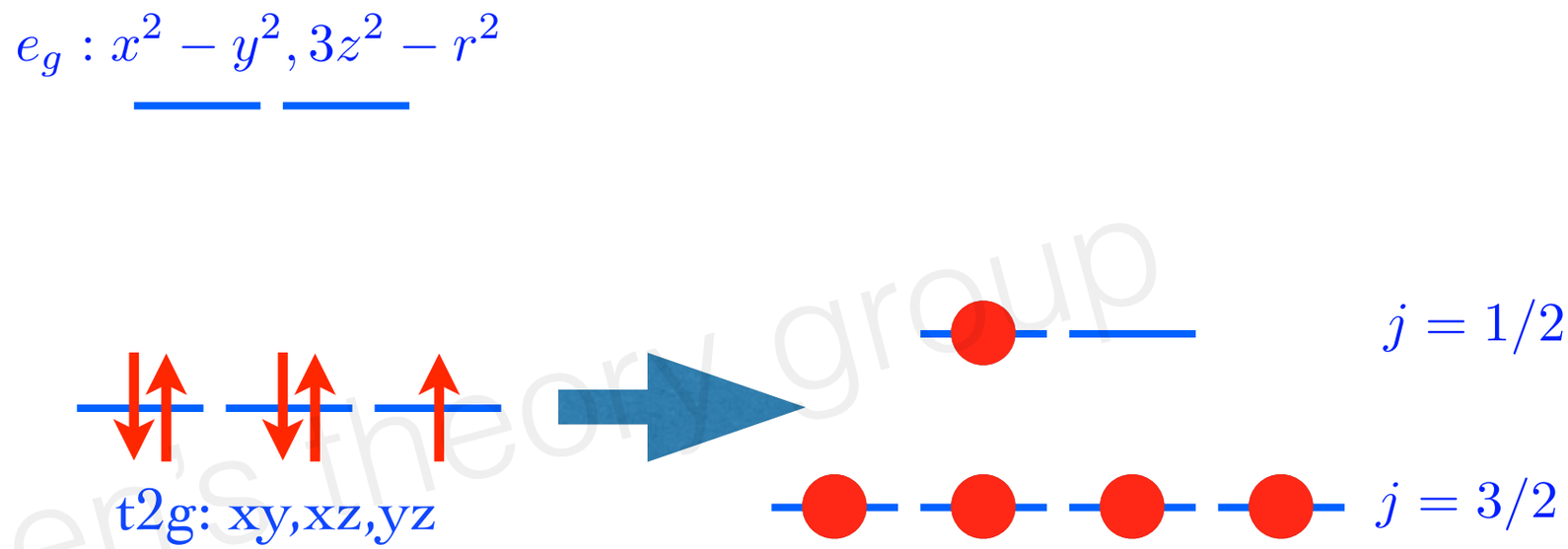
Why Ir ion behaves as a spin-1/2 ?

t_{2g} orbitals in octahedral crystal field



$\mathrm{Ir}^{4+} : 5d^5$

IrO6 octahedron



Crystal electric field

Spin-orbit coupling

$$\langle \{t_{2g}\} | \mathbf{L} | \{t_{2g}\} \rangle = -\mathbf{l}, \quad H_{soc} = -\lambda \mathbf{l} \cdot \mathbf{S}, \quad \mathbf{j} = \mathbf{l} + \mathbf{S}$$

It is interesting to look at how the magnetic moment M = L+2S = -l+2S varies.

BTW, SOC is quenched for eg orbitals.

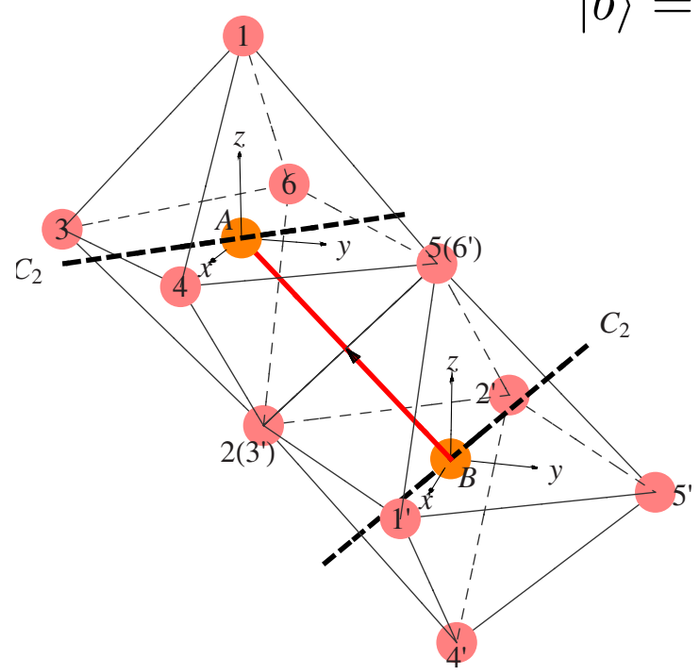
Gang Chen, Balents PRB 2008, B.J. Kim etc, Science 2008, G. Jackeli, Khaliullin PRL 2009

Exchange interaction: direct

Spin-orbit entangled j=1/2 doublet

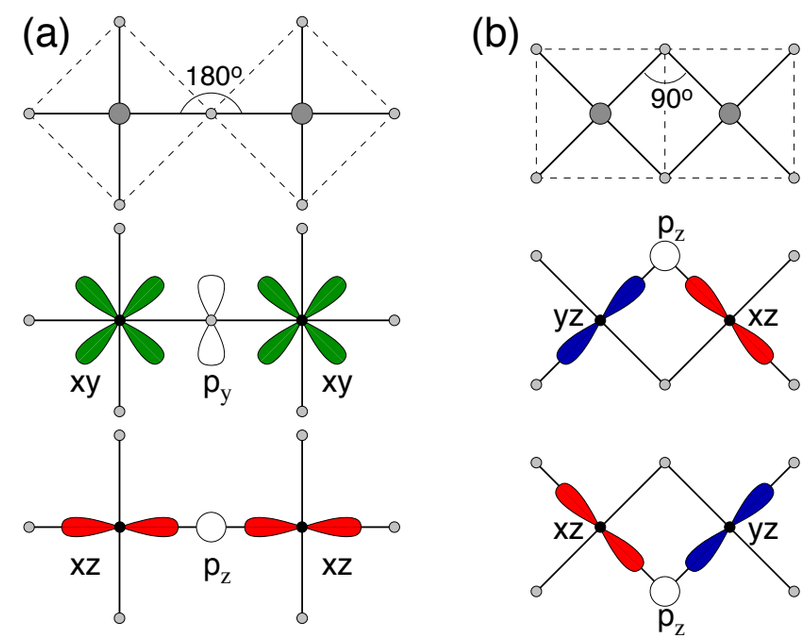
$$|a\rangle = \frac{1}{\sqrt{3}}(|d_{xy,\uparrow}\rangle + |d_{yz,\downarrow}\rangle + i|d_{zx,\downarrow}\rangle),$$

$$|b\rangle = \frac{1}{\sqrt{3}}(|d_{xy,\downarrow}\rangle - |d_{yz,\uparrow}\rangle + i|d_{zx,\uparrow}\rangle),$$



two neighboring IrO_6 octahedra:
they share 2 oxygens.

