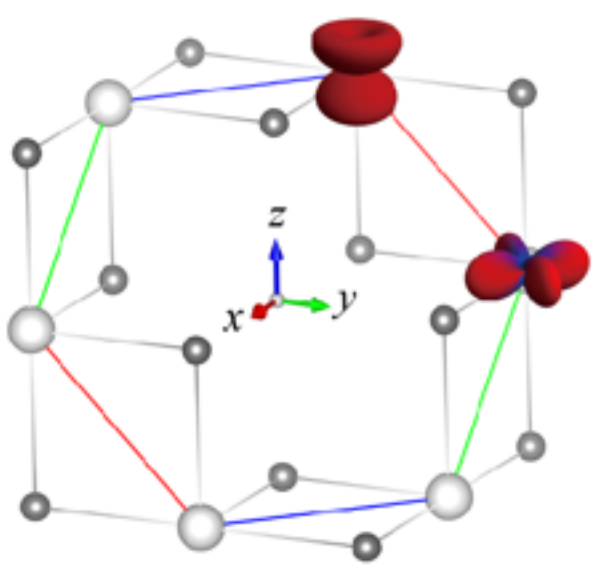
Emergent SU(4) symmetry and quantum spin-orbital liquid in α-ZrCl3



arXiv:1709.05252

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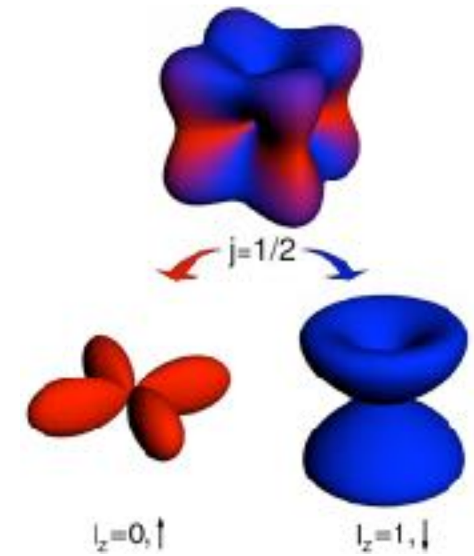
Outline

- Introduction to quantum spin-orbital liquids
- Material proposal
- Derivation of the emergent SU(4) symmetry
- 3D generalization, etc.
- Summary

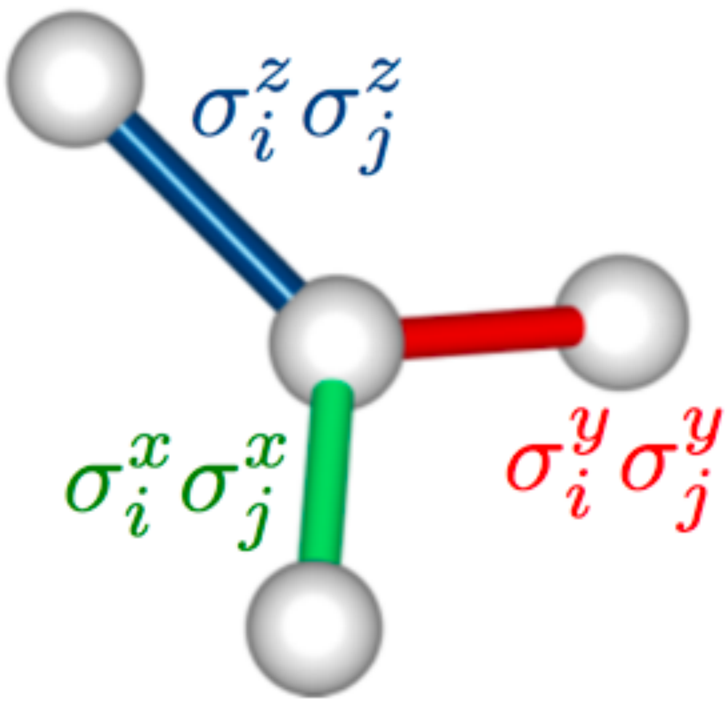
Frustration from spin-orbit coupling



Why does it happen?

- SOC usually **reduces** the symmetry of the spin space from SU(2) to the point group.

- => Kitaev-type interactions!



Exchange frustration

e.g. iridates,
Ru-compounds/MOFs

strong spin-orbit coupling (SOC) materials

https://www.fmq.uni-stuttgart.de/en/takagi-group/research_profile/

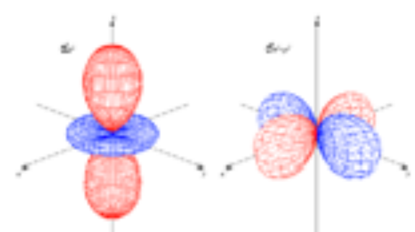
G. Jackeli and G. Khaliullin, PRL **102**, 017205 (2009).

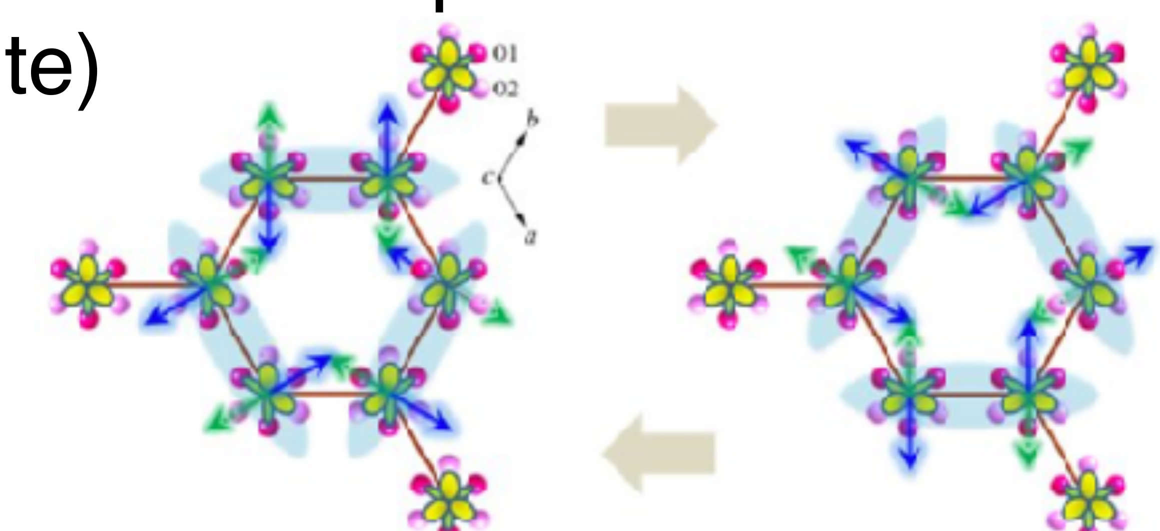
http://www.thp.uni-koeln.de/~hermanns/talks/KitaevSL.pdf

