Below the Mott gap:

cluster Mott insulators and spin liquids

GANG CHEN

ArXiv 1402.5425 **(PRL 2014),**
1408.1963

Collaborators: Hae-Young Kee, Yong-Baek Kim

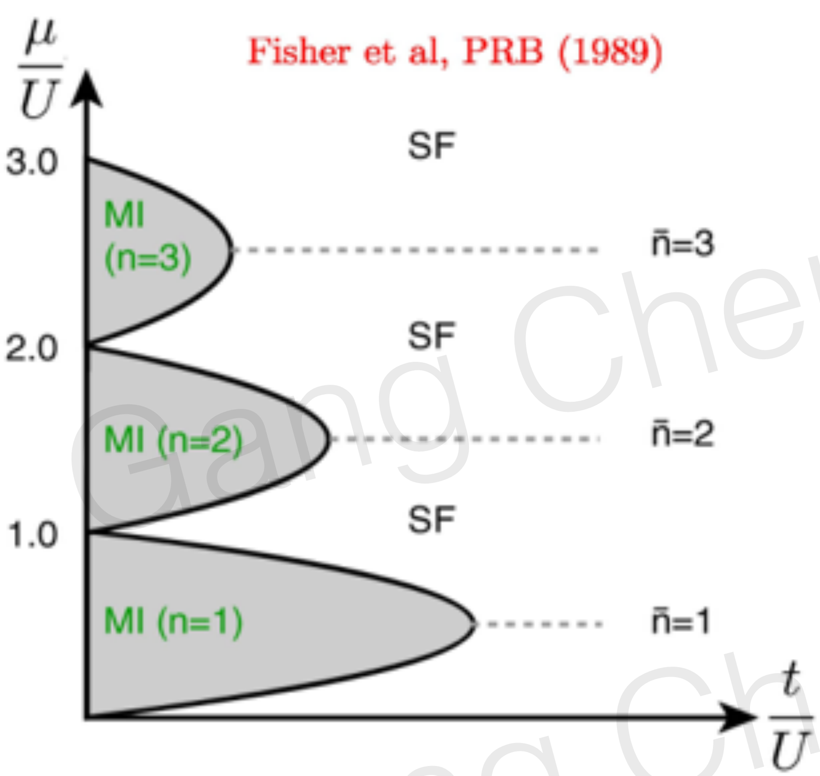
Outline

- Introduction and Motivation
- A 2D cluster Mott insulator: $LiZn_2Mo_3O_8$
- The theory of cluster Mott insulator in 2D
- Summary

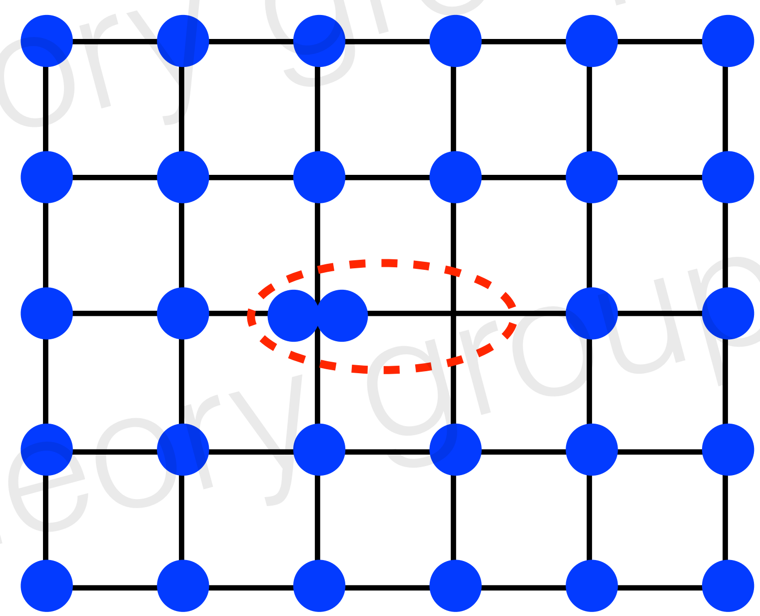
Matthew Fisher

Boson Hubbard model

$$H = -t\sum_{i,j}(b_i^\dagger b_j + h.c.) + \sum_i U n_i(n_i - 1) - \mu n_i$$



SF = Superfluid
MI = Mott insulator



Particle-hole excitation in the
Mott insulator costs energy ~ U (Mott gap).
nothing below the Mott gap.

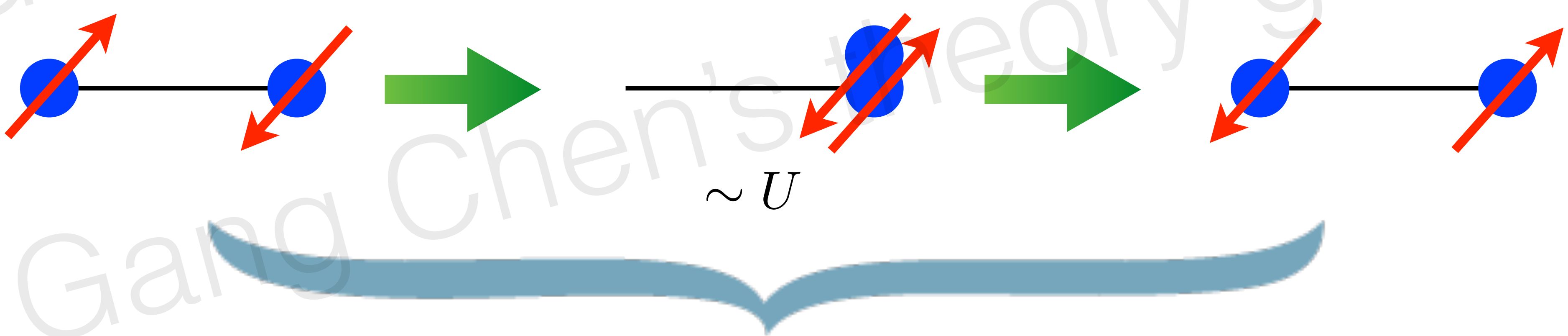
P. W. Anderson

Fermion Hubbard model

$$H = -t \sum_{ij,\sigma} (c^\dagger_{i\sigma} c_{j\sigma} + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

Below the Mott gap: superexchange of spins

Electron carries spin. Even though the position of the electron is frozen, the spins are still active.



$$H = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad J_{ij} \sim \mathcal{O}(t^2/U)$$

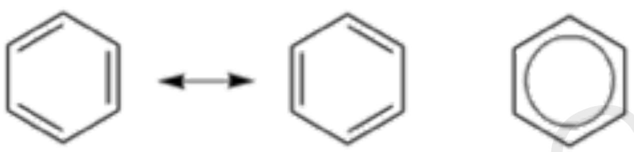
The idea of **resonant valence bor**

P. W. Anderson

RESONATING VALENCE BONDS: A NEW KIND OI

P. W. Anderson

type would be insulating; it would represent an alternative state to the Néel antiferromagnetic state for S = 1/2. An estimate of



benzene molecule

Pauling's RVB state of benzene molecule

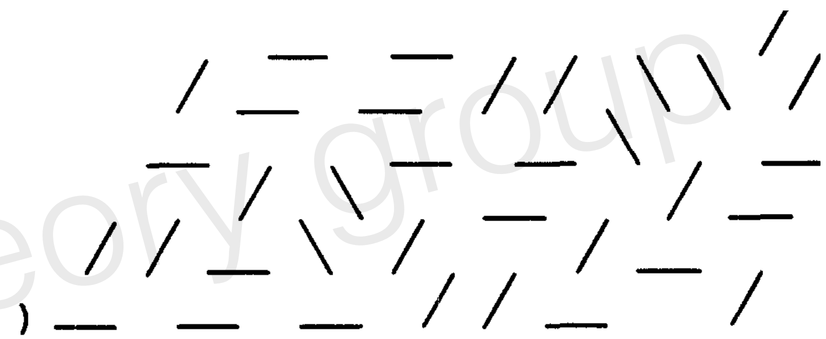


FIG. 3

Random arrangements of pair bonds on a triangle lattice. (a) Shows a regular ar-

$$— = \frac{1}{\sqrt{2}}\left[\uparrow\!—\!\downarrow - \downarrow\!—\!\uparrow\right]$$

Anderson's spin singlet RVB states, then possible application to high-Tc superconductor in 1987.

It is NOT a Landau symmetry breaking state. This brings up an **old and fundamental question**, how do we characterize phase of matter? Does spin liquid even exist?

it is very illuminating to trace the motivation of great physicists.

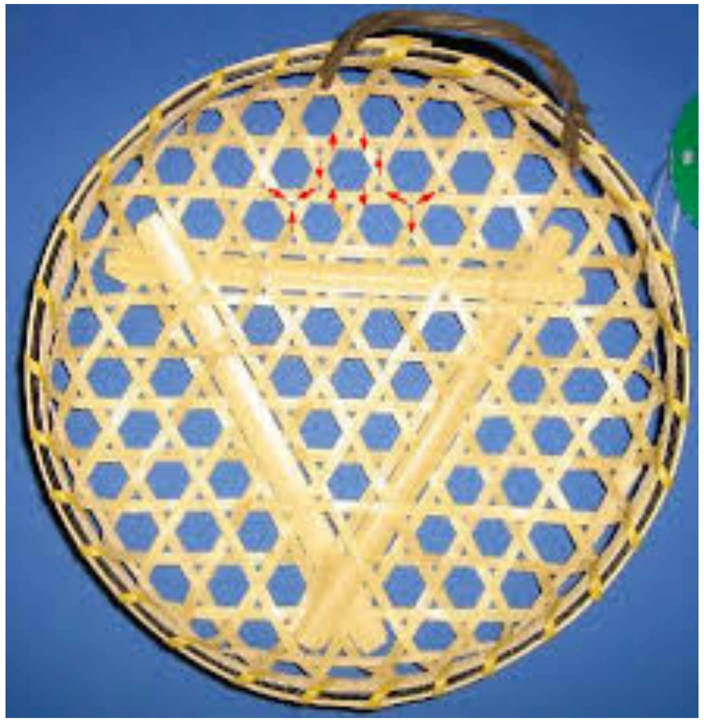
One-slide introduction to quantum spin liquids

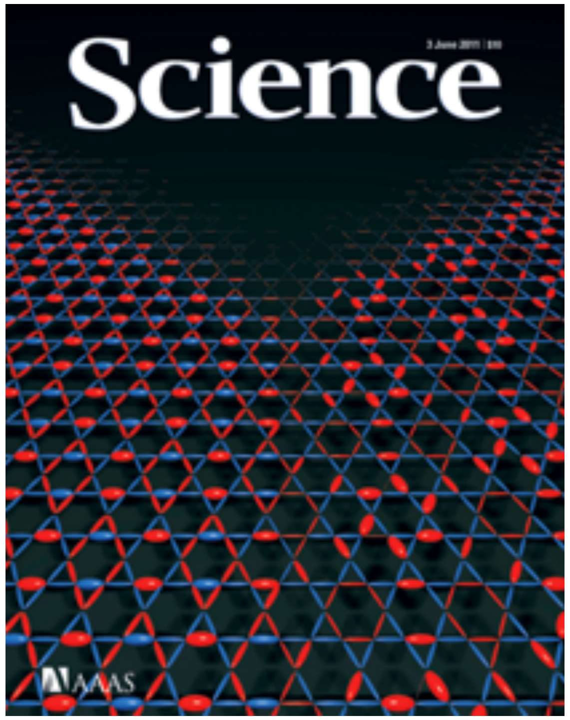
one slide introduction t
liquids

The existence of spin liquid (in **theory**) is well established and is supported by

- Exactly solvable models: e.g. Kitaev model and its variants
- Classification: many many spin liquids (X.-G. Wen, etc)
- Numerical studies: DMRG, quantum Monte Carlo, exact diagonalization, etc

QSL is a **new phase of matter**, and is not characterized by symmetry, but characterized by an emergent gauge structure and deconfined excitations that carry fractional (spin) quantum numbers.





S. White

H.C. Jiang

a semi-realistic model study:
Z_2 spin liquid for Kagome Heisenberg model

What's needed? Experiments, and the connection from theory to experiments!

Candidate spin liquid materials

- 2D triangular and Kagome lattice

  organics: kappa-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$, $EtMe_3Sb[Pd(dmit)_2]_2$, κappa–$H_3(Cat\text{-}EDT\text{-}TTF)_2$ herbertsmithite ($ZnCu_3(OH)_6Cl_2$), $Ba_3NiSb_2O_9$, $Ba_3CuSb_2O_9$, $LiZn_2Mo_3O_8$, $ZnCu_3(OH)_6Cl_2$ volborthite ($Cu_3V_2O_7(OH)_2$), $BaCu_3V_2O_3(OH)_2$, $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$, Na_2IrO_3, $CsCu_2$($CsCu_2Br_4$, $NiGa_2S_4$, He-3 layers on graphite, etc

- 3D pyrochlore, hyperkagome, FCC lattice, diamond lattice, etc

  $Na_4Ir_3O_8$, IrO_2, Ba_2YMoO_6, $Yb_2Ti_2O_7$, $Pr_2Zr_2O_7$, $Pr_2Sn_2O_7$, $Tb_2Ti_2O_7$, $Nd_2Zr_2O_7$, $FeSc_2S_4$, etc

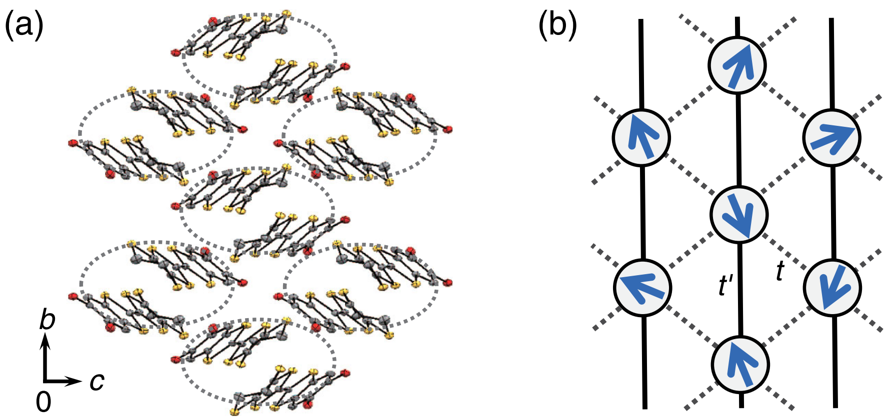
- Ultracold atom and molecules on optical lattices: temperature is too high now.

if you have any q
material, we can

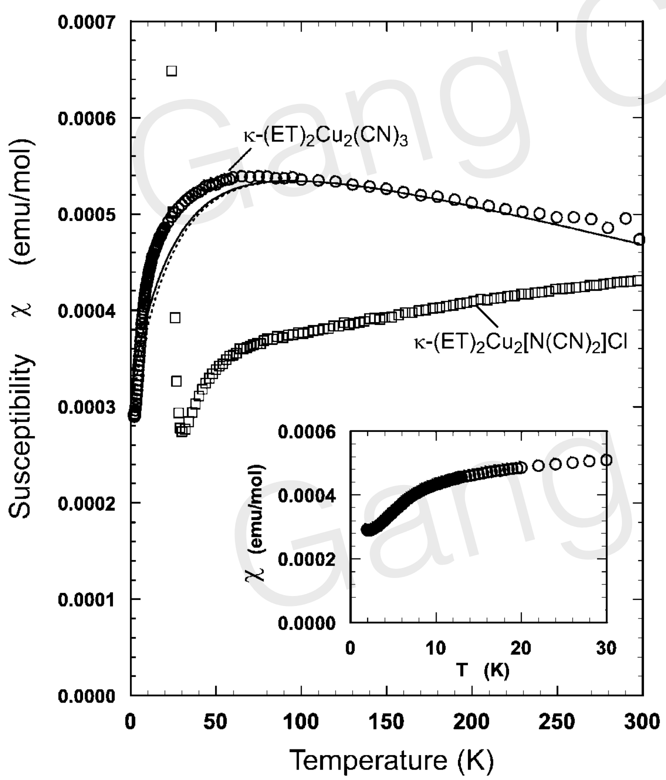
Some candidate materials have already been ruled out.
Not being a QSL does not necessarily mean the physics is not interesting !