Gang Chen, Balents PRB 2008



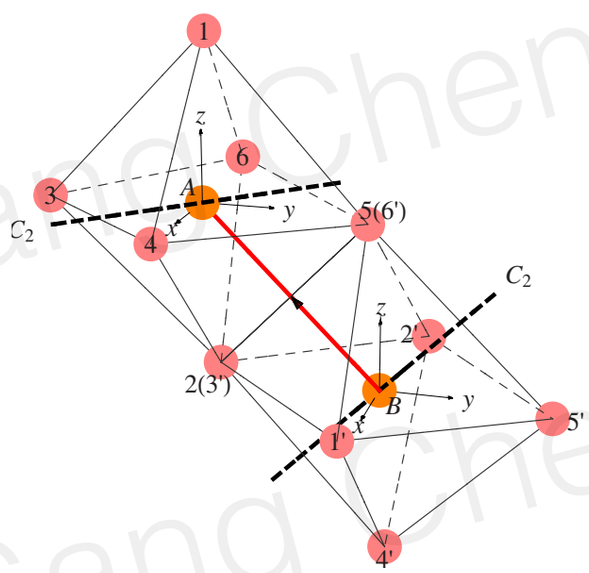
Na2IrO3: Jackeli, Khaliullin PRL 2009

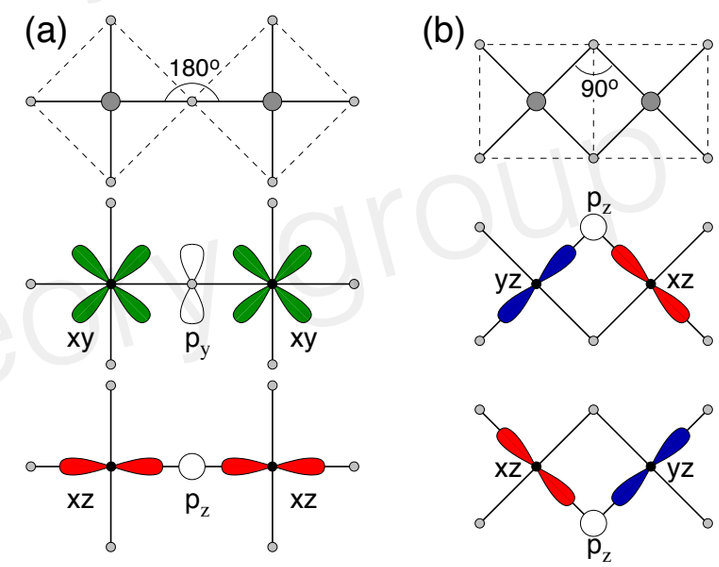
Surprisingly, direct hopping gives us a Heisenberg model !
This is very special especially since orbitals have orientations.

Exchange interaction: indirect

Remark: almost all iridates have the same local structure,

- IrO6 form an octahedron,
- Neighboring IrO6 octahedra share 2 oxygens,
- Ir-O-Ir bond angle is close to be 90 degrees.
- The microscopic analysis may apply to many other iridate families.





$$\mathcal{H}_{AB} = -JS_A^x S_B^x + JS_A^y S_B^y + JS_A^z S_B^z$$
$$= -2JS_A^x S_B^x + J\mathbf{S}_A \cdot \mathbf{S}_B$$

Kitaev-Heisenberg term for x bond after including CEF splitting among t2g orbitals

$$\mathcal{H}_{ij}^{(\gamma)} = -JS_i^\gamma S_j^\gamma$$

Kitaev term for gamma bond after including Hund's coupling

Lesson learned

- SOC creates a local moment that entangles spin and orbital degrees of freedom.

- The exchange interaction is often anisotropic in both spin space and real space (or position space).

- Although often in antiferromagnets, SOC, e.g., via Dzyaloshinskii -Moriya interaction, is thought to remove accidental degeneracy and favor order. The Kitaev model is a counterexample, showing that in some cases strong SOC can suppress ordering. However, one should be aware of both possibilities.

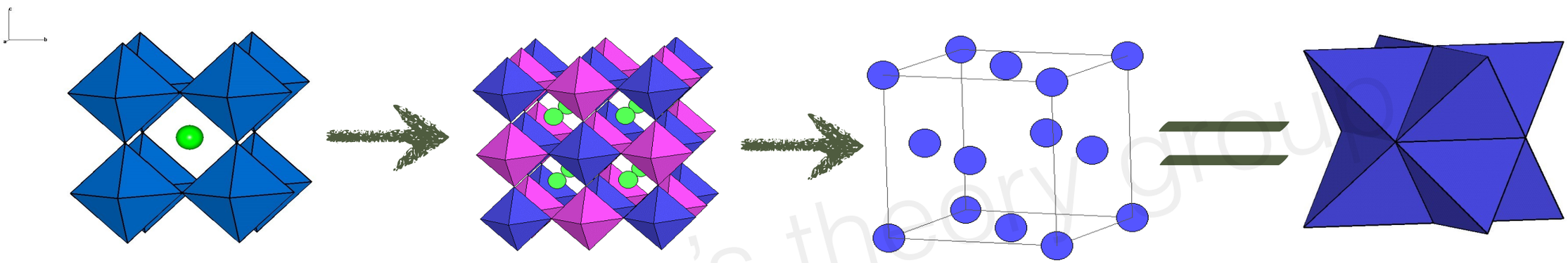
Also see talks by Prof Yu Yue and Dr Lou Jie