Quantum spin-orbital liquid

- Known candidate: honeycomb-like $Ba_3CuSb_2O_9$ (BCSO)
  - Cu^{2+} in the octahedral coordination: both spin/orbital degeneracy (2 x 2 states per site)

wikipedia





- No magnetic order / spin freezing

http://satoru.issp.u-tokyo.ac.jp/research_BCSO.html

- No Jahn-Teller transition / orbital freezing

$$
\begin{aligned}
\mathcal{H}_{ST} = \frac{4(t')^2}{U}\sum_{\langle ij\rangle}\Big\{ & -\frac{1}{1+J/U}\mathcal{P}_{ij}^{S=0}\Big[\frac{2t}{t'}\mathbf{T}_i\cdot\mathbf{T}_j - \frac{4t}{t'}T_i^yT_j^y + (1-t/t')^2(\mathbf{n}_{ij}\cdot\mathbf{T}_i)(\mathbf{n}_{ij}\cdot\mathbf{T}_j) \\
& -\frac{1}{2}(1-(t/t')^2)(\mathbf{n}_{ij}\cdot\mathbf{T}_i+\mathbf{n}_{ij}\cdot\mathbf{T}_j)+\frac{1}{4}(1+(t/t')^2)\Big] \\
& -\frac{1}{1-J/U}\mathcal{P}_{ij}^{S=0}\Big[\frac{4t}{t'}T_i^yT_j^y - \frac{1}{2}(1-(t/t')^2)(\mathbf{n}_{ij}\cdot\mathbf{T}_i+\mathbf{n}_{ij}\cdot\mathbf{T}_j)+\frac{1}{2}(1+(t/t')^2)\Big] \\
& +\frac{1}{1-3J/U}\mathcal{P}_{ij}^{S=1}\Big[\frac{2t}{t'}\mathbf{T}_i\cdot\mathbf{T}_j + (1-t/t')^2(\mathbf{n}_{ij}\cdot\mathbf{T}_i)(\mathbf{n}_{ij}\cdot\mathbf{T}_j) - \frac{1}{4}(1+(t/t')^2)\Big]\Big\},
\end{aligned}
$$

where

$$\mathcal{P}_{ij}^{S=0} = \frac{1}{4} - \mathbf{S}_i\cdot\mathbf{S}_j, \quad \mathcal{P}_{ij}^{S=1} = \frac{3}{4} + \mathbf{S}_i\cdot\mathbf{S}_j \qquad (9)$$

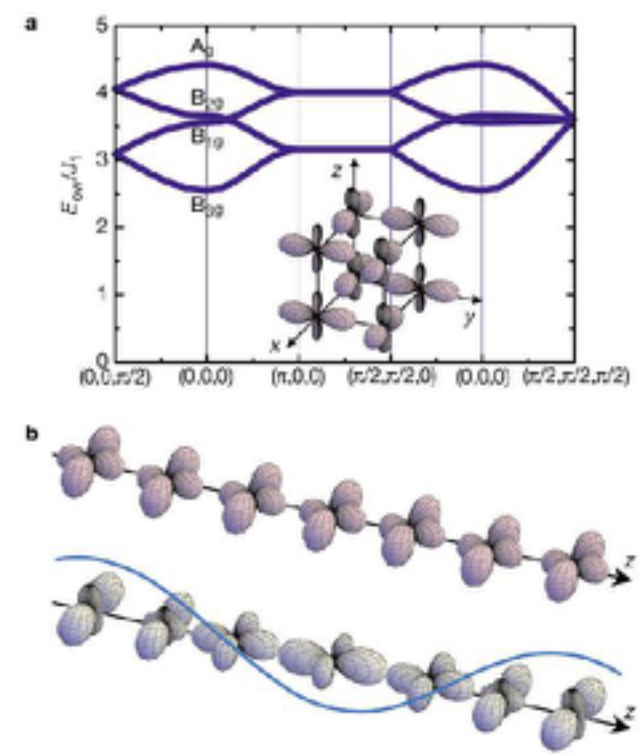
A. Smerald and F. Mila, PRB, **90**, 094422 (2014).

No SOC, though…

New fractionalized excitation: orbitalon

cf. orbital wave spectrum observed in $LaMnO_3$
E. Saitoh et al., Nature **410**, 180 (2001).

	spin sector	orbital sector
NG boson	magnon (spin wave)	orbiton (orbital wave)
fermionic excitation	spinon	orbitalon



- In QSOL, spinon excitations coexist with fractionalized orbital excitations: orbitalons.
- In BCSO, EXAFS/dynamical JT effect excludes LRO/SSB, but this is still an indirect evidence for the QSOL state.

SU(2)xSU(2) Kugel-Khomskii models

- If we write spin as S_i and orbital as T_i then the Hamiltonian can be written by these two spin-1/2 operators.

- For example, assuming the SU(2)xSU(2) symmetry for both the spin and orbital degrees of freedom, the Hamiltonian can generally be written as

orbital d.o.f.

$$H = J \sum_{\langle ij \rangle} \left(\boldsymbol{S}_i \cdot \boldsymbol{S}_j + c_1 \right) \boxed{\left(\boldsymbol{T}_i \cdot \boldsymbol{T}_j + c_2 \right)} + c_3 .$$

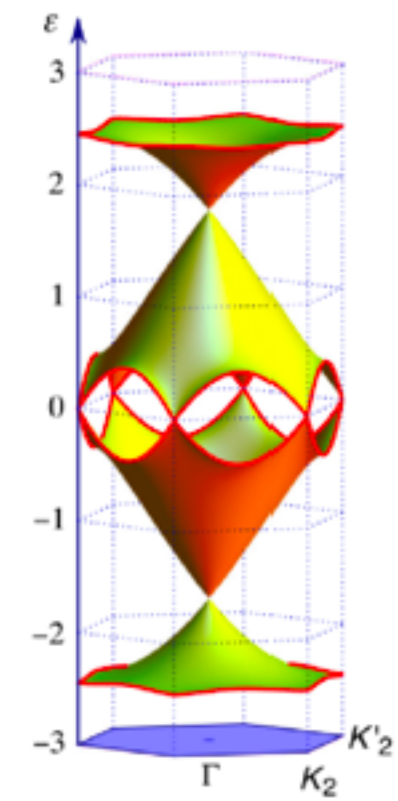
K. I. Kugel and D. I. Khomskii, Sov. Phys. Usp. **25**, 231 (1982).

Quantum spin-orbital liquid (QSOL) in the SU(4) Heisenberg model

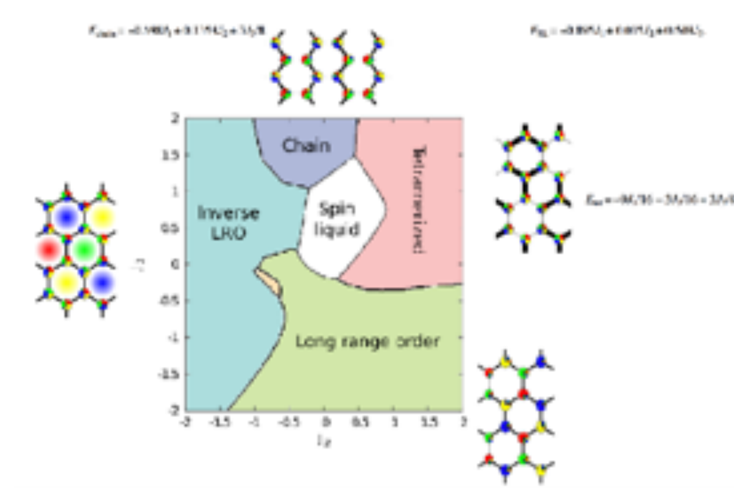
- Variational Monte-Carlo studies suggest the SU(4) Heisenberg model on the honeycomb lattice hosts QSOL with pi-flux Dirac dispersions:

$$H = J \sum_{\langle ij \rangle} \Big(\mathbf{S}_i \cdot \mathbf{S}_j + \frac{1}{4} \Big) \Big(\mathbf{T}_i \cdot \mathbf{T}_j + \frac{1}{4} \Big)$$

P. Corboz *et al.*, Phys. Rev. X **2**, 041013 (2012).



- Theoretically, this is only one well-established example of QSOL with fractionalized excitations and with a finite stable window.



http://www2.yukawa.kyoto-u.ac.jp/ws/2016/sun2016/archive/PresenFiles/week2/Lajko.pdf

Two effects of the enlarged symmetry

- **Quantum fluctuation gets stronger**:
  the classical ground state becomes more degenerate
  - SU(2): only Néel state ↑↓↑↓↑↓↑↓
  - SU(4): more candidates ABABAB / ABCABC / ABCDABCD
- **Lieb-Schultz-Mattis (LSM) condition is changed**:
  The existence of fractionalized excitations is guaranteed by the LSM theorem.
  - SU(2): even/odd, while SU(4): whether a multiple of 4 or not
  - The honeycomb SU(2) model can be trivial, but SU(4) cannot

Note: LSM-Affleck theorem

- For SU(2), even: can be trivial, odd: nontrivial
- For SU(N), multiple of N fundamental rep.: can be trivial, otherwise nontrivial (gapless/GSD)
- This is because trivial representation can only be constructed from N fundamental representations.
- General statement: only when the number of boxes/unit cell is a multiple of N, the ground state can be trivially gapped.

