Orbitals physics: basics and some novel development

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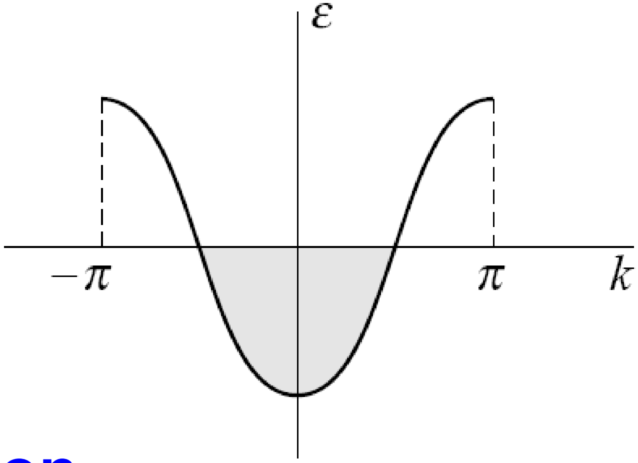
Outline

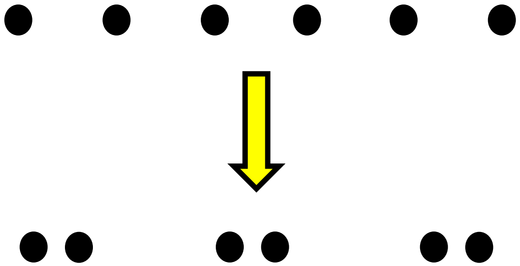
- Introduction
- Role of local geometry in spin-orbital ordering: face-sharing octahedra
- Reduction of dimensionality due to orbital ordering
- Orbital-selective Peierls transition; molecular orbitals agains Hund's rule and suppression of double exchange by molecular orbital formation
- Orbital ordering against spin-orbit interaction
- Some quantum effects for orbitals
- Conclusions

Band structure

$$\mathcal{H}_b = \sum_{\boldsymbol{k},\sigma} \varepsilon(\boldsymbol{k})\, c^\dagger_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} \qquad \varepsilon(\boldsymbol{k}) = -2t(\cos k_x + \cos k_y + \cos k_z)$$

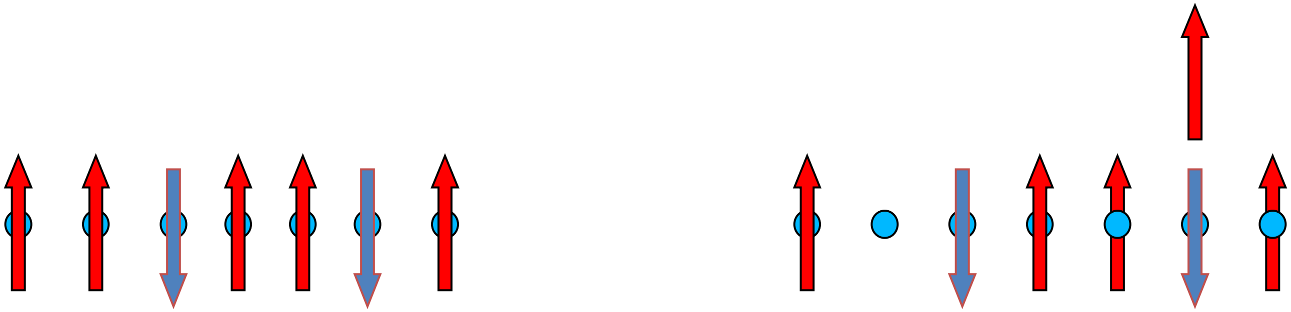


Peierls transition



In this case dimerization opens a gap at the Fermi-surface and make the 1d system insulating

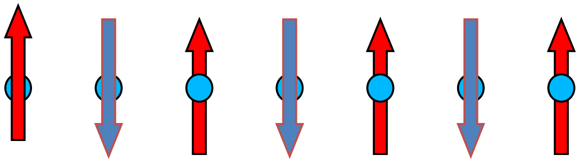
STRONGLY CORRELATED ELECTRONS



$$H = \sum t_{ij}^{\alpha\beta} c^{+}_{i\alpha\sigma} c_{j\beta\sigma} + \sum_{\alpha\sigma\neq\beta\sigma'} U n_{i\alpha\sigma} n_{i\beta\sigma'}$$

$$- \sum_{\alpha\neq\beta} J_H\left(\tfrac{3}{4} + \mathbf{S}_{i\alpha}\mathbf{S}_{i\beta}\right).$$

$$H_{eff} = \frac{2t^2}{U} \sum_{(ij)} \mathbf{S}_i \mathbf{S}_j .$$



Orbital physics

Not a completely new topic: active in ~1970-th ("Cooperative Jahn-Teller effect")

Orbital ordering;

structural phase transitions;

coupling to magnetism (Goodenough-Kanamori-Anderson rules)

New life/fashionable: (HTSC); CMR

Recent development:

- *reduced dimensionality due to orbital ordering*;
- orbitals & frustrations;
- *orbital-induced Peierls transition*
- *orbital-selective dimerization; molecular orbitals against double exchange*
- *role of local geometry*
- *orbital ordering vs spin-orbit interaction*
- quantum effects

Orbital degrees of freedom: 3d, l=2, 2l+1=5 different orbitals.

Crystal field splitting

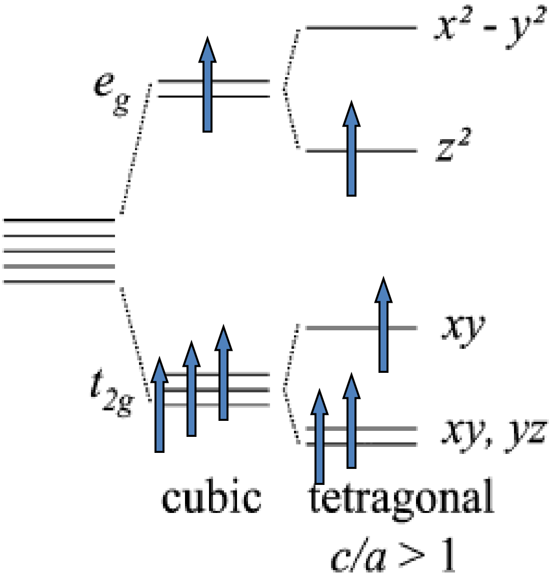


Fig. 1. Schematic form of the crystal field splitting of *d*-levels of transition metal in octahedral coordination.

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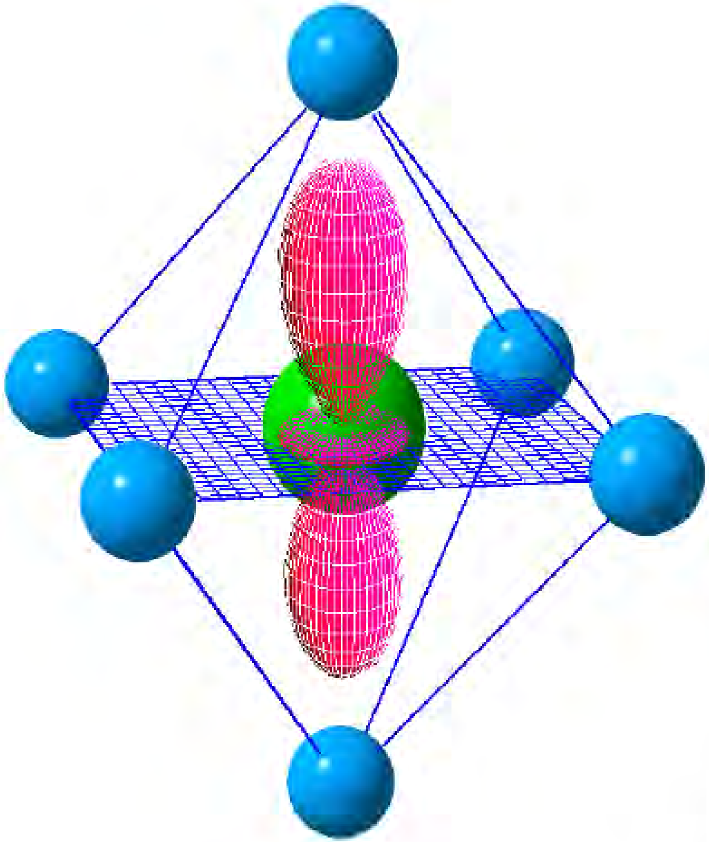
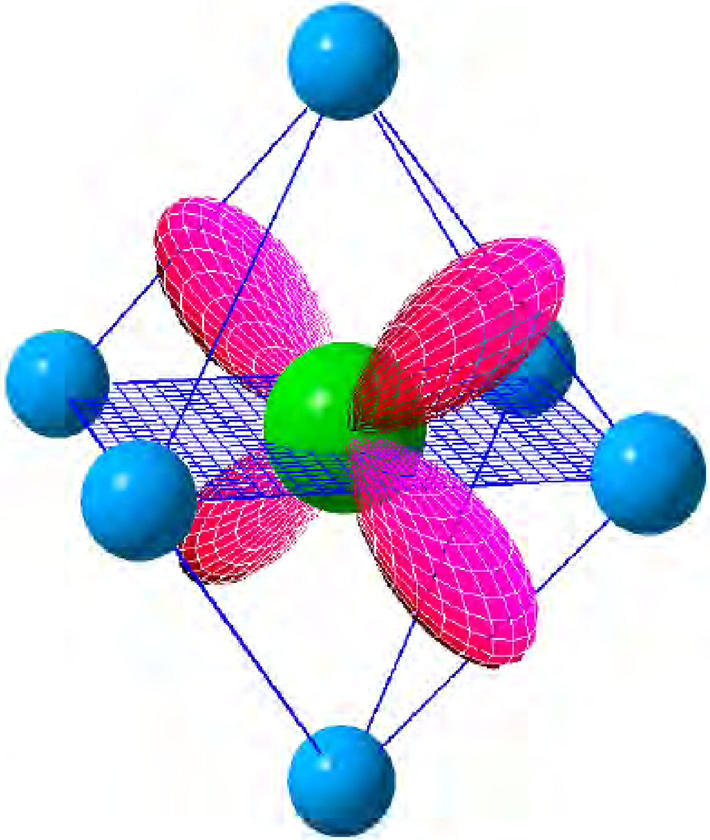
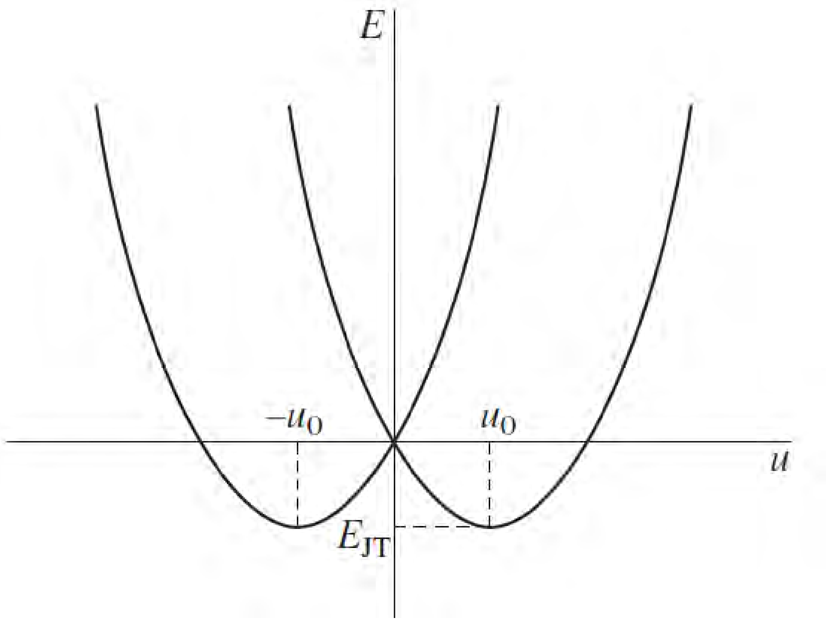


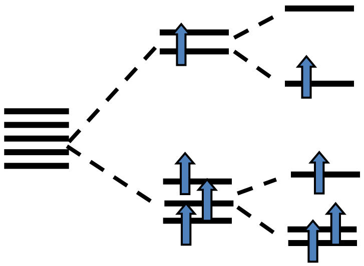


Jahn-Teller effect

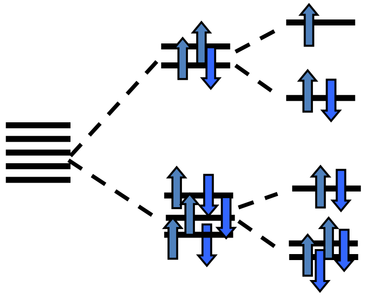


$$E = -gu + Bu^2/2$$

d^4 (Mn^{3+}, Cr^{2+})

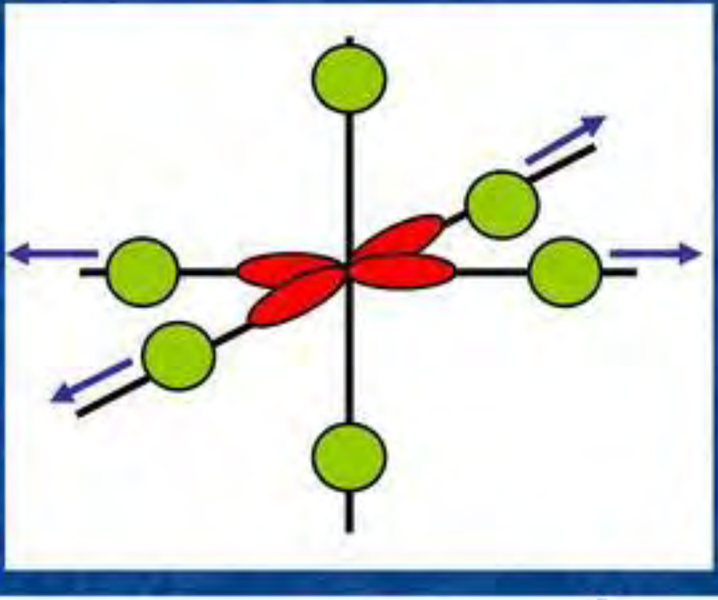


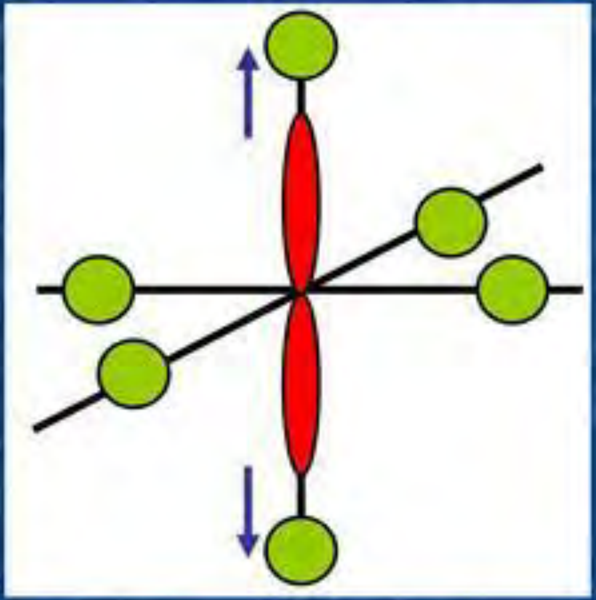
d^9 (Cu^{2+}, Ag^{2+})

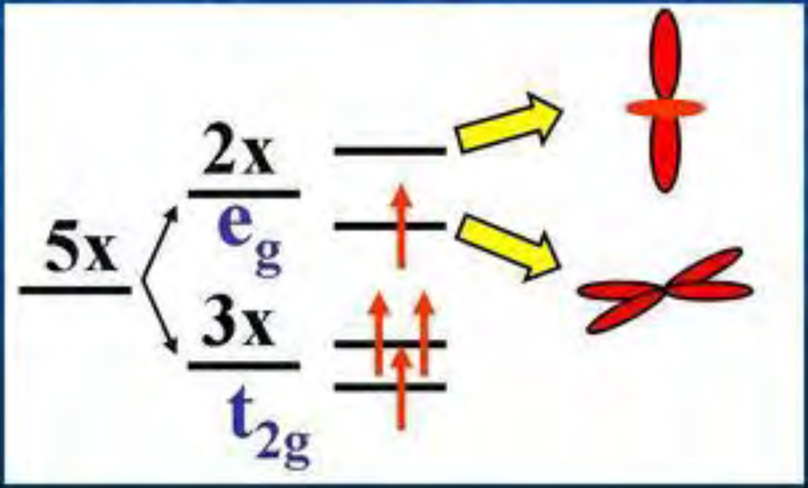


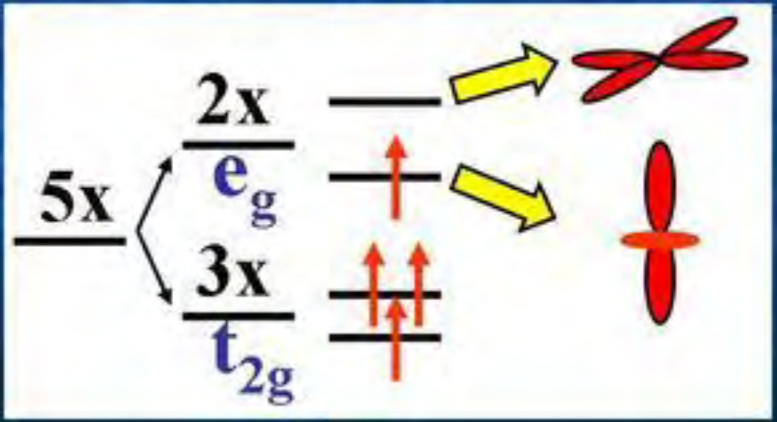
Lifting of degeneracy: lattice

Crystal field splitting of e_g levels → Jahn-Teller distortion



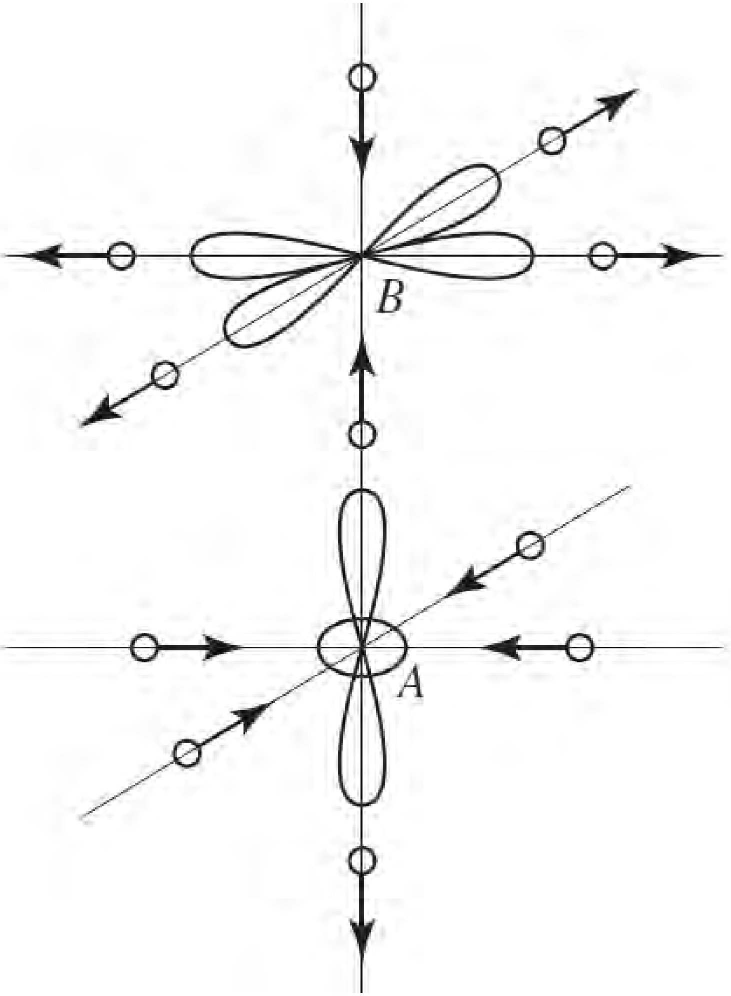






Mechanisms of *cooperative Jahn-Teller effect*, or *orbital ordering* in concentrated solids:

Interaction via lattice distortions



Schematics of superexchange

(“Kugel-Khomskii model”)

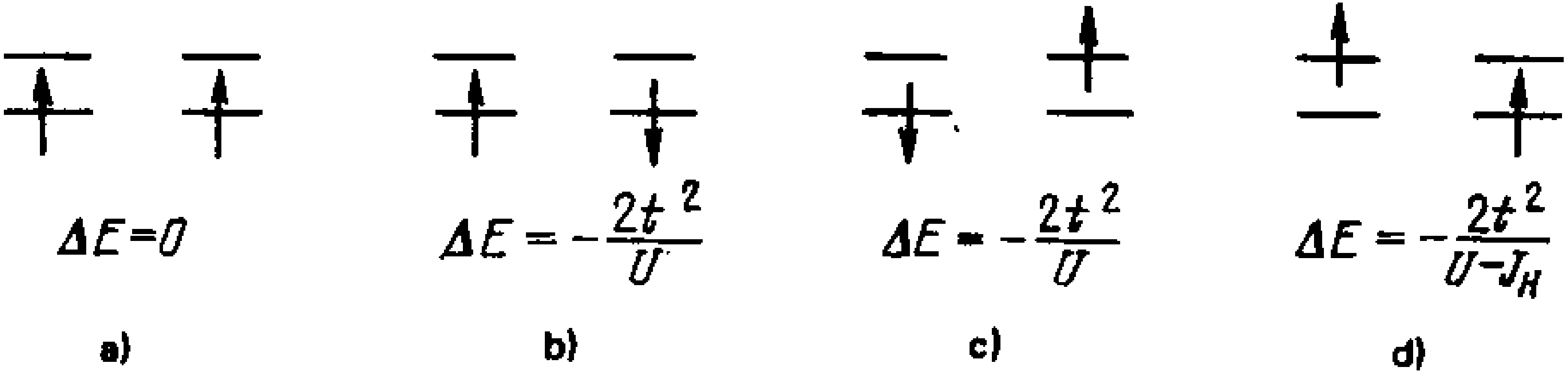
Nondegenerate levels

$\Delta E = 0$

$\Delta E = -\frac{2t^2}{U}$

Double degenerate levels

$t_{11} = t_{22} = t, \;\; t_{12} = 0$



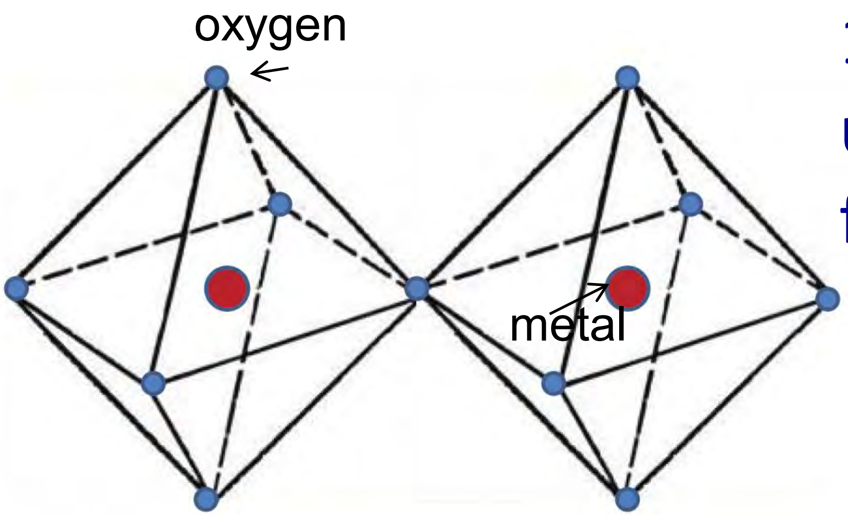
$\Delta E = 0$ a)

$\Delta E = -\frac{2t^2}{U}$ b)

$\Delta E = -\frac{2t^2}{U}$ c)

$\Delta E = -\frac{2t^2}{U - J_H}$ d)

Octahedra with common corners



180º M-O-M angle,
usual situation
for perovskite-like structures

Doubly degenerate case, one electron or hole per *e_g* level

S =1/2 (spin variables), τ = 1/2 (orbital variables)

Schematic structure of the effective spin-orbital Hamiltonian

$$H_{eff} \sim \frac{t^2}{U}\left(J_1 SS + J_2 \tau\tau + J_3 SS\tau\tau\right)$$

Orbital terms can be rather anisotropic and even different for different axes!

Simplified model

$t_{11} = t_{22} = t, \; t_{12} = 0$

$$H_{eff} = \frac{t^2}{U} \sum_{\langle i,j \rangle} \left(\frac{1}{2} + 2\vec{s}_i \vec{s}_j\right)\left(\frac{1}{2} + 2\vec{\tau}_i \vec{\tau}_j\right)$$

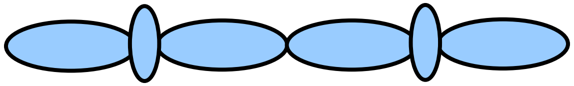
has not only SU(2)× SU(2), but even **SU(4)** symmetry. Unfortunately *for simple geometries, like in perovskites, this case is not realized*

The Hund's rule coupling $-JS_{i\alpha}S_{i\beta}$ also gives contribution

$\sim \frac{t^2}{U}\frac{J}{U}\left(SS + \tau\tau + SS\tau\tau \right)$ with other combinations of ($S\tau$)

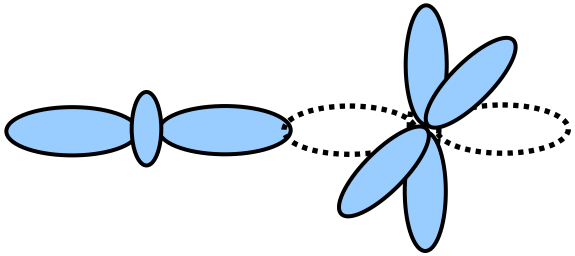
Goodenough-Kanamori-Anderson rules

1. Exchange interaction of two half-filled orbitals is strong and antiferromagnetic (**AFM**)



$$J_{AFM} = \frac{2t^2}{U}$$

2. Exchange interaction of half-filled and empty (or doubly-filled) orbitals is weak and ferromagnetic (**FM**)



$$J_{FM} = -\frac{2t^2 J_H}{U(U - J_H)}$$

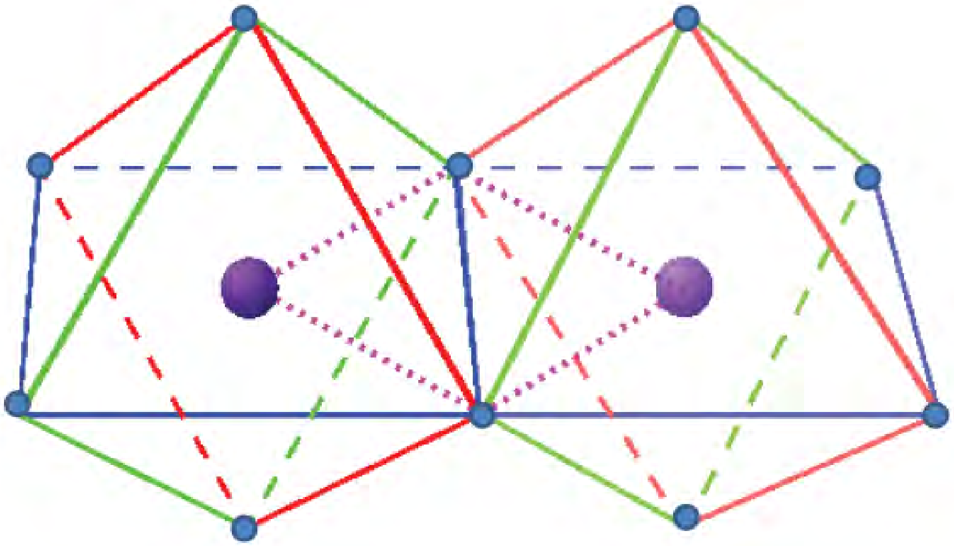
“General rule” for 180º M-O-M angle:

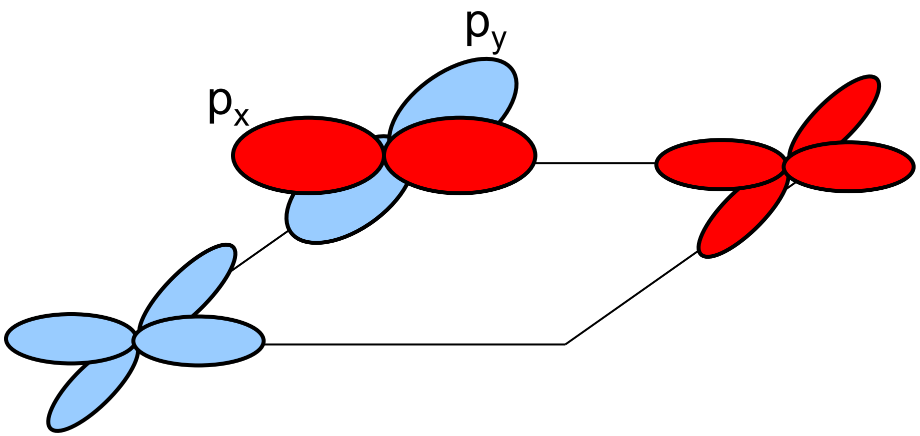
Ferro orbitals ⟷ antiferro spins
antiferro orbitals ⟷ ferro spins

Has become a “common knowledge”,
but be careful, only for 180º!

For edge-sharing octahedra, 90º M-O-M angle,
the situation is very different !

For systems with common edge, with 90 M-O-M angle, the situation is different and more complicated: for e_g electrons exchange is ferromagnetic for every orbital occupation; for t_{2g} electrons – depends on orbitals occupied; and there may be $t_{2g} – e_g$ antiferro. exchange; etc.





Same x2-y2 orbitals, but **ferromagnetic** exchange!

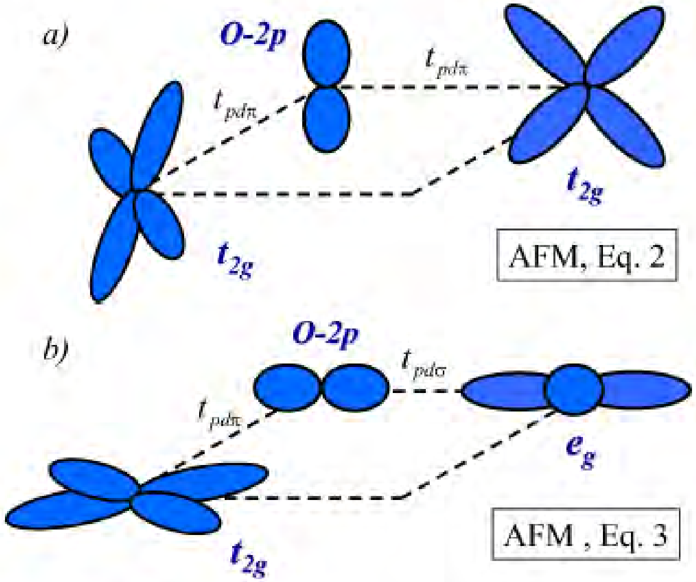


FIG. 3: (color online). Typical orbital ordering between two occupied TM $d-$orbitals via the same O$-2p$ orbital, which results to AFM interaction for the case of 90° $TM-O-TM$ bond.

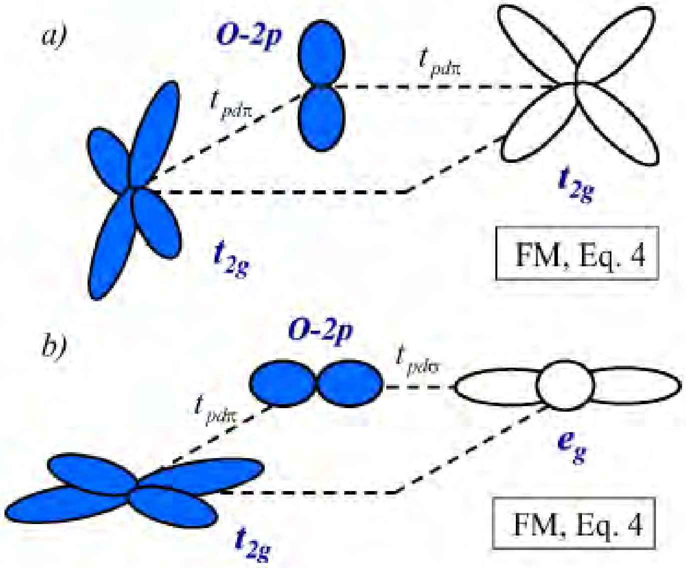


FIG. 4: (color online). Typical orbital ordering between occupied (filled) and unoccupied (unfilled) $d-$orbitals of TM via the same O$-2p$ orbital, which results to FM interaction for the case of 90° $TM-O-TM$ bond.

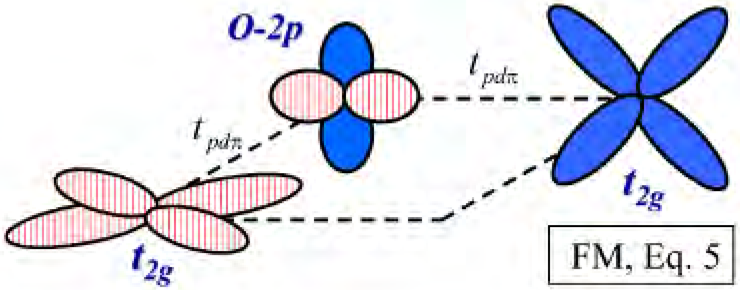
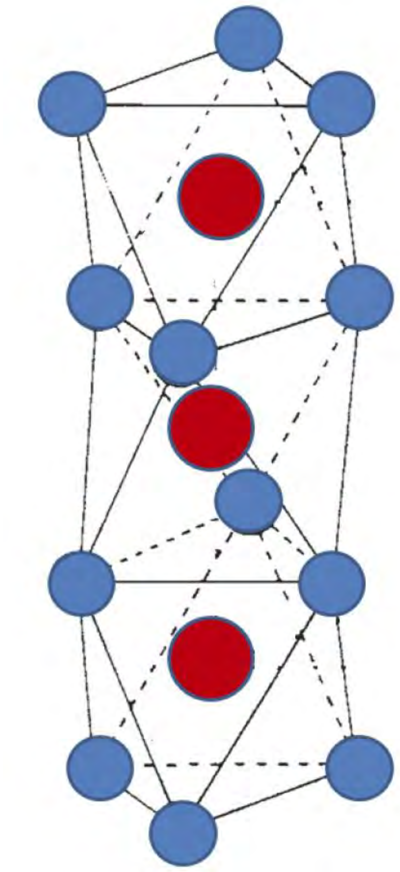


FIG. 5: (color online). Typical orbital ordering between two occupied $d-$orbitals of TM via *different* O$-2p$ orbitals, which results in a FM interaction for the case of 90° $TM-O-TM$ bond.

● Our problem: “the third case”, face-sharing



A lot is done and known for MO_6 octahedra with *common corners* (∠ O-M-O ~180º) or *common edges* (∠ O-M-O ~ 90º)

However, almost nothing for face-sharing geometry!

A lot of examples:

hexagonal crystals: $BaCoO_3$, $BaVS_3$, $CsCuCl_3$, containing infinite columns of face-sharing octahedra;

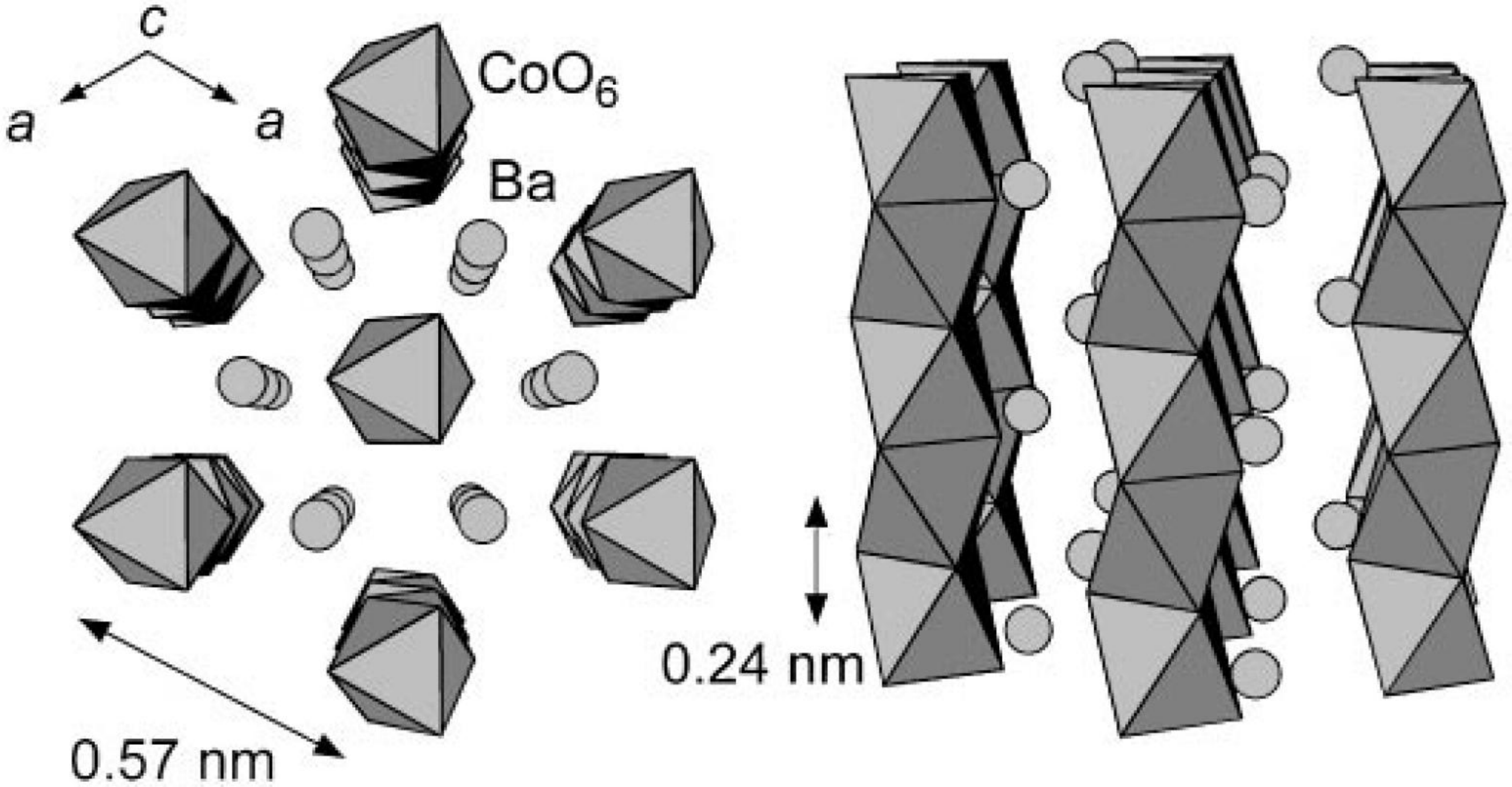
systems with face-sharing blocks: $BaIrO_3$, $BaRuO_3$, $Ba_4Ru_3O_{10}$;

systems of general formula $Ba_3(M1)(M2)_2O_9$, M1= Li, Na; Ca, Sr, Co,...; Y, La, … with face-sharing $M2O_6$ octahedra of transition metals, separated by $M1O_6$ octahedra (which have common corners with $M2O_6$)

Our aim: to analyze exchange interaction in such geometry.

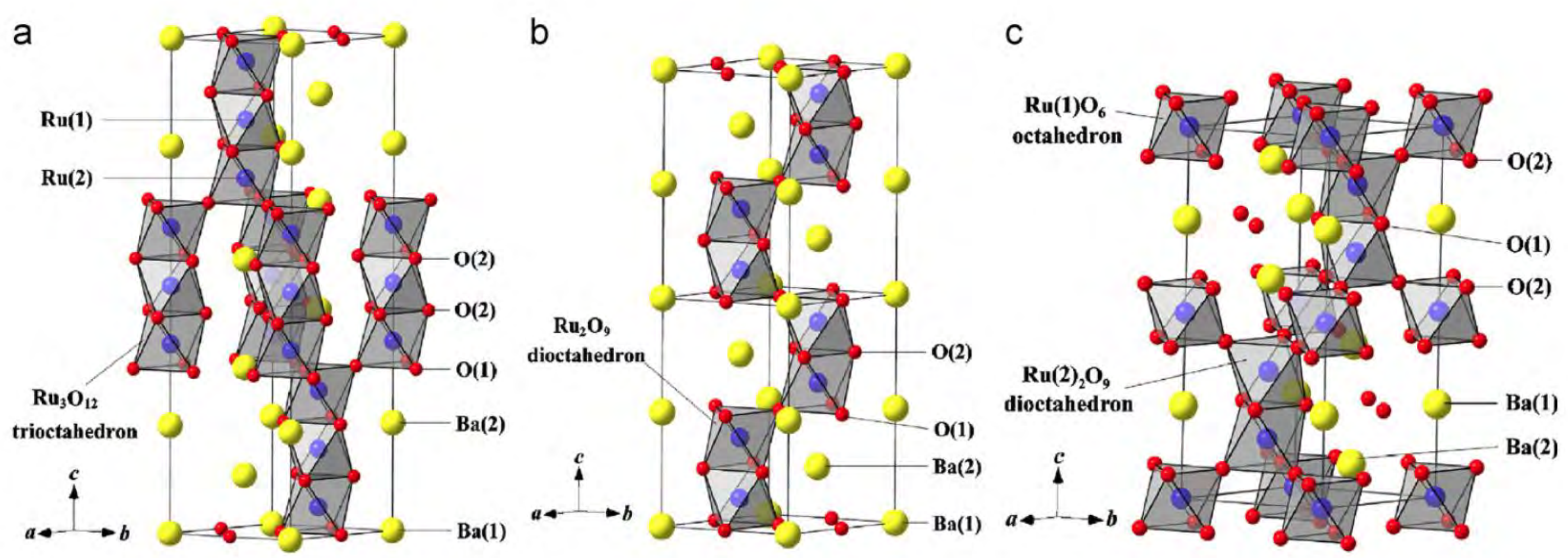
Calculations are rather tedious but straightforward

Crystal structure of $BaCoO_3$



K. Yamaura *et al.*, J. Solid State Chem. 146, 96 (1999)

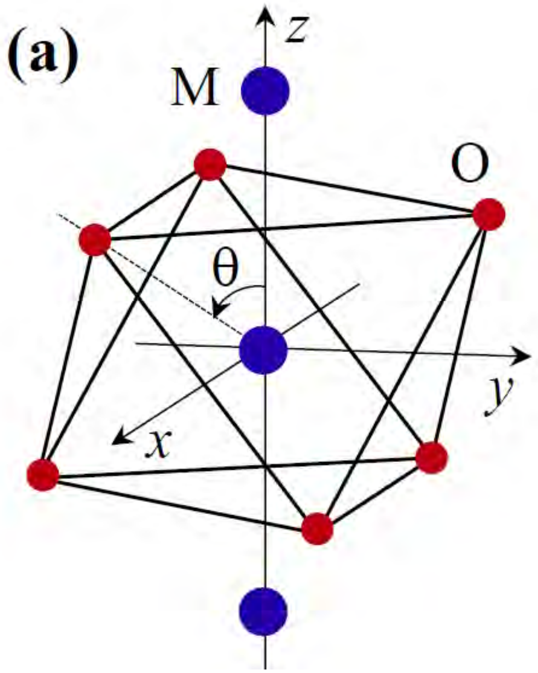
Crystallographic forms of $BaRuO_3$



(a) 9R form, (b) 4H form and (c) 6H form. The RuO_6 octahedra are represented by geometrical coordination (Ru at the center, O at corners). The unit cells are outlined.

