Lecture Notes

Introduction to Strongly Correlated Electron Systems

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Introduction to strongly correlated electron systems

I. Introduction

Brief summary of electrons in solids, origin of strong electron correlations

II. Classes of strongly correlated electron systems

(a) Transition metal compounds: 3d-electrons

- Hubbard model, Mott insulator, metal-insulator transition
- Spin, charge, and orbital degrees of freedom and ordering phenomena, selected materials

(b) Heavy fermion systems: 4f (5f) – electrons

- The Kondo effect, heavy fermion systems, non-Fermi liquid behavior,
- Quantum phase transitions, unconventional superconductivity, selected materials

(c) Nanoscale structures:

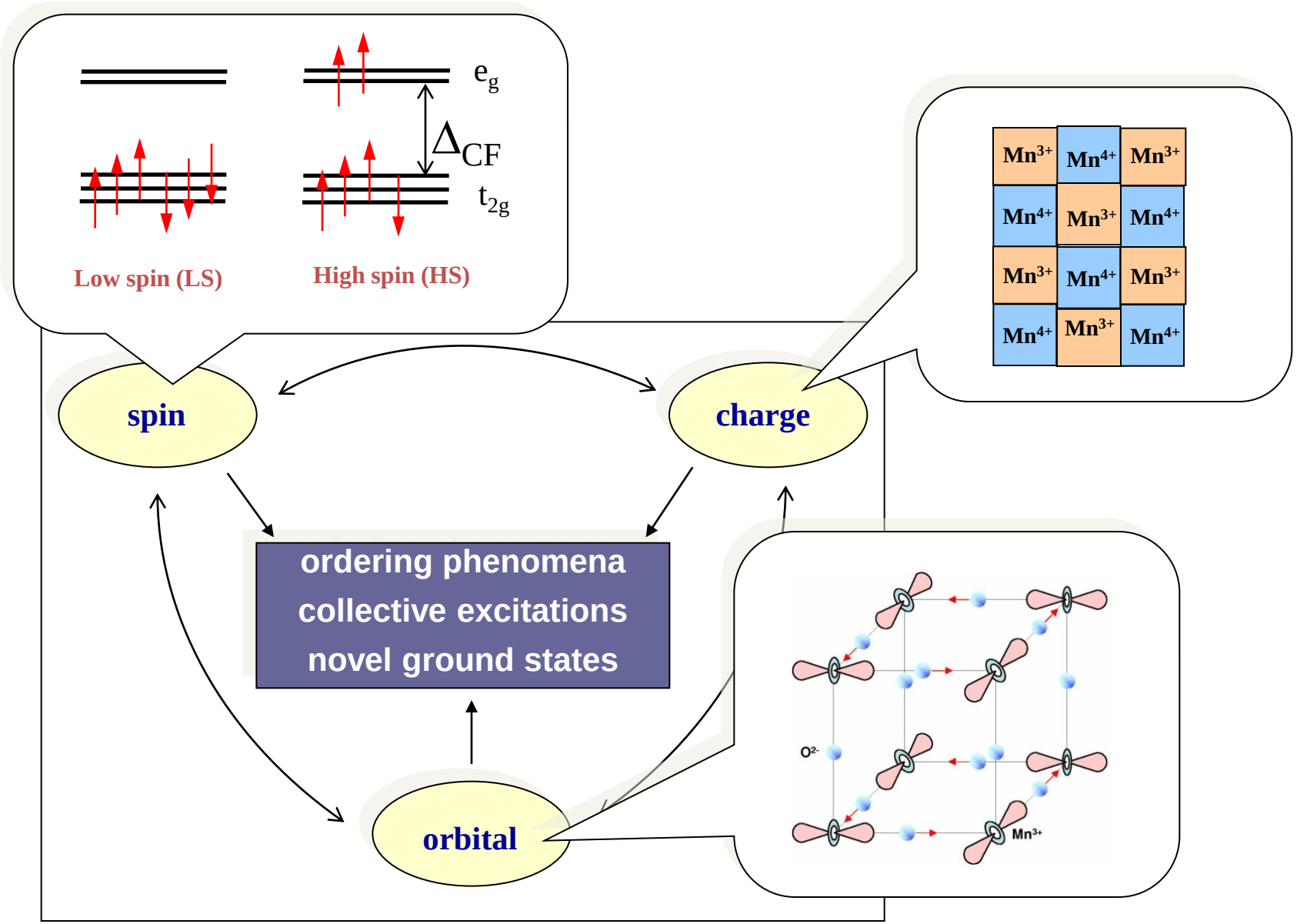
- Quantum confinement, unusual properties for potential applications