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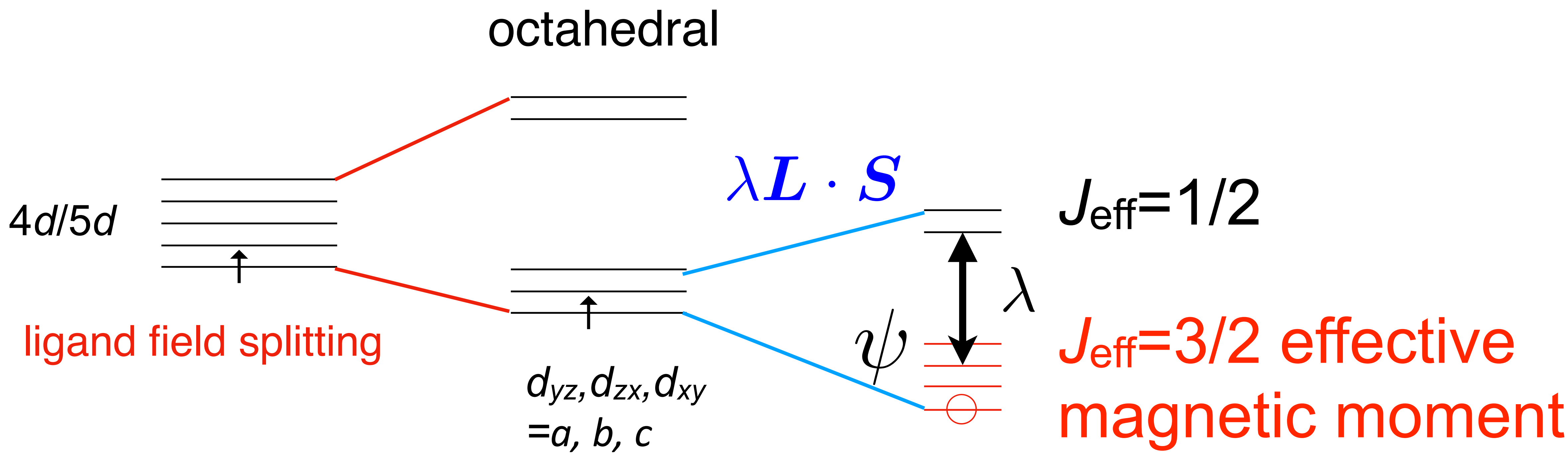
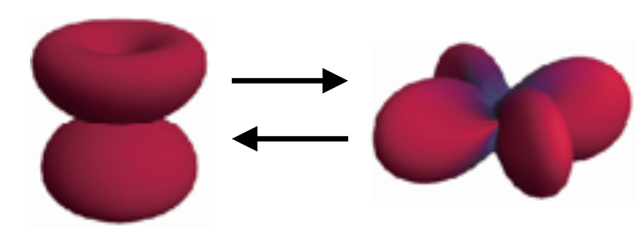
d^1 electronic configuration





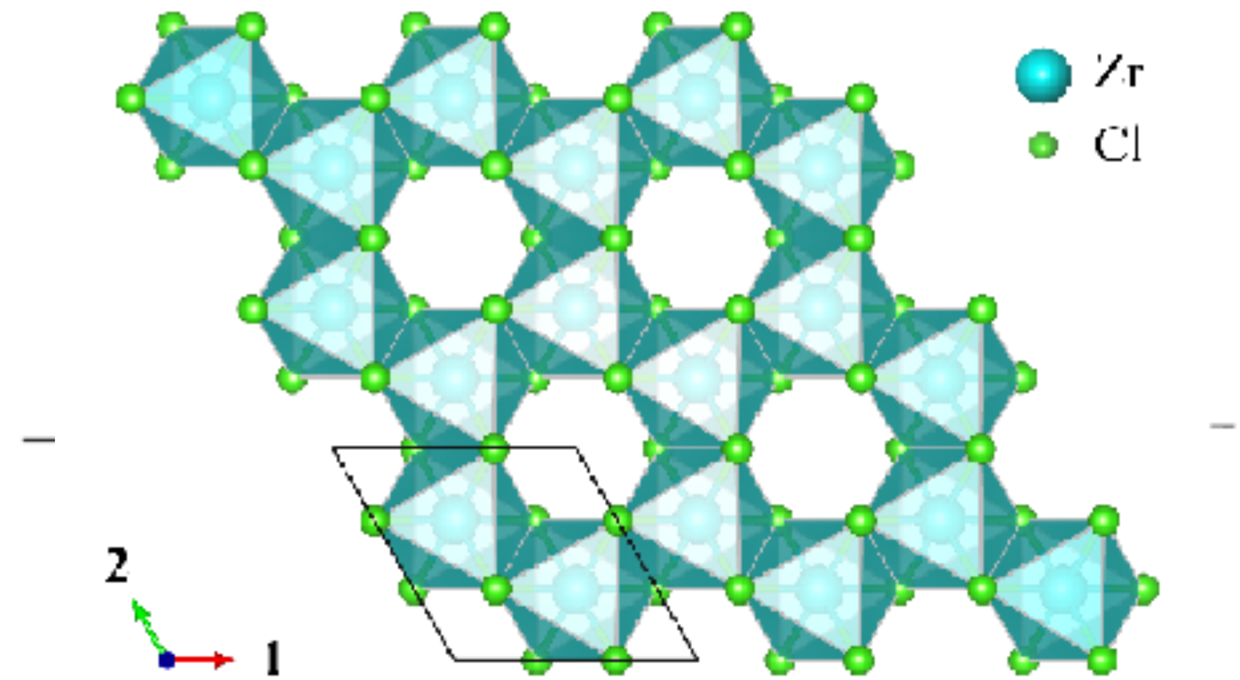
Ti^{3+}, Zr^{3+}, Hf^{3+} d^1 S=1/2, L=1

- Six-fold degenerate d^1 ground state splits into the J_{eff}=1/2 doublet and the J_{eff}=3/2 quartet by spin-orbit coupling (SOC).

α-ZrCl$_3$

IV group

4*d*, 5*d* metal
=strong SOC



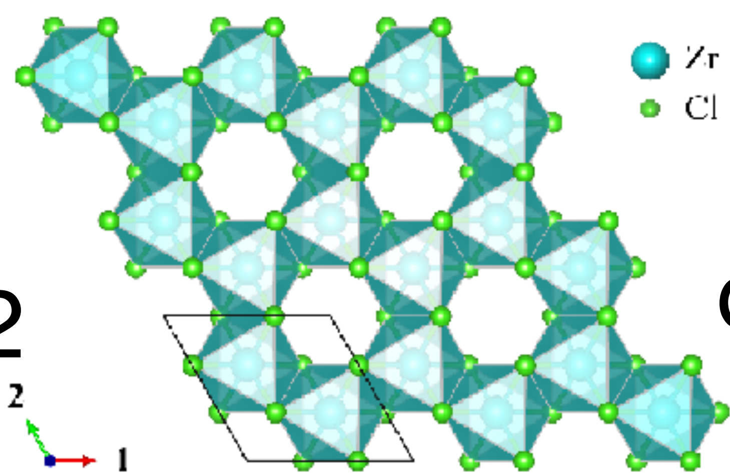
$$3ZrCl_4\ _{(gas)} + Zr_{(solid)} \rightarrow 4ZrCl_3\ _{(solid)}$$

