Орбитальные степени свободы в непроводящих соединениях переходных металлов

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Materials under consideration

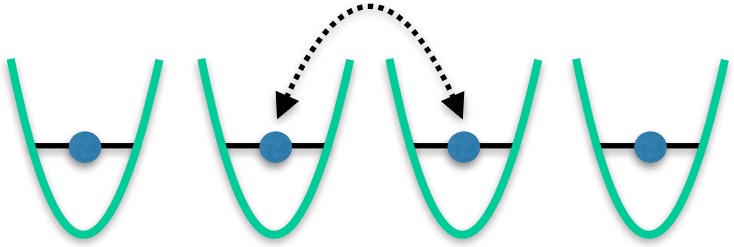
Conductors

SemiConductors

Superconductors

Insulators

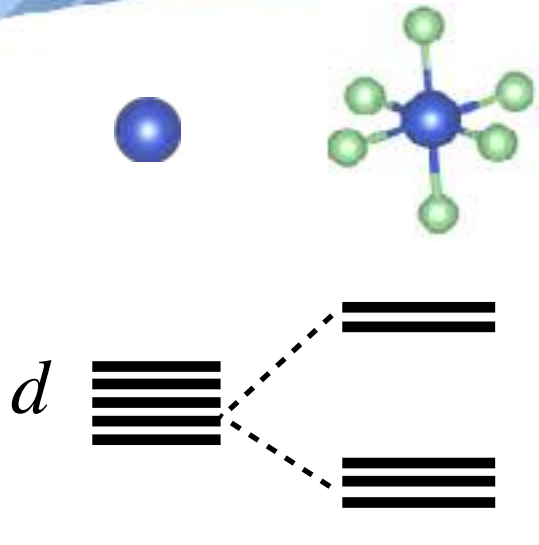
- localized electrons
- not-completely filled *d*- or *f*-shell



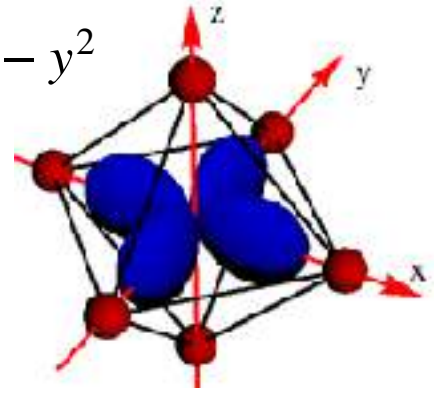
Or materials with the metal-insulator transition

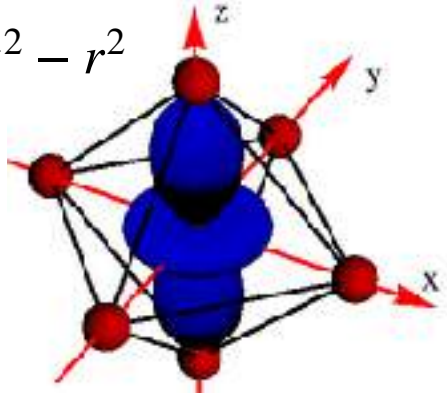
Examples: NiO, $LaMnO_3$, La_2CuO_4 etc.

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



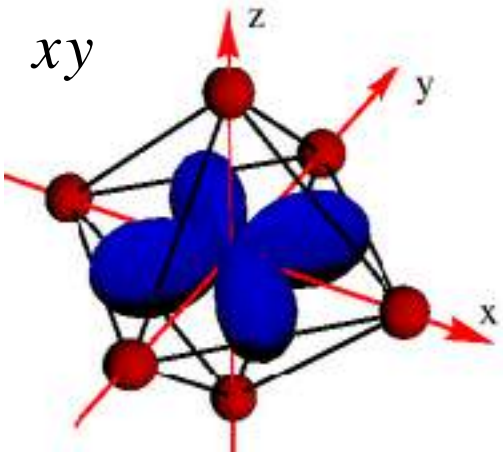
e_g

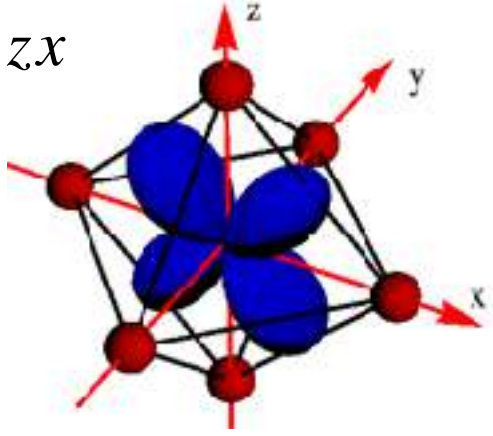


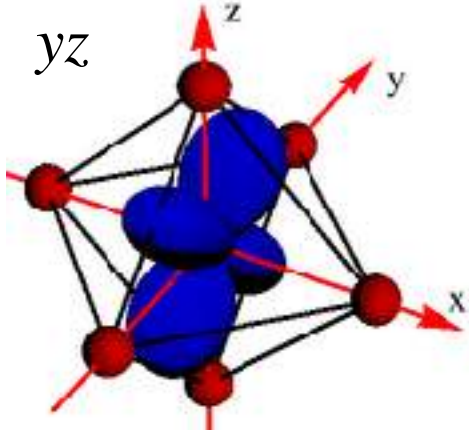


Directed **to** ligands

t_{2g}



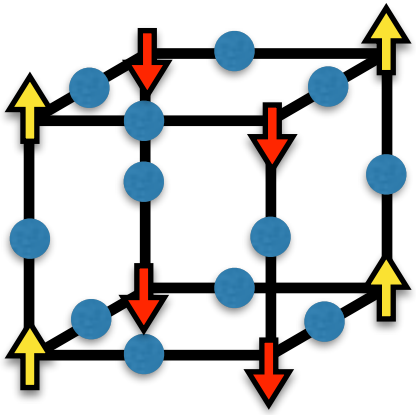




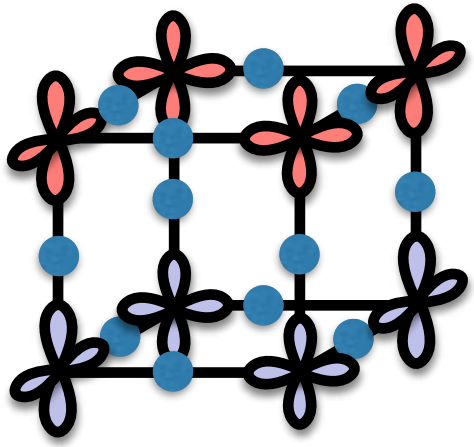
Directed **away** from ligands

Orbital degrees of freedom

Spin degrees of freedom



Orbital degrees of freedom



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

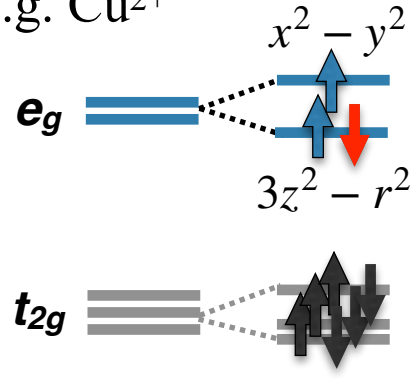
pseudospin operators $\hat{\vec{\tau}}$

for $s = 1/2$

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

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

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

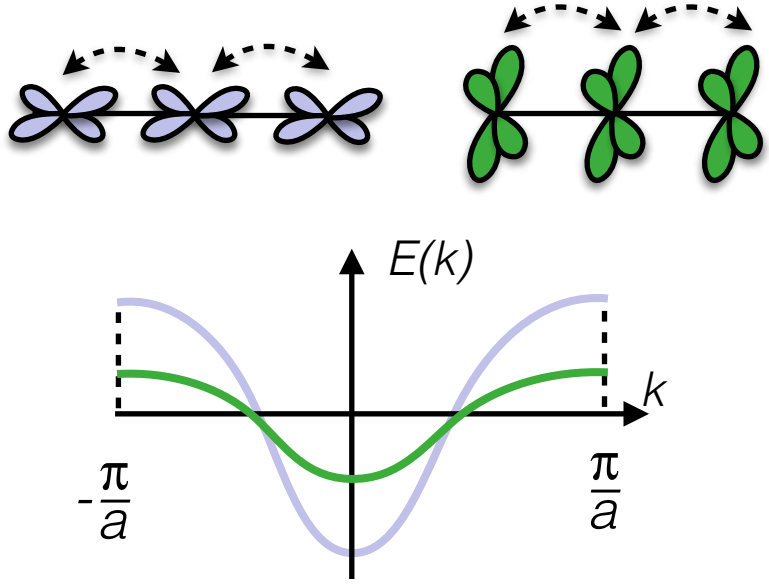
1. Orbitals are coupled with other degrees of freedom

Jahn-Teller effect

Goodenough-Kanamori-Anderson rules

Kugel-Khomskii-like models

2. Orbitals have directional character



Orbital-selective Mott transition

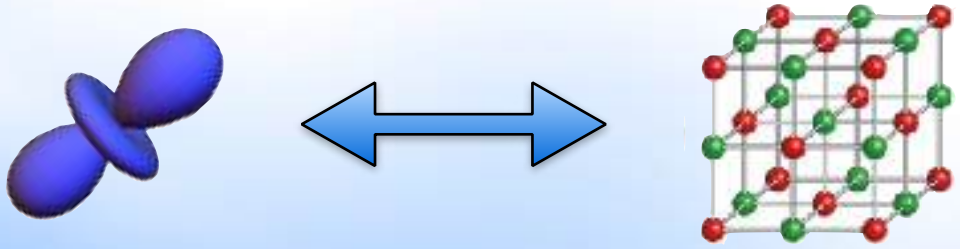
Orbital-selectivity and Magnetism

Orbitally-assisted Peierls effect

3. Spin-orbit coupling - lecture on Sunday

Interplay of different degrees of freedom:

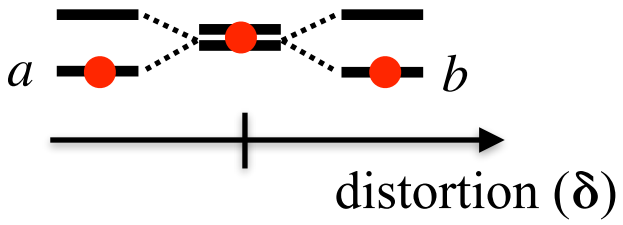
Jahn-Teller effect



Jahn-Teller effect in a nutshell

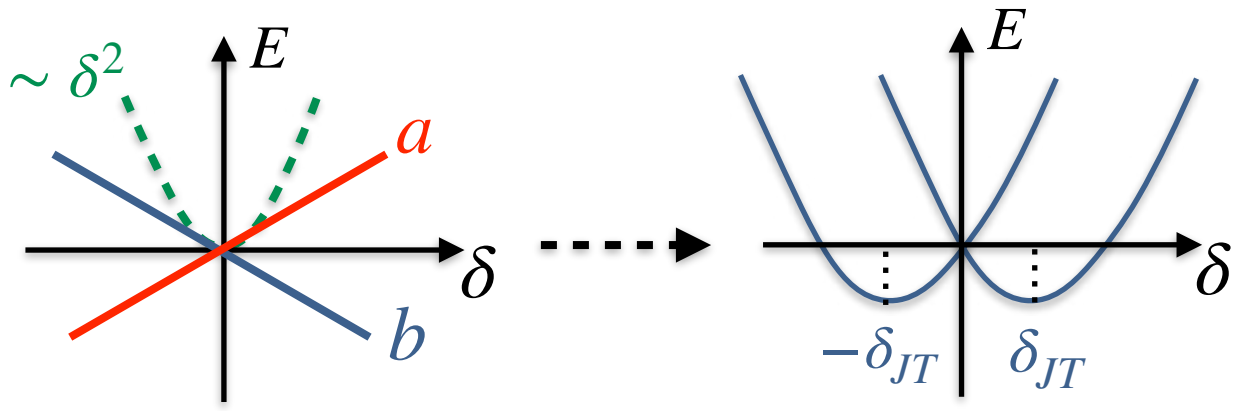
Let's consider a model two-levels (a & b) system in a certain surrounding

Idea



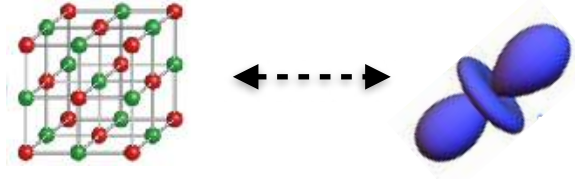
$$E_{JT} = \pm g\,|\delta|$$

Coupling with lattice



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

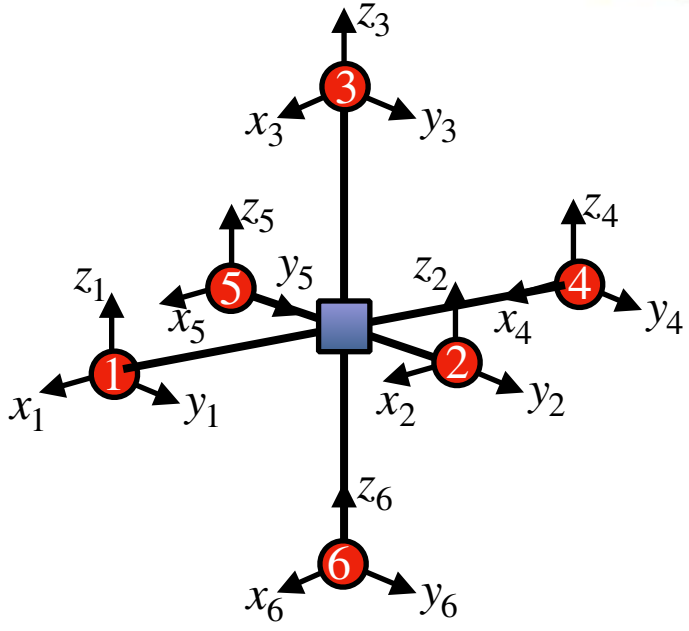
"Orbital-lattice" coupling



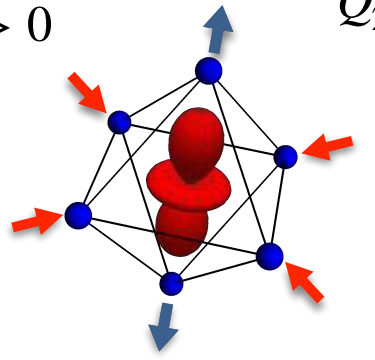
Normal vibration modes (octahedron)

Mode	Transformation properties		Displacements
Q_1	A_{1g}		$[(x_1 - x_4) + (y_2 - y_5) + (z_3 - z_6)]/\sqrt{16}$
Q_2	E_g	$\varepsilon,\ x^2 - y^2$	$[(x_1 - x_4) - (y_2 - y_5)]/2$
Q_3		$\theta,\ 3z^2 - r^2$	$[2(z_3 - z_6) - (x_1 - x_4) - (y_2 - y_5)]/\sqrt{12}$
Q_4	T_{2g}	$\xi,\ yz$	$[(z_2 - z_5) + (y_3 - y_6)]/2$
Q_5		$\eta,\ zx$	$[(x_3 - x_6) + (z_1 - z_4)]/2$
Q_6		$\zeta,\ xy$	$[(y_1 - y_4) + (x_2 - x_5)]/2$
Q_7	T_{1u}	x	$[x_2 + x_3 + x_5 + x_6]/2$
Q_8		y	$[y_1 + y_3 + y_4 + y_6]/2$
Q_9		z	$[z_1 + z_2 + z_4 + z_5]/2$
Q_{10}	T_{1u}	x	$[x_1 + x_4]/\sqrt{2}$
Q_{11}		y	$[y_2 + y_5]/\sqrt{2}$
Q_{12}		z	$[z_3 + z_6]/\sqrt{2}$
		$\cdots$	

