# Quantum spin liquids and unconventional superconductivity in honeycomb materials

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A. Ralko, and JM, PRL 124, 217203 (2020); M. F. López, and JM, PRB (2020); JM, M. F. López, and B. J. Powell, PRB (2021).



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#### Outline

- Motivation: unconventional superconductivity in strongly correlated 2D materials.
- Novel chiral quantum spin liquids in honeycomb Kitaev magnets.
- Unconventional superconductivity in decorated honeycomb materials.
- Conclusions and outlook.

# Superconductivity in strongly correlated 2D materials



#### insulator

- Superconductivity arises in proximity to the Mott insulator: what is the mechanism?
- What is the connection (if any) between quantum spin liquids and superconductivity?
- Role of flat bands, Dirac points,...on electronic properties and superconductivity.

# Anderson's RVB theory of cuprate superconductivity

Ground state of the Heisenberg model on a triangular lattice is an RVB state (1973):



**RVB Mott insulator** 

# Anderson's RVB theory of cuprate superconductivity

Ground state of the Heisenberg model on a triangular lattice is an RVB state (1973):



Under hole doping, the ground state of the t-J model is a high-Tc superconductor (1987):

TT /4

\

$$H_{t-J} = PTP + J \sum_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad P = \prod_i (1 - n_i \uparrow n_i \downarrow)$$
oped holes
$$P |\Phi\rangle = P \left[ \sum_{\vec{r}, \vec{r}'} \varphi(\vec{r} - \vec{r}') c^{\dagger}_{\vec{r}} c^{\dagger}_{\vec{r}'} \downarrow \right]^{N/2} |0\rangle$$
High To currend uptor

High-Tc superconductor

# Key ingredients for quantum spin liquids

- Small spins, s=1/2 favor quantum fluctuations.
- Geometrical frustration:



• Strong spin-orbit coupling:



Broholm, et. al., Science (2020). Savary and Balents, Rep. Prog. Phys. (2017).

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#### Quantum spin liquids in honeycomb materials

• Can novel chiral quantum spin liquids arise in Kitaev magnets?



#### Quantum spin liquids in honeycomb materials

• Can novel chiral quantum spin liquids arise in Kitaev magnets?

- Is there a quantum spin liquid in the Heisenberg model on the decorated honeycomb lattice?
- Can superconductivity arise by doping the half-filled decorated honeycomb lattice?





#### Novel chiral quantum spin liquids in Kitaev magnets

A. Ralko, and JM, PRL **124**, 217203 (2020).

#### Quantum spin liquid in $\alpha$ -RuCl<sub>3</sub>



Y. Kasahara, et. al., Nature 559, (2018)

# Kitaev spin model $H_{K} = \sum_{\langle ij \rangle} K_{\gamma} \sigma_{i}^{\gamma} \sigma_{j}^{\gamma} = \sum_{\langle ij \rangle} K_{x} \sigma_{i}^{x} \sigma_{j}^{x} + K_{y} \sigma_{i}^{y} \sigma_{j}^{y} + K_{z} \sigma_{i}^{z} \sigma_{j}^{z}$



A. Y. Kitaev, Ann. Phys. (2006).

#### Exact solution to the Kitaev model

Spins are represented through four Majorana fermions:



 $b^x, b^y, b^z =$  bond Majorana fermion c = matter Majorana fermion

$$\sigma^{x} = ib^{x}c$$
  

$$\sigma^{y} = ib^{y}c$$
  

$$\sigma^{z} = ib^{z}c$$

$$H_{K} = \frac{i}{4} \sum_{\langle ij \rangle} \hat{A}_{ij} c_{i} c_{j} = \frac{i}{4} \sum_{\langle ij \rangle} 2K_{\gamma} \hat{u}_{ij}^{\gamma} c_{i} c_{j}$$
$$\hat{u}_{ij}^{\gamma} = i b_{i}^{\gamma} b_{j}^{\gamma}, \ \hat{u}_{ji}^{\gamma} = -\hat{u}_{ij}^{\gamma}, \ \hat{A}_{ij} = -\hat{A}_{ji}$$
$$\left[\hat{u}_{ij}^{\gamma}, H_{K}\right] = 0, \ u_{ij} = \pm 1 \quad \text{Fix } \mathbb{Z}_{2} \text{ gauge fields quadratic H!}$$



• Quantum spin liquid with gapless Majorana excitations and two Dirac cones.

# Effect of a weak magnetic field

Applying a weak magnetic field to the Kitaev model:

$$V = -\sum_{j} (h_x \sigma_j^x + h_y \sigma_j^y + h_z \sigma_j^z)$$

Leads up to third order in the field:

$$H_{\rm eff}^{(3)} \sim -\frac{h_x h_y h_z}{{\rm K}^2} \sum_{j,k,l} \sigma_j^x \sigma_k^y \sigma_l^z, \label{eq:eff}$$



Majorana fermions on honeycomb lattice with n. n. n. chiral amplitudes:



- Gapped chiral quantum spin liquid with non-zero Chern number,  $\nu = \pm 1$ .
- Topological Majorana edge state gives rise to a half-quantized thermal conductivity.



#### Beyond the Kitaev model

- No exact solution to Kitaev model + moderate/strong magnetic fields, Heisenberg terms and/or the Dzyaloshinskii-Moriya contribution.
- We consider the general model:

$$H = H_{K} + H_{B} + H_{DM}$$
$$H_{B} = -\sum_{i} \mathbf{B} \cdot \mathbf{S}_{i}$$
$$H_{DM} = \sum_{\langle\langle ij \rangle\rangle} \mathbf{D}_{ij} \cdot \mathbf{S}_{i} \times \mathbf{S}_{j}$$

A. Ralko, and J. Merino, PRL (2020).

#### Majorana mean-field theory

• We introduce a HF mean-field decoupling of the Majoranas:

$$(\sigma_{i}^{\gamma}\sigma_{j}^{\gamma})_{HF} \approx \left\langle \frac{i}{2}b_{i}^{\gamma}c_{i}\right\rangle \frac{i}{2}b_{j}^{\gamma}c_{j} + \left\langle \frac{i}{2}b_{j}^{\gamma}c_{j}\right\rangle \frac{i}{2}b_{i}^{\gamma}c_{i} - \left\langle \frac{i}{2}b_{i}^{\gamma}c_{i}\right\rangle \left\langle \frac{i}{2}b_{j}^{\gamma}c_{j}\right\rangle \frac{i}{2}b_{j}^{\gamma}c_{j} \right\rangle \frac{Magnetic}{channel} \\ - \left\langle \frac{i}{2}b_{i}^{\gamma}b_{j}^{\gamma}\right\rangle \frac{i}{2}c_{i}c_{j} - \left\langle \frac{i}{2}c_{i}c_{j}\right\rangle \frac{i}{2}b_{i}^{\gamma}b_{j}^{\gamma} + \left\langle \frac{i}{2}b_{i}^{\gamma}b_{j}^{\gamma}\right\rangle \left\langle \frac{i}{2}c_{i}c_{j}\right\rangle + Spin liquid channel \\ - \left\langle \frac{i}{2}b_{i}^{\gamma}c_{j}\right\rangle \frac{i}{2}b_{j}^{\gamma}c_{i} - \left\langle \frac{i}{2}b_{j}^{\gamma}c_{i}\right\rangle \frac{i}{2}b_{i}^{\gamma}c_{j} + \left\langle \frac{i}{2}b_{i}^{\gamma}c_{j}\right\rangle \left\langle \frac{i}{2}b_{j}^{\gamma}c_{i}\right\rangle$$

• Together with the constraints to recover actual spin Hilbert space:

$b^z c + b^x b^y = 0$	60 self-consistent non-linear
$b^{y}c - b^{x}b^{z} = 0$	coupled equations for
$b^x c + b^y b^z = 0$	Kitaev+Heisenberg+DM

# Majorana mean-field theory

Spectrum of pure Kitaev model



### Beyond the Kitaev model

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$$H_{DM} = \sum_{\langle\langle ij \rangle\rangle} \mathbf{D}_{ij} \cdot \mathbf{S}_{i} \times \mathbf{S}_{j}$$

• Take magnetic field in the [1,1,1] direction:  $\mathbf{B}=B(1,1,1)/\sqrt{3}$ 

Kitaev model under a magnetic field



A. Ralko, and J. Merino, PRL (2020).

Kitaev model under a magnetic field



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- We take the magnetic field in the [1,1,1] direction:  $\mathbf{B}=B(1,1,1)/\sqrt{3}$
- We take a DM field in the [0,0,1] direction:  $\mathbf{D}=D(0,0,1)/\sqrt{3}$
- Obtain K-B-D phase diagram.

### Full phase diagram



### Full phase diagram



### Full phase diagram



# Beyond MMFT: exact diagonalization of K-B-D model



- An intermediate phase is found at sufficiently large:  $B \sim K$
- Gap in intermediate phase is enhanced by the DM interaction.



# Unconventional superconductivity in decorated honeycomb materials

JM, M. F. López, and B. J. Powell, PRB (2021).

M. F. López, and JM, PRB (2020).

# $Mo_3S_7(dmit)_3$ and $Rb_3TT \cdot 2H_2O$ materials

Mo<sub>3</sub>S<sub>7</sub>(dmit)<sub>3</sub>



Rosa Llusar, et. al., JACS (2004).

 $Rb_3TT \cdot 2H_20$ 



Y. Shuku et. al., Chem. Commun. (2018).

#### Tight-binding model for Mo<sub>3</sub>S<sub>7</sub>(dmit)<sub>3</sub> and Rb<sub>3</sub>TT·2H<sub>2</sub>O



- Dirac cones: non-trivial topology under significant spin-orbit coupling.
- Coulomb interaction effects enhanced in proximity to flat bands as in TBG.

#### Minimal strongly correlated model

Hubbard model on a decorated honeycomb lattice:

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

At half-filling and U, U>>t, t<sub>c</sub> the Hubbard model maps onto:

$$\mathcal{H} = J \sum_{\langle j,k \rangle} \vec{S}_j \cdot \vec{S}_k$$

Is the ground state of the Heisenberg model on a decorated honeycomb a quantum spin liquid?

At finite hole doping consider the t-J model:

$$H = -t_c \sum_{\langle ij \rangle, \sigma} P_G(c_{i\sigma}^{\dagger}c_{j\sigma} + H.c.)P_G - t \sum_{\langle ij \rangle, \sigma} P_G(c_{i\sigma}^{\dagger}c_{j\sigma} + H.c.)P_G + J_c \sum_{\langle ij \rangle, \sigma} \vec{S}_i \vec{S}_j + J \sum_{\langle ij \rangle, \sigma} \vec{S}_i \vec{S}_j$$

Can unconventional superconductivity arise under hole doping? Which is the role played by the flat bands and the Dirac cones ?

# RVB spin liquid on the decorated honeycomb lattice?

**Exact diagonalization 42-sites** 

Tensor network T=0 phase diagram Lattice Triangular Kagomé Star -0.2172-0.1842-0.3091 $e_0$  $m^+/m^+_{class}$ 0.386 0.000 0.122 -Dimer VBS Resonating  $J_c$  Dimer VBS  $J = J_c = 1$ 0.6 star △ kagome o 0.5 triangular 🗆 0.4  $\Delta 0.3$ Spin gap 0.2 Ō Richter et. al., PRB (2004)- $\frac{J_c}{-} \sim 1.1$ 0.1  $\frac{J_c}{I} \ll 1$  $\frac{J_c}{I} \gg 1$ 36 24 18

0

0

0.02

0.04

1/N

0.06

0.08

• Ground state at J=J<sub>c</sub> is a spin disordered Valence Bond Solid.

Jahromi, Orus, PRB (2018)

• Strongly suppressed long range AF order with large singlet-triplet spin gap.

# RVB spin liquid on the decorated honeycomb lattice?



Exact diagonalization on 42-sites



$$\langle \mathbf{S}_i \mathbf{S}_j \rangle^{\Delta \to \Delta} = -0.591$$
  
 $\langle \mathbf{S}_i \mathbf{S}_j^{\Delta} \rangle = -0.168$ 

 $\langle \mathbf{S_i S_j} \rangle^{\Delta \to \Delta} = -0.573 \\ \langle \mathbf{S_i S_j} \rangle^{\Delta} = -0.191$ 

# RVB spin liquid on the decorated honeycomb lattice?



• NN-RVB state is a good candidate for the ground state of Heisenberg model on the DHL.

At non-zero hole doping we explore the t<sub>c</sub>-t-J<sub>c</sub>-J model:

$$H = -t_{c} \sum_{\langle \alpha i, \alpha j \rangle \sigma} P_{G}(c_{\alpha i \sigma}^{\dagger} c_{\alpha j \sigma} + c_{\alpha j \sigma}^{\dagger} c_{\alpha i \sigma})P_{G} - t \sum_{\langle A i, B i \rangle, \sigma} P_{G}(c_{A i \sigma}^{\dagger} c_{B i \sigma} + c_{B i \sigma}^{\dagger} c_{A i \sigma})P_{G}$$
$$+ J_{c} \sum_{\langle \alpha i, \alpha j \rangle} \left( \vec{S}_{\alpha i} \cdot \vec{S}_{\beta j} - \frac{n_{\alpha i} n_{\beta j}}{4} \right) + J \sum_{\langle A i, B i \rangle} \left( \vec{S}_{A i} \cdot \vec{S}_{B i} - \frac{n_{A i} n_{B i}}{4} \right) \qquad P_{G} = \prod_{i} (1 - n_{i \uparrow} n_{i \downarrow})$$

Introducing bond singlet operators:  $h_{\alpha i,\beta j}^{\dagger} = \frac{1}{\sqrt{2}} \left( c_{\alpha i\uparrow}^{\dagger} c_{\beta j\downarrow}^{\dagger} - c_{\alpha i\downarrow}^{\dagger} c_{\beta j\uparrow}^{\dagger} \right)$ 

$$\sum_{\langle \alpha i,\beta j\rangle} \left( \vec{\boldsymbol{S}}_{\alpha i} \cdot \vec{\boldsymbol{S}}_{\beta j} - \frac{n_{\alpha i} n_{\beta j}}{4} \right) = -\sum_{\langle \alpha i,\beta j\rangle} h_{\alpha i,\beta j}^{\dagger} h_{\alpha i,\beta j}$$

Performing a Hartree-Fock-Bogoliubov decoupling of the free energy:

$$\Phi = -\frac{1}{\beta} \sum_{m,\mathbf{k},\sigma} \ln\left(1 + e^{-\beta\omega_m(\mathbf{k})}\right) - \sum_{m,\mathbf{k}} \omega_m(\mathbf{k}) + 6N_s\mu + \int_{\langle\alpha i,\alpha j\rangle} \left(|\Delta_{\alpha i,\alpha j}|^2 + |\chi_{\alpha i,\alpha j}|^2\right) + \int_{\langleA i,B i\rangle} \left(|\Delta_{A i,B i}|^2 + |\chi_{A i,B i}|^2\right)$$
$$\Delta_{\alpha i,\beta j} = \langle h_{\alpha i,\beta j} \rangle \quad \chi_{\alpha i,\beta j} = \langle h_{\alpha i,\beta j} \rangle \quad \text{Gutzwiller approx: } (J/t, J'/t) \to (\tilde{J}/\tilde{t}, \tilde{J}'/\tilde{t}) = \frac{2}{\delta(1+\delta)} (J/t, J'/t)$$



• Unconventional superconductivity: extended-s, extended-d and f-wave singlet pairing!



Unconventional superconductivity: extended-s, extended-d and f-wave singlet pairing!

![](_page_41_Figure_1.jpeg)

- In the honeycomb lattice s\* and d-wave singlet pairing occur. (Black-Schaffer, Doniach PRB(2007))
- In the decorated honeycomb lattice f-wave singlet pairing is allowed by the decoration.

![](_page_42_Figure_0.jpeg)

![](_page_43_Figure_0.jpeg)

![](_page_44_Figure_1.jpeg)

### Conclusions

- Kitaev magnets under magnetic fields and /or DM can host novel chiral quantum spin liquids.
- An RVB quantum spin liquid is a good candidate for the ground state of the Heisenberg model on the decorated honeycomb lattice.
- Extended s\*, d\* and f-wave singlet superconductivity can arise in decorated honeycomb lattices under hole doping.

#### Outlook:

- Theory: analyze rich variety of superconducting pairing states emerging in decorated lattices.
- Experiments: search for unconventional superconductivity in DHLs under doping!

Thank you for your attention!