http://www.compoundchem.com/2015/11/17/oxidation-states/

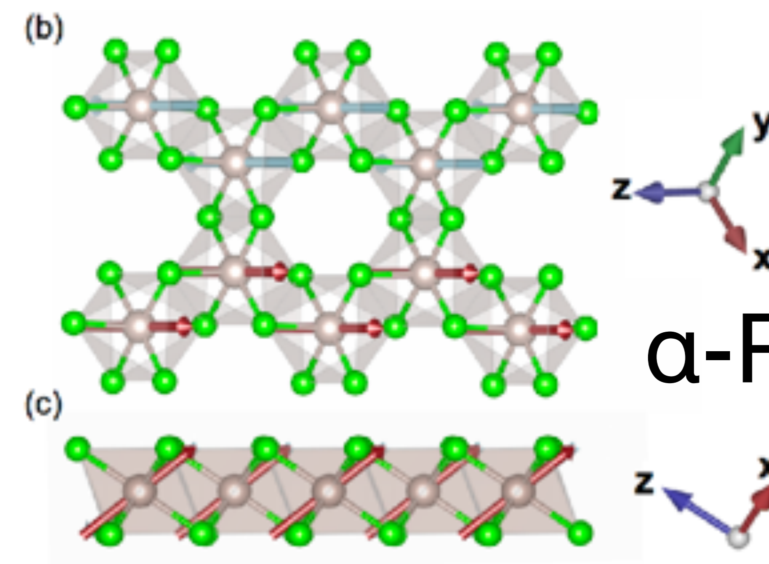
- First reported in B. Swaroop and S. N. Flengas, Can. J. Chem. **42**, 1495 (1964), Can. J. Phys. **42**, 1886 (1964).

α-**Zr**Cl_3 with **strong** SOC

J_{eff}=3/2



α-$ZrCl_3$



α-$RuCl_3$

J_{eff}=1/2

- Basically, the same structure as α-$RuCl_3$, a Kitaev candidate.

- At least the 6-fold degeneracy lifts to **the 4-fold ground state with a quarter filling**, which leads to the effective Hubbard model on the J_{eff}=3/2 quartet.

S. M. Winter *et al.*, PRB **93**, 214431 (2016).

Construct a 4-flavor Hubbard model

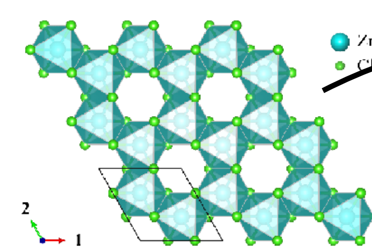
In the limit $\lambda \to \infty$, ψ : 4-component J_{eff}=3/2 spinor

hopping term

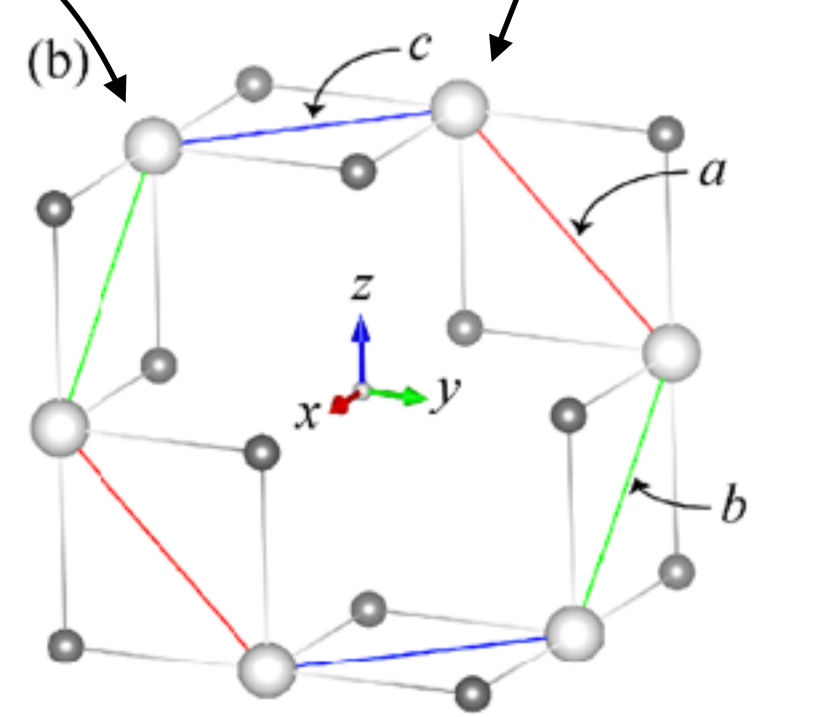
Hubbard term

$$H = \boxed{-\frac{t}{\sqrt{3}} \sum_{\langle ij \rangle} \psi_i^\dagger U_{ij} \psi_j + h.c.} + \boxed{\frac{U}{2} \sum_j \psi_j^\dagger \psi_j (\psi_j^\dagger \psi_j - 1).}$$

$$U_{ij} = \begin{cases} U^a & (\langle ij \rangle \in a) \\ U^b & (\langle ij \rangle \in b) \\ U^c & (\langle ij \rangle \in c) \end{cases}$$



4 orbitals ψ on each site



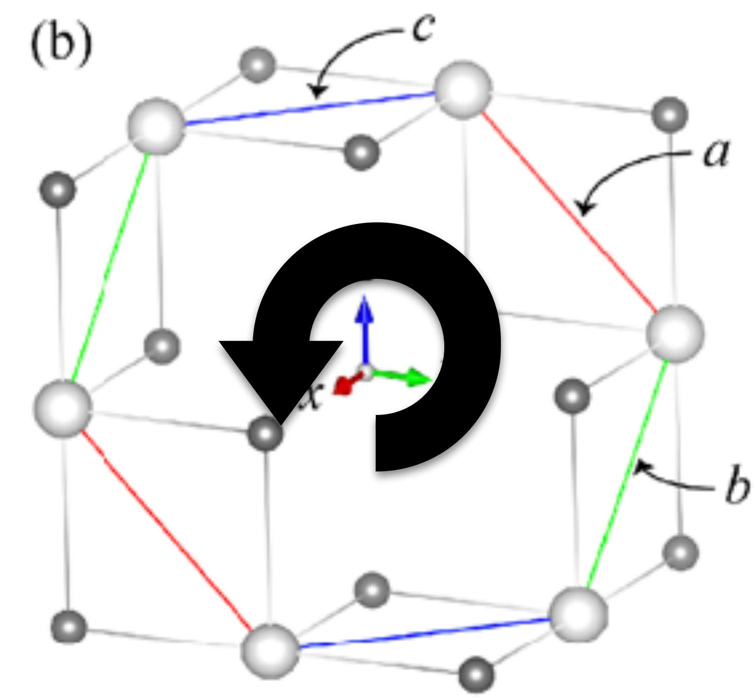
- U_{ij} depends on the “bond plane”

$$U^a = \begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{pmatrix}, U^b = \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, U^c = \begin{pmatrix} 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix}.$$

Miracle: 4x4 multiplication

- U_{ij} depends on the “bond plane”

$$U^a = \begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{pmatrix}, U^b = \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, U^c = \begin{pmatrix} 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix}.$$



- U_{ij} obeys the following equation, which is important later

$$\prod_{\langle ij \rangle \in p} U_{ij} = U^a U^b U^c U^a U^b U^c = -I.$$

for each hexagon *p*.