III. Pressure effect on the ground state properties:

- Recent experimental results on heavy fermions and transition metal compounds

IV. Summary and open discussion

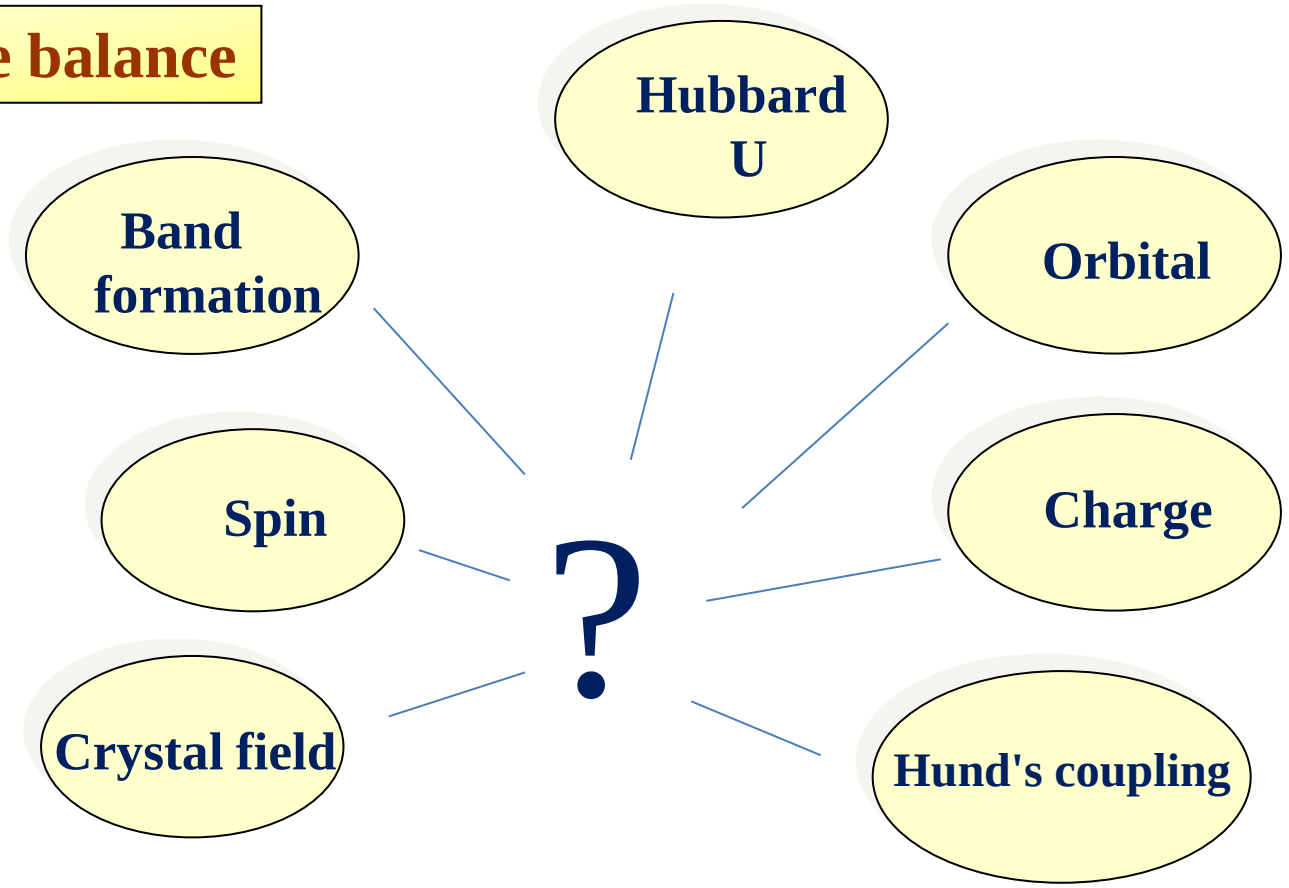
Spin, Charge, and Orbital degrees of freedom



Metal insulator transition is driven by an interplay between these degrees of freedom!

Transition metal systems and electron correlations

Delicate balance



systems can be quite close to the borderline U~ W (t)

Thus many interesting transitions to unusual ground states can occur by changing T, P, filling, structure, etc.