3. Beyond iridates: multipolar order, exciton magnetism, etc

3.1 Multipolar orders in double perovskites

Ordered double perovskites

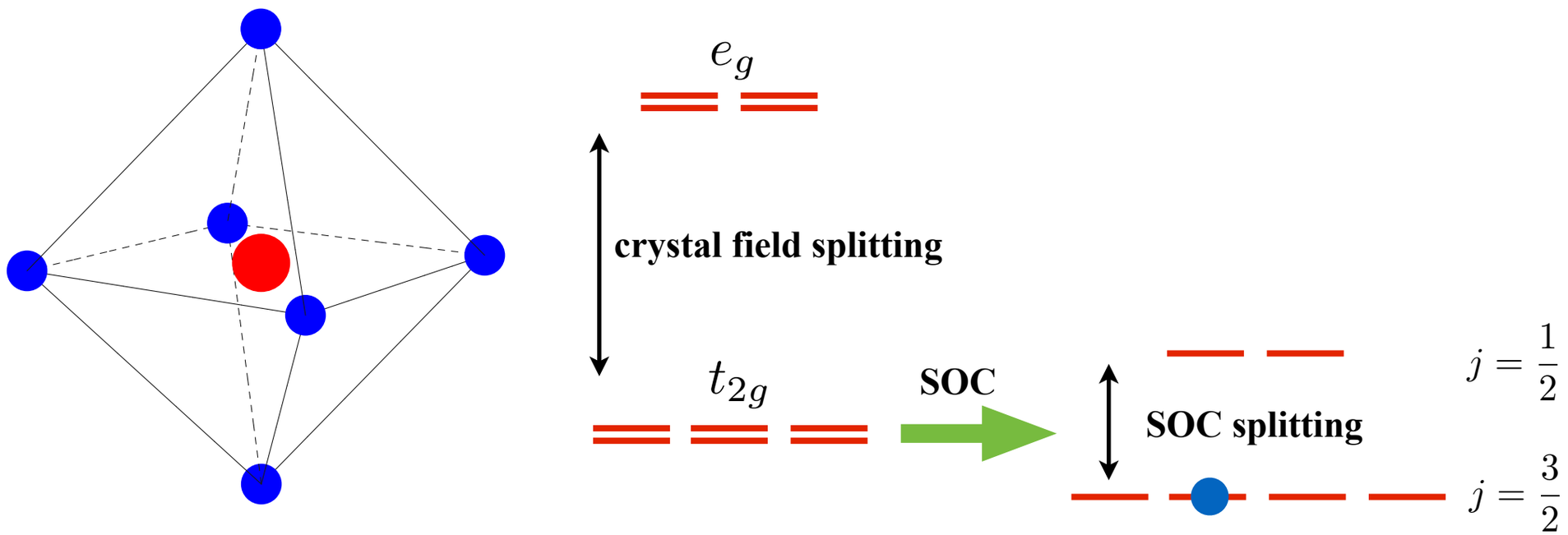
FCC ordered double perovskites $A_2BB'O_6$



Compound	B' config.	crystal structure	$\theta_{\rm CW}$	$\mu_{\rm eff}(\mu_B)$	magnetic transition	frustration parameter f
Ba_2YMoO_6	$Mo^{5+}(4d^1)$	cubic	-91K	1.34	PM down to 2K	$f \gtrsim 45$
Ba_2YMoO_6	$Mo^{5+}(4d^1)$	cubic	-160K	1.40	PM down to 2K	$f \gtrsim 80$
Ba_2YMoO_6	$Mo^{5+}(4d^1)$	cubic	-219K	1.72	PM down to 2K	$f \gtrsim 100$
La_2LiMoO_6	Mo^{5+} (4d^1)	monoclinic	-45K	1.42	PM to 2K	$f \gtrsim 20$
Sr_2MgReO_6	$Re^{6+}(5d^1)$	tetragonal	-426K	1.72	spin glass, $T_G \sim 50$K	$f \gtrsim 8$
Sr_2CaReO_6	$Re^{6+}(5d^1)$	monoclinic	-443K	1.659	spin glass, $T_G \sim 14$K	$f \gtrsim 30$
Ba_2CaReO_6	$Re^{6+}(5d^1)$	cubic to tetragonal (at $T \sim 120$K)	-38.8K	0.744	AFM $T_c = 15.4$K	$f \sim 2$
Ba_2LiOsO_6	$Os^{7+}(5d^1)$	cubic	-40.48K	0.733	AFM $T_c \sim 8$K	$f \gtrsim 5$
Ba_2NaOsO_6	$Os^{7+}(5d^1)$	cubic	-32.45K	0.677	FM $T_c \sim 8$K	$f \gtrsim 4$
Ba_2NaOsO_6	$Os^{7+}(5d^1)$	cubic	~ -10K	~ 0.6	FM $T_c = 6.8$K	$f \gtrsim 4$

Gang Chen, Rodrigo Pereira, Balents, PRB 2010

Microscopic consideration



$\mathrm{Re}^{6+}, \mathrm{Os}^{7+}, \mathrm{Mo}^{5+} : 5d^1 \text{ or } 4d^1$

One electron in the t_{2g} manifold

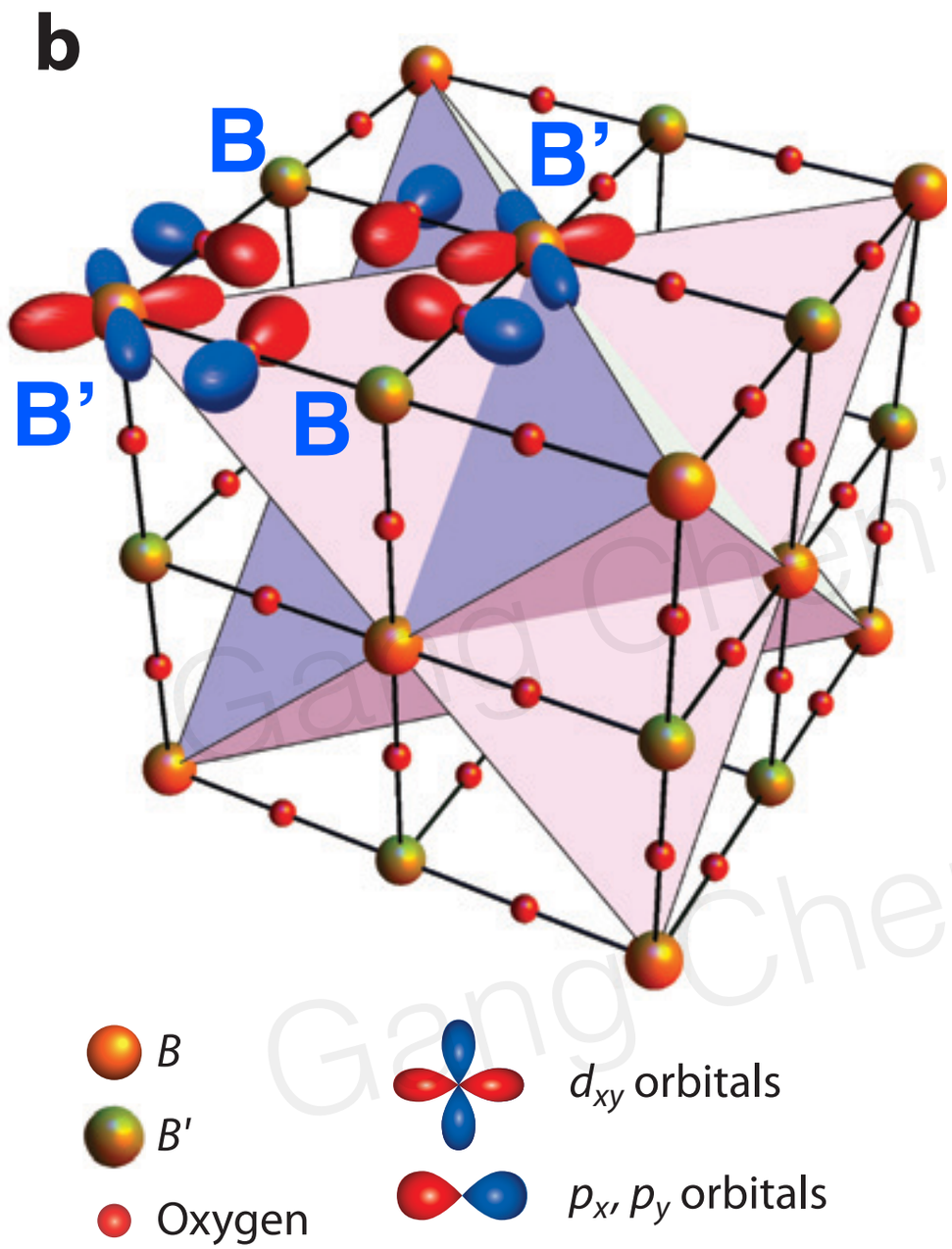
$$\mathcal{P}_{\frac{3}{2}}\, \boldsymbol{S}\, \mathcal{P}_{\frac{3}{2}} = \frac{1}{3}\, \boldsymbol{j},$$

$$\mathcal{P}_{\frac{3}{2}}\, \boldsymbol{l}\, \mathcal{P}_{\frac{3}{2}} = \frac{2}{3}\, \boldsymbol{j}\ .$$

$$\boldsymbol{M} \equiv \mathcal{P}_{\frac{3}{2}} [2\boldsymbol{S} + (-\boldsymbol{l})] \mathcal{P}_{\frac{3}{2}} = 0\ .$$

Although hybridization with oxygen p orbitals could increase the magnetic moment, it is a general fact that SOC strongly suppresses magnetic moment for the d^1 electron configuration.

Interaction between local moments



* Orbitals have orientation.

* AFM exchange in **XY** plane only involves **xy** orbitals

$$\mathcal{H}^{\mathrm{XY}}_{\text{ex-1}} = J \sum_{\langle ij \rangle \in \mathrm{XY}} \left(\boldsymbol{S}_{i,xy} \cdot \boldsymbol{S}_{j,xy} - \frac{1}{4} n_{i,xy} n_{j,xy} \right)$$

$$H_{soc} = -\lambda \sum_i \mathbf{l}_i \cdot \mathbf{S}_i$$

We need to express everything in terms of the effective spin operator j. We need to project the orbital dependent spin operators onto j=3/2 quadruplets.

Spin-orbital entanglement in the j=3/2 quadruplet

* Project orbital resolved spin into j=3/2 manifold

$$\tilde{S}^x_{i,xy} = \frac{1}{4} j^x_i - \frac{1}{3} j^z_i j^x_i j^z_i$$
$$\tilde{S}^y_{i,xy} = \frac{1}{4} j^y_i - \frac{1}{3} j^z_i j^y_i j^z_i$$
$$\tilde{S}^z_{i,xy} = \frac{3}{4} j^z_i - \frac{1}{3} j^z_i j^z_i j^z_i$$
$$\tilde{n}_{i,xy} = \frac{3}{4} - \frac{1}{3} (j^z_i)^2,$$

Moment	Symmetry	Operator
Dipole	Γ_4	$M^x = j^x$ $M^y = j^y$ $M^z = j^z$
Quadrupole	Γ_3	$Q^{3z^2} = [3(j^z)^2 - \boldsymbol{j}^2]/\sqrt{3}$ $Q^{x^2-y^2} = (j^x)^2 - (j^y)^2$
	Γ_5	$Q^{xy} = \overline{j^x j^y}/2$ $Q^{yz} = \overline{j^y j^z}/2$ $Q^{xz} = \overline{j^z j^x}/2$
Octupole	Γ_2	$T_{xyz} = \sqrt{15}/6\overline{j^x j^y j^z}$
	Γ_4	$T^x_\alpha = (j^x)^3 - [\overline{j^x (j^y)^2} + \overline{(j^z)^2 j^x}]/2$ $T^y_\alpha = (j^y)^3 - [\overline{j^y (j^z)^2} + \overline{(j^x)^2 j^y}]/2$ $T^z_\alpha = (j^z)^3 - [\overline{j^z (j^x)^2} + \overline{(j^y)^2 j^z}]/2$
	Γ_5	$T^x_\beta = \sqrt{15}[\overline{j^x (j^y)^2} - \overline{(j^z)^2 j^x}]/6$ $T^y_\beta = \sqrt{15}[\overline{j^y (j^z)^2} - \overline{(j^x)^2 j^y}]/6$ $T^z_\beta = \sqrt{15}[\overline{j^z (j^x)^2} - \overline{(j^y)^2 j^z}]/6$

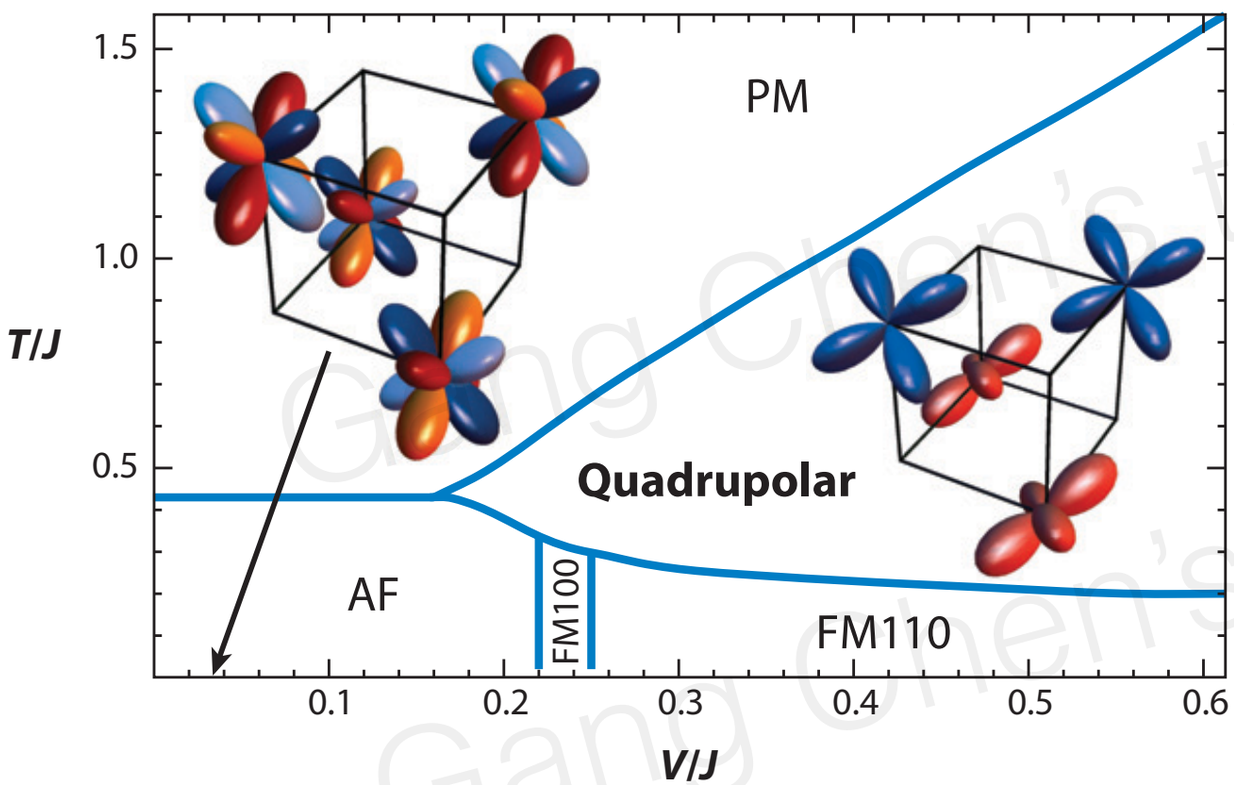
TABLE I. Multipole moments within a cubic Γ_8 quartet. Bars over symbols indicate the sum with respect to all the possible permutations of the indices, e.g. $\overline{j^x (j^y)^2} = j^x (j^y)^2 + j^y j^x j^y + (j^y)^2 j^x$.

* These are not just dipole moment, also involve **quadrupole, octupole** moments.

* The exchange interaction is very non-Heisenberg !!

Novel phases due to the multipolar exchange

$$\mathcal{H}^{\mathrm{XY}}_{\mathrm{quad}} = \sum_{\langle ij\rangle \in \mathrm{XY}} \left[-\frac{4V}{3}(n_{i,xz} - n_{i,yz})(n_{j,xz} - n_{j,yz}) \; + \frac{9V}{4} n_{i,xy} n_{j,xy} \right]$$

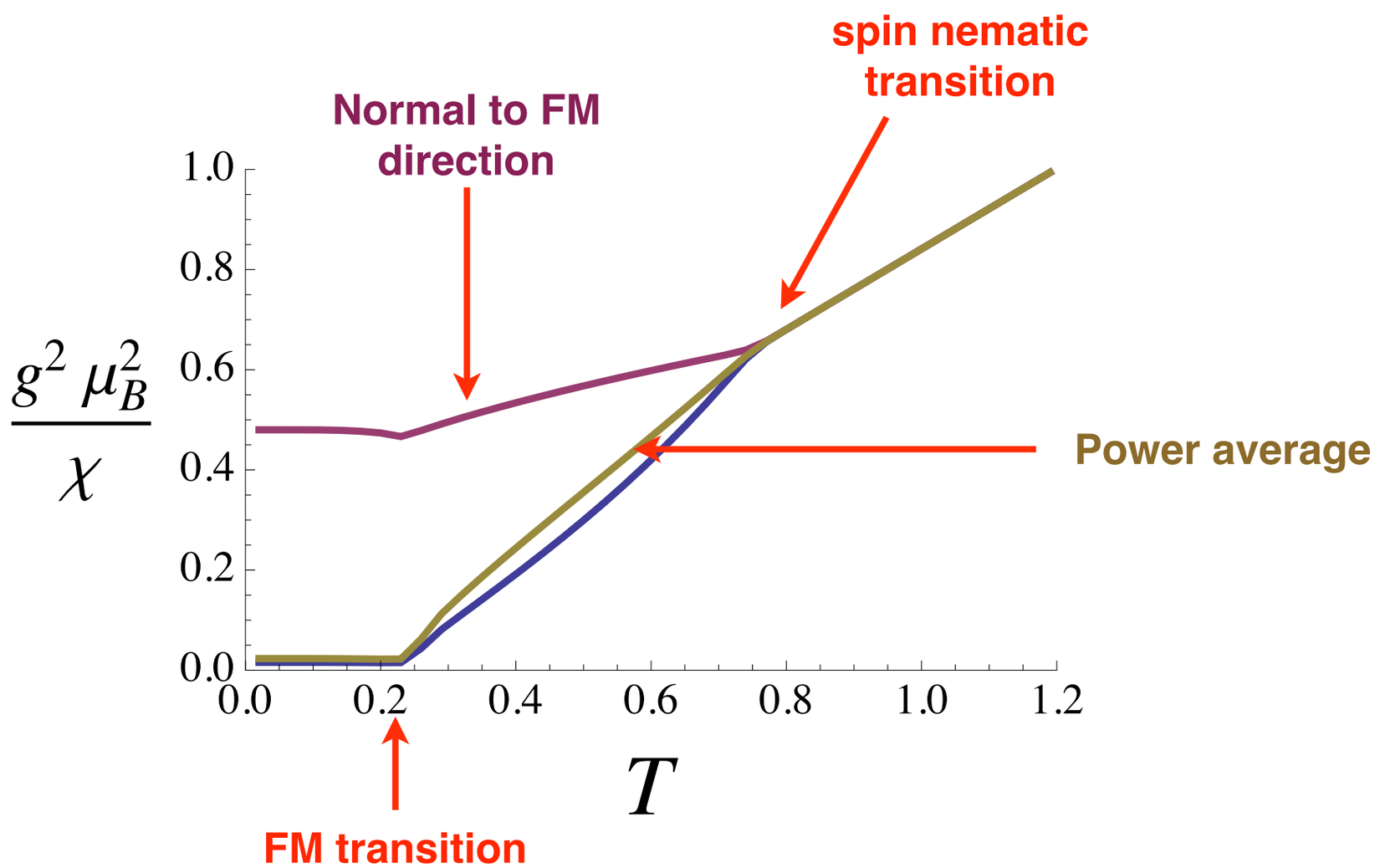


Finite temperature phase diagram: include an electric quadrupole interaction

1. Finite-T quadrupolar ordering
   - no magnetic dipolar order
   - no time reversal symmetry breaking
   - spin nematics

2. Low temperature FM phase with small or no FM interaction
   - electric quadrupole interaction wants nearby electrons to take different orbital occupation
   - AFM interaction wants nearby spins to be AFM, but the orbital occupations would be identical.
   - The compromise of these two interactions is an FM state with two sublattice ordering structure.