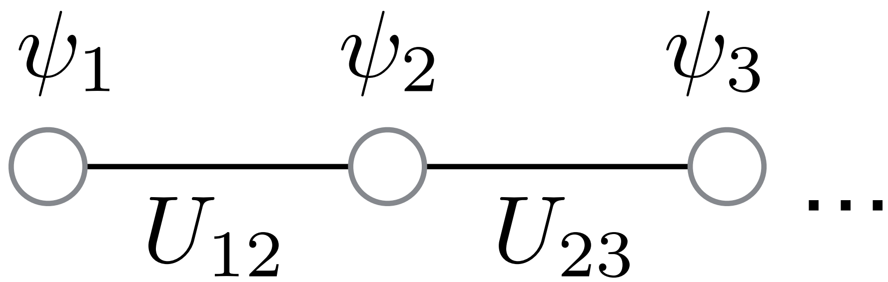
- From this, we can find a gauge transformation:

$$\psi'_j = g_j \cdot \psi_j,$$
$$U'_{ij} = g_i U_{ij} g_j^\dagger, \text{ with } U'_{ij} = \eta_{ij} I$$

$$g_j \in SU(4)$$
$$\eta_{ij} = \pm 1$$

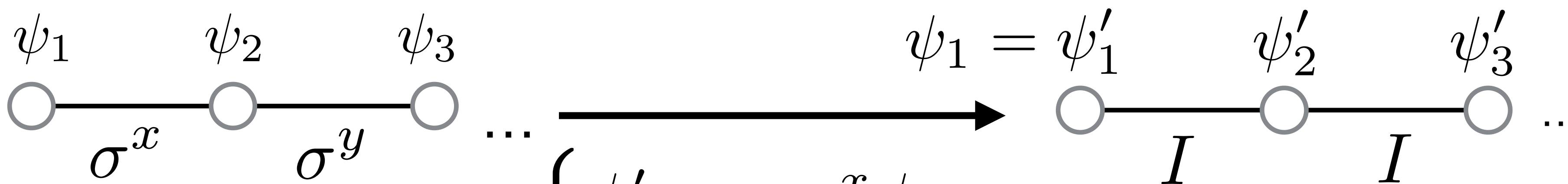
Gauge transformation in 1D

- In 1D chains, gauge transformation is just a multiplication of the string operator



$$g_i = \prod_{j=1}^{i-1} U_{j,j+1}.$$

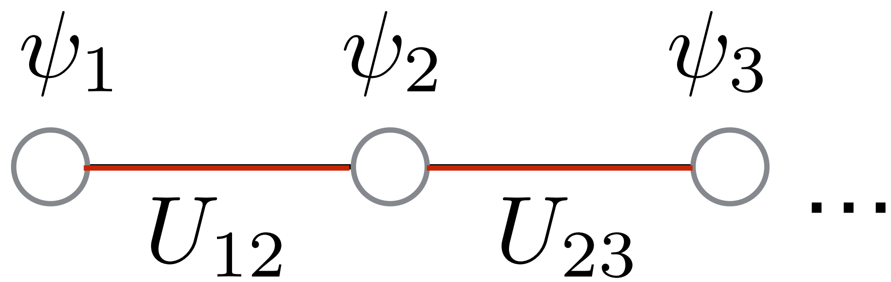
e.g.



$$\begin{cases} \psi_2' &= \sigma^x \psi_2 \\ \psi_3' &= \sigma^x \sigma^y \psi_3 \end{cases}$$

It’s SU(2) but the same for SU(4)

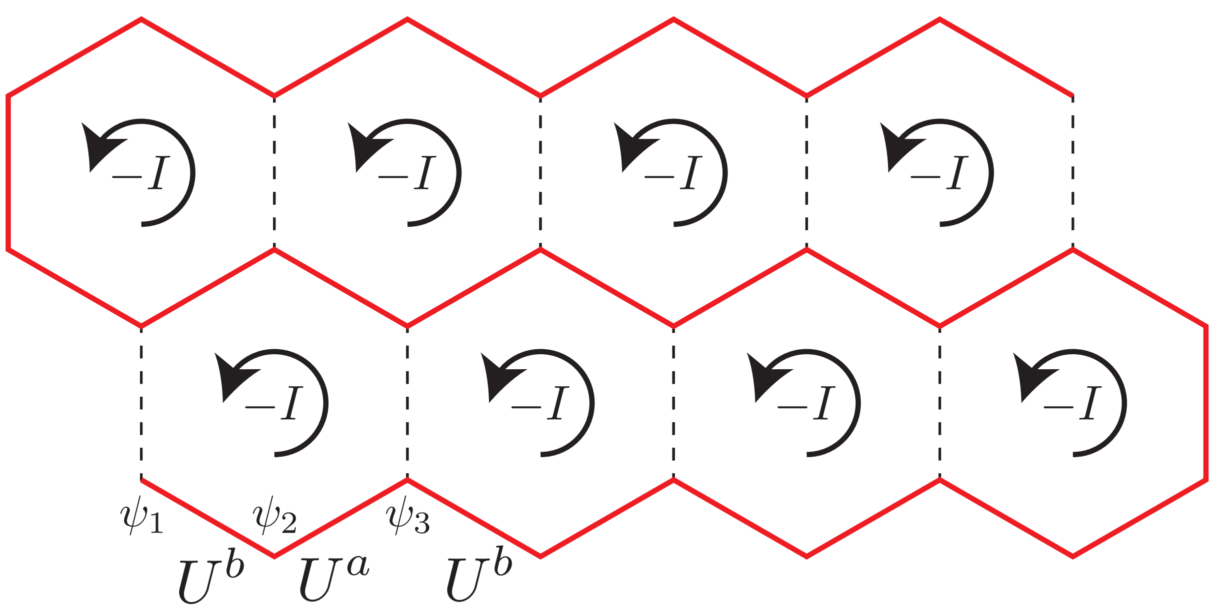
Gauge transformation in 2D



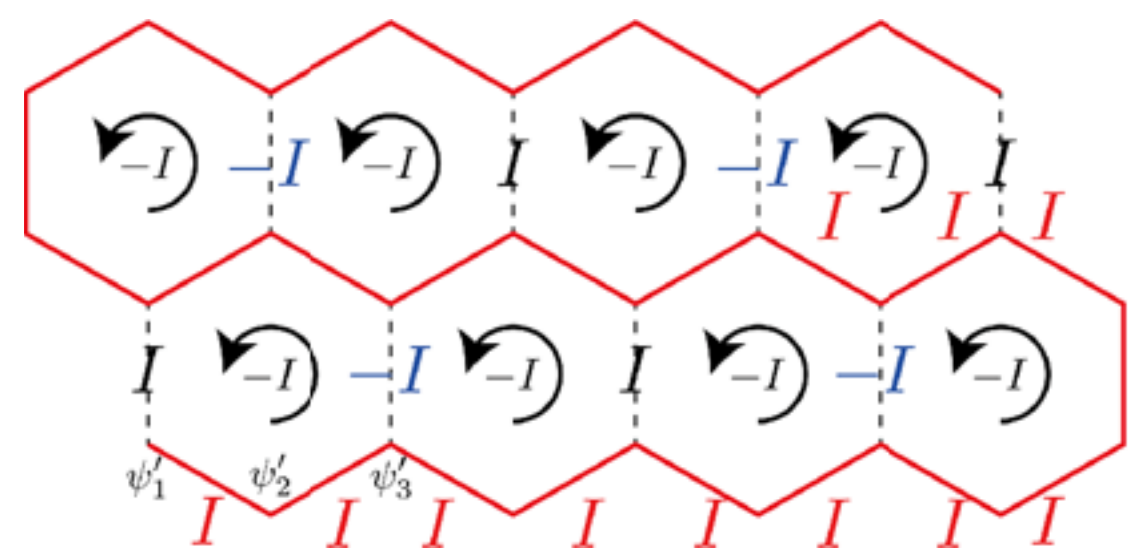
$$g_i = \prod_{j=1}^{i-1} U_{j,j+1}.$$

Constraint: $\prod_{\langle ij\rangle \in p} U_{ij} = \prod_{\langle ij\rangle \in p} U'_{ij} = -I.$