J.G. Zhao *et al.,* J. Solid State Chem. 180, 2816 (2007)

e_g electrons, ideal face-sharing octahedra



e_g doublet for two neighboring magnetic ions M1 and M2 along the chain (in trigonal axes)

$$| \, d_1 \rangle \; = \; \frac{1}{\sqrt{3}} \, | \, x^2 - y^2 \rangle - \sqrt{\frac{2}{3}} \, | \, xz \rangle$$

$$| \, e_1 \rangle \; = \; -\frac{1}{\sqrt{3}} \, | \, xy \rangle - \sqrt{\frac{2}{3}} \, | \, yz \rangle$$

$$| \, d_2 \rangle \; = \; \frac{1}{\sqrt{3}} \, | \, x^2 - y^2 \rangle + \sqrt{\frac{2}{3}} \, | \, xz \rangle$$

$$| \, e_2 \rangle \; = \; -\frac{1}{\sqrt{3}} \, | \, xy \rangle + \sqrt{\frac{2}{3}} \, | \, yz \rangle$$

e_g electrons, direct exchange

Hopping integrals in terms of Slater-Koster parameters

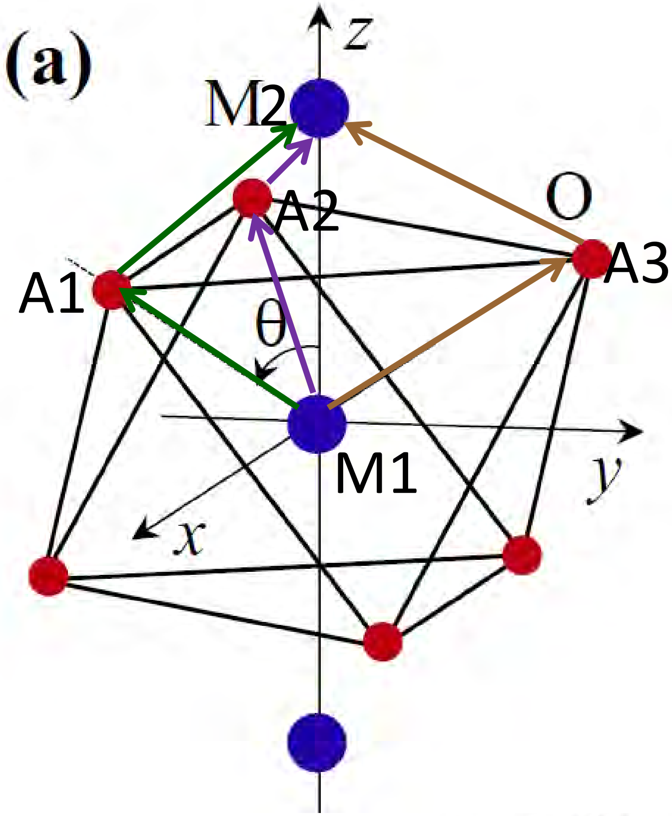
$$\begin{aligned} t_{|xy\rangle,|xy\rangle} &= t_{|x^2-y^2\rangle,|x^2-y^2\rangle} = V_{dd\delta} \\ t_{|yz\rangle,|yz\rangle} &= t_{|xz\rangle,|xz\rangle} = V_{dd\pi} \end{aligned}$$

$$\boxed{t_{direct} = t_{|d_2\rangle|d_1\rangle} = t_{|e_2\rangle|e_1\rangle} = \frac{1}{3}V_{dd\delta} - \frac{2}{3}V_{dd\pi}}$$

$$\boxed{t_{|e_2\rangle|d_1\rangle} = t_{|e_2\rangle|d_1\rangle} = 0}$$

e_g electrons, superexchange via anions

3 M-O-M superexchange paths, transformed into each other by rotation at 180º about *z* axis (via A1, A2, A3)



via A1

$$t_{|d_2\rangle|d_1\rangle} = t_1 \quad t_{|e_2\rangle|e_1\rangle} = t_2$$

$$t_{|e_2\rangle|d_1\rangle} = t_{|e_2\rangle|d_1\rangle} = t_3$$

via A2

$$\begin{aligned} t'_1 &= t_1 \cos^2 \frac{2\pi}{3} + t_2 \sin^2 \frac{2\pi}{3} + t_3 \sin \frac{4\pi}{3} \\ t'_2 &= t_1 \sin^2 \frac{2\pi}{3} + t_2 \cos^2 \frac{2\pi}{3} - t_3 \sin \frac{4\pi}{3} \\ t'_3 &= \frac{t_2 - t_1}{2} \sin \frac{4\pi}{3} + t_3 \cos \frac{4\pi}{3} \end{aligned}$$

Similarly via A3 → *t''*

$$t^{viaO} = t + t' + t''$$

$$t_1^{viaO} = t_2^{viaO} = \frac{3}{2}(t_1 + t_2) \quad t_3^{viaO} = 0$$

Outcome: e_g electrons, effective Hamiltonian

For face-sharing geometry,
we arrive at the symmetric **SU(4)** orbital model

$$H_{eff} = \frac{t^2}{U} \sum_{\langle i,j \rangle} (\frac{1}{2} + 2\vec{s}_i \vec{s}_j)(\frac{1}{2} + 2\vec{\tau}_i \vec{\tau}_j)$$

with $t = t_{direct} + t^{via\,\mathrm{O}}$

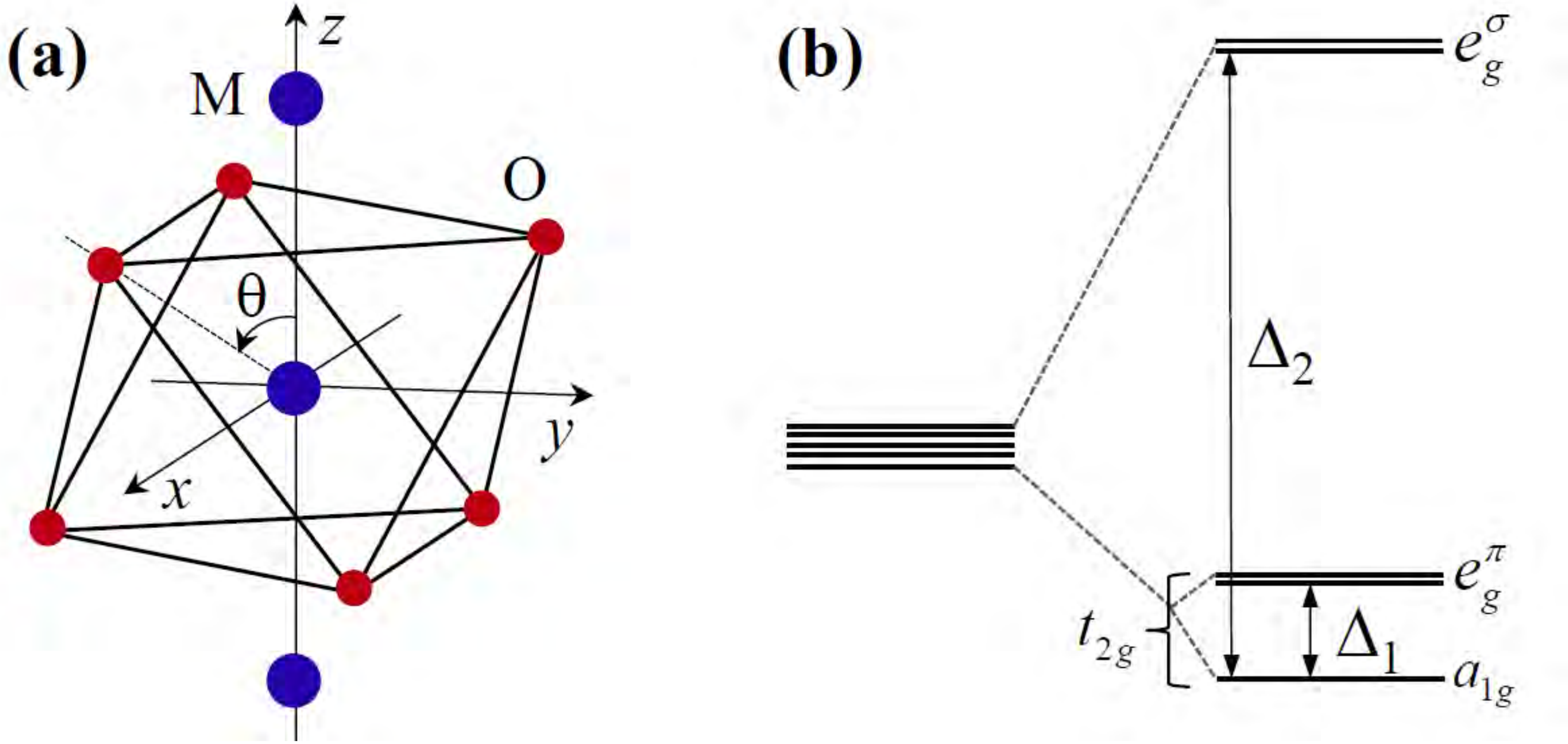
Again, the terms with the Hund's rule coupling constant $\sim \frac{t^2}{U} \frac{J}{U}$

have different orbital structure, such as

$$[2(\vec{\tau}_i \vec{\tau}_j - \tau_i^z \tau_j^z) - (\frac{1}{2} + 2\vec{s}_i \vec{s}_j)(\frac{1}{2} - 2\tau_i^z \tau_j^z)]$$

K.I. Kugel, D.I. Khomskii, A.O. Sboychakov, S.V. Streltsov,
Phys. Rev. B **91**, 155125 (2015)

Same result for t_{2g} level, with splitting in trigonal crystal field



For electrons at e_g^π levels with face-sharing octahedra – the same SU(4) spin-orbital Hamiltonian !

● Strong SOC: projection to j=1/2

1. Octahedra with *common corner (*180 degree M-O-M bonds): **Heisenberg** interaction

$$H \sim \frac{t^2}{U}\mathbf{jj}$$

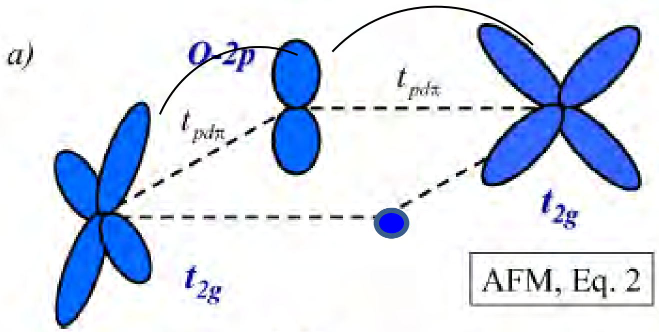
2. Octahedra with *common edge* (90 degree M-O-M bonds): **Kitaev** (may be + Heisenberg)

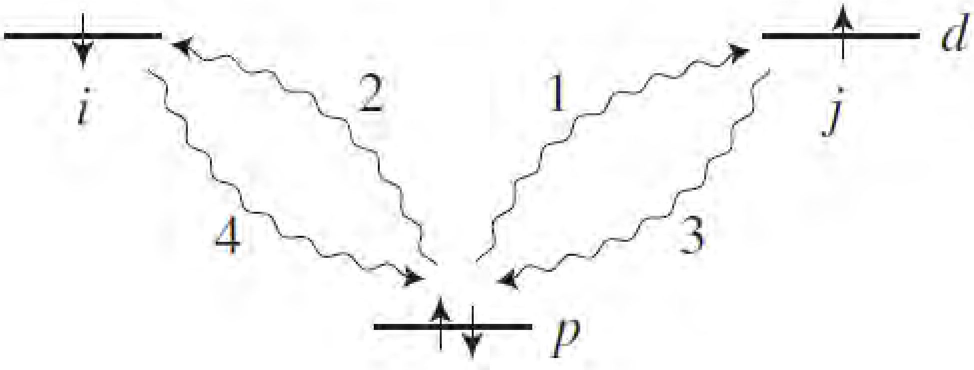
$$H \sim \frac{t^2 J}{UU} j_z j_z + H_{Heis}$$

3. Octahedra with *common face:* **Heisenberg**

$$H \sim \frac{t^2}{U}\mathbf{jj}$$

- **Note:** for charge-transfer insulators also the second case (common edge) gives *not Kitaev, but the usual Heisenberg* interaction in terms of **j**=1/2!





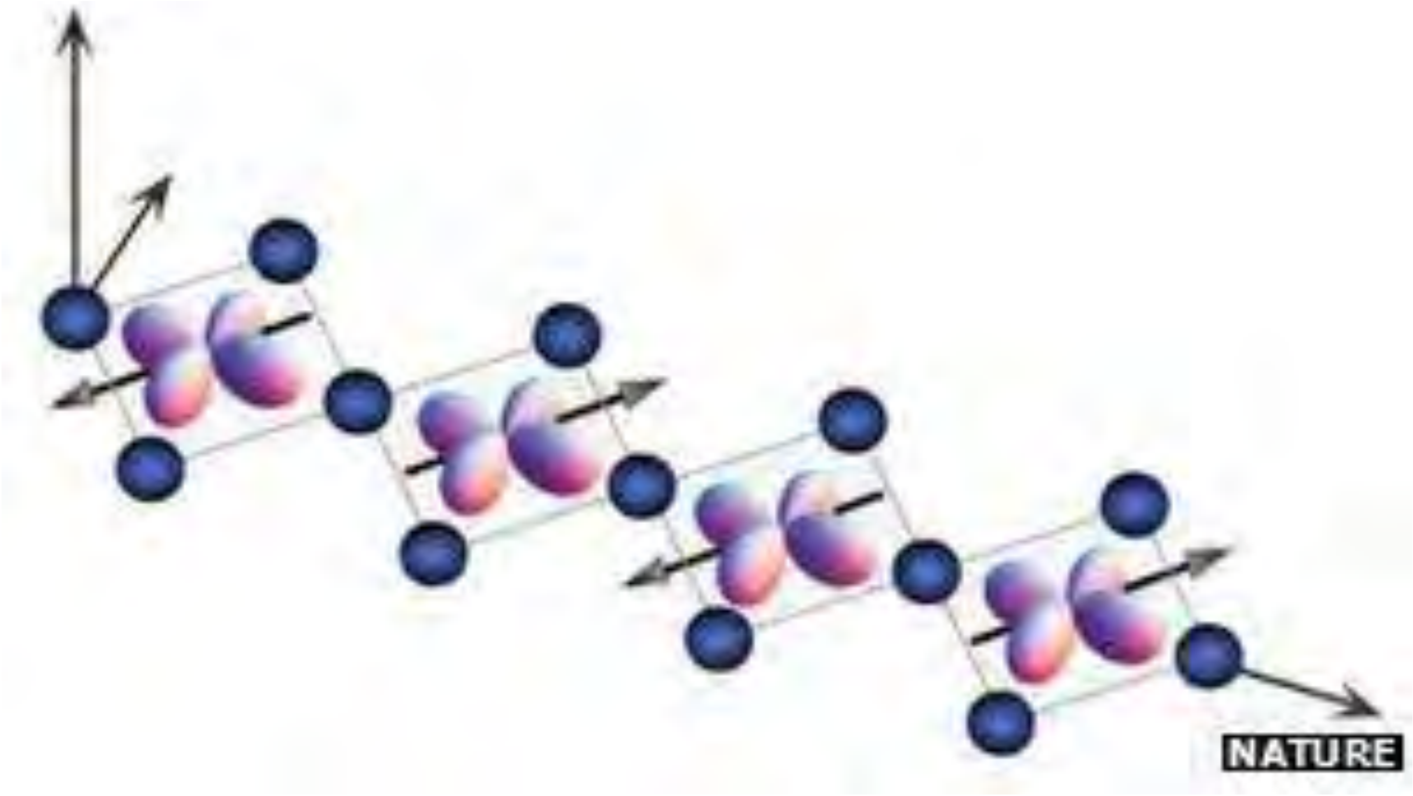
Electrons (or holes) hop *to the same oxygen* and back. In effect it is *not the amplitides* via different oxygens which add (and cancel for j=1/2, to give Kitaev), but the probablities add → **Heisenberg interaction ~ t^2/U**

(was already in the first PRL paper by Jackeli and Khaliullin, in the footnote; largely forgotten!)

Which situations are met in experiment?

Common corner (180 degrees M-O-M bonds): 1d; 2d; 3d

1D: e.g. **Sr_2CuO_3**

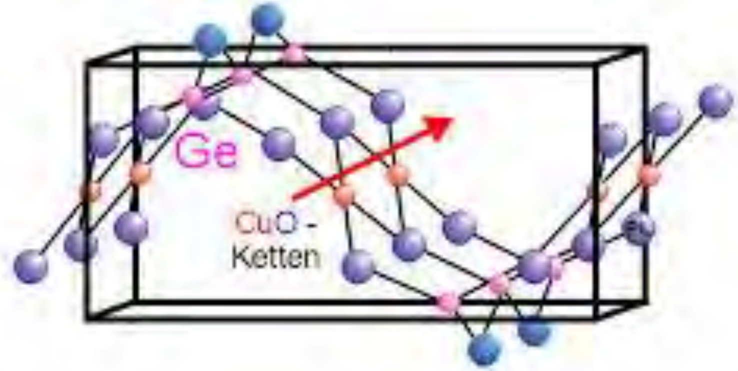


2d: **La_2CuO_4**, etc

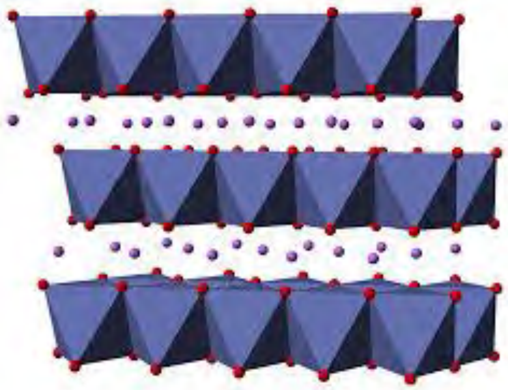
3d: **perovskites** (**e.g.** **$LaMnO_3$, $BiFeO_3$**, ...)

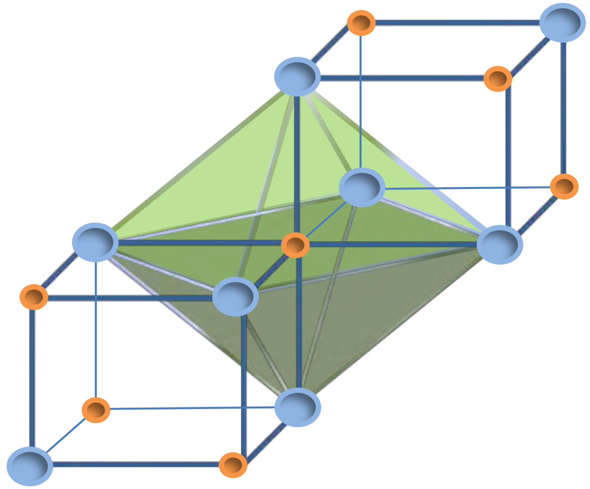
Common face (~90 degrees M-O-M bonds)

1d: e.g. **$CuGeO_3$; $KCuO_2$, ...**



2d: many triangular, kagome, honeycomb systems (Li_xCoO_2; Na_2IrO_3, ...)