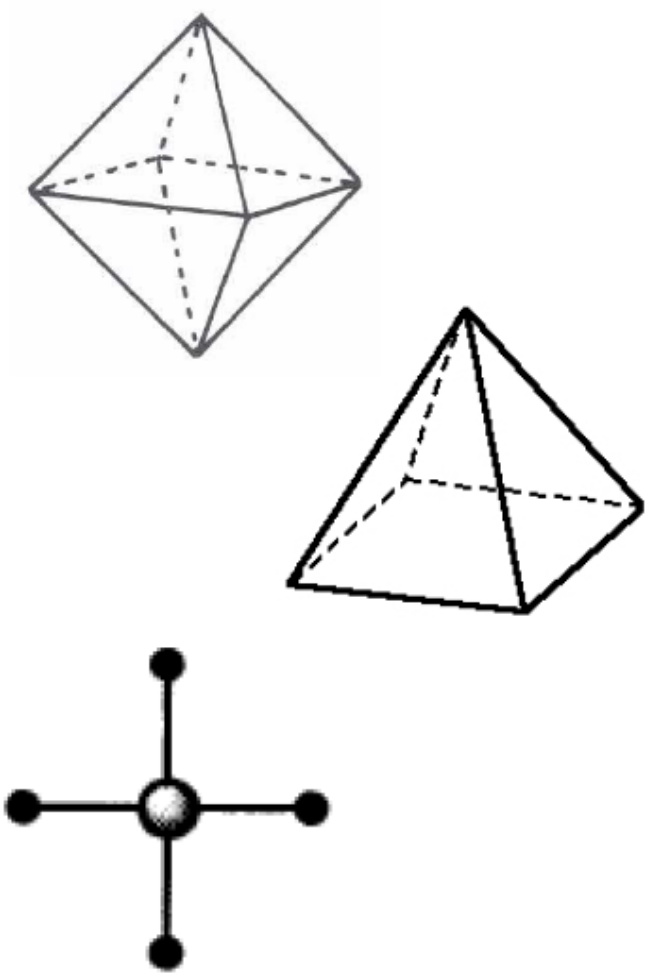
more discussion with examples later!

Review of some background concepts relevant to transition metal oxide systems

Transition metal oxides building blocks

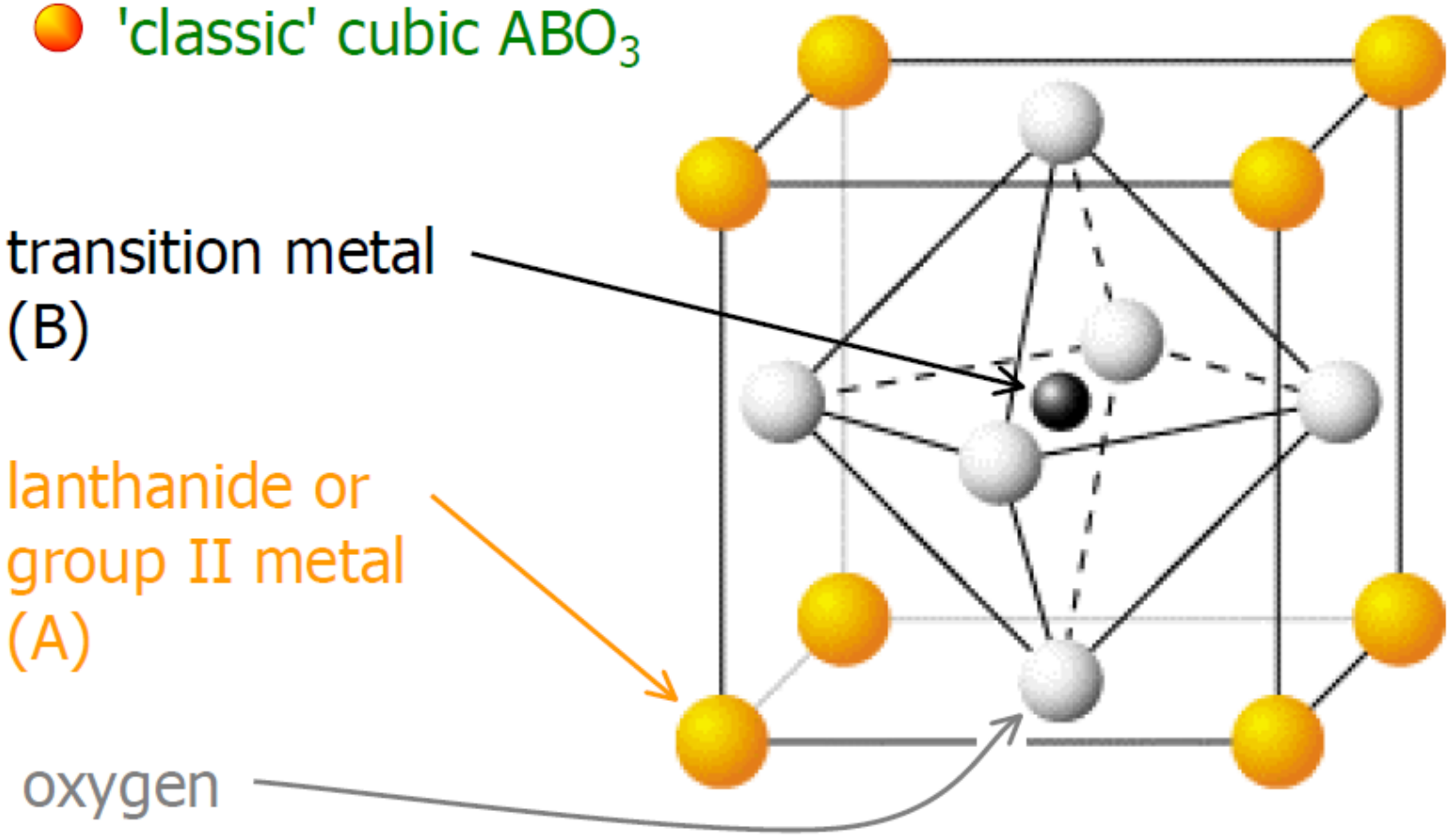
Just like all crystalline solids, TM-oxides are built up of regular repeat units such as:

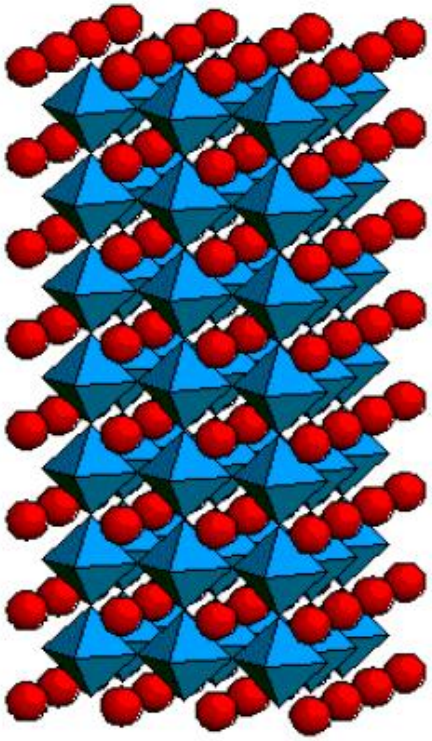
- TM-O_6 octahedron
- TM-O_5 square pyramid
- TM-O_4 plaquette



Very large class of transition metal (and other) oxides

- 'classic' cubic ABO_3

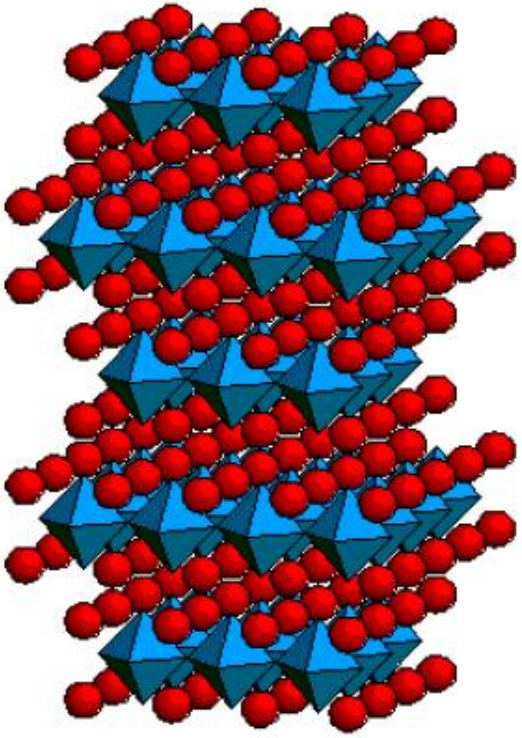




$n = \infty$

ABO_3

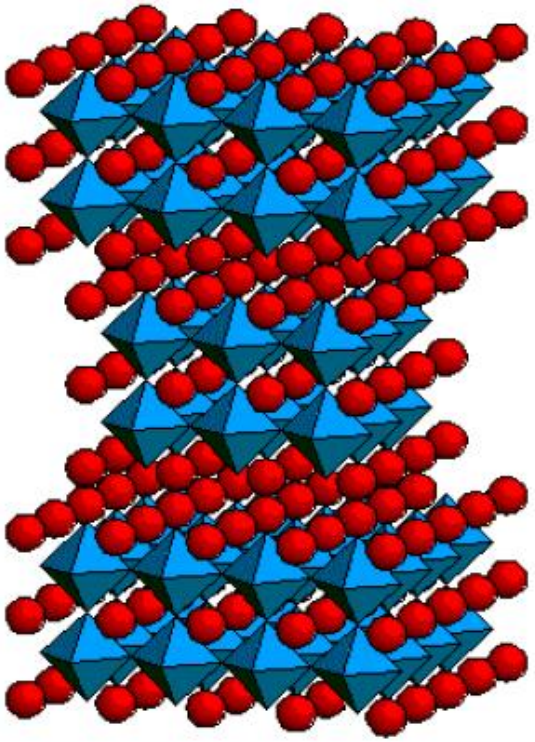
perovskite



$n = 1$

A_2BO_4

K_2NiF_4



$n = 2$

$A_3B_2O_7$

bilayer

pic: Matt Rosseinsky

Orbitals

Orbitals in atoms, molecules and solids

- Pauli exclusion principle

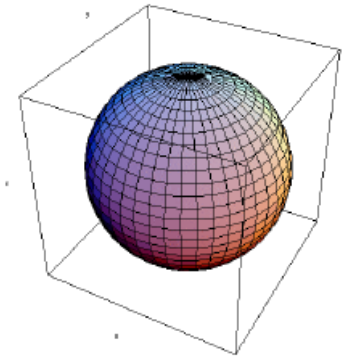
  max. two electrons per orbital, spins opposed

- Degeneracy and relative energy

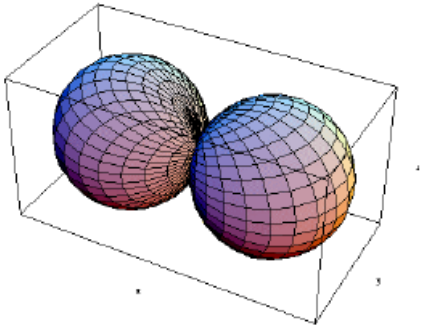
  1 x 1s, 1 x 2s, 3 x 2p, 1 x 3s, 3 x 3p, 1 x 4s, 5 x 3d

Is and 2 orbitals

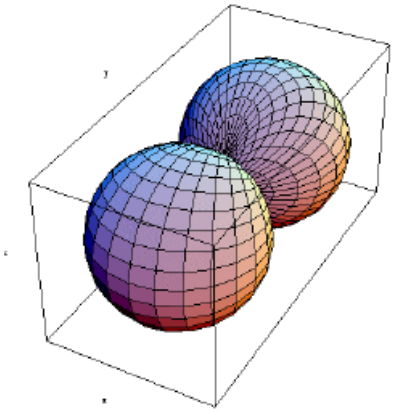
1s



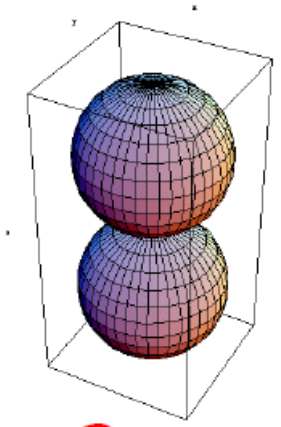
images: http://buffer.bu.edu/acrosby/orbitals



