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 against 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

\[ \mathcal{H}_b = \sum_{k, \sigma} \varepsilon(k) c_{k\sigma}^{\dagger} c_{k\sigma} \]
\[ \varepsilon(k) = -2t(\cos k_x + \cos k_y + \cos k_z) \]

Peierls transition

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

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

\[ - \sum_{\alpha \neq \beta} J_H (\frac{3}{4} + S_{i\alpha} S_{i\beta}) \]

\[ H_{\text{eff}} = \frac{2t^2}{U} \sum_{(ij)} S_i S_j \]
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\textsubscript{g} levels $\rightarrow$ Jahn-Teller distortion

\[
\begin{align*}
\frac{5x}{2x} & \quad \frac{2x}{3x} \\
\frac{e_g}{t_{2g}} & \quad \frac{t_{2g}}{e_g}
\end{align*}
\]
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

\[ t_{11} = t_{22} = t, \ t_{12} = 0 \]

\[ \Delta E = 0 \]

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

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

\[ \Delta E = -\frac{2t^2}{U-J_H} \]
Octahedra with common corners

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

$S = 1/2$ (spin variables), $\tau = 1/2$ (orbital variables)

Schematic structure of the effective spin-orbital Hamiltonian

$$H_{\text{eff}} \sim \frac{t^2}{U} \left\{ J_1 S S + J_2 \tau \tau + J_3 S S \tau \tau \right\}$$

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

\[ t_{11} = t_{22} = t, \ t_{12} = 0 \]

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

has not only SU(2) \( \times \) 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

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

\[
J_{FM} = -\frac{2t^2J_H}{U(U - J_H)}
\]
"General rule" for 180° M-O-M angle:

Ferro orbitals ↔ antiferro spins
antiferro orbitals ↔ ferro spins

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

For edge-sharing octahedra, 90° 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* \(x_2-y_2\) 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 in AFM interaction for the case of $90^\circ$ 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 in FM interaction for the case of $90^\circ$ 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 $90^\circ$ TM – O – TM bond.
Our problem: “the third case”, face-sharing

A lot is done and known for MO$_6$ octahedra with common corners ($\angle O$-$M$-$O \sim 180^\circ$) or common edges ($\angle O$-$M$-$O \sim 90^\circ$)

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$_4$Ru$_3$O$_{10}$;
- systems of general formula Ba$_3$(M1)(M2)$_2$O$_9$, 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$_3$

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.

$e_g$ 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

\[ t_{|xy\rangle,|xy\rangle} = t_{|x^2-y^2\rangle,|x^2-y^2\rangle} = V_{dd\delta} \]
\[ t_{|yz\rangle,|yz\rangle} = t_{|xz\rangle,|xz\rangle} = V_{dd\pi} \]

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

\[ t_{|e_2\rangle|d_1\rangle} = t_{|e_2\rangle|d_1\rangle} = 0 \]
$e_g$ electrons, superexchange via anions

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

\[ t_{|d_2\rangle|d_1\rangle} = t_1 \quad t_{|e_2\rangle|e_1\rangle} = t_2 \quad \text{via A1} \]
\[ t_{|e_2\rangle|d_1\rangle} = t_{|e_2\rangle|d_1\rangle} = t_3 \quad \text{via A2} \]

\[ t'_1 = t_1 \cos^2 \frac{2\pi}{3} + t_2 \sin^2 \frac{2\pi}{3} + t_3 \sin \frac{4\pi}{3} \]
\[ t'_2 = t_1 \sin^2 \frac{2\pi}{3} + t_2 \cos^2 \frac{2\pi}{3} - t_3 \sin \frac{4\pi}{3} \]
\[ t'_3 = \frac{t_2 - t_1}{2} \sin \frac{4\pi}{3} + t_3 \cos \frac{4\pi}{3} \]