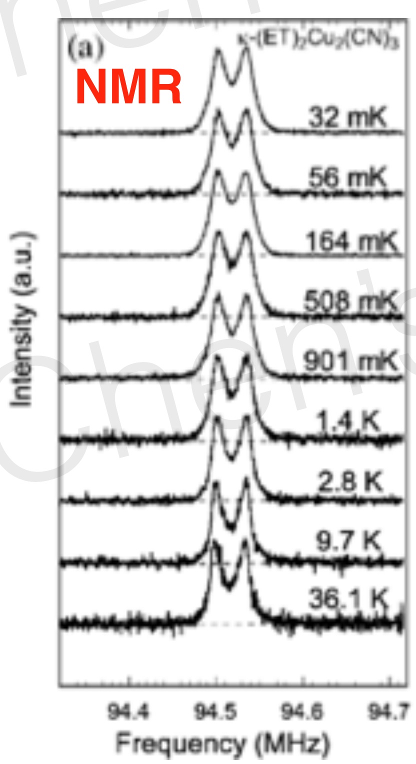
Organic spin liquids?

Kanoda



kappa-(BEDT-TTF)2Cu2(CN)3,
EtMe3Sb[Pd(dmit)2]2,
kappa–H3(Cat-EDT-TTF)2 **a new one!**





* No magnetic order down to 32mK
* Constant spin susceptibility at zero temperature

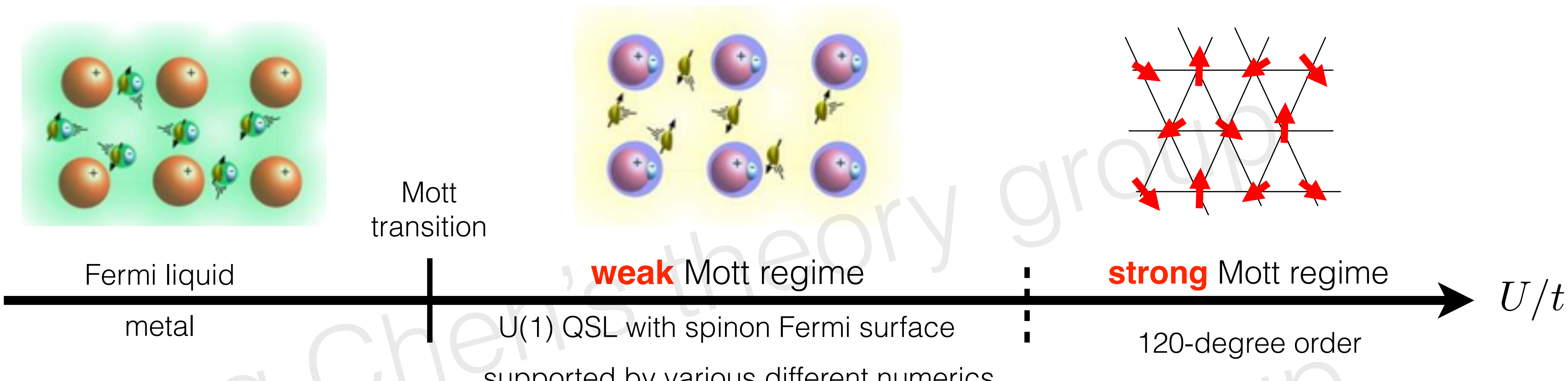
Other experiments: transport,
heat capacity, optical absorption, etc,
Unfortunately, **no neutron scattering** so far.

- Theoretical understanding: expected phase diagram

$$H = -t \sum_{\langle ij \rangle, \sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + h.c. + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

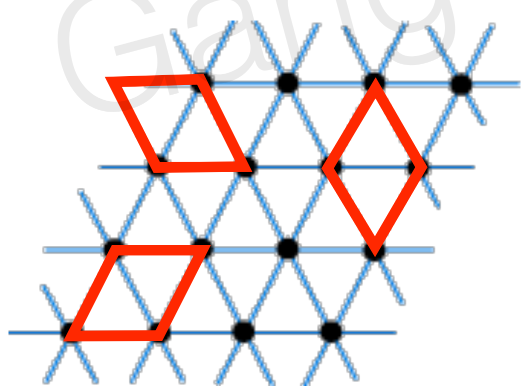
Sung-Sik Lee T Senthil P Lee

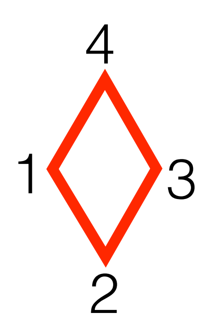
Senthil's cartoon



- **Physical mechanism** for weak Mott insulator spin liquids: perturbation in t/U

$$H_{\text{pert}} = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + K \sum_{1234} (P_{1234} + P_{1234}^{-1}) + \cdots$$





4-site ring exchange

$$\begin{aligned} &(\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_3 \cdot \mathbf{S}_4) \\ +&(\mathbf{S}_1 \cdot \mathbf{S}_4)(\mathbf{S}_2 \cdot \mathbf{S}_3) \\ -&(\mathbf{S}_1 \cdot \mathbf{S}_3)(\mathbf{S}_2 \cdot \mathbf{S}_4) \end{aligned}$$

Motrunich

Remark (on the mechanism NOT the properties):

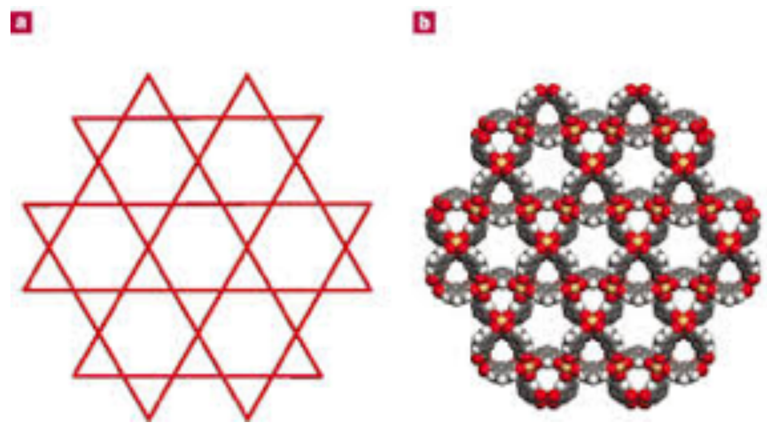
1. There is no sharp distinction between the charge fluctuations in the weak and strong Mott regimes.
2. Strong charge fluctuation in the weak Mott regime is a quantitative description.
3. Interesting physics occurs in the spin sector, but charge sector is completely trivial !

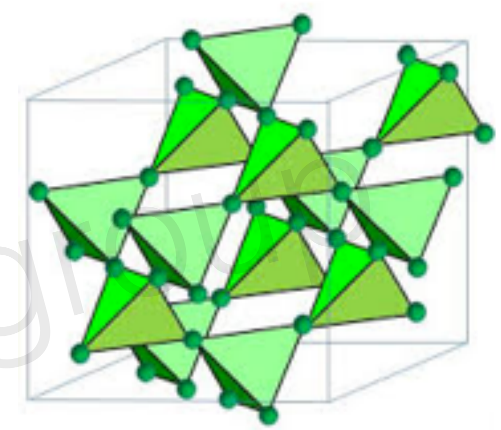
Question / observation (this goes beyond just spin liquid):

1. What if the change fluctuation is very strong, and in the most extreme case, the charge sector forms a **quantum charge liquid Mott insulator**? (tomorrow)
2. What if the charge fluctuation leads to **some structure in the charge** sector? Spin sector is surely to be influenced in a non-trivial way. This would lead to a **striking experimental** consequence. If it is observed, it gives us confidence on the theoretical framework that we are developing.

Cluster Mott Insulator: a new class of Mott insulators

Electrons (or bosonic particles) are localized on some cluster units instead of the lattice sites. These cluster units build the lattice.





triangle clusters in kagome
(**J. Atwood, nature mat 2002)**

tetrahedral cluster in pyrochlore

A large class of cluster magnets (Mott insulators)

$Mg_2Mo_3O_8$, $Mn_2Mo_3O_8$, $Fe_2Mo_3O_8$, $Co_2Mo_3O_8$, $Ni_2Mo_3O_8$, $Zn_2Mo_3O_8$, $Cd_2Mo_3O_8$

$LiScMo_3O_8$, $LiYMo_3O_8$, $LiInMo_3O_8$, $LiSmMo_3O_8$, $LiGdMo_3O_8$, $LiTbMo_3O_8$, $LiDyMo_3O_8$, $LiHoMo_3O_8$, $LiErMo_3O_8$, $LiYbMo_3O_8$

NbO_2, $Mg_3Nb_6O_{11}$, $Ba_{1.14}Mo_8O_{16}$, $NaMo_4O_6$, $GaTa_4Se_8$, $GaNb_4S_8$, $GaNb_4Se_8$,
many organic materials……

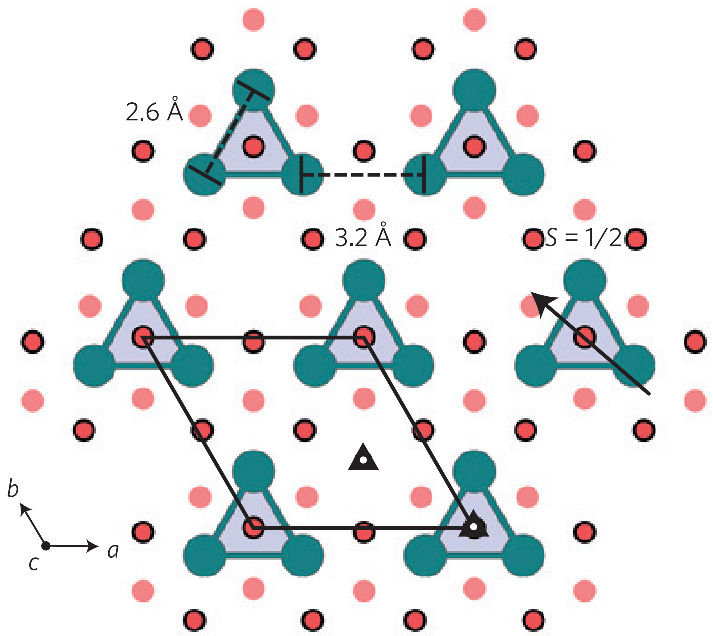
Cluster magnets can even be systematically fabricated in organic chemistry !

My Goal

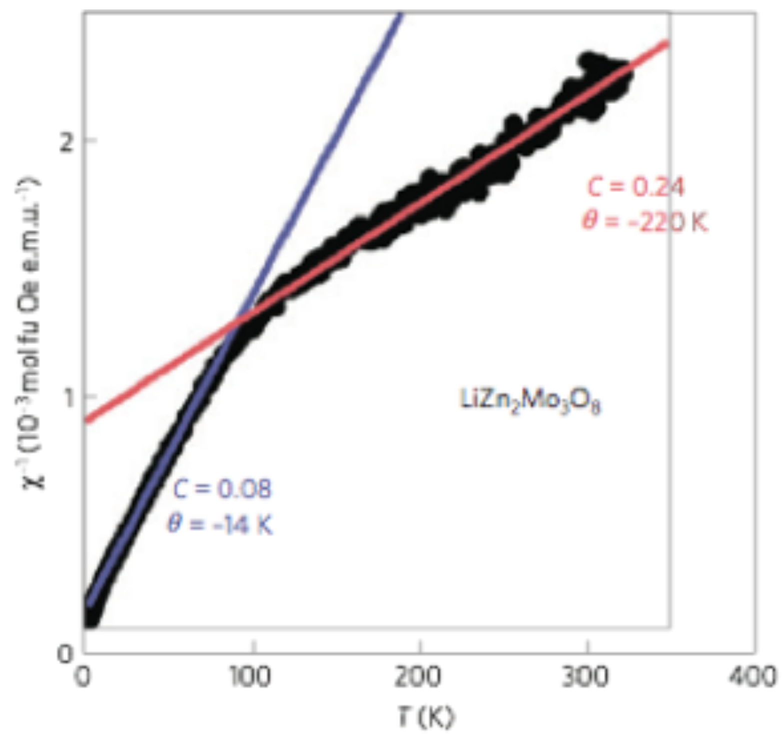
1. Introduce the notion of cluster Mott insulator (they are interesting and they exist in nature, actually quite a lot, never been studied)
2. Develop a **new theoretical framework** to understand the **universal features** of charge and spin fluctuation, and show the relation between the simple idea of cluster charge localization to something deep (**quantum dimer model and lattice gauge theory**)
3. Apply to illustrative examples and explain the puzzling experiments in $LiZn_2Mo_3O_8$.

