RSF Russian Science Foundation

Orbital degrees of freedom
in condensed matter physics

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THE BEATLES

ORBITALS: HERE, THERE AND EVERYWHERE

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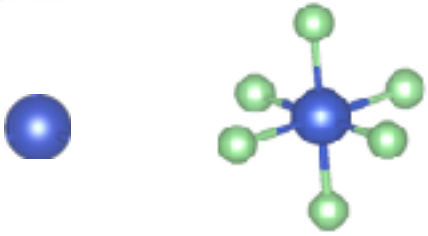
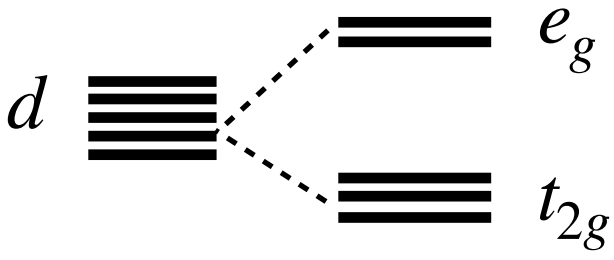
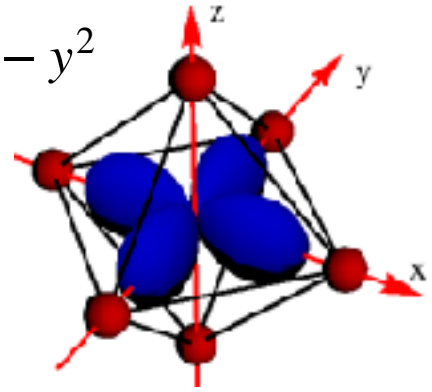
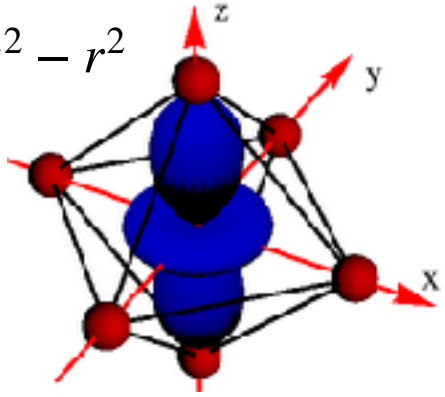
Introduction: *d*-orbitals in a crystal, cubic harmonics





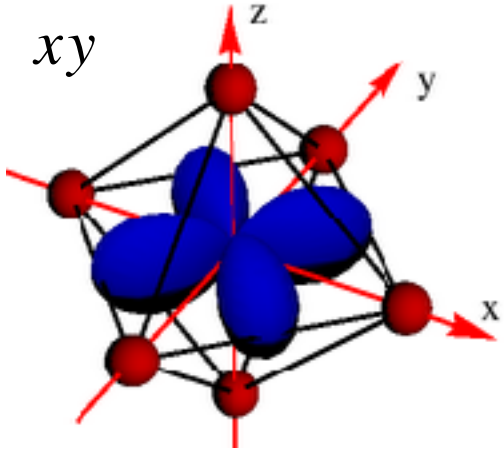
e_g

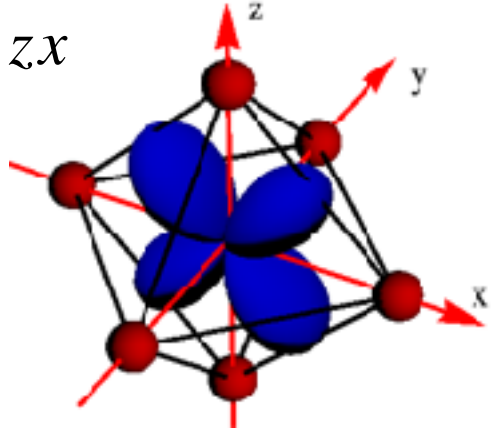


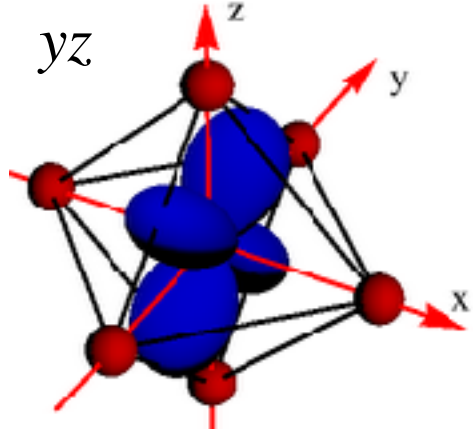


Directed **to** ligands

t_{2g}



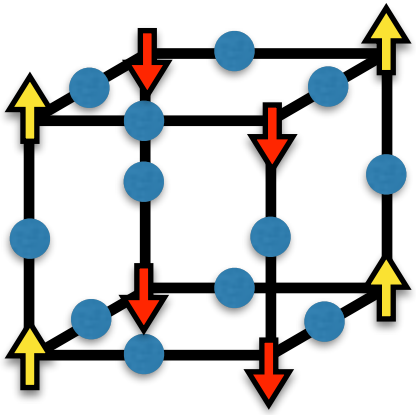




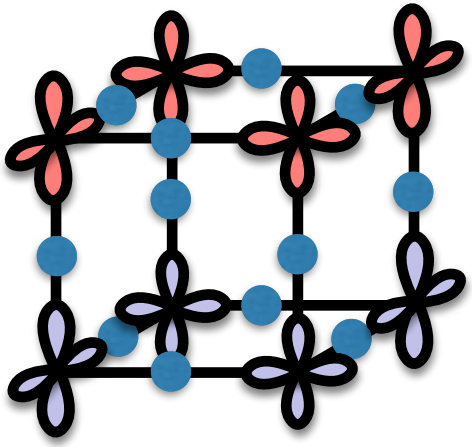
Directed **away** from ligands

Orbital degrees of freedom

Spin degrees of freedom



Orbital degrees of freedom



Math: **spin operators** $\hat{\vec{S}}$

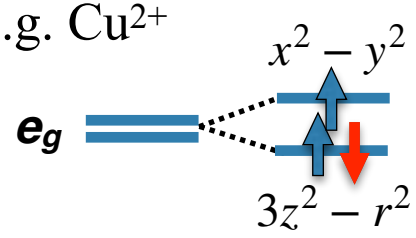
for $s = 1/2$

$$\langle \downarrow | \hat{S}^z | \downarrow \rangle = -1/2$$

$$\langle \uparrow | \hat{S}^z | \uparrow \rangle = 1/2$$

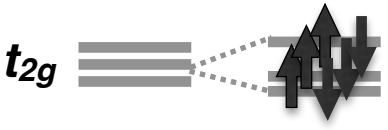
pseudospin operators $\hat{\vec{\tau}}$

e.g. Cu^{2+}



$$\langle x^2 - y^2 | \hat{\tau}^z | x^2 - y^2 \rangle = -1/2$$

$$\langle z^2 | \hat{\tau}^z | z^2 \rangle = 1/2$$



● Ligands

Orbital degrees of freedom

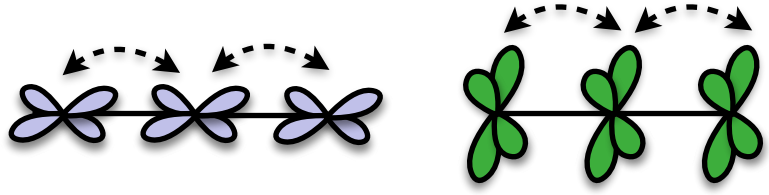
1. Orbitals are coupled with other degrees of freedom

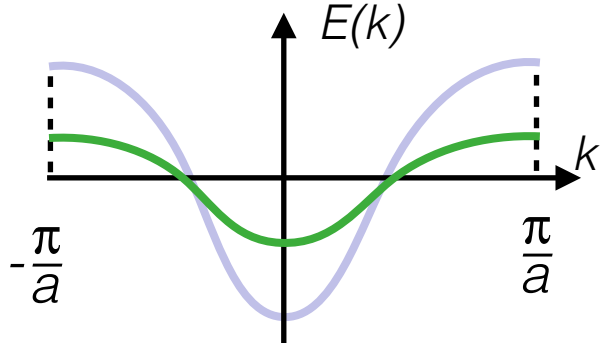
Jahn-Teller effect

Goodenough-Kanamori-Anderson rules

Kugel-Khomskii-like models

2. Orbitals have directional character





Orbital-selective Mott transition

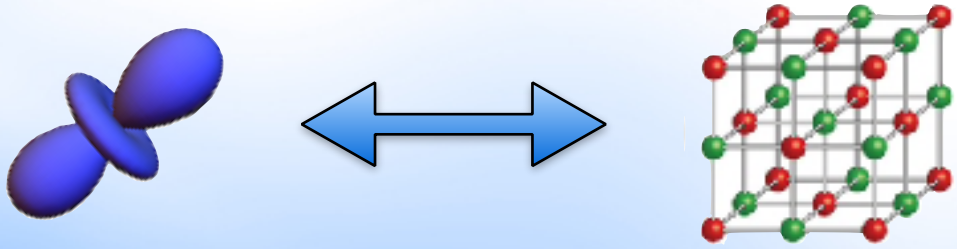
Orbital-selectivity and Magnetism

Orbitally-assisted Peierls effect

3. Spin-orbit coupling - beyond the scope of this lecture

1. Interplay of different degrees of freedom:

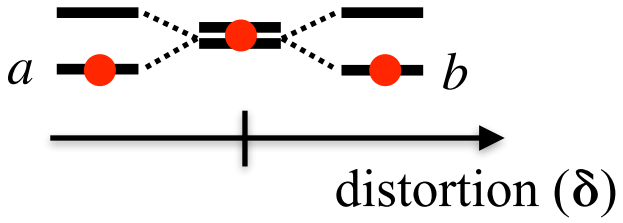
Jahn-Teller effect



Jahn-Teller effect in a nutshell

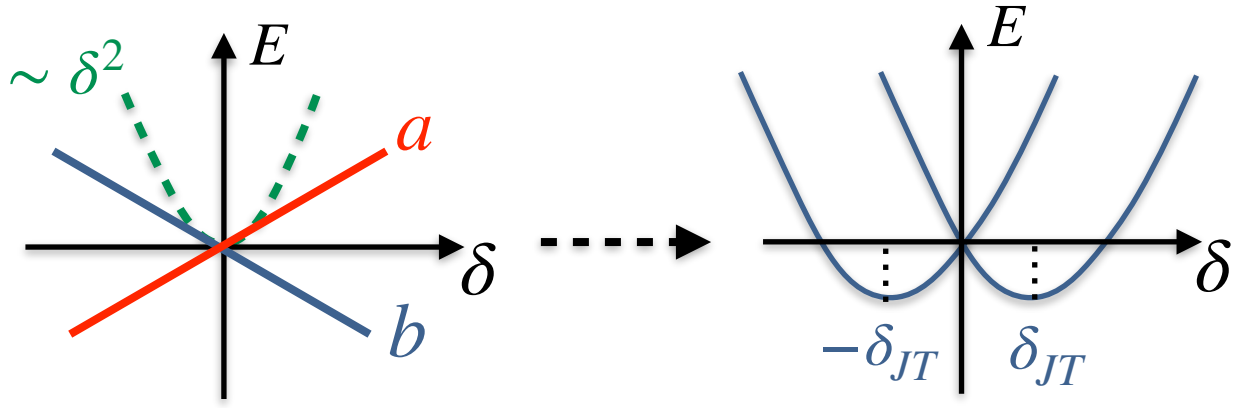
Let's consider a model two-levels (a & b) system in a certain surrounding

Idea



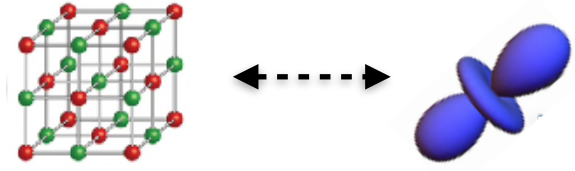
$$E_{JT} = \pm g\,|\delta|$$

Coupling with lattice



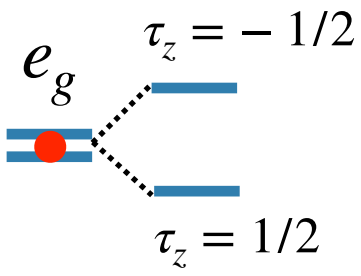
Thus, the system aims to spontaneously lift orbital degeneracy by distorting surrounding