One experimental consequence of the spin nematic order



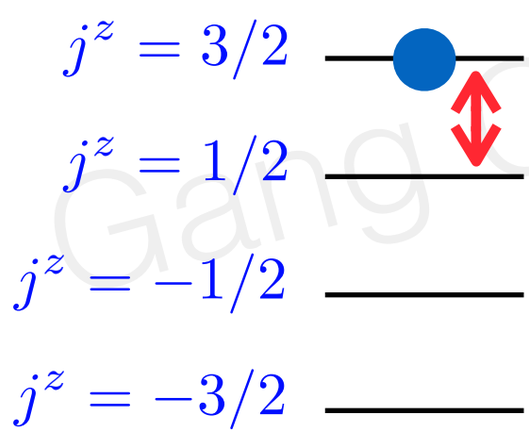
The presence of double Curie-Weiss regimes at finite temperature
The change of the Curie behavior is because the spin nematics modifies the effective local spin moment.

Origin of strong quantum fluctuation

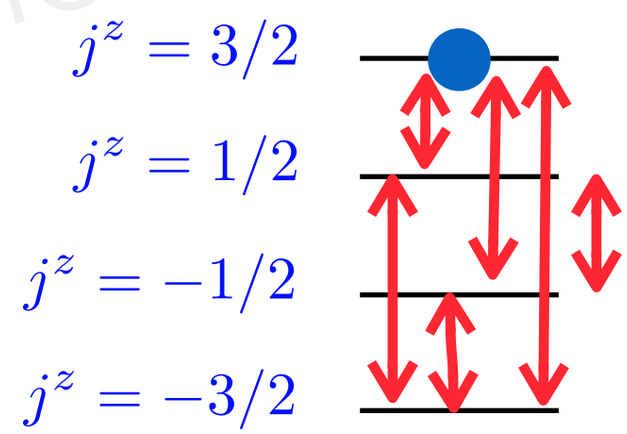
Near the origin, the quantum fluctuation is found to be very strong, is expected to melt the magnetic order and may lead to spin liquid ground state.

This is different from the simple understanding that large spin moment tends to behave classically.

The underlying reason is that the multipolar interaction allows spins to quantum tunnel among all spin states. The electrons are more delocalized in the local spin space.

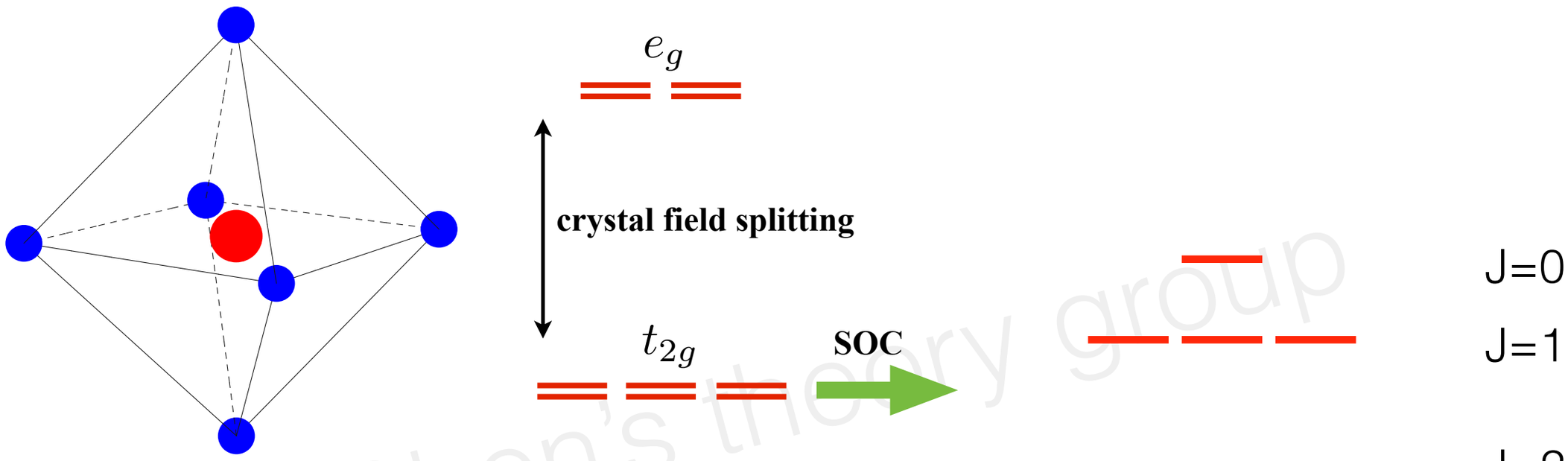


pair-wise Heisenberg case



mutipolar interaction
(similar to SU(4) models)

d^2 double perovskites



$\mathrm{Re}^{5+}, \mathrm{Os}^{6+} : 4d^2 \text{ or } 5d^2$

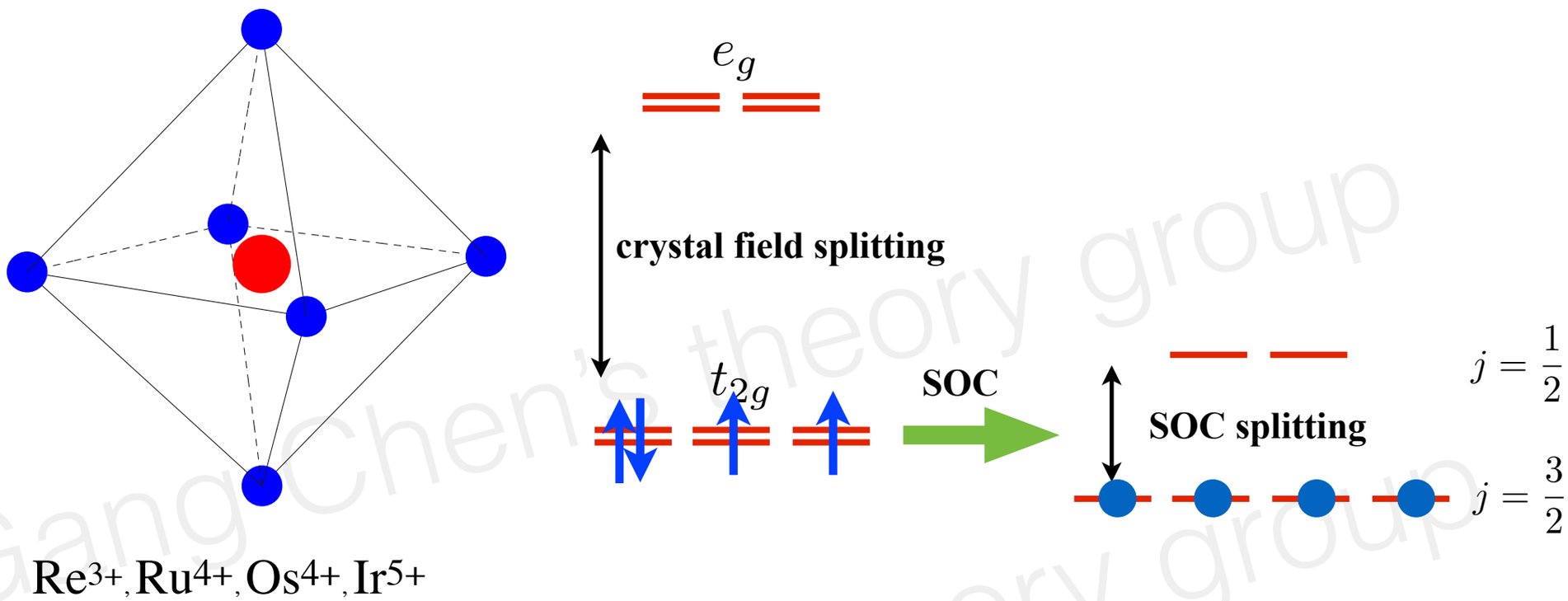
$$|\mathrm{X}\rangle = \frac{1}{\sqrt{2}}(|xy\rangle_1|xz\rangle_2 - |xy\rangle_2|xz\rangle_1)$$
$$|\mathrm{Y}\rangle = \frac{1}{\sqrt{2}}(|xy\rangle_1|yz\rangle_2 - |xy\rangle_2|yz\rangle_1)$$
$$|\mathrm{Z}\rangle = \frac{1}{\sqrt{2}}(|xz\rangle_1|yz\rangle_2 - |xz\rangle_2|yz\rangle_1)$$