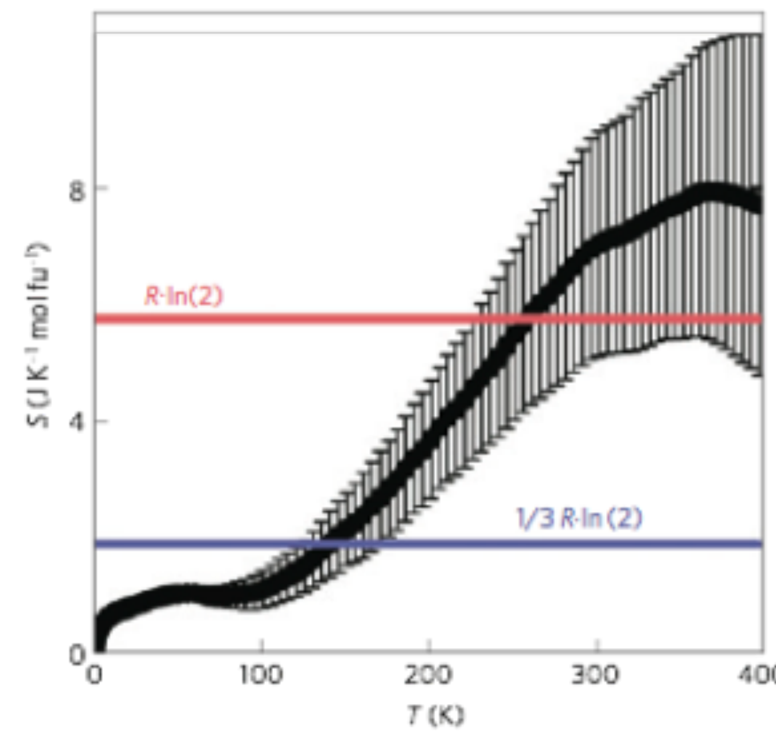
T. McQueen

One striking experiment on $LiZn_2Mo_3O_8$



Nature Material 2012





- Why striking and difficult? Neither model works.
  1. Triangular lattice Heisenberg model
  2. Triangular lattice Hubbard model at 1/2 filling

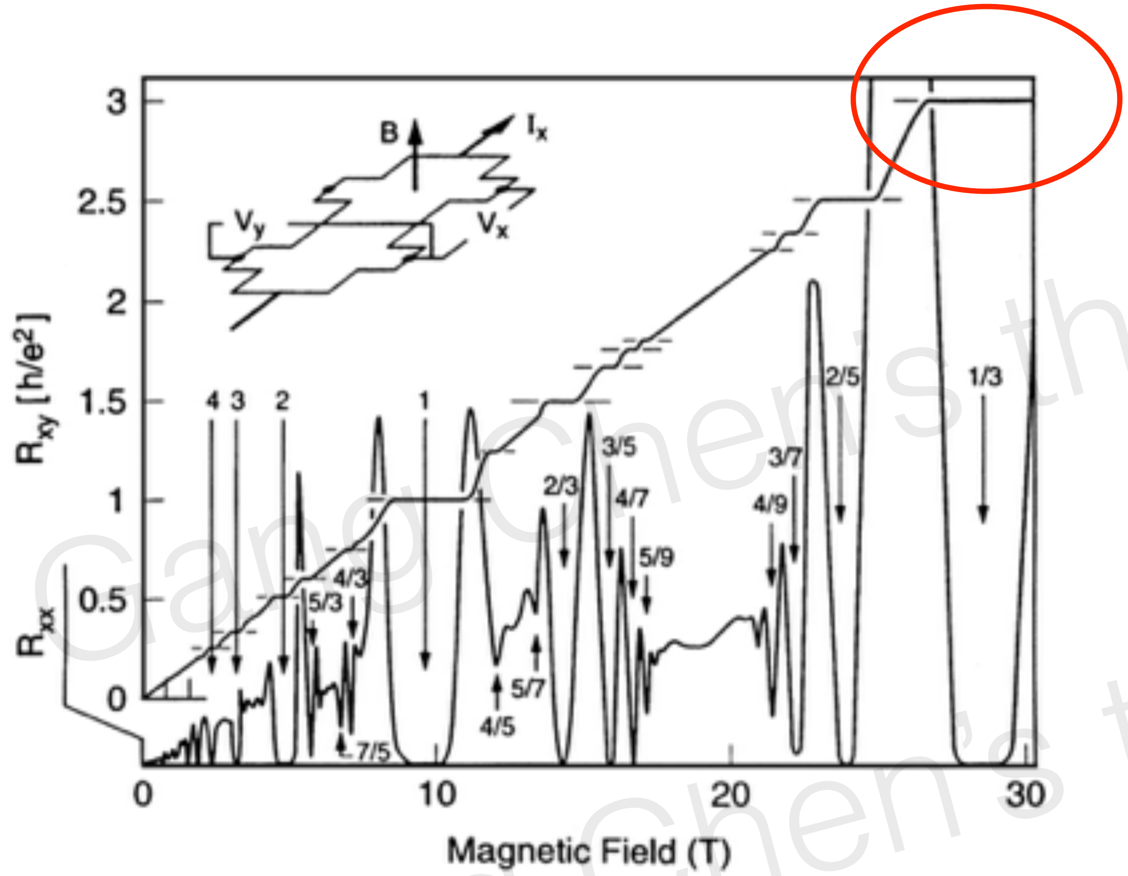
- Further low-temperature experiments: NMR, muSR, neutron scattering, proposed as a spin liquid candidate.

FQHE (Tsui, Stormer, and Gossard)

1st exotic phase known to us

Tsui

Laughlin



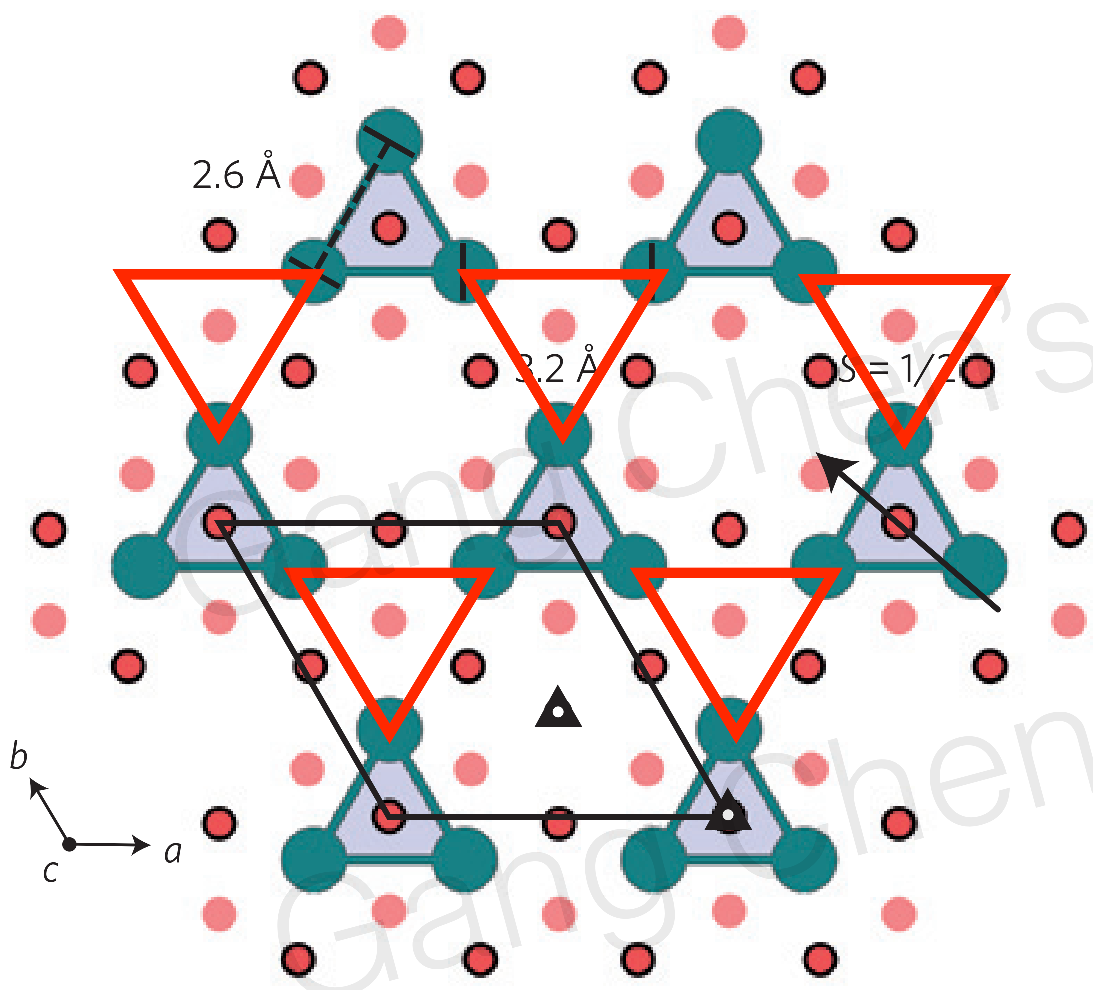
Xiao-Gang Wen: all the electrons in the Laughlin state are dancing collectively.

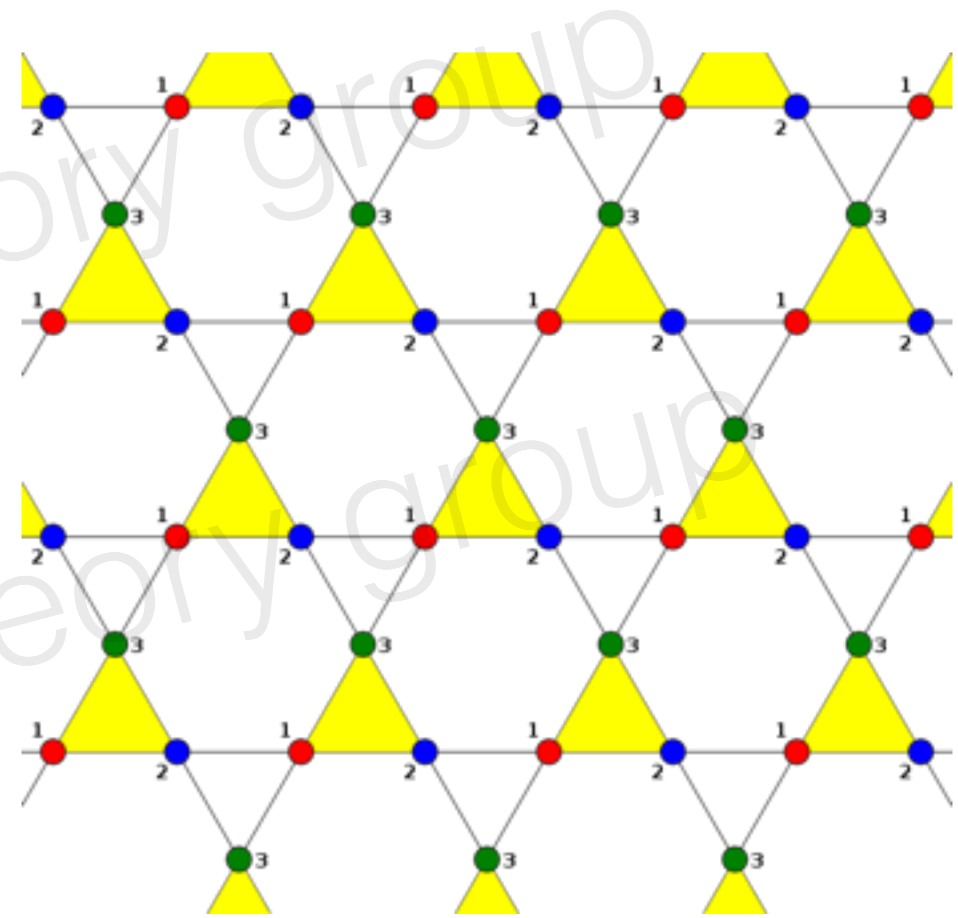
What do electrons do in $LiZn_2Mo_3O_8$?
Any collective behaviours?

What to do next?

1. Explain the “fractional spin susceptibility” at finite temperature;
2. Explain the low-temperature (or ground state) properties, and introduce the theoretical framework.