$2p_x$

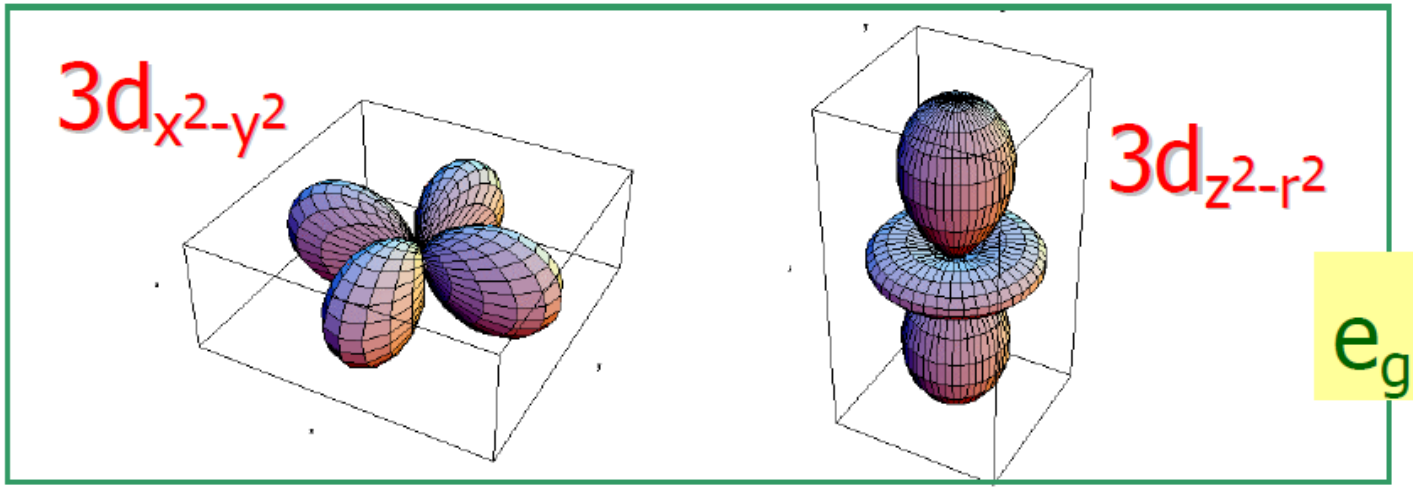


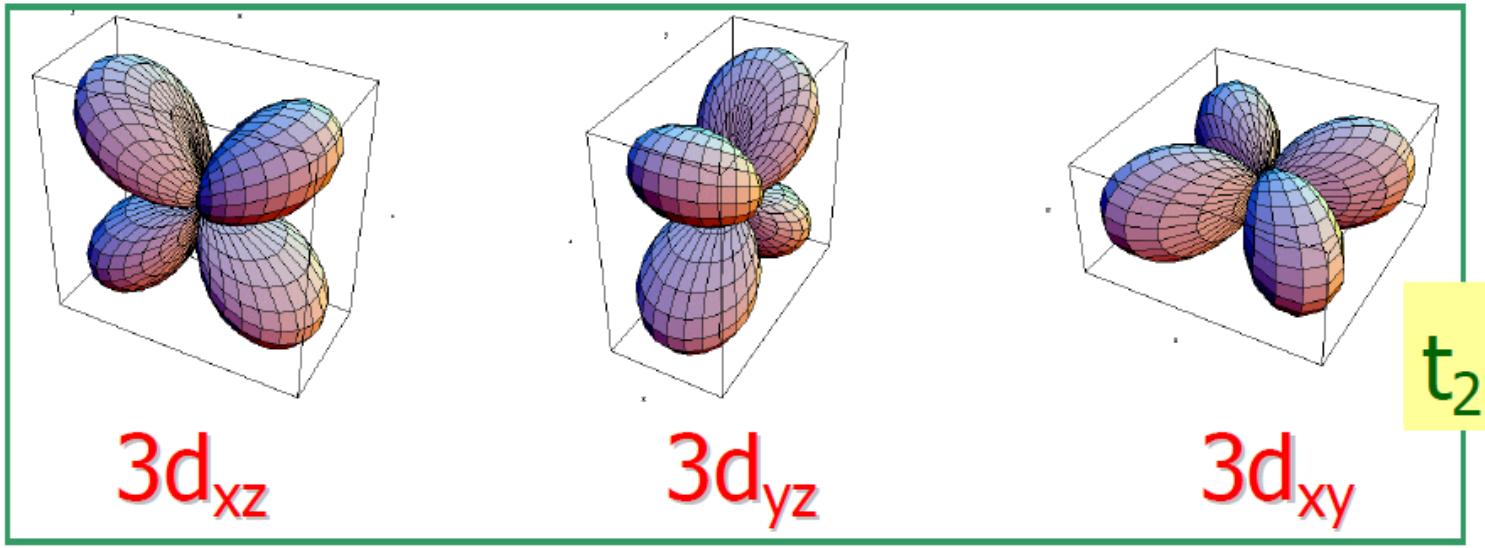
$2p_y$



$2p_z$

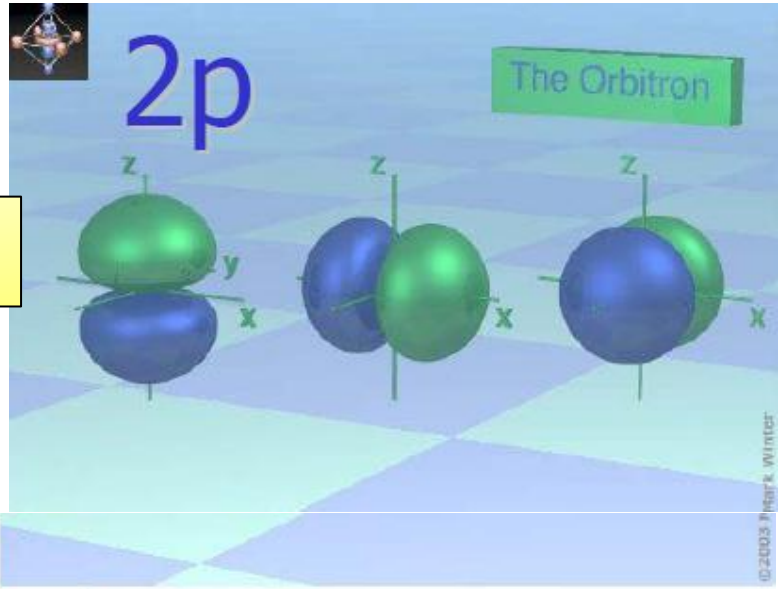
3d orbitals

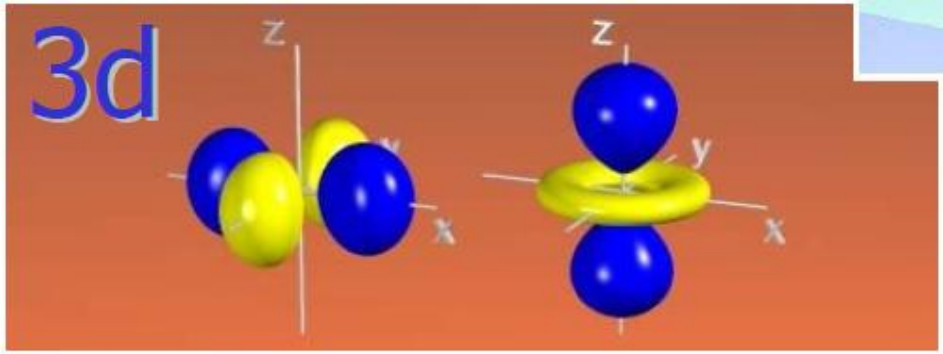




Note:

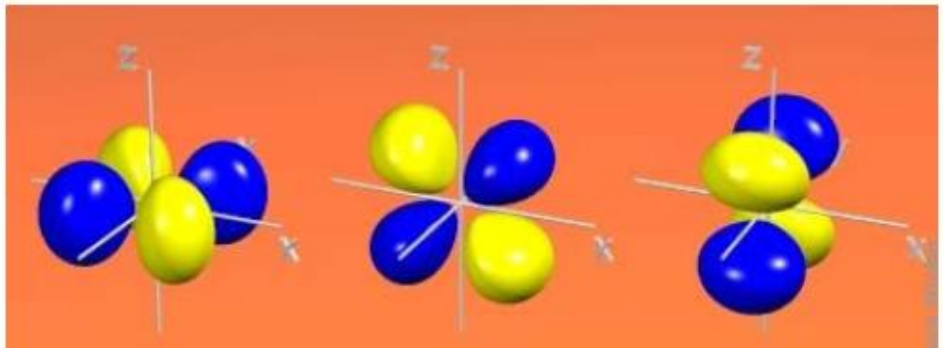
Sign change in wave functions!





e_g

σ-bonding to ligands



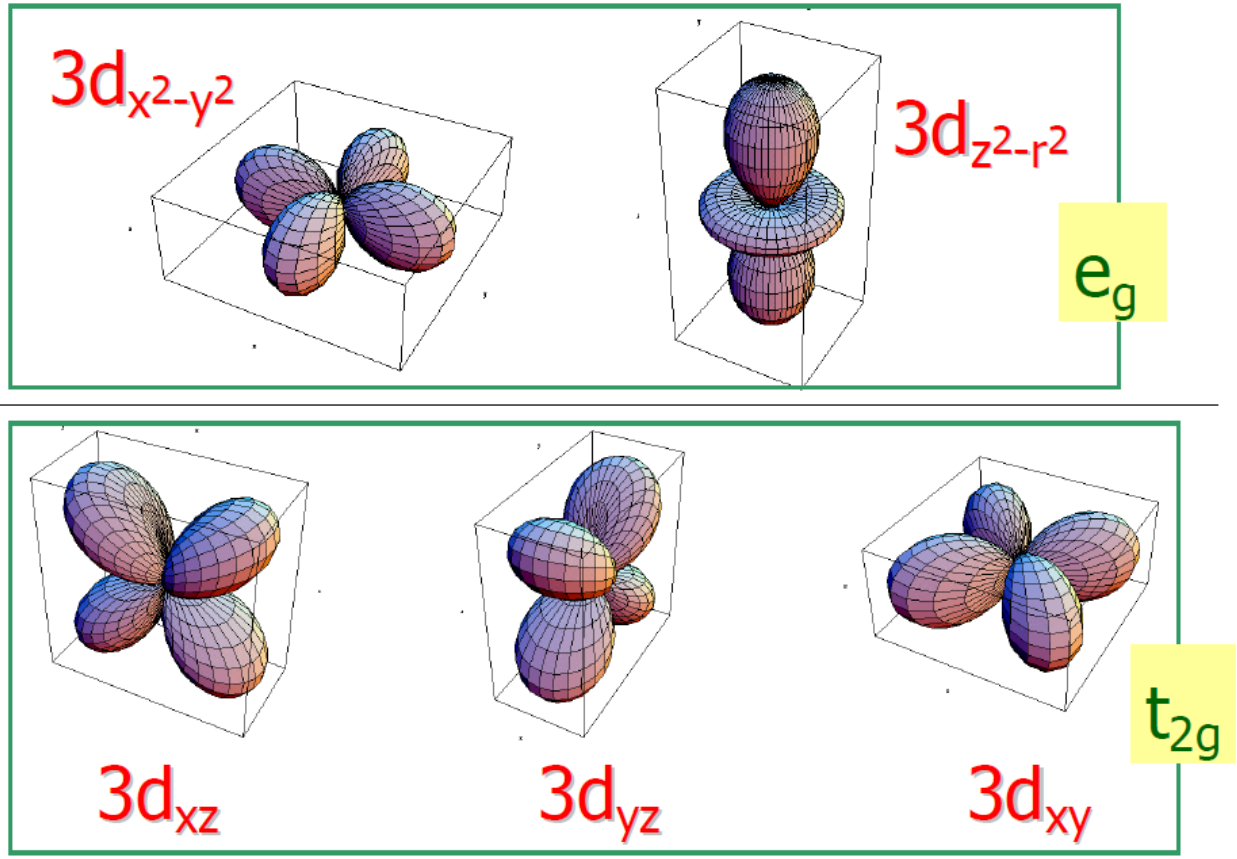
t_{2g}

π-bonding to ligands

3d orbitals in central potential of a free atom/ ion

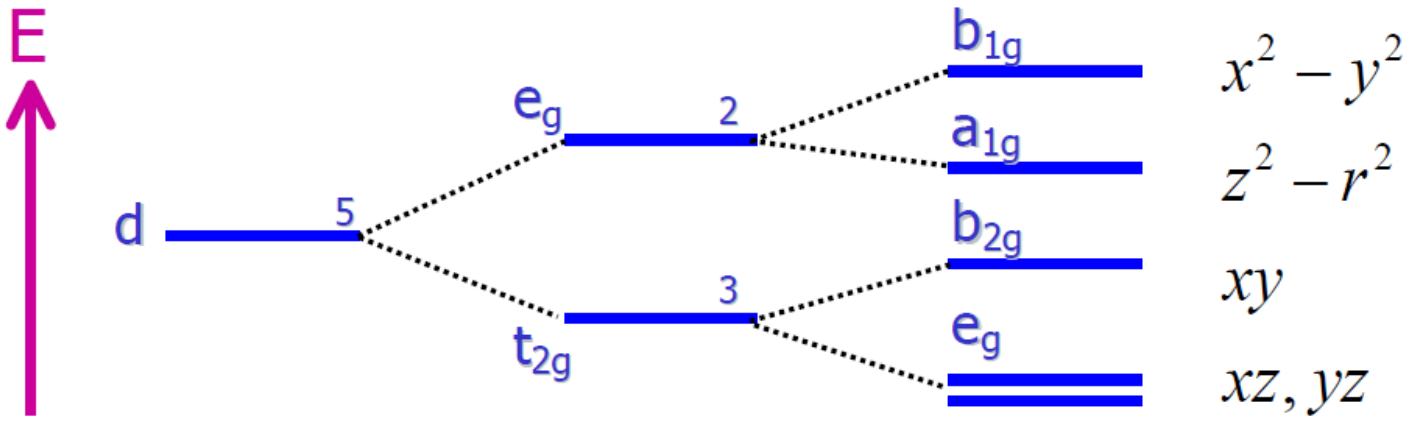
5-fold degenerate 3d orbitals

3d: n=3, ℓ=2, m_ℓ= -2,-1,0,1,2 ⟶ 5 orbitals

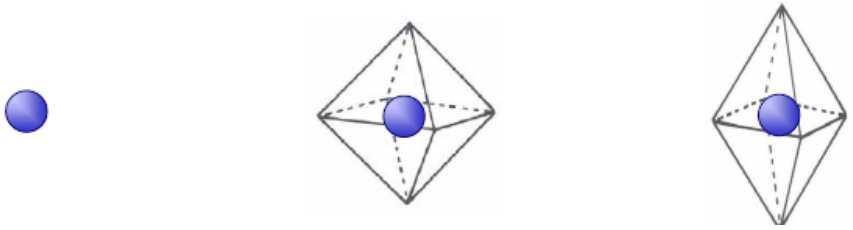


Crystal electric field energy

Coulomb potentials in oxides lead to lifting of the orbital degeneracy of the 3d levels:

