Emergent SU(4) symmetry and quantum spin-orbital liquid in $\alpha$-ZrCl$_3$

arXiv:1709.05252

Masahiko G. Yamada
the Institute for Solid State Physics, the University of Tokyo
with Masaki Oshikawa (ISSP) and George Jackeli (MPI-FKF)
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.

Exchange frustration

- e.g. iridates, Ru-compounds/MOFs

strong spin-orbit coupling (SOC) materials


https://www.thp.uni-koeln.de/~hermanns/talks/KitaevSL.pdf
Quantum spin-orbital liquid

- Known candidate: honeycomb-like Ba$_3$CuSb$_2$O$_9$ (BCSO)
- Cu$^{2+}$ in the octahedral coordination: both spin/orbital degeneracy (2 x 2 states per site)
- No magnetic order / spin freezing
- No Jahn-Teller transition / orbital freezing

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

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

No SOC, though…
New fractionalized excitation: orbitalon

cf. orbital wave spectrum observed in LaMnO$_3$

<table>
<thead>
<tr>
<th></th>
<th>spin sector</th>
<th>orbital sector</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG boson</td>
<td>magnon (spin wave)</td>
<td>orbiton (orbital wave)</td>
</tr>
<tr>
<td>fermionic excitation</td>
<td>spinon</td>
<td>orbitalon</td>
</tr>
</tbody>
</table>

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

$$H = J \sum_{\langle ij \rangle} \left( S_i \cdot S_j + c_1 \right) \left( T_i \cdot T_j + c_2 \right) + c_3.$$

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:

\[
H = J \sum_{\langle ij \rangle} \left( S_i \cdot S_j + \frac{1}{4} \right) \left( T_i \cdot T_j + \frac{1}{4} \right)
\]


• 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 $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$
  - 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.
Outline

• Introduction to quantum spin-orbital liquids
• Material proposal
• Derivation of the emergent SU(4) symmetry
• 3D generalization, etc.
• Summary
$d^1$ electronic configuration

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

- $\text{Ti}^{3+}$, $\text{Zr}^{3+}$, $\text{Hf}^{3+}$ $d^1$ $S=1/2$, $L=1$
$\alpha$-ZrCl$_3$ with strong SOC

- Basically, the same structure as $\alpha$-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 $J_{\text{eff}}=3/2$ quartet.

S. M. Winter et al., PRB 93, 214431 (2016).
Construct a 4-flavor Hubbard model

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

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

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

- $U_{ij}$ depends on the “bond plane”

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

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

$g_j \in SU(4)$

$\eta_{ij} = \pm 1$
Gauge transformation in 1D

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

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

\[
\begin{align*}
\psi_1 & \quad \psi_2 & \quad \psi_3 \\
U_{12} & \quad U_{23} & \quad \cdots
\end{align*}
\]

e.g.

\[
\begin{align*}
\psi_1 & \quad \psi_2 & \quad \psi_3 \\
\sigma^x & \quad \sigma^y & \quad \cdots
\end{align*}
\]

\[
\begin{align*}
\psi_1 &= \psi_1' \\
\psi_2' &= \sigma^x \psi_2 \\
\psi_3' &= \sigma^x \sigma^y \psi_3
\end{align*}
\]

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

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

\[
H' = -\frac{t}{\sqrt{3}} \sum_{\langle ij \rangle} \eta_{ij} \psi^\dagger_i \psi_j' + h.c. + \frac{U}{2} \sum_j \psi^\dagger_j \psi_j' (\psi^\dagger_j \psi_j' - 1).
\]
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-ZrCl₃ corresponds to $B \sim 6000 \text{T}$.

cf. The highest magnetic field in ISSP

B ~ 985T

*Emergent B in skyrmions

B ~ 40-400T

http://www.issp.u-tokyo.ac.jp/
Phase diagram of the $\pi$-flux Hubbard model

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

Direct Mott transition? Ordered phase?

GW=Gutzwiller projection
From Hubbard to Heisenberg

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

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

\[ H = J \sum_{\langle ij \rangle} \left( \mathbf{S}_i \cdot \mathbf{S}_j + \frac{1}{4} \right) \left( \mathbf{T}_i \cdot \mathbf{T}_j + \frac{1}{4} \right) \]

- The flux sector does not matter in this limit.

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 $\pm 1$.
- Honeycomb and some 3D lattices obey this condition.
- How we use the anticommutation relations determines the flux sector 0 or $\pi$. 
Some examples

- Hyperoctagon (10,3)-a lattice:

- $8^2 \cdot 10$-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
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 division of glide/screw.

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

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

MGY, V. Dwivedi, and M. Hermanns, PRB 96, 155107 (2017).
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 $\alpha$-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.