$LiZn_2Mo_3O_8$ structure



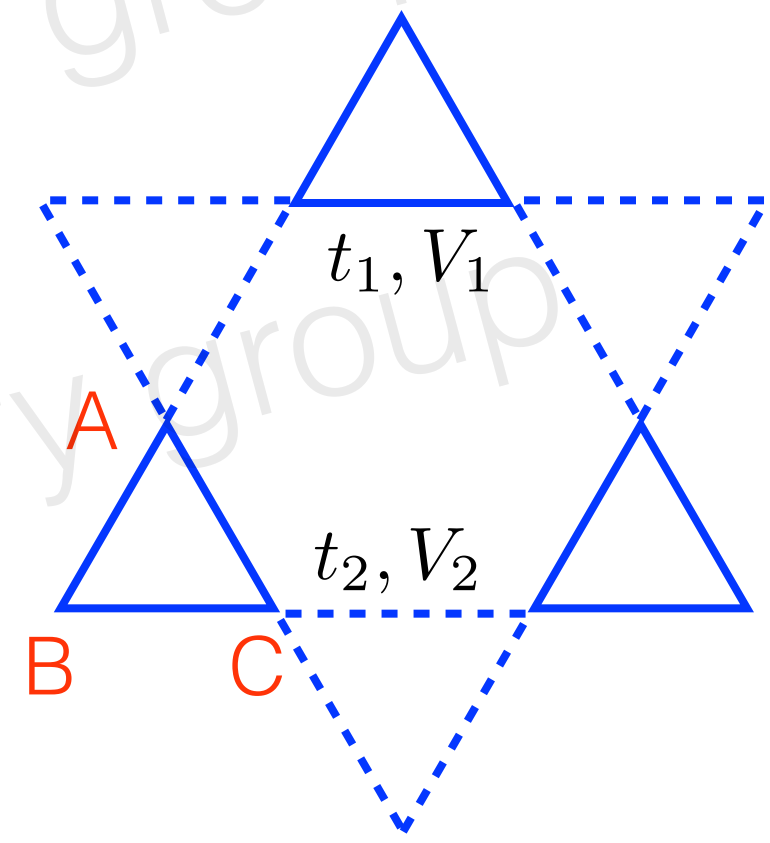


Model

Claim: a single-band extended Hubbard model on an anisotropic Kagome lattice with **1/6 electron filling.**

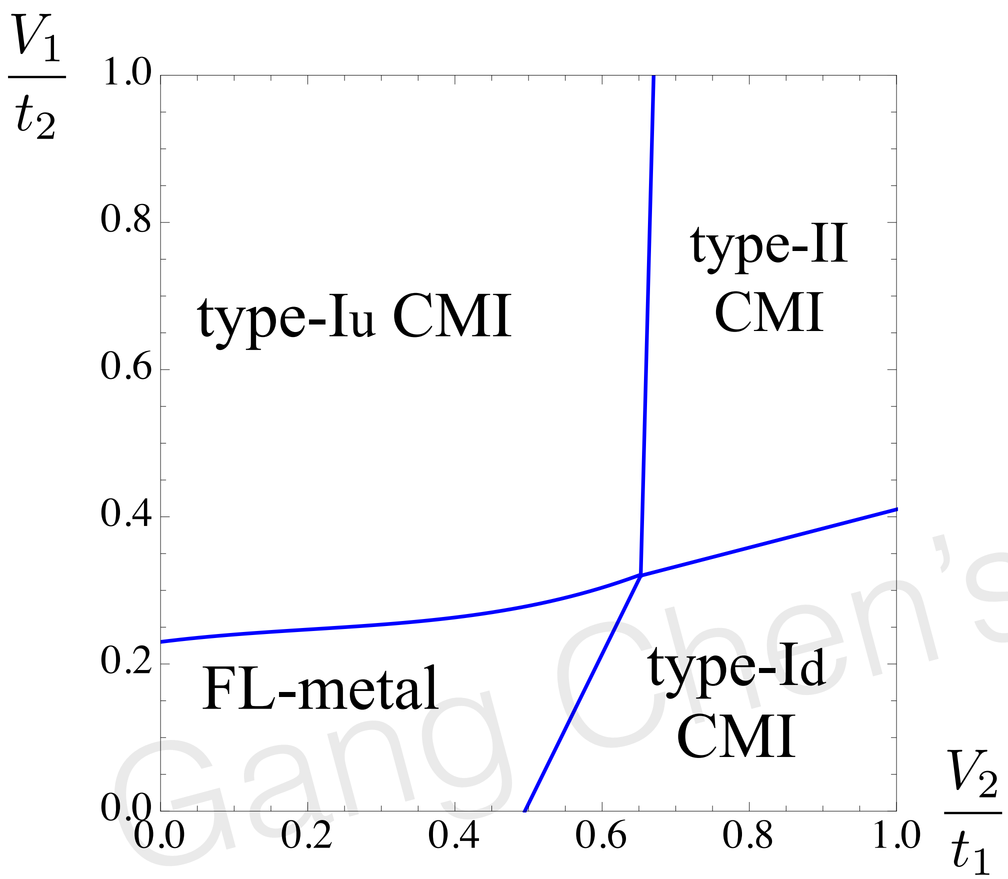
- Minimal model allowed by symmetry [require quantum chemistry understanding]

$$H = \sum_{\langle ij \rangle \in \mathrm{u}} [-t_1(c^\dagger_{i\sigma} c_{j\sigma} + h.c.) + V_1 n_i n_j] + \sum_{\langle ij \rangle \in \mathrm{d}} [-t_2(c^\dagger_{i\sigma} c_{j\sigma} + h.c.) + V_2 n_i n_j] + \sum_i \frac{U}{2}(n_i - \frac{1}{2})^2,$$



* Large U alone **cannot** localize the electron.
* V_1 and V_2 are needed: because it is 4d orbital, and also to localize the electron in the clusters.

Generic phase diagram



spin sector is spin liquid

Here **t1/t2** = 4, no qualitative difference for different **t1/t2**

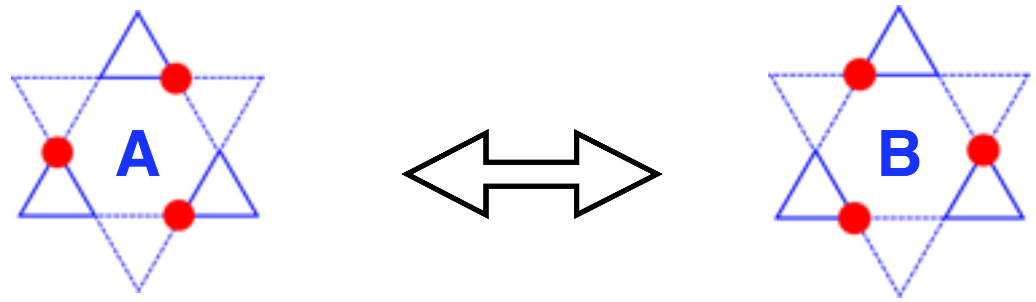
V2 is small, V1 is large

snapshots of electron occupation in type-I CMI

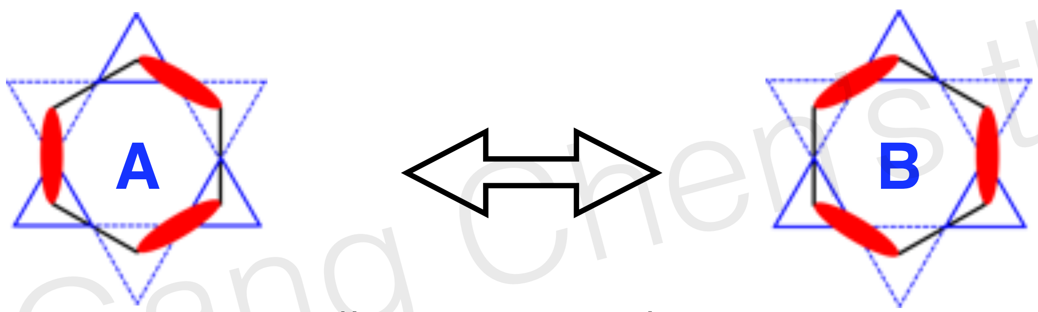
- A "simple" understanding:

* Electrons are localized in **one** type of triangles in type-I CMI;
* Electrons are localized in **both** types of triangles in type-II CMI.

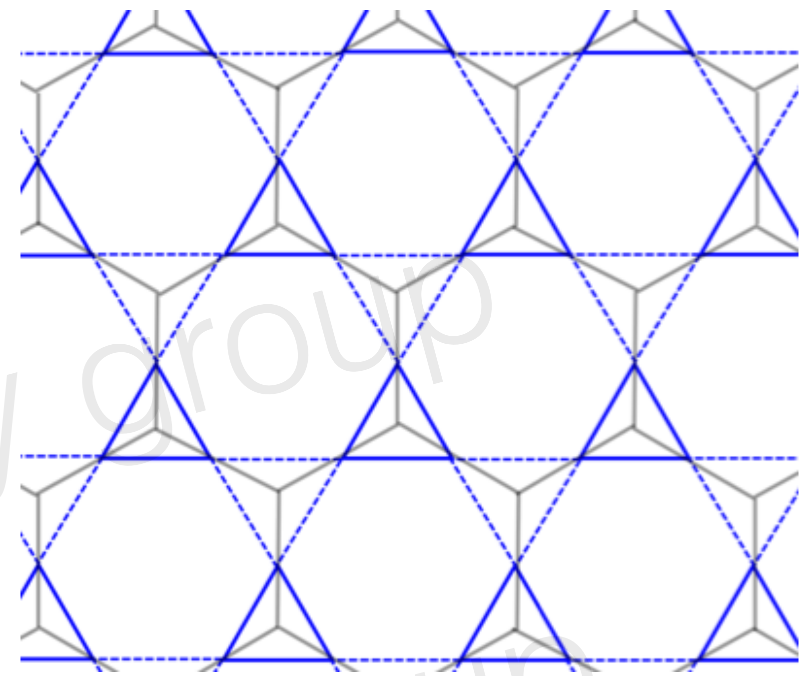
Sub-Mott-gap process: correlated electron motion



3rd order process in type-II CMI

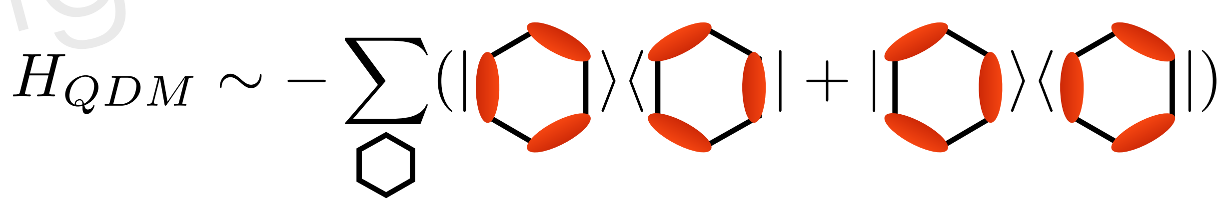


dimer resonating



Dual honeycomb lattice and Kagome lattice

This collective tunnelling process **preserves the center of mass** of 3 electrons !



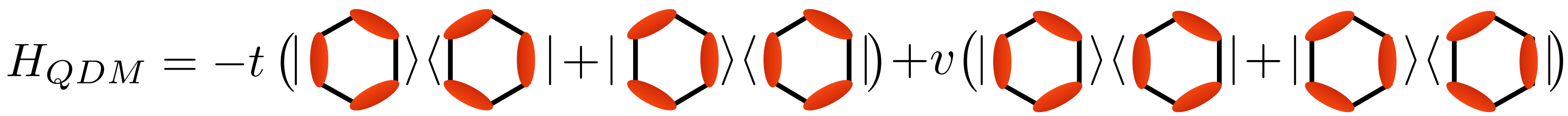
Type-II CMI: plaquette charge order via QDM

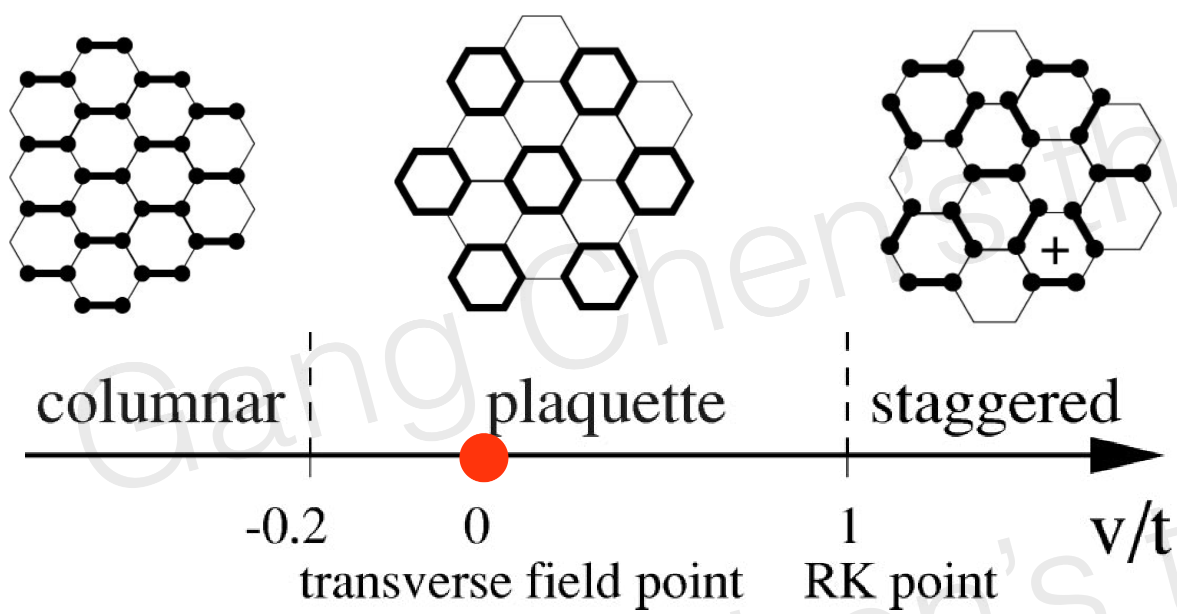
R. Moessner

S. Sondhi

P. Chandra

- A model study in 2001





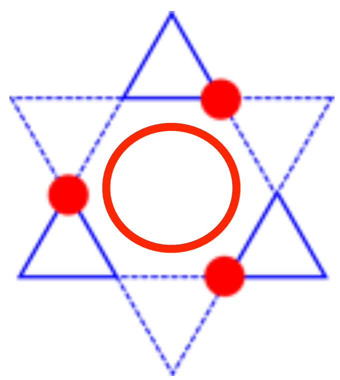
- **plaquette charge order**

- Remarks:

  * The plaquette charge order is a **local charge "RVB"**.
    (This is not Anderson's spin singlet RVB).
  * One may simply view each resonating hexagon as a benzene molecule.
  * It is a collective behaviour of 3 electrons.
  * It is a **quantum** effect.

- High energy d.o.f. (charge) usually influences low energy d.o.f. (spin). More practically, low d.o.f serves as a probe of the physical properties of the high energy d.o.f..