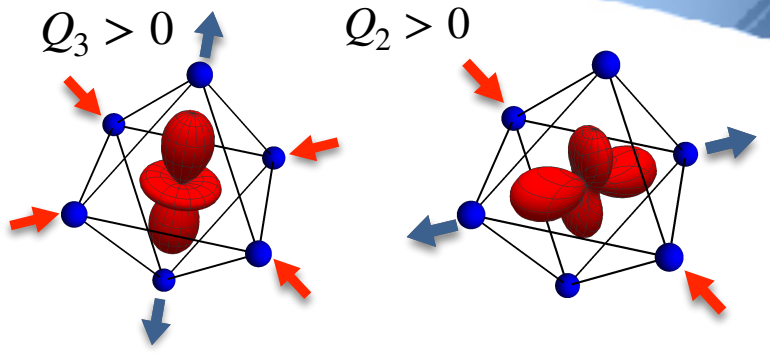
"Orbital-lattice" coupling



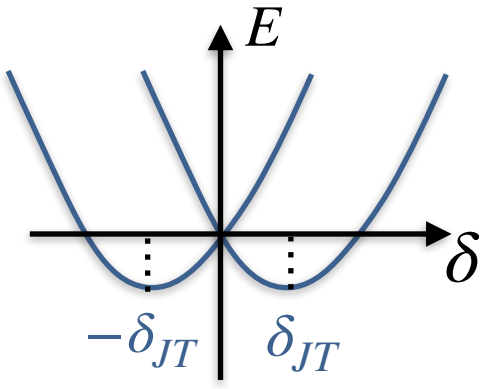
Introduction: Jahn-Teller $e \otimes E$ problem

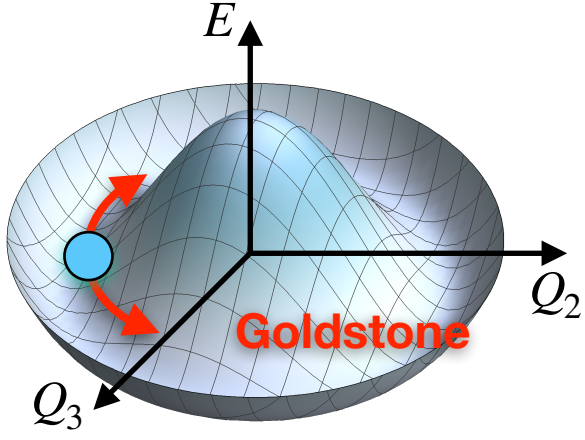
More realistic situation:
e_g-levels and E-distortions
(i.e. Q_2, Q_3)
e.g. Mn^{3+} or Cu^{2+}





$$E_{JT} = \pm g\,|\delta| + \frac{B\delta^2}{2} \quad \dashrightarrow \quad \hat{H}_{JT} = -g(\hat{\tau}_z Q_3 + \hat{\tau}_x Q_2) + \frac{B}{2}(Q_3^2 + Q_2^2)$$

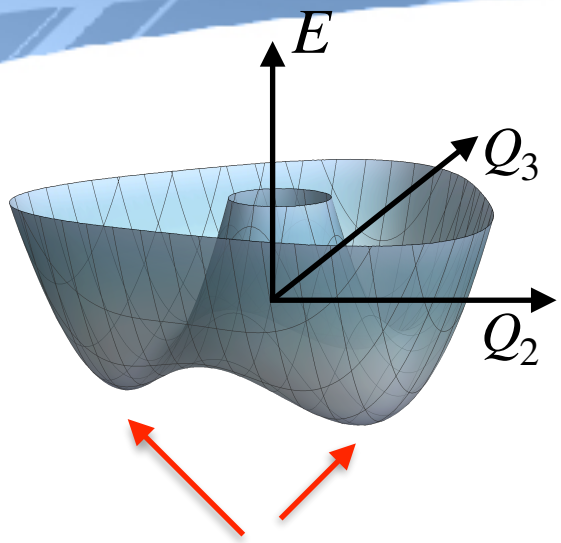




Harmonic approximation: Highly degenerate ground state

Introduction: Jahn-Teller $e \otimes E$ problem

for an isolated octahedron



Anharmonicity

	Claimed compressed	Turned out elongated
$NaMn_7O_{12}$	Nature Mat. 3, 48 (2004)	PRB 89, 201115 (2014)
$Cs_2CuCl_2Br_2$	Cryst. Gr. Des. 10, 4456 (2010)	PRB 86, 035109 (2012)

Elongated octahedra!

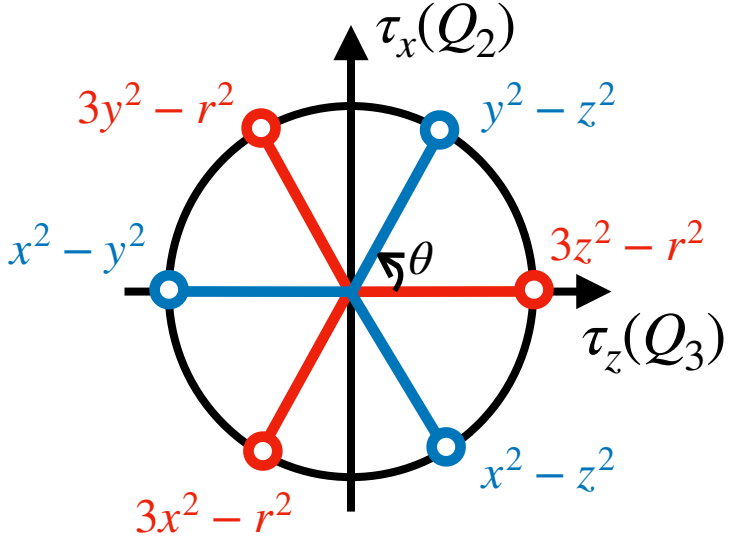
Most of octahedra with e_g-ions (Cu^{2+}, Mn^{3+}) are elongated!

Distortion ⟷ **Orbital**

Distortions: $|\theta\rangle = \cos(\theta)Q_3 + \sin(\theta)Q_2$

Orbitals: $|\theta\rangle = \cos(\theta/2)\,|z^2\rangle + \sin(\theta/2)\,|x^2 - y^2\rangle$

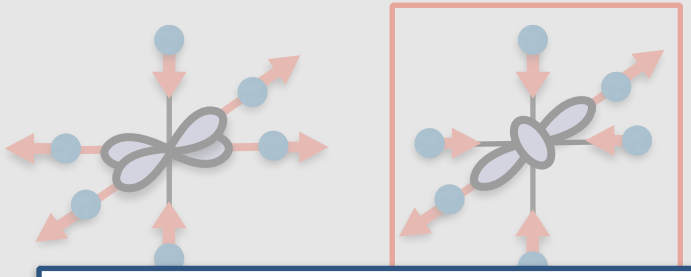
θ parametrizes both distortions and orbitals



Cooperative Jahn-Teller distortions

(electron-lattice mechanism of orbital ordering)

How to pack octahedra?



Anharmonic effects stabilize this!

We must keep V the same

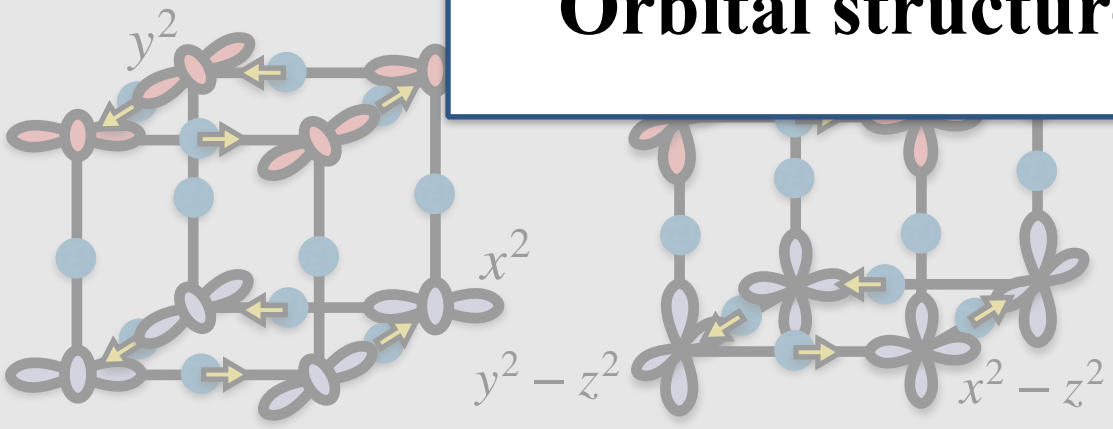
$$\sum_{i \neq j} J_{ij} \vec{\tau}_i \vec{\tau}_j \qquad J_{ij} \sim g^2/B$$

Lattice distortions

↕

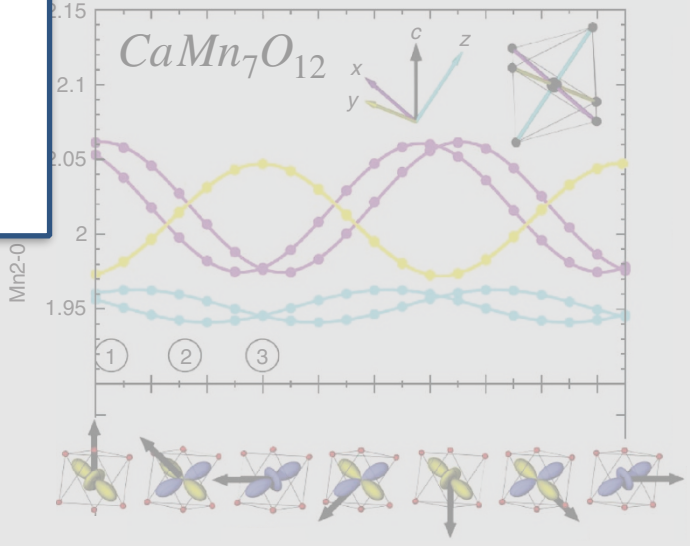
Orbital structure

$LaMnO_3$ (Mn^{3+}, e_g^1)



electrons are plotted

holes are plotted

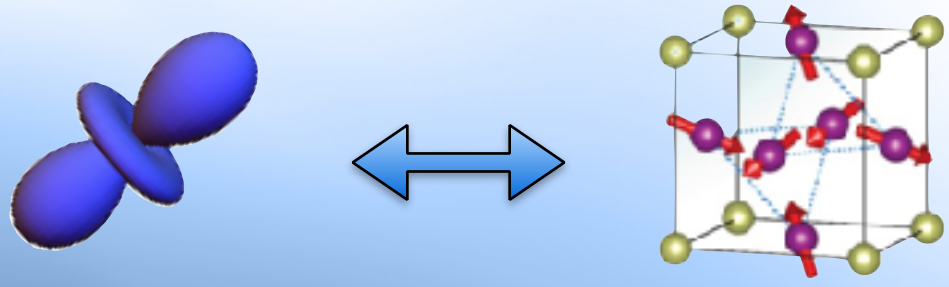


N. Perkins et al., Nature Communications 3, 1277 (2012)

1. Interplay of different degrees of freedom:

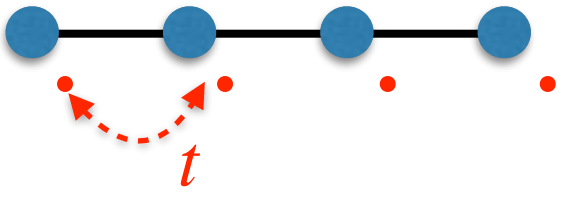
Orbitals - Magnetism

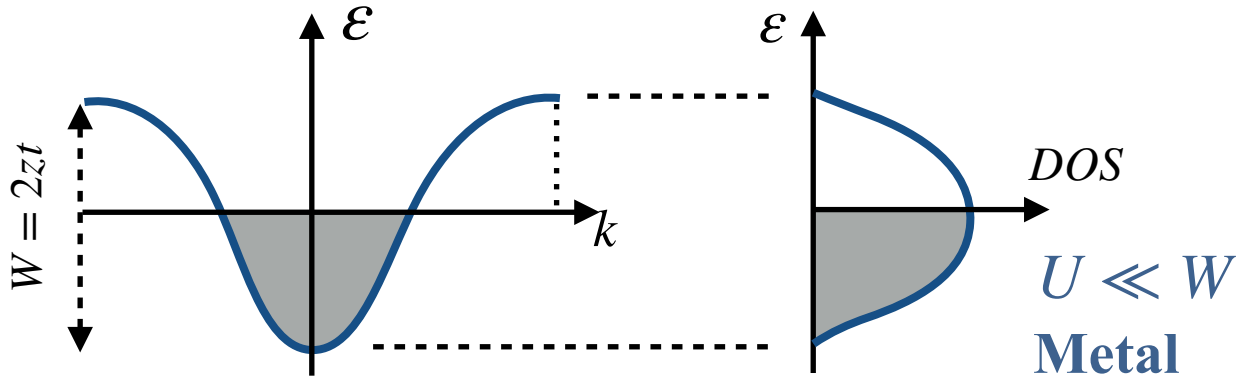
(Kugel-Khomskii-like models)