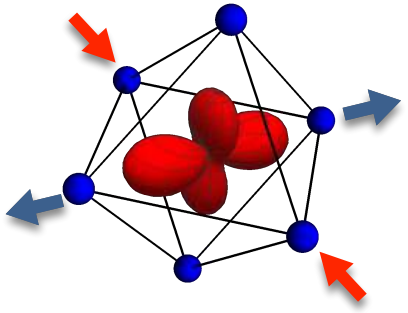
g



$Q_3 > 0$



$Q_2 > 0$

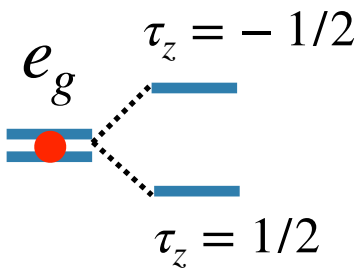


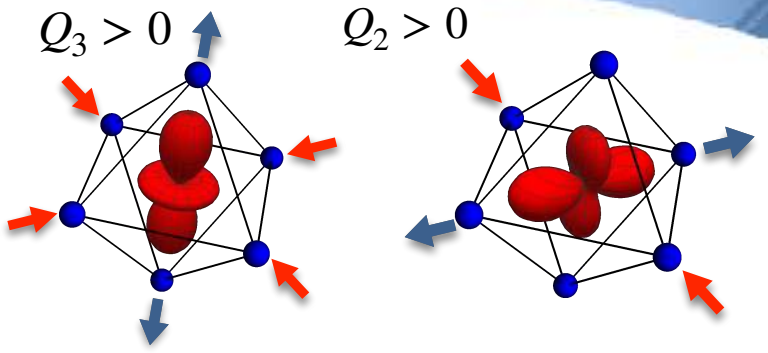
$$E_{JT} = \pm g\,|\,\delta\,| + \frac{B\delta^2}{2}$$

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

for an isolated octahedron

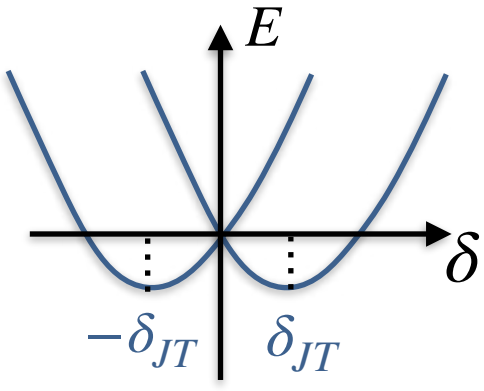
More realistic situation:
e_g-levels and E-distortions
(i.e. Q_2, Q_3)
e.g. Mn^{3+} or Cu^{2+}

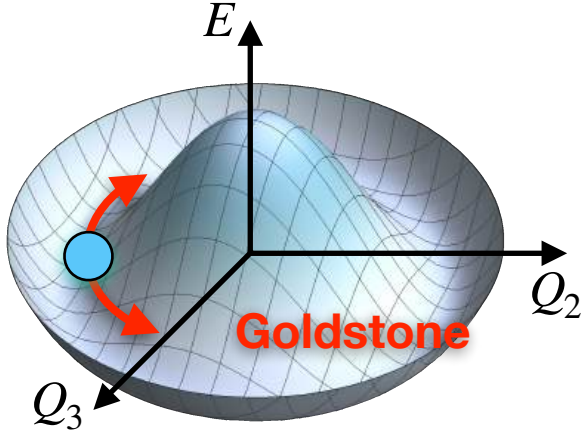




$$E_{JT} = \pm g\,|\delta| + \frac{B\delta^2}{2} \quad \dashrightarrow \quad \hat{H}_{JT} = -g(\hat{\tau}_z Q_3 + \hat{\tau}_x Q_2) + \frac{B}{2}(Q_3^2 + Q_2^2)$$

* from Wigner-Eckart theorem

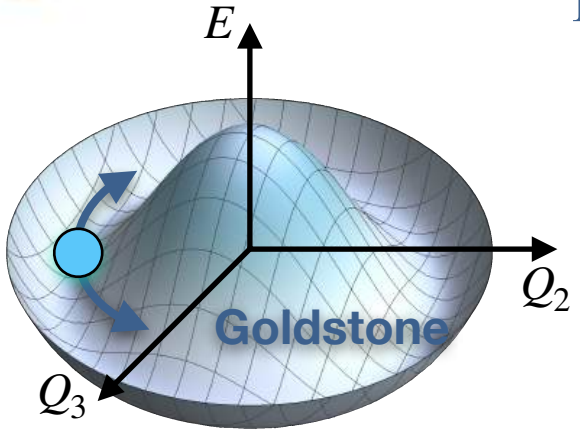




Harmonic approximation: Highly degenerate ground state

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

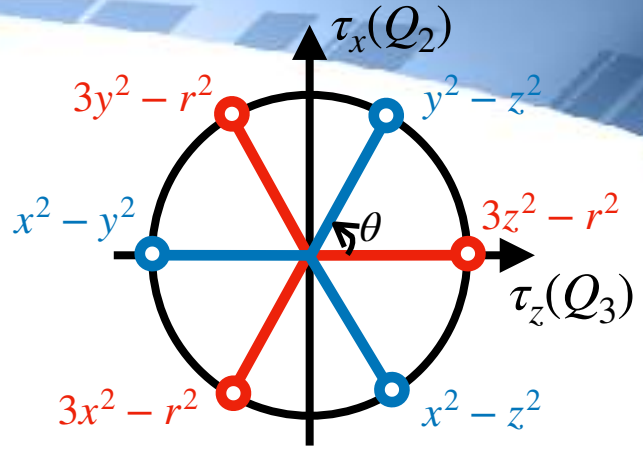
for an isolated octahedron



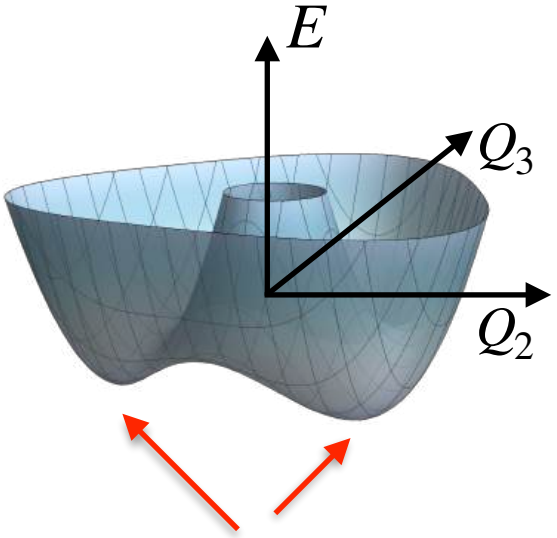
Harmonic approximation

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

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



Distortion ⟷ **Orbital**



Elongated octahedra!

Anharmonicity

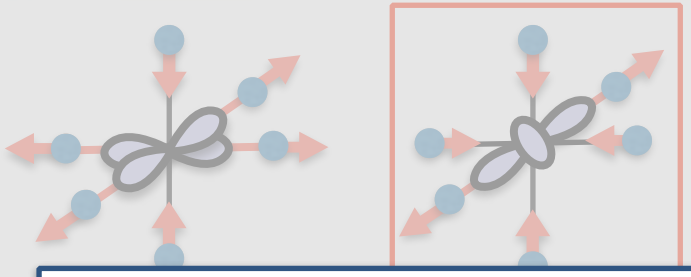
	Claimed compressed	**Turned out elongated**
$NaMn_7O_{12}$	Nature Mat. 3, 48 (2004)	PRB 89, 201115 (2014)
$Cs_2CuCl_2Br_2$	Cryst. Gr. Des. 10, 4456 (2010)	PRB 86, 035109 (2012)

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

Cooperative Jahn-Teller distortions

(electron-lattice mechanism of orbital ordering)

How to pack octahedra?



Anharmonic effects stabilize this!

We must keep V the same

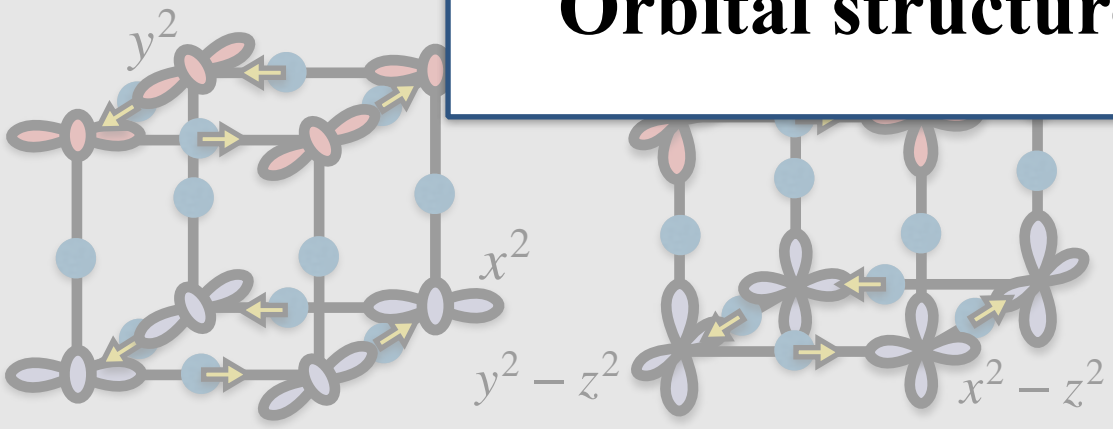
$$\sum_{i \neq j} J_{ij} \vec{\tau}_i \vec{\tau}_j \qquad J_{ij} \sim g^2/B$$

Lattice distortions

↕

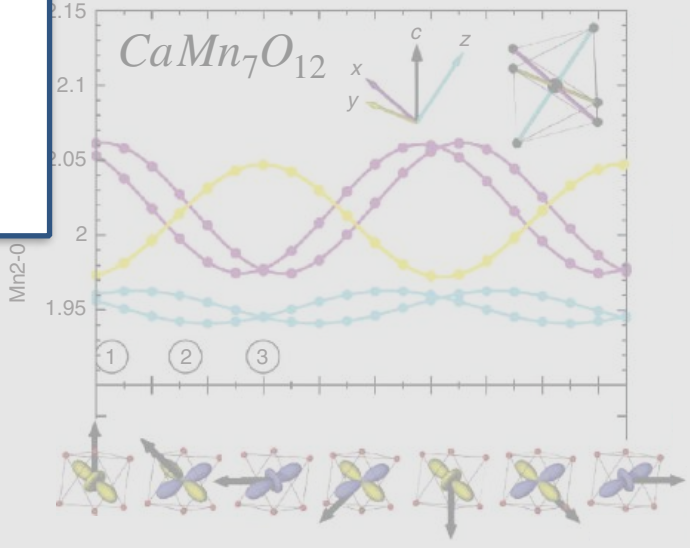
Orbital structure

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



electrons are plotted

holes are plotted

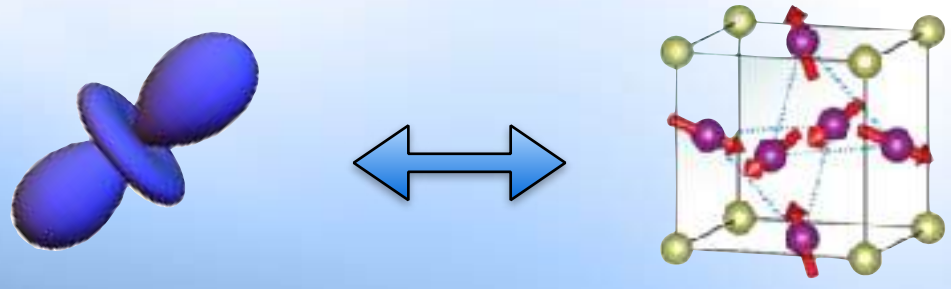


N. Perkins et al., Nature Communications 3, 1277 (2012)

Interplay of different degrees of freedom:

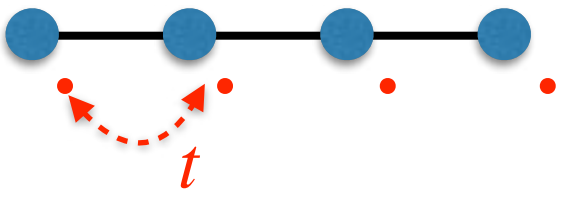
Exchange interaction

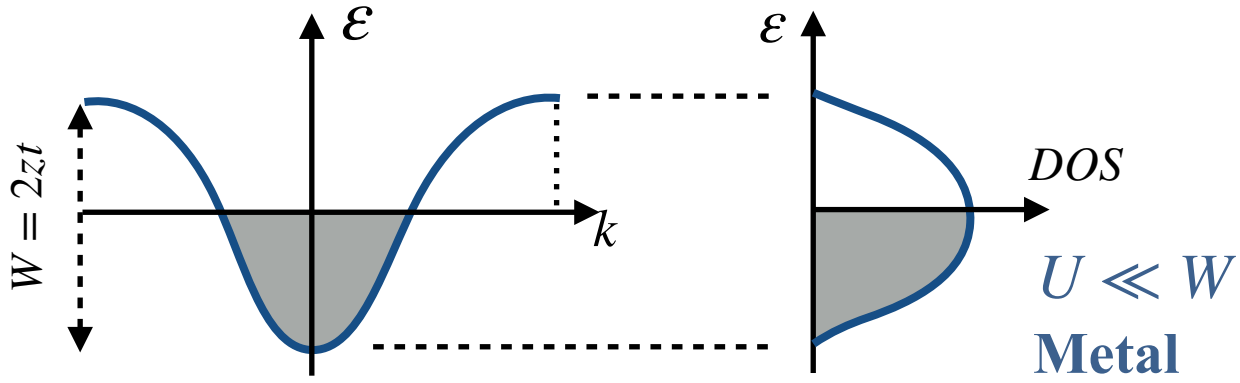
Kugel-Khomskii-like models



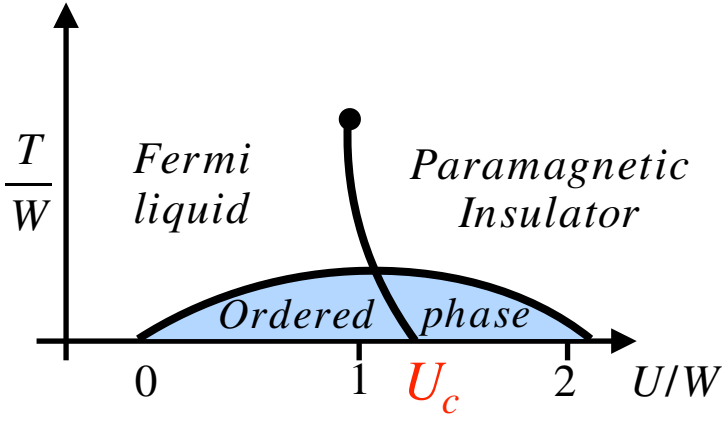
Mott-Hubbard transition in a nutshell

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

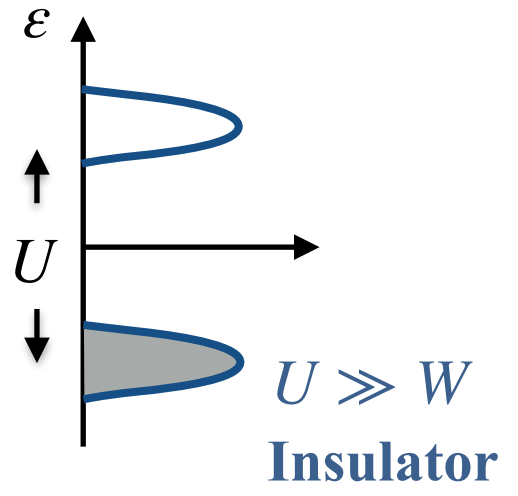




Hubbard model: $H = -t \sum_{\langle ij \rangle \sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$



Metal-Insulator (Mott-Hubbard) transition!

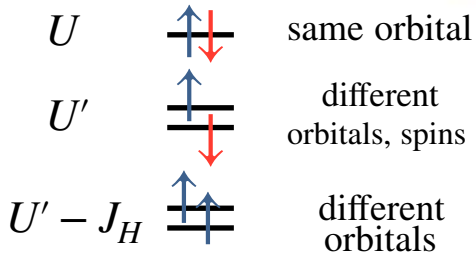


U - on-site Coulomb repulsion

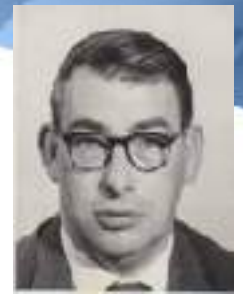
Localized electrons and correlation effects

Many-band Hubbard model:

$$H_K = U\sum_m n_{m\uparrow}n_{m\downarrow} + U'\sum_{m\neq m'} n_{m\uparrow}n_{m'\downarrow} + (U'-J_H)\sum_{m<m',\sigma} n_{m\sigma}n_{m'\sigma}$$
$$-J_H\sum_{m\neq m'} c^\dagger_{m\uparrow}c_{m\downarrow}c^\dagger_{m'\downarrow}c_{m'\uparrow} + J_H\sum_{m\neq m'} c^\dagger_{m\uparrow}c^\dagger_{m\downarrow}c_{m'\downarrow}c_{m'\uparrow}$$



J_H – Hund's exchange!



John Hubbard

$$H_U = \left(4J_H - \frac{U}{2}\right)\hat{N} + (U-3J_H)\frac{\hat{N}^2}{2} - J_H\left(2\hat{S}^2 + \frac{\hat{L}^2}{2}\right)$$

3-band model in non-standard notations

Polar model (Shubin-Vonsovski)

Electron correlations in narrow energy bands

By J. Hubbard

Theoretical Physics Division, A.E.R.E., Harwell, Didcot, Berks

(*Communicated by B. H. Flowers, F.R.S.—Received* 23 *April* 1963)

On the Electron Theory of Metals.

By S. Schubin and S. Wonsowsky.

Sverdlovsk Physical Technical Institute.

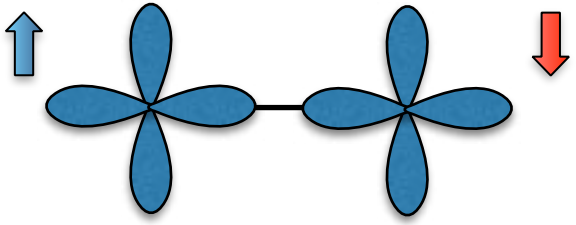
(Communicated by R. H. Fowler, F.R.S.—Received December 29, 1933.)

V. Irkhin, S.S.
JSNM 35, 2135 (2022)

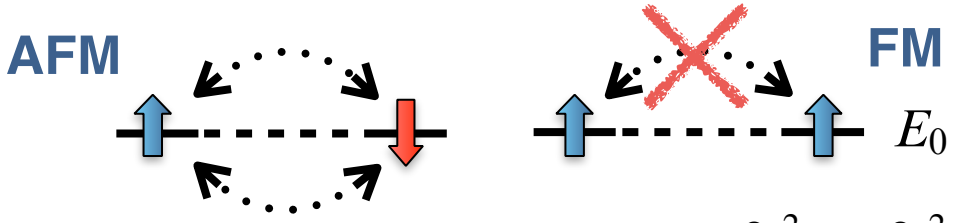
Introduction: Orbitals and spins

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

Ferro-orbital order



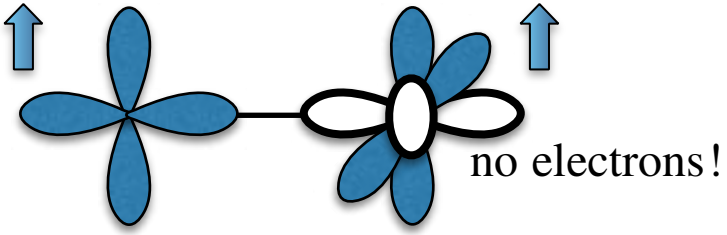
1 electron per orbital 1 electron per orbital



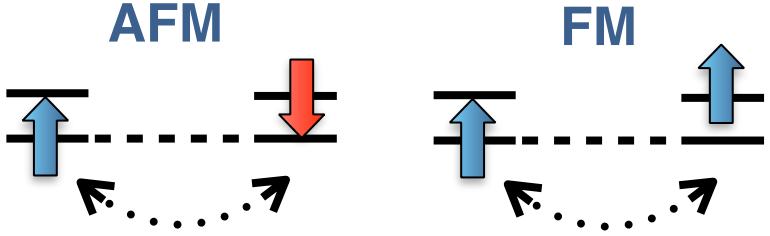
$$J_A = E_{FM} - E_{AFM} = 2E_0 - (2E_0 - \frac{2t^2}{U}) = \frac{2t^2}{U}$$

strong AFM

AntiFerro-orbital order



1 electron per orbital 1 electron per orbital

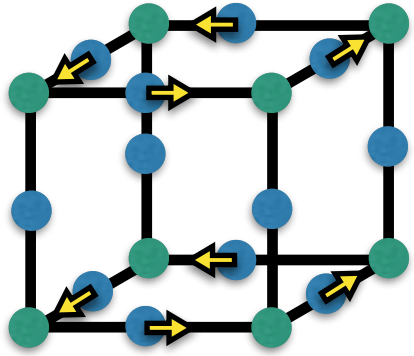


$$J_F = E_{FM} - E_{AFM} = 2E_0 - \frac{2t^2}{U - J_H} - 2E_0 + \frac{2t^2}{U} \sim -\frac{t^2 J_H}{U^2}$$

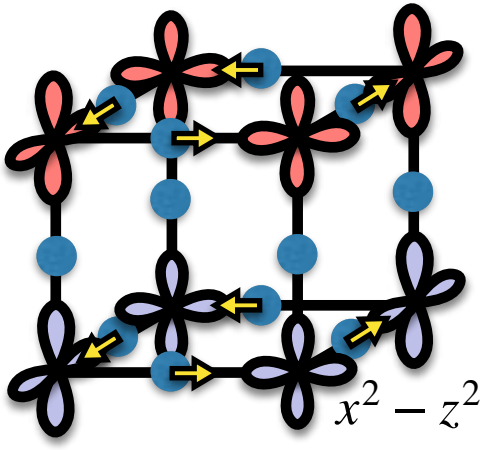
weak FM

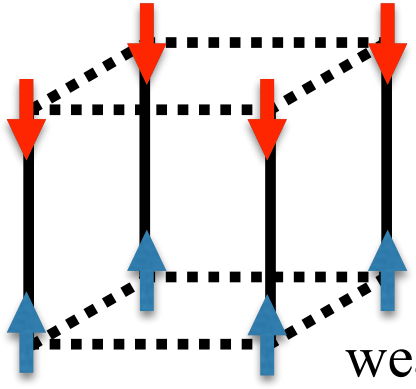
Modification of magnetic structure by orbitals

If we know local distortions



We can understand which orbitals are occupied



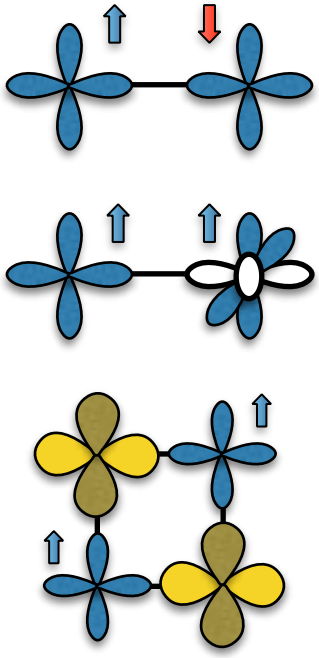


Stong AFM

weak FM

We can find a magnetic order!

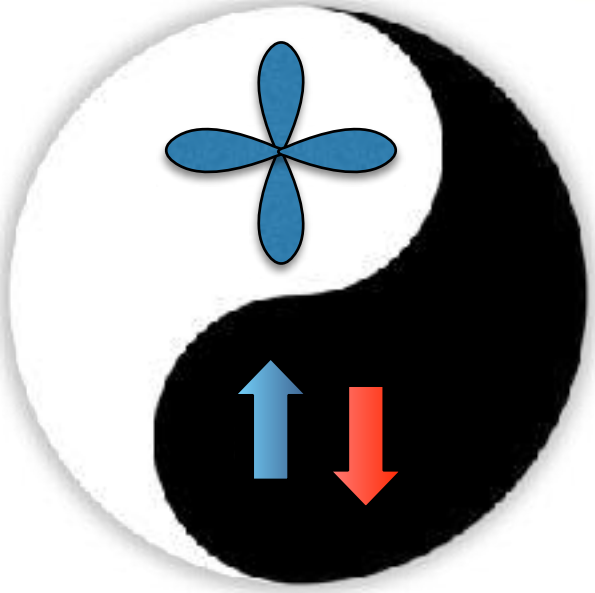
Goodenough - Kanamori - Anderson rules
connect orbitals and spins



Ferro-orbital => AFM

Antiferro-orbital => FM

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



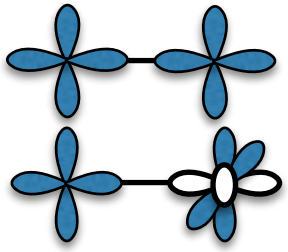
John Goodenough
1922-2023
Nobel prize
2019

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



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

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

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

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

$\downarrow$

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

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

FM

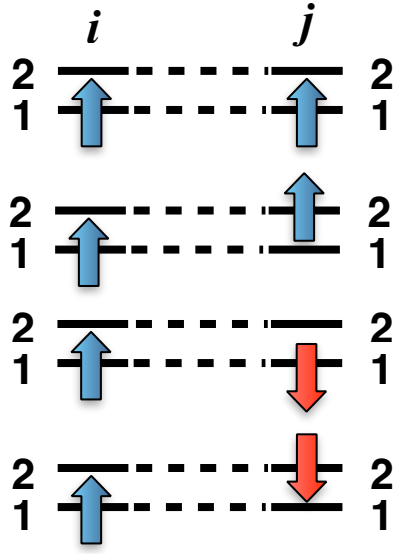
	T_C
$YTiO_3$	30 K
$BaNaOs_2O_6$	7 K
$NaCrGe_2O_6$	6 K

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 exchange 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

Exchange 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:

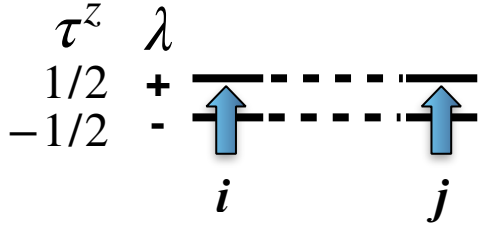
$$\hat{H} = \sum_{i\neq j} t_{ij}^{ab} c_{ia\sigma}^{\dagger} c_{jb\sigma} + \frac{1}{2}\sum_{i} U_{ab} n_{ia\sigma} n_{ib\sigma'} \left(1 - \delta_{ab}\delta_{\sigma\sigma'}\right)$$
$$- \sum_{i,a\neq b} J_H^{ab} \left(c_{ia\sigma}^{\dagger} c_{ia\sigma'} c_{ib\sigma'}^{\dagger} c_{ib\sigma} + c_{ia\sigma}^{\dagger}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

Kugel-Khomskii Hamiltonian:

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

Kugel-Khomskii model
derivation

Let's consider a lattice with two orbitals at each site



λ numerates orbitals

Hamiltonian describing exchange interaction can by obtained by the 2nd order of perturbation theory with respect to electron hopping

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

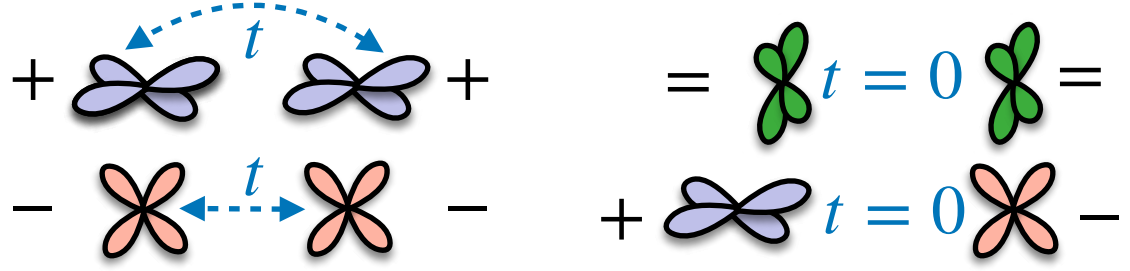
sites — orbitals — spins — energy of the perturbed state

Approximations:

A. $t_{++} = t_{--} = t$

$\lambda = \lambda', \quad \lambda'' = \lambda'''$

E.g.



B. $\langle \hat{H}_1 \rangle = \tilde{U}$ we don't distinguish energies of different excited states

Kugel-Khomskii model
derivation

$$\hat{H}_{eff} = -\sum_{i\neq j}\sum_{\lambda\lambda'}\sum_{\sigma\sigma'}\frac{t^2}{\tilde{U}}c^{\dagger}_{i\lambda\sigma}c_{j\lambda\sigma}c^{\dagger}_{j\lambda'\sigma'}c_{i\lambda'\sigma'} = -\sum_{i\neq j}\sum_{\lambda\lambda'}\frac{t^2}{\tilde{U}}\left(\sum_{\sigma}c^{\dagger}_{i\lambda\sigma}c_{i\lambda'\sigma}(1-c^{\dagger}_{j\lambda'\sigma}c_{j\lambda\sigma}) - \sum_{\sigma\neq\sigma'}c^{\dagger}_{i\lambda\sigma}c_{i\lambda'\sigma'}c^{\dagger}_{j\lambda'\sigma'}c_{j\lambda\sigma}\right)$$

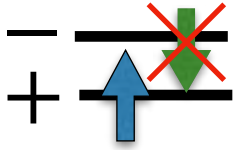
Spin space (spins)

$$c^{\dagger}_{i\uparrow}c_{i\uparrow} = \hat{n}_{i\uparrow} = 1/2 + \hat{S}^z_i, \quad c^{\dagger}_{i\uparrow}c_{i\downarrow} = \hat{S}^+_i$$
$$c^{\dagger}_{i\downarrow}c_{i\downarrow} = \hat{n}_{i\downarrow} = 1/2 - \hat{S}^z_i, \quad c^{\dagger}_{i\downarrow}c_{i\uparrow} = \hat{S}^-_i$$

Orbital space (pseudospins)

$$c^{\dagger}_{i+}c_{i+} = \hat{n}_{i+} = 1/2 + \hat{\tau}^z_i, \quad c^{\dagger}_{i+}c_{i-} = \hat{\tau}^+_i$$
$$c^{\dagger}_{i-}c_{i-} = \hat{n}_{i-} = 1/2 - \hat{\tau}^z_i, \quad c^{\dagger}_{i-}c_{i+} = \hat{\tau}^-_i$$

i.e. e.g. what $c^{\dagger}_{i\uparrow+}c_{i\downarrow-}$ does? It **acts in both spin and orbital spaces** raising both spin and pseudospin



$$c^{\dagger}_{i\uparrow+}c_{i\downarrow-} = \hat{\tau}^+_i\hat{S}^+_i$$

$$\hat{H}_{eff} = \sum_{i\neq j}\hat{H}_{++} + \hat{H}_{+-} + \hat{H}_{-+} + \hat{H}_{--}$$

$\lambda = +, \lambda' = +$

Expand the sum over orbitals explicitly

$$\hat{H}_{\pm\pm} = -\frac{t^2}{\tilde{U}}\left(\frac{1}{2} \pm \hat{\tau}^z_i\right) + \frac{t^2}{\tilde{U}}\left(\frac{1}{2} \pm \hat{\tau}^z_i\right)\left(\frac{1}{2} \pm \hat{\tau}^z_j\right)\left[\frac{1}{2} + 2\hat{\vec{S}}_i\hat{\vec{S}}_j\right], \quad \hat{H}_{\pm\mp} = \frac{t^2}{\tilde{U}}\hat{\tau}^{\pm}_i\hat{\tau}^{\mp}_j\left[\frac{1}{2} + 2\hat{\vec{S}}_i\hat{\vec{S}}_j\right]$$

Highly (and not really) symmetric Kugel-Khomskii model

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

so-called *SU(4)* symmetric Kugel-Khomskii model

Assume spins are coupled ferromagnetically, i.e. $\langle \hat{S}_i^z \hat{S}_j^z \rangle = 1/4$

In a mean-field $E_{AFM} = \frac{t^2}{\tilde{U}} \sum_{i \neq j} \left(\frac{1}{2} + 2\langle \hat{\tau}_i^z \hat{\tau}_j^z \rangle \right)$

Minimum at $\langle \hat{\tau}_i^z \hat{\tau}_j^z \rangle = -1/4$ i.e. antiferro-orbital ordering*

Reproduces GKA rules

Kugel-Khomskii model (perovskite with e_g-electrons)

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

** Mean-field approximation is a very poor approach in a general case, see e.g. PRL 82, 836 (1998)*

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

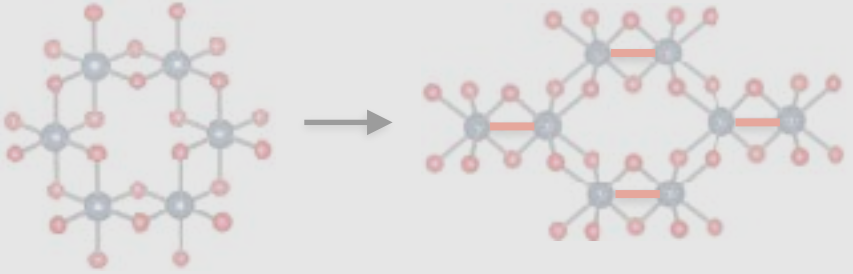
Heisenberg model

↕

Kugel-Khomskii model

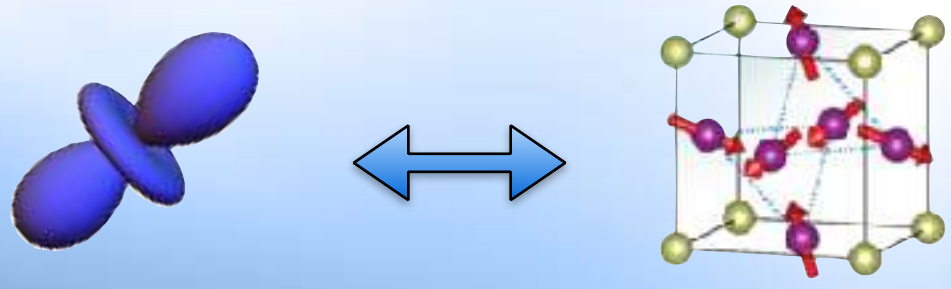
M. Yamada et al., PRL 121, 97201 (2018)

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

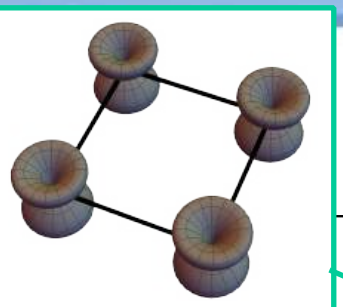


Interplay of different degrees of freedom:

Some examples



Example 1: 3-band Hubbard model with 1 electron on the square lattice (= Sr_2VO_4)



Dipoles

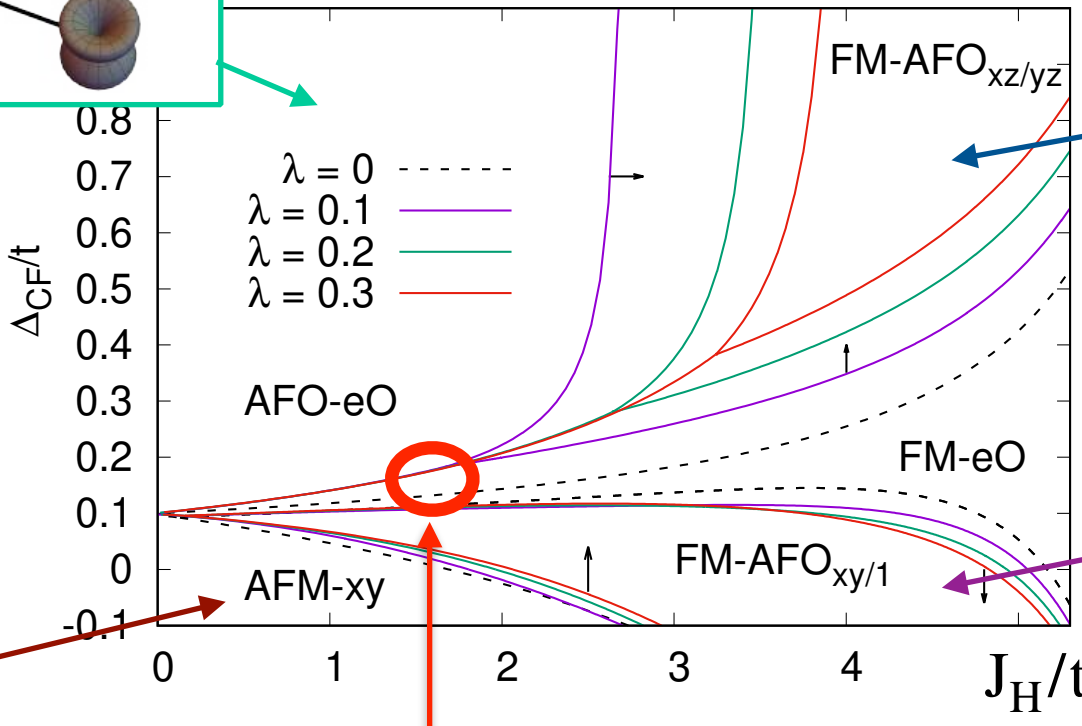
$$\langle S \rangle = \langle L \rangle = 0$$

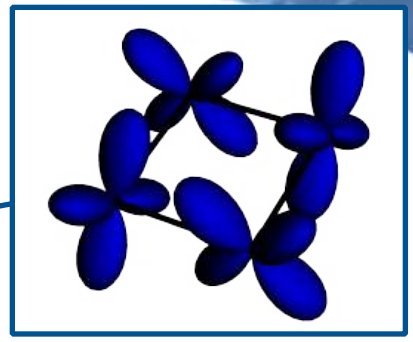
Octupoles

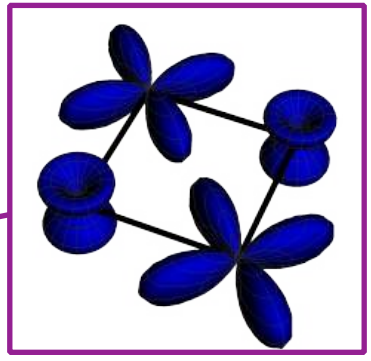
$$\langle T_x^\alpha \rangle \neq 0, \ \langle T_x^\beta \rangle \neq 0$$

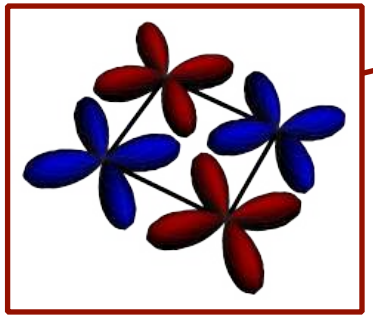
$$T_x^\alpha = J_x^3 - \frac{1}{2}(\overline{J_x J_y^2} + \overline{J_z^2 J_x})$$

$$T_x^\beta = \frac{\sqrt{15}}{6}(\overline{J_x J_y^2} - \overline{J_z^2 J_x})$$



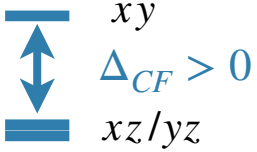






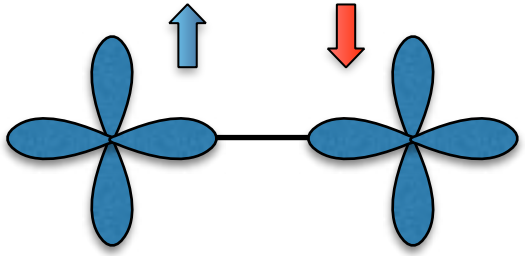
Realistic parameters for Sr_2VO_4

Orbitals matter!



P. Igoshev, V. Irkhin, S.S. arXiv:2406.07386

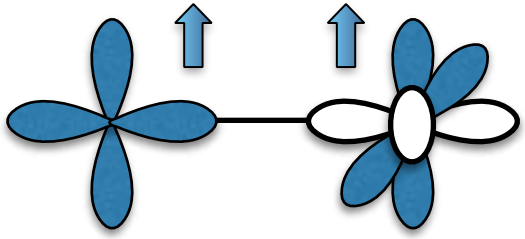
Example 2: Reduction of dimensionality
Modulation of the exchange interaction



Ferro-orbital => AFM

strong

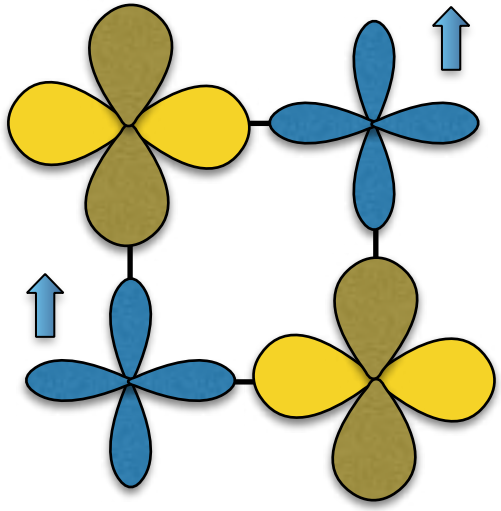
$$J_A = \frac{2t^2}{U}$$



Antiferro-orbital => FM

weak

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



90^0 via orthogonal p-orbitals => FM

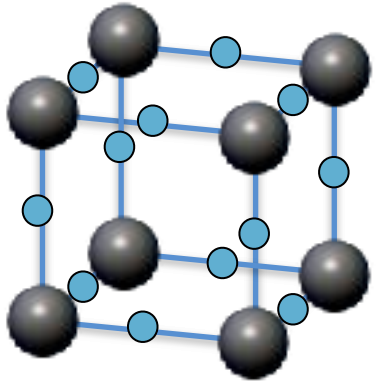
weak

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

Example 2: Reduction of dimensionality
Modulation of the exchange interaction

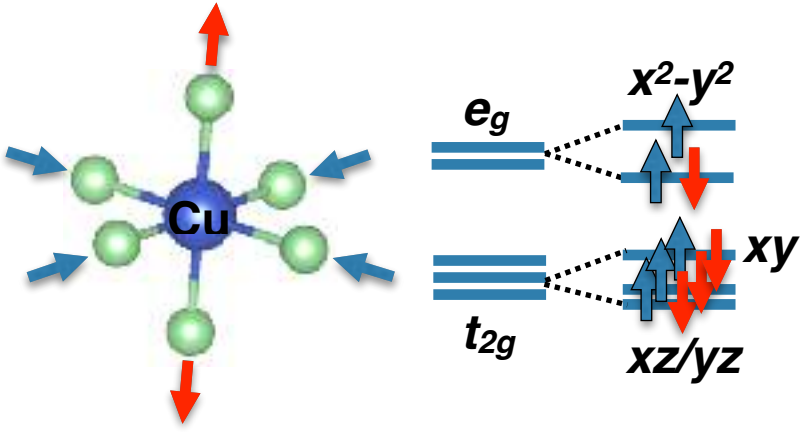
$KCuF_3$

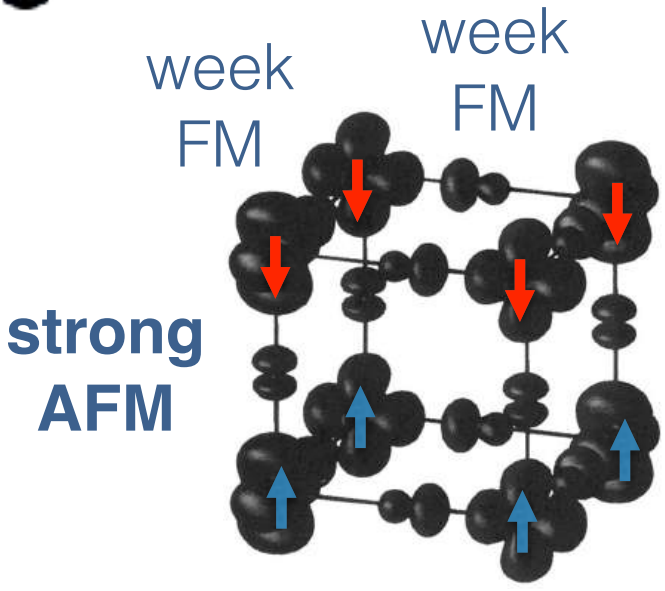
Crystal structure:
perovskite (3D)



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 !!!

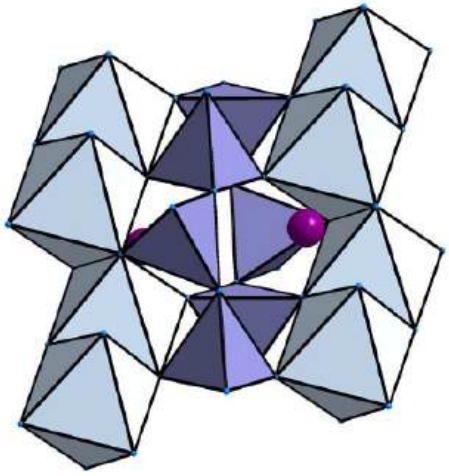
Orbitals reduce dimensionality: 3D ⟶ 1D

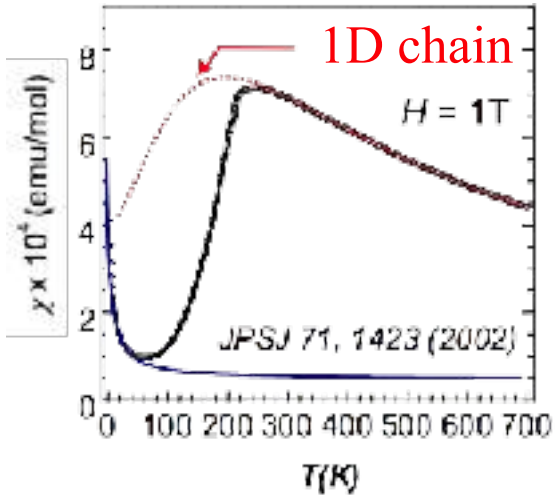
Example 3: Dimerization driven by orbital ordering

$NaTiSi_2O_6$

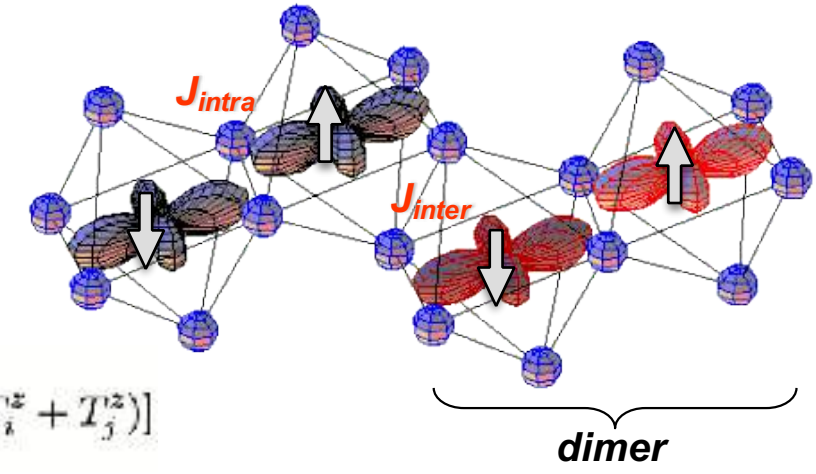
Crystal structure: pyroxene (1D)

Ti^{3+} ($3d^1$, S=1/2) →





Orbital ordering: (LDA+U)



$$H^{\mathrm{Ti}} = |\mathbf{J}^{\mathrm{Ti}}| \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j \times$$

$$[\frac{1}{4} + T_i^z T_j^z + \frac{(-1)^i}{2}(T_i^z + T_j^z)]$$

Exchange constants:

In dimer: J_{intra} = *396 K* (AFM)
inter-dimer: J_{inter} = *-5 K* (FM)

S.S., O. Popova, D. Khomskii
PRL 96, 249701 (2006)