- Spin state reconstruction

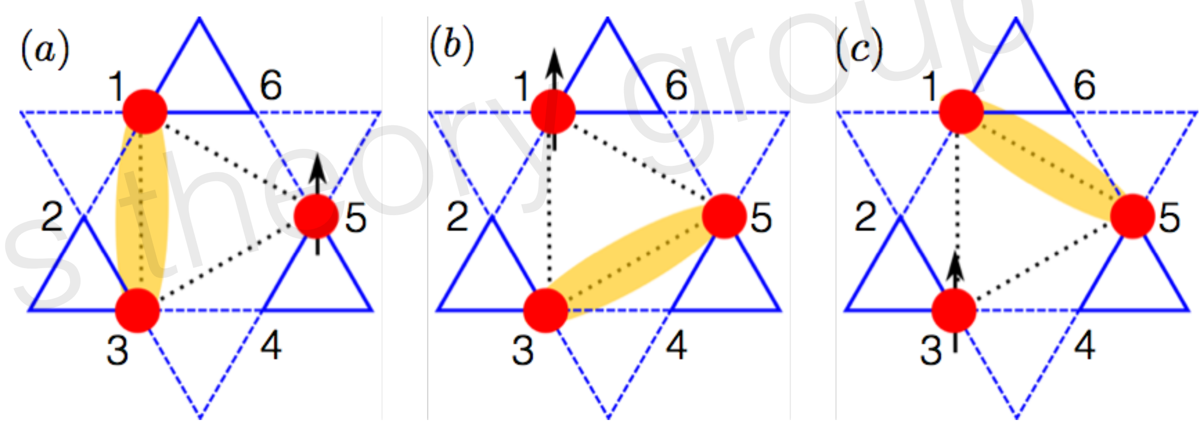


$$\frac{1}{2}\otimes\frac{1}{2}\otimes\frac{1}{2}=\frac{1}{2}\oplus\frac{1}{2}\oplus\cancel{\frac{3}{2}}$$

K. Kugel

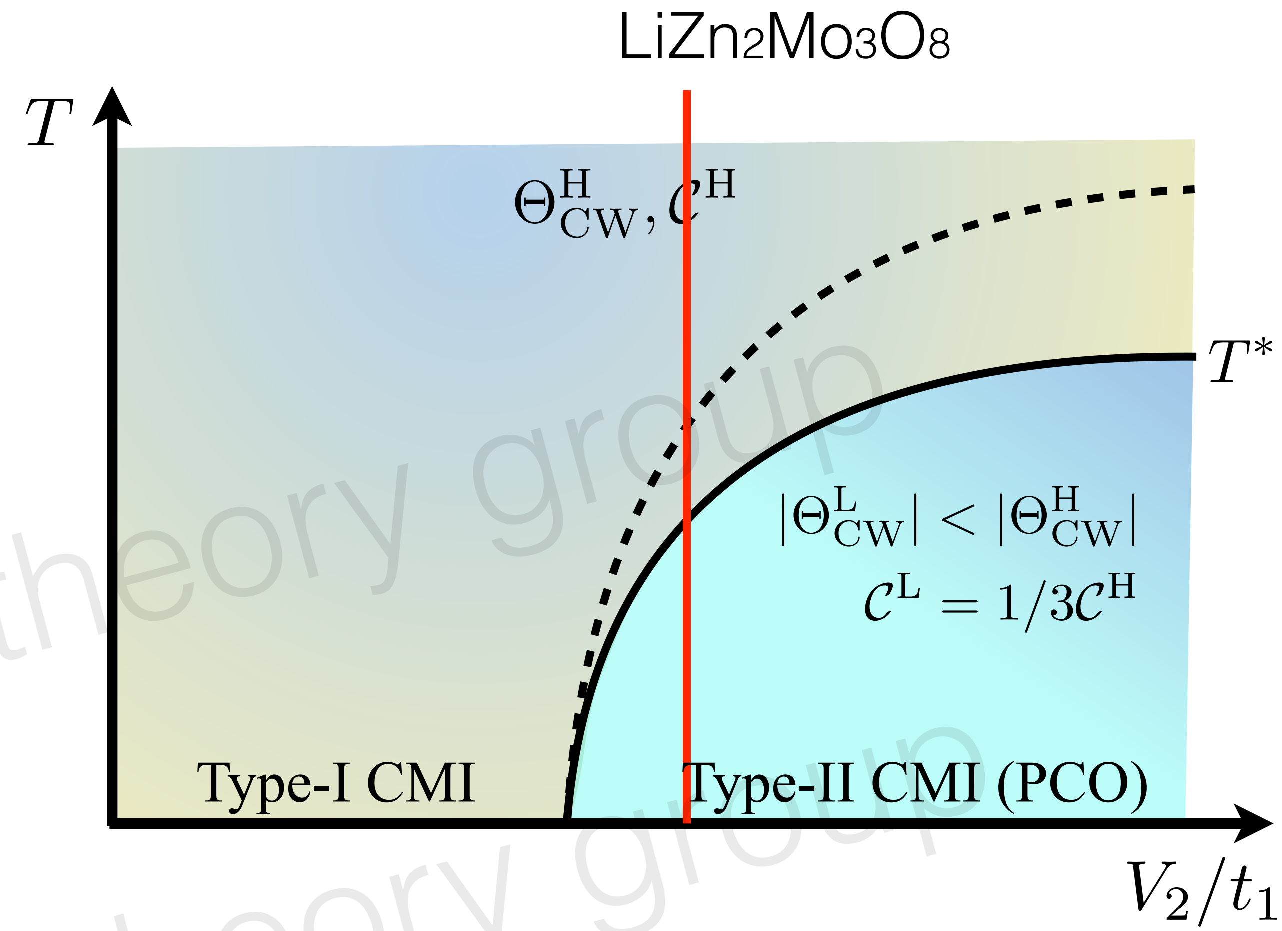
D. Khomskii

The total spin S_{tot} =1/2;
Pseudospin $\mathcal{T}$ = 1/2, nonmagnetic

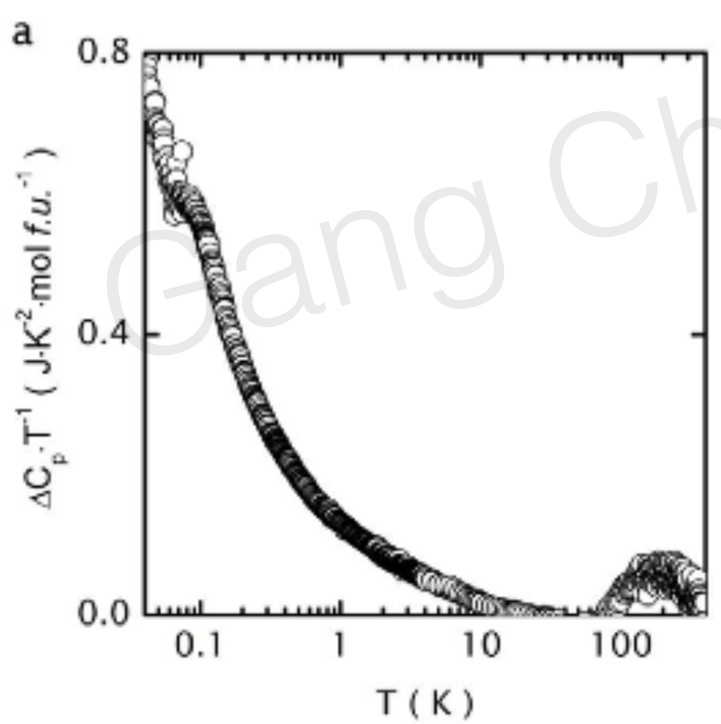


An effective Kugel-Khomskii model on the **emergent triangular lattice**

Explanation for fractional spin susceptibility at finite temperatures



type-II CMI (PCO)



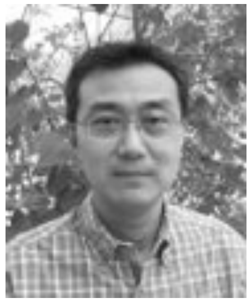
1. Expect 1st order finite temperature transition, peak at ~100K, (was interpreted as Li freezing.) smeared out 1st transition?
2. High resolution X-ray, RIXS
3. Nuclear quadrupolar resonance: electric field gradient (suggested to me by Baskaran)

What to do next?

1. Explain the “fractional spin susceptibility” at finite temperature;
2. Explain the low-temperature (or ground state) properties, and introduce the theoretical framework.

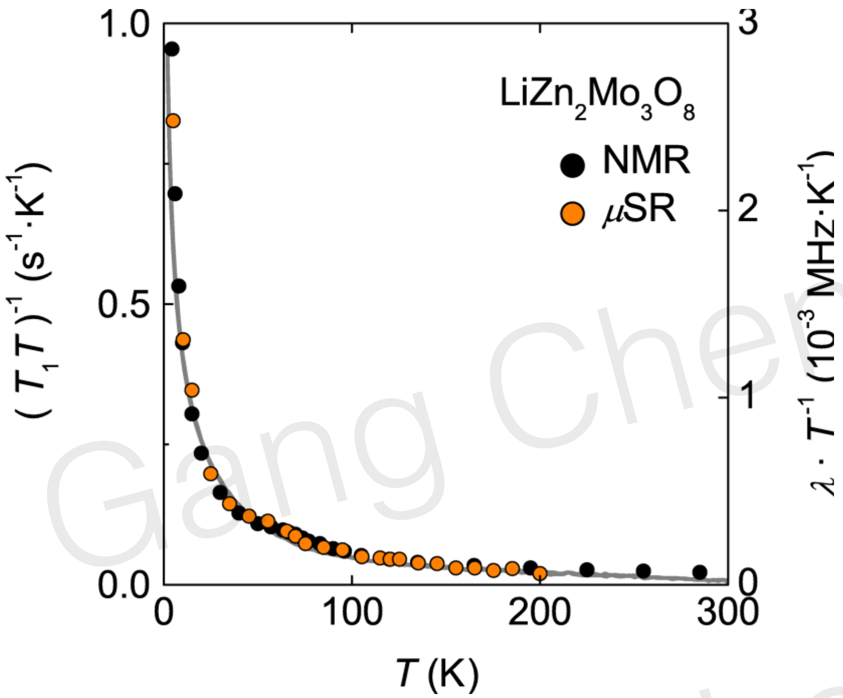
Low-temperature experiments

T. Mcqueen

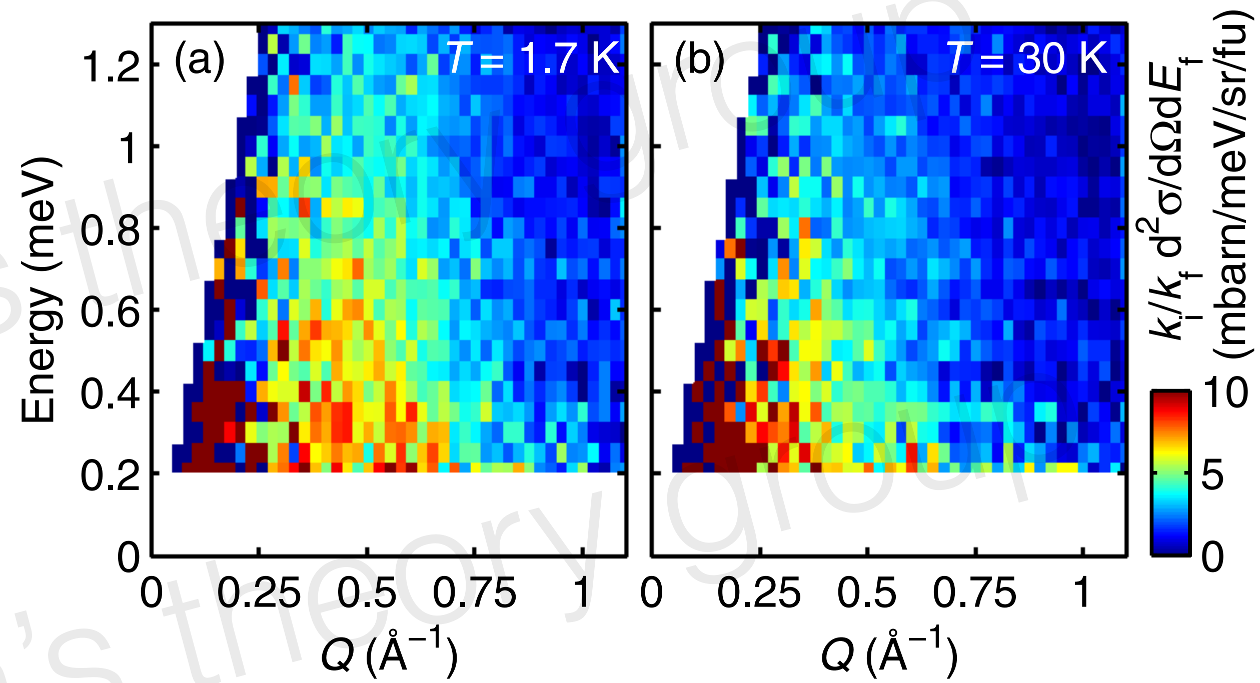


T. Imai

C. Broholm



NMR + muSR



Inelastic neutron scattering

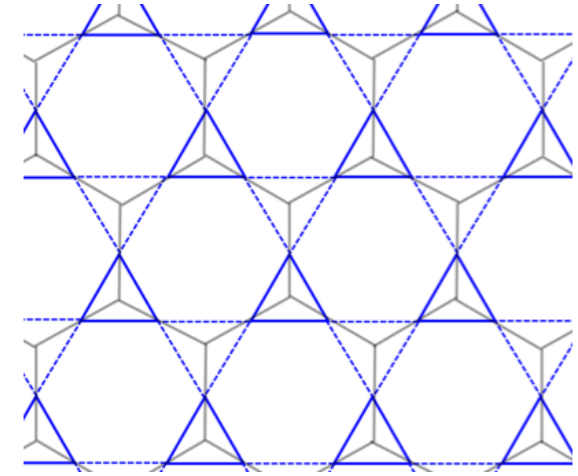
- No magnetic order is detected.
- The behaviour is compatible with a **gapless** spin liquid state.