3d: e.g. **B-sites of a spinel**

Common edge:

1d : many

2d, 3d: is it ever possible?

Common edge:

1d : many

2d, 3d: is it ever possible?

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2d, 3d: is it ever possible?

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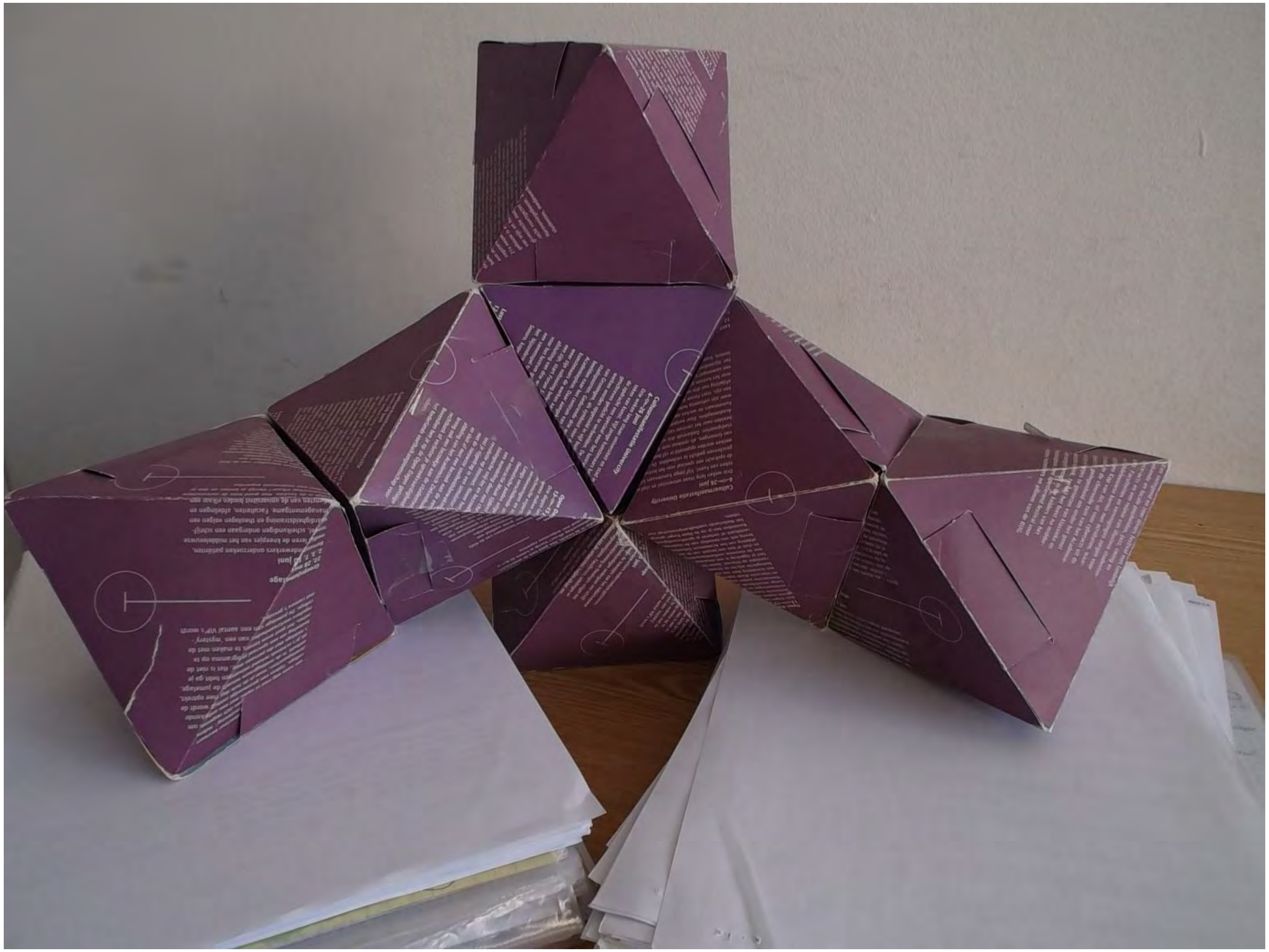
2d, 3d: is it ever possible?

Common edge:

1d : many

2d, 3d: is it ever possible?



● Orbitals, *reduced dimensionality* and spin gaps in correlated systems close to Mott transitions

1d → 0d: NaTiSi2O6 (singlet dimers) *PRL **96**, 249701 (2006)*

1d → 0d: TiOCl (spin-Peierls --- Peierls) *PRL **102**, 056406 (2009)*

1d → 0d: hollandites **K2V8O16; K2Cr8O16** *PRL **107**, 266402 (2011)*

2d square → 0d : La4Ru2O10 (singlet dimers) *PRL **96**, 256402 (2006)*

2d honeycomb → 0d : Li2RuO3 (singlet dimers) *PRL **100**, 147203 (2008)*

Na2IrO3 (molecular orbitals on hexagons) *PRL **109**, 197201 (2012)*

2d triangular → 0d: LiVO2 (singlets on triangles) *PRL **78**, 1323 (1997)*

3d spinel → 1d: MgTi2O4 (Peierls transition) *PRL **94**, 156402 (2005)*

CuIr2O4

3d spinel → 1d: MgV2O4 (triplet dimers) *PRL **101**, 256403 (2008)*

3d pyrochlore → 1d: Tl2Ru2O7 (Haldane chain) *Nature Materials **5**, 471 (2006)*

D.Kh. Physica Scripta (Comments Cond.Mat.Phys.) **72**, CC8 (2005)
D.Kh. Progr.Theor. Phys. Suppl.**159**, 319 (2005)

PYROXENES

Spodumene:
$LiAlSi_2O_6$

Diopside:
$CaMgSi_2O_6$

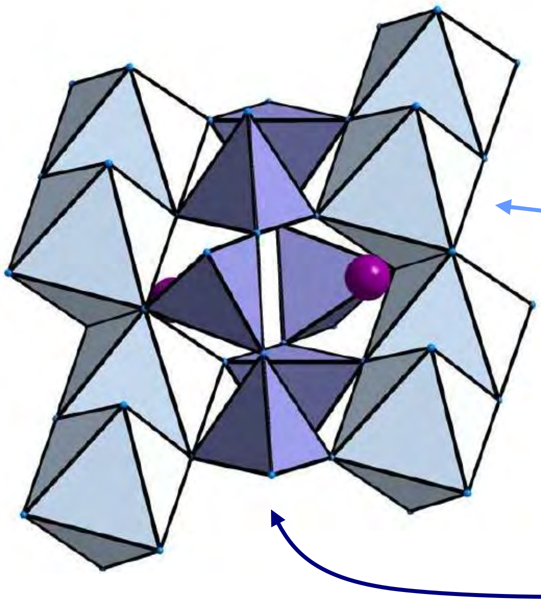
Aegirine:
$NaFeSi_2O_6$

Kosmochlore:
$NaCrSi_2O_6$

Jade:
$NaAlSi_2O_6$–

Minerals

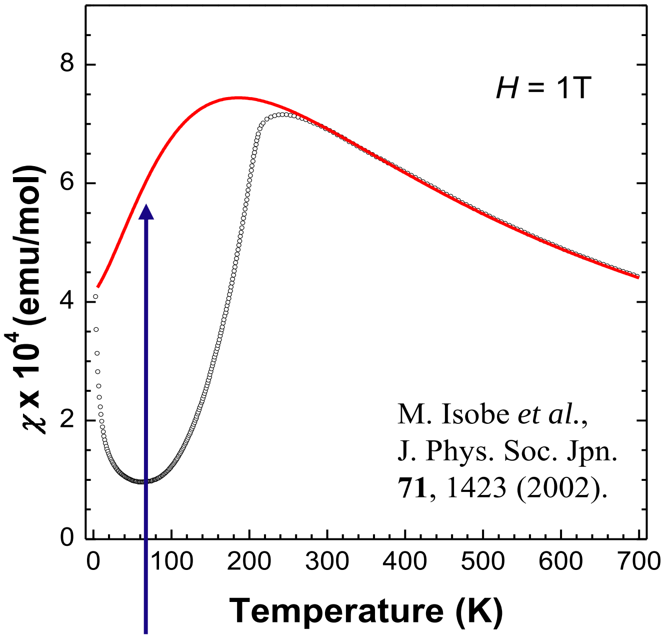
Crystal structure of pyroxenes



Isolated chains of
***$Me^{3+}O_6$ octahedra,** sharing*
common edge, divided by
$(Si,Ge)O_4$ tetrahedra

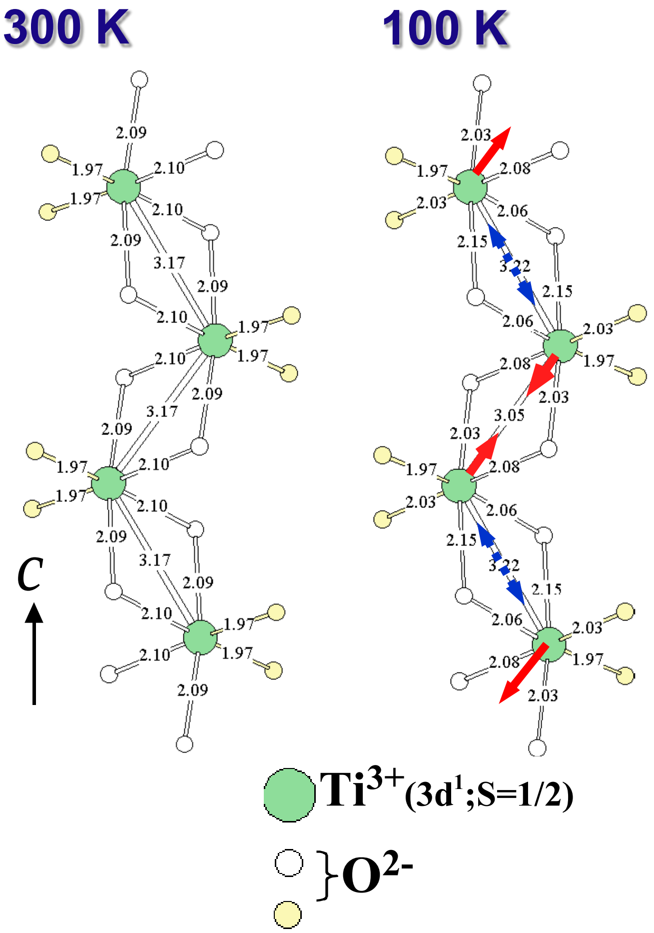
1d ⟶ 0d

Spin gap in $NaTiSi_2O_6$

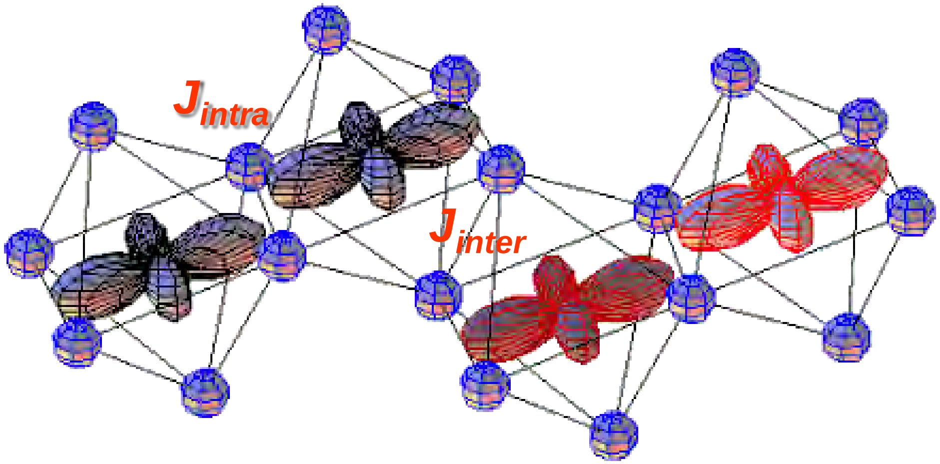


M. Isobe *et al.*, J. Phys. Soc. Jpn. **71**, 1423 (2002).

Bonner-Fisher curve for the S=1/2 Heisenberg linear AFM chain J/k_B = 295 K



Natural explanation - formation of Ti-Ti singlet dimers!



U_{dd} = 3.3 eV, J_H= 0.8 eV

Energy gap: 1.8 eV

Exchange in a dimer J_{intra} = *396 K* (AFM)

Between dimers J_{inter} = *-5 K* (FM)

$NaTiSi_2O_6$ – chain consisting of dimers !

Orbital ordering reduces dimensionality from 1-d to 0-d

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

3d ⟶ 1d

$KCuF_3$:

(cf. K_2CuF_4
La_2CuO_4)

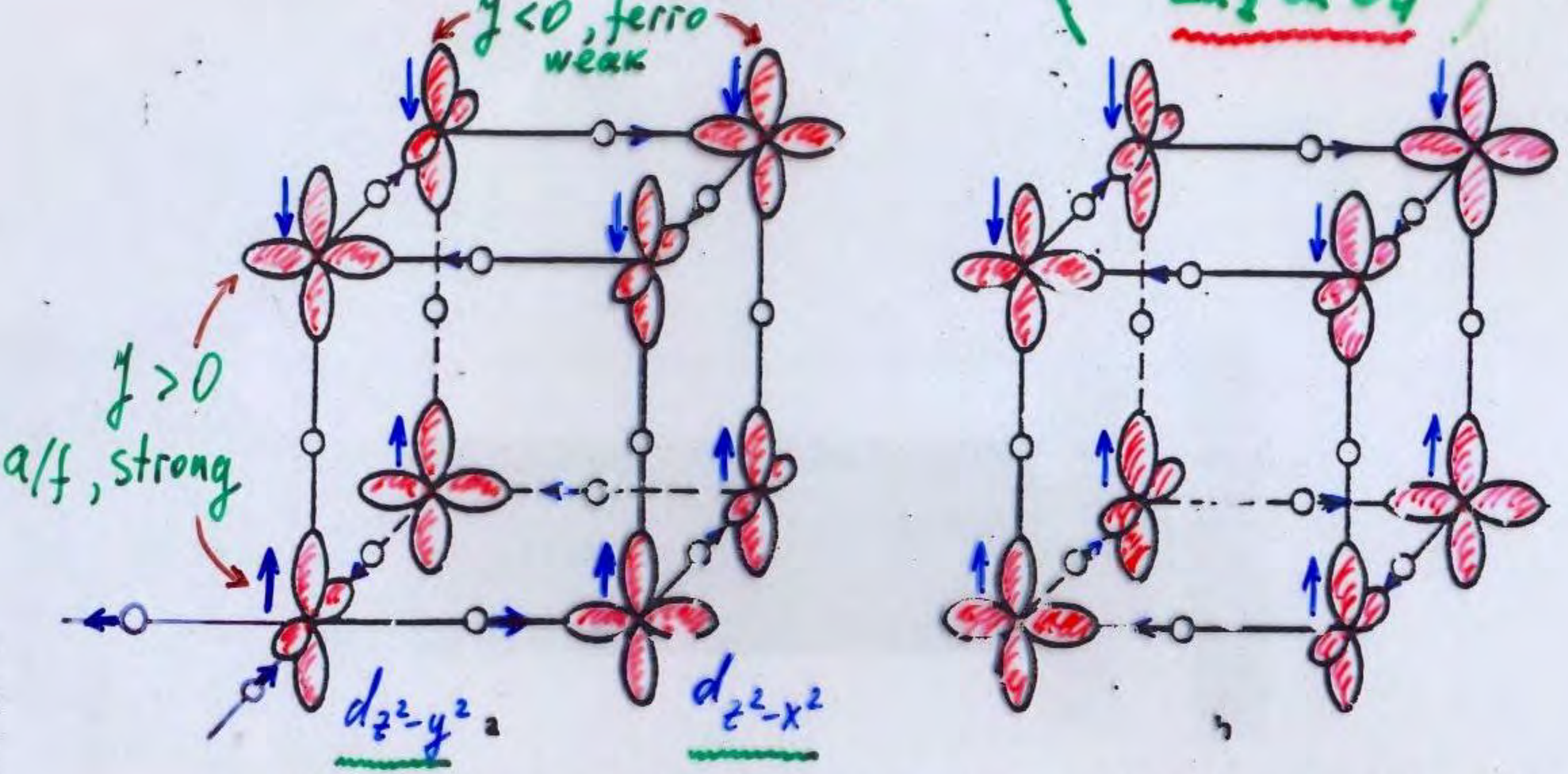


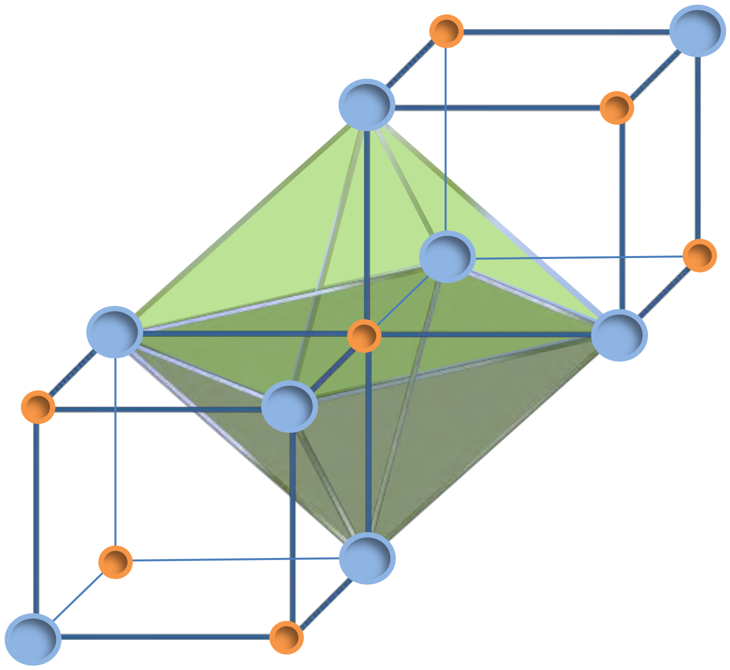
FIG. 3. Two equivalent types of ordering of singly-occupied orbitals in perovskites, obtained in the superexchange model. The figure shows the anion displacements produced for a hole orbital (Cu^{2+} ion).

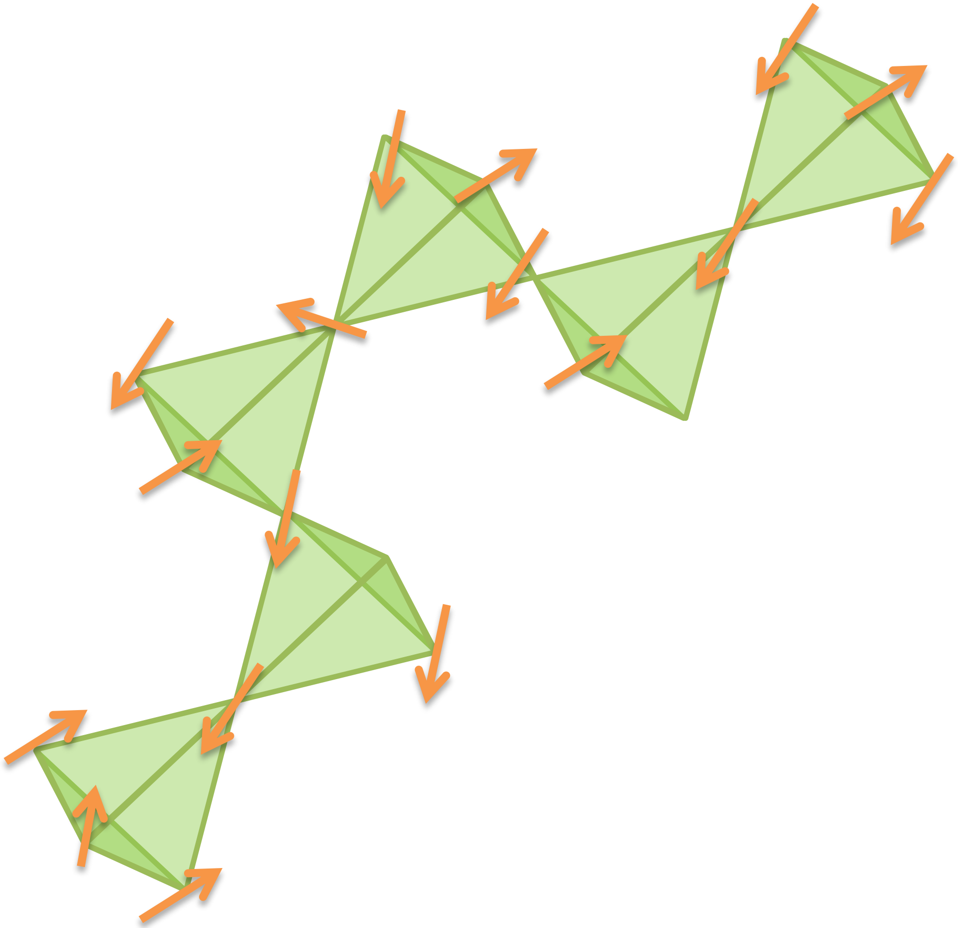
- Nearly cubic, but 1-d antiferromagnet!

in the plane perpendicular to the c axis, the orbital

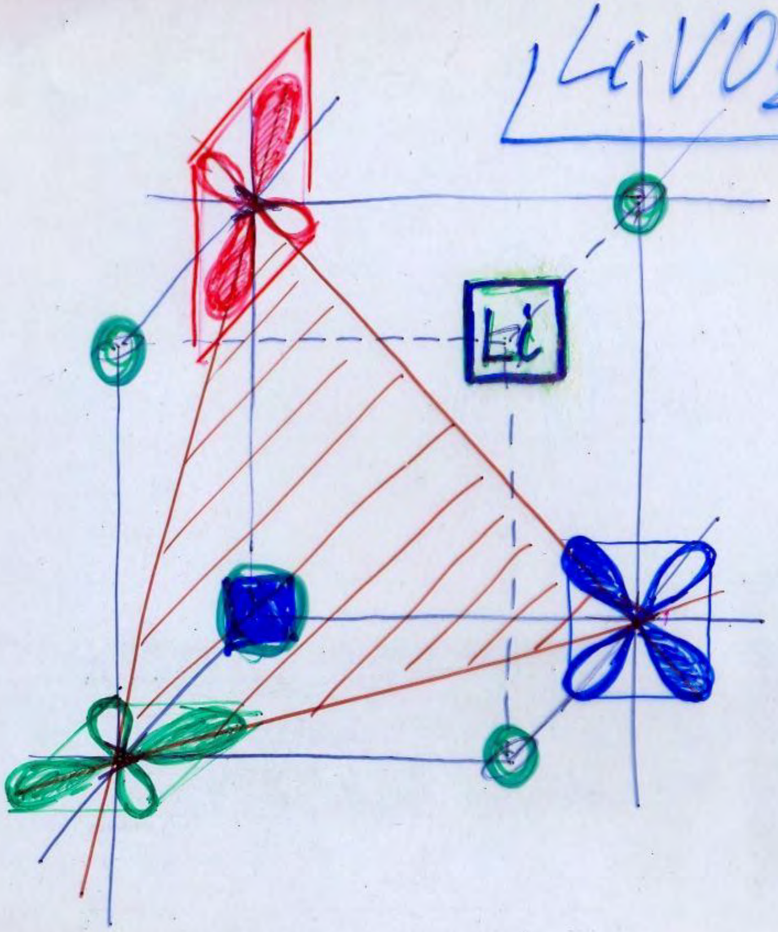
3d → 1d

Spinels





LiVO$_2$



I order phase transition at 450 K
semiconductor - semiconductor,
spin gap opens at $T < T_c$

Formation of isomorphic Ir^{3+} and Ir^{4+} octamers and spin dimerization in the spinel CuIr$_2$S$_4$

**Paolo G. Radaelli[*], Y. Horibe[†‡§], Matthias J. Gutmann[*],
Hiroki Ishibashi[§‖], C. H. Chen[†], Richard M. Ibberson[*], Y. Koyama[‡],
Yew-San Hor[§], Valery Kiryukhin[§] & Sang-Wook Cheong[§]**

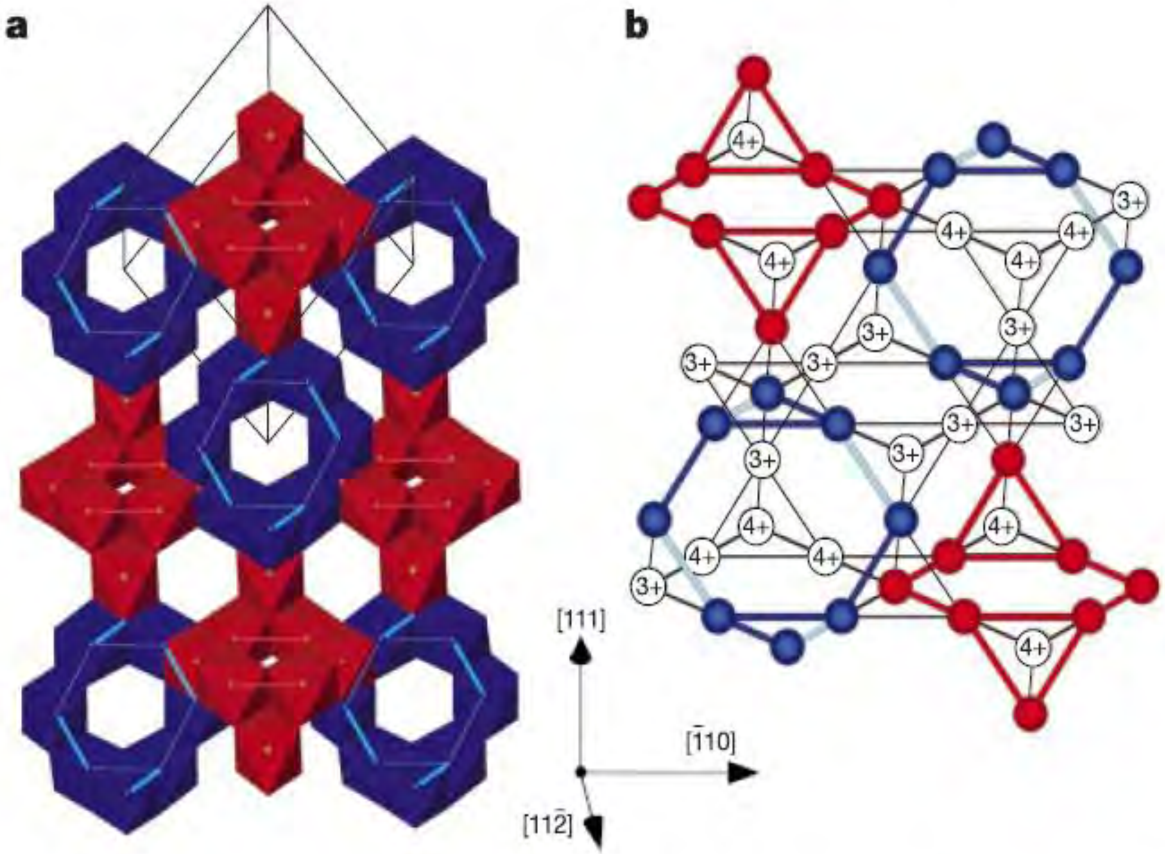


Figure 2 The low-temperature crystal structure of CuIr$_2$S$_4$. **a**, Schematic representation of

create a 3D impression of the stacking and to pro

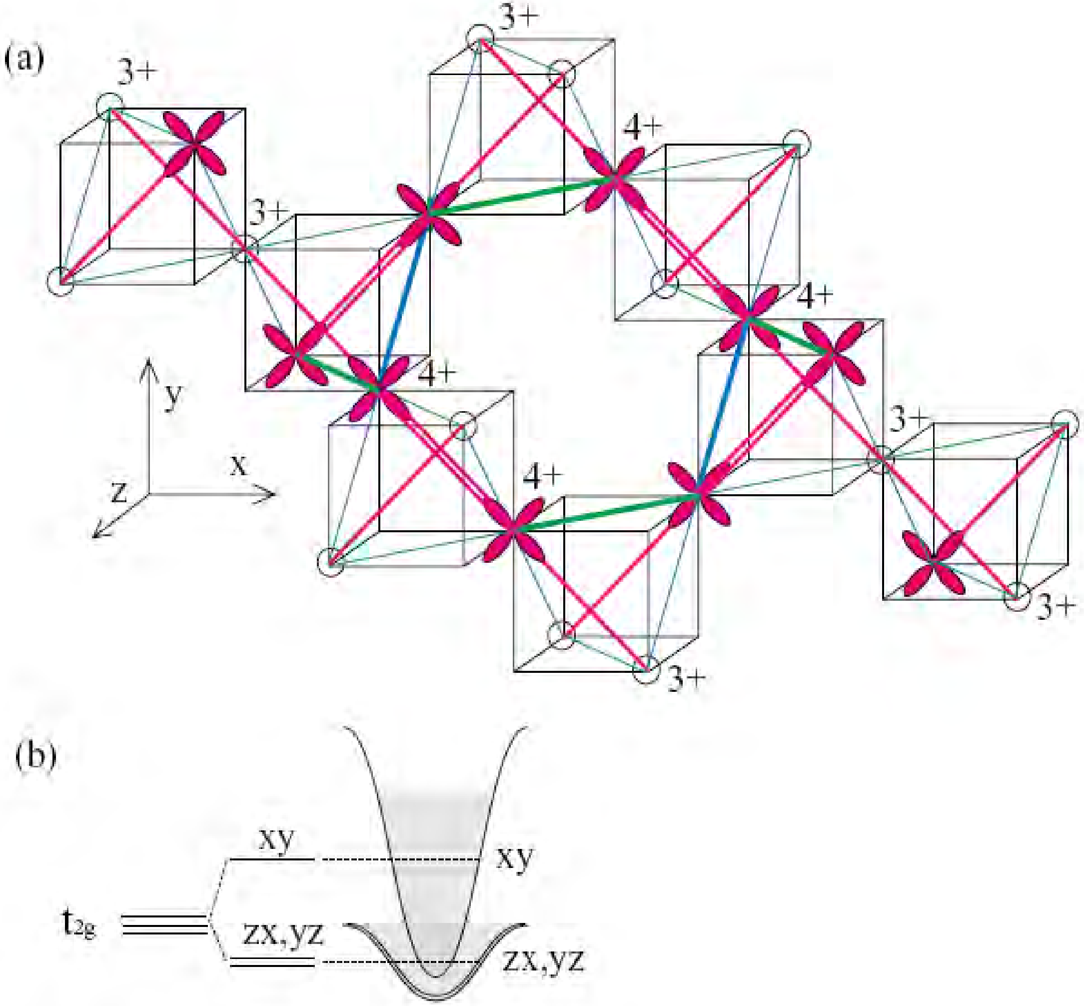
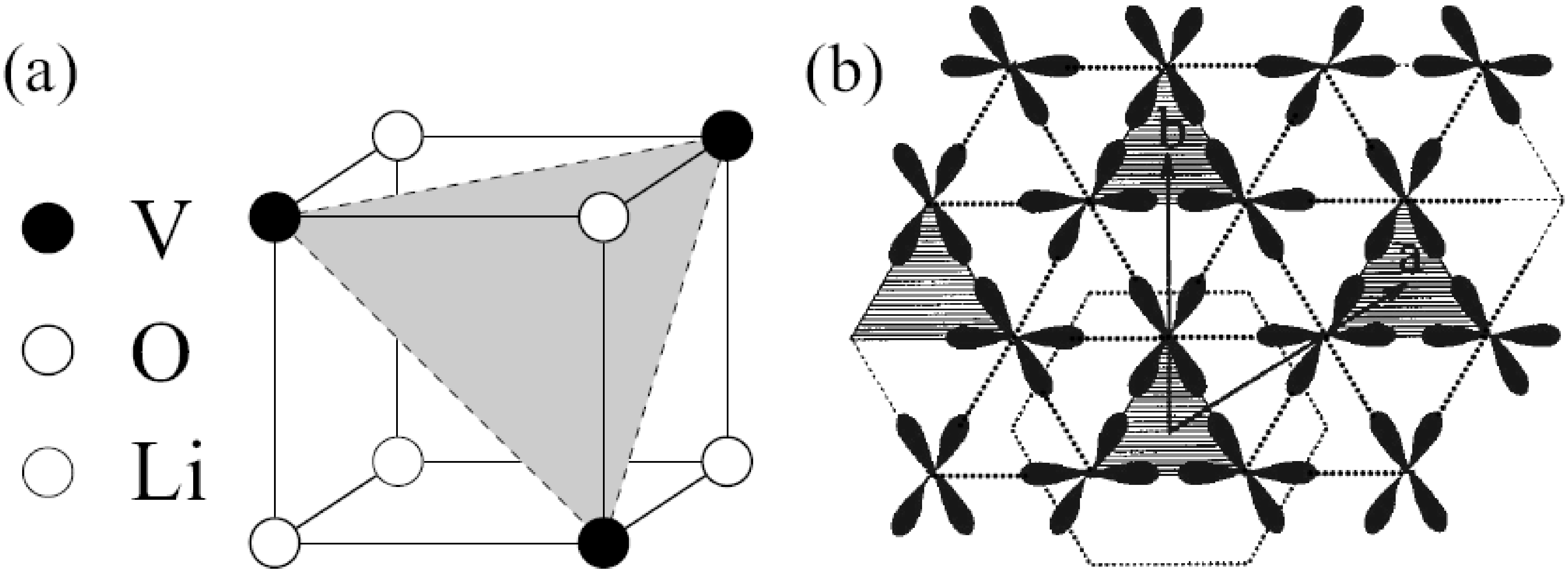


FIG. 2: (a) Charge and orbital ordering in $\mathrm{CuIr_2S_4}$. Octamer is shown by thick lines, short singlet bonds — by double lines. (b) Schematic electronic structure of $\mathrm{CuIr_2S_4}$.

D.Kh. & T.Mizokawa, PRL 94, 156402 (2005)



g. 3. Schematic crystal structure (a) and orbital ordering (b) in LiVO$_2$, by Ref.

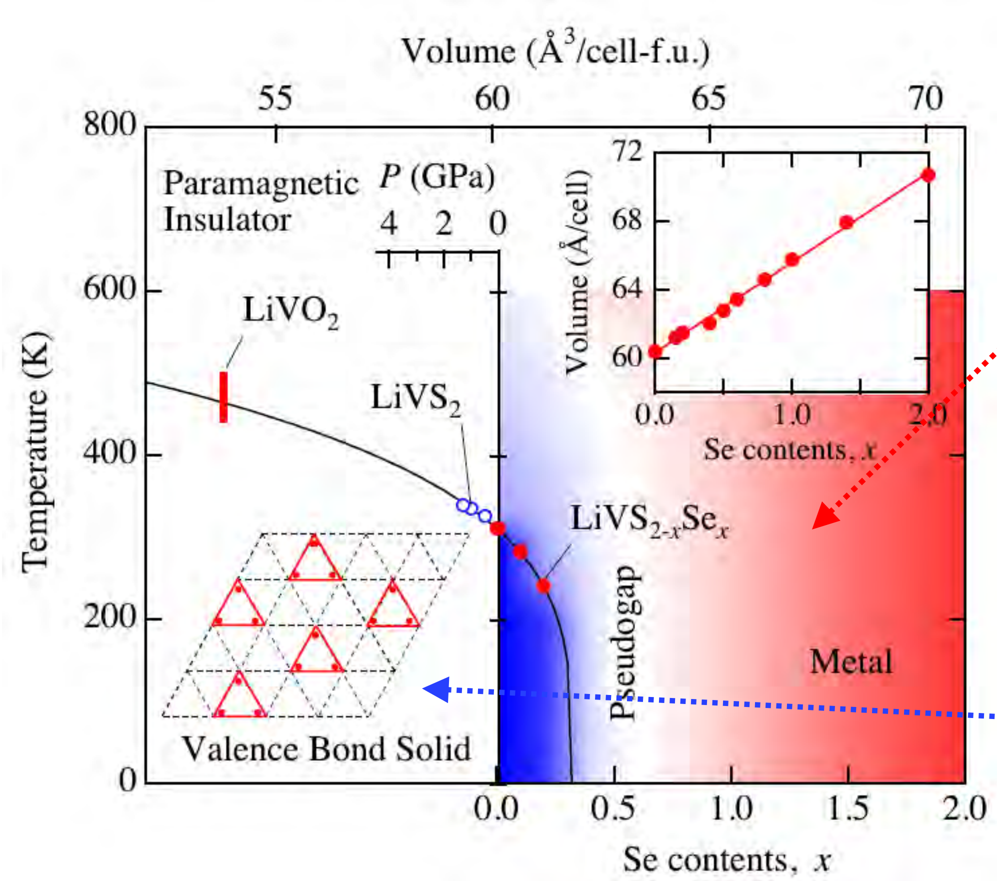
Same in **TiI$_2$** (G.Meyer); in **LiVS$_2$** (H.Takagi)

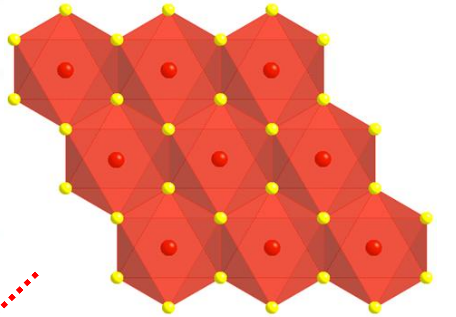
And the bonds in shaded (singlet) triangles become much **shorter!** Average **V-V** distance is 2.84Å is shorter than $R_c^{Goodenough}$ ~ 2.94Å; after trimerization **V-V**$_{short}$=**2.56**Å; **V-V**$_{long}$=3.02Å (**V-V**$_{metal}$=**2.62**Å!)

H.Pen, G.Sawatzky, D.Kh. et al., PRL **78**, 1323 (1997)

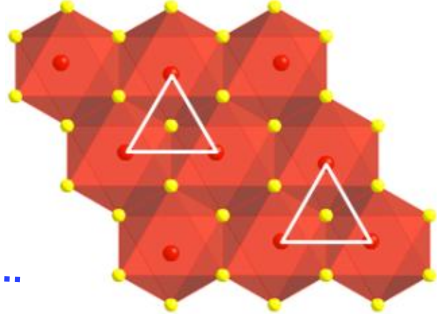
N. Katayama, M. Nohara, H. Takagi

- **Phase diagram of $LiVO_2$, $LiVS_2$ and $LiVSe_2$**, which consists of a **frustrated $3d^2$ lattice**.

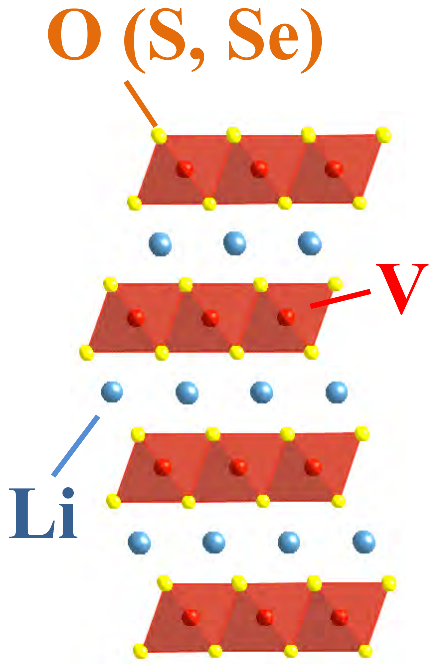




2D-triangular lattice



Valence Bond Solid
(V "trimer" cluster)



- The formation of **pseudogap in metallic phase** close to the critical boundary of the **metal to Valence Bond Solid insulator transition**.

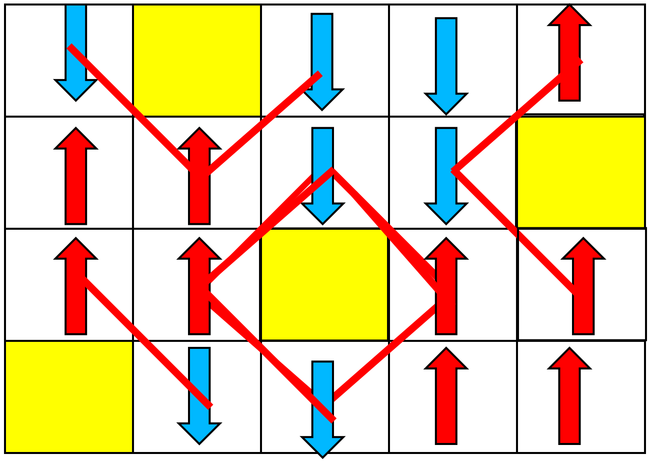
Larger molecular clusters:

Singlets on squares: **CaV_4O_9**

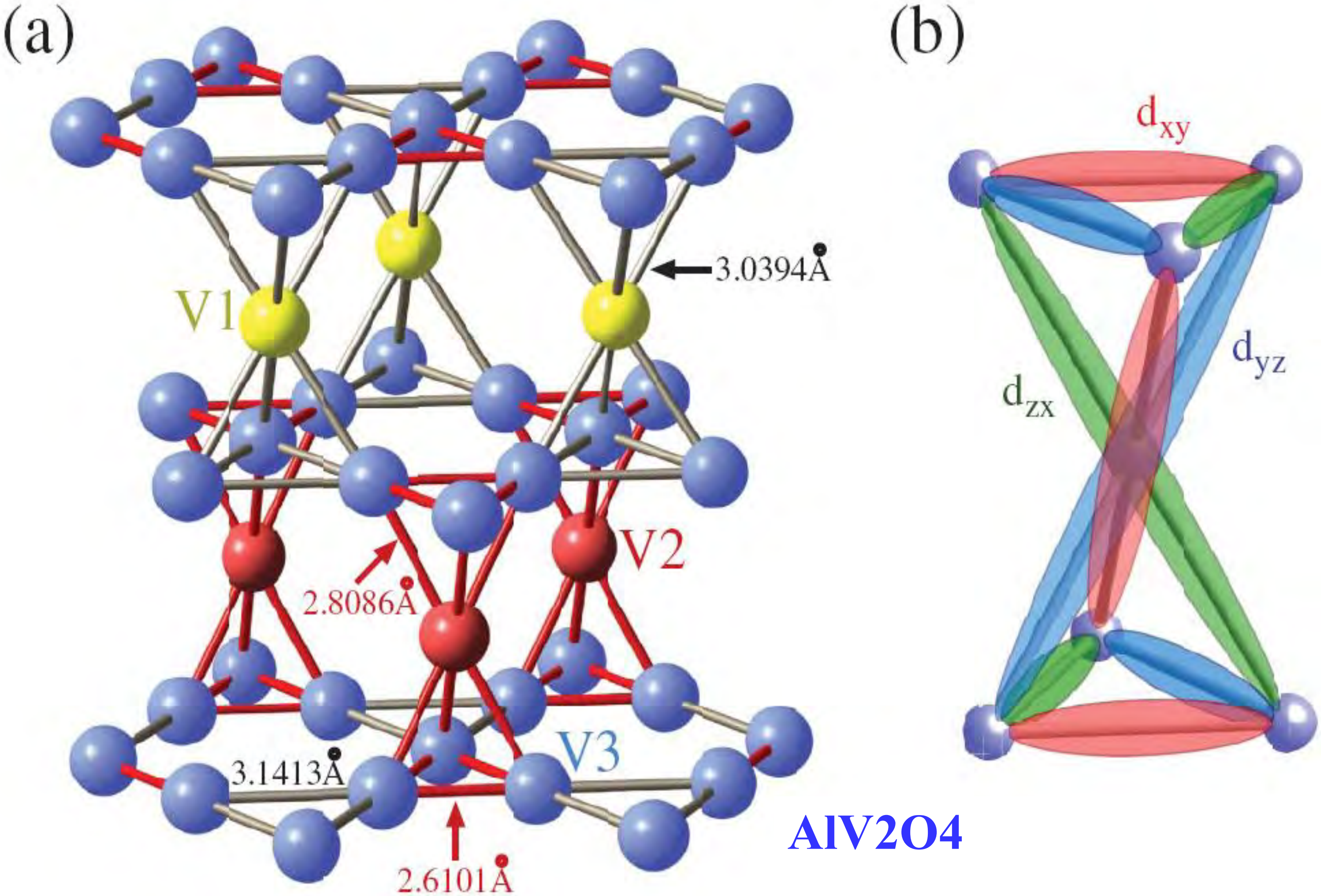
Origin of Spin Gap in CaV4O9: Effects of Frustration and Lattice Distortions

O. A. Starykh, M. E. Zhitomirsky, D. I. Khomskii, R. R. P. Singh, and K. Ueda, Phys. Rev.Lett., 77, 2558 (1996)

Similar structure in Fe-deficient **K2Fe4Se5 !**



"Molecular " superstructures in the solid

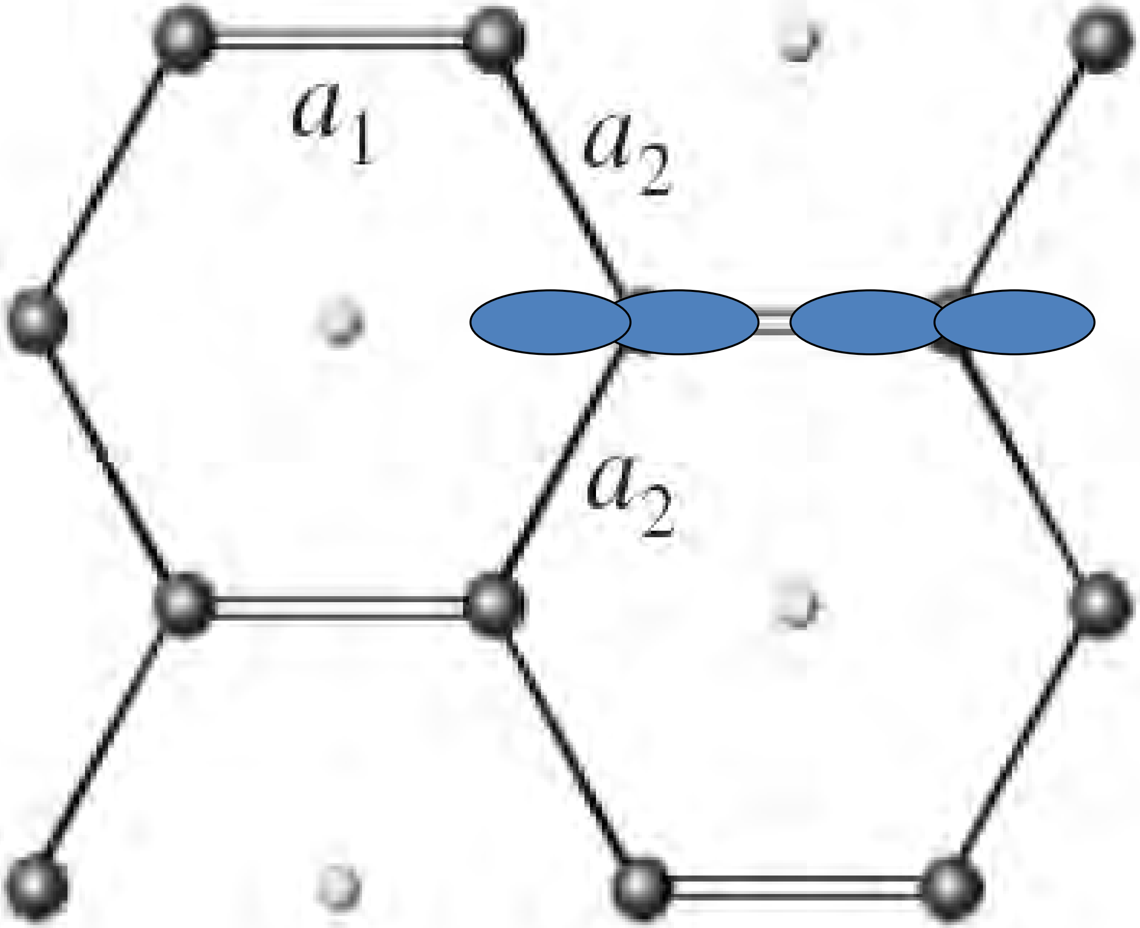


AlV2O4

Horibe et al., PRL **96**, 086406 (2006)

V-V$_{metal}$=2.62Å

t_{g2} orbitals on a **honeycomb** lattice: direct dd-hopping - reduction to 0-dimensional case!



nal of the Physical Society of Japan
. 76, No. 3, March, 2007, 033705
007 The Physical Society of Japan

New-Type Phase Transition of Li_2RuO_3 with Honeycomb Structure

Yoko MIURA, Yukio YASUI, Masatoshi SATO,
Naoki IGAWA[1], and Kazuhisa KAKURAI[1]

Department of Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602
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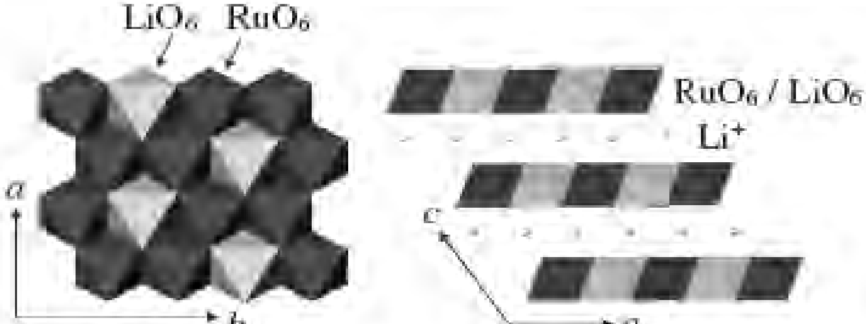
Tokai-mura, Naka-gun, Ibaraki 319-1195

(Received November 28, 2006; accepted January 10, 2007; published February 26, 2007)

A new-type structural transition has been found in Li_2RuO_3 with a honeycomb lattice of edge-sharing RuO_6 octahedra. With decreasing temperature T, the electrical resistivity exhibits an anomalous increase at $T = T_c \sim 540$ K, suggesting the (metal-to-insulator)-like transition, and the magnetic susceptibility also shows a sharp decrease. Detailed structure analyses have revealed that the high-temperature space group $C2/m$ changes to $P2_1/m$ at T_c. The most striking fact is that a significant reduction of the bond lengths is found between two of the six Ru–Ru pairs of the hexagon in the low-temperature phase, indicating a new-type phase transition driven by the formation of the molecular orbits of these Ru–Ru pairs.

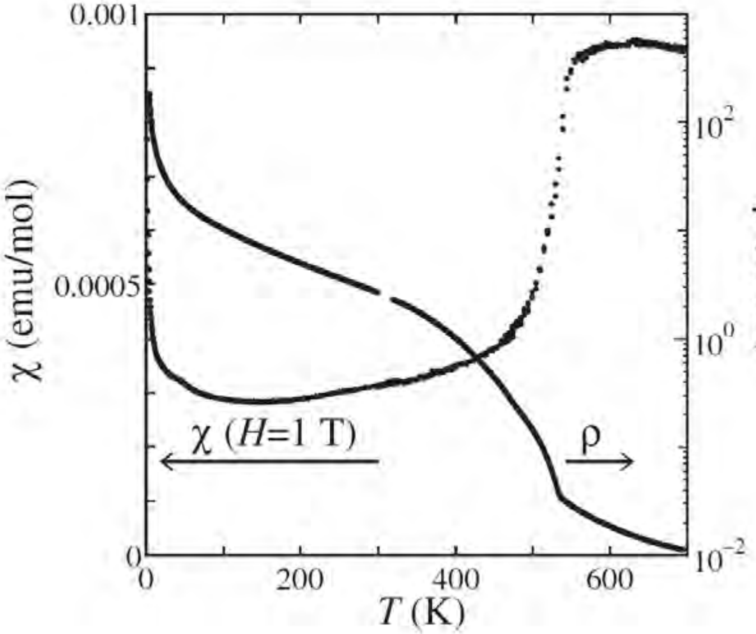
KEYWORDS: Li_2RuO_3, honeycomb structure, structural transition
DOI: 10.1143/JPSJ.76.033705

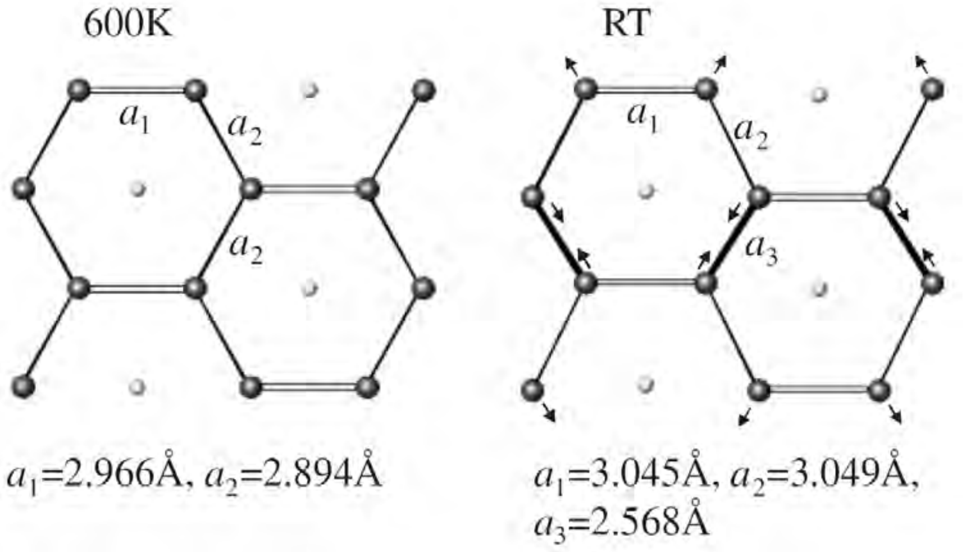
Compounds with the honeycomb lattice often present
eresting behavior originating from their characteristic
uctures. For example, in the course of the studies on the
ysical properties of localized spin systems of $A_3T_2SbO_6$
$= Na, Li$; $T = Cu, Ni, Co$) and $Na_2T_2TeO_6$ on the
storted) honeycomb lattice, spin gap behaviors have been
und for T = Cu,[1–3] while magnetic transitions to the spin-
dered state have been observed for T = Co and Ni.[4]



Experimental observations: Li_2RuO_3

Miura et al JPSJ'07





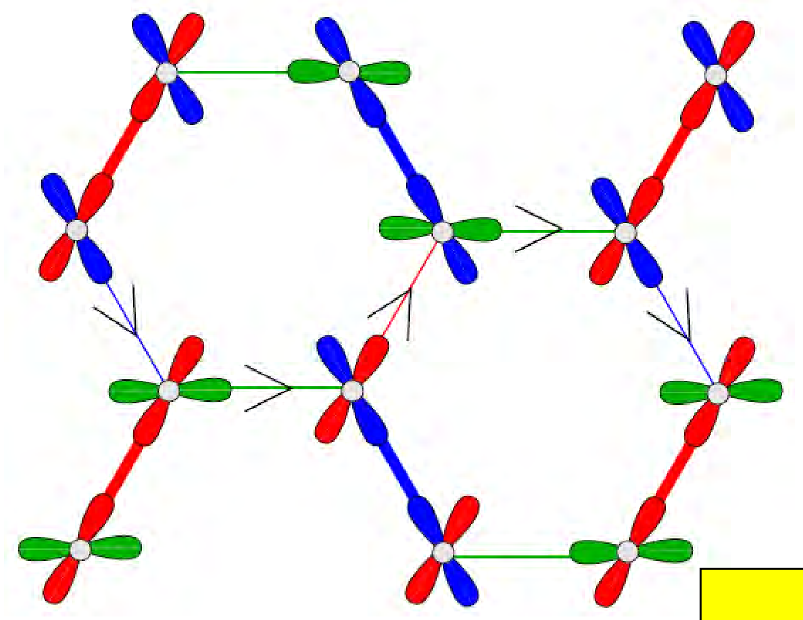
a_1=2.966Å, a_2=2.894Å

a_1=3.045Å, a_2=3.049Å, a_3=2.568Å

Possible spin-singlet dimerized phase in 2D ?!

The ground state manifold

Conclusion: The ground state manifold is generated by hard-core dimer coverings: Extensive orientational degeneracy

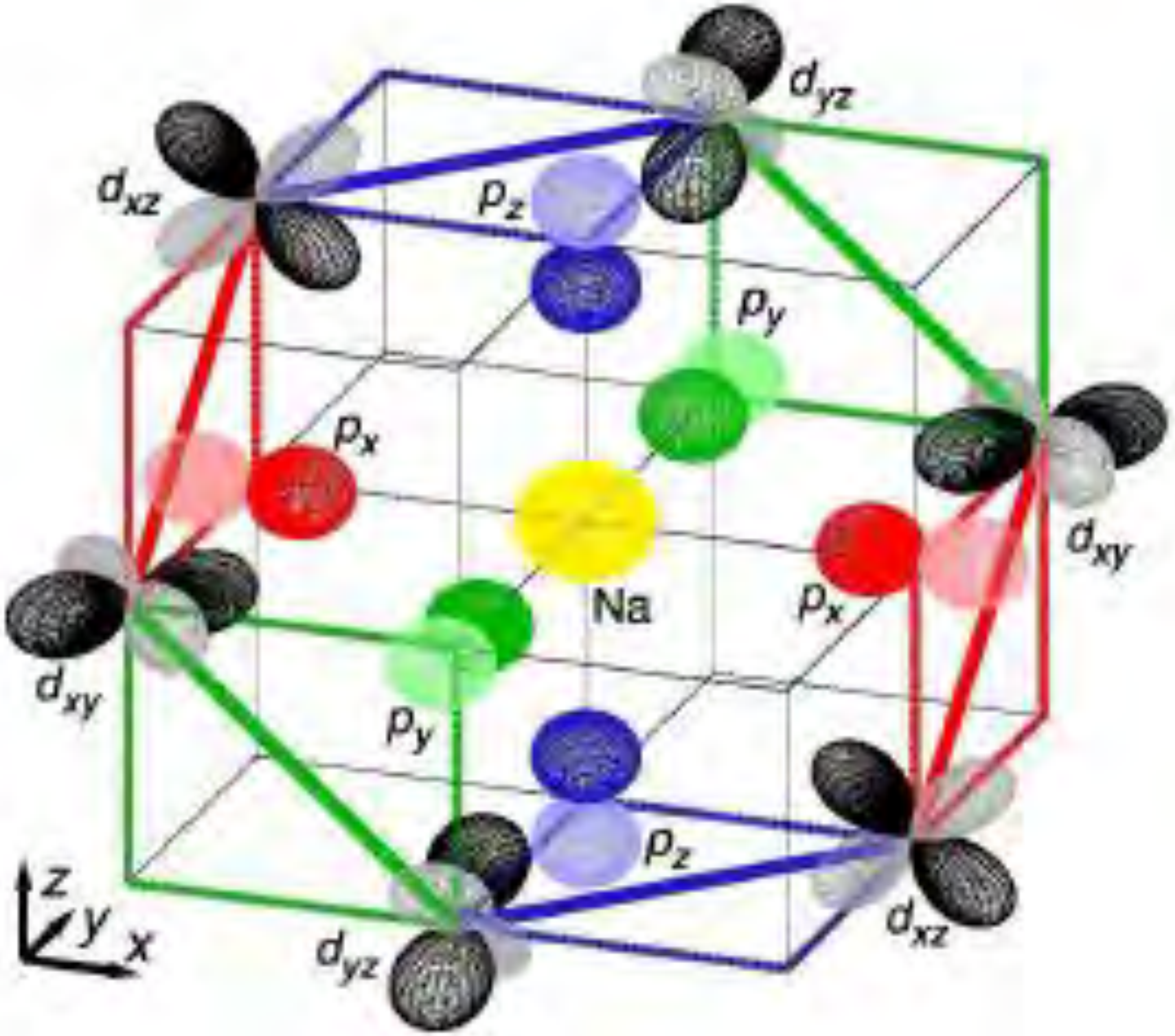


Each spin is bound into spin-singlet

Spin Gap

G.Jackeli and D.Kh., PRL **100**, 147203 (2008)

Na2IrO3

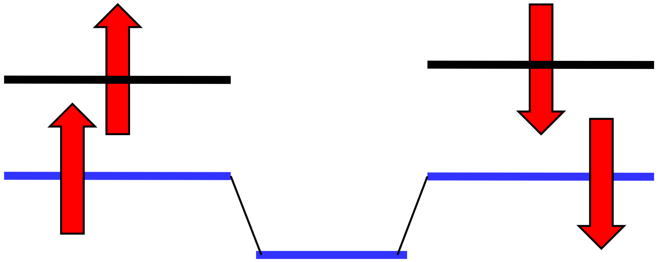


I. Mazin et al., PRL **109**, 197201 (2012)

Orbital-selective Peierls transition (MO against Hund !)

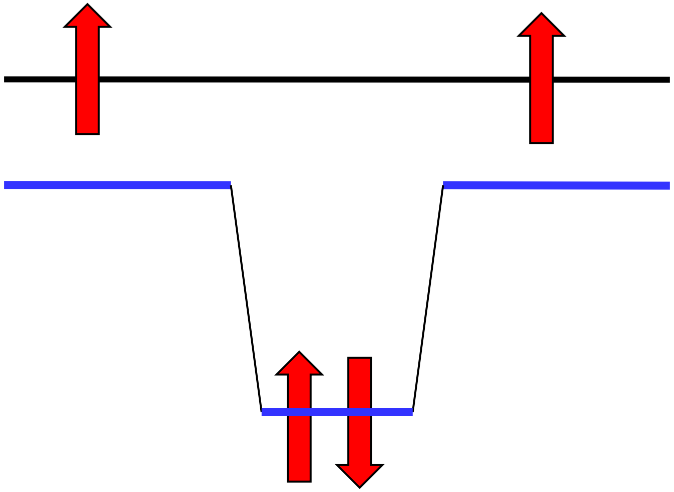
S.V. Streltsov and D.I. Khomskii,
Phys. Rev. B 89, 161112(R) (2014)

State of a dimer with 4 electrons, with J(Hund)>t



$E = -2J_H - t^2/J_H$

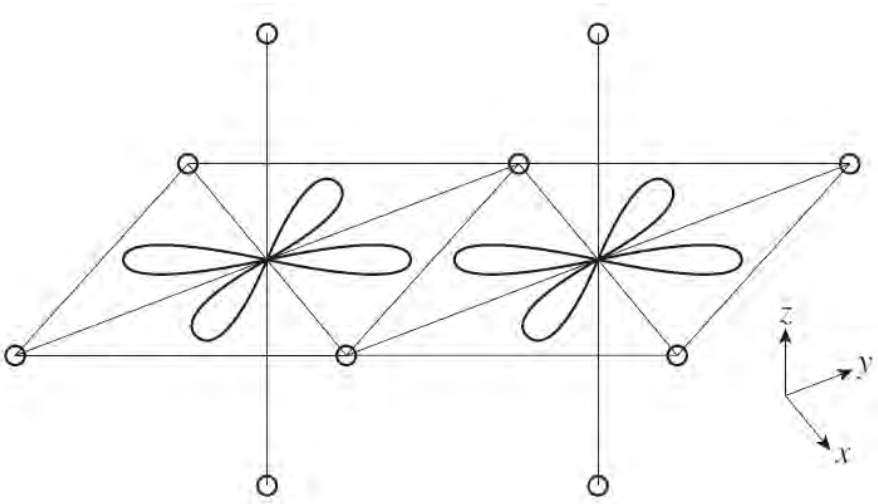
MO state of a dimer with 4 electrons, with t>J(Hund)



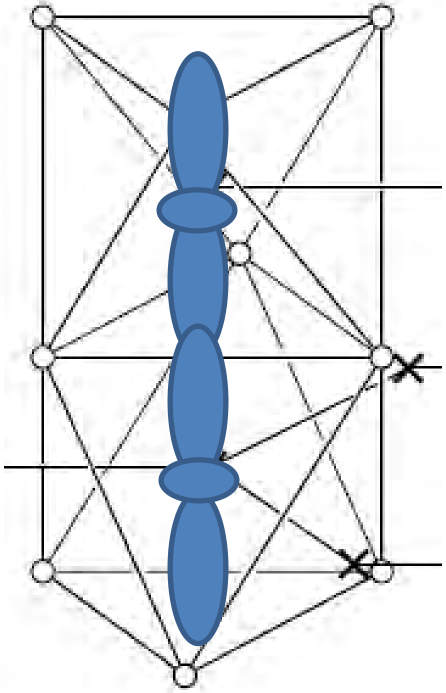
$E = -2t$

For large hopping one orbital form singlet bonding molecular orbital, at the expence of the Hund’s coupling. Second electron is decoupled and does what it wants.

Typical cases of strong direct metal-metal overlap/hopping:



Common edge (xy-orbitals)



Common face (a_{1g} orbitals)

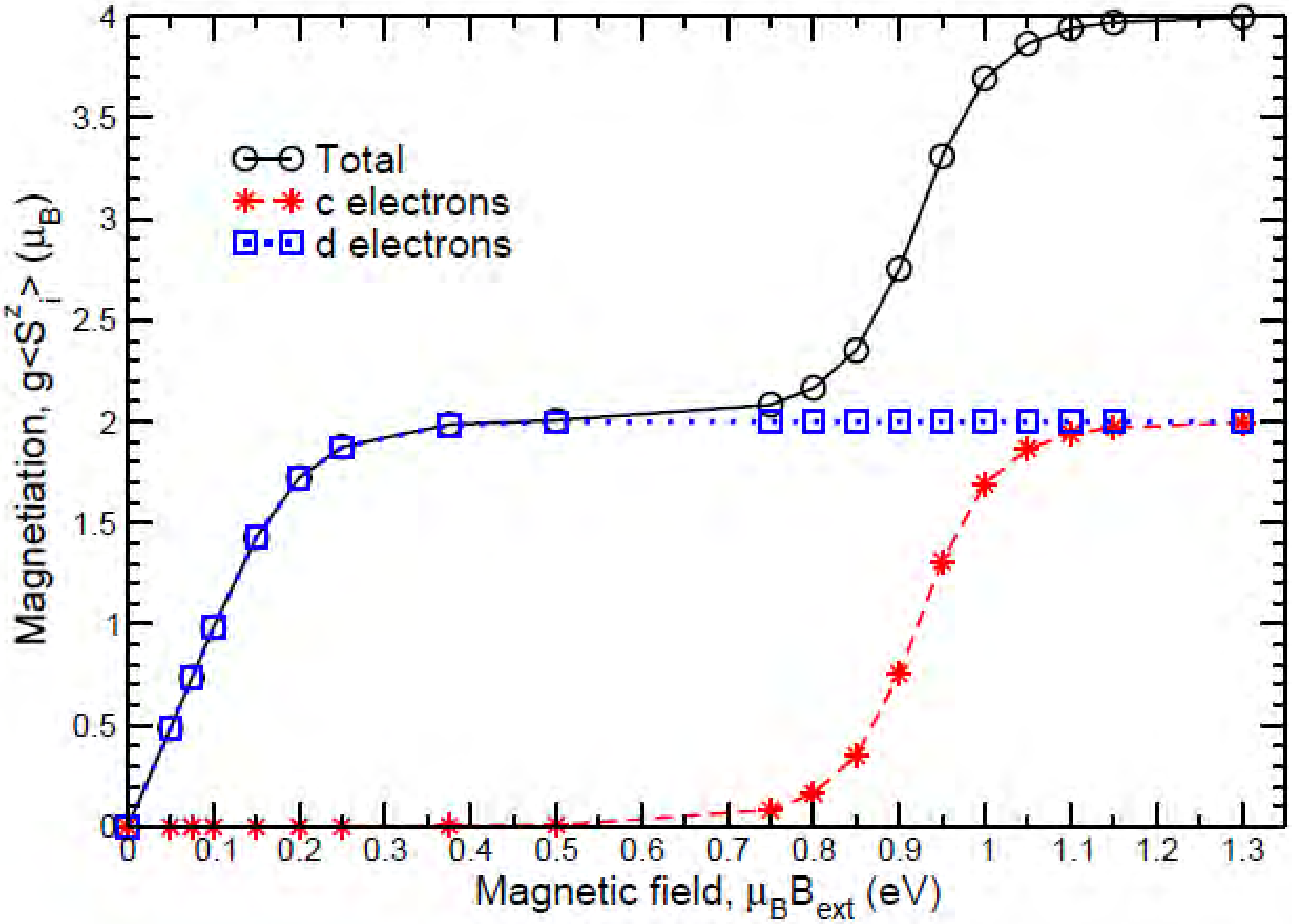


FIG. 2: (color online). Results of the C-DMFT calculations. The total and partial magnetization per dimer. $t' = 0.1$ eV, $t_c = 12t'$, $t_d = 2t'$, $J_H = t'$, $U = 10t'$.

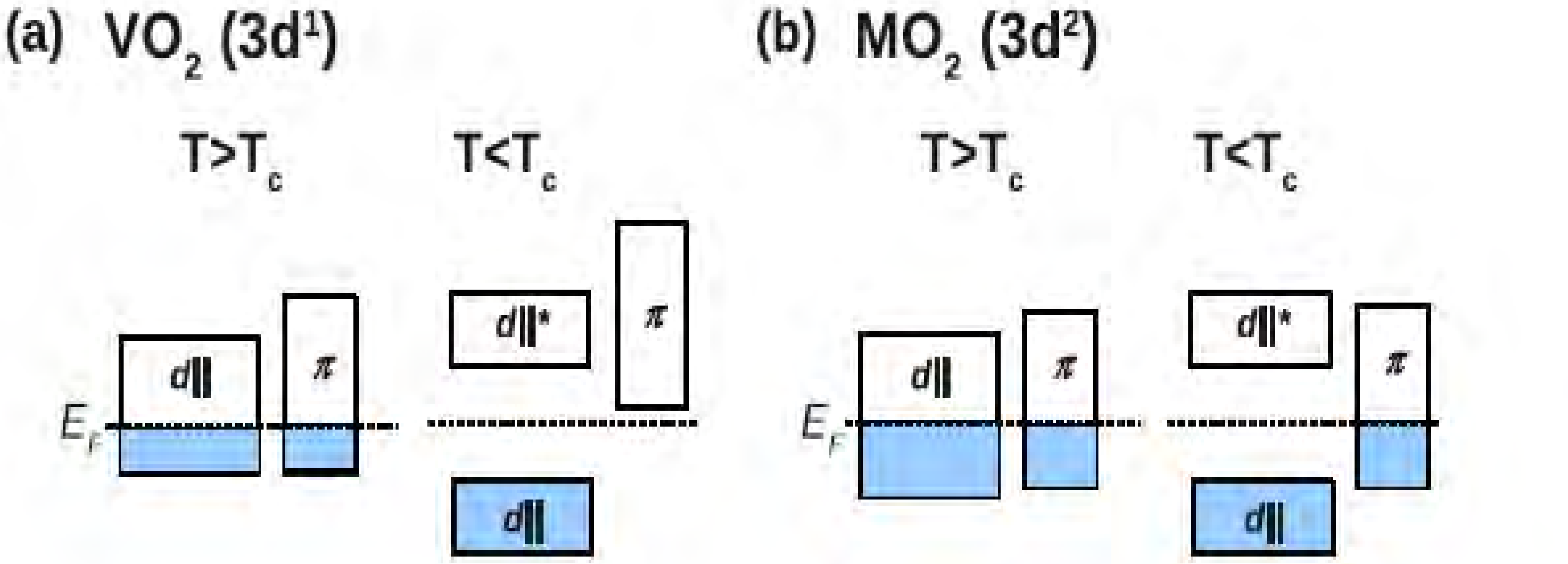


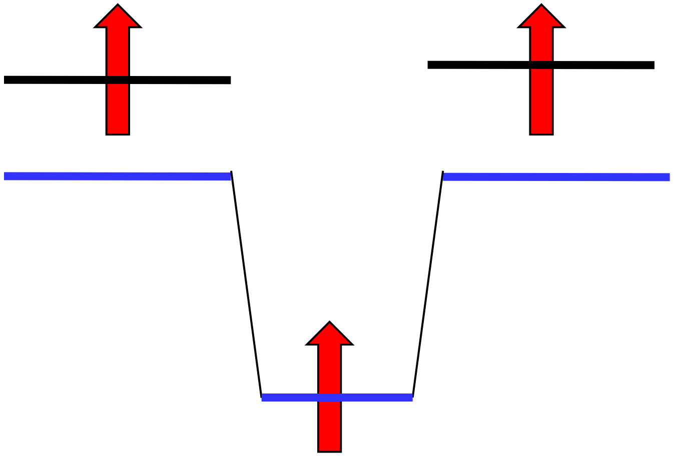
FIG. 4: (color online). Schematic band structures below and above Peierls transition in VO_2 and MoO_2. The notations are taken as in Ref. 19.

VO2: one d-electron, singlet dimers below metal-insulator transition

MoO2: two d-electrons per site. **Metal, but with dimers!** I.e. one d-electron forms singlet MO (metal-metal bond), and the second electron forms a conduction band

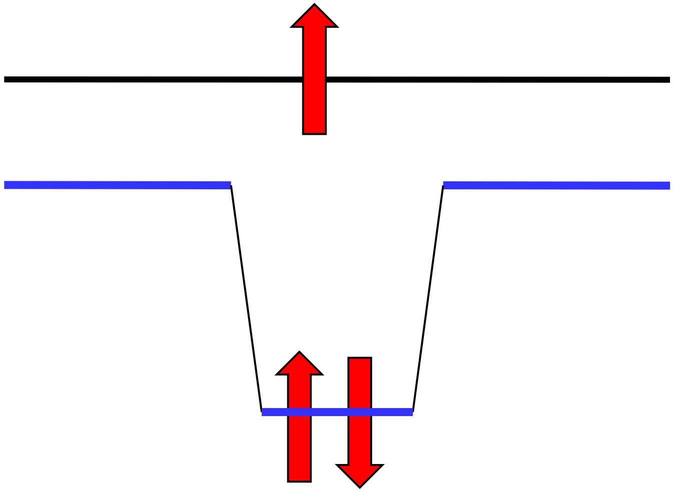
Orbitally-selective Peierls transition: molecular orbitals vs double exchange

DE state of a dimer with 3 electrons



$E = -t - J_H$

MO state of a dimer with 3 electrons



$E = -2t$

Other possible systems:

Ba3MRu2O9

M=Na, …; Ru5.5+ (d^3/d^2)
M=Ca; Co; …; Ru5+(d3)
M=Y, La, ….; Ru4.5+ (d^4.d^3)

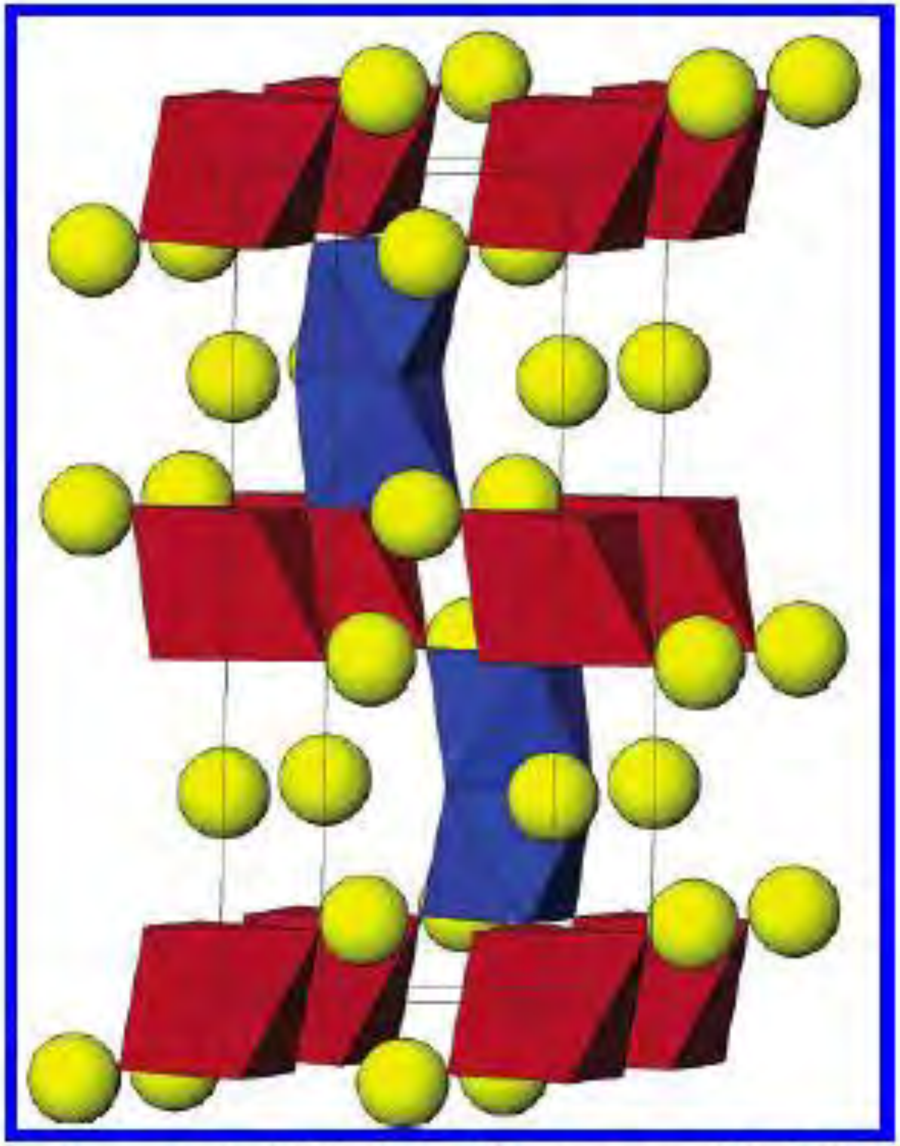
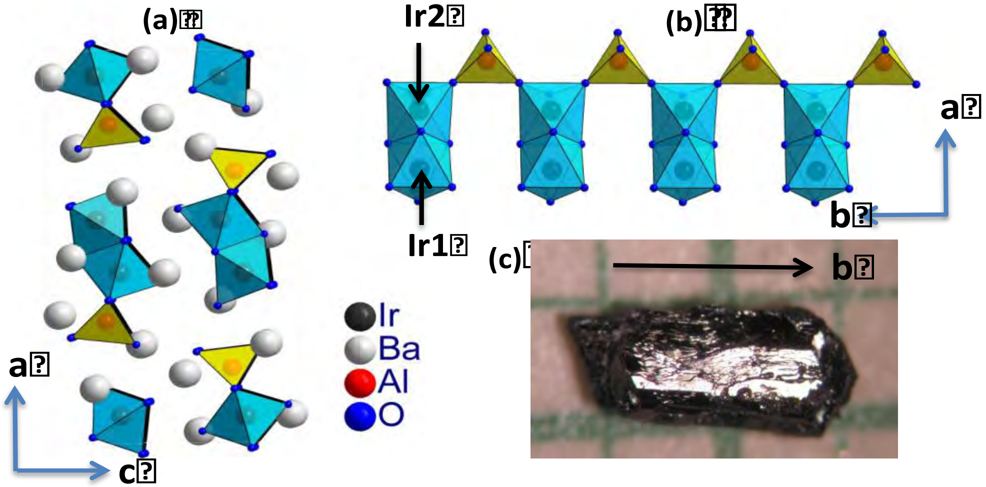


Figure 2. Approximate [110] view of the structure of $Ba_3MRu_2O_9$ (M = Li, Na) consisting of blue RuO_6 face-sharing bi-octahedra cornered shared to red MO_6 (M = Li, Na) octahedra singles. Barium cations are shown as yellow spheres.

Ba5 Al Ir2 O11

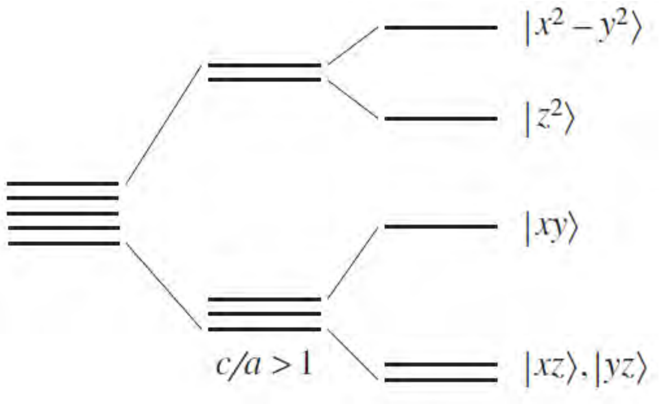
arXiv:1505.00877 (5 May 2015) Covalency and spin-orbit coupling against double exchange: anomalous behaviour of the dimer-chain iridate Ba5AlIr2O11
S.V. Streltsov, J. Terzic, J. C. Wang, Feng Ye, D.I. Khomskii, W. H. Song, S. J. Yuan, S. Aswartham, G. Cao



The analysis (experimental and theoretical) shows that here we have the same story: formation of a singlet molecular orbital for two electrons (holes)/dimer, with one hole with S=1/2/dimer remaining “free” (and ordering below 5K).
Strong SOC on Ir helps this tendency! (but itself is not enough to strongly reduce magnetic moment)

Orbital ordering vs spin-orbit coupling

For 3d systems (λ small) SOC is often treated in a mean field approximation

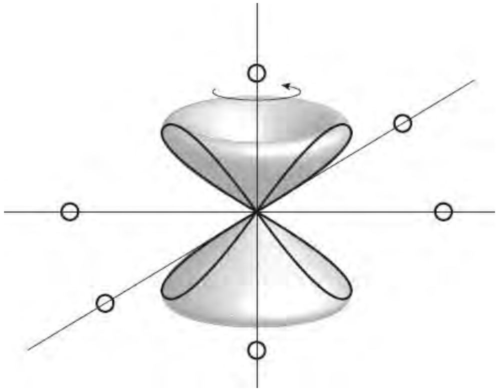


e_g, orbital moment quenched

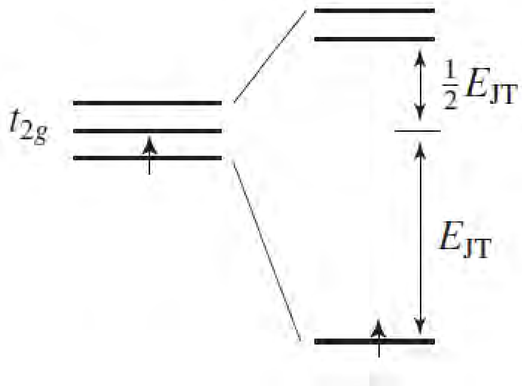
t_{2g}, l_{eff} =1
|xy> = $|l^z=0\rangle$
|xz, yz>= $|l^z=+/-1\rangle$

$$|1\rangle \sim -\frac{1}{\sqrt{2}}(|xz\rangle + i|yz\rangle)$$

$$|-1\rangle \sim \frac{1}{\sqrt{2}}(|xz\rangle - i|yz\rangle)$$

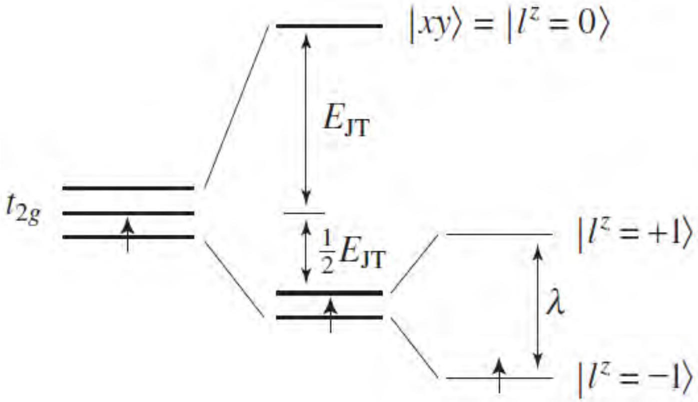


Jahn-Teller dominated regime



$E = -E_{JT}$, c/a < 0

Spin-orbit dominated regime



$E = -E_{JT}/2 - \lambda/2$, c/a >0

E_{JT} vs λ

In effect:

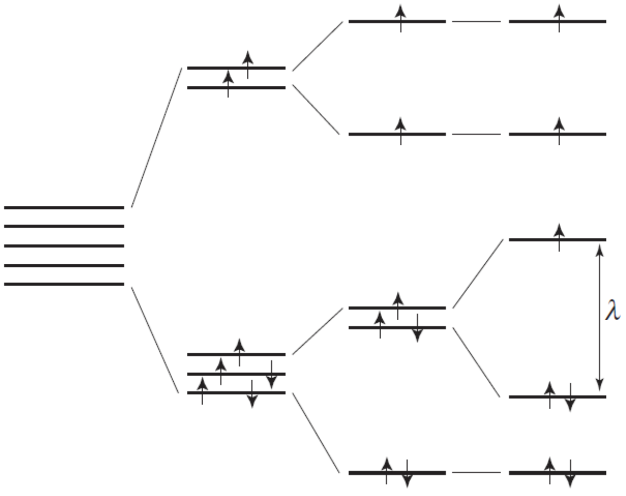
if $E_{JT} > \lambda$, system evolves according to JT scenario (orbital ordering of real orbitals)

if $E_{JT} > \lambda$, system evolves according to SO (orbital ordering of complex orbitals)

Distortion of O6 octahedra are **opposite**!