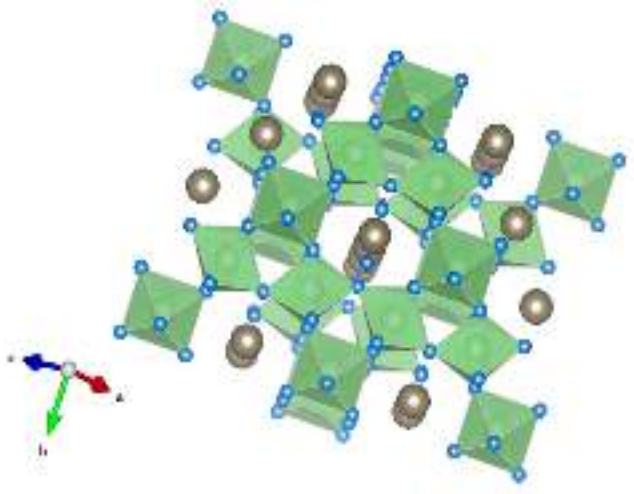
Orbitals reduce dimensionality: 1D → 0D

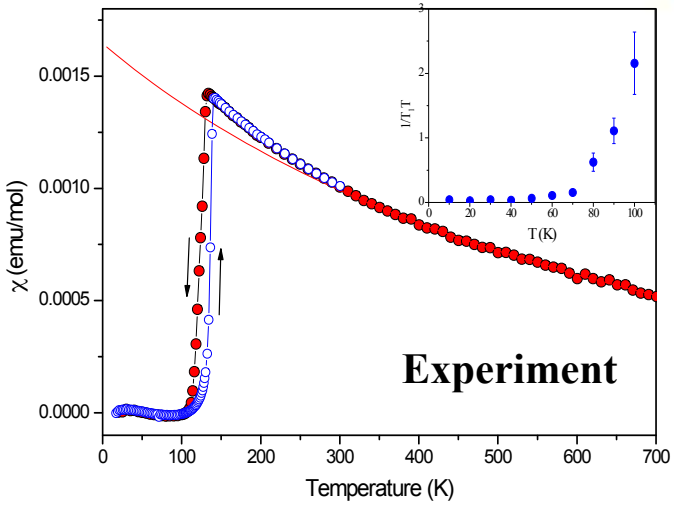
Example 4: Formation of a Haldane chain due to orbital ordering

$Tl_2Ru_2O_7$

Crystal structure: pyrochlore (3D)

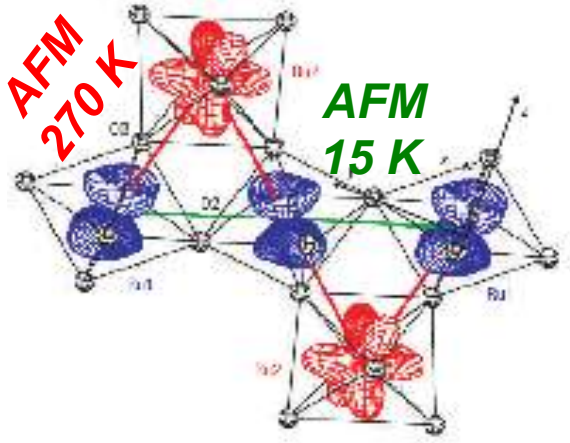
Ru^{4+} ($4d^4$, $S=1$)





Orbital ordering: (LDA+U)

Ru^{4+}



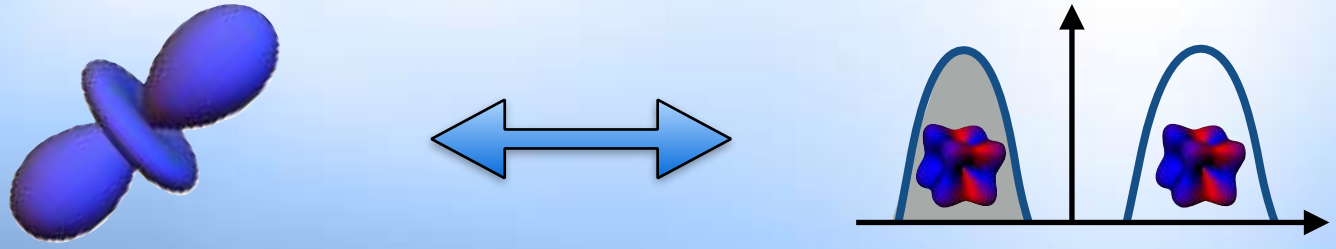
AFM chain $S=1$: Haldane chains

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

Orbitals reduce dimensionality: 3D → 1D

Directional character of orbitals:

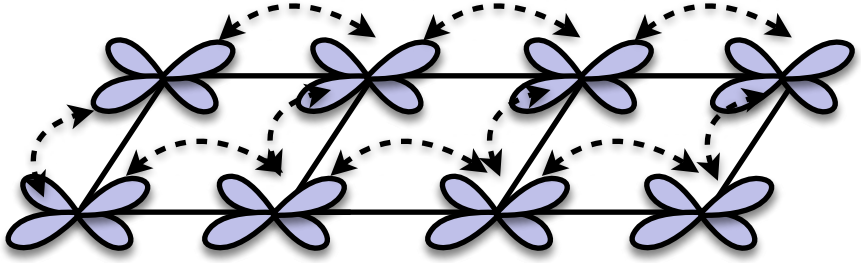
Electronic structure:
Orbital-selective Mott transition



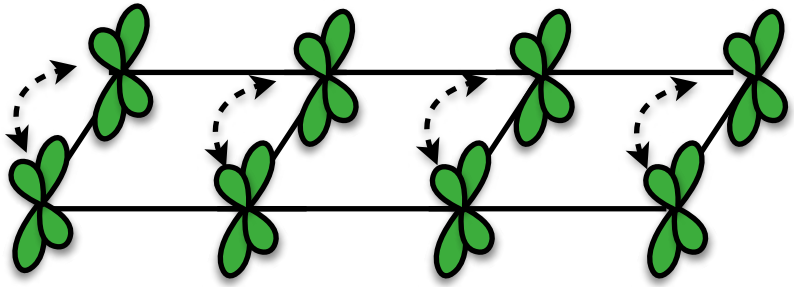
Directional character of orbitals

t_{2g} orbitals on the square lattice

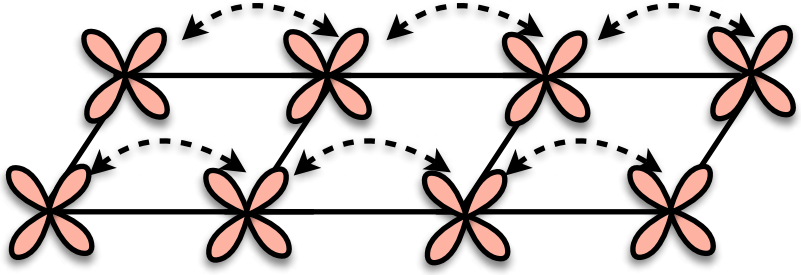
xy – orbital

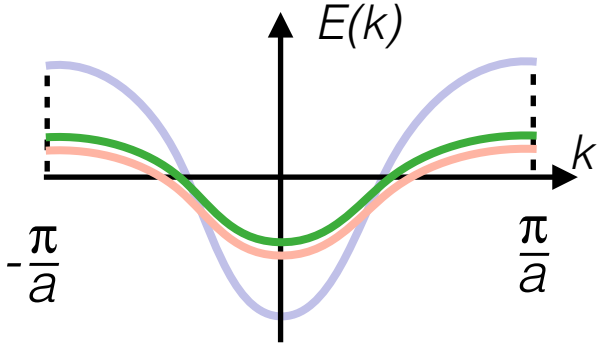


yz – orbital



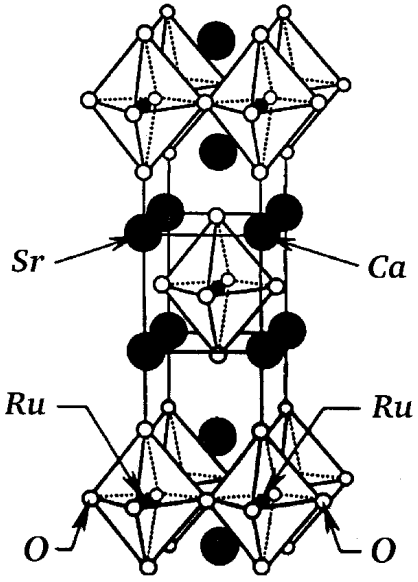
xz – orbital



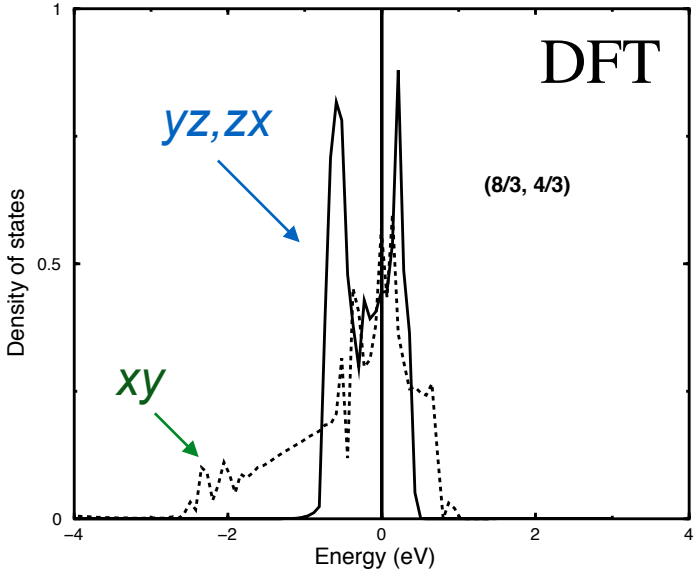


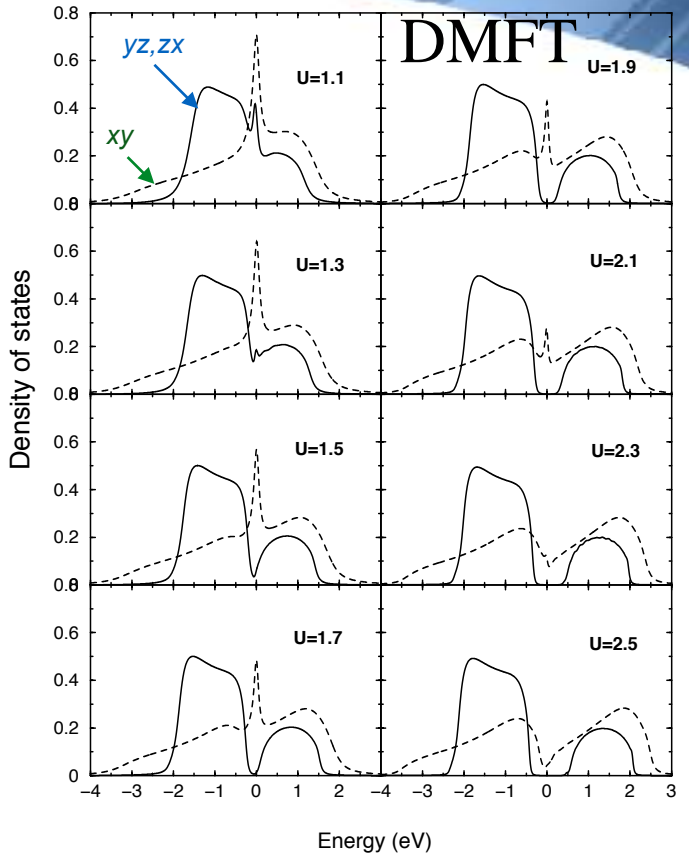
Orbitals can have a very different dispersion, which can be reflected on e.g. transport properties

Orbital-selective Mott (OSM) transition



$Ca_{2-x}Sr_xRuO_4$





Layered structure: Square lattice

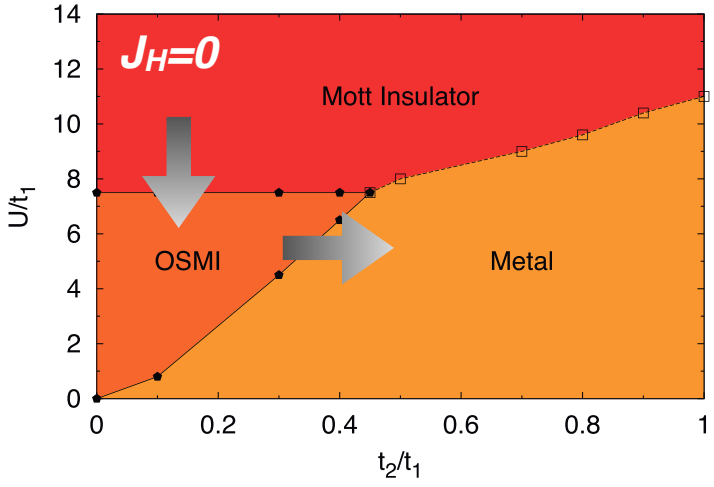
Orbital-selective Mott transition: Mott transition can occur separately for different orbitals

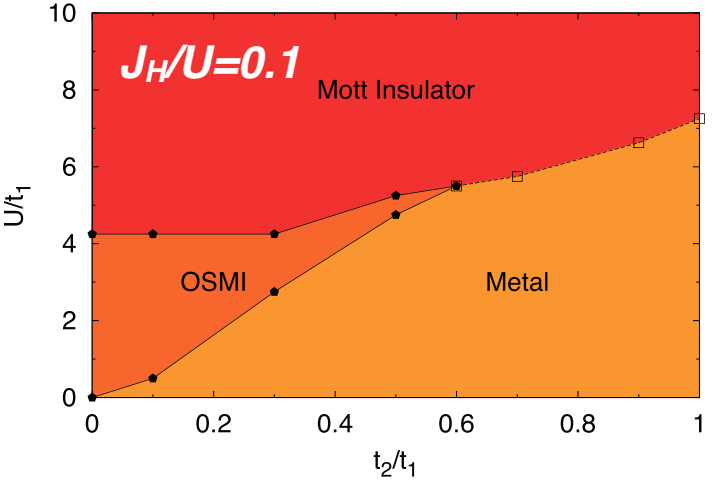
Critical U_c: 1.5 eV for xz/yz orbitals
2.5 eV for xy orbital

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

Orbital-selectivity: effect of Hund's coupling and orbital mixing

2D Square lattice, two orbitals, half-filling (2 electrons/site)





$$\mathcal{H} = \mathcal{H}_{\text{kin}} + \mathcal{H}_{\text{int}}$$

α - orbital index

$$\mathcal{H}_{\text{kin}} = -\sum_{\langle i,j\rangle,\alpha,\sigma} t_\alpha c^\dagger_{i,\alpha,\sigma} c_{j,\alpha,\sigma} + \text{h.c.},$$

$$\mathcal{H}_{\text{int}} = U\sum_{i,\alpha} n_{i,\alpha,\uparrow} n_{i,\alpha,\downarrow} + U'\sum_{i,\sigma,\sigma'} n_{i,1,\sigma} n_{i,2,\sigma'}$$

$$- J_H\sum_{i,\sigma,\sigma'} c^\dagger_{i,1,\sigma} c_{i,1,\sigma'} c^\dagger_{i,2,\sigma'} c_{i,2,\sigma} - J_H\sum_i (c^\dagger_{i,1,\uparrow} c^\dagger_{i,1,\downarrow} c_{i,2,\uparrow} c_{i,2,\downarrow} + \text{h.c.})$$

Effect of orbital mixing ($t_{mm'} \neq 0$)

(1) Destabilization of the Orbital-selective Mott state

Effect of the Hund's coupling:

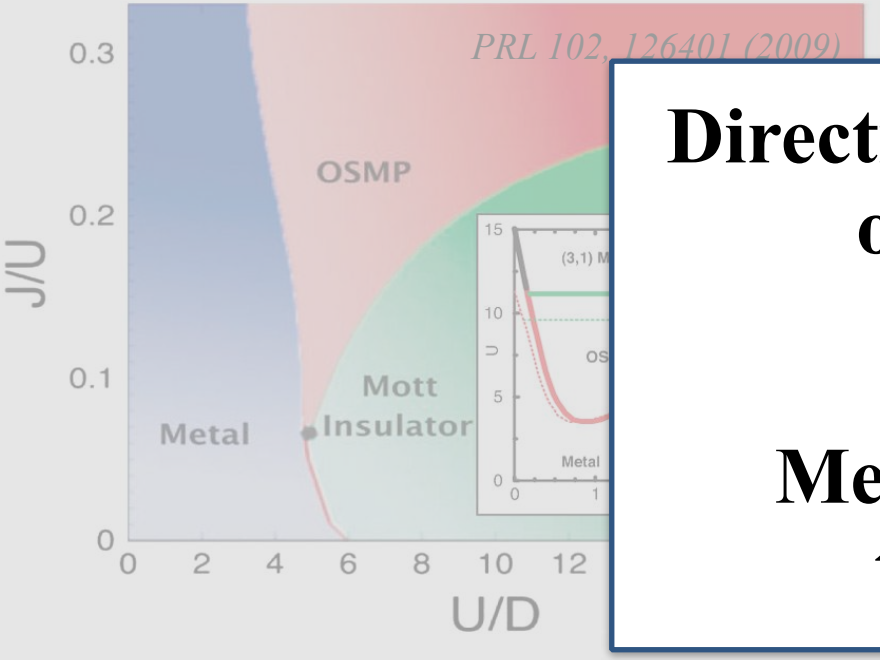
(1) Stabilization of Mott phase

(2) Stabilization of the Orbital-selective Mott state

Tocchio et al., JPCM 28, 105602 (2016)

Orbital-selective Mott (OSM) transition

OSM transition is possible
even in the case of the same bandwidths



$$H = -t \sum (d^{\dagger}_{im\sigma} d_{jm\sigma} + \text{H.c.}) + \sum_{i,m\sigma} \varepsilon_m d^{\dagger}_{im\sigma} d_{im\sigma}$$

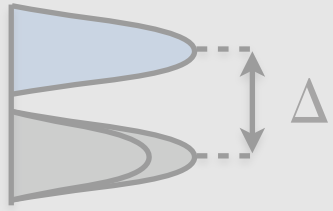
$$\left(U - \frac{J}{2}\right) \sum_{i,m>m'} n_{im} n_{im'}$$

$$(d^{\dagger}_{im\uparrow} d^{\dagger}_{im\downarrow} d_{im'\uparrow} d_{im'\downarrow} + \text{H.c.})].$$

Directional character of orbitals

↓

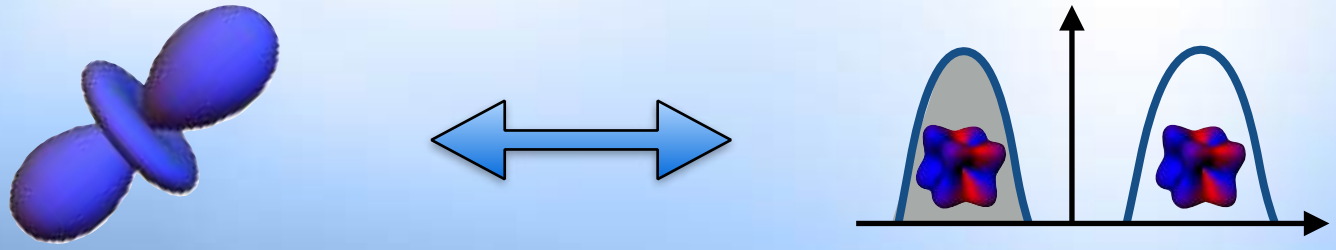
Metal-insulator transition



With J we increase energy difference between high-spin and low-spin configurations
(and suppress orbital fluctuations)

Directional character of orbitals:

Orbital-selectivity and magnetic properties



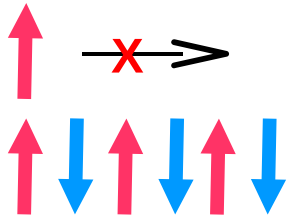
Double exchange as an orbital-selective effect

Double exchange is a natural realization of the orbital-selectivity

Itinerant electrons (e.g. e_g electrons)

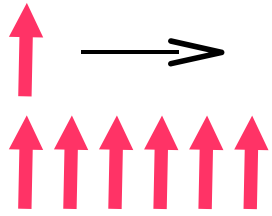
Localized electrons (e.g. t_{2g} electrons)

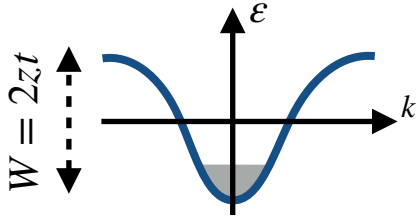
AFM



No energy gain due to hoppings!

FM





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

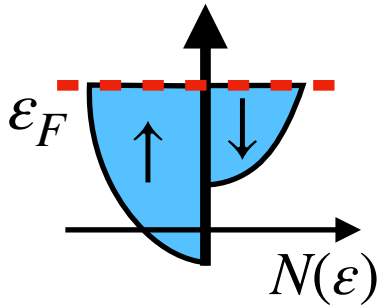
Double-exchange mechanism of ferromagnetism

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

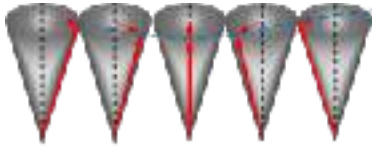
Examples: CrO_2, CMR manganates etc.

Orbital-selective behaviour: localized and itinerant magnetism on the same ion

Itinerant magnetism

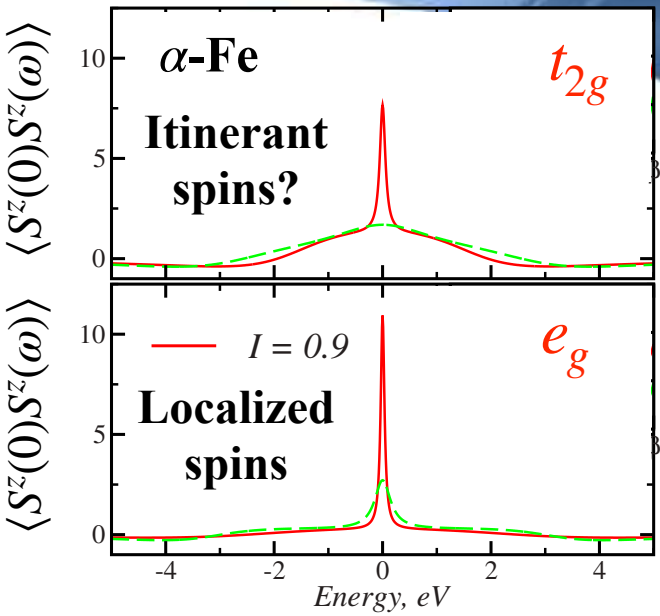


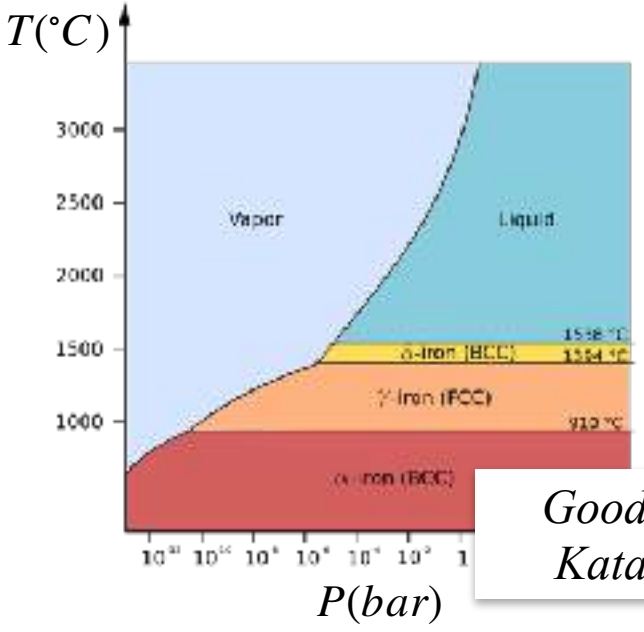
Localized spins



Dynamical mean-field theory:

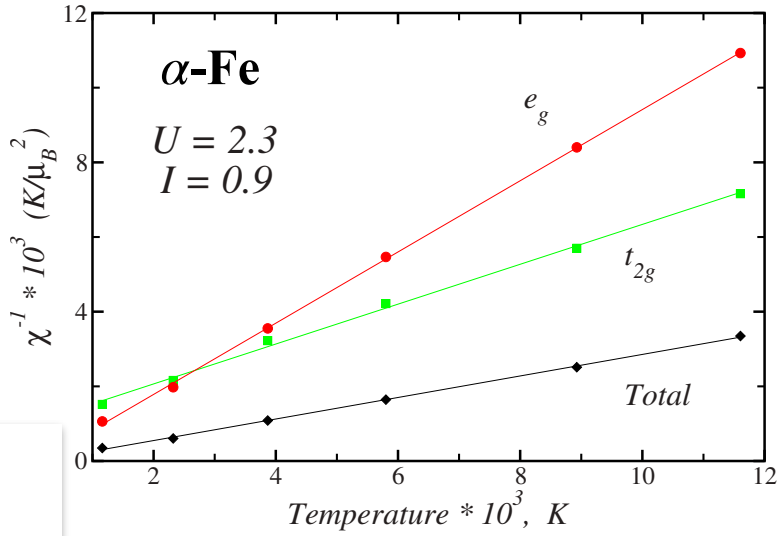
HWHM of $\langle S^z(0)S^z(\omega)\rangle$
$\sim$ 1/"lifetime"





Electrons of the same shell (d) can behave differently depending on the symmetry

Orbital-selective behaviour!



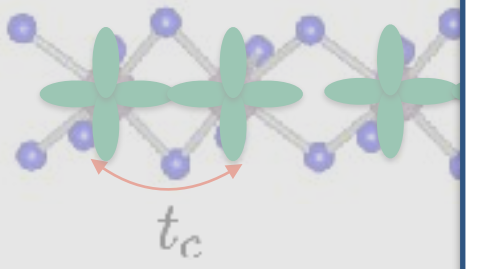
Goodenough, Phys. Rev. 120, 67 (1960)
Katanin et al., PRB 81, 045117 (2010)

Extreme case:
Orbital-selectivity in low-dimensional magnets

E.g. a dimerized chain

Two different orbitals *c* and *d*

$t_c \gg t_d$



Directional character of orbitals

↓

Magnetic properties

Examples

$CuIr_2S_4$ *Nat. Com. 10, 3638 (2019)*

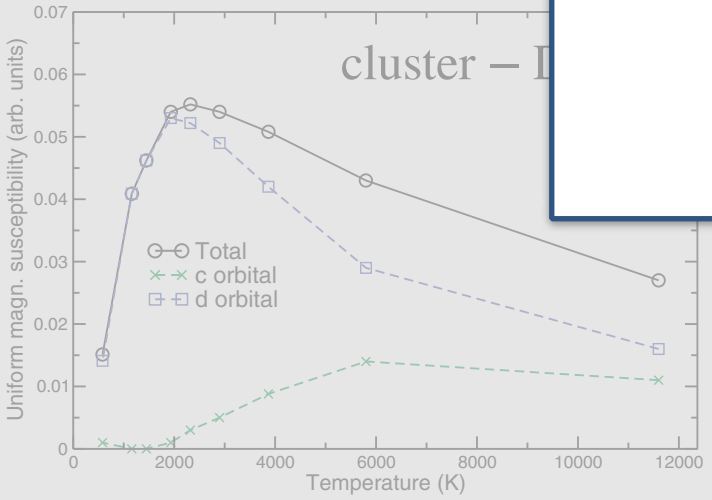
$BaCeRu_2O_9$ *JACS 141, 9928 (2019)*

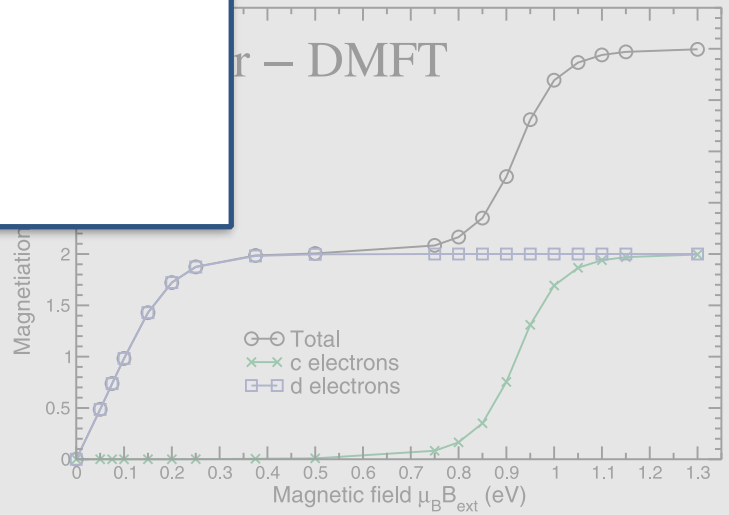
PRB 100, 045131 (2019)

PRL 122, 106401 (2019)

PRB 98, 201105(R) (2018)

skii PNAS 113, 10491 (2016)



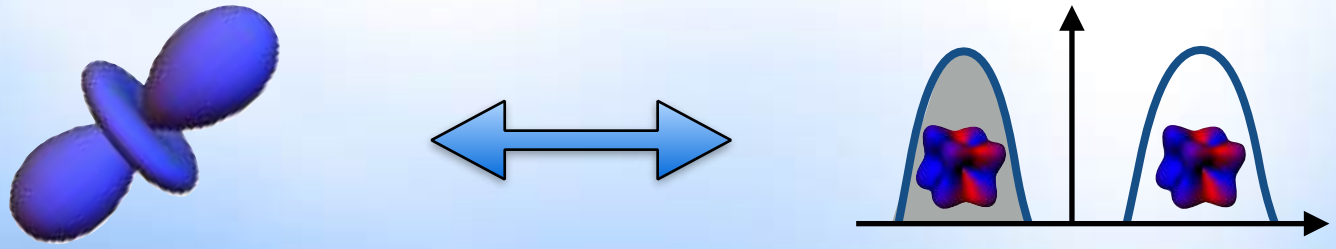


c and *d* orbitals "work" at different ***T***

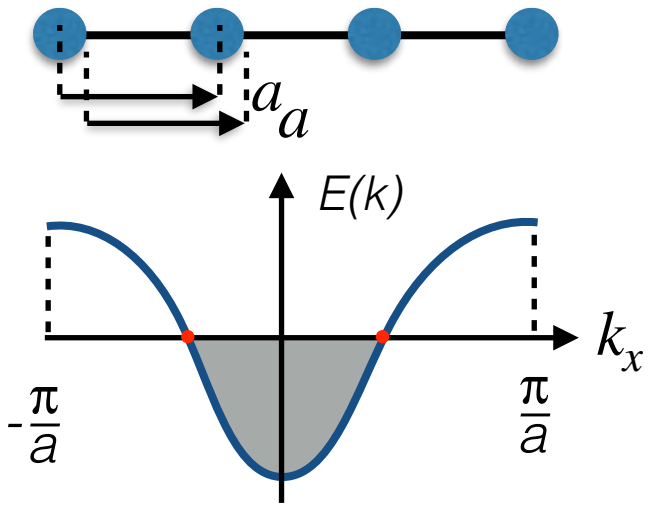
c and *d* orbitals "work" at different ***B***

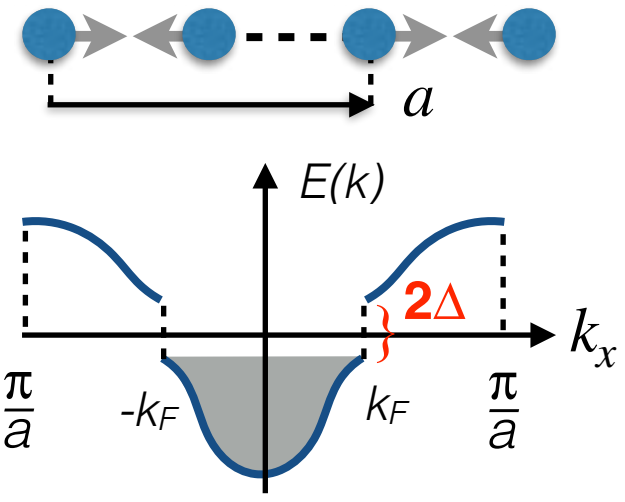
Directional character of orbitals:

Orbitally-induced Peierls transition

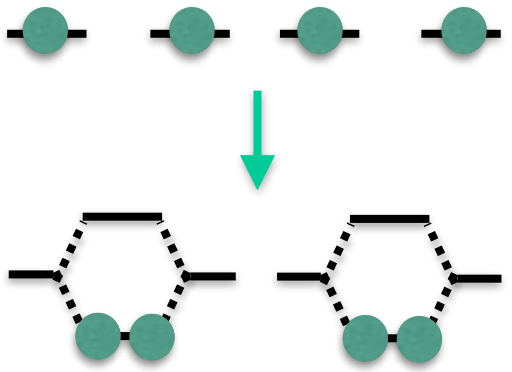


Peierls transition - simplest case of
1D + half-filling (1 electron/site)





On a "Chemical language"



Instability at $|Q| = 2k_F$

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

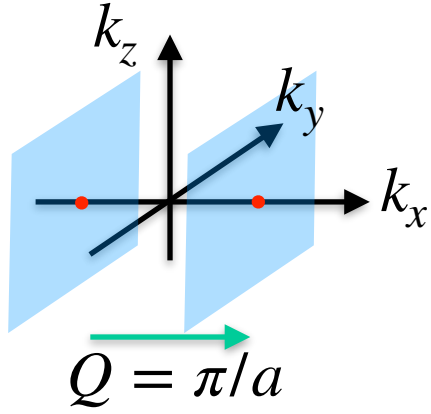
Gain in kinetic energy: $\sim -|\Delta|^2 \ln|\Delta|$

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

Physical mechanism: nesting of the Fermi surface

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

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



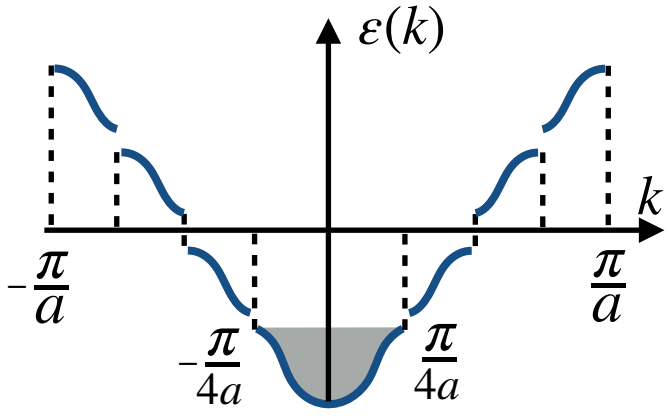
Factor I: lattice deformations are possible for other fillings!

Peierls transition - away from half-filling

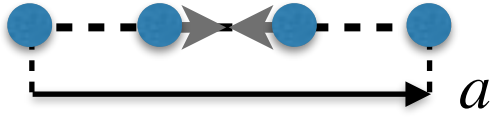
Peierls transition: 1D chain Instability at $|Q| = 2k_F$

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

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

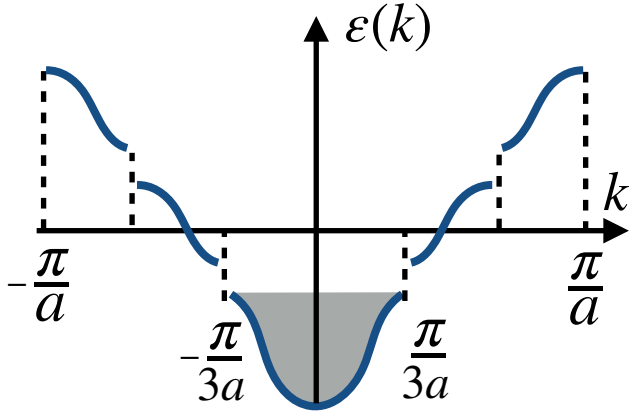


Tetramerization

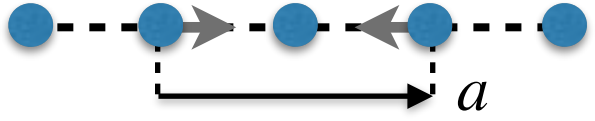


1/3 electron/site:

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



Trimerization

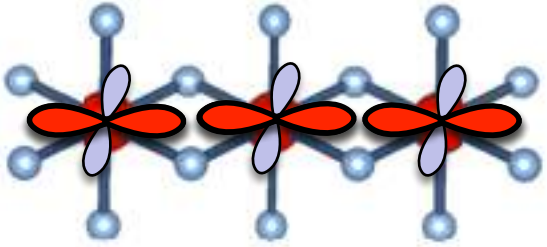


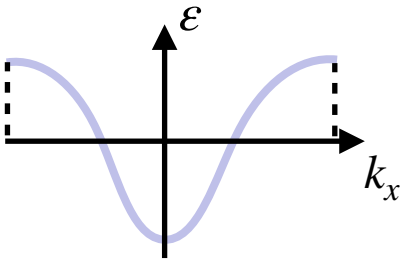
Peierls transition - importance of orbital degrees of freedom

Factor II: Orbital-selectivity with respect to Peierls transition

E.g. edge-sharing geometry

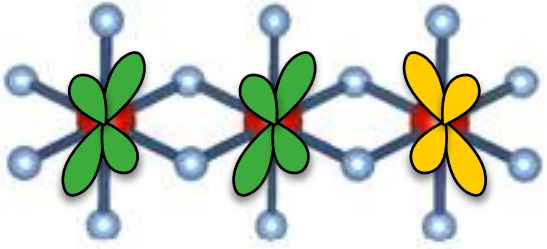
xy

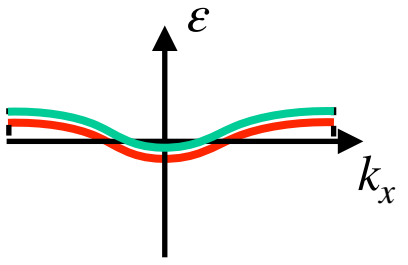




- Wide nearly 1D bands susceptible to Peierls transition

xz/yz

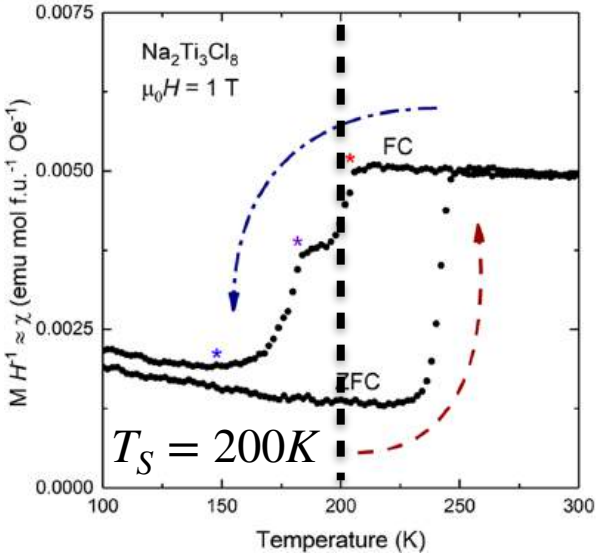




- Localized bands susceptible to U;
- Crystal-field can strongly change position of the band;

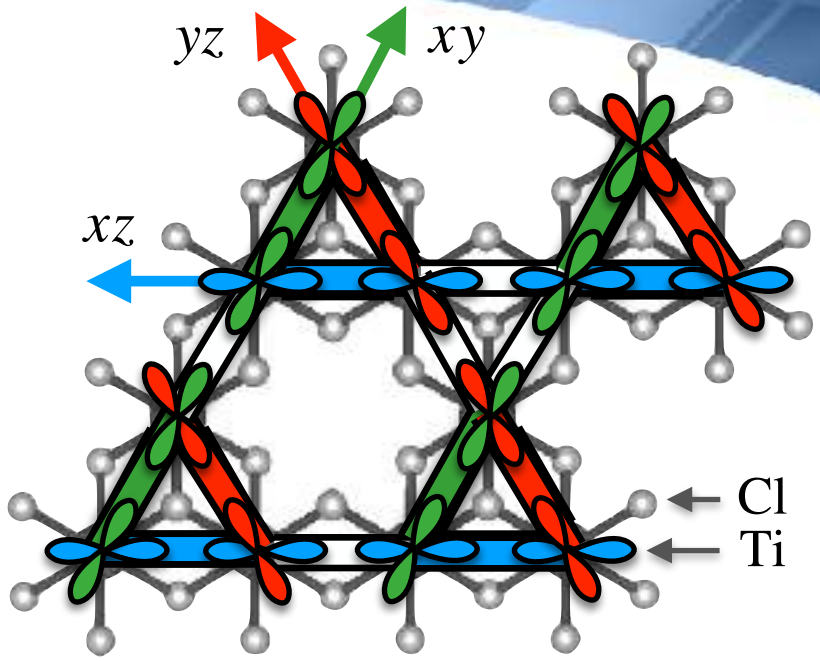
Orbitally-induced Peierls effect: Kagome lattice

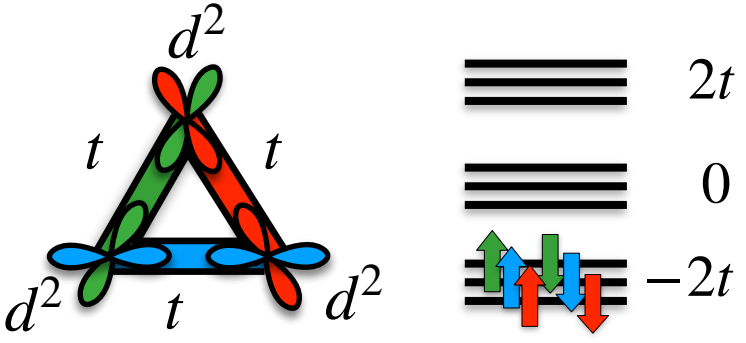
$Na_2Ti_3Cl_8$: Ti^{2+}: d^2 $(S=1)$

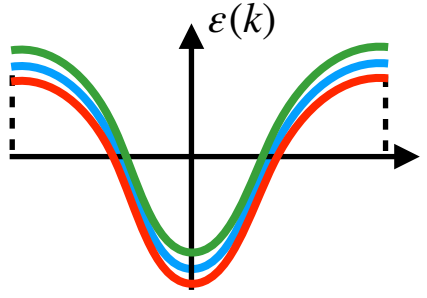


Angew. Chem ***34***, *71 (1995)*
ZAAC ***643***, *2063 (2017)*
Inorg. Chem ***58***, *11941 (2019)*
PRL ***124***, *167203 (2020)*

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







Three 1D bands!

Band filling: 1/2

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

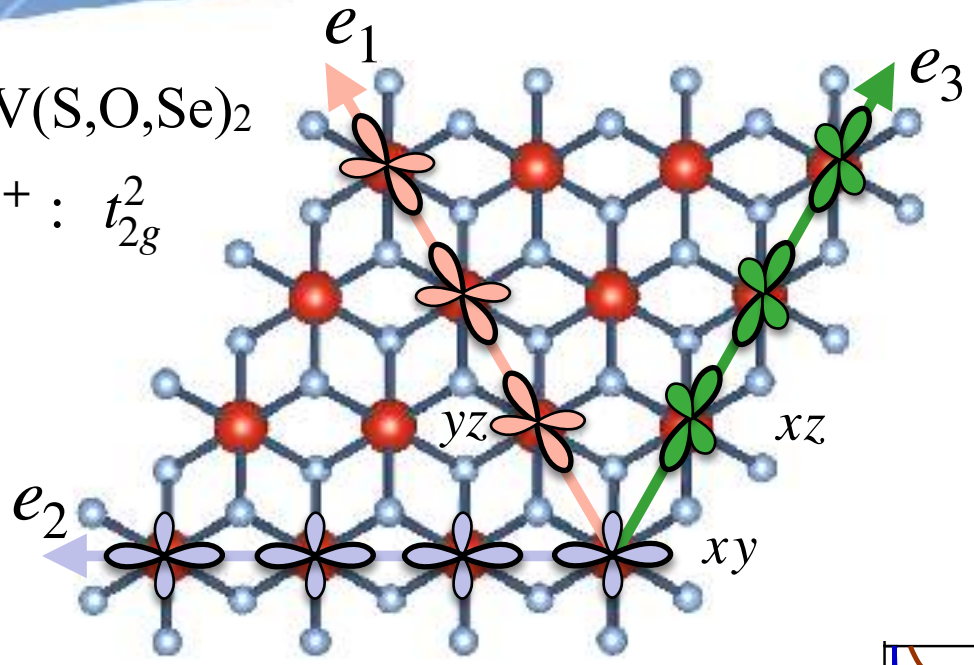
Trimerization = Dimerization along each direction

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

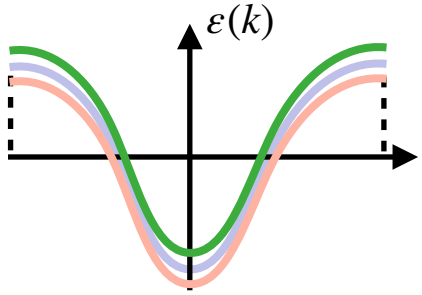
Orbitally-induced Peierls:
another lattice, but again trimerization

$LiV(S,O,Se)_2$

$V^{3+}: \; t_{2g}^2$



Assumption: the most important is a direct overlap between *d*-orbitals

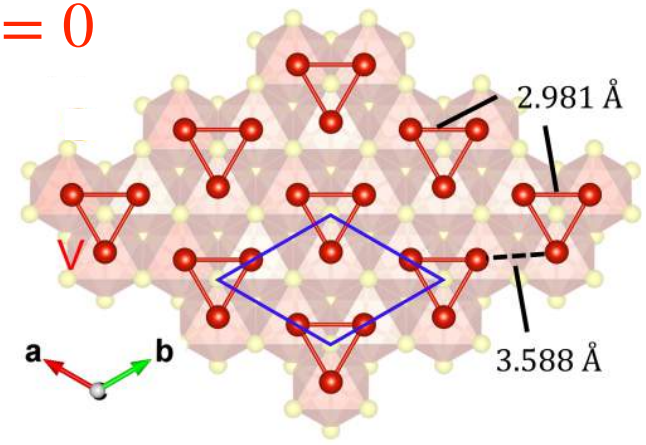


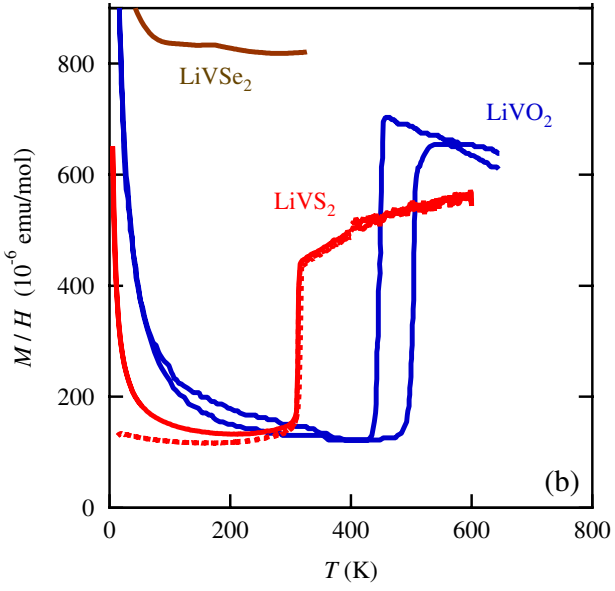
Three 1D bands!

Number of holes

$n_o = 1/3$

$S = 0$





Pen et al.,
PRL 78, 1323 (1997)

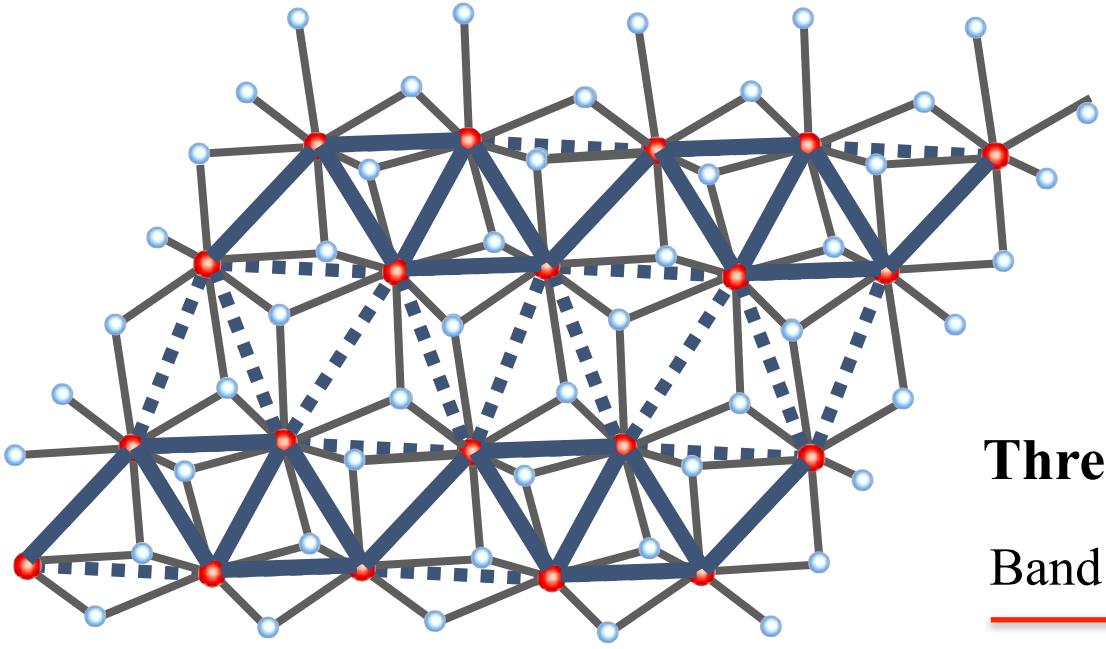
Katayama et al.,
PRL 103, 146405 (2009)

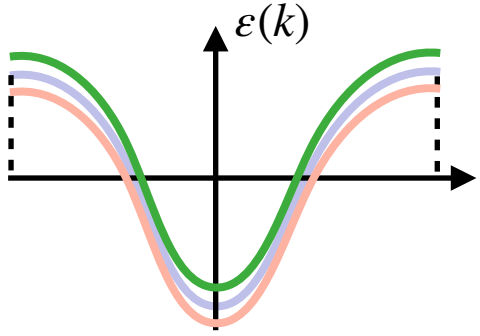
Kojima et al.,
PRB 100, 235120 (2019)

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

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

⇩

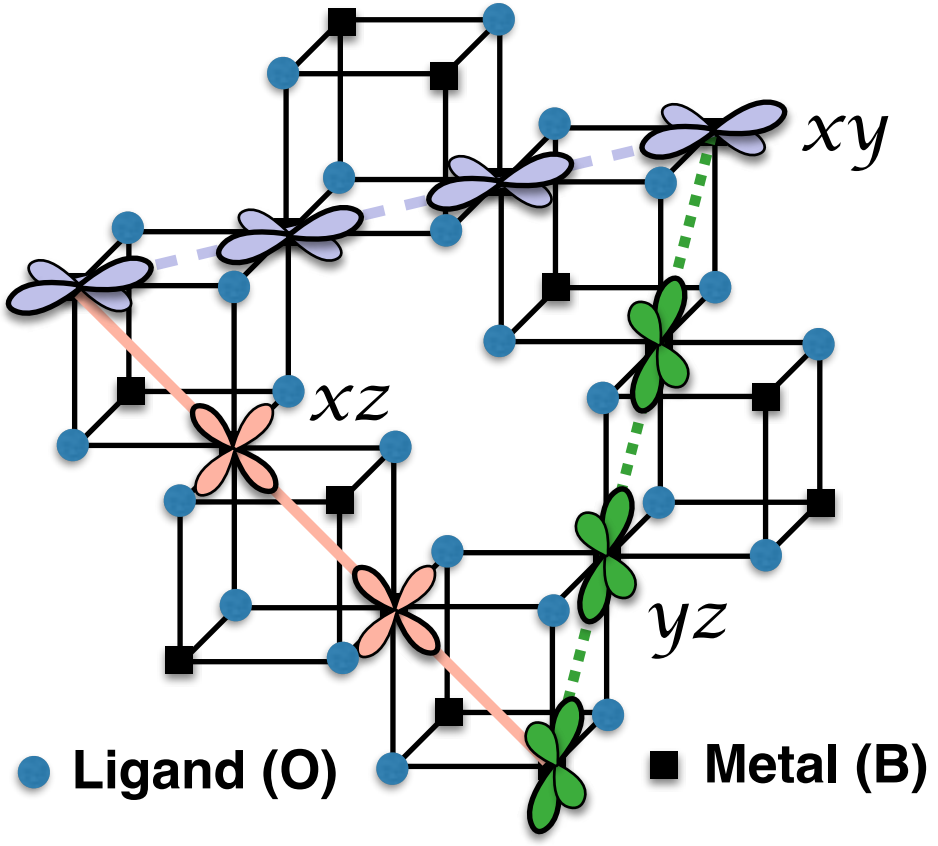
Formation of "diamond necklace"

Dimerization in three directions!

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

Reduction of dimensionality
Orbitally-induced Peierls effect

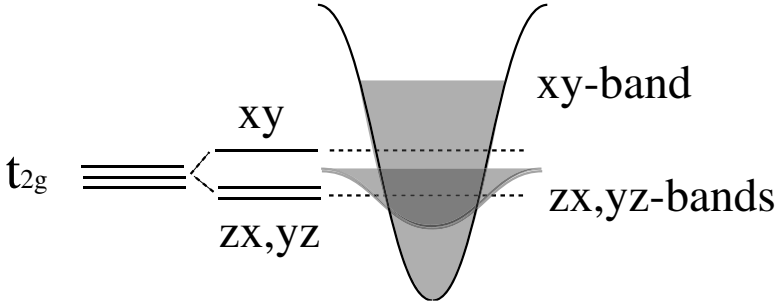
Spinels (3D structure): AB_2O_4



Natural formation of 1D bands due to orbitals…

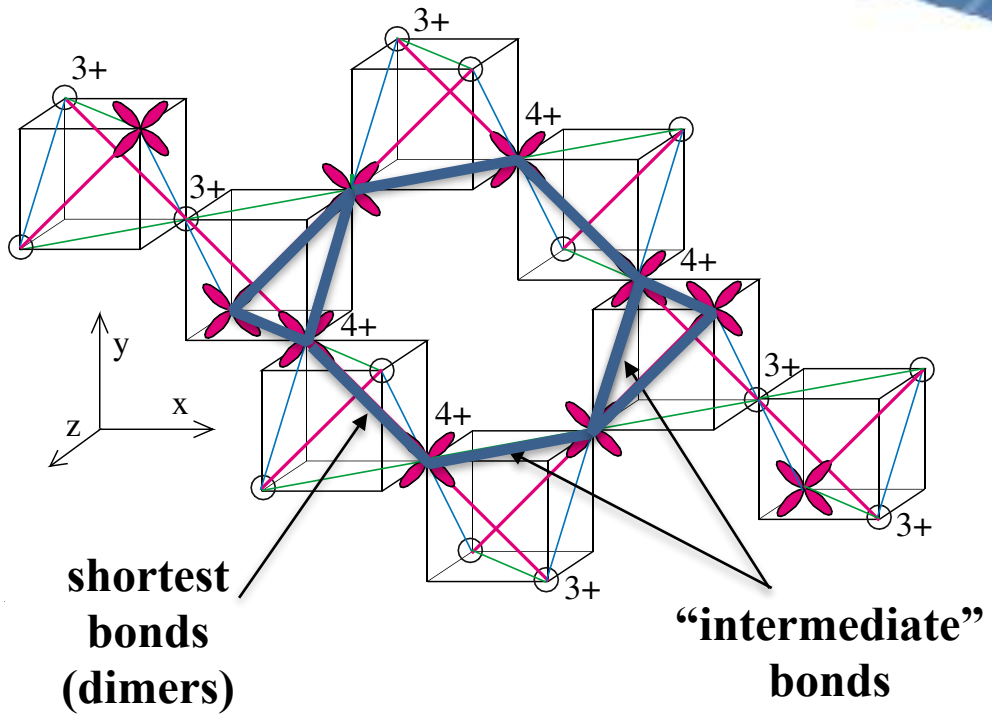
Orbitally induced Peierls effect:
Tetramerization in spinel $CuIr_2S_4$

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



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

1/2 holes
in *xy* band



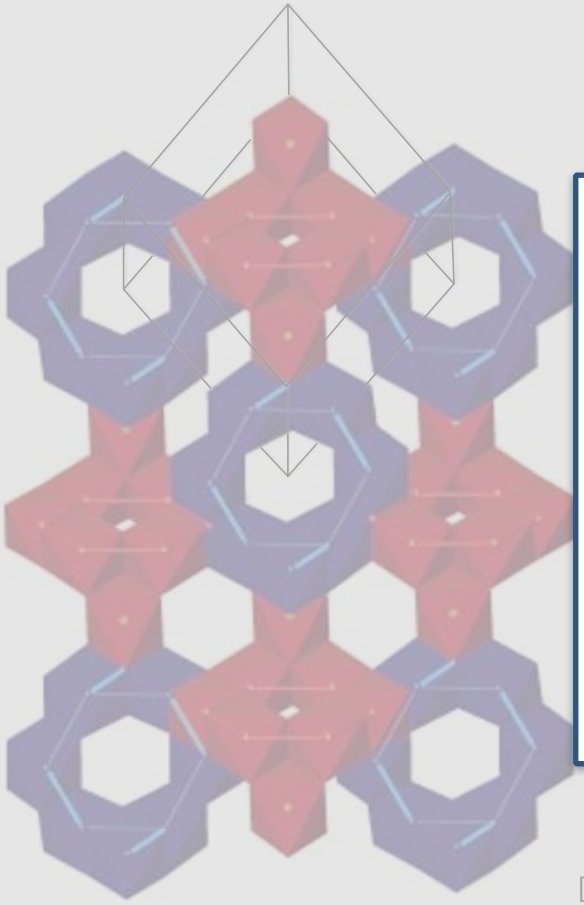
Band filling: 1/4

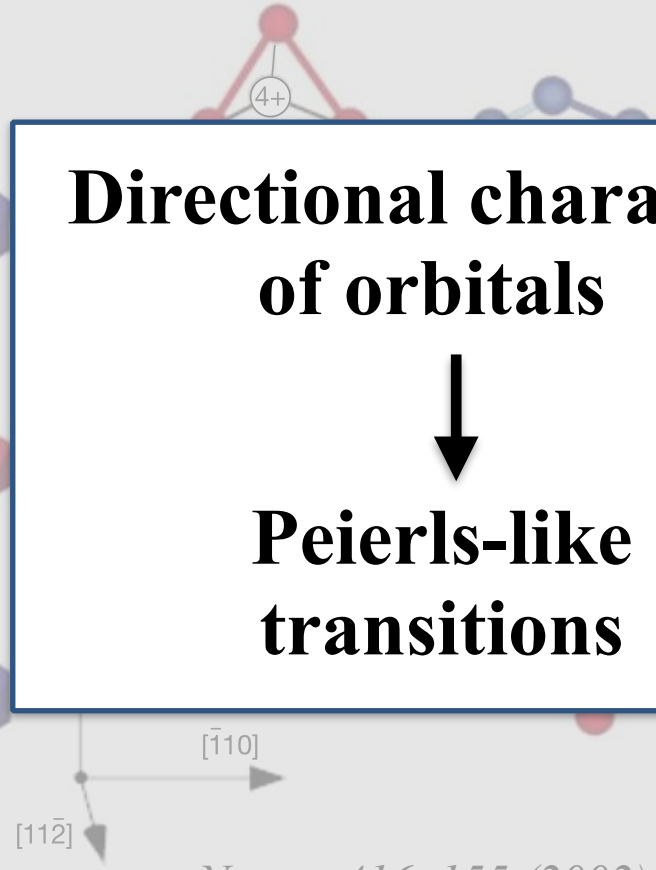
⇩

Tetramerization!

Khomskii and Mizokawa, PRL 94, 156402 (2005)

Orbitally induced Peierls effect:
Tetramerization in spinel $CuIr_2S_4$

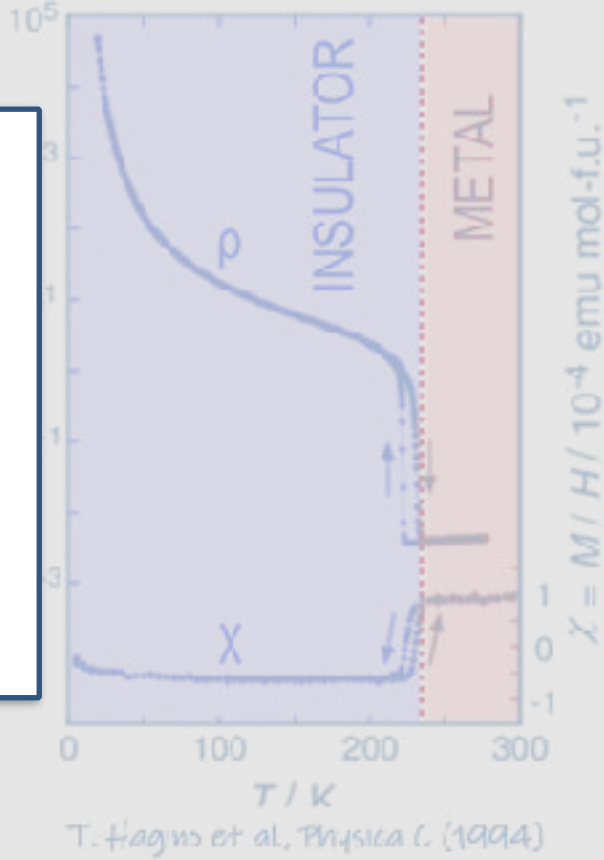




Directional character of orbitals

↓

Peierls-like transitions



Nature 416, 155 (2002)

Reduction of dimensionality due to orbital degrees of freedom

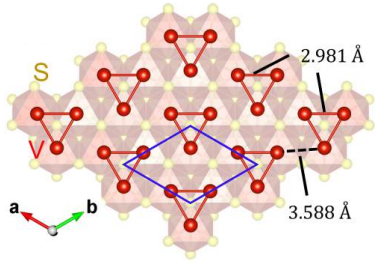
Other examples

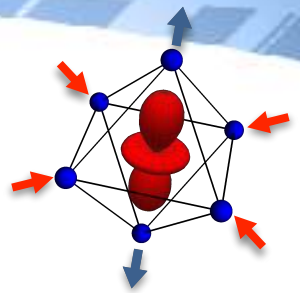
$1D \rightarrow 0D$ chains→dimers	$NaTiSi_2O_6$ [57, 58]
$1D \rightarrow 0D$ chains→dimers	TiOCl [59]
$2D \rightarrow 0D$ triangular lattice → trimers	$LiVO_2$ [60, 61]
$2D \rightarrow 0D$ square lattice → dimers	$La_4Ru_2O_{10}$ [62]
$2D \rightarrow 0D$ depleted square lattice → tetramers	CaV_9O_9 [63, 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)

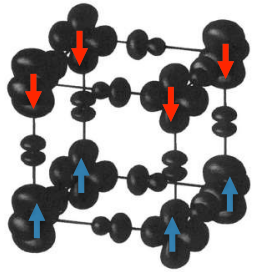
Take-home messages

- Orbitals can **affect the crystal structure**

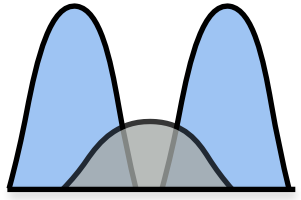




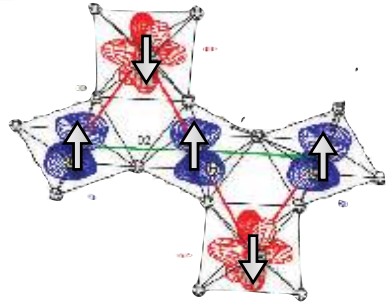
- Orbitals can **define magnetic properties**



- 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)