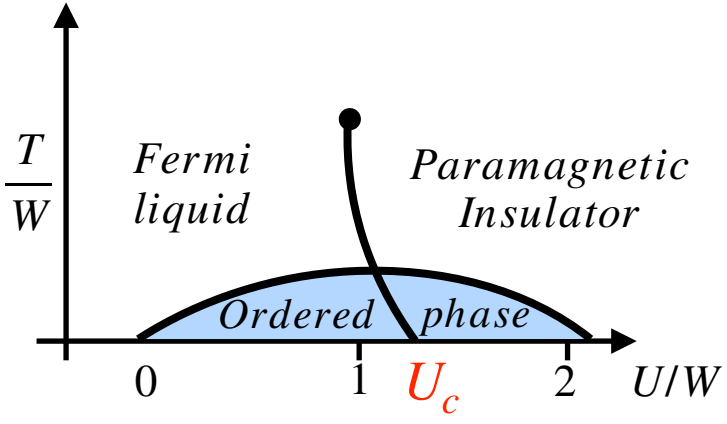
Mott-Hubbard transition in a nutshell

$$H_{kin} = -t \sum_{\langle ij \rangle \sigma} c^{\dagger}_{i\sigma} c_{j\sigma} \xrightarrow{\text{Fourier}} \sum_{\mathbf{k}\sigma} \varepsilon(\mathbf{k}) c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}$$

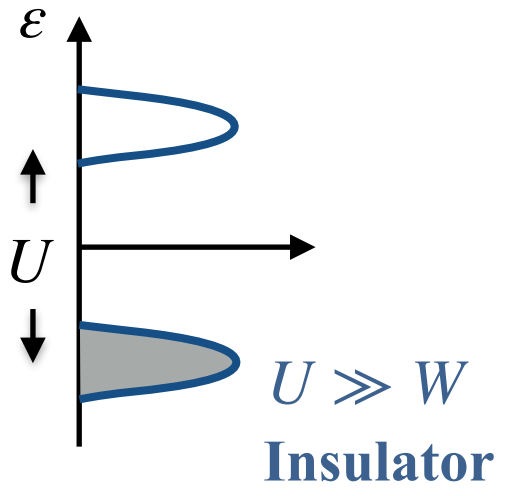




Hubbard model: $H = -t \sum_{\langle ij \rangle \sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$



Metal-Insulator (Mott-Hubbard) transition!

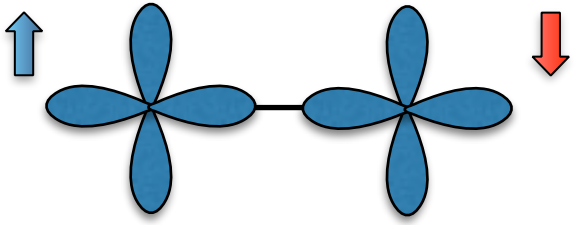


U - on-site Coulomb repulsion

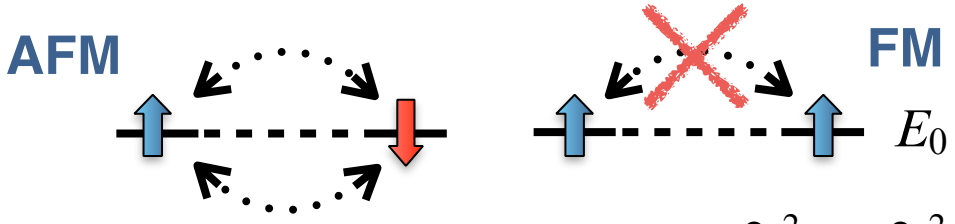
Introduction: Orbitals and spins

Heisenberg model: $\hat{H} = J \sum_{i \neq j} \hat{\vec{S}}_i \hat{\vec{S}}_j$

Ferro-orbital order



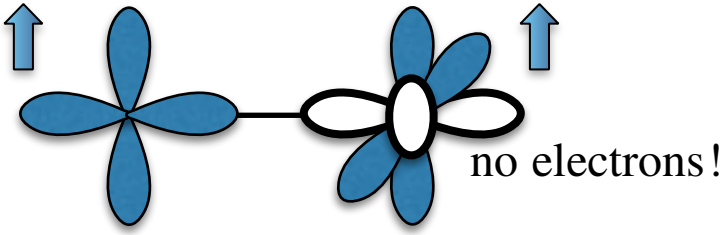
1 electron per orbital 1 electron per orbital



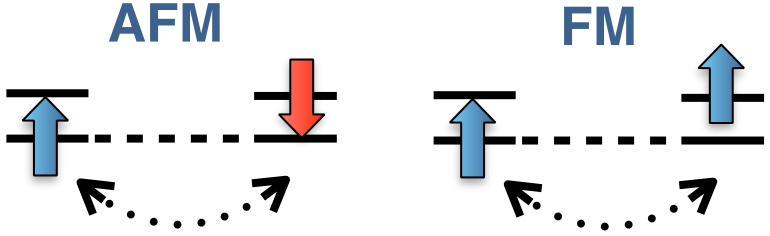
$$J_A = E_{FM} - E_{AFM} = 2E_0 - (2E_0 - \frac{2t^2}{U}) = \frac{2t^2}{U}$$

strong AFM

AntiFerro-orbital order



1 electron per orbital 1 electron per orbital

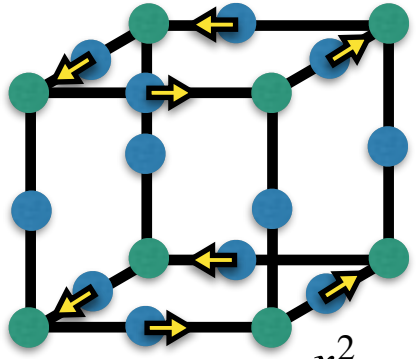


$$J_F = E_{FM} - E_{AFM} = 2E_0 - \frac{2t^2}{U - J_H} - 2E_0 + \frac{2t^2}{U} \sim -\frac{t^2 J_H}{U^2}$$

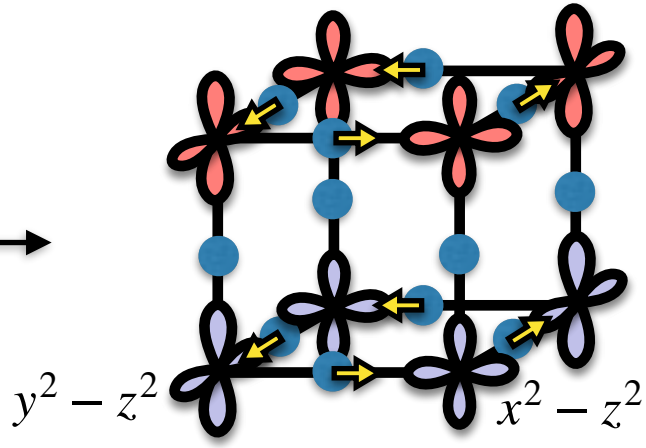
weak FM

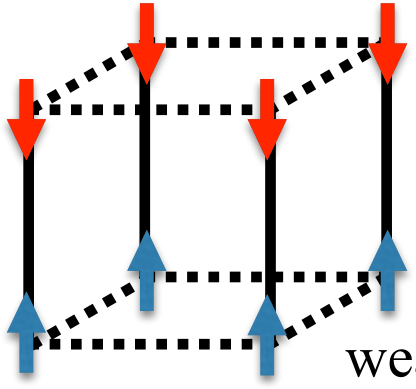
Modification of magnetic structure by orbitals

If we know local distortions



We can understand which orbitals are occupied



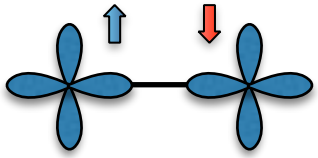


Stong AFM

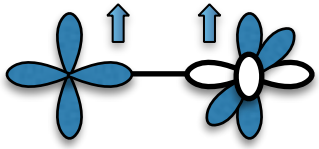
weak FM

We can find a magnetic order!

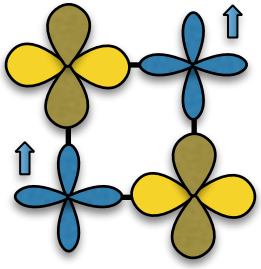
Goodenough - Kanamori - Anderson rules
connect orbitals and spins



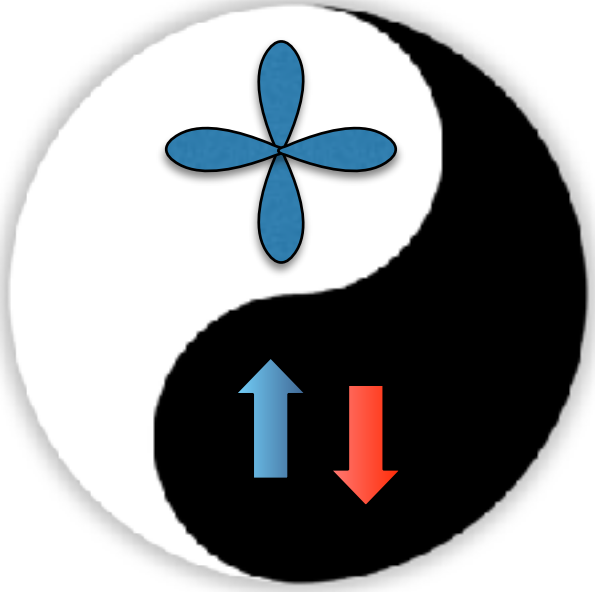
Ferro-orbital => AFM



Antiferro-orbital => FM



90^0 via orthogonal *p*-orbitals => FM



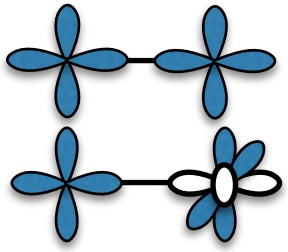
John Goodenough
1922
Nobel prize
2019

Junjiro Kanamori
1930-2012

Philip Anderson
1923-2020
Nobel prize
1977

Goodenough - Kanamori - Anderson rules
connect orbitals and spins

Important general trend in insulating transition metal oxides



$J_{AFM} \sim t^2/U$

$|J_{FM}| \sim t^2 J_H/U^2$

$$\frac{J_{AFM}}{|J_{FM}|} \sim \frac{U}{J_H}$$

$U \sim 10$ eV, $J_H \sim 1$ eV

$$J_{AFM} \sim 10\,|J_{FM}|$$

This is the reason why most of insulating transition metal oxides with localized electrons are AFM

FM

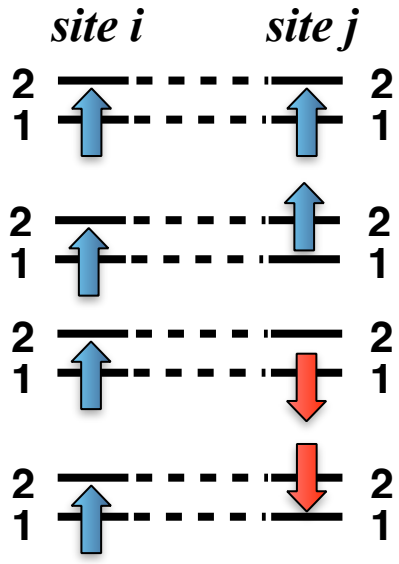
	T_C
$YTiO_3$	30 K
$BaNaOs_2O_6$	7 K
$NaCrGe_2O_6$	6 K

AFM

	T_N	μ_{eff}	
NiO	520 K	$4.6\mu_B$	AFM-II
CoO	291 K	$5.1\mu_B$	AFM-II
$KNiF_3$	275 K	$4.7\mu_B$	Γ
$LaFeO_3$	750 K	$3.0\text{-}4.4\mu_B$	Γ
FeS	600 K	$5.25\mu_B$	Γ

Orbitals and spins: Kugel-Khomskii model
and electronic mechanism of orbital ordering

Two levels with hoppings between the same orbitals



$\delta E = 0$

$\delta E = -\dfrac{2t^2}{U - J_H}$

$\delta E = -\dfrac{2t^2}{U}$

$\delta E = -\dfrac{2t^2}{U}$

The maximum energy gain is when electrons occupy <u>different</u> orbitals

Electrons can decide by themselves (without lattice), which orbitals to occupy

Electronic mechanism of orbital order

Pseudo-spin operators:

$\hat{\tau}^z|1\rangle = 1/2|1\rangle$

$\hat{\tau}^z|2\rangle = -1/2|2\rangle$

Hubbard model:

$$\hat{H} = \sum_{i\neq j} t_{ij}^{ab} c_{ia\sigma}^{\dagger} c_{jb\sigma} + \frac{1}{2}\sum_{i} U_{ab} n_{ia\sigma} n_{ib\sigma'} \left(1 - \delta_{ab}\delta_{\sigma\sigma'}\right)$$
$$- \sum_{i,a\neq b} J_H^{ab} \left(c_{ia\sigma}^{\dagger} c_{ia\sigma'} c_{ib\sigma'}^{\dagger} c_{ib\sigma} + c_{ia\sigma}^{\dagger} c_{ib\sigma} c_{ia\sigma'}^{\dagger} c_{ib\sigma'} \right)$$

Kugel-Khomskii Hamiltonian:

$$\hat{H}_{KK} = \sum_{i\neq j} J_{ij}^{S} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + J_{ij}^{\tau} \hat{\tau}_i \hat{\tau}_j + 4 J_{ij}^{S\tau} (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j)(\hat{\tau}_i \hat{\tau}_j), \quad J^S = \frac{2t^2}{U}\left(1 - \frac{J_H}{U}\right), \quad J^{\tau} = J^{S\tau} = \frac{2t^2}{U}\left(1 + \frac{J_H}{U}\right)$$

Introduction: Orbitals and spins
electronic (or KK) mechanism of orbital ordering

Heisenberg model
(spins only)

$$\hat{H} = J \sum_{i \neq j} \hat{\vec{S}}_i \hat{\vec{S}}_j$$

Kugel-Khomskii-like models (spins+orbitals)
Sov. Phys.- Usp. ***25****, 231 (1982)*

$$\hat{H}_{KK} = \frac{t^2}{\tilde{U}} \sum_{i \neq j} \left(\frac{1}{2} + 2 \hat{\vec{\tau}}_i \hat{\vec{\tau}}_j \right) \left[\frac{1}{2} + 2 \hat{\vec{S}}_i \hat{\vec{S}}_j \right]$$

There is a coupling between orbitals and spins
in materials with orbital (quasi) degeneracy (don't mix with spin-orbit interaction)

Kugel-Khomskii model
(perovskite with e_g-electrons)

$$H_{\text{эфф}} = \frac{t^2}{U} \sum_{(i,j)_z} \left\{ 8 \mathbf{S}_i \mathbf{S}_j \left[\tau_i^z \tau_j^z \left(1 + \frac{J_H}{U} \right) + \tau_j^z + \frac{1}{4} \left(1 - \frac{J_H}{U} \right) \right] + \right.$$
$$\left. + 2 \left[\tau_i^z \tau_j^z \left(1 + \frac{J_H}{U} \right) - \tau_j^z \right] \right\} + \frac{t^2}{U} \sum_{(i,j)_{x,y}} \left\{ 2 \mathbf{S}_i \mathbf{S}_j \left[\tau_i^z \tau_j^z \left(1 + \frac{J_H}{U} \right) \right. \right.$$
$$- 2 \tau_j^z + \left(1 - \frac{J_H}{U} \right) \pm 2 \sqrt{3} \left(1 + \frac{J_H}{U} \right) \tau_i^z \tau_j^x \mp 2 \sqrt{3} \tau_j^x +$$
$$+ 3 \left(1 + \frac{J_H}{U} \right) \tau_i^x \tau_j^x \Big] + \frac{1}{2} \left[\tau_i^z \tau_j^z \left(1 + \frac{J_H}{U} \right) - \right.$$
$$\left. \left. - 2 \tau_j^z \pm 2 \sqrt{3} \left(1 + \frac{J_H}{U} \right) \tau_i^z \tau_j^x \pm 2 \sqrt{3} \tau_j^x + 3 \left(1 + \frac{J_H}{U} \tau_i^x \tau_j^x \right] \right\} \right.$$

Kugel-Khomskii model:
realization of a highly symmetric model

$$\hat{H}_{eff} = \sum_{i\neq j,k\neq l} \sum_{\{\lambda\}} \sum_{\sigma\sigma'} \frac{t_{\lambda\lambda'} t_{\lambda''\lambda'''}}{E_0 - \langle H_1 \rangle} c^{\dagger}_{i\lambda\sigma} c_{j\lambda'\sigma} c^{\dagger}_{k\lambda''\sigma'} c_{l\lambda'''\sigma'}$$

Excited level spectrum $\langle H_1 \rangle$ and a hopping structure $t_{ij}^{\lambda\lambda'}$ are the origin of all complications!

General expression for

*P. Igoshev, S.S., K.Kugel, JMMM **587**, 171315 (2023)*

Exchange interaction

↕

Orbital structure

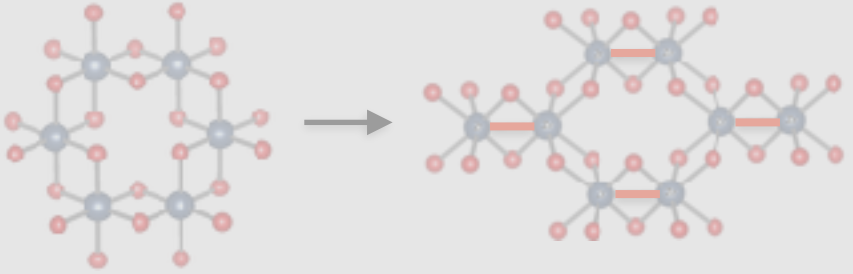
Heisenberg model

↕

Kugel-Khomskii model

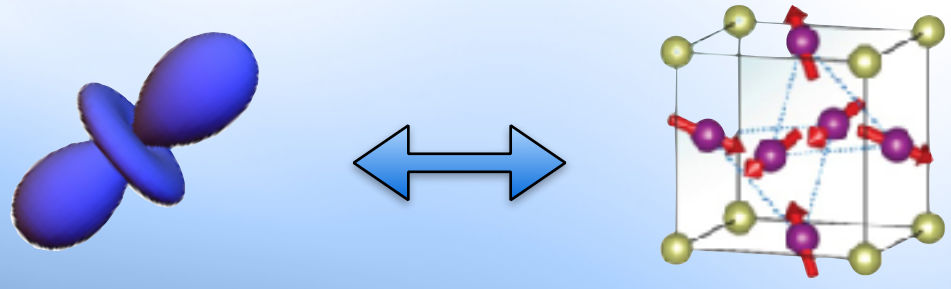
M. Yamada et al., PRL 121, 97201 (2018)

Note also possibility of dimerization
A. Ushakov, I. Solovyev, S.S.,
JETP Letters 112, 642 (2020)

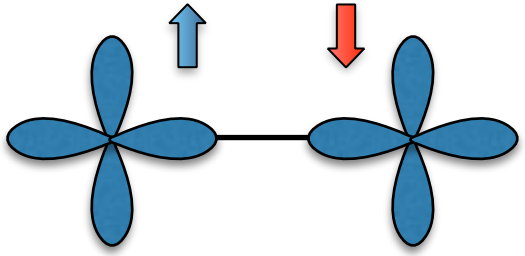


1. Interplay of different degrees of freedom:

Some examples



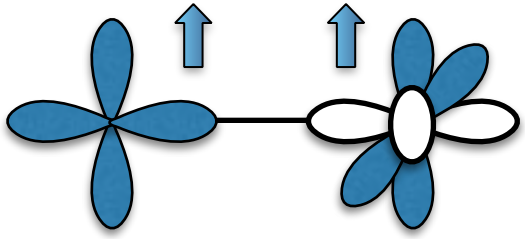
Example 2: Reduction of dimensionality
Modulation of the exchange interaction



Ferro-orbital => AFM

strong

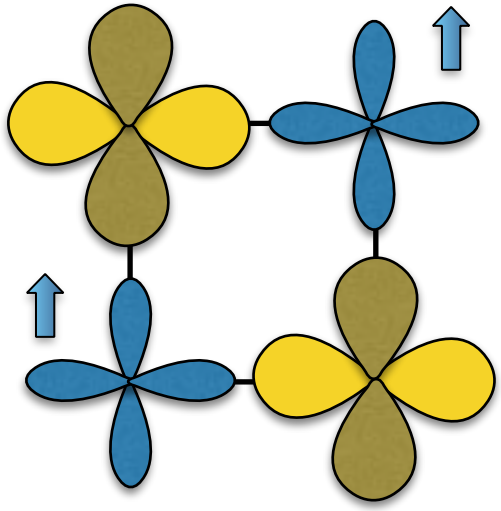
$$J_A = \frac{2t^2}{U}$$



Antiferro-orbital => FM

weak

$$J_F \approx -\frac{2t^2 J_H}{U^2}$$



90^0 via orthogonal p-orbitals => FM

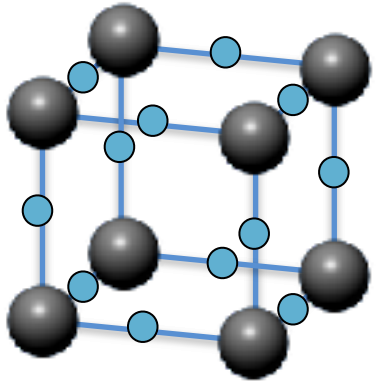
weak

$$J_F \approx -\frac{2t^2 J_H}{U^2}$$

Example 2: Reduction of dimensionality
Modulation of the exchange interaction

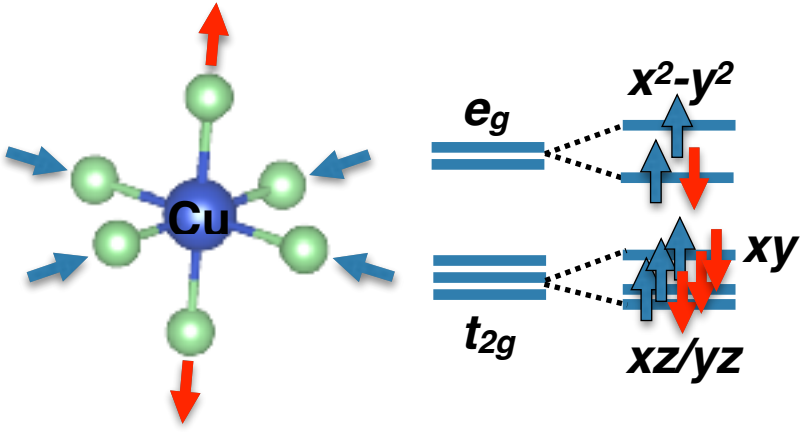
$KCuF_3$

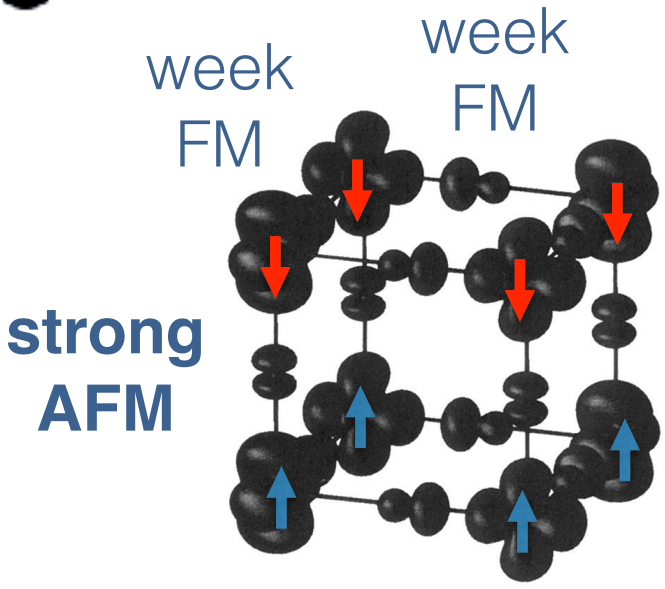
Crystal structure:
perovskite (3D)



Cu^{2+} ($3d^9$)

Jahn-Teller distortions:





AFM
S=1/2
chains!

Kugel & Khomskii, JETP 37, 725 (1973)

$KCuF_3$ - One of the best 1D antiferromagnet !!!

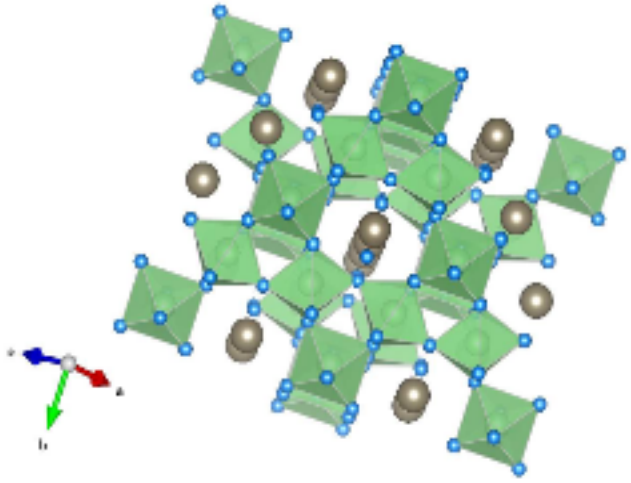
Orbitals reduce dimensionality: 3D ⟶ 1D

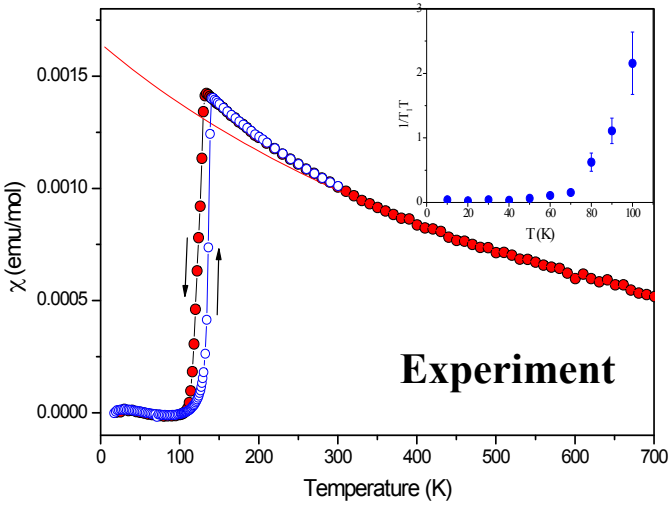
Example 4: Formation of a Haldane chain due to orbital ordering

$Tl_2Ru_2O_7$

Crystal structure: pyrochlore (3D)

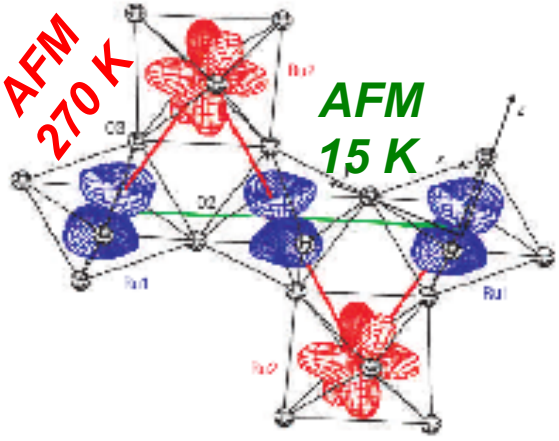
Ru^{4+} ($4d^4$, $S=1$)





Orbital ordering: (LDA+U)

Ru^{4+}



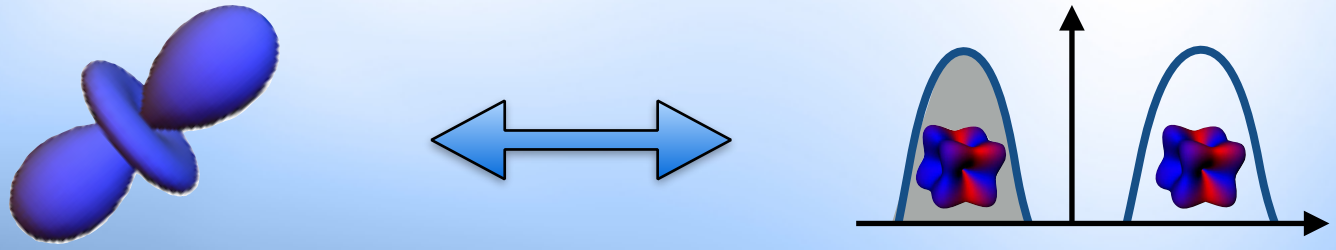
AFM chain $S=1$: Haldane chains

S. Lee, S.S. et al., Nature Material ***5****, 471 (2006)*

Orbitals reduce dimensionality: 3D → 1D

2. Directional character of orbitals:

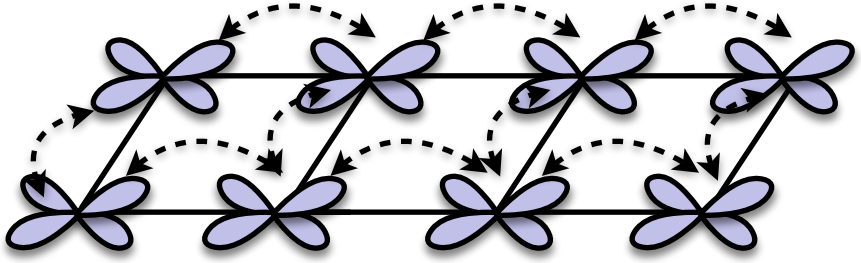
Electronic structure:
Orbital-selective Mott transition



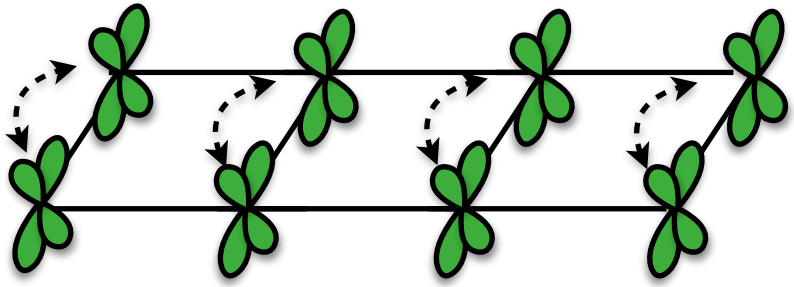
Directional character of orbitals

t_{2g} orbitals on square lattice

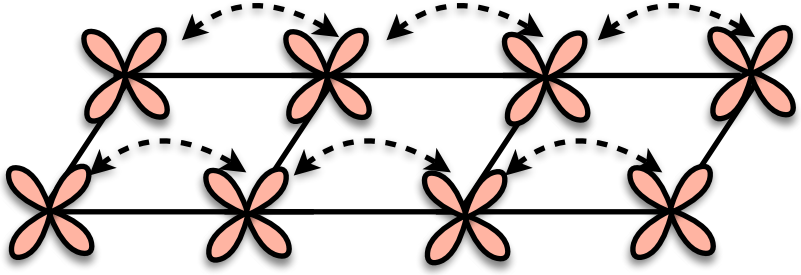
xy – orbital

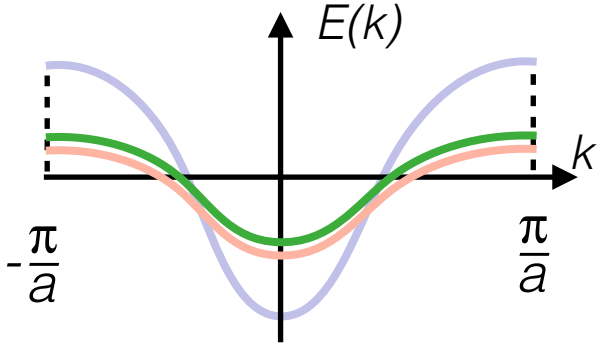


yz – orbital



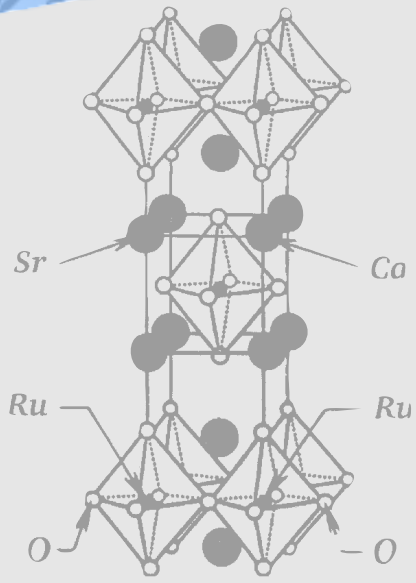
xz – orbital





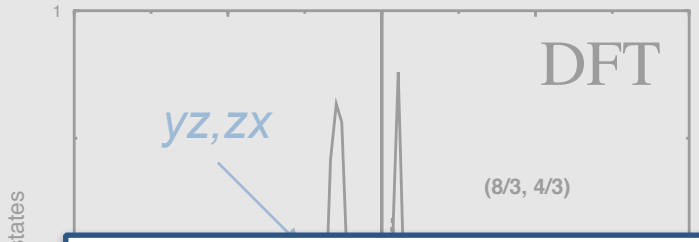
Orbitals can have a very different dispersion, which can be reflected on e.g. transport properties

Orbital-selective Mott (OSM) transition



$Ca_{2-x}Sr_xRuO_4$

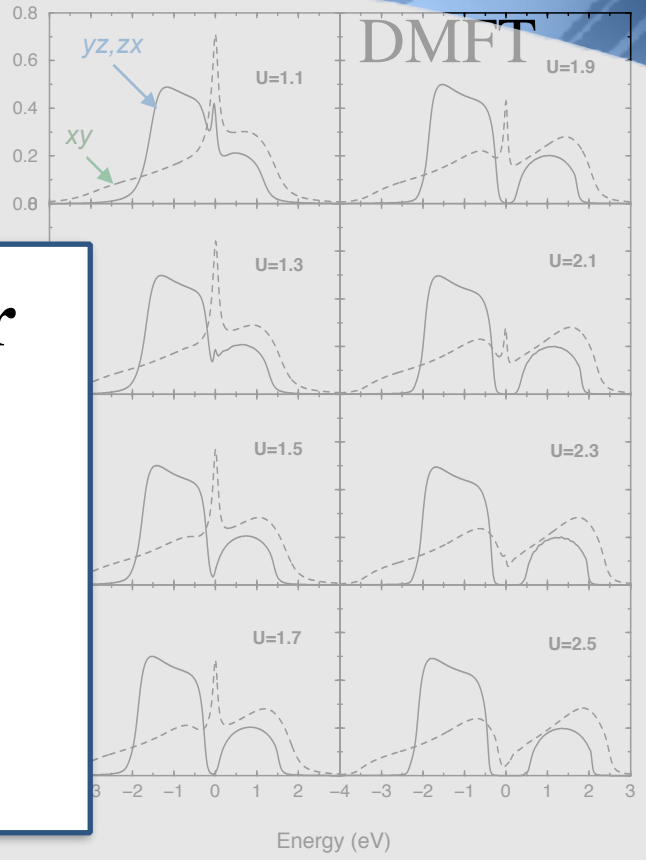
Layered structure: Squar



Directional character of orbitals

↓

Metal-insulator transition



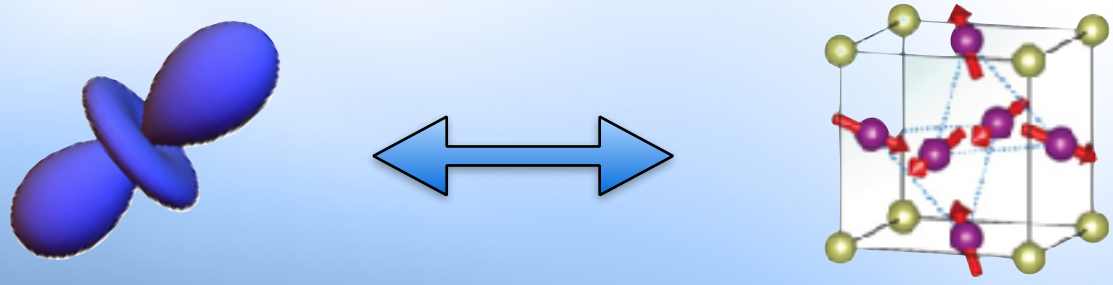
Orbital-selective Mott transition: Mott transition can occur separately for different orbitals

Critical U_c: 1.5 eV for xz/yz orbitals
2.5 eV for xy orbital

Anisimov et al., Eur. Phys. J. B 25, 191 (2002)