Similarly via A3 $\rightarrow t''$

\[ t_{\text{via } O} = t + t' + t'' \]

\[ t_{\text{via } O} = t_{\text{via } O} = \frac{3}{2} (t_1 + t_2) \quad t_{\text{via } O} = 0 \]
**Outcome:** $e_g$ electrons, effective Hamiltonian

For face-sharing geometry, we arrive at the symmetric $\text{SU}(4)$ orbital model

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

with \( t = t_{\text{direct}} + t_{\text{via O}} \)

Again, the terms with the Hund’s rule coupling constant have different orbital structure, such as

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

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

For electrons at $e_g^{\pi}$ levels with face-sharing octahedra – the same SU(4) spin-orbital Hamiltonian!
1. Octahedra with *common corner* (180 degree M-O-M bonds): **Heisenberg** interaction

\[ H \sim \frac{t^2}{U} \vec{j}_j \vec{j}_j \]

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**

\[ H \sim \frac{t^2}{U} \vec{j}_j \vec{j}_j \]
\textbf{Note:} for charge-transfer insulators also the second case (common edge) gives \textit{not Kitaev, but the usual Heisenberg} interaction in terms of \( j=1/2 \! \)!

Electrons (or holes) hop \textit{to the same oxygen} and back. In effect it is \textit{not the amplitides} via different oxygens which add (and cancel for \( j=1/2 \!), to give Kitaev), but the probablities add \( \rightarrow \text{Heisenberg interaction} \sim t^2/U \)

(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$_2$CuO$_3$

2d: La$_2$CuO$_4$, etc

3d: perovskites (e.g. LaMnO$_3$, BiFeO$_3$, ....)
**Common face** (~90 degrees M-O-M bonds)

1d: e.g. CuGeO3; KCuO2, ...

2d: many triangular, kagome, honeycomb systems (Li\_xCoO2; Na2IrO3, ...)

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?
Common edge:

1d: many

2d, 3d: is it ever possible?
Common edge:

1d : many

2d, 3d: is it ever possible?
Common edge:

1d: many

2d, 3d: is it ever possible?
Orbitals, \textit{reduced dimensionality} and spin gaps in correlated systems close to Mott transitions

1d \rightarrow 0d: NaTiSi\textsubscript{2}O\textsubscript{6} (singlet dimers) \hspace{1cm} \textit{PRL 96}, 249701 (2006)

1d \rightarrow 0d: TiOC\textsubscript{l} (spin-Peierls --- Peierls) \hspace{1cm} \textit{PRL 102}, 056406 (2009)

1d \rightarrow 0d: hollandites K\textsubscript{2}V\textsubscript{8}O\textsubscript{16}; K\textsubscript{2}Cr\textsubscript{8}O\textsubscript{16} \hspace{1cm} \textit{PRL 107}, 266402 (2011)

2d square \rightarrow 0d: La\textsubscript{4}Ru\textsubscript{2}O\textsubscript{10} (singlet dimers) \hspace{1cm} \textit{PRL 96}, 256402 (2006)

2d honeycomb\rightarrow 0d: Li\textsubscript{2}RuO\textsubscript{3} (singlet dimers) \hspace{1cm} \textit{PRL 100}, 147203 (2008)

\hspace{1cm} Na\textsubscript{2}IrO\textsubscript{3} (molecular orbitals on hexagons) \hspace{1cm} \textit{PRL 109}, 197201 (2012)

2d triangular\rightarrow 0d: Li\textsubscript{VO}\textsubscript{2} (singlets on triangles) \hspace{1cm} \textit{PRL 78}, 1323 (1997)

3d spinel \rightarrow 1d: MgTi\textsubscript{2}O\textsubscript{4} (Peierls transition) \hspace{1cm} \textit{PRL 94}, 156402 (2005)

\hspace{1cm} CuIr\textsubscript{2}O\textsubscript{4}

3d spinel \rightarrow 1d: MgV\textsubscript{2}O\textsubscript{4} (triplet dimers) \hspace{1cm} \textit{PRL 101}, 256403 (2008)