E Fradkin

S Kivelson

S. Sondhi

R. Moessner



- **Quantum Dimer Model = Lattice Gauge Theory**;
  bipartite: compact U(1) gauge theory,
  non-bipartite: Z_2 gauge theory.

$$H_{QDM} \sim -\sum_{\hexagon}\big(|\hexagon\rangle\langle\hexagon| + |\hexagon\rangle\langle\hexagon|\big)$$

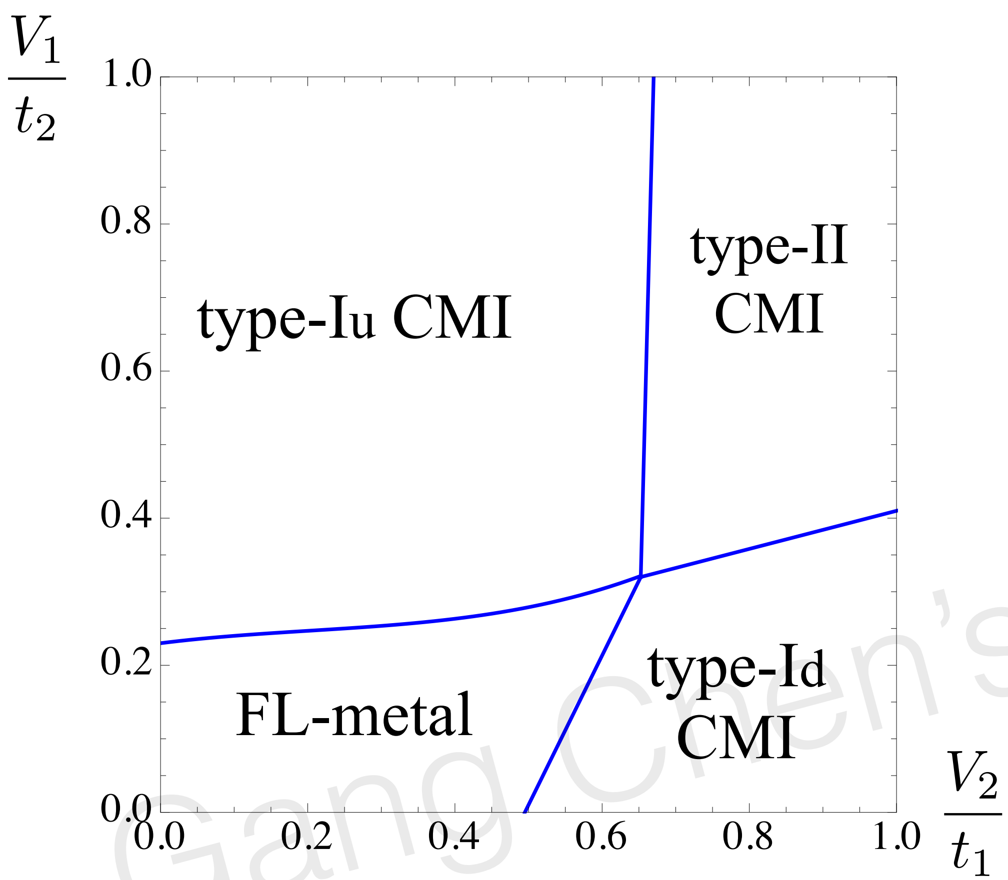
A. Polyakov

- Charge sector is described by a compact U(1) gauge theory on the dual honeycomb lattice. Having one electron in each triangle is like a Gauss' law constraint.

- The PCO in type-II CMI can be understood as the confining phase of compact U(1) gauge theory in 2D.

- This implies 3D CMI supports **change fractionalization** !

type-I CMI as a Higgs' phase



Phase number conjugation $[\phi_{\mathbf{r}}, n_{\mathbf{r}'}] = i\delta_{\mathbf{r}\mathbf{r}'}$

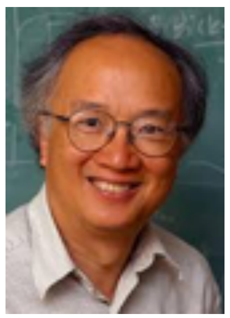
- In type-I CMI, one charge boson is condensed, and the internal U(1)c gauge field in the charge sector is Higgsed, but the U(1)sp gauge field remains deconfined.

- Only in type-I CMI, the triangular cluster can be viewed as a supersite of the triangular lattice, and the system is **smoothly connected** to triangular Hubbard model at 1/2 filling.

S Florens

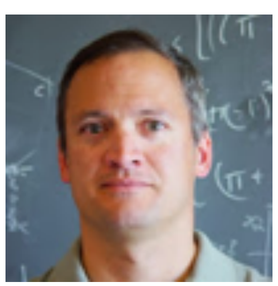
A Georges

Sung-Sik Lee



P Lee

E Fradkin



L Balents

Framework: a new parton construction

- The slave rotor construction is used to describe the **conventional Mott insulator,** e.g. triangular lattice Hubbard model at 1/2 filling

$$c_{i\sigma} = e^{-i\theta_i} f_{i\sigma}$$

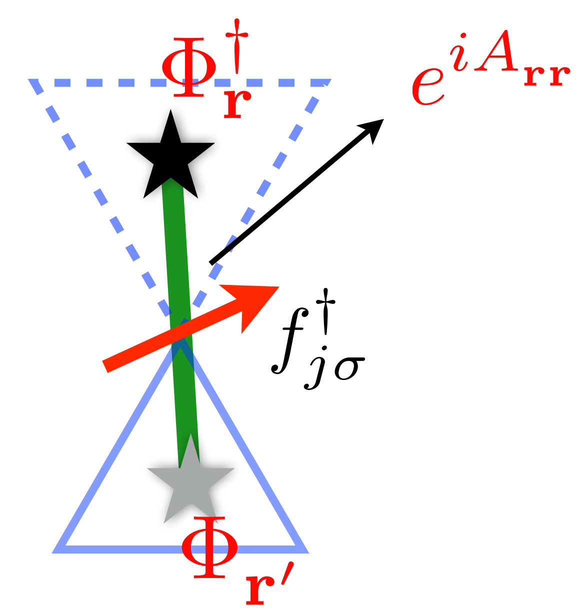
one U(1) gauge field

charge-q_e spinless boson

charge-neutral spin-1/2 fermion

- A new parton gauge construction is required for cluster Mott insulators to **capture additional U(1) gauge structure** in the charge sector

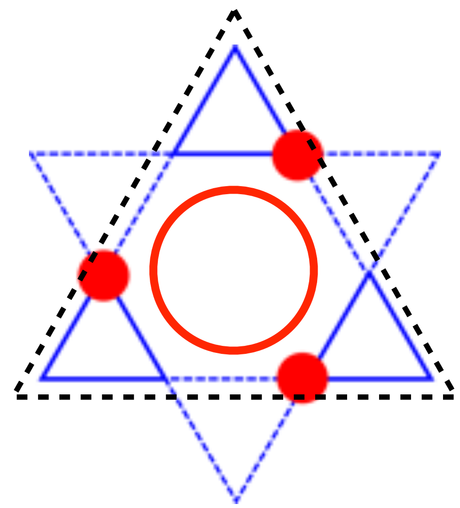
$$\boxed{c^\dagger_{j\sigma} \sim f^\dagger_{j\sigma} \Phi^\dagger_{\mathbf{r}} \Phi_{\mathbf{r}'} e^{iA_{\mathbf{rr}'}}}$$



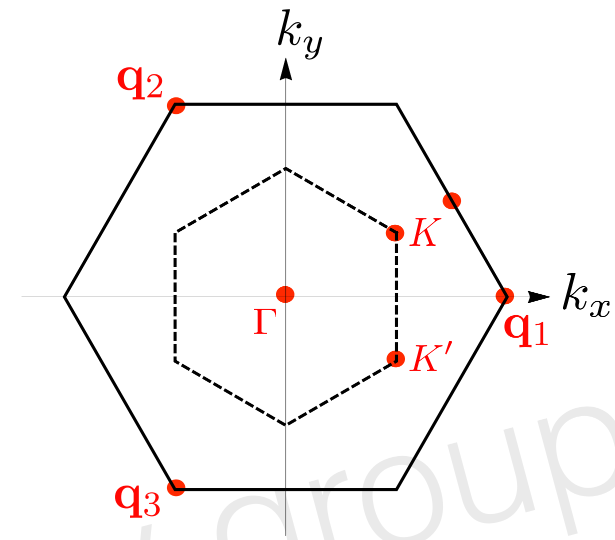
two U(1) gauge fields: $U(1)_c \times U(1)_{sp}$

Hastings' theorem: spin liquid of type-II CMI

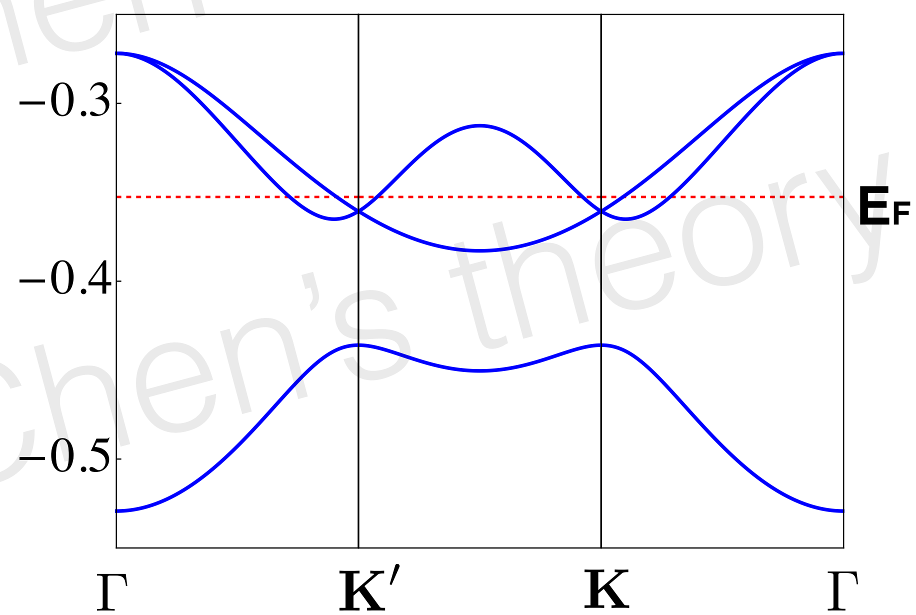
M. Hastings



tripled unit cell,
host 3 electrons

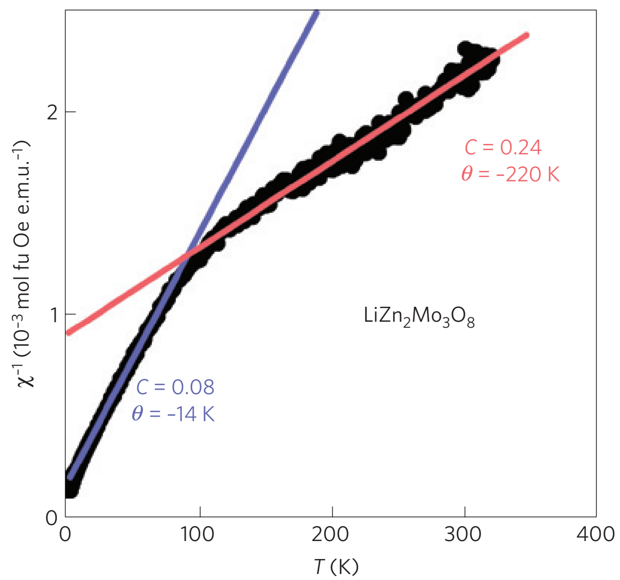


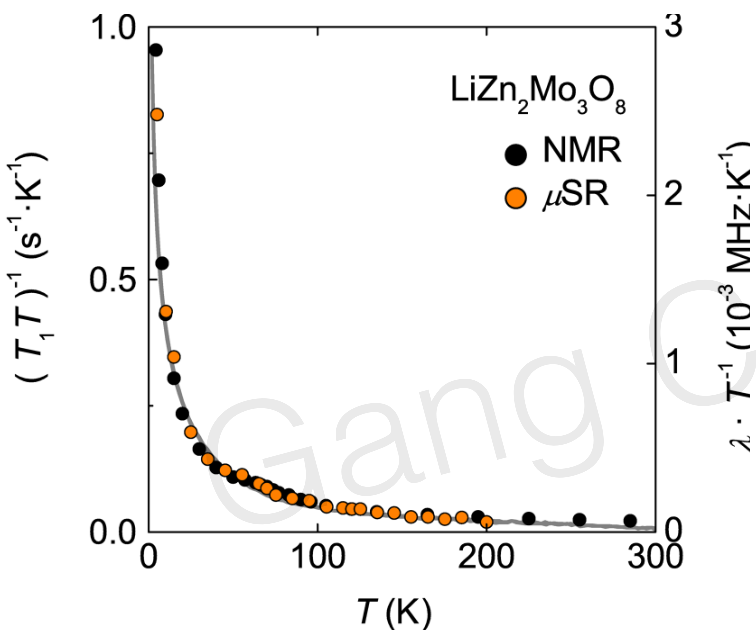
Brillouin zone of
type-I & type-II CMIs

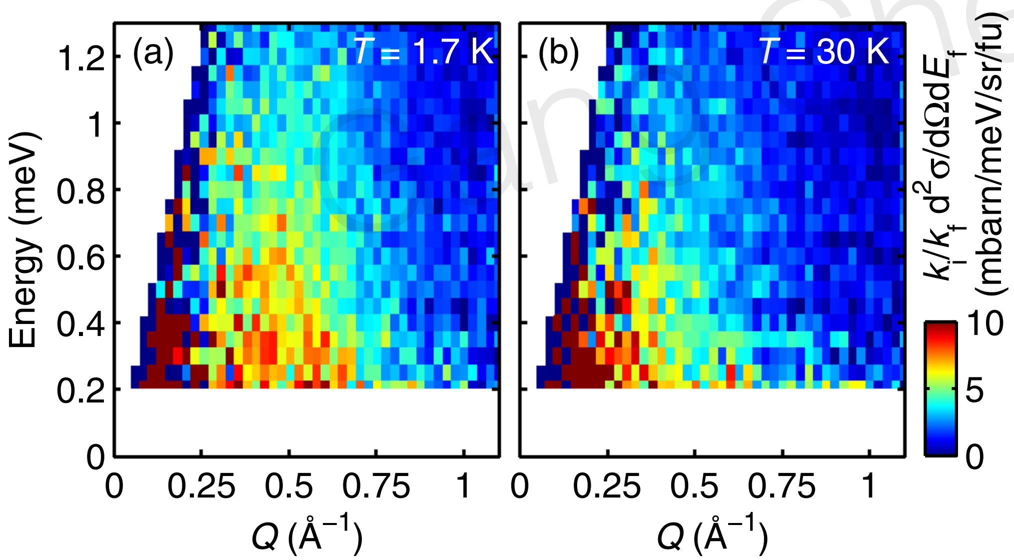


PCO splits the spinon band, creates a direct band gap, and narrows the effective bandwidth.