We need to consider the electron interaction: Hund's rule suggests S=1 and the orbital wavefunction of two electrons is antisymmetrized. Again, these 3 antisymmetrized orbital state can be thought as l=1.
SOC is still active.

Gang Chen, Balents PRB 2011

3.2 Exciton magnetism

Four electrons in the t2g manifold: J=0 ?

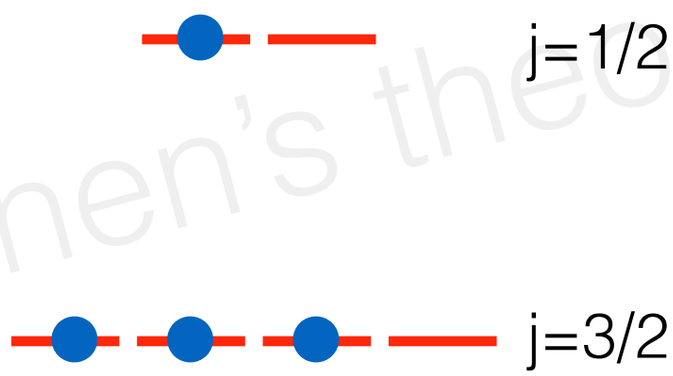


If we look at the d^4 configuration at a single site, the ground state is a trivial Jeff=0 singlet in the strong SOC limit.

Even if we include Hund's coupling, the ground state remains to be a singlet.

Gang Chen, Balents PRB 2011

Apparently, some of the materials in this family are magnetic,
e.g. R2Os2O7, La2RuO3, Sr2NiIrO6, etc.
What is the reason for them to be magnetic?



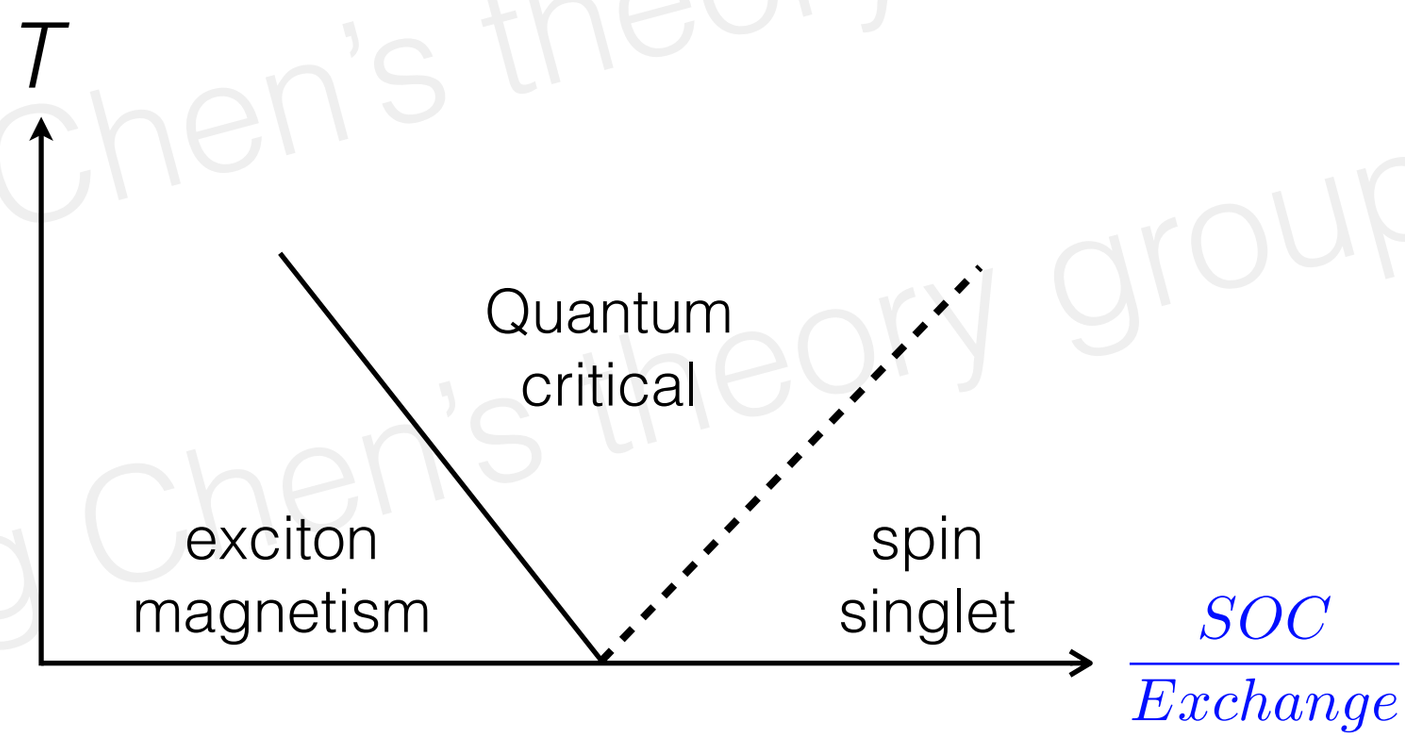
In the strong SOC limit, the exciton like excitation costs a finite energy gap. The gap is of the order of spin orbit coupling.