2. Directional character of orbitals:

Orbital-selectivity and magnetic properties



Double exchange as an orbital-selective effect

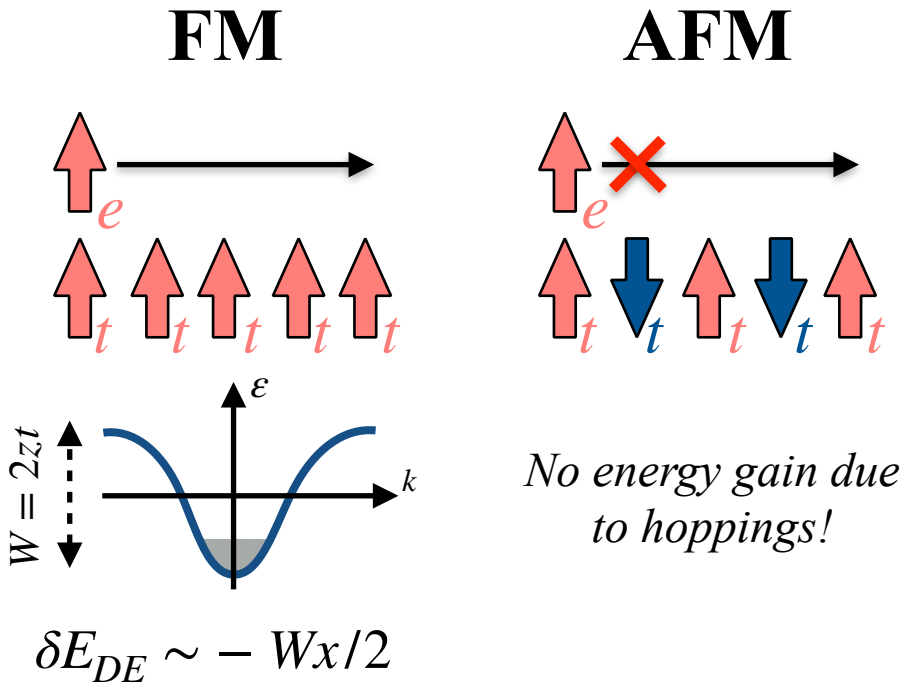
Double exchange is a natural realization of the orbital-selectivity

Itinerant electrons (e.g. e_g electrons)

Localized electrons (e.g. t_{2g} electrons)

Double-exchange mechanism of ferromagnetism

C. Zener, Phys. Rev. 82, 403 (1951)

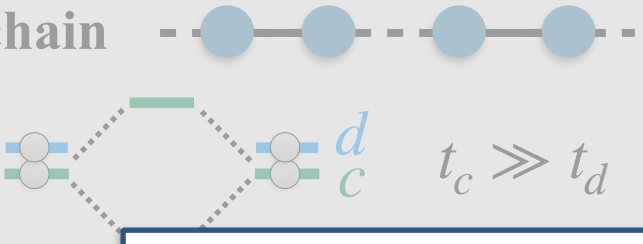


$$\delta E_{DE} \sim -Wx/2$$

Examples: CrO_2, CMR manganates etc.

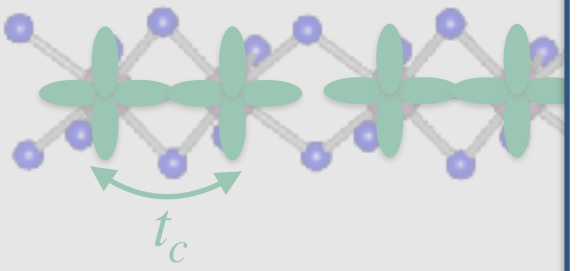
Extreme case:
Orbital-selectivity in low-dimensional magnets

E.g. a dimerized chain



Two different orbitals *c* and *d*

$t_c \gg t_d$



Examples

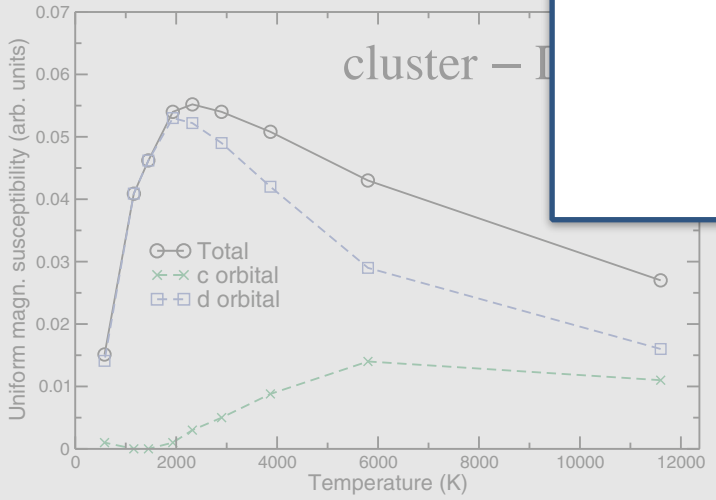
$CuIr_2S_4$	*Nat. Com. 10, 3638 (2019)*
$BaCeRu_2O_9$	*JACS 141, 9928 (2019)*
	PRB 100, 045131 (2019)
	PRL 122, 106401 (2019)
	PRB 98, 201105(R) (2018)

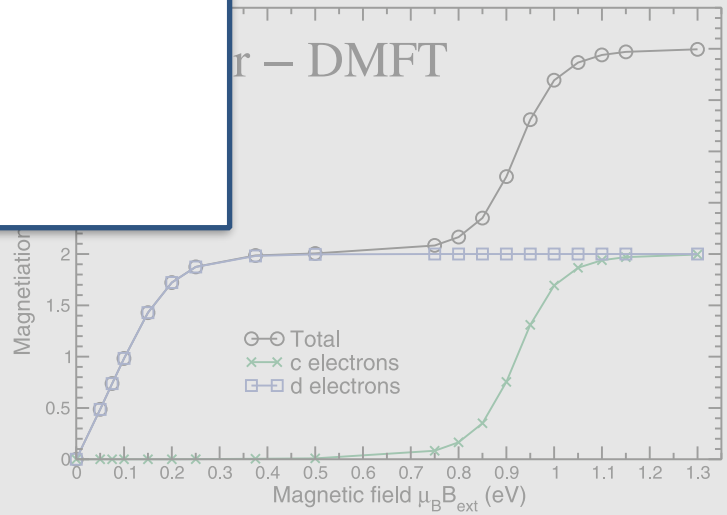
skii PNAS 113, 10491 (2016)

Directional character of orbitals

↓

Magnetic properties

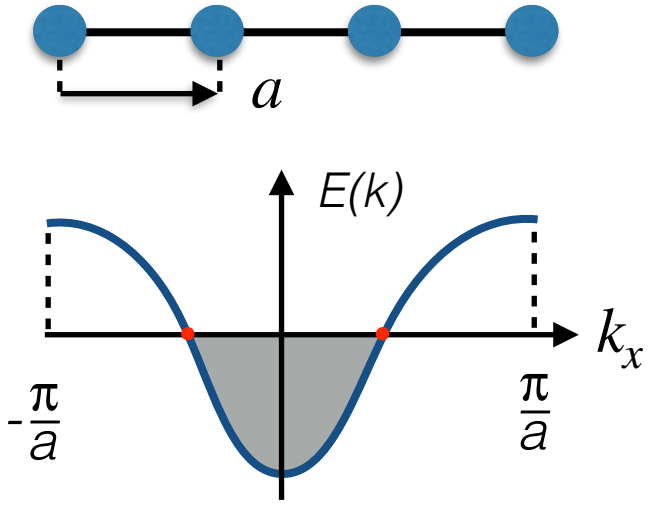


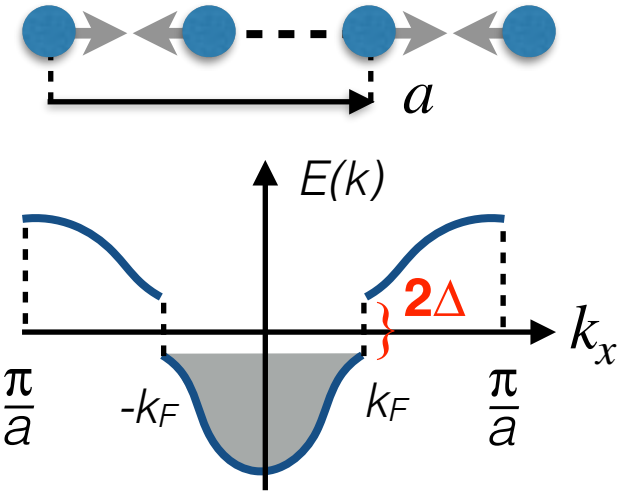


c and *d* orbitals "work" at different ***T***

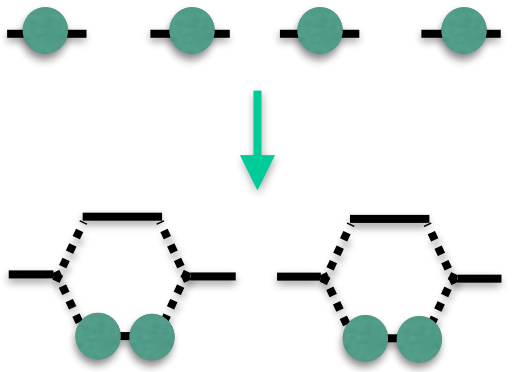
c and *d* orbitals "work" at different ***B***

Peierls transition - simplest case of
1D + half-filling (1 electron/site)





On a "Chemical language"



Instability at $|Q| = 2k_F$

Half-filling: $|k_F| = \pi/2a, |Q| = \pi/a$

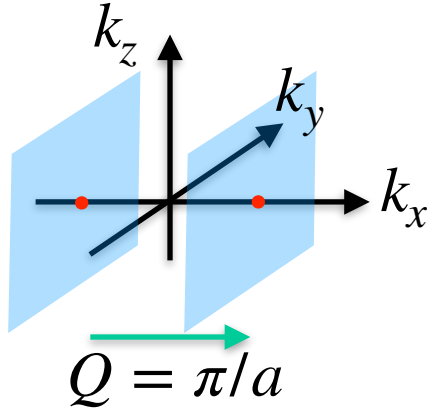
Gain in kinetic energy: $\sim -|\Delta|^2 \ln|\Delta|$

Loss in elastic energy: $\sim |\Delta|^2$

Physical mechanism: nesting of the Fermi surface

$$\chi_0'(\vec{Q}, \omega = 0) =$$

$$= \frac{1}{\Omega} \sum_{\vec{k}} \frac{f(\varepsilon(\vec{k})) - f(\varepsilon(\vec{k} + \vec{Q}))}{\varepsilon(\vec{k}) - \varepsilon(\vec{k} + \vec{Q})}$$



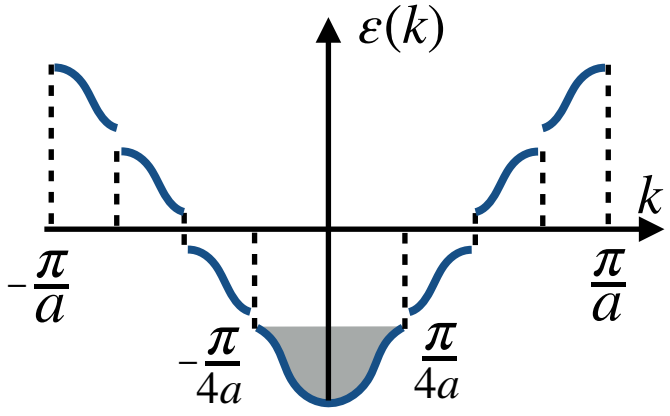
Factor I: lattice deformations are possible for other fillings!

Reduction of dimensionality
Orbitally-induced Peierls effect

Peierls transition: 1D chain Instability at $|Q| = 2k_F$

quarter-filling (1/2 electron/site):

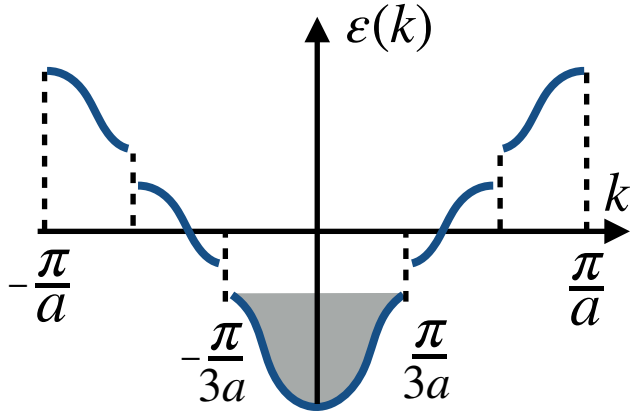
$$|k_F| = \frac{\pi}{4a} \qquad |Q| = \frac{\pi}{2a}$$



Tetramerization

1/3 electron/site:

$$|k_F| = \frac{\pi}{3a} \qquad |Q| = \frac{2\pi}{3a}$$



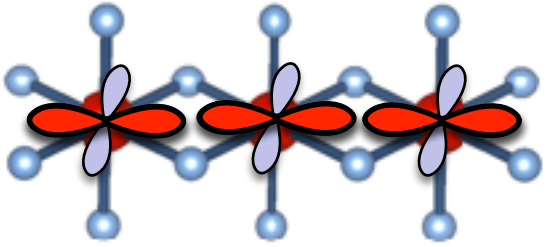
Trimerization

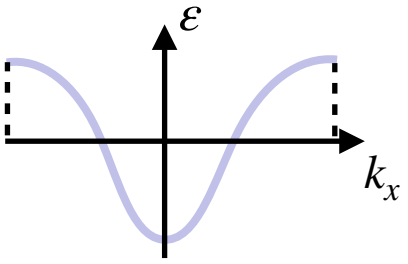
Peierls transition - importance of orbital degrees of freedom

Factor II: Orbital-selectivity with respect to Peierls transition

E.g. edge-sharing geometry

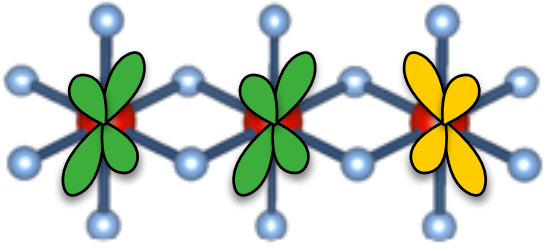
xy

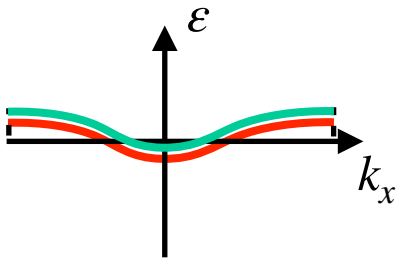




- Wide nearly 1D bands susceptible to Peierls transition

xz/yz

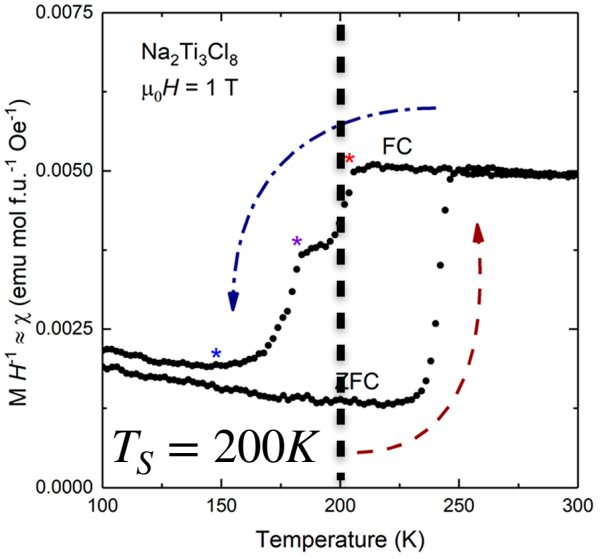




- Localized bands susceptible to U;
- Crystal-field can strongly change position of the band;

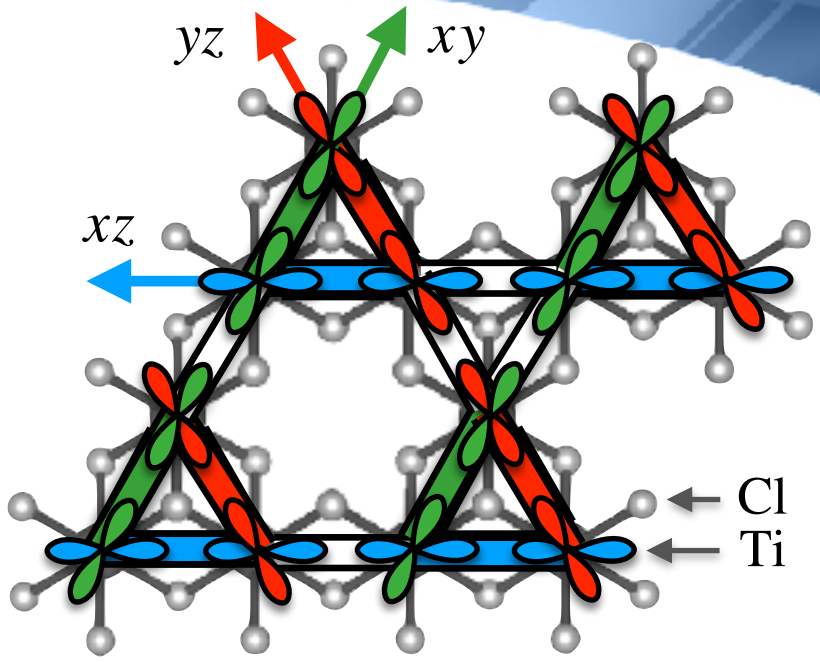
Orbitally-induced Peierls effect: Kagome lattice

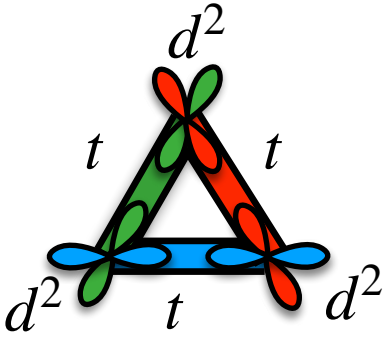
$Na_2Ti_3Cl_8$: Ti^{2+}: d^2 $(S=1)$

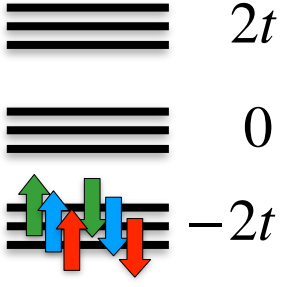


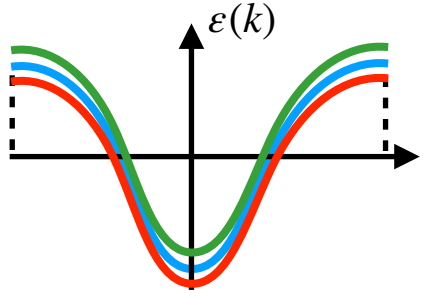
Angew. Chem ***34***, *71 (1995)*
ZAAC ***643***, *2063 (2017)*
Inorg. Chem ***58***, *11941 (2019)*
PRL ***124***, *167203 (2020)*

- Trimerization at 200 K;
- Non-magnetic state T<200 K









Three 1D bands!

Band filling: 1/2

***S=0* ground state!**

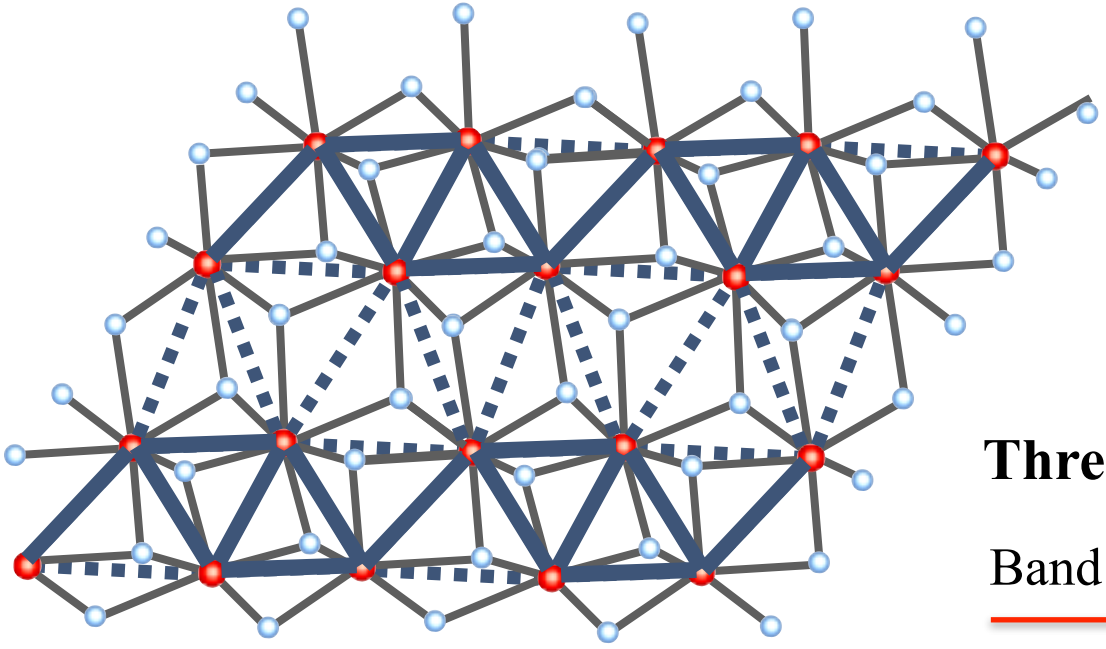
Trimerization = Dimerization along each direction

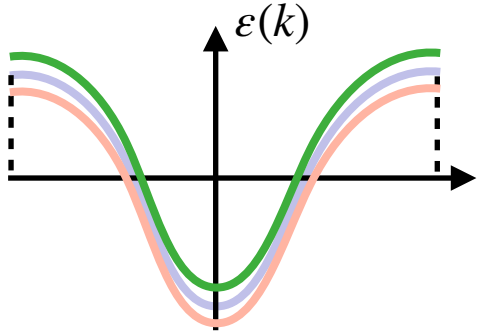
D. Khomskii, T. Mizokawa, S.S. PRL 127, 049701 (2021)

Orbitally-induced Peierls effect: Triangular lattice

ReS_2: diamond necklace

ReS_2 $\quad Re^{4+}: \; t_{2g}^3 \; (n_e = 3)$





Three 1D bands

Band filling: 1/2

$$k_F = \frac{\pi}{2a}, Q = \frac{\pi}{a}$$

⇩

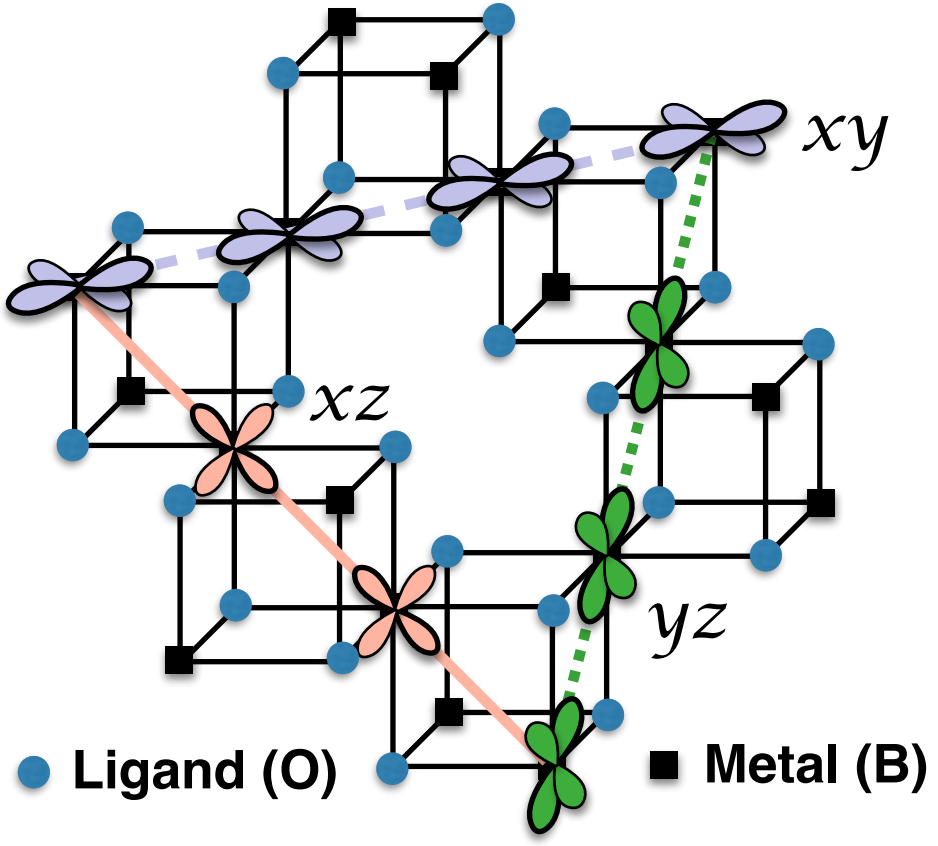
Formation of "diamond necklace"

Dimerization in three directions!