Implication to susceptibility from bandwidth and filling







Prediction: low-T QSL

- U(1) QSL with spinon Fermi surfaces
  * strongly coupled field theory, still under active research

$$C_v \sim T^{2/3}, \quad \chi \sim \text{const}$$

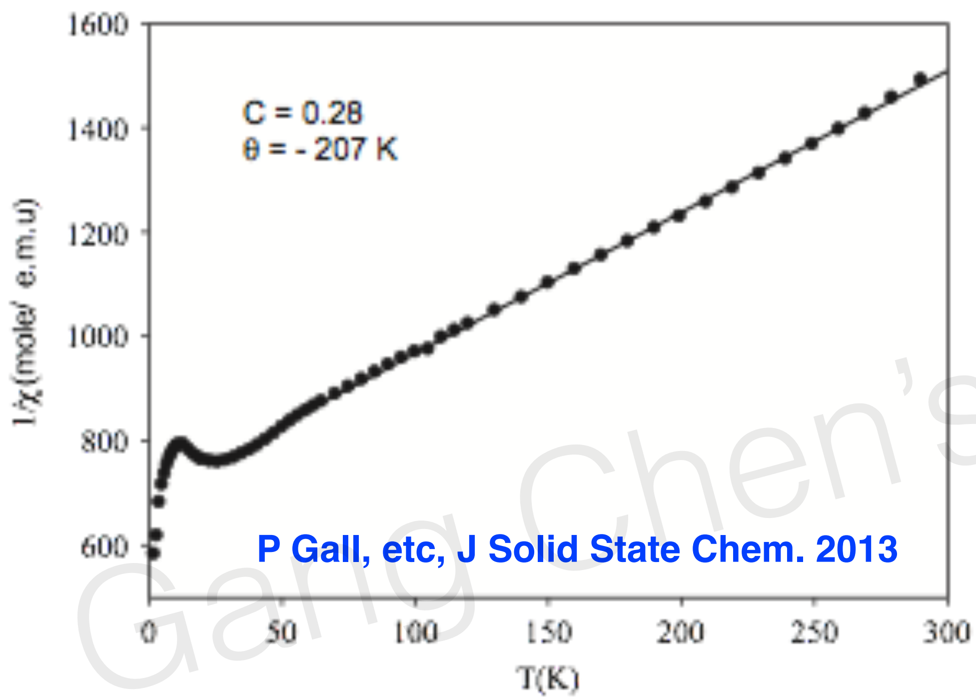
at very low temperature (<1K), but may be hard to observe.

- Large density of low-energy spin excitations
  because of the reduced bandwidth

$$1/(T_1 T) \propto D(E_F)^2$$

- It would be nice to compare the prediction from the spinon band structure in future work. Single crystal data and better resolution are preferred.

Where is type-I CMI?

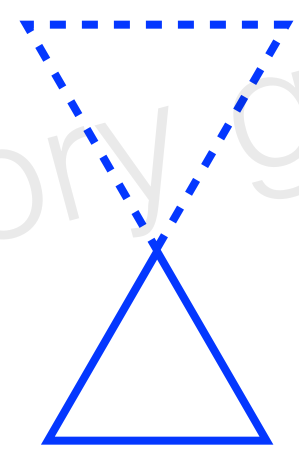


no susceptibility anomaly !
Li2InMo3O8 as a type-I CMI ?
quantum spin liquid ?

type-I CMI is a triangular lattice spin liquid

	$[\text{Mo-Mo}]_u$	$[\text{Mo-Mo}]_d$	λ	e^-/Mo_3
$LiZn_2Mo_3O_8$	2.6Å	3.2Å	1.23	7
$Li_2InMo_3O_8$	2.54Å	3.25Å	1.28	7
$ScZnMo_3O_8$	2.58Å	3.28Å	1.27	7

a simple phenomenological parameter



$$\lambda = \frac{[\text{Mo-Mo}]_d}{[\text{Mo-Mo}]_u}$$

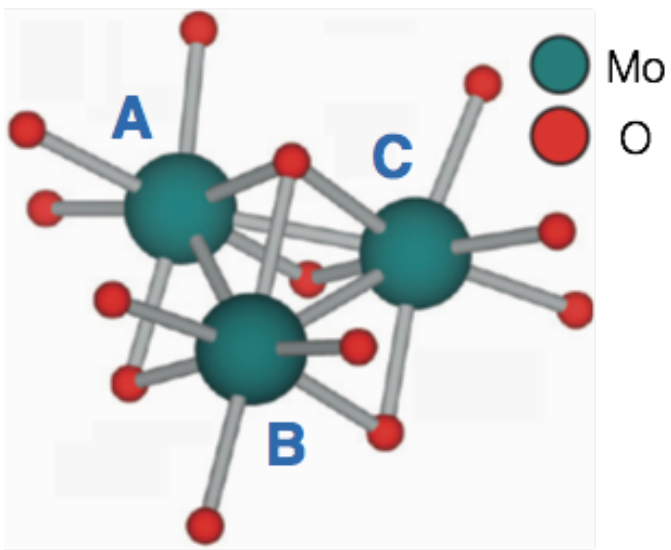
Question / observation **(this goes beyond just spin liquid):**

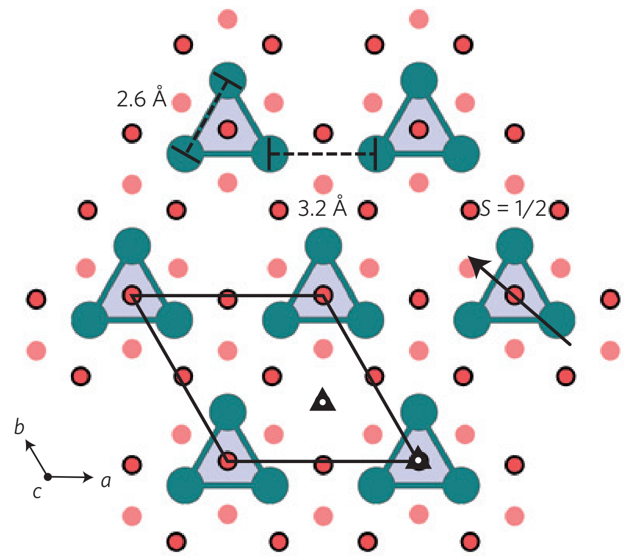
1. What if the change fluctuation is very strong, and in the most extreme case, the charge sector forms a **quantum charge liquid Mott insulator**? (tomorrow)
2. What if the charge fluctuation leads to **some structure in the charge** sector? Spin sector is surely to be influenced in a non-trivial way. This would lead to a **striking experimental** consequence. If it is observed, it gives us confidence on the theoretical framework that we are developing.

Summary

- I provide specific examples to illustrate some of the physics in cluster Mott insulators.
- There is a very interesting interplay between the charge and spin degrees of freedom in both 2D and 3D cluster Mott insulators, maybe also with **disorders** in the future!
- Cluster Mott insulators are new physical systems that may host various emergent and exotic physics.

Quantum chemistry: molecular orbitals and bands



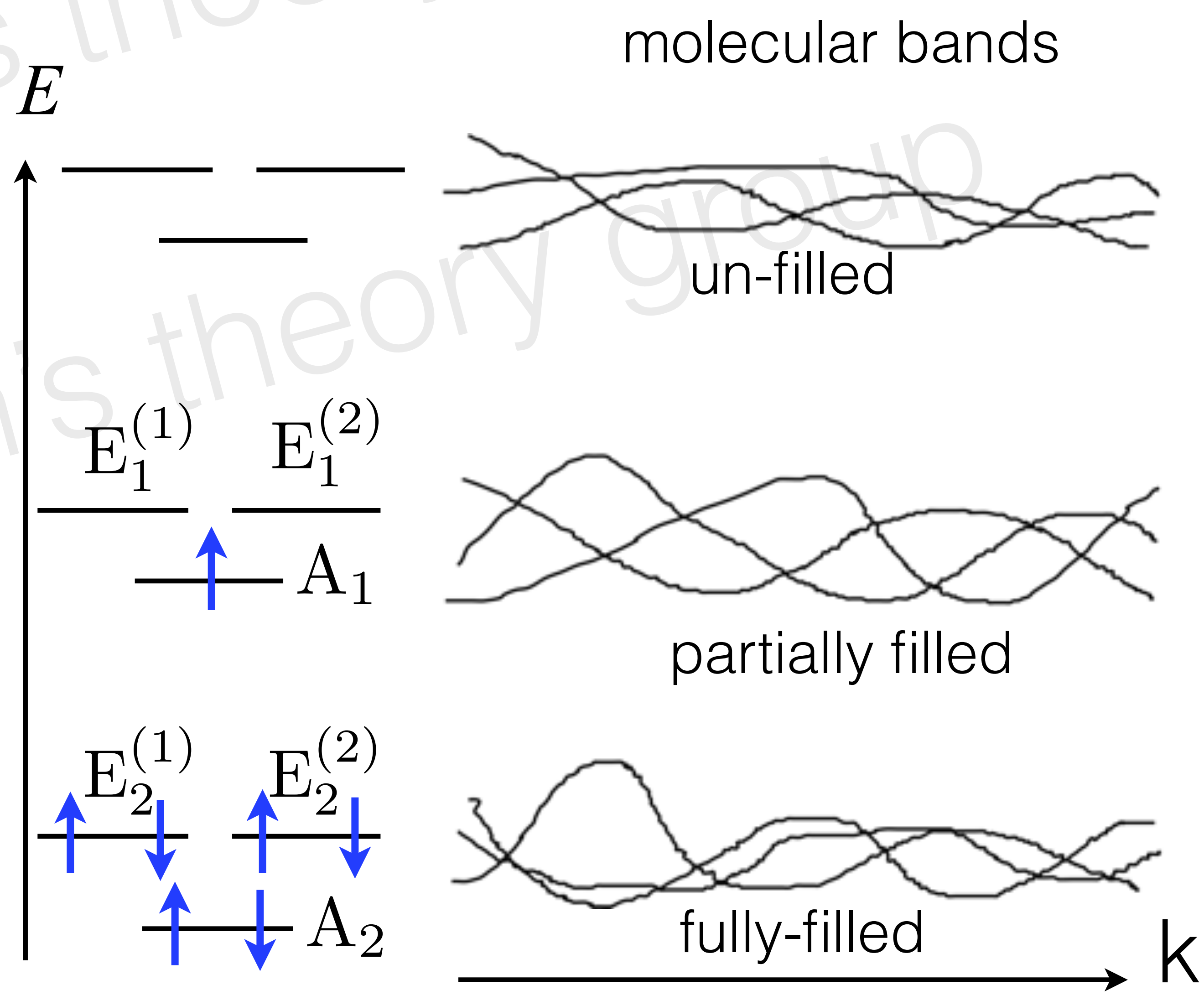


Triangular lattice of Mo_3O_{13} clusters

$$|A_1\rangle = \frac{1}{\sqrt{3}}\left[|\psi_1\rangle_A + |\psi_1\rangle_B + |\psi_1\rangle_C\right],$$

$$|E_1^{(1)}\rangle = \frac{1}{\sqrt{3}}\left[|\psi_1\rangle_A + e^{i\frac{2\pi}{3}}|\psi_1\rangle_B + e^{-i\frac{2\pi}{3}}|\psi_1\rangle_C\right]$$

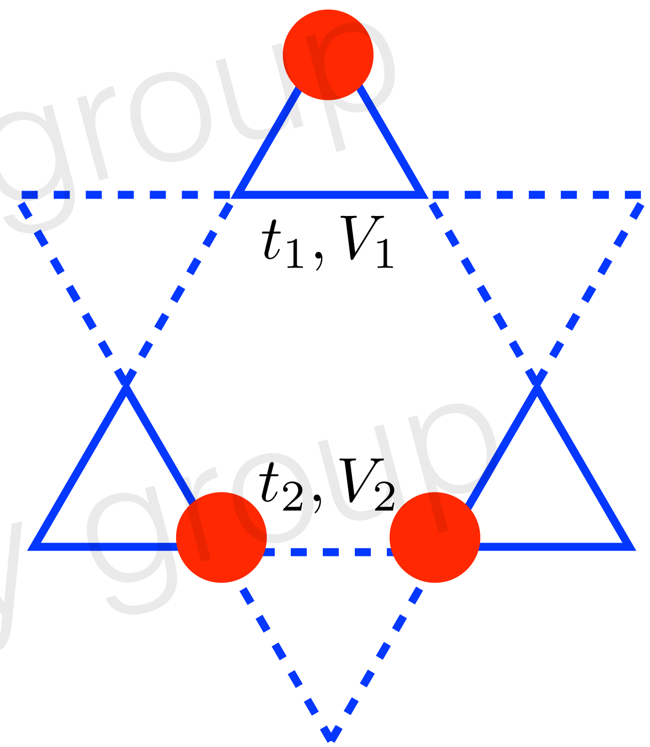
$$|E_1^{(2)}\rangle = \frac{1}{\sqrt{3}}\left[|\psi_1\rangle_A + e^{-i\frac{2\pi}{3}}|\psi_1\rangle_B + e^{i\frac{2\pi}{3}}|\psi_1\rangle_C\right]$$



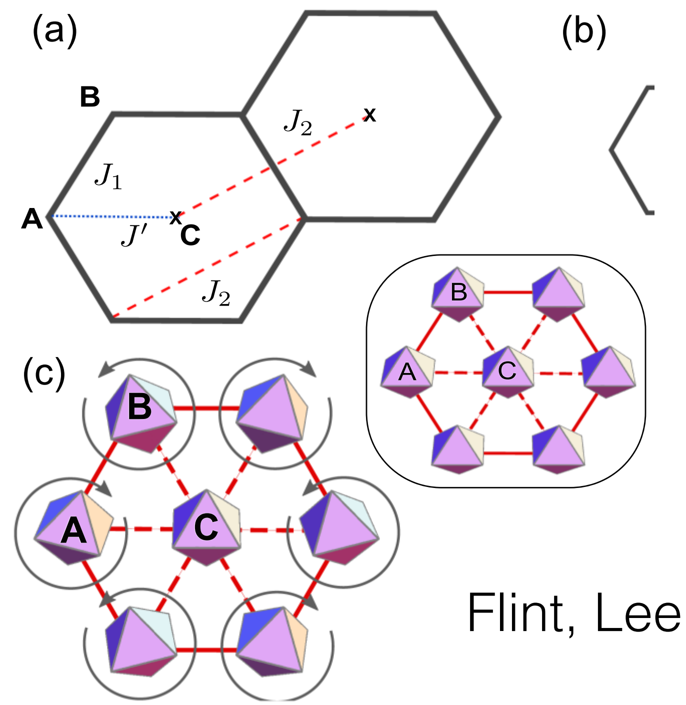
Instead of a multi-molecular-band model on a triangular lattice, we go back to the atomic state on each Mo site and build an extended Hubbard model from there.

Minimal model allowed by symmetry

$$
\begin{aligned}
H = & \sum_{\langle ij \rangle \in \mathrm{u}} [-t_1 (c^\dagger_{i\sigma} c_{j\sigma} + h.c.) + V_1 n_i n_j] \\
& + \sum_{\langle ij \rangle \in \mathrm{d}} [-t_2 (c^\dagger_{i\sigma} c_{j\sigma} + h.c.) + V_2 n_i n_j] \\
& + \sum_i \frac{U}{2} (n_i - \frac{1}{2})^2,
\end{aligned}
$$



Physical meaning of electron operator,
Large U alone cannot localize the electron.
V_1 and V_2 are needed: because it is 4d orbital,
and also to localize the electron in the clusters.