Khaliullin PRL 2013

Phase transition

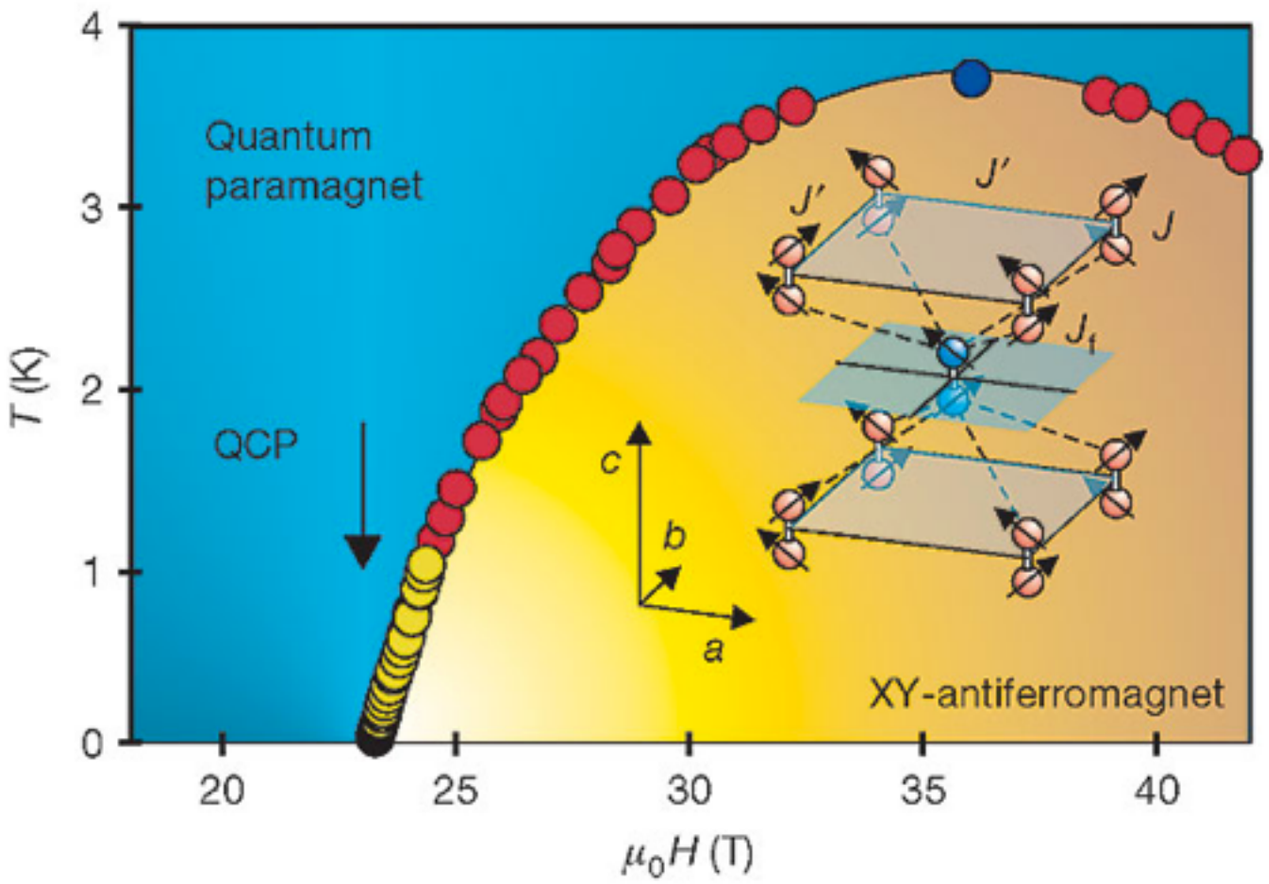
The exchange interaction between the local moments renders kinetic energy to the gapped excitons. When the kinetic energy gain overcomes the SOC gap, the exciton will condense and lead to magnetism.

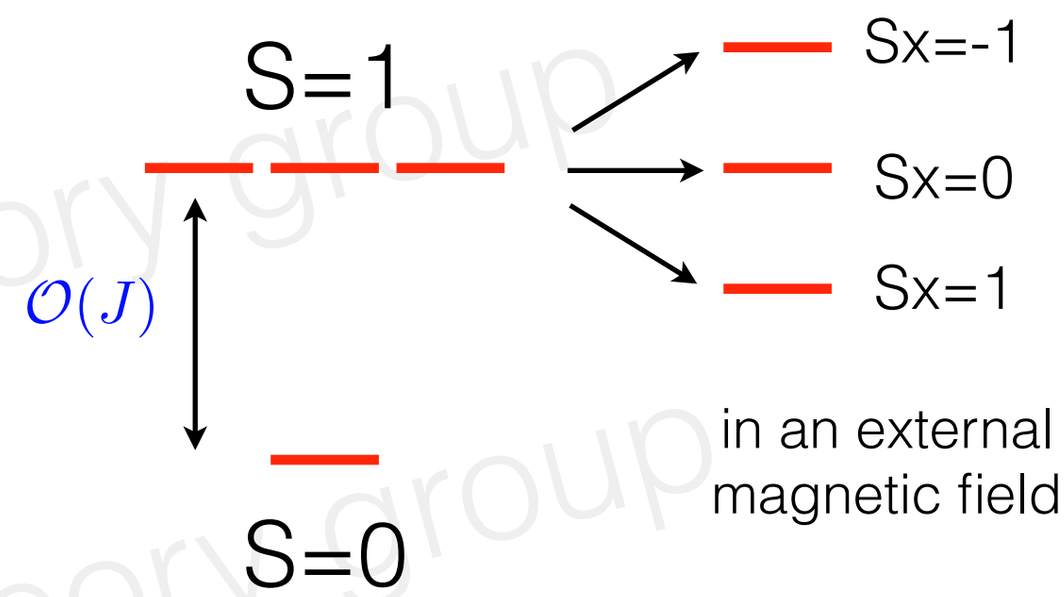
$$H = H_{soc} + H_{exchange}$$



It would be interesting to push the system to the transition point and study the quantum phase transition.

Similar idea: triplon condensation driven by external magnetic field





An external magnetic field splits the triplon bands and brings down the Sx=1 band, when this band touches the zero energy, the triplon will condense and lead to magnetic ordering.

Sebastian etc, Nature 2006

4. Summary

This is a young and active field and is still under rapid development.

We argue that spin-orbit coupled Mott insulator may provide an arena to realize various novel and exotic quantum phases.

We explain the highly anisotropic spin exchange interaction for various local moments with spin-orbital entanglement.

We discuss in details the physics of multipolar phase due to the spin-orbital entanglement.

Thank you !