Phase factor: $\eta_{ij} = \pm 1.$



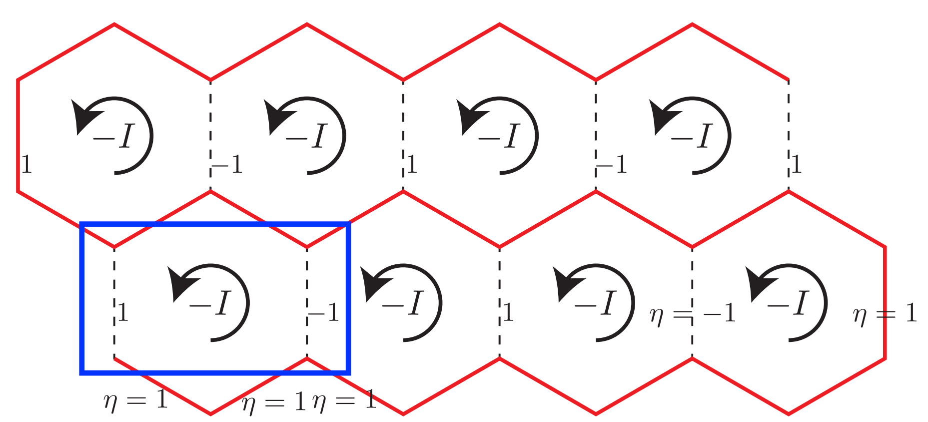
Applying SU(2)
gauge transformation
for **the red line**



$$H' = -\frac{t}{\sqrt{3}} \sum_{\langle ij\rangle} \eta_{ij} \psi_i'^{\dagger} \psi'_j + h.c. + \frac{U}{2} \sum_j \psi_j'^{\dagger} \psi'_j (\psi_j'^{\dagger} \psi'_j - 1).$$

π-flux SU(4) Hubbard model on the honeycomb lattice

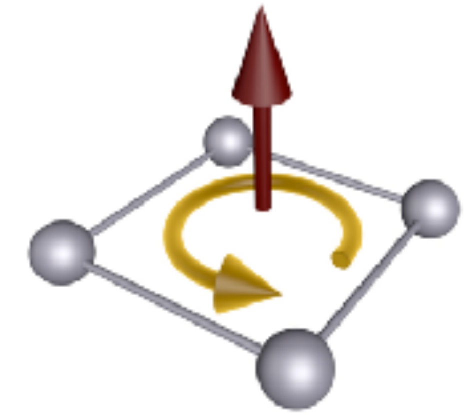
- The gauge transformation keeps the flux inside the plaquette, then the unit cell is effectively doubled. $\prod_{\langle ij\rangle \in p} U_{ij} = -I.$



- Global SU(4) symmetry becomes explicit. Some bonds have a -1 factor to keep the condition.

$$H' = -\frac{t}{\sqrt{3}} \sum_{\langle ij\rangle} \eta_{ij} \psi_i'^{\dagger} \psi_j' + h.c. + \frac{U}{2} \sum_j \psi_j'^{\dagger} \psi_j' (\psi_j'^{\dagger} \psi_j' - 1).$$

π-flux



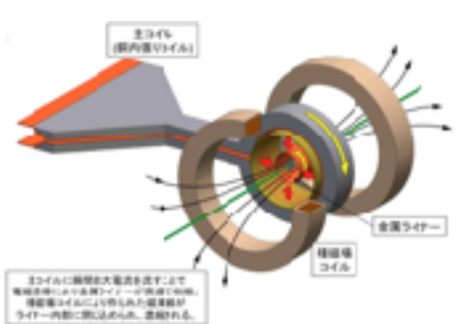
https://www.pks.mpg.de/topart18/

- From SOC, electrons feel an effective magnetic field, which is called orbital flux.

- **Orbital flux engineering** in strong SOC materials will allow us to explore an unprecedented effective magnetic field in real materials.

- π-flux in α-$ZrCl_3$ corresponds to B ~ **6000T**.

cf. The highest magnetic field in ISSP



B ~ 985T

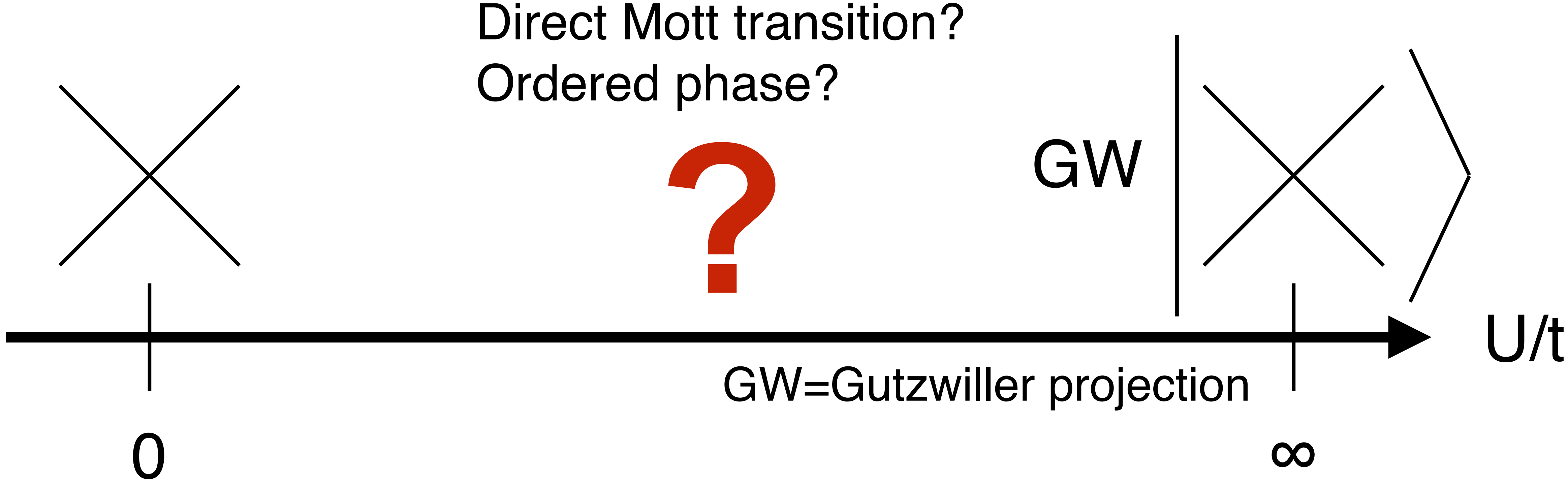
http://www.issp.u-tokyo.ac.jp/

*Emergent B in skyrmions

B ~ 40-400T

Phase diagram of the π-flux Hubbard model

- In the free limit (U=0), the π-flux Hubbard model is Dirac semimetal.
- In the Mott insulator limit (U=∞), this will become π-flux Dirac spin-orbital liquid without charge.



From Hubbard to Heisenberg

$$H' = -\frac{t}{\sqrt{3}} \sum_{\langle ij \rangle} \eta_{ij} \psi_i'^\dagger \psi_j' + h.c. + \frac{U}{2} \sum_j \psi_j'^\dagger \psi_j' (\psi_j'^\dagger \psi_j' - 1).$$

- Since the electron is 1/4-filled, this Hubbard model can be mapped to the SU(4) Heisenberg model in the large U limit.