Beginning of 3d series (**Ti, V**) – JT dominates; heavy 3d elements (**Fe, Co**) – SOC dominates

Co^{2+} ($3d^7$) :



Co2+ - one t_{2g}-hole. SO regime – tetragonal distortion with c/a<1 (**CoO; KCoF3**)

t_{2g} levels are splitted both by tetragonal [001] and trigonal [111] distortions

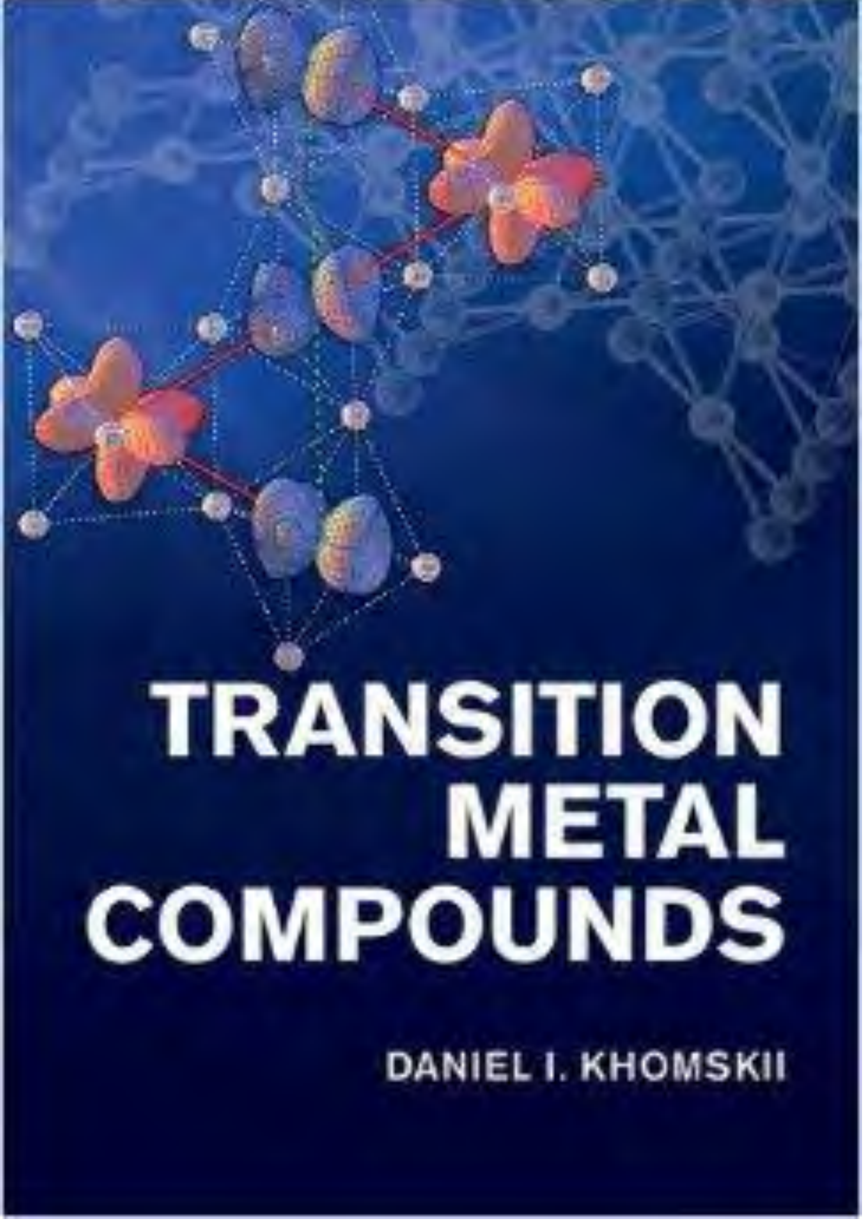
Co2+ - (almost) always **tetragonal**

Fe2+(d^6) (one electron on top of half-filled shell: **trigonal** distortion (**FeO; KFeF3**). **Why?**

Ca2RuO4 below metal-insulator transition: octahedra distorted, c/a<1. **Usual JT ordering?**

SOC $\sim Z^?$

Usual answer SOC $\sim Z^4$

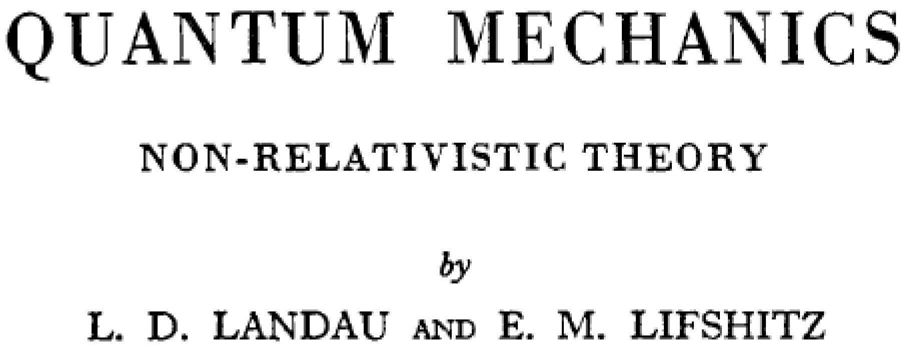


Transition Metal Compounds Hardcover

by Daniel I. Khomskii

Describing all aspects of the physics of transition metal compounds, this book provides a comprehensive overview of this unique and diverse class of solids. Beginning with the basic concepts of the physics of strongly correlated electron systems, the structure of transition metal ions, and the behaviours of transition metal ions in crystals, it goes on to cover more advanced topics such as metal-insulator transitions, orbital ordering, and novel phenomena such as multiferroics, systems with oxygen holes, and high-Tc superconductivity. Each chapter concludes with a summary of key facts and concepts, presenting all the most important information in a consistent and concise manner. Set within a modern conceptual framework, and providing a complete treatment of the fundamental factors and mechanisms that determine the properties of transition metal compounds, this is an invaluable resource for graduate students, researchers and industrial practitioners in solid state physics and chemistry, materials science, and inorganic chemistry.

SOC ~Z^?

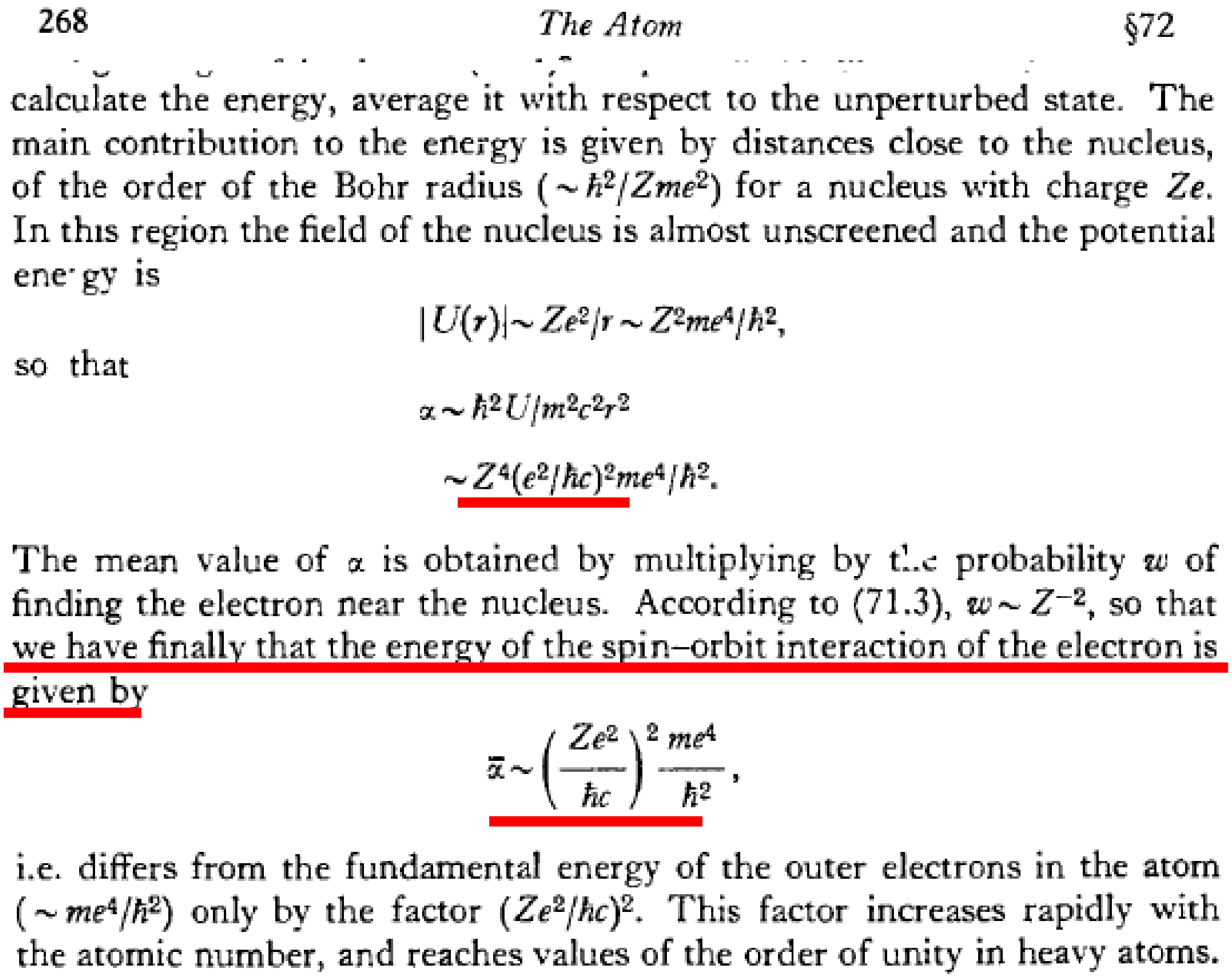


QUANTUM MECHANICS

NON-RELATIVISTIC THEORY

by

L. D. LANDAU AND E. M. LIFSHITZ



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calculate the energy, average it with respect to the unperturbed state. The main contribution to the energy is given by distances close to the nucleus, of the order of the Bohr radius ($\sim \hbar^2/Zme^2$) for a nucleus with charge Ze. In this region the field of the nucleus is almost unscreened and the potential energy is

$$|U(r)| \sim Ze^2/r \sim Z^2me^4/\hbar^2,$$

so that

$$\begin{aligned}\alpha &\sim \hbar^2 U/m^2c^2r^2\\ &\sim Z^4(e^2/\hbar c)^2 me^4/\hbar^2.\end{aligned}$$

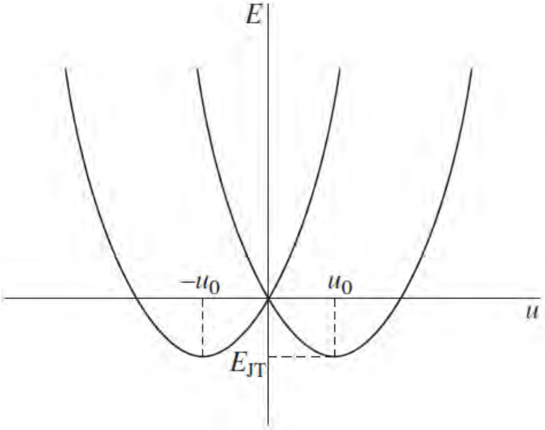
The mean value of α is obtained by multiplying by the probability w of finding the electron near the nucleus. According to (71.3), $w \sim Z^{-2}$, so that we have finally that the energy of the spin–orbit interaction of the electron is given by

$$\bar{\alpha} \sim \left(\frac{Ze^2}{\hbar c}\right)^2 \frac{me^4}{\hbar^2},$$

i.e. differs from the fundamental energy of the outer electrons in the atom ($\sim me^4/\hbar^2$) only by the factor $(Ze^2/\hbar c)^2$. This factor increases rapidly with the atomic number, and reaches values of the order of unity in heavy atoms.

Quantum effects in orbitals:

Static and dynamic Jahn-Teller effect



$$|\Psi_i\rangle_{\mathrm{ad}} = |\psi_i\rangle|\phi\rangle \quad \Longrightarrow \quad \begin{aligned} |\Psi_1\rangle &= |\psi_1\rangle|\phi_1\rangle \\ |\Psi_2\rangle &= |\psi_2\rangle|\phi_2\rangle \end{aligned}$$

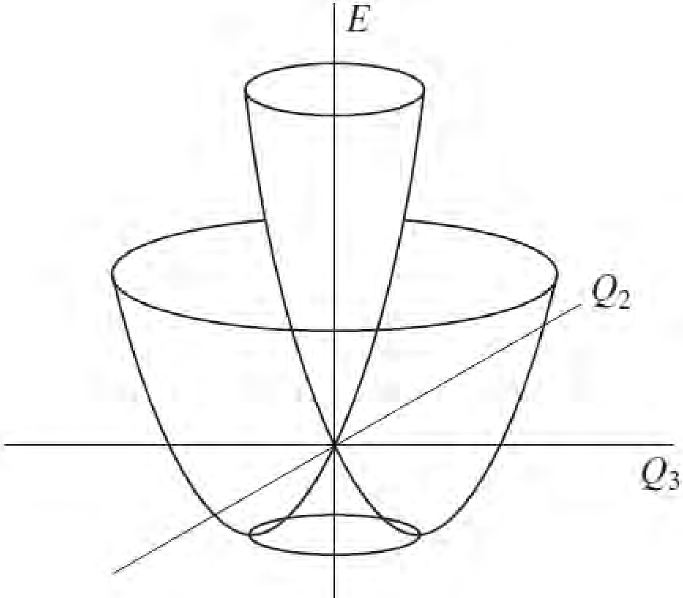
$$A_{12} = {}_{\mathrm{ad}}\langle\Psi_1|\hat{A}|\Psi_2\rangle_{\mathrm{ad}} = \langle\psi_1|\hat{A}|\psi_2\rangle$$

$$\Big\Downarrow$$

$$A_{12} = \langle\Psi_1|\hat{A}|\Psi_2\rangle = \langle\psi_1|\hat{A}|\psi_2\rangle\langle\phi_1|\phi_2\rangle$$

Ham reduction factor

$$\mathcal{H}_{\mathrm{JT}}^{(e_g)} = -\frac{1}{2}g\left\{(c_1^\dagger c_1 - c_2^\dagger c_2)Q_3 + (c_1^\dagger c_2 Q_2 + \mathrm{h.c.})\right\}$$



System *freely rotates* around the trough.
Rotational quantization

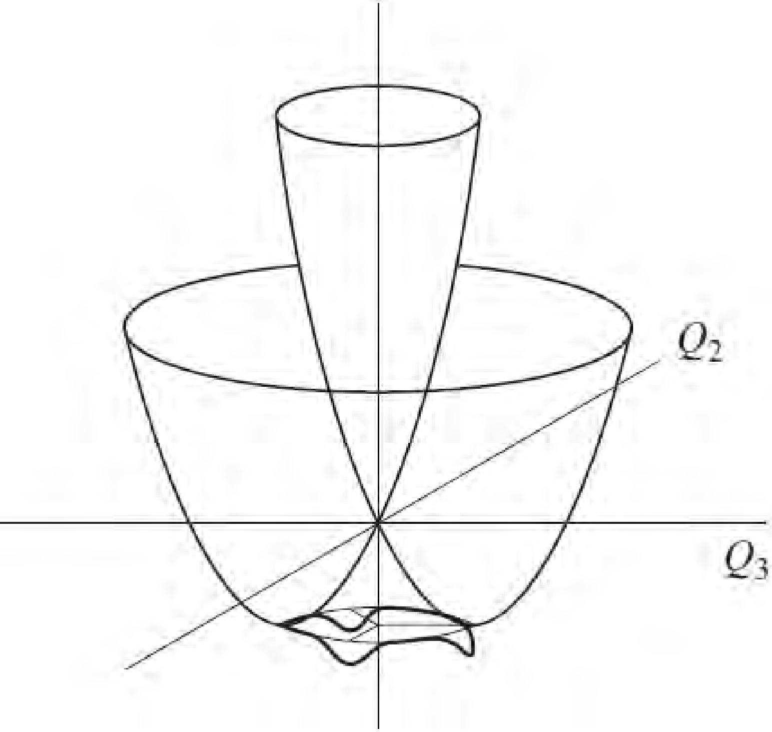
Geometric phase (Longuet-Higgins et al., Proc.Roy.Soc. **A244**, 1 (1958))

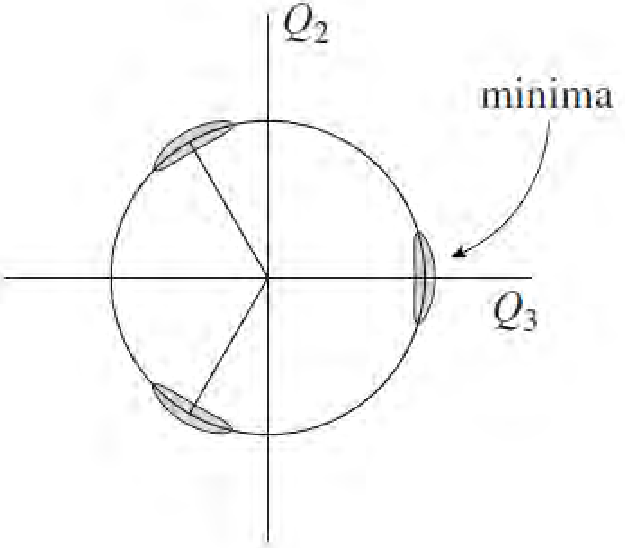
$$|\theta\rangle = \cos\frac{\theta}{2}\,|z^2\rangle + \sin\frac{\theta}{2}\,|x^2 - y^2\rangle$$

$$|\tilde{\theta}\rangle = \cos\tilde{\theta}\,|Q_3\rangle + \sin\tilde{\theta}\,|Q_2\rangle$$

Conical intersection

$E_2 \sim \gamma \cos 3\theta$





Lifts the degeneracy or not?

The same symmetry – gives the same systematic of terms, with E_g doublet and A singlet. **Which is the ground state?**

The outcome depends on the strength of anisotropy; conical point!
(Koizumi, H. and Bersuker, I. B. (1999), *Phys. Rev. Lett.* **83**, 3009)

How important can it all be in concentrated solids?

Conclusions

- Orbital ordering and cooperative Jahn-Teller effect determine to a large extend the behavior of transition metal compounds
- Details of orbital and spin ordering strongly depend on local geometry: the cases of common corner and common face of MO6 octahedra are much different from the case of common edge
- Directional character or orbitals often leads to a reduction of effective dimensionality of the system. This, in particular, favors formation of "molecules" in solids - partial delocalization of electrons on certain clusters (dimers; trimers, heptamers, …)
- Especially strong are these effects in systems close to Mott transition; step-wise Mott transition
- Orbitally-selective Peierls transition is in principle possible, especially in 4d and 5d-systems
- Singlet molecular orbital formation can counteract the double-exchange mechanism of ferromagnetism
- Orbital ordering and real spin-orbit interaction may counteract each other.
- Quantum (vibronic) effects: are they important for concentrated solids?
- *Orbital physics is quite rich and produces new and new surprises !*