Flint, Lee 2013

1. It requires lattice degrees of freedom to work in a *special* way to generate the honeycomb lattice.

2. It may also need a large spin gap, not seem to be supported by J1-J2 honeycomb lattice model because both the “orphan” spins and honeycomb spins contribute to the spin susceptibility.

$$\chi \sim \frac{\#_1}{T - \Theta_{CW}^L} + \#_2 e^{-\frac{\Delta}{T}}$$

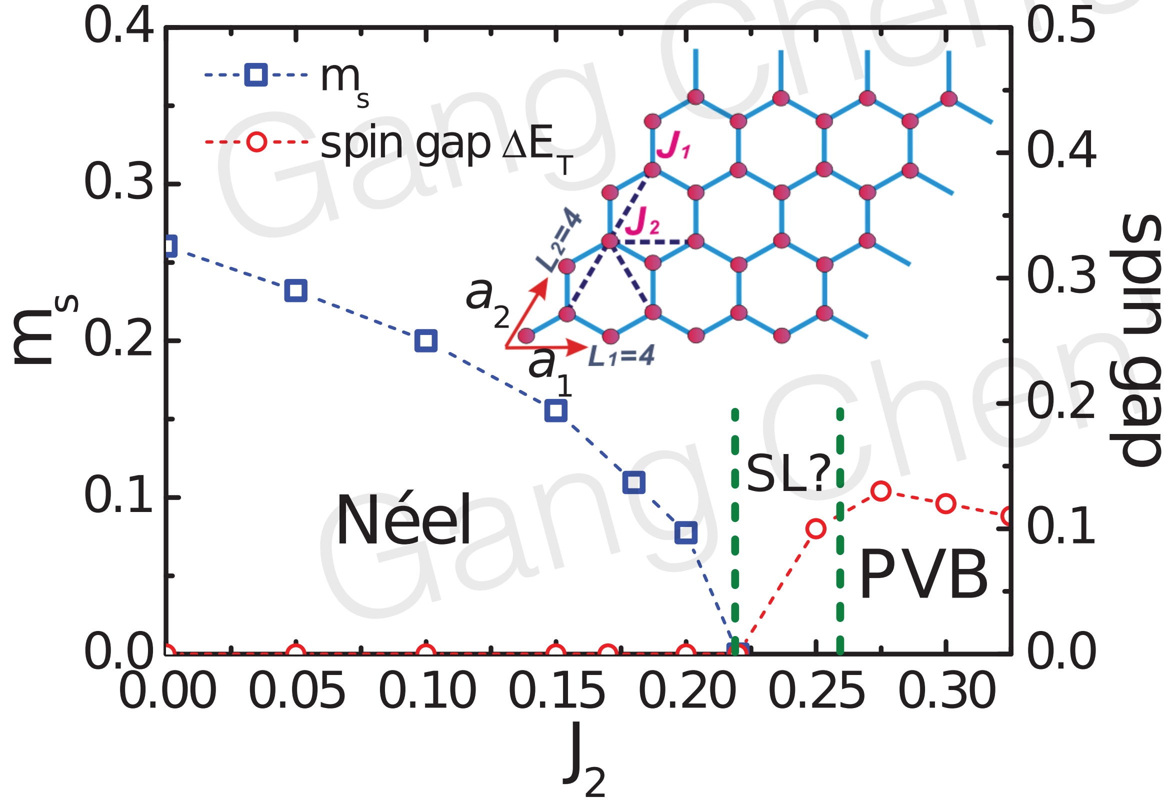
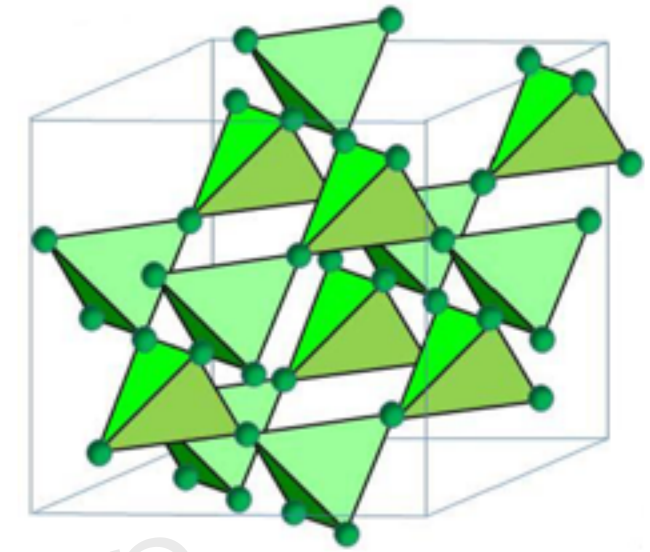


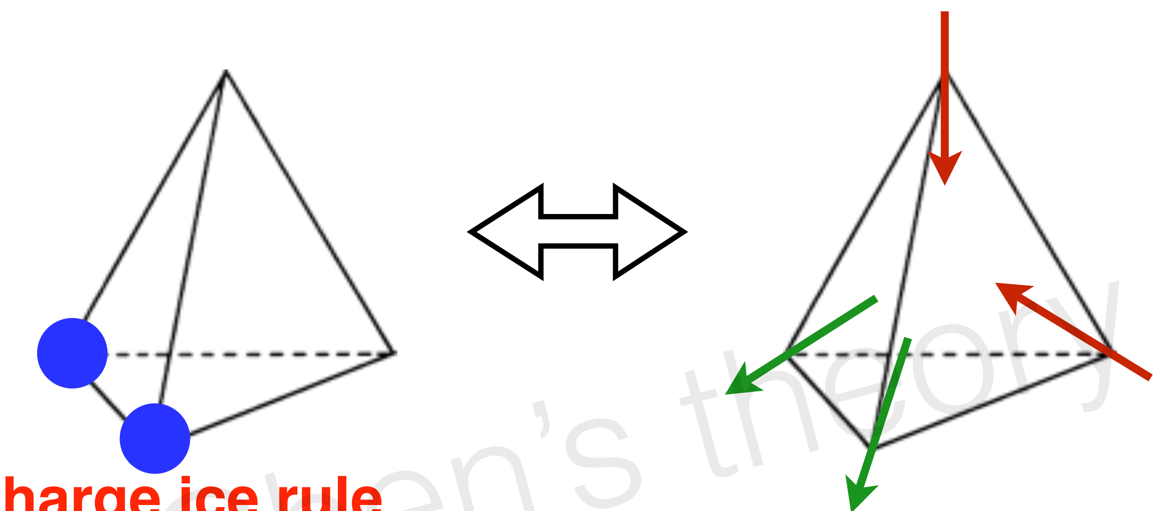
FIG. 1. (Color online) Phase diagram of the spin-$\frac{1}{2}$ J_1-J_2 honeycomb Heisenberg model for $J_2 \leqslant 0.35$ obtained by our SU(2) DMRG studies. With increasing J_2, the model has a Néel phase for $J_2 \lesssim 0.22$ and a PVB phase for $0.25 \lesssim J_2 \lesssim 0.35$. Between these two phases, there is a small region that exhibits no order in our calculations. The main panel shows Néel order parameter m_s and spin gap ΔE_T. The inset is the sketch of the J_1-J_2 honeycomb lattice on a $N = 2 \times L_1 \times L_2$ torus (here with four unit cells, $L_1 = L_2 = 4$, along the two primitive vector directions).

D. Sheng, L. Motrunich, M. Fisher 2012

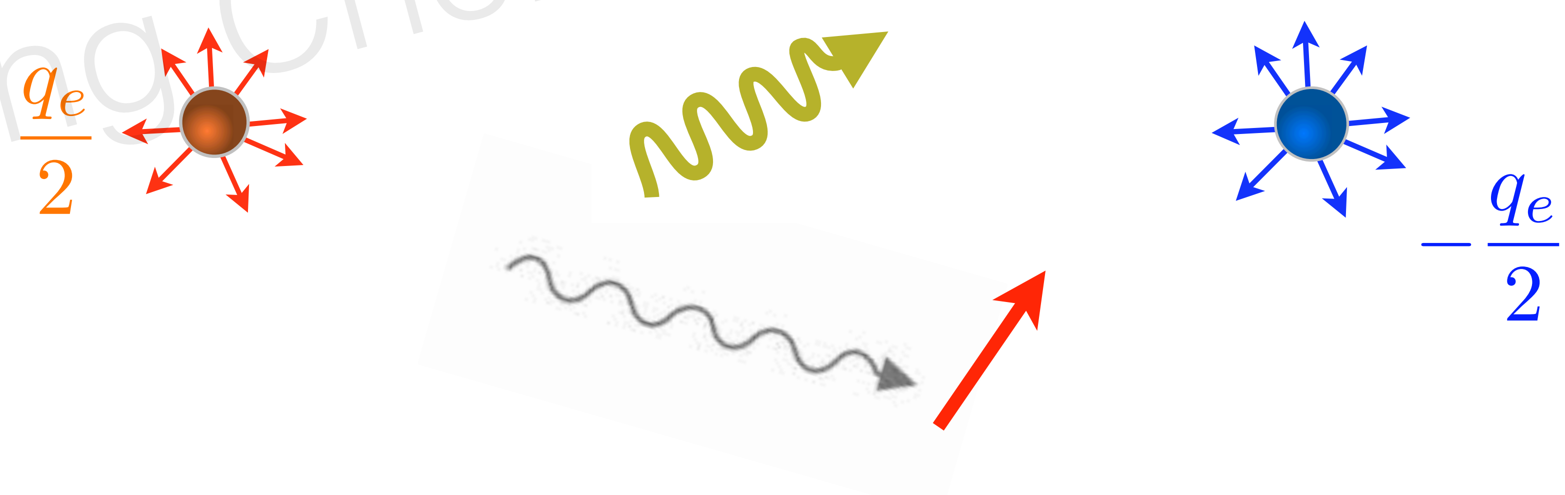
3D CMI as **quantum charge ice**



$$H = -t\sum_{\langle ij\rangle,\sigma}(c^{\dagger}_{i\sigma}c_{j\sigma} + h.c.) - \mu\sum_i n_i + V\sum_{\langle ij\rangle} n_i n_j + \frac{U}{2}\sum_i (n_i - \frac{1}{2})^2$$



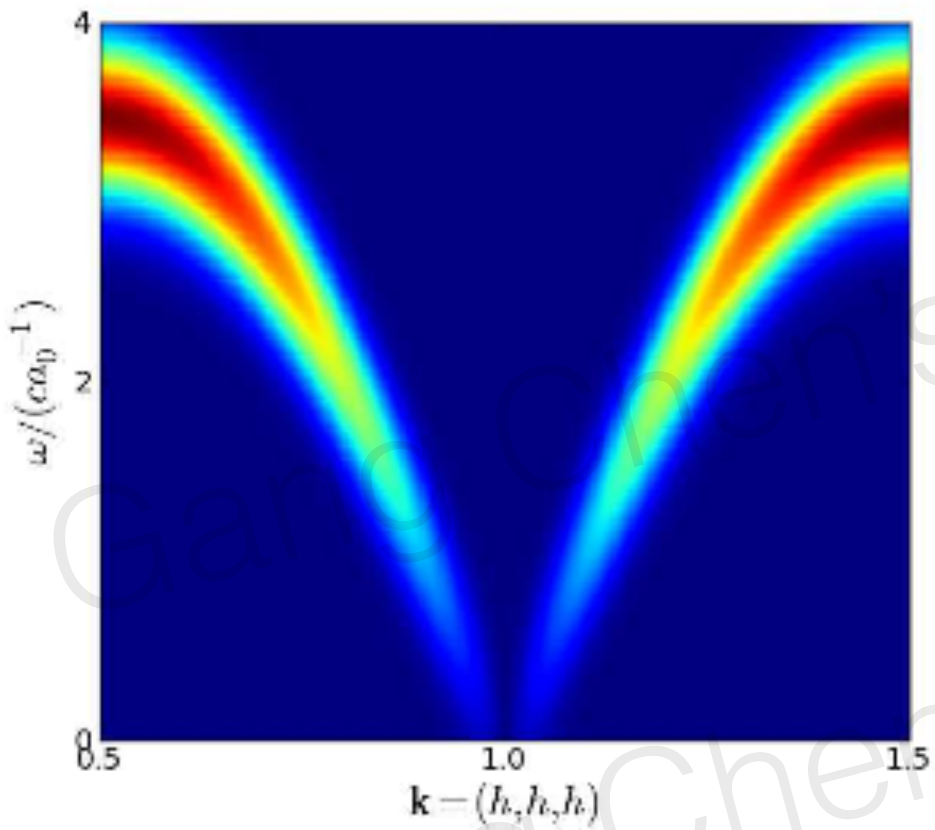
- Low-energy physics of the charge is described by an **emergent (compact) quantum electrodynamics** in 3+1D. Charge excitation carries **1/2 the electron charge** !



- (Inelastic) X-ray scattering measures U(1) gauge field correlation in the charge sector

$$\mathrm{Im}[E^{\alpha}_{-\mathbf{k},-\omega} E^{\beta}_{\mathbf{k},\omega}] \propto [\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{\mathbf{k}^2}]\, \omega\, \delta(\omega - v|\mathbf{k}|),$$

$$\mathbf{E}_{\mathbf{r}+\frac{1}{2}\mathbf{e}_\mu} \equiv L^z_{\mathbf{r},\mathbf{r}+\mathbf{e}_\mu} \frac{\mathbf{e}_\mu}{|\mathbf{e}_\mu|} = (n_{\mathbf{r}+\frac{1}{2}\mathbf{e}_\mu} - \tfrac{1}{2}) \frac{\mathbf{e}_\mu}{|\mathbf{e}_\mu|}$$



$$I(\omega) \sim \omega$$

emergent light in quantum charge ice !

$$\langle E^{\alpha}_{-\mathbf{k}} E^{\beta}_{\mathbf{k}} \rangle \propto \delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{\mathbf{k}^2}$$

Pinch points in equal-time charge structure factor at T > ring hopping. “classical charge ice”

Hermele etc 2004
N Shannon etc 2012,
L Savary etc 2012