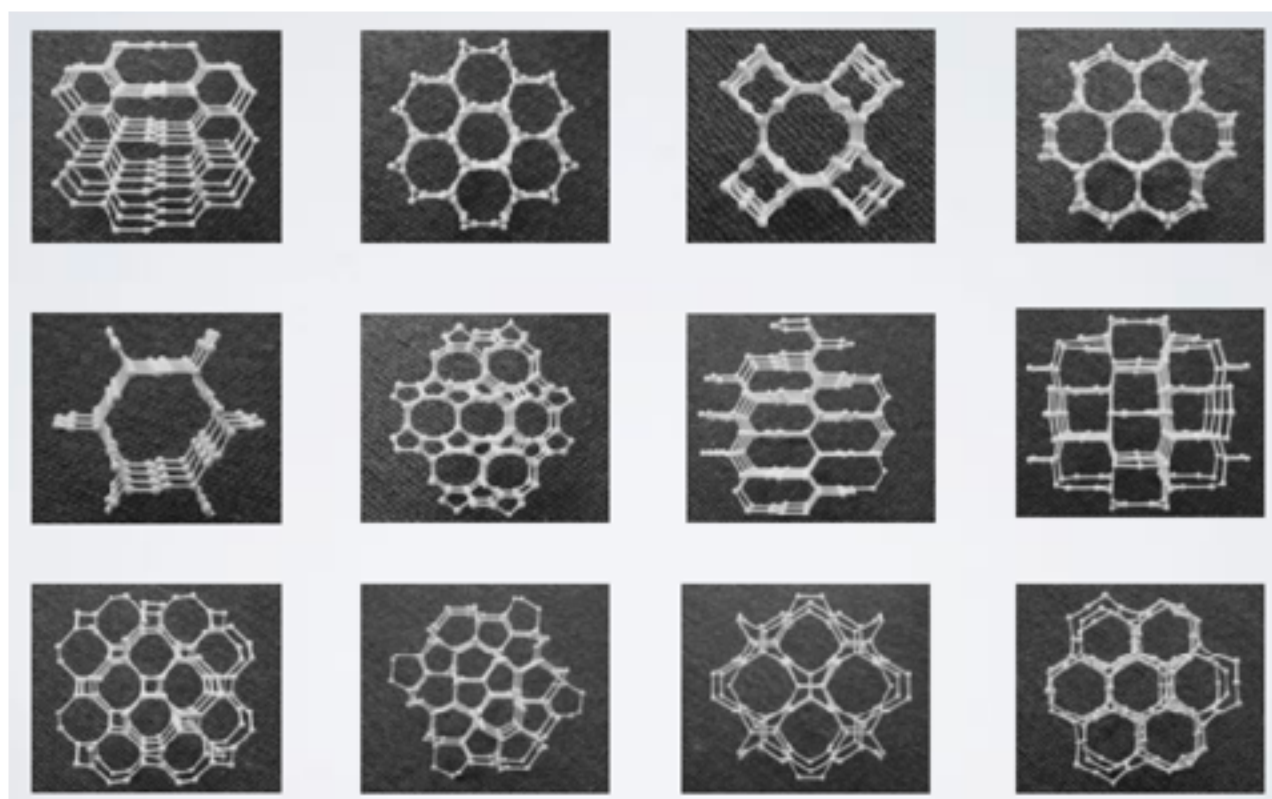
$$H = J \sum_{\langle ij \rangle} \Big(\mathbf{S}_i \cdot \mathbf{S}_j + \frac{1}{4} \Big) \Big(\mathbf{T}_i \cdot \mathbf{T}_j + \frac{1}{4} \Big)$$

- The flux sector does not matter in this limit.

cf. Derivation in another way: W. M. H. Natori, *et al.*, arXiv:1802.00044

How about 3D tricoordinated lattices?

- There are many 3D generalizations of the honeycomb lattice with trivalent vertices.



http://www.thp.uni-koeln.de/~hermanns/talks/KitaevSL.pdf

Conditions to become *SU*(4)

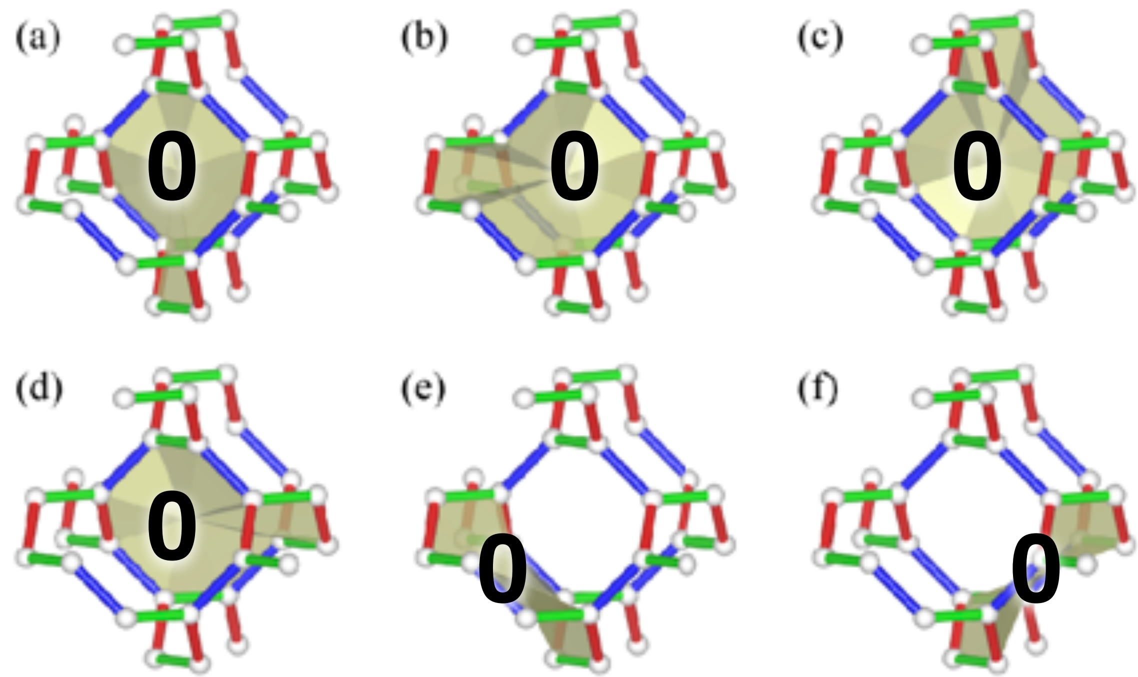
- *U*'s obey Majorana-like anticommutation relations:
$$\{U^\alpha, U^\beta\} = 2\delta^{\alpha\beta} I.$$
- Then, if the same color appears even times in each loop, the flux becomes Abelian ±1.

- Honeycomb and some 3D lattices obey this condition.

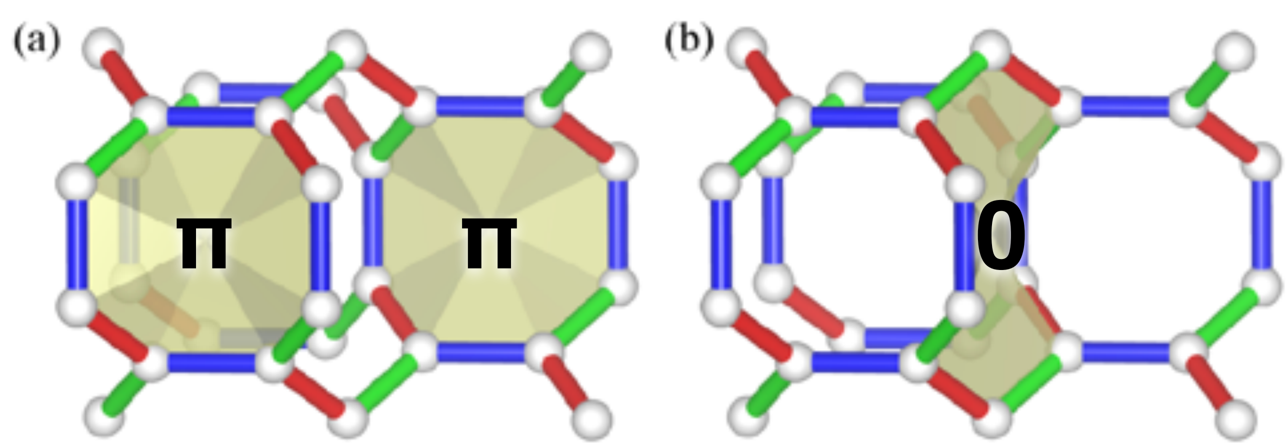
- How we use the anticommutation relations determines the flux sector 0 or π.