3d pyrochlore\rightarrow 1d: Tl\textsubscript{2}Ru\textsubscript{2}O\textsubscript{7} (Haldane chain) \hspace{1cm} \textit{Nature Materials 5}, 471 (2006)


Jade: \( \text{NaAlSi}_2\text{O}_6 \)

Spodumene: \( \text{LiAlSi}_2\text{O}_6 \)

Aegirine: \( \text{NaFeSi}_2\text{O}_6 \)

Diopside: \( \text{CaMgSi}_2\text{O}_6 \)

Kosmochlore: \( \text{NaCrSi}_2\text{O}_6 \)

Jade: \( \text{NaAlSi}_2\text{O}_6 \)
Isolated chains of $\text{Me}^{3+}\text{O}_6$ octahedra, sharing common edge, divided by $(\text{Si,Ge})\text{O}_4$ tetrahedra

Crystal structure of pyroxenes
Spin gap in Na$\text{TiSi}_2\text{O}_6$

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!

Exchange in a dimer

\[ J_{\text{intra}} = 396 \text{ K} \] (AFM)

Between dimers

\[ J_{\text{inter}} = -5 \text{ K} \] (FM)

\[ U_{dd} = 3.3 \text{ eV}, \ J_H = 0.8 \text{ eV} \]

Energy gap: 1.8 eV

\( \text{NaTiSi}_2\text{O}_6 \) – chain consisting of dimers!

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

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

3d → 1d
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 Culr$_2$S$_4$

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Figure 2 The low-temperature crystal structure of Culr$_2$S$_4$. a, Schematic representation of create a 3D impression of the stacking and to pro
FIG. 2: (a) Charge and orbital ordering in CuIr$_2$S$_4$. Octamer is shown by thick lines, short singlet bonds — by double lines. (b) Schematic electronic structure of CuIr$_2$S$_4$. 

D.Kh. & T.Mizokawa, PRL 94, 156402 (2005)
Fig. 3. Schematic crystal structure (a) and orbital ordering (b) in LiVO₂, by Ref.

Same in TiI₂ (G.Meyer); in LiVS₂ (H.Takagi)

And the bonds in shaded (singlet) triangles become much **shorter**! Average V-V distance is 2.84Å is shorter than \( R_{\text{c, Goodenough}} \sim 2.94\text{Å}; \) after trimerization \( V-V_{\text{short}}=2.56\text{Å}; V-V_{\text{long}}=3.02\text{Å} \) (V-V_{\text{metal}}=2.62Å!)

Phase diagram of LiVO$_2$, LiVS$_2$ and LiVSe$_2$, which consists of a frustrated $3d^2$ lattice.

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: $\text{CaV}_4\text{O}_9$

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


Similar structure in Fe-deficient K2Fe4Se5!
“Molecular “ superstructures in the solid

(a)

(b)

AlV2O4

Horibe et al., PRL 96, 086406 (2006)
$t_g_2$ orbitals on a honeycomb lattice: direct dd-hopping - reduction to 0-dimensional case!
New-Type Phase Transition of Li$_2$RuO$_3$ with Honeycomb Structure

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A new-type structural transition has been found in Li$_2$RuO$_3$ 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$_2$RuO$_3$, honeycomb structure, structural transition
DOI: 10.1143/JPSJ.76.033705

Compounds with the honeycomb lattice often present interesting behavior originating from their characteristic structures. For example, in the course of the studies on the physical properties of localized spin systems of A$_3$T$_2$SbO$_6$ ($A =$ Na, Li; $T =$ Cu, Ni, Co) and Na$_2$T$_2$TeO$_6$ on the (distorted) honeycomb lattice, spin gap behaviors have been found for $T =$ Cu,$^{1-3}$ while magnetic transitions to the spin-ordered state have been observed for $T =$ Co and Ni.$^4$
Experimental observations: Li$_2$RuO$_3$

