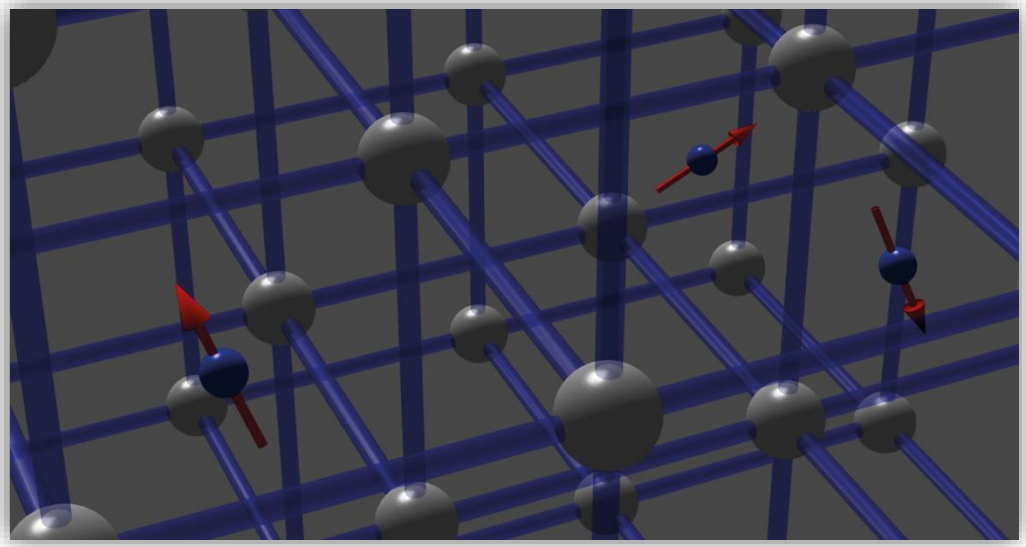
Frustrated Magnetic Materials from an ab initio prespective



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Institute of Theoretical Physics
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Germany

GOETHE UNIVERSITÄT FRANKFURT AM MAIN

Highly Frustrated Magnetism
Tutorial, July 9th 2018,
UC Davis

- ***What are frustrated magnetic materials :***

  why are they special?

- ***Microscopic description***

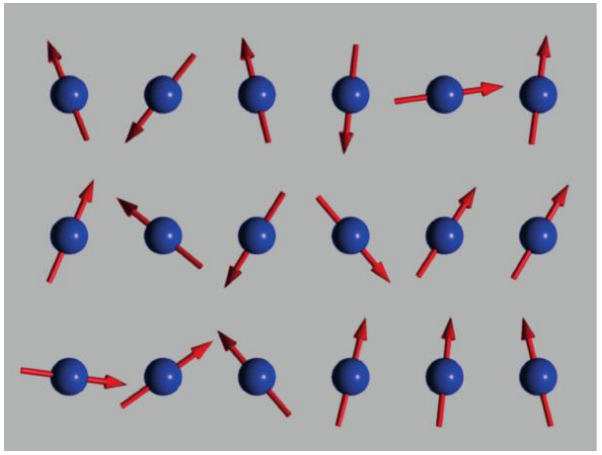
  → *from first principles to model Hamiltonians*

- ***Predict systems with unconventional properties?***

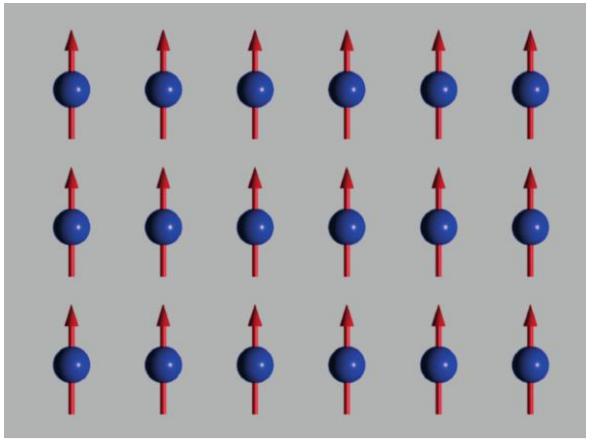
- ***Examples***

exotic phases beyond …

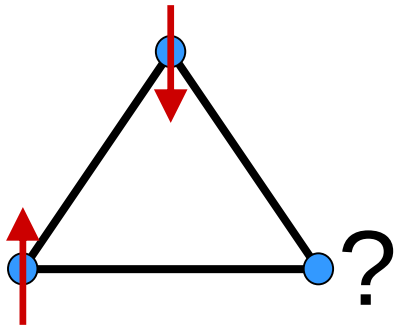
paramagnetism



ferro- / antiferromagnetism



P.W. Anderson
Mat.Res.Bull 8, 153 (1973)



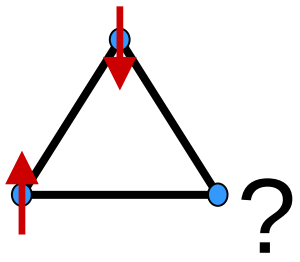
- Importance of **quantum effects** to induce new types of **non-ordered states**
  (*spin liquid, resonating valence bond state*, …)

- Ways out of classical magnetic order:

1. **Low dimensionality**

(1D Chains)

2. **Geometric frustration**



(Kagome, Triangular,…)

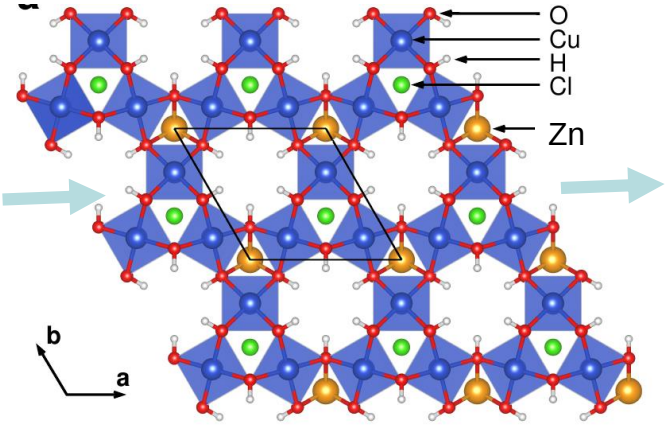
3. **Hamiltonian engineering**

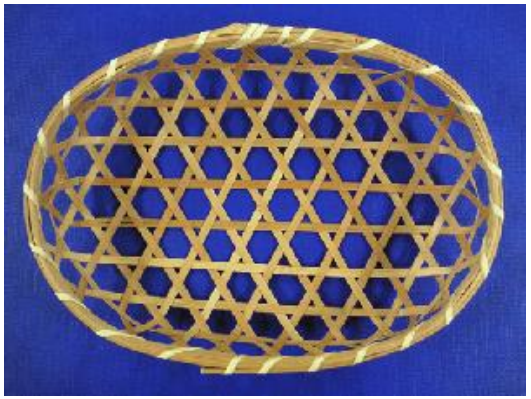
(Hamiltonian with only non-conmuting terms. Anisotropic interactions)

(Honeycomb, …)

Herbertsmithite : spin ½ kagome lattice

$ZnCu_3(OH)_6Cl_2$





Herbertsmithite : spin ½ kagome lattice
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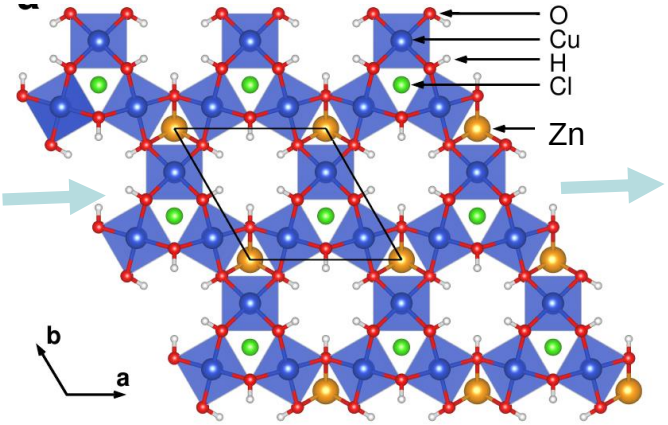
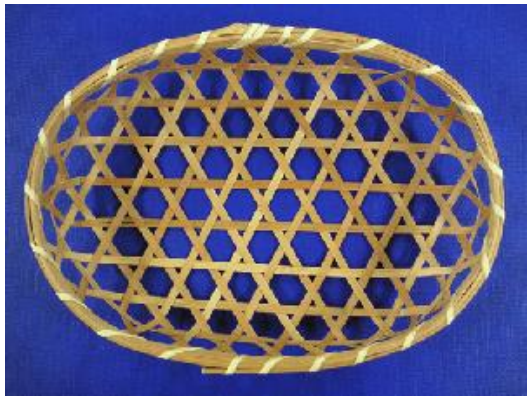
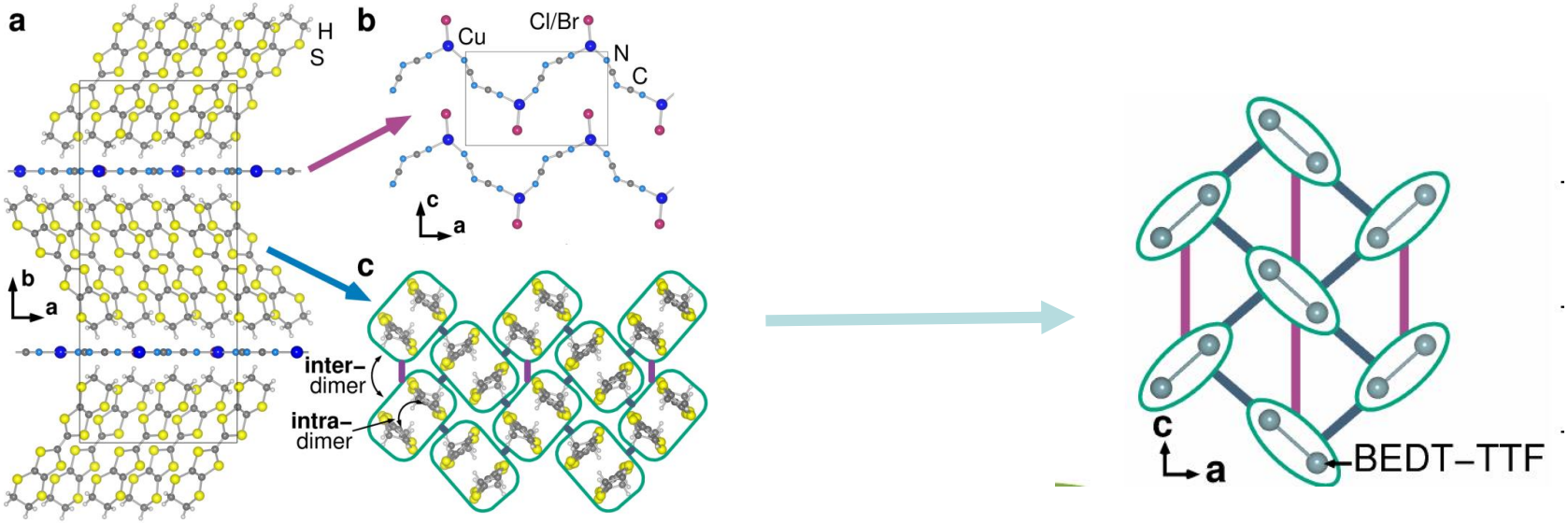




$(BEDT\text{-}TTF)_2X$: spin ½ triangular lattice

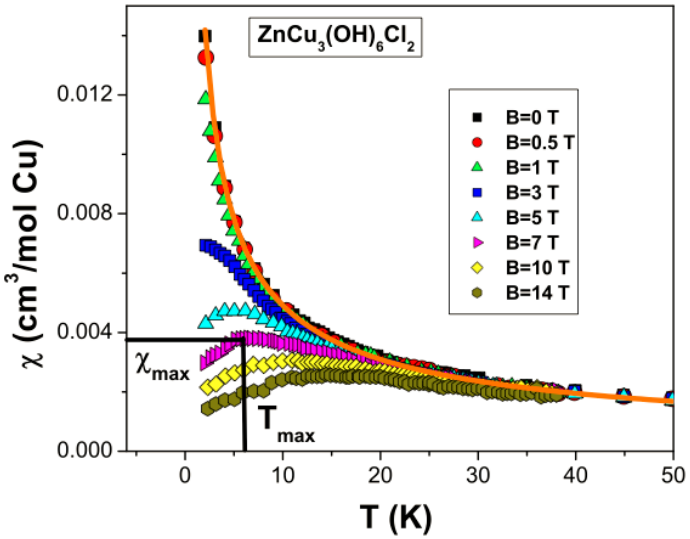


Geometric Frustration

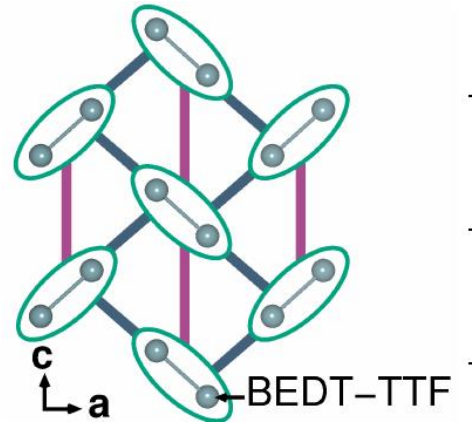
Herbertsmithite : spin ½ kagome lattice
$ZnCu_3(OH)_6Cl_2$

F. Bert, P. Mendels
*JPSJ **79**, 011001 (2010)*

J.S. Helton et al.
*PRL **104**, 147201 (2010)*

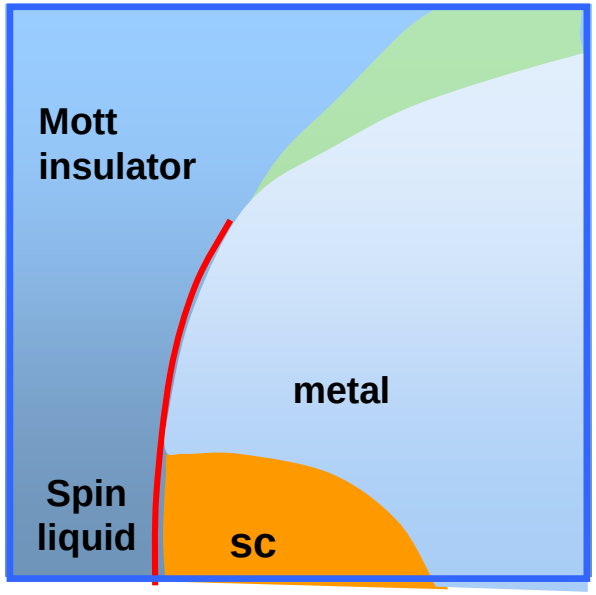


κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$



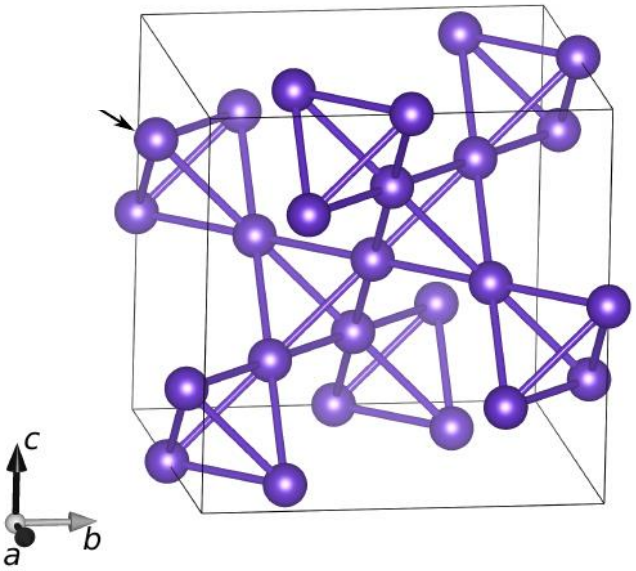
Shimizu et al.PRL
***91,** 107001 (2003)*

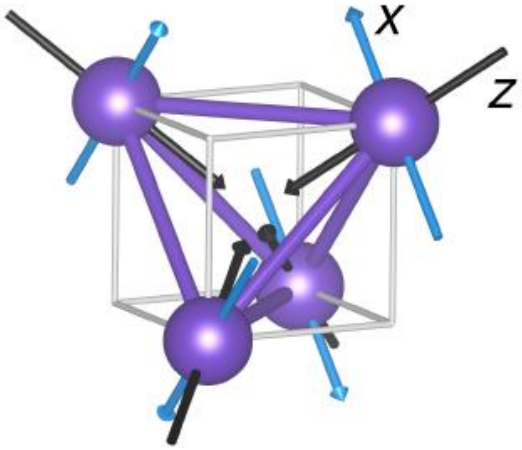
Manna et al. PRL
***104,** 016403 (2010)*



Mott insulators

pyrochlore lattices $A_2B_2O_7$: corner-sharing B_4 tetrahedra

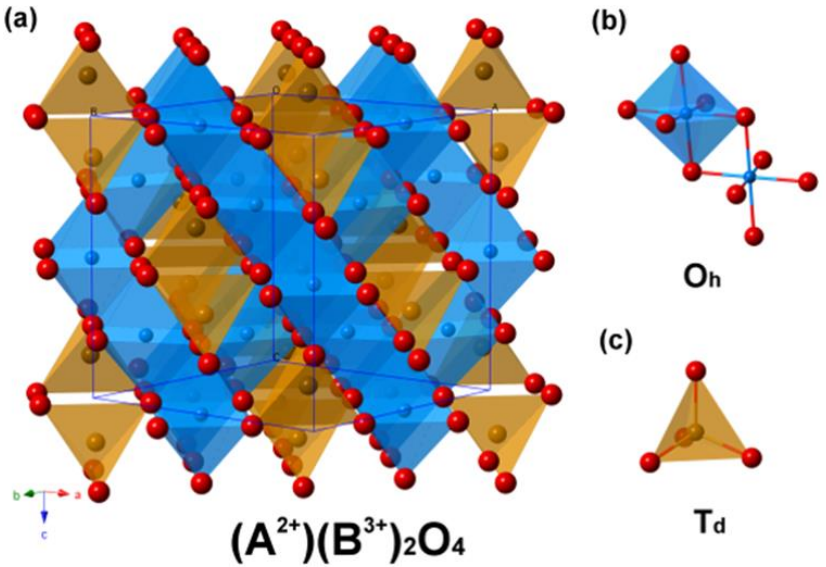




spinel lattices AB_2O_4:

corner-sharing B_4 tetrahedra

B = transition-metal ion



Spin Hamiltonian

$$\mathcal{H} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \cdot \mathbf{\Gamma}_{ij} \cdot \mathbf{S}_j$$

(Isotropic Heisenberg Exchange)

(Dzyaloshinskii-Moriya Term)

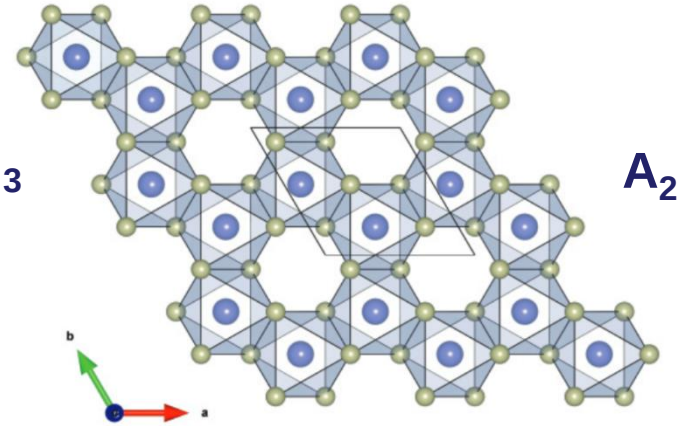
(Symmetric Term)

strongest interaction

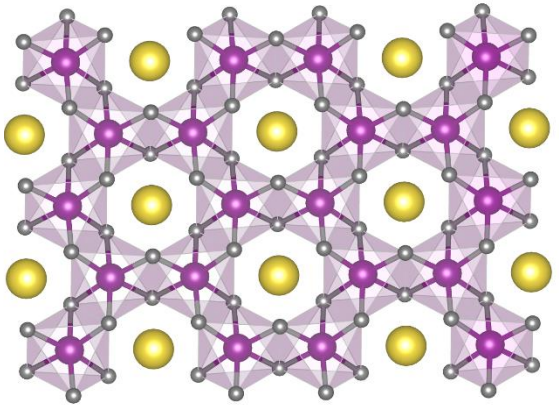
Geometric Frustration

Kitaev Materials

α-$RuCl_3$



A_2IrO_3 (A = Li, Na)



$$\mathcal{H} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \cdot \mathbf{\Gamma}_{ij} \cdot \mathbf{S}_j$$

(Isotropic Heisenberg Exchange)

(Dzyaloshinskii-Moriya Term)

(Symmetric Term)

Hamiltonian engineering

strongest interaction

bond-dependent

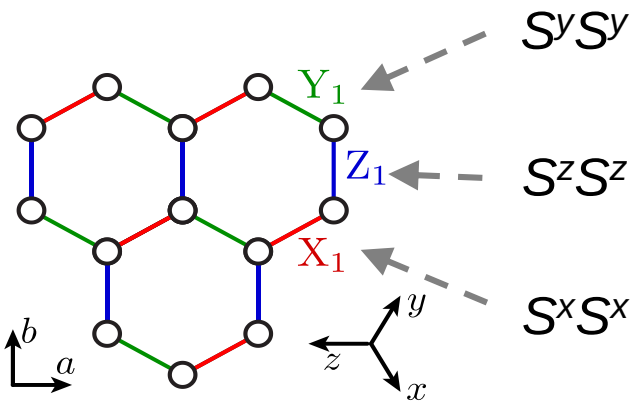
$$\mathcal{H} = K S_i^\gamma S_j^\gamma$$

Kitaev Honeycomb Model

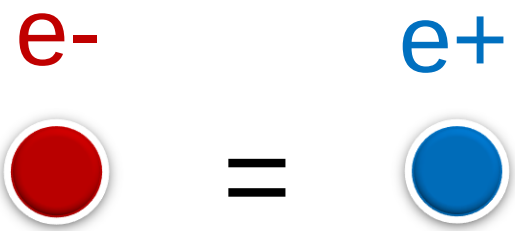
Alexei Kitaev, Annals of Physics 321, 2 (2006)

- Exactly solvable
  Z_2 spin-liquid ground state
  with gapless Majorana fermions
  and static gapped fluxes

$$\mathcal{H} = K S_i^\gamma S_j^\gamma$$



Majorana Fermions



$$c_i^\dagger = c_i \quad , \quad c_i^2 = 1 \quad , \quad \{c_i, c_j\} = 0$$

Ettore Majorana

How does the solution work?

1. Write spin-operators in terms of four Majorana fermions:

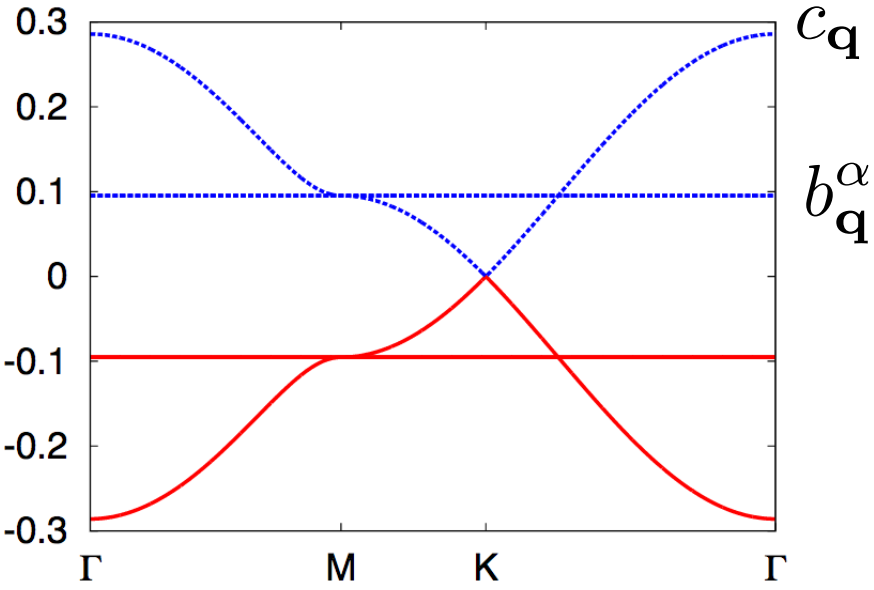
$$S_i^x = ib_i^x c_i$$
$$S_i^y = ib_i^y c_i$$
$$S_i^z = ib_i^z c_i$$

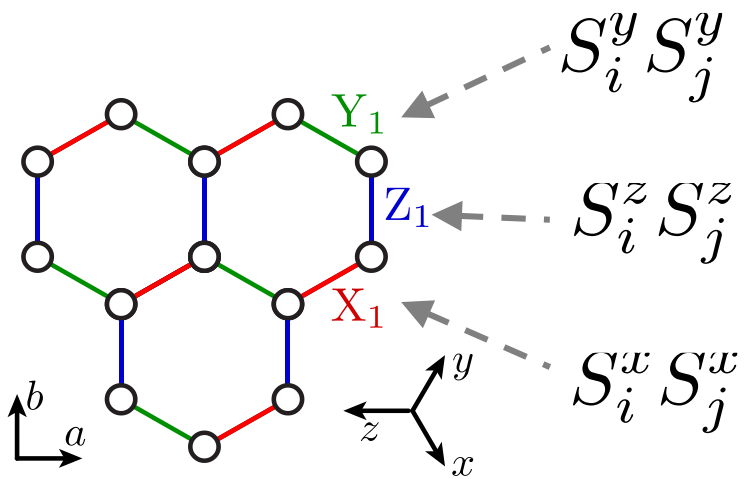
These are related to normal fermions like:

$$c_i = \frac{1}{2}(f_i^\dagger + f_i) \qquad c_i^\dagger = c_i \quad , \quad c_i^2 = 1 \quad , \quad \{c_i, c_j\} = 0$$

2. When we write Hamiltonian in this basis, b-fermions can only hop on one bond-type, and c-fermions can hop on all bonds.

e.g. $S_i^z S_j^z = b_i^z b_j^z c_i c_j$





Schaffer, Bhattacharjee, YB Kim arXiv:1206.5814

Kitaev Honeycomb Model

◆ Conventional to write: $\mathcal{H} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \cdot \mathbf{\Gamma}_{ij} \cdot \mathbf{S}_j$

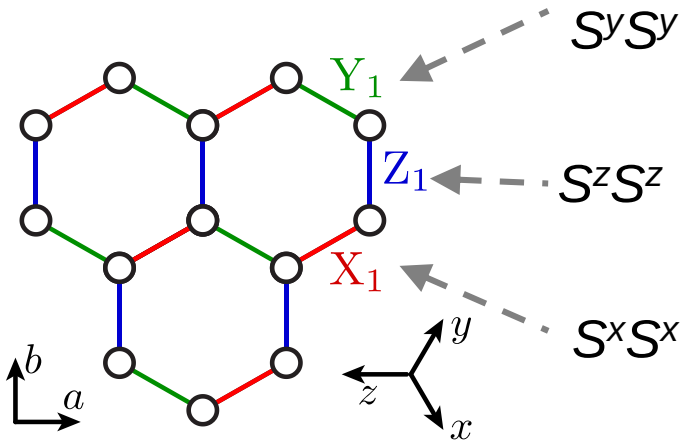
J_{ij}	$\mathbf{D}_{ij}$	$\mathbf{\Gamma}_{ij}$
(Isotropic Exchange)	*(Dzyaloshinskii-Moriya Term)*	*(Symmetric Term)*

General Interactions

$$J_{ij} = 0 \qquad \begin{matrix} D^a_{ij} = 0 & \Gamma^{ab}_{ij} = 0 \\ D^b_{ij} = 0 & \Gamma^{ac}_{ij} = 0 \\ D^c_{ij} = 0 & \Gamma^{bc}_{ij} = 0 \end{matrix} \qquad \Gamma^{aa}_{ij}, \Gamma^{bb}_{ij}, \Gamma^{cc}_{ij} = \begin{cases} K \\ 0 \end{cases}$$

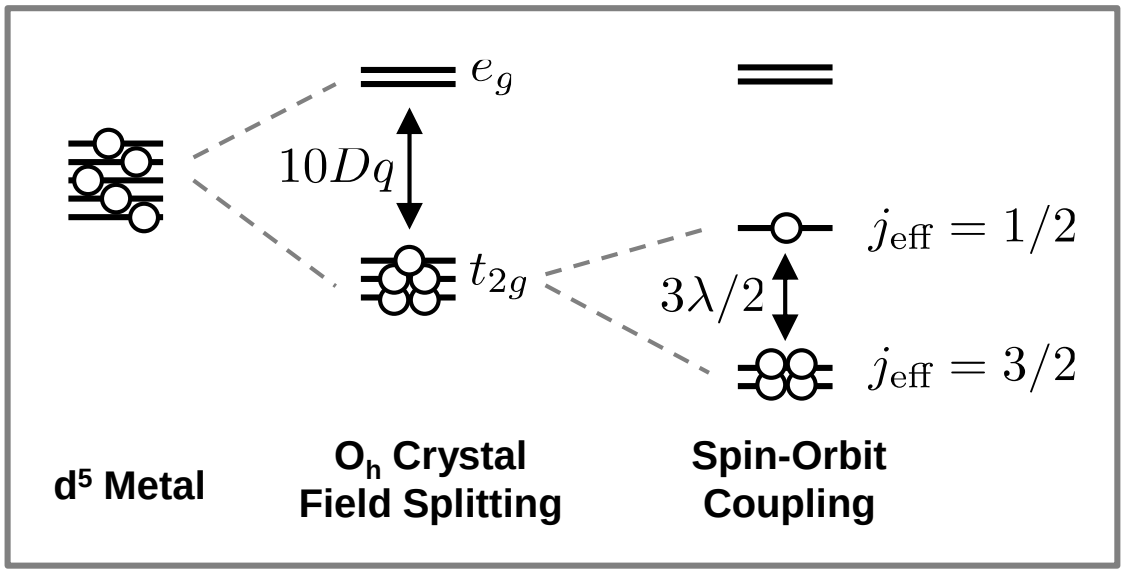
(Depending on orientation of the bond.)

Kitaev Model

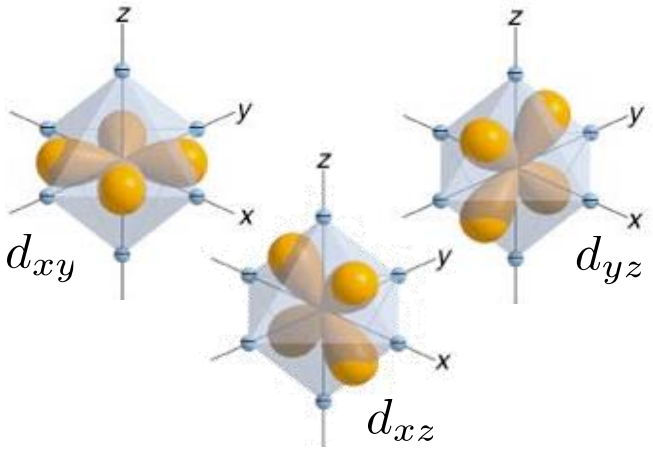


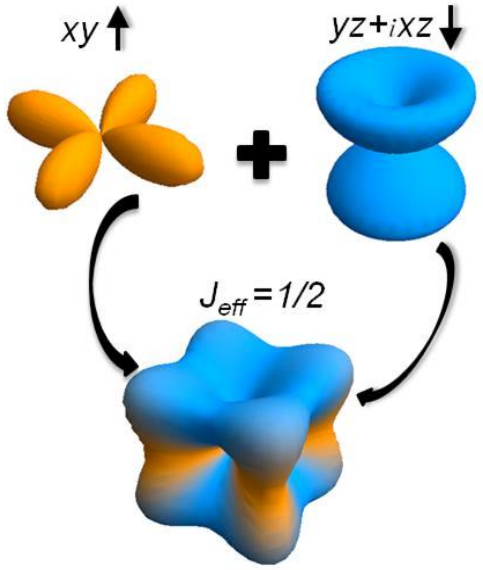
Kitaev Honeycomb Model – Relation to Real Materials

How to engineer dominant Kitaev terms?



$j_{\rm eff} = 1/2$ *States:*





- For **d^5 metals** in an **O_h crystal field**, with **large SOC vs. CFS**, low energy degrees of freedom are jeff = ½ moments.

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

J. Chaloupka, G. Jackeli, G. Khaliullin PRL 105, 027204 (2012)

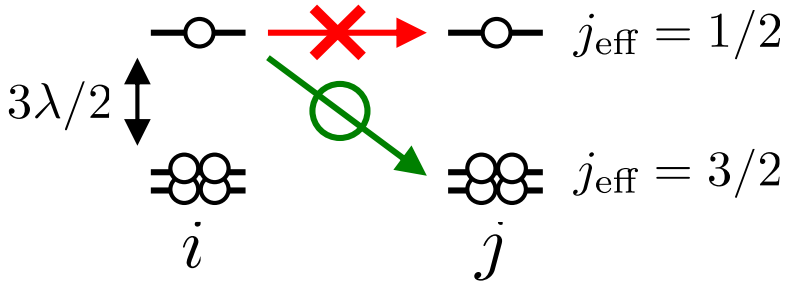
Khaliullin,Maekawa PRL 85, 3950 (2000), Khaliullin, Horsch, Oles PRL 86, 3879 (2001)

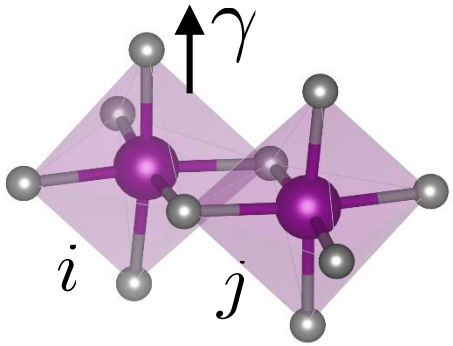
Kitaev Honeycomb Model – Relation to Real Materials

How do we engineer dominant Kitaev terms?

◆ For **d^5 metals** in an **O_h crystal field**, with **large SOC vs. CFS**, low energy degrees of freedom are jeff = ½ moments.

Jackeli, Khaliullin PRL 102, 017205 (2009)





◆ When such metals are **edge-sharing**

$$J_{ij} \sim 0$$

◆ When such metals have **inversion symmetry**,

$$\mathbf{D}_{ij} = 0 \qquad \mathbf{\Gamma}_{ij} = 0 + \mathcal{O}(J_H t^2)$$

◆ Subleading term from effective **Hund's coupling** between j_{eff} = ½ states to the m_j = ±3/2 states that is Ising-like.

$$\mathcal{H} = K S_i^\gamma S_j^\gamma \qquad K \sim \frac{J_H t^2}{2U + 3\lambda})^2$$

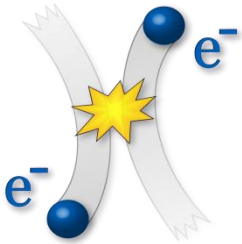
How do we extract the spin model Hamiltonian from first principles?

Material ←→ Model

microscopic description

- N electrons M ions

Coulomb repulsion



$$T_s = \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m_e}, \qquad V_{e-e} = \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{k,k',k\neq k'}^{N} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_{k'}|}$$

$$T_i = \sum_{l=1}^{M} \frac{\mathbf{P}_l^2}{2M_l}, \qquad V_{i-i} = \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{l,l',l\neq l'}^{M} \frac{e^2}{|\mathbf{R}_l - \mathbf{R}_{l'}|}$$

$$V_{e-i} = \sum_{l=1}^{M}\sum_{k=1}^{N} v^i(|\,\mathbf{R}_l - \mathbf{r}_k\,|)$$

- many-body Schrödinger equation:

$$(T_s + T_i + V_{e-e} + V_{e-i} + V_{i-i})\Psi = E\Psi$$

$$\Psi = \Psi(\{\mathbf{r}_k, \sigma_k\}, \{\mathbf{R}_l\})$$

- adiabatic approximation:

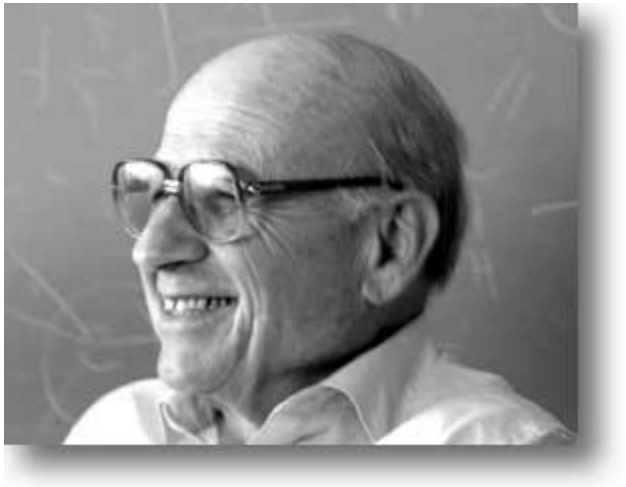
$$(T_s + V_{e-e} + V_{ext})\Phi = E_e\Phi$$

$$\Phi = \Phi(\{\mathbf{r}_k, \sigma_k\})$$

- 10^{23} coupled equations!!!

Density Functional Theory

Walter Kohn
Nobel Prize in Chemistry 1998



Hohenberg-Kohn Theorem:

The groundstate energy of a system of interacting particles
is a functional of the groundstate density ρ(r): E [ρ(r)]

Kohn-Sham Ansatz:

Replace interacting many-body problem: $E = E[\rho]$

with a non-interacting problem with all many-body effects in a XC functional

Kohn-Sham Ansatz

Replace interacting many-body problem:

$$E = E[\rho]$$

with a non-interacting problem with all many-body effects in a XC functional:

$$E[\rho] = T_S[\rho] + E_{ext}[\rho] + E_H[\rho] + E_{xc}[\rho]$$

$$(T + V_{ei}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}))\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{occ} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$$

$$V_H = e^2 \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}$$

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

Variational principle !

Bloch wavefunctions

Local Density Approximation (LDA)

$$E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \hat{E}_{xc}(n(\mathbf{r}))$$

Kohn, Sham (1964)

Local Density Approximation (LDA)

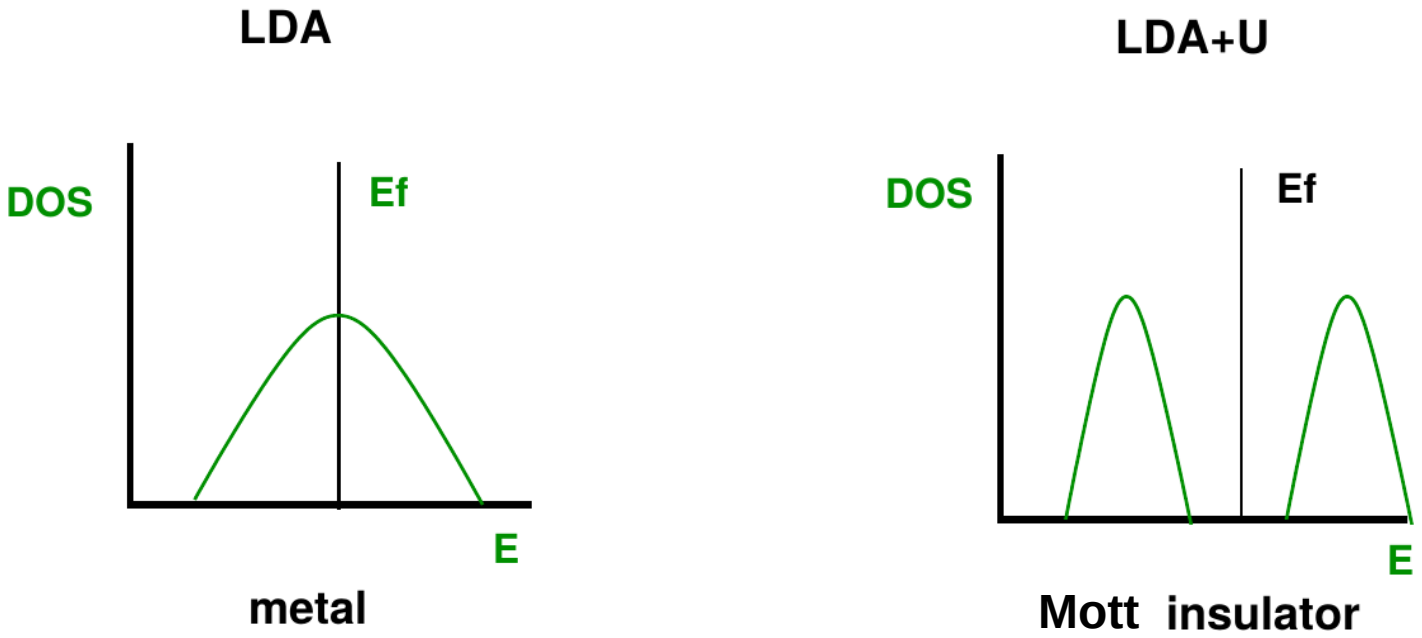
$$E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \hat{E}_{xc}(n(\mathbf{r}))$$

Kohn, Sham (1964)

LDA+U

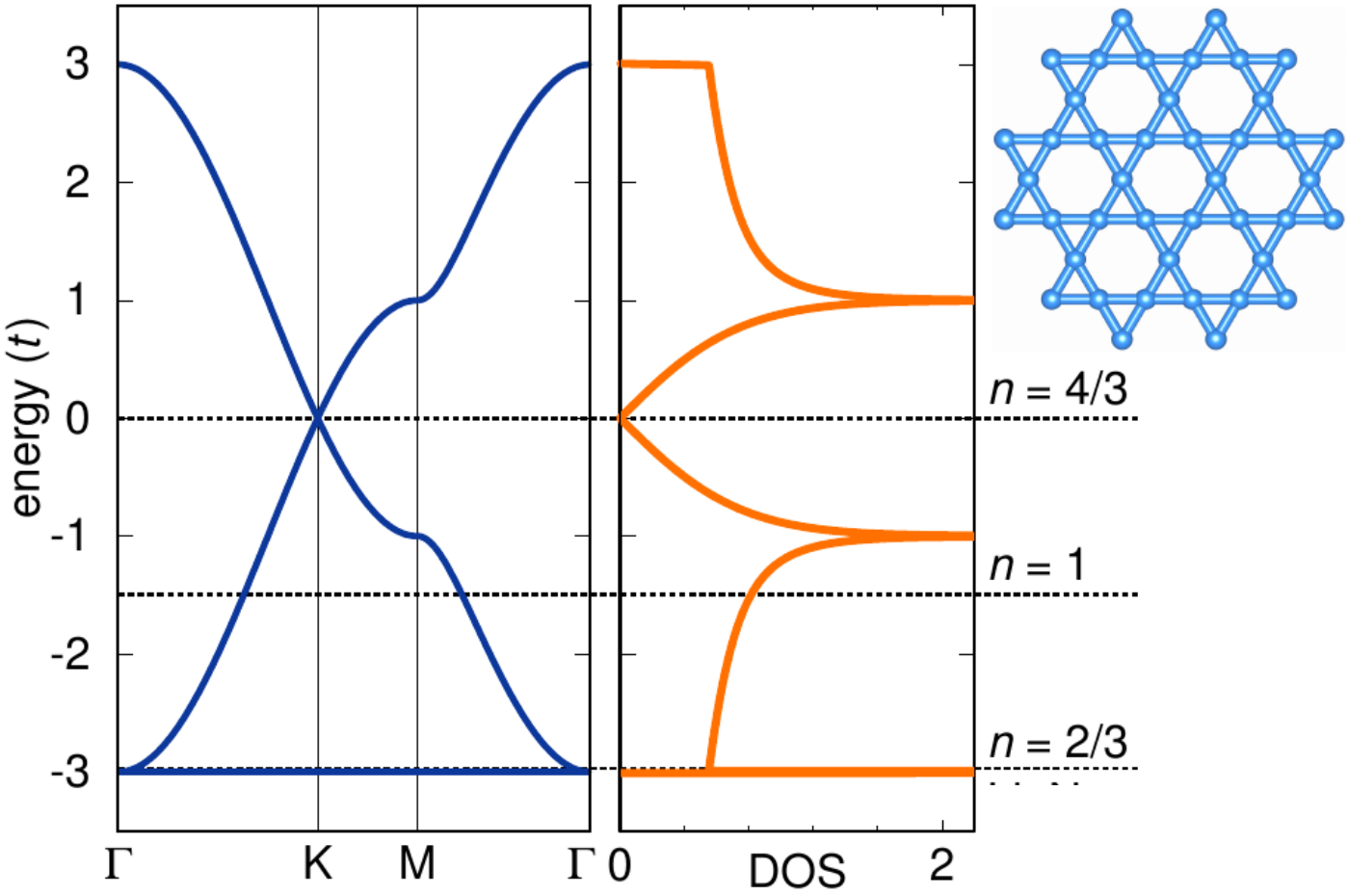
Anisimov,Zaanen,Andersen PRB 44, 943 (1991)

$$E = E^{LDA} - \frac{U}{2}N(N-1) + \frac{J}{2}[N^{\uparrow}(N^{\uparrow}-1) + N^{\downarrow}(N^{\downarrow}-1)] + \frac{U}{2}\sum_{j,k,\sigma} n_{j,\sigma} n_{k,-\sigma} + \frac{1}{2}(U-J)\sum_{i \neq j,\sigma} n_{i,\sigma} n_{j,\sigma}$$



Example: Kagome lattice

Nearest-neighbor hopping tight-binding

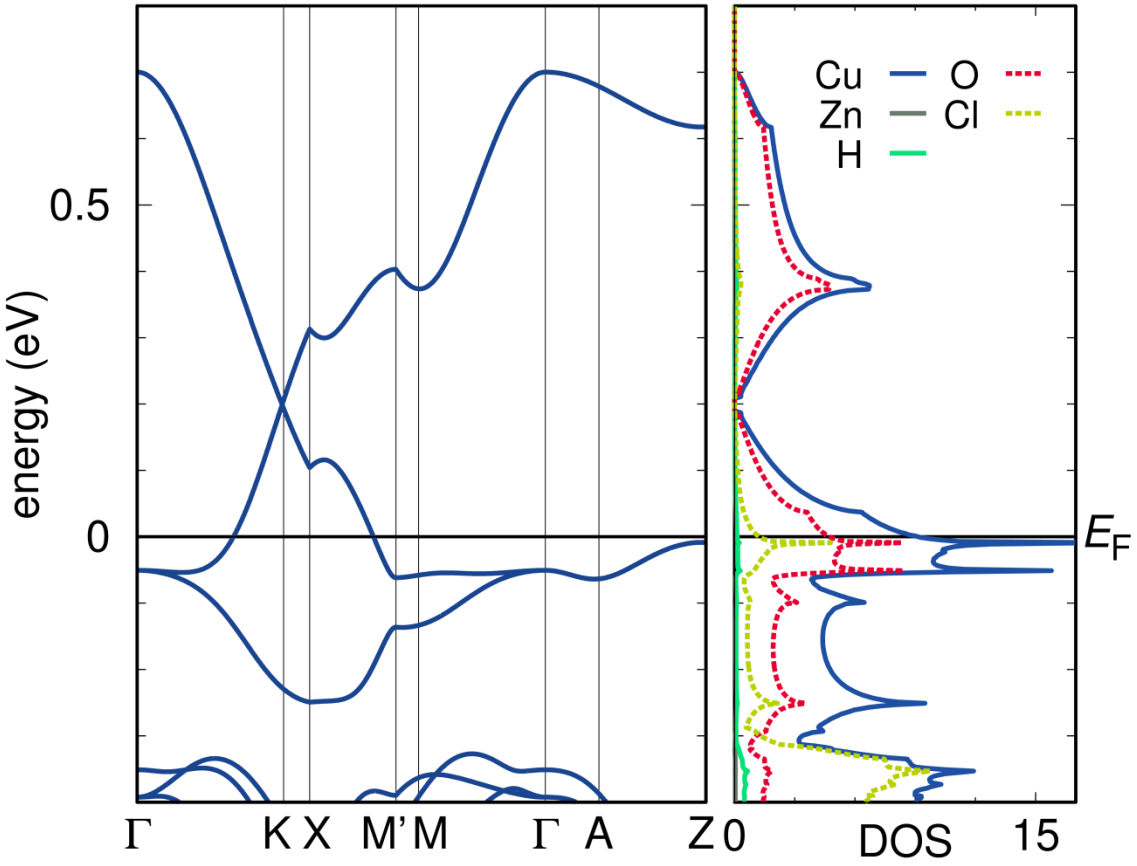


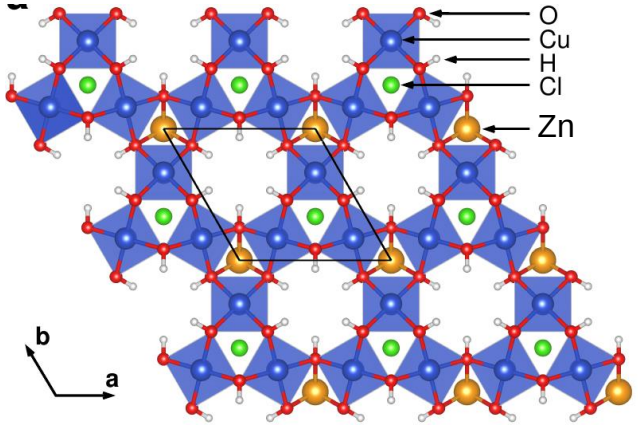
Herbertsmithite

$ZnCu_3(OH)_6Cl_2$

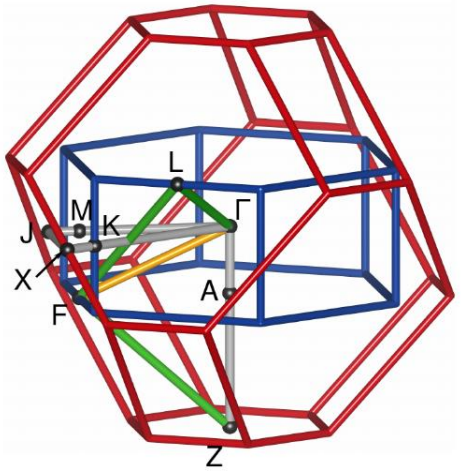
Kagome lattice of spin ½ Cu

DFT-GGA calculation/FPLO basis





Cu d_{x2-y2} bands

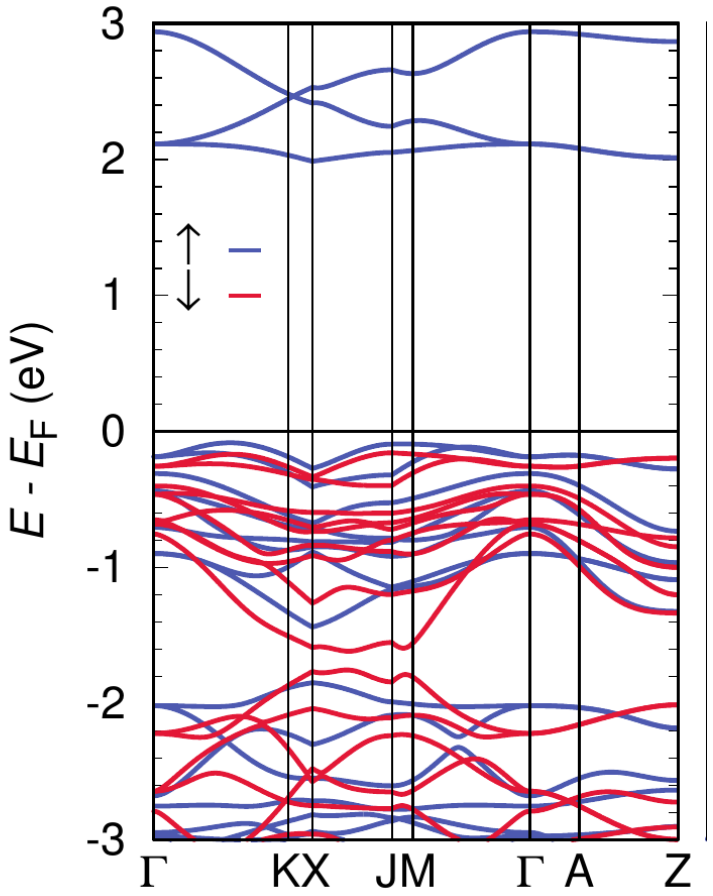


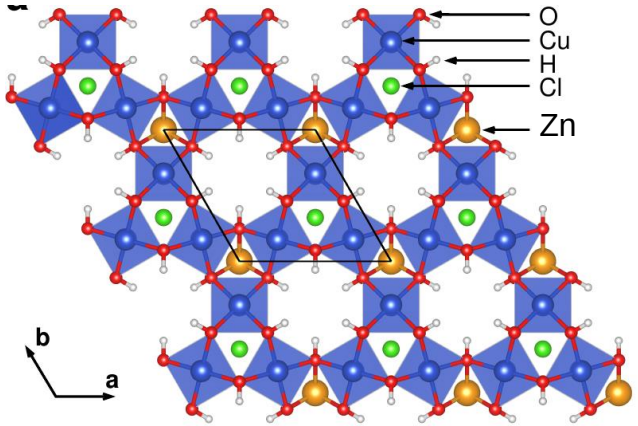
Herbertsmithite
$ZnCu_3(OH)_6Cl_2$

Kagome lattice of spin ½ Cu

n=1

DFT-GGA+U





Cu d_{x2-y2} bands

Mott insulator

nature of spin liquid

*PRB **88**, 075106 (2013)*
*PRB **97**, 020104(R) (2018)*

Spin model

$$\mathcal{H} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \cdot \mathbf{\Gamma}_{ij} \cdot \mathbf{S}_j$$

Total energy calculations (isotropic case):

- Map the energy differences of frozen collinear spin configurations in DFT supercell calculations onto a spin-1/2 Heisenberg model and evaluate J in the dimer approximation

$$H = -2J\mathbf{S}_i\mathbf{S}_j$$

$$E_{FM} = -J\left[S_T(S_T+1) - 2S(S+1)\right]$$

$$E_{AFM} = J\left[2S(S+1)\right]$$

$$\Delta E = \frac{E_{FM} - E_{AFM}}{2} = -\frac{J}{2}S_T(S_T+1)$$

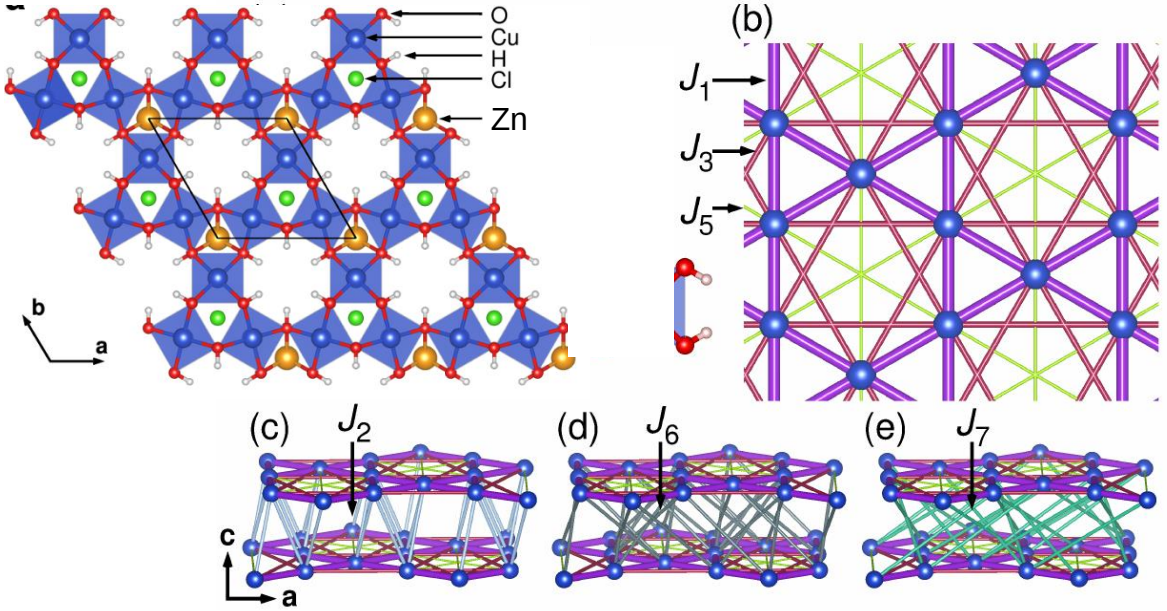
mind the neighbors‘ scaling factors!

Spin model

Total energy calculations (isotropic case):

Herbertsmithite
$ZnCu_3(OH)_6Cl_2$

*PRB **88**, 075106 (2013)*



name	d_{Cu-Cu}	type	J_i (K) $U=6$ eV
kagomé layer couplings			
J_1	3.4171	kagomé nn	182.4
J_3	5.91859	kagomé 2nd nn	3.4
J_5	6.8342	kagomé 3rd nn	−0.4
interlayer couplings			
J_2	5.07638	interlayer 1st nn	5.3
J_4	6.11933	interlayer 2nd nn	−1.5
J_6	7.00876	interlayer 3rd nn	−6.4
J_7	8.51328	interlayer 4th nn	3.0
J_9	9.17347	interlayer 6th nn	2.5

J_i determined from total GGA+U energies of 9 spin configurations in 2x1x2 supercells

→ agreement with experiment

What about anisotropic spin hamiltonians?

$$\mathcal{H} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \cdot \mathbf{\Gamma}_{ij} \cdot \mathbf{S}_j$$

spin-orbit coupling

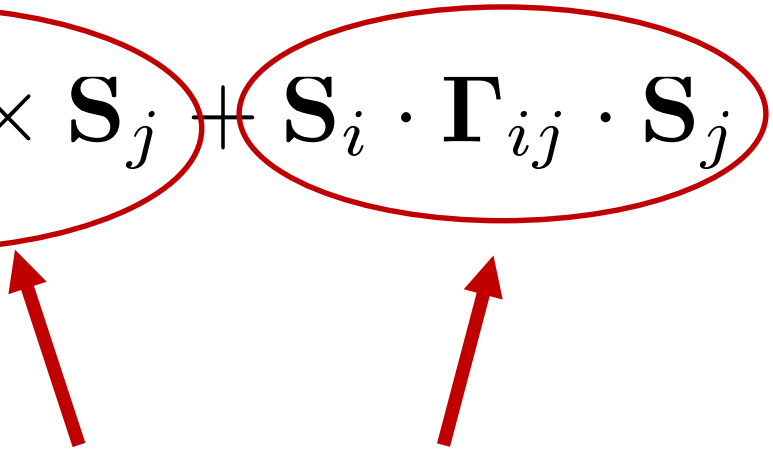
(relevant for non-centrosymmetric systems, Kitaev, …)

- The method of total energy calculations requires **relativistic non-collinear spin configurations**

  → implementation of LDA+U and non-collinear spin calculations is problematic in some basis sets
  → may provide unreliable results
  → (f.i. elk calculations are ok but computationally very heavy)

What about anisotropic spin hamiltonians?

$$\mathcal{H} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \cdot \mathbf{\Gamma}_{ij} \cdot \mathbf{S}_j$$

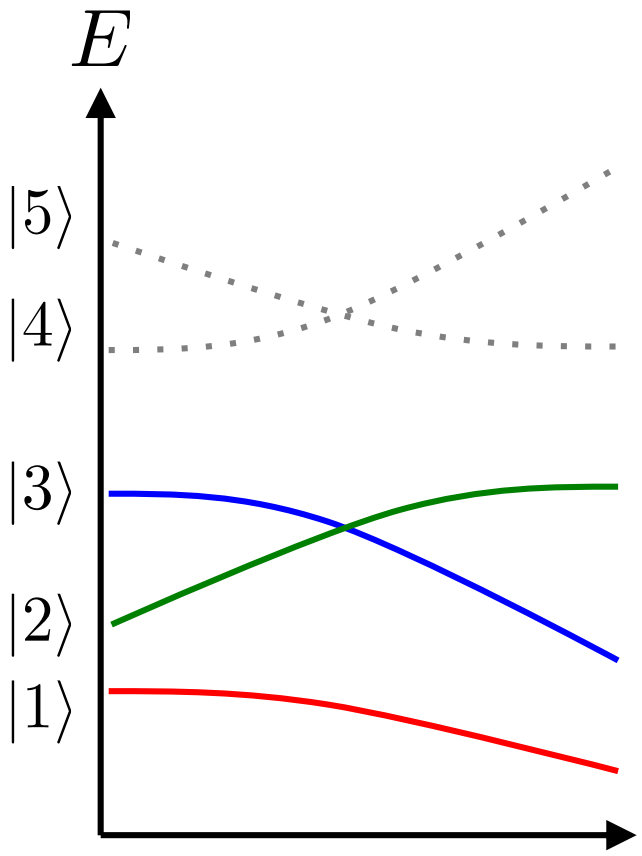


spin-orbit coupling

(relevant for non-centrosymmetric systems, Kitaev, …)

→ we will consider an alternative method → obtain the low-energy spin Hamiltonian from numerical projection

Reminder: Low-Energy Hamiltonian from Perturbation Theory



Total Hamiltonian:

$$\mathcal{H} = \mathcal{H}_0 + V$$

Projection Operators:

$$\mathbb{P} = |1\rangle\langle 1| + |2\rangle\langle 2| + |3\rangle\langle 3|$$

$$\mathbb{Q} = 1 - \mathbb{P}$$

Effective Low-Energy Hamiltonian:

$$\mathcal{H}_{\text{eff}} = \mathbb{P}\mathcal{H}\mathbb{P} + \mathbb{P}V\mathbb{Q}(E - \mathcal{H}_0)^{-1}\mathbb{Q}V\mathbb{P} + \ldots$$

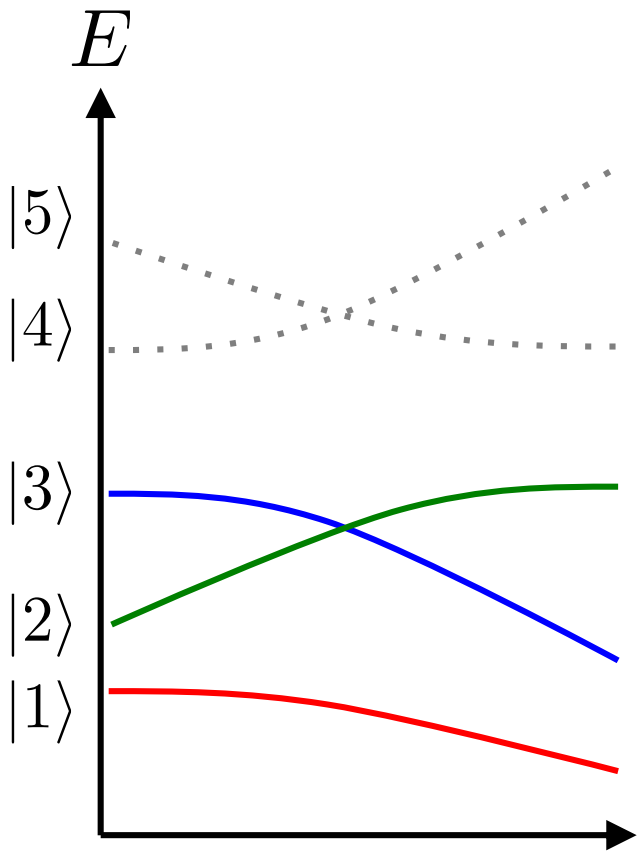
Exact Low-Energy States:

$$c_n|n'\rangle = |n\rangle + (E - \mathcal{H}_0)^{-1}\mathbb{Q}V|n\rangle + \ldots$$

Perturbation theory provides:

1. Approximate energies (up to computed order).
2. Mapping from exact states to low-energy space.

Low-Energy Hamiltonian from Numerical Projection



Exact Low-Energy States:

$$c_n|n'\rangle = |n\rangle + (E - \mathcal{H}_0)^{-1}\mathbb{Q}V|n\rangle + \ldots$$

We want a mapping:

$$|n'\rangle \rightarrow |n\rangle$$

1. Maximizes $\langle n'|n\rangle$
2. Preserve all symmetries.

1. Apply projection numerically:

$$\mathbb{P}|n'\rangle = (1/c_n)|n\rangle$$

2. Orthonormalize obtained states numerically:

$$(1/c_n)|n\rangle \rightarrow |n\rangle$$

The “correct” choice is symmetric (Löwdin) orthonormalization:

Overlap Matrix:

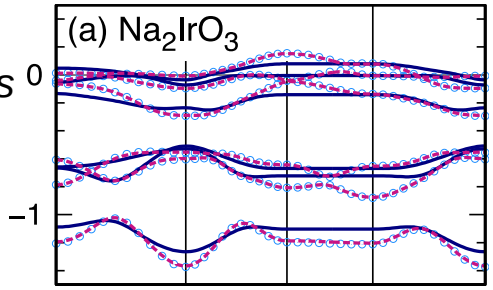
$$S_{nm} = \langle n'|\mathbb{P}|m'\rangle$$

Final Mapping:

$$|n\rangle \leftarrow \sum_m [\mathbf{S}^{1/2}]_{mn}\mathbb{P}|m'\rangle$$

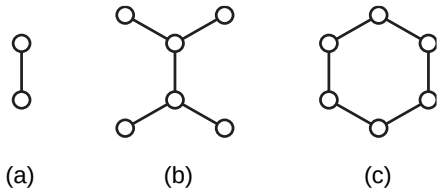
Low-Energy Hamiltonian from Numerical Projection

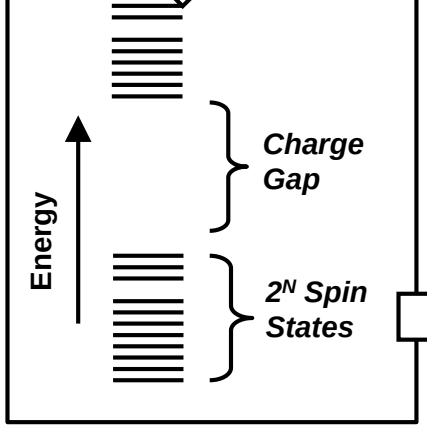
-1. Obtain hopping integrals from DFT + wannier basis:



S. M. Winter, K. Riedl, R. Valenti PRB 95, 060404(R) (2017); (Supplemental Material) Riedl et al. PRB 94, 014410 (2016)

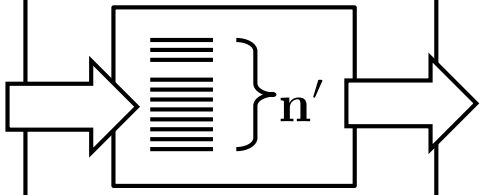
0. Exactly diagonalize full t_{2g} model (hopping + SOC + CF+ Hund + Coulomb) on finite clusters :





1. Obtain “exact” energies and eigenstates.

2. Keep only lowest energy states.



3. Define reference basis (f.i. j_{eff} = ½ states for Kitaev systems)

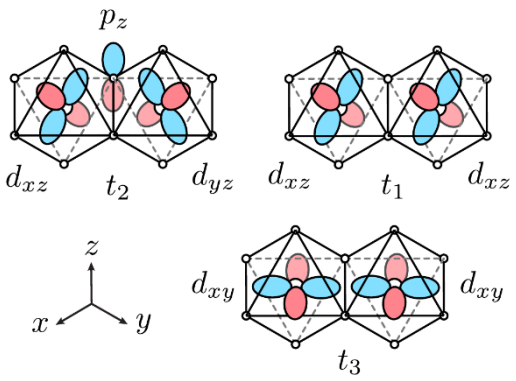
$$\mathbf{S} = (\mathbf{n}')^\dagger \mathbb{P} \mathbf{n}'$$

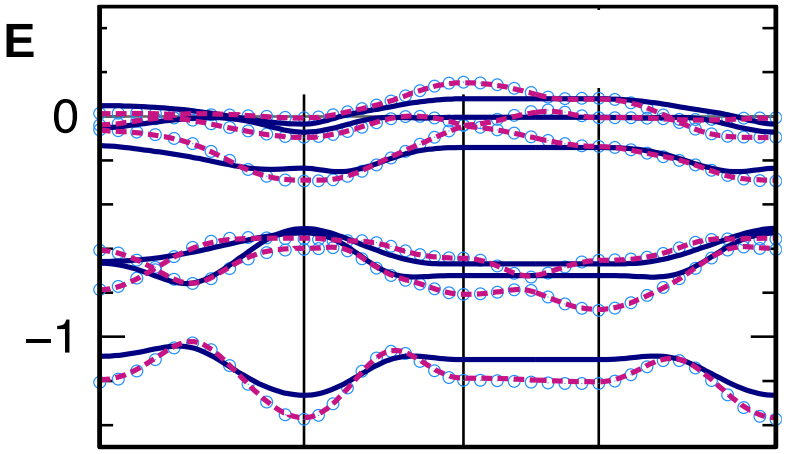
$$\mathcal{H}_{\text{eff}} = \mathbb{P}\mathbf{S}^{-1/2}\mathcal{H}\mathbf{S}^{-1/2}\mathbb{P}$$

4. Perform projection.

Ab initio-based Kitaev Honeycomb Model

1. Obtain hopping integrals from DFT:





BZ

$$\mathcal{H}_{tot} = \mathcal{H}_{\rm hop} + \mathcal{H}_{\rm CF} + \mathcal{H}_{\rm SO} + \mathcal{H}_U$$

$$\begin{aligned}\mathcal{H}_U &= U \sum_{i,a} n_{a,\uparrow} n_{i,a,\downarrow} + (U' - J_{\rm H}) \sum_{i,a<b,\sigma} n_{i,a,\sigma} n_{i,b,\sigma} \\ &+ U' \sum_{i,a\neq b} n_{i,a,\uparrow} n_{i,b,\downarrow} - J_{\rm H} \sum_{i,a\neq b} c^\dagger_{i,a\uparrow} c_{i,a\downarrow} c^\dagger_{i,b\downarrow} c_{i,b\uparrow} \\ &+ J_{\rm H} \sum_{i,a\neq b} c^\dagger_{i,a\uparrow} c^\dagger_{i,a\downarrow} c_{i,b\downarrow} c_{i,b\uparrow}\end{aligned}$$

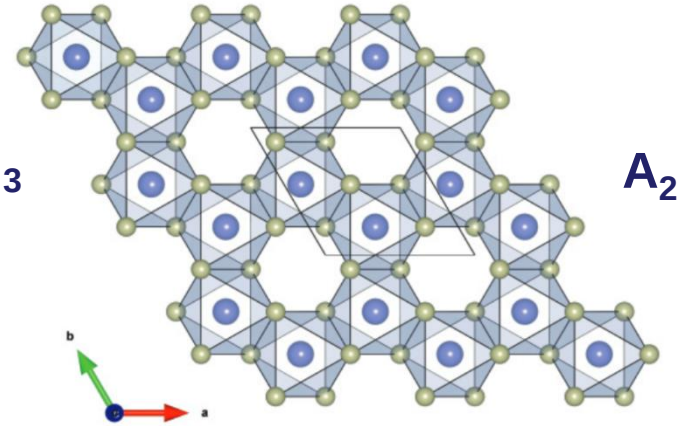
$$\mathcal{H}_{\rm hop} = -\sum_{ij} \vec{\mathbf{c}}^\dagger_i \; \{\mathbf{T}_{ij} \otimes \mathbb{I}_{2\times 2}\} \; \vec{\mathbf{c}}_j$$

$$\mathcal{H}_{\rm CF} = -\sum_{i} \vec{\mathbf{c}}^\dagger_i \; \{\mathbf{E}_{i} \otimes \mathbb{I}_{2\times 2}\} \; \vec{\mathbf{c}}_i$$

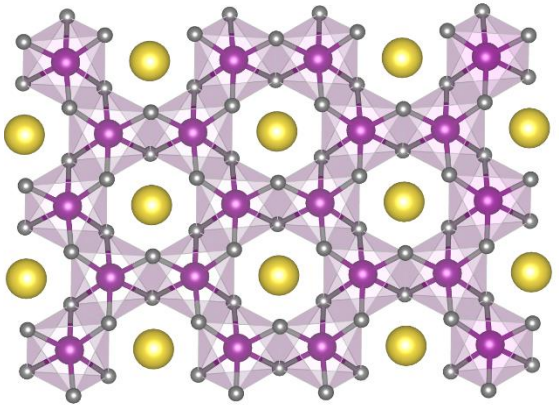
$$\mathcal{H}_{\rm SO} = \frac{\lambda}{2} \sum_i \vec{\mathbf{c}}^\dagger_i \begin{pmatrix} 0 & -i\sigma_z & i\sigma_y \\ i\sigma_z & 0 & -i\sigma_x \\ -i\sigma_y & i\sigma_x & 0 \end{pmatrix} \vec{\mathbf{c}}_i$$

Example: *Kitaev* Materials

α-$RuCl_3$



A_2IrO_3 (A = Li, Na)



$$\mathcal{H} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \cdot \mathbf{\Gamma}_{ij} \cdot \mathbf{S}_j$$

(Isotropic Heisenberg Exchange)

(Dzyaloshinskii-Moriya Term)

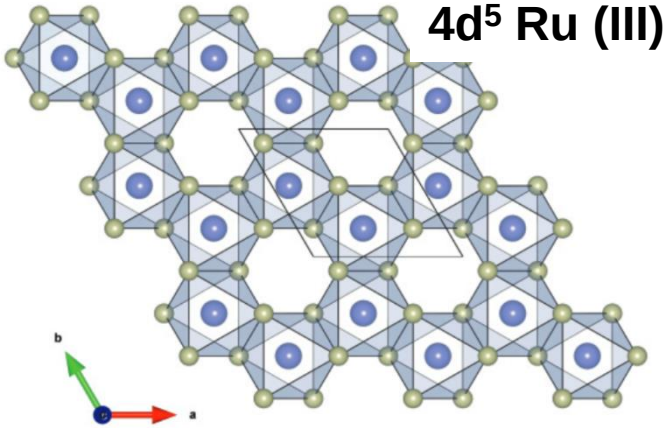
(Symmetric Term)

strongest interaction

bond-dependent

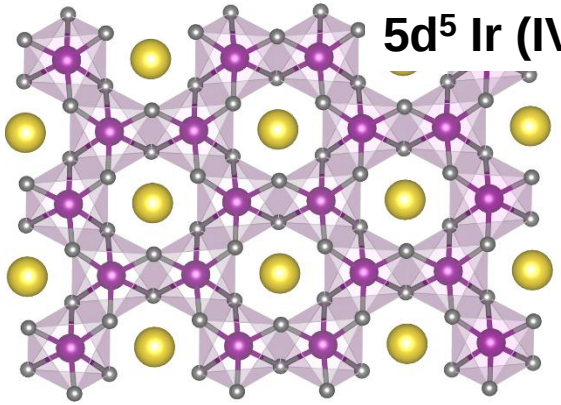
$$\mathcal{H} = K S_i^\gamma S_j^\gamma$$

Real materials



$4d^5$ Ru (III)

α-$RuCl_3$



$5d^5$ Ir (IV)

A_2IrO_3 (A = Li, Na)

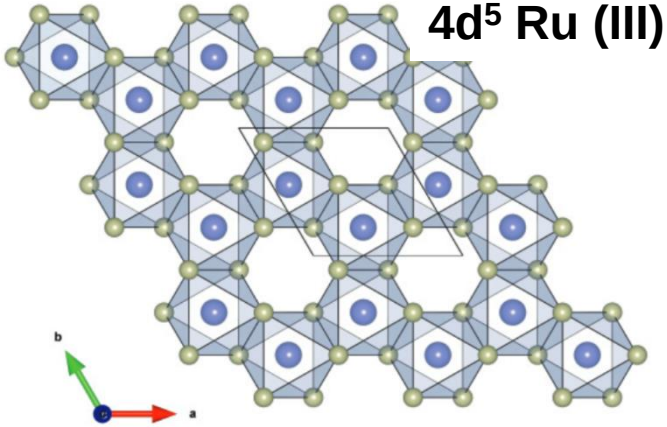
- IrO_6 crystal-field splitting t_{2g}-e_g ~ 2-3eV
- Δ_T trigonal-field splitting ~ 75meV
- t2g bandwidth W ~ 1.5eV
  - O-assisted hoppings
  - direct hoppings
- **spin-orbit coupling** λ ~ 0.5eV
- Hubbard U ~ 1 – 2 eV
- Hund's coupling J_H ~ 0.5 eV

Mazin, Jeschke, Foyevtsova, Valenti, Khomskii PRL 109, 197201 (2012)

Foyevtsova, Jeschke, Mazin, Khomskii ,Valenti PRB 88, 035107 (2013)

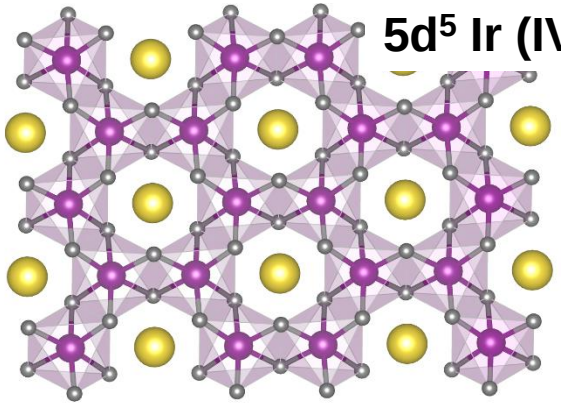
Quasi-molecular orbitals

Itinerant description



$4d^5$ Ru (III)

α-$RuCl_3$

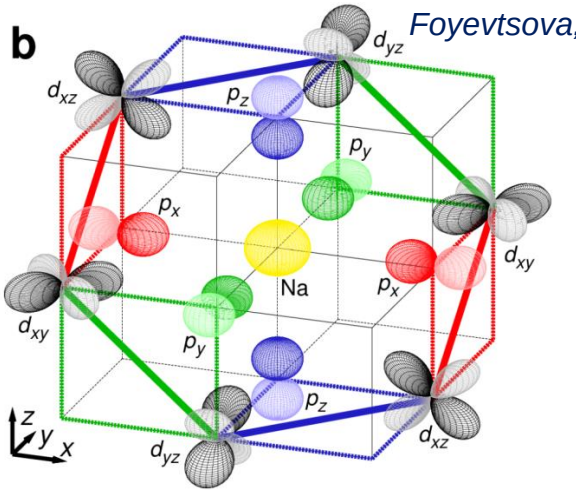


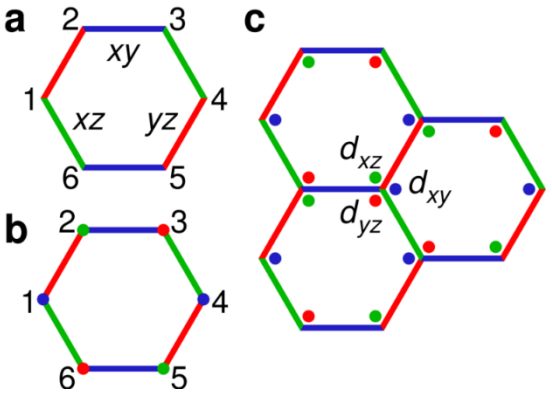
$5d^5$ Ir (IV)

A_2IrO_3 (A = Li, Na)

Mazin, Jeschke, Foyevtsova, Valenti, Khomskii PRL 109, 197201 (2012)

Foyevtsova, Jeschke, Mazin, Khomskii ,Valenti PRB 88, 035107 (2013)





“quasi-molecular orbitals” QMO

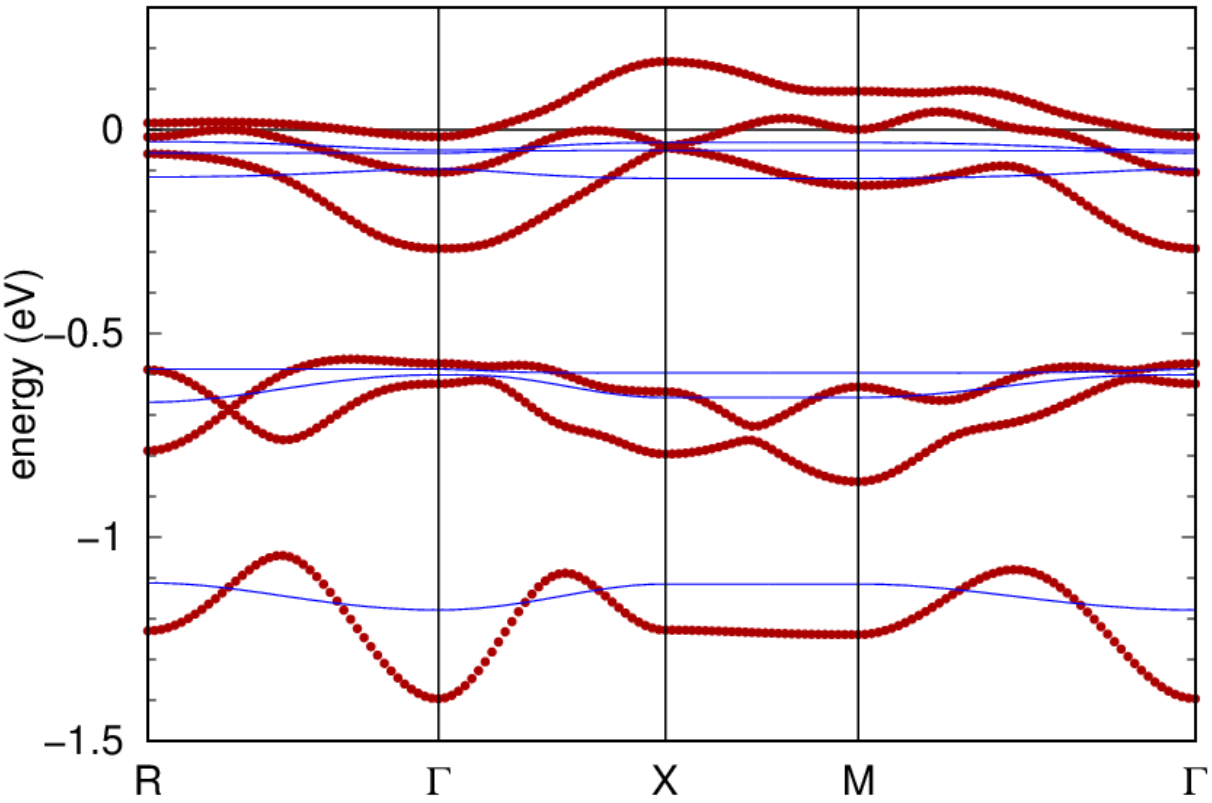
linear combination of the 6 states on a particular hexagon

The GGA hamiltonian is diagonal in this basis

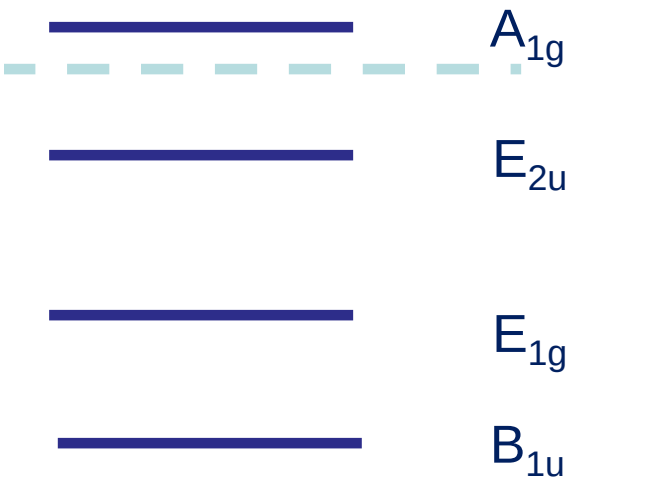
Na_2IrO_3: electronic structure

DFT non-relativistic calculation: one electron hoppings (FPLO)

+ **projective Wannier functions**



molecular orbital states:



Non-relativistic DFT bandstructure

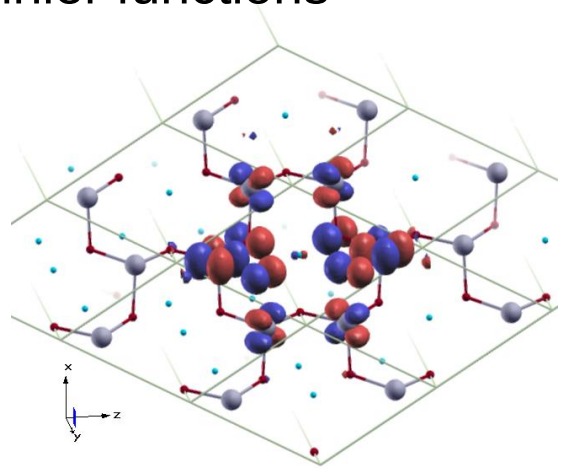
Contribution of molecular orbitals:

n.n. + n.n.n hoppings + trigonal distortion

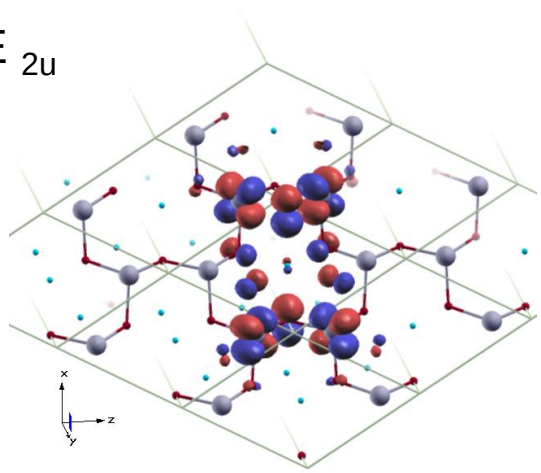
Na_2IrO_3: calculated quasi-molecular orbitals

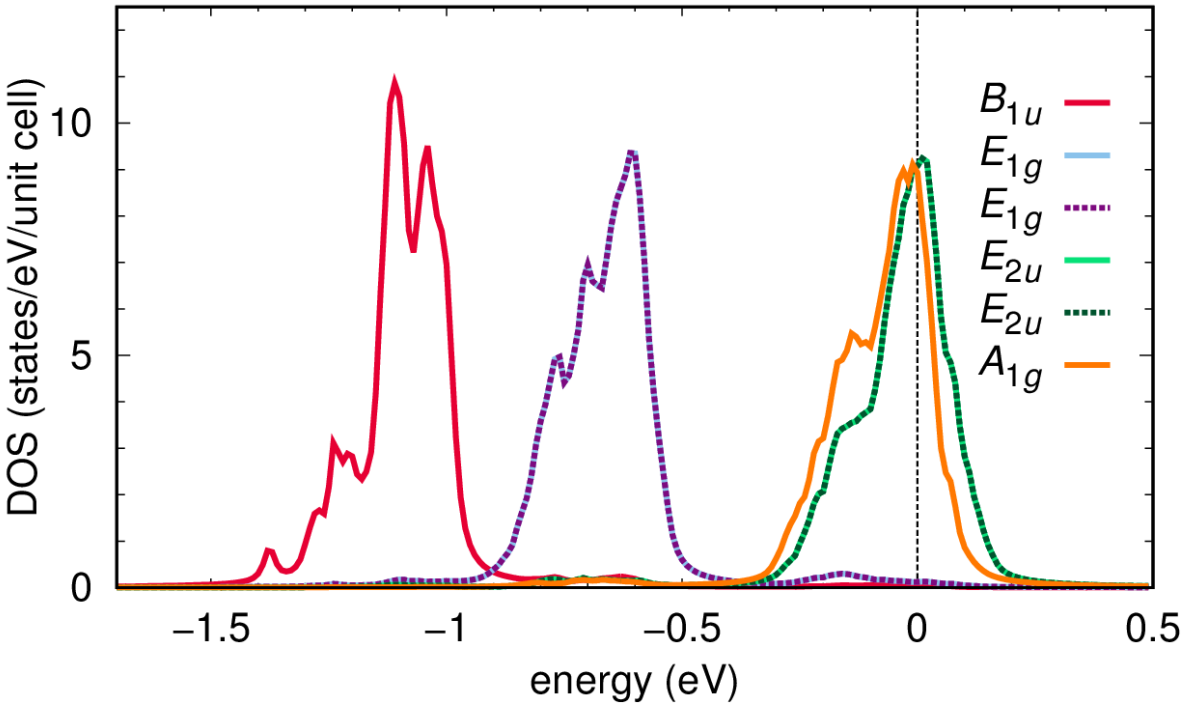
- Wannier functions

A_{1g}

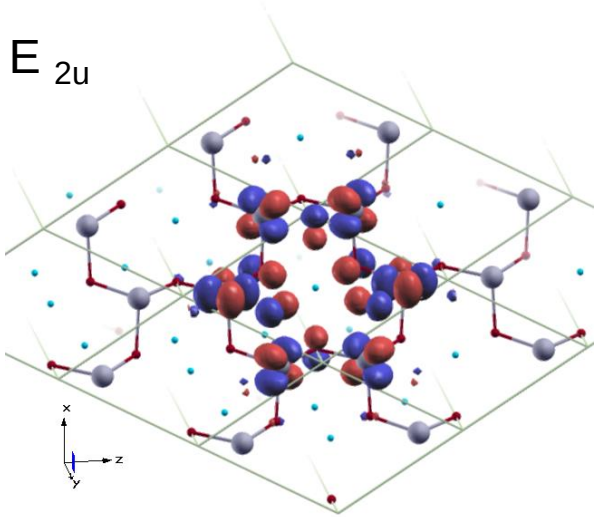


E_{2u}



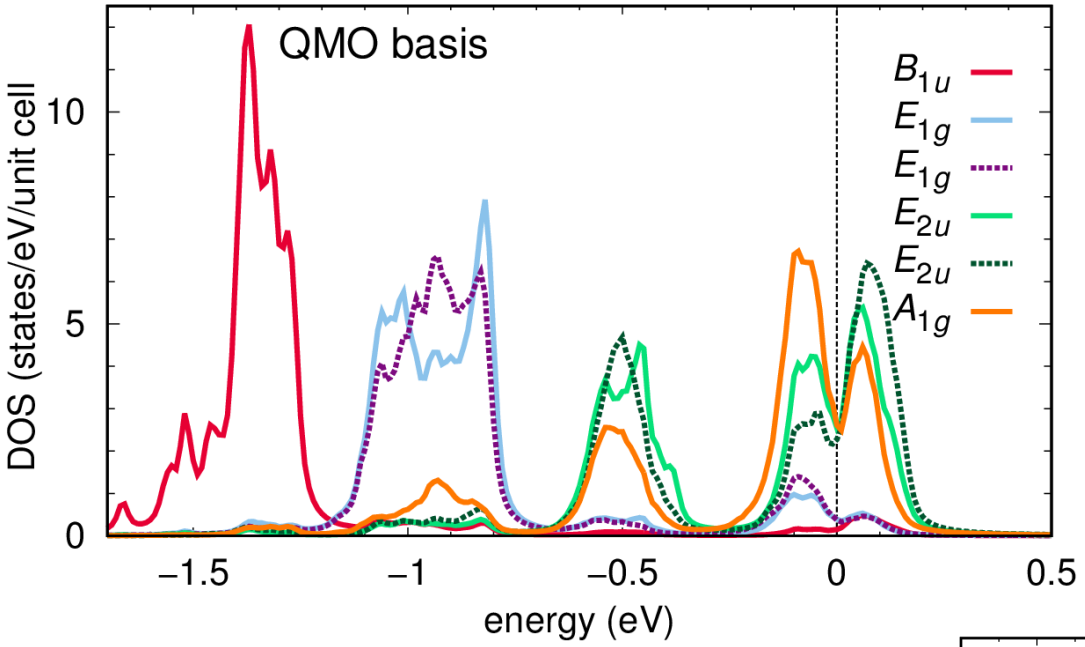


E_{2u}



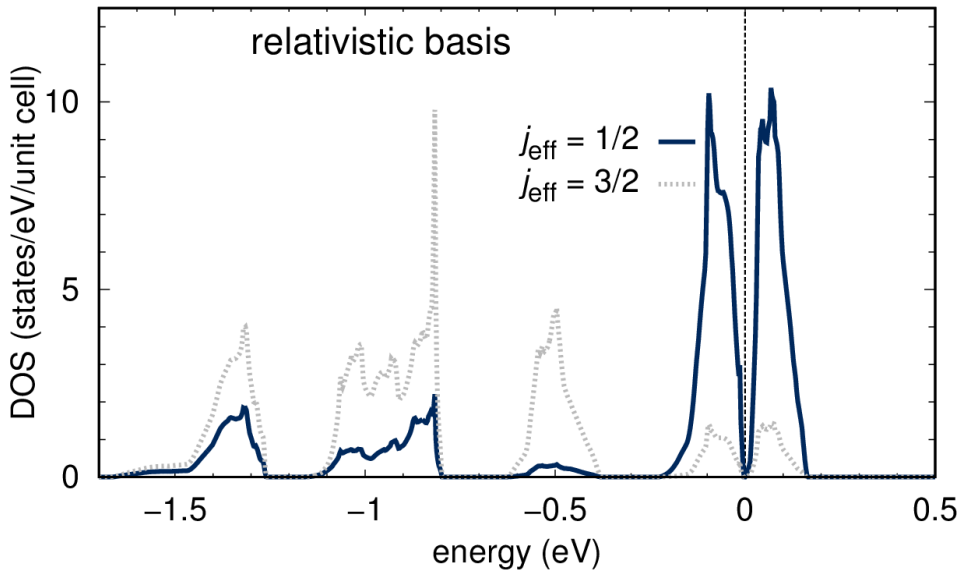
Na_2IrO_3: spin-orbit coupling

- states at the Fermi level in **relativistic** DFT calculations:



$j_{eff}=1/2, j_{eff}^{z}=1/2> =$
$(|xy\uparrow>+ |yz\downarrow> + i\ |xz\downarrow>)/\sqrt{3}$

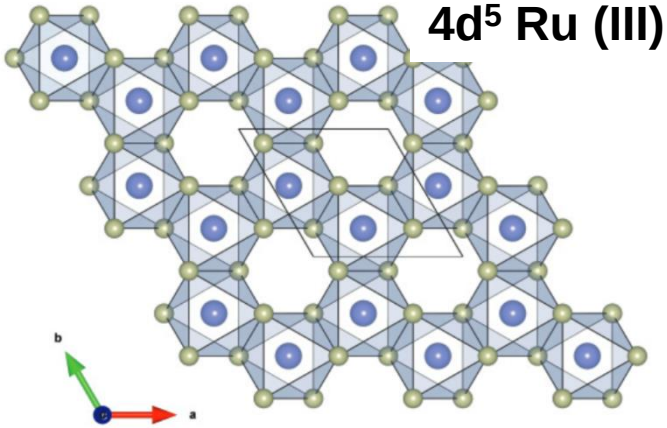
$j_{eff}=1/2, j_{eff}^{z}=-1/2> =$
$(-|xy\downarrow>+ |yz\uparrow> - i\ |xz\uparrow>)/\sqrt{3}$



Hubbard U: widens the gap

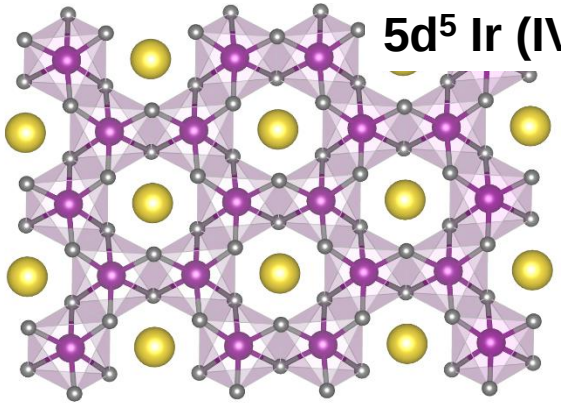
RIXS: H. Gretarsson et al. PRL (2013)
j_{eff}=1/2, j_{eff}=3/2

localized description



4d^5 Ru (III)

α-RuCl$_3$

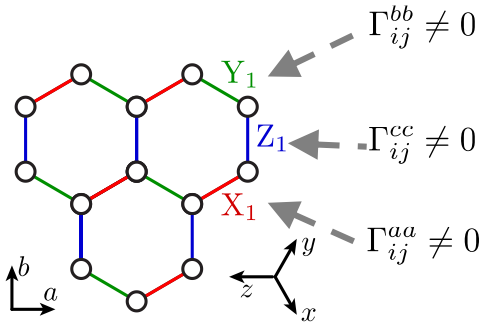


5d^5 Ir (IV)

A$_2$IrO$_3$ (A = Li, Na)

- Due to **competing energy scales**, difficult to optimize Kitaev interactions:

$$\mathcal{H} = K S_i^\gamma S_j^\gamma \qquad K \sim \frac{J_H t^2}{(2U + 3\lambda)^2}$$



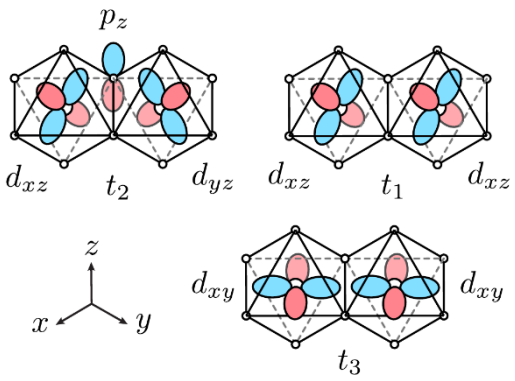
- **Distortions** and **direct metal-metal hopping** give additional interactions:

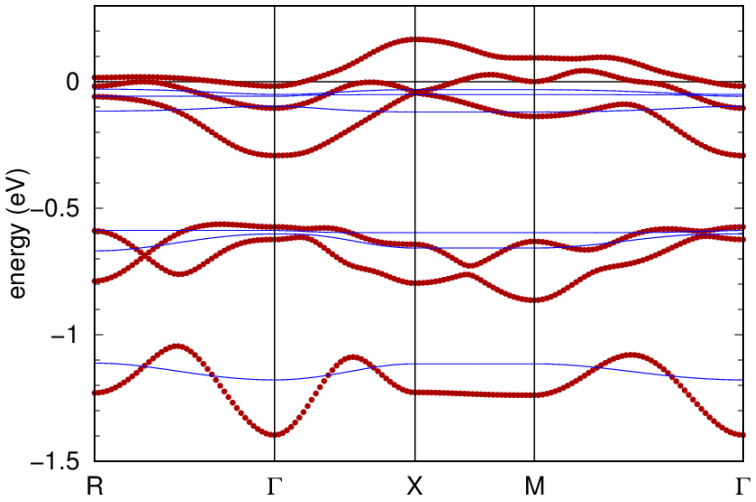
$$\mathcal{H} = \begin{pmatrix} S_i^x & S_i^y & S_i^z \end{pmatrix} \begin{pmatrix} J & \Gamma & \Gamma' \\ \Gamma & J & \Gamma' \\ \Gamma' & \Gamma' & J+K \end{pmatrix} \begin{pmatrix} S_j^x \\ S_j^y \\ S_j^z \end{pmatrix}$$

- Remanent itinerancy makes **second** and **third neighbour interactions** much more important.

Ab initio-based Kitaev Honeycomb Model

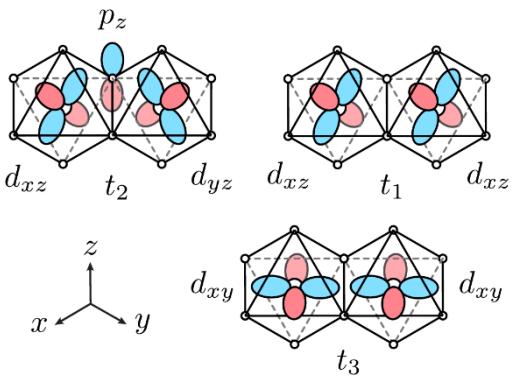
1. Obtain hopping integrals from DFT:

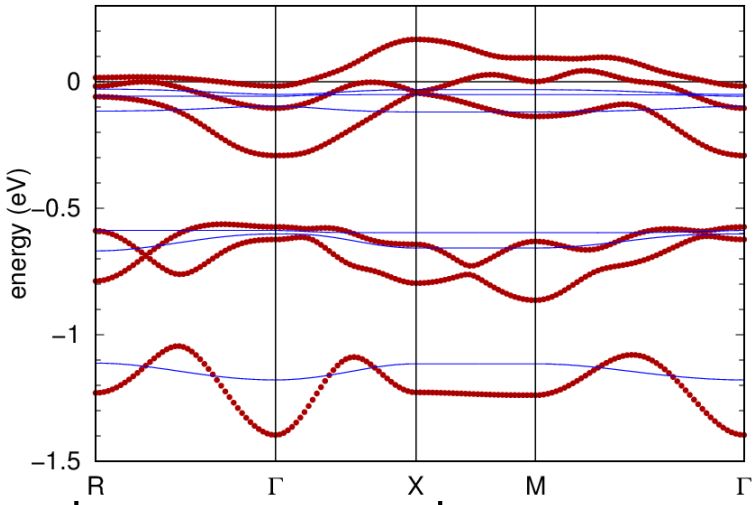




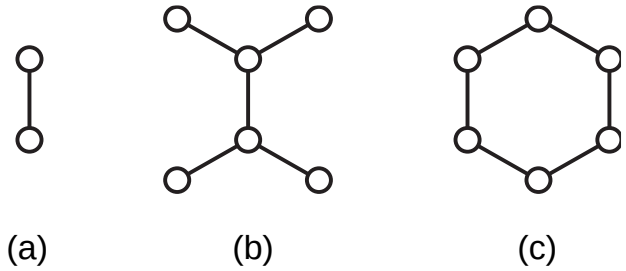
Ab initio-based Kitaev Honeycomb Model

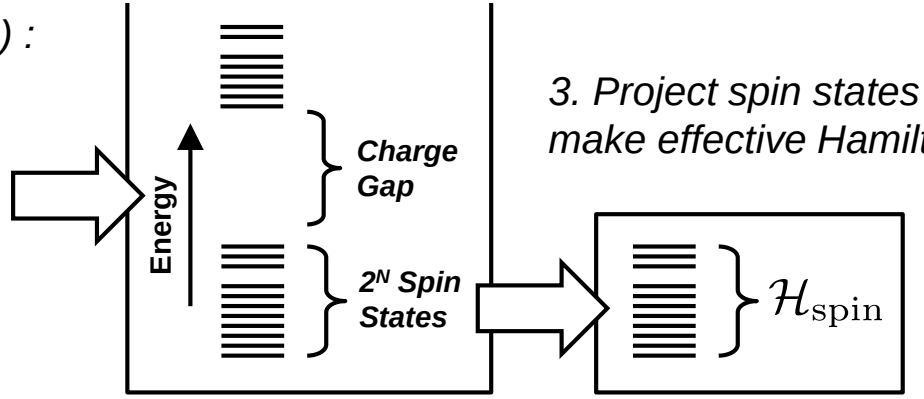
1. Obtain hopping integrals from DFT:





2. Exactly diagonalize full t_{2g} model (hopping + SOC + Hund + Coulomb) :





3. Project spin states to make effective Hamiltonian:

◆ H_{spin} reproduces **exact spectrum** and respects **all symmetries** of t_{2g} cluster model.

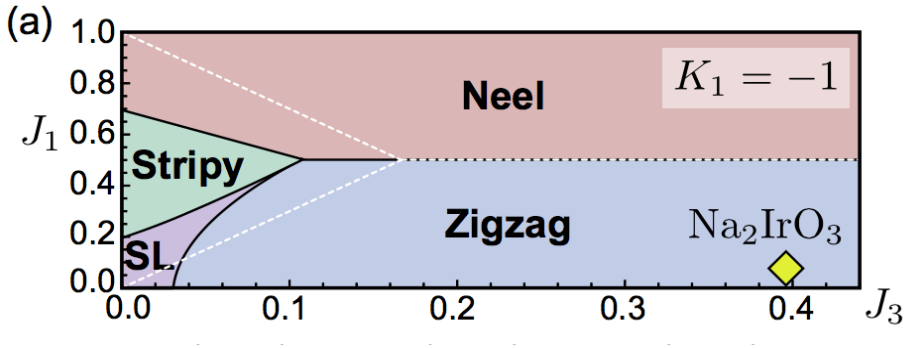
Winter.Li.Jeschke.Valenti PRB 93. 214431 (2016)

Winter,Riedl,Maximov,Chernyshev,Honecker,Valenti Nature Comm. 8, 1152 (2017)

Ab initio-based Kitaev Honeycomb Model

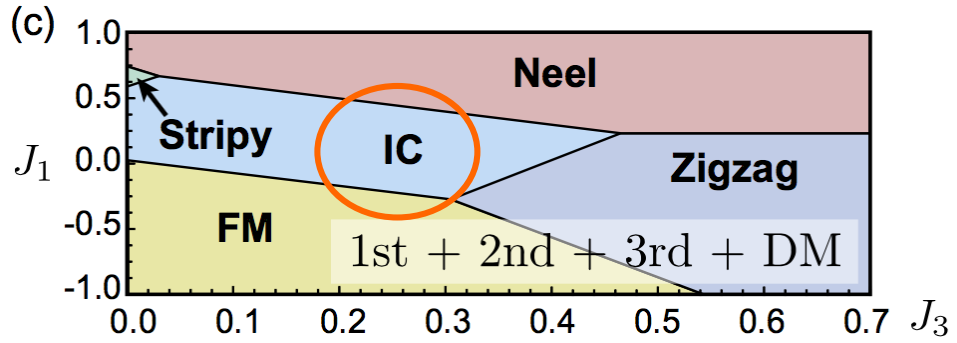
Na_2IrO_3

- Kitaev terms dominant at first neighbour.
- Zigzag order enforced by large J_3.
- $\chi_{||} < \chi_{\perp}$ from small off-diagonal terms.



α-Li_2IrO_3

- Spiral order from 2nd neighbour DM, anisotropic interactions.
- $\chi_{||} > \chi_{\perp}$ from large off-diagonal terms.



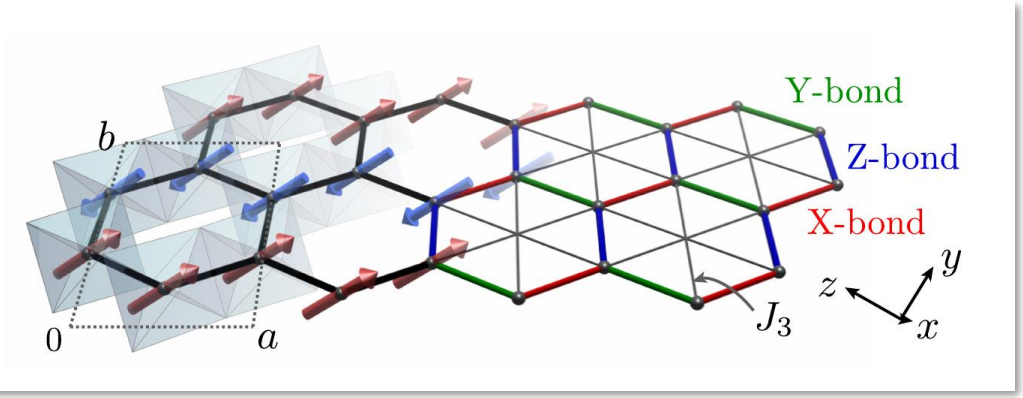
Minimal model

$$\mathcal{H} = \sum_{\langle i,j \rangle} J_1 \ \mathbf{S}_i \cdot \mathbf{S}_j + K_1 S_i^{\gamma} S_j^{\gamma} + \Gamma_1 (S_i^{\alpha} S_j^{\beta} + S_i^{\beta} S_j^{\alpha})$$

$$+ \sum_{\langle\langle\langle i,j \rangle\rangle\rangle} J_3 \ \mathbf{S}_i \cdot \mathbf{S}_j$$

Ab initio-based Kitaev Honeycomb Model

α-$RuCl_3$



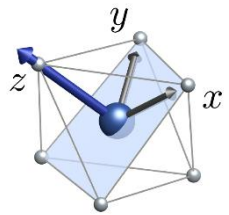
- Zigzag order enforced by large J_3.
- Large off-diagonal Γ_1 terms.
- $\chi_{||} > \chi_{\perp}$ from large Γ_1 terms.

Minimal model

$$\mathcal{H} = \sum_{\langle i,j \rangle} J_1 \, \mathbf{S}_i \cdot \mathbf{S}_j + K_1 S_i^{\gamma} S_j^{\gamma} + \Gamma_1 (S_i^{\alpha} S_j^{\beta} + S_i^{\beta} S_j^{\alpha}) + \sum_{\langle\langle\langle i,j \rangle\rangle\rangle} J_3 \, \mathbf{S}_i \cdot \mathbf{S}_j$$

observed moment direction→departure from Kitaev
Chaloupka,Khaliullin PRB 92, 024413 (2015)

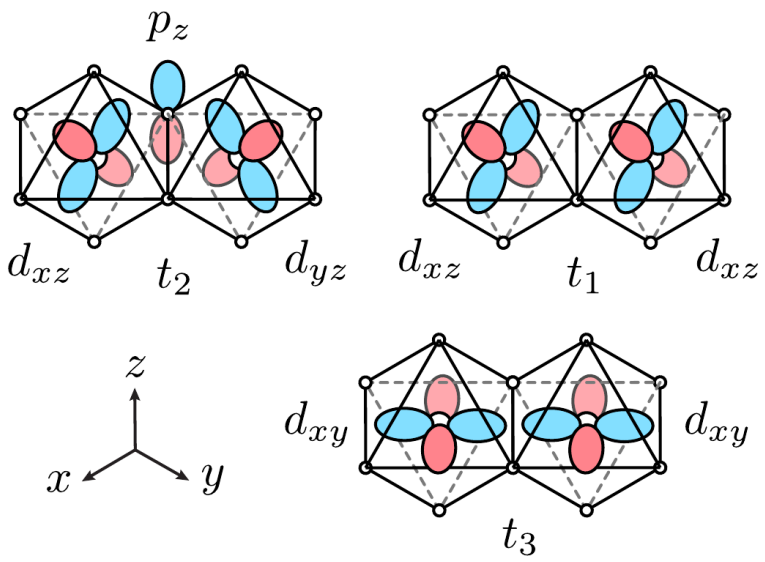
J_1 = -0.5, K_1 = -5.0, Γ_1 = +2.5, J_3 = +0.5 meV



Frankfurt/IFW Dresden/Toronto

Kitaev Honeycomb Model – Complete Models

- Interactions very sensitive to bonding geometry.



$$J_{ij} = \frac{4\mathbb{A}}{9}(2t_1 + t_3)^2 - \frac{8\mathbb{B}}{9}\left\{9t_4^2 + 2(t_1 - t_3)^2\right\}$$

$$K_{ij} = \frac{8\mathbb{B}}{3}\left\{(t_1 - t_3)^2 + 3t_4^2 - 3t_2^2\right\}$$

$$\Gamma_{ij} = \frac{8\mathbb{B}}{3}\left\{2t_2(t_1 - t_3) + 3t_4^2\right\}$$

$$\Gamma'_{ij} = \frac{8\mathbb{B}}{3}\left\{t_4(3t_2 + t_3 - t_1)\right\}$$

Winter,Li,Jeschke,Valenti PRB 93, 214431 (2016)

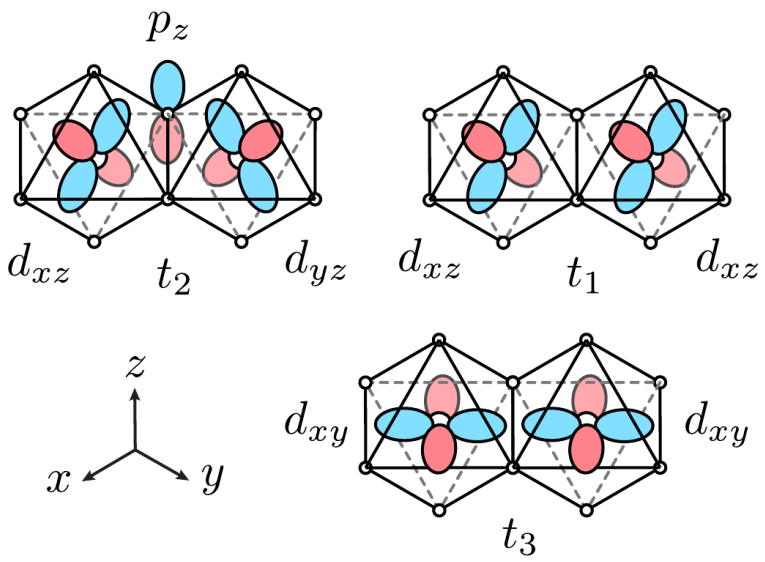
Rau, Lee, Kee PRL 112, 077204 (2014)

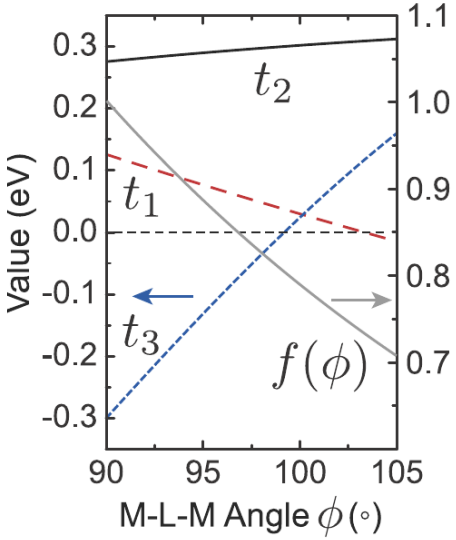
A ~ 1/U B ~ $J_H/3U^2$

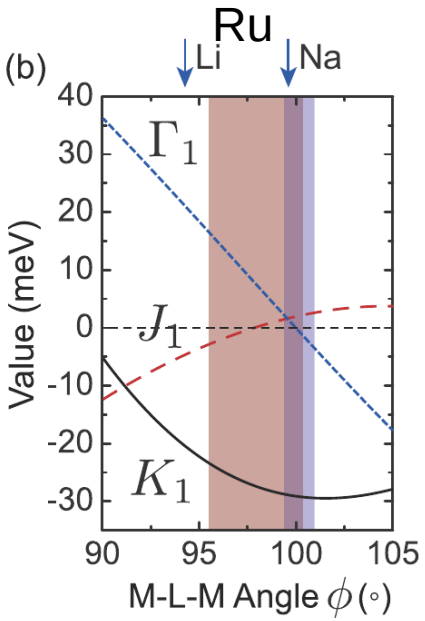
Winter,Tsirlin,Daghofer,van den Brink,Singh,Gegenwart,Valenti Review (2018)

Kitaev Honeycomb Model – Complete Models

- Interactions very sensitive to bonding geometry.







$$J_{ij} = \frac{4\mathbb{A}}{9}(2t_1 + t_3)^2 - \frac{8\mathbb{B}}{9}\{9t_4^2 + 2(t_1 - t_3)^2\}$$

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Winter,Li,Jeschke,Valenti PRB 93, 214431 (2016)

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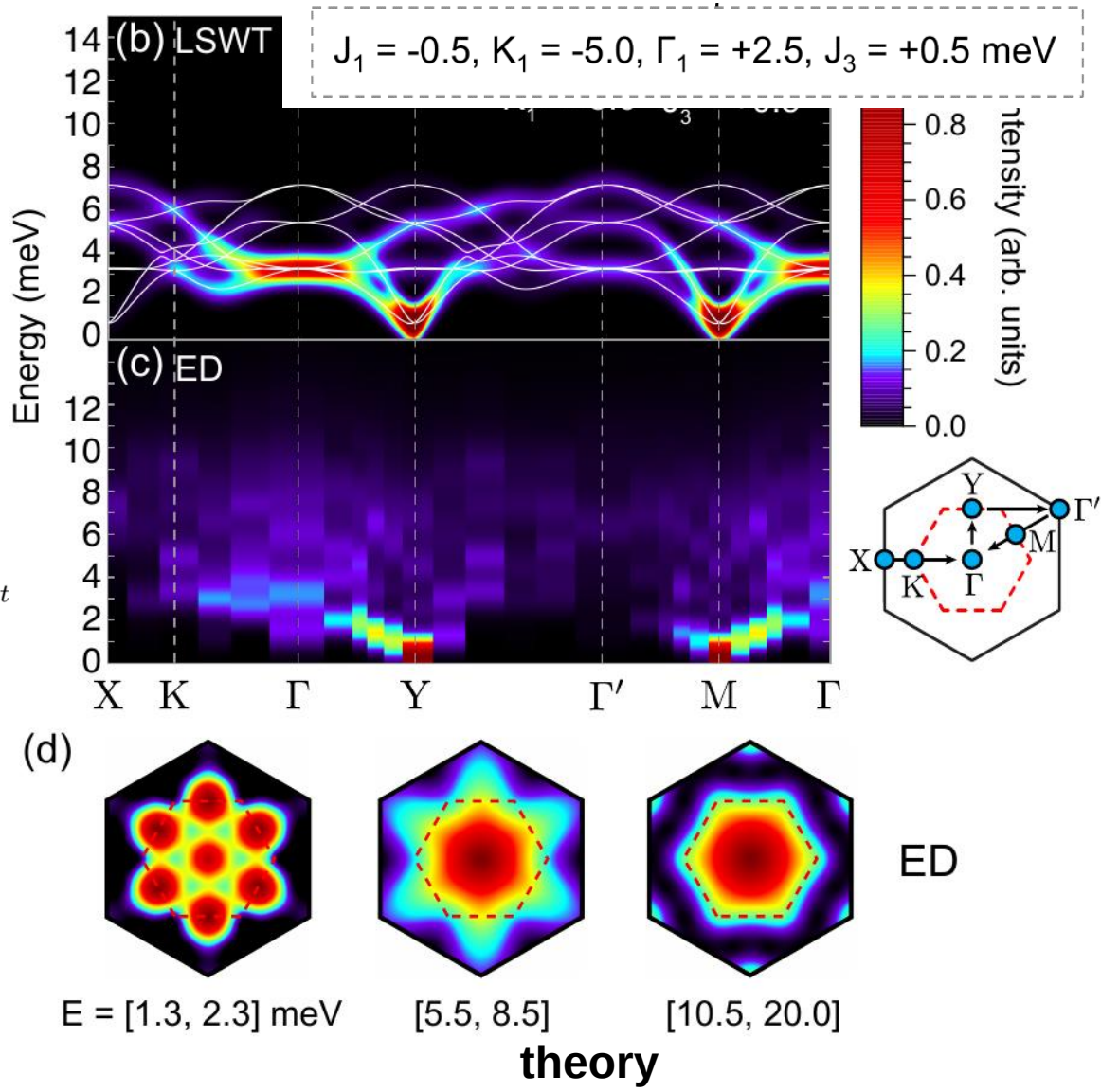
ordered phase

Excitations – INS α-$RuCl_3$

Exact Diagonalization (ED)

$$\mathcal{I}(\mathbf{k},\omega) \propto f^2(\mathbf{k}) \int dt \sum_{\mu,\nu} (\delta_{\mu,\nu} - k_\mu k_\nu / k^2) \times$$
$$\times \sum_{i,j} \langle S_i^\mu(t) S_j^\nu(0) \rangle e^{-i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j) - i\omega t}$$



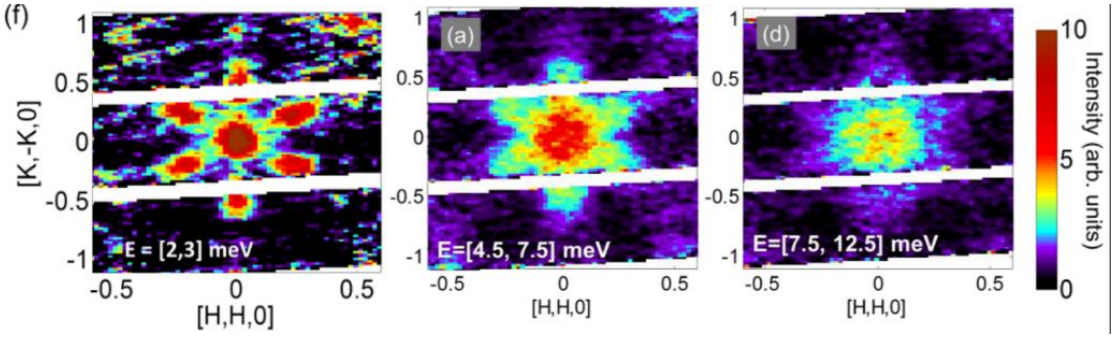
ordered phase

Excitations – INS α-$RuCl_3$

J_1 = -0.5, K_1 = -5.0, Γ_1 = +2.5, J_3 = +0.5 meV

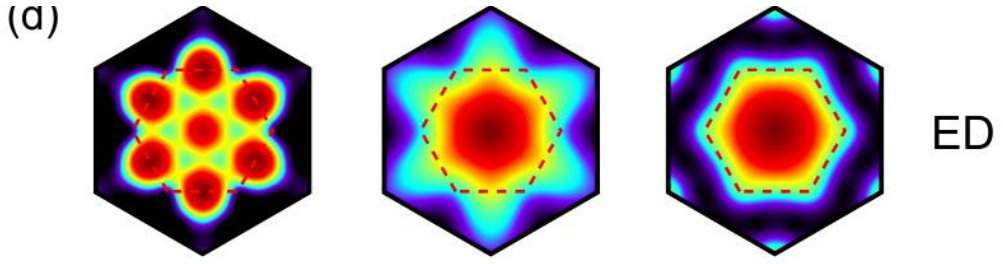
experiment

Banerjee et al. Science 356, 1055 (2017)



Nature of the continuum?

Majorana excitations?
←→
multimagnon decay?

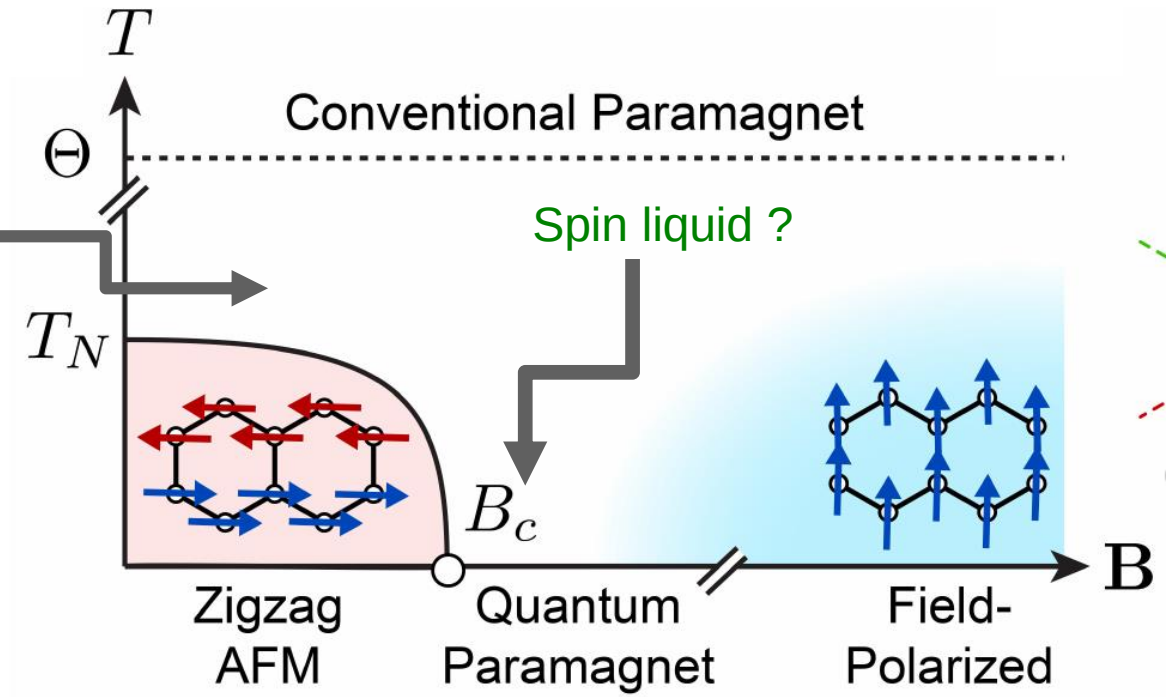


theory

Nature of excitations and magnetic field effects α-$RuCl_3$

Winter,Riedl,Maximov,Chernyshev,Honecker,Valenti Nature Comm. 8, 1152 (2017)

$$\mathcal{H} = \sum_{\langle ij \rangle} J_1 \, \mathbf{S}_i \cdot \mathbf{S}_j + K_1 S_i^\gamma S_j^\gamma + \Gamma_1 \left(S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha \right) + \sum_{\langle\langle\langle ij \rangle\rangle\rangle} J_3 \, \mathbf{S}_i \cdot \mathbf{S}_j - \mu_B \sum_i \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}_i$$



majorana excitations ←→ Breakdown of magnons excitation?

Kitaev model → Γ model

Gohlke et al. PRB 97, 075126 (2018)

Barnejee et al. npj Quant. Mat. 3, 8 (2018)

Rousochatzakis, Perkins PRL 118, 147204 (2017)

Winter,Riedl,Kaib,Coldea,Valenti PRL 120, 077203 (2018)

Summary

- ***Microscopic description of frustrated magnetic materials***

→ ***from first principles to spin model Hamiltonians***

$$\mathcal{H} = J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \cdot \mathbf{\Gamma}_{ij} \cdot \mathbf{S}_j$$

- ***Predict systems with unconventional properties***

Challenges and opportunities ?

Collaborators

Theory:

Steve Winter (Frankfut)
Ying Li (Frankfurt)
Kira Riedl (Frankfurt)
David Kaib (Frankfurt)
Harald Jeschke (Okayama)
Daniel Khomskii (Köln)
Igor Mazin (NRL, Washington DC)
Andreas Honecker (Paris)
Sasha Chernyshev, Pavel Maximov (UC Irvine)

Experiment:

Radu Coldea, Roger Johnson (Oxford)
Steve Blundell, Franz Lang (Oxford)
Cornelius Krellner (Frankfurt)
Philipp Gegenwart (Augsburg)

Financial support: German Science Foundation DFG