Some examples

- Hyperoctagon (10,3)-*a* lattice:



- $8^2.10$-*a* lattice:

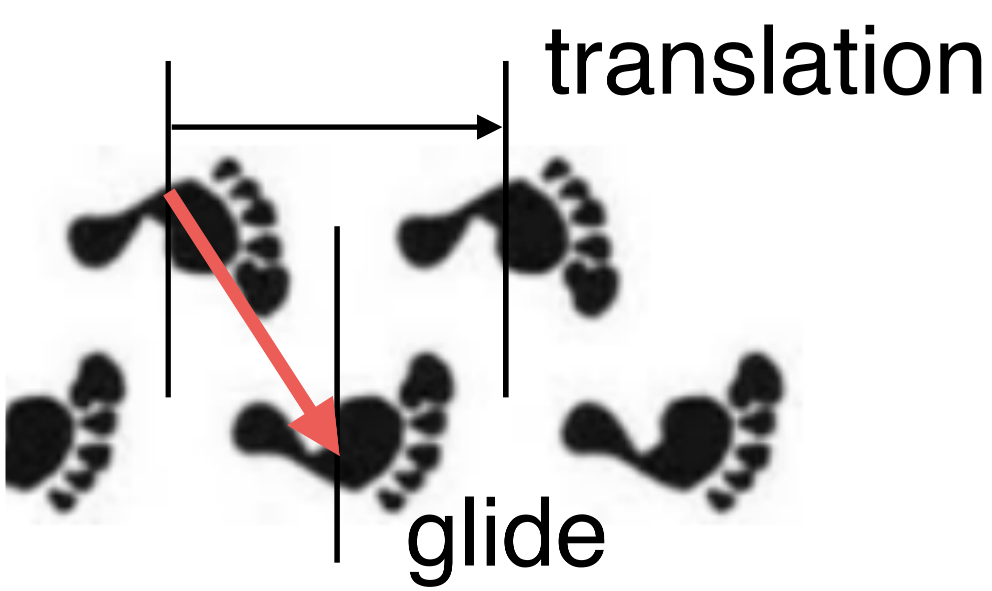


etc.

Nonsymmorphic symmetries

- Most materials/lattices are nonsymmorphic: 157 out of 230 space groups.
- e.g. The hyperoctagon lattice has a screw axis inside the square spirals and a glide mirror plane.
- Divided by those nonsymmorphic symmetries, The unit cell will be effectively reduced.

This is why gapless semimetallic phases are protected in nonsymmorphic materials.



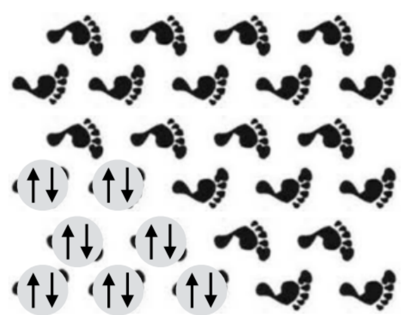
https://sites.google.com/site/hwatanabephys/research

H. Watanabe *et al.*, PNAS **112**, 14551 (2015).

QSOL can also be protected by space group symmetries

- Even if the number of sites/u.c. is a multiple of 4, the nonsymmorphic symmetry sometimes protects the QSOL state.

"Extended LSMA theorem"



- This is because the effective unit cell is reduced by the devision of glide/screw.

TABLE I. Tricoordinated lattices discussed in this Letter. Space groups are shown in number indices. Nonsymmorphic ones are underlined. n is the number of sites per unit cell.

Wells' notation	Lattice name	SU(4)	120° bond	n	Space group	LSMA
(10,3)-a	hyperoctagon	✓[a]	✓	4	214	✓[b]
(10,3)-b	hyperhoneycomb	✓[a]	✓	4	70	✓[b]
(10,3)-d	–	✓[a]	–	8	52	✓[b]
(9,3)-a	hypernonagon	–	–	12	166	–
8^2.10-a	–	✓	✓	8	141	–
(8,3)-b	hyperhexagon	✓	✓	6	166	✓[c]
–	stripyhoneycomb	✓	✓	8	66	–
(6,3)	2D honeycomb	✓	✓	2		✓[d]

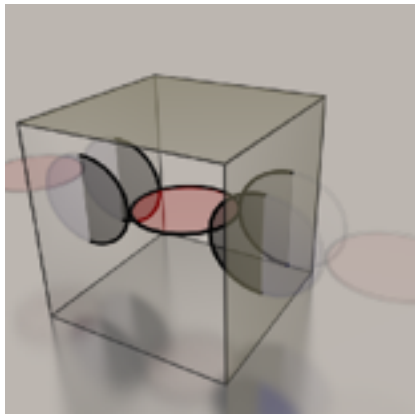
[a] The product of hopping matrices along every elementary loop is unity, resulting in the SU(4) Hubbard model with zero flux.
[b] Nonsymmorphic symmetries of the lattice are enough to protect a QSOL state, i.e. hosting an XSOL state.
[c] Although the model has a π flux, with an appropriate gauge choice the unit cell is not enlared. Therefore, the LSMA theorem straightforwardly applies to the π-flux SU(4) Hubbard model.
[d] While the standard LSMA theorem is not effective for the π-flux SU(4) Hubbard model here, the magnetic translation symmetry works to protect a QSOL state [47].

https://sites.google.com/site/hwatanabephys/research

H. Watanabe *et al.*, PNAS **112**, 14551 (2015).

Crystalline spin liquids and crystalline spin-orbital liquids

- A crystalline spin liquid (XSL) is defined as a (gapless) spin liquid where the gapless point is protected by the space group symmetry.



e.g. a nodal line is protected by the glide mirror symmetry.

MGY, V. Dwivedi, and M. Hermanns, PRB **96**, 155107 (2017).

- In the same way, hyperoctagon, hyperhoneycomb, etc. *SU*(4) Heisenberg models can be called **crystalline spin-orbital liquids (XSOL)** due to their nonsymmorphic symmetries.

Signatures for the SU(4) symmetry between spin & orbital excitations

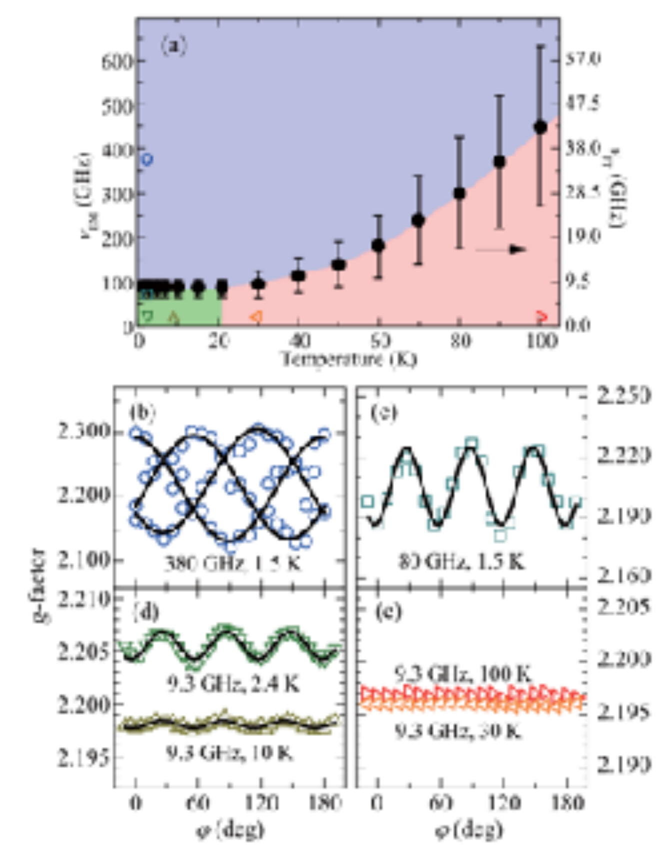
- Finite-frequency ESR (electron spin resonance) is known to be a very good signature of the quantum orbital fluctuations.

Y. Han *et al.*, PRB 92, 180410(R) (2015).

- Use NMR for spins and ESR for orbitals!

- If the typical time scales coincide between the two, this suggests a symmetry between spin & orbital.

- SU(4) may change the universality class of critical phenomena.



Summary

- We have proposed α-$ZrCl_3$ as a candidate material for the SU(4) Hubbard / Heisenberg model on the honeycomb lattice.
- Especially, the SU(4) Heisenberg model is expected to host QSOL, so we found a new candidate for quantum spin-orbital liquids.
- EXAFS (extended X-ray absorption fine structure) and ESR will confirm the absence of orbital ordering, but it is still challenging to observe orbital excitations.