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)
Na$_2$IrO$_3$

I. Mazin et al., PRL 109, 197201 (2012)
**Orbital-selective Peierls transition**

**(MO against Hund !)**

State of a dimer with 4 electrons, with $J(\text{Hund}) > t$

\[ E = -2t - \frac{t^2}{J_H} \]

MO state of a dimer with 4 electrons, with $t > J(\text{Hund})$

\[ E = -2t \]

For large hopping one orbital form singlet bonding molecular orbital, at the expense 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, $t_c = 12t'$, $t_d = 2t'$, $J_H = t'$, $U = 10t'$. 
**VO$_2$:** one d-electron, singlet dimers below metal-insulator transition

**MoO$_2$:** 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

**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.
**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:

\[ \text{Ba}_3\text{MRu}_2\text{O}_9 \]

- \( M = \text{Na}, \ldots; \) Ru\( ^{5.5+} \) \( (d^3/d^2) \)
- \( M = \text{Ca}; \text{Co}; \ldots; \) Ru\( ^{5+} \) (d3)
- \( M = \text{Y}, \text{La}, \ldots; \) Ru\( ^{4.5+} \) \( (d^4.d^3) \)

*Figure 2.* Approximate [110] view of the structure of \( \text{Ba}_3\text{MRu}_2\text{O}_9 \) \( (M = \text{Li}, \text{Na}) \) consisting of blue \( \text{RuO}_6 \) face-sharing bi-octahedra cornered shared to red \( \text{MO}_6 \) \( (M = \text{Li}, \text{Na}) \) octahedra singles. Barium cations are shown as yellow spheres.
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 ($\lambda$ small) SOC is often treated in a mean field approximation

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

**Jahn-Teller dominated regime**

$|x^2 - y^2\rangle$, orbital moment quenched

$t_{2g}, \quad |l_{eff} = 1\rangle$

$|xy\rangle$ = $|l_z = 0\rangle$

$|xz, yz\rangle = |l_z = +/ - 1\rangle$

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

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

**Spin-orbit dominated regime**

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

$E_{JT} \text{ vs } \lambda$
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\(^7\))**: Co\(^{2+}\) - 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

**Co\(^{2+}\) - (almost) always tetragonal**

**Fe\(^{2+}\)(d\(^6\))** (one electron on top of half-filled shell: trigonal distortion (FeO; KFeF3). Why?

**Ca\(^{2+}\)RuO\(^4\)** below metal-insulator transition: octahedra distorted, \( c/a < 1 \). **Usual JT ordering**?
SOC $\sim Z$?

Usual answer $SOC \sim Z^4$
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.
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

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

so that

$$\alpha \sim \hbar^2 U/m^2c^2r^2 \sim Z^4(e^2/\hbar c)^2me^4/h^2.$$

The mean value of $\alpha$ 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

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

i.e. differs from the fundamental energy of the outer electrons in the atom ($\sim me^4/h^2$) 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

\[ |\Psi_i\rangle_{ad} = |\psi_i\rangle|\phi\rangle \quad \Rightarrow \quad |\Psi_1\rangle = |\psi_1\rangle|\phi_1\rangle \]
\[ |\Psi_2\rangle = |\psi_2\rangle|\phi_2\rangle \]

\[ A_{12} = \text{ad}\langle \Psi_1|\hat{A}|\Psi_2\rangle_{ad} = \langle \psi_1|\hat{A}|\psi_2\rangle \]
\[ = \langle \Psi_1|\hat{A}|\Psi_2\rangle = \langle \psi_1|\hat{A}|\psi_2\rangle\langle \phi_1|\phi_2\rangle \]

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

System freely rotates around the trough.
Rotational quantization


\[ |\theta\rangle = \cos \frac{\theta}{2} |z^2\rangle + \sin \frac{\theta}{2} |x^2 - y^2\rangle \]
\[ |\tilde{\theta}\rangle = \cos \tilde{\theta} |Q_3\rangle + \sin \tilde{\theta} |Q_2\rangle \]

**Conical intersection**
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?**


**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!