D. Khomskii, S.S. Chem. Rev. 121, 2992 (2021)

Reduction of dimensionality
Orbitally-induced Peierls effect

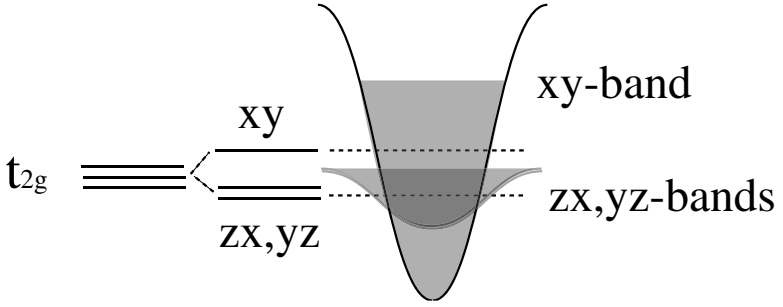
Spinels (3D structure): AB_2O_4



Natural formation of 1D bands due to orbitals…

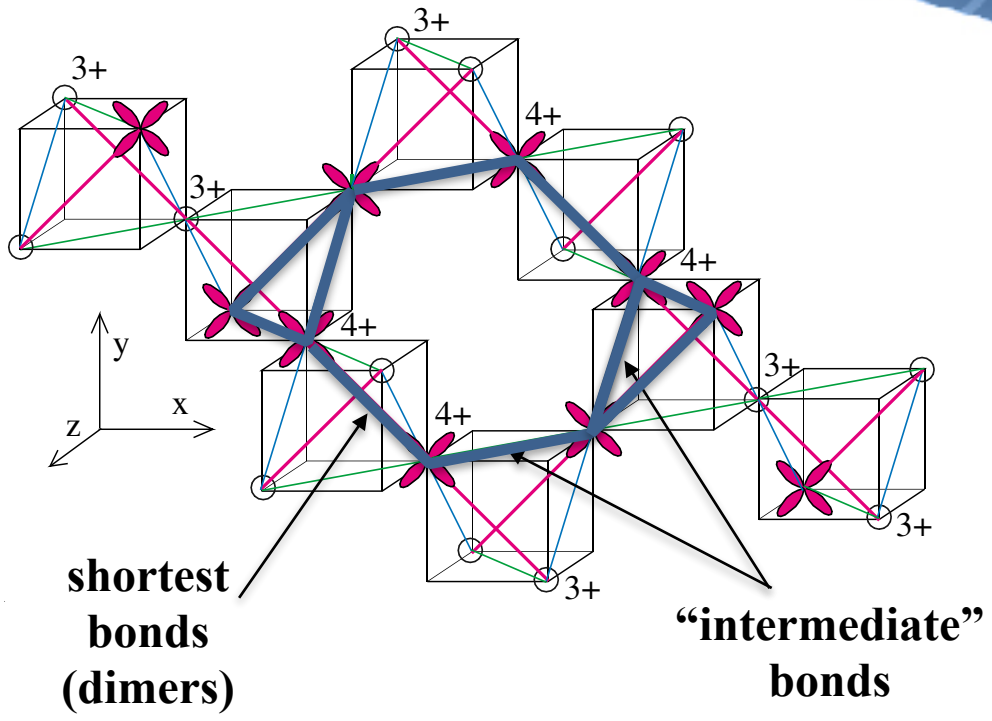
Orbitally induced Peierls effect:
Tetramerization in spinel $CuIr_2S_4$

$CuIr_2S_4$: spinel **$Ir^{3.5+}$: $d^{5.5}$**



tetragonal elongation
(*xz/yz* orbitals are
"frozen")

1/2 holes
in *xy* band



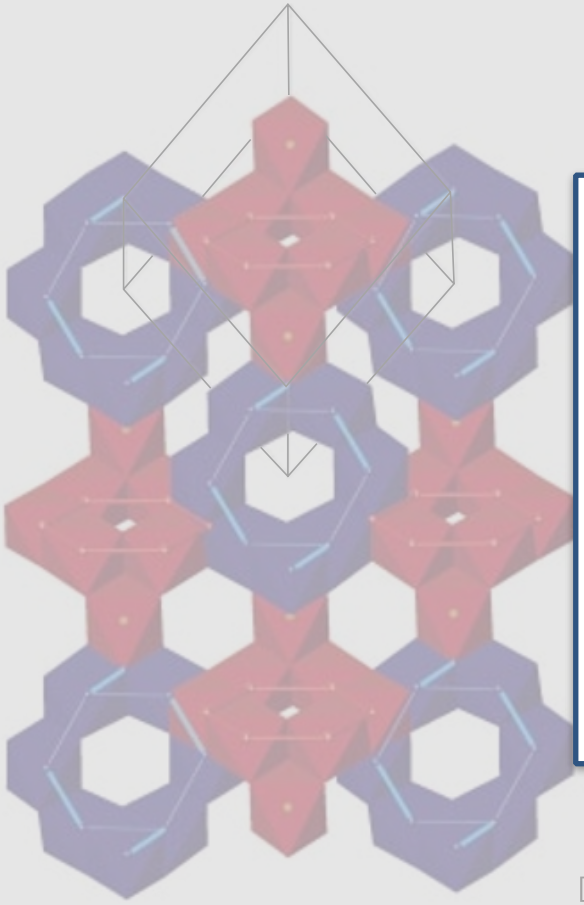
Band filling: 1/4

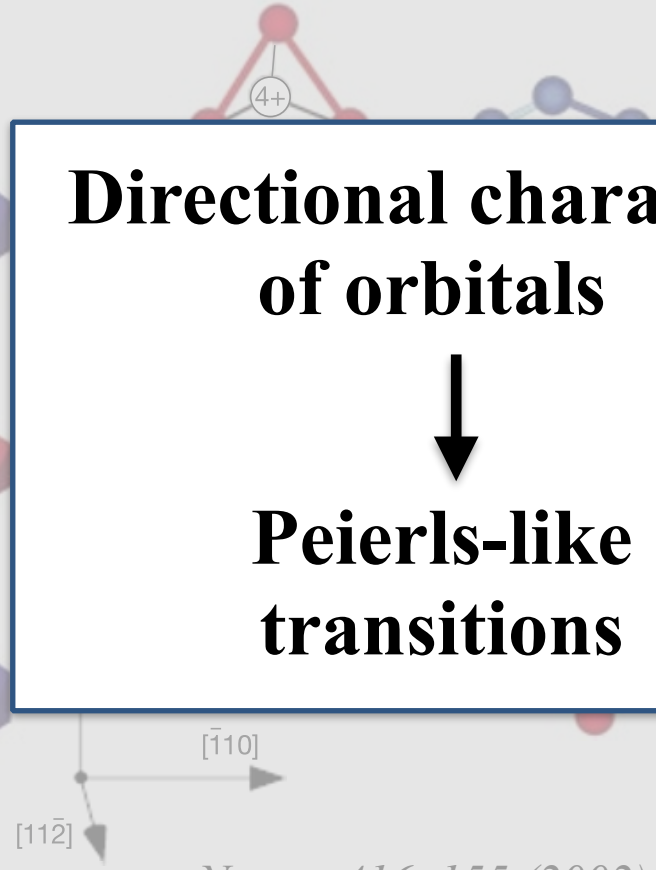
⇩

Tetramerization!

Khomskii and Mizokawa, PRL 94, 156402 (2005)

Orbitally induced Peierls effect:
Tetramerization in spinel $CuIr_2S_4$

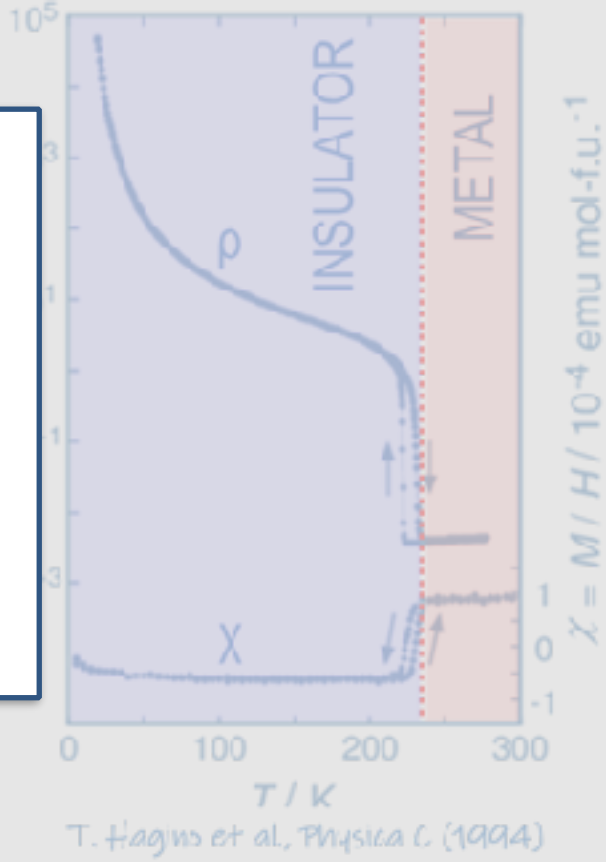




Directional character of orbitals

↓

Peierls-like transitions



Nature 416, 155 (2002)

Reduction of dimensionality due to orbital degrees of freedom

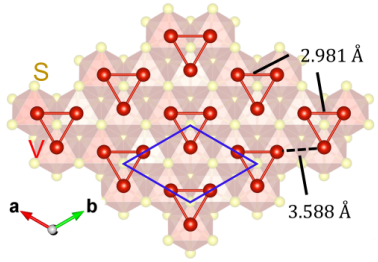
Other examples

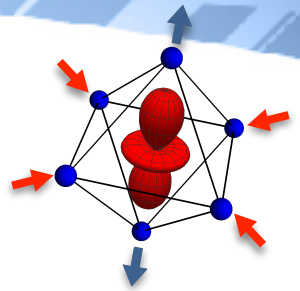
$1D \rightarrow 0D$ chains→dimers	$NaTiSi_2O_6$ [57, 58]
$1D \rightarrow 0D$ chains→dimers	TiOCl [59]
$2D \rightarrow 0D$ triangular lattice → trimers	$LiVO_2$ [60, 61]
$2D \rightarrow 0D$ square lattice → dimers	$La_4Ru_2O_{10}$ [62]
$2D \rightarrow 0D$ depleted square lattice → tetramers	CaV_9O_9 [63, 64]
$3D \rightarrow 0D$ hollandite → tetramers	$K_2Cr_8O_{16}$ [65, 66]
$3D \rightarrow 0D$ spinel → tetramers/trimers	AlV_2O_4 [67, 68]
$3D \rightarrow 0D$ spinel → octamers	$CuIr_2S_4$ [69, 70]
$3D \rightarrow 1D$ spinel → chains → dimers	$MgTi_2O_4$ [70, 71]
$3D \rightarrow 1D$ perovskite → chains	$KCuF_3$ [72]
$3D \rightarrow 1D$ pyrochlore → chains	$Tl_2Ru_2O_7$ [73]

D. Khomskii, *S.S.* Chem. Rev. 121, 2992 (2021)

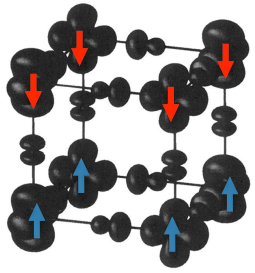
Take-home messages

- Orbitals can **affect the crystal structure**

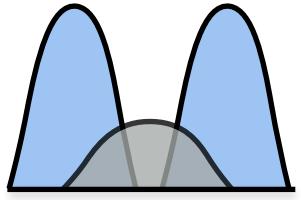




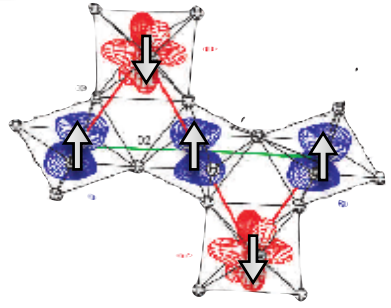
- Orbitals can **define magnetic properties**



- There are plenty of **orbital-selective effects:** Mott transition, magnetic properties



- Orbitals may **reduce dimensionality** of a magnetic subsystem



S.S. and D. Khomskii, Physics-Uspekhi 60, 1121 (2017)
D. Khomskii and S.S. Chem. Rev. 121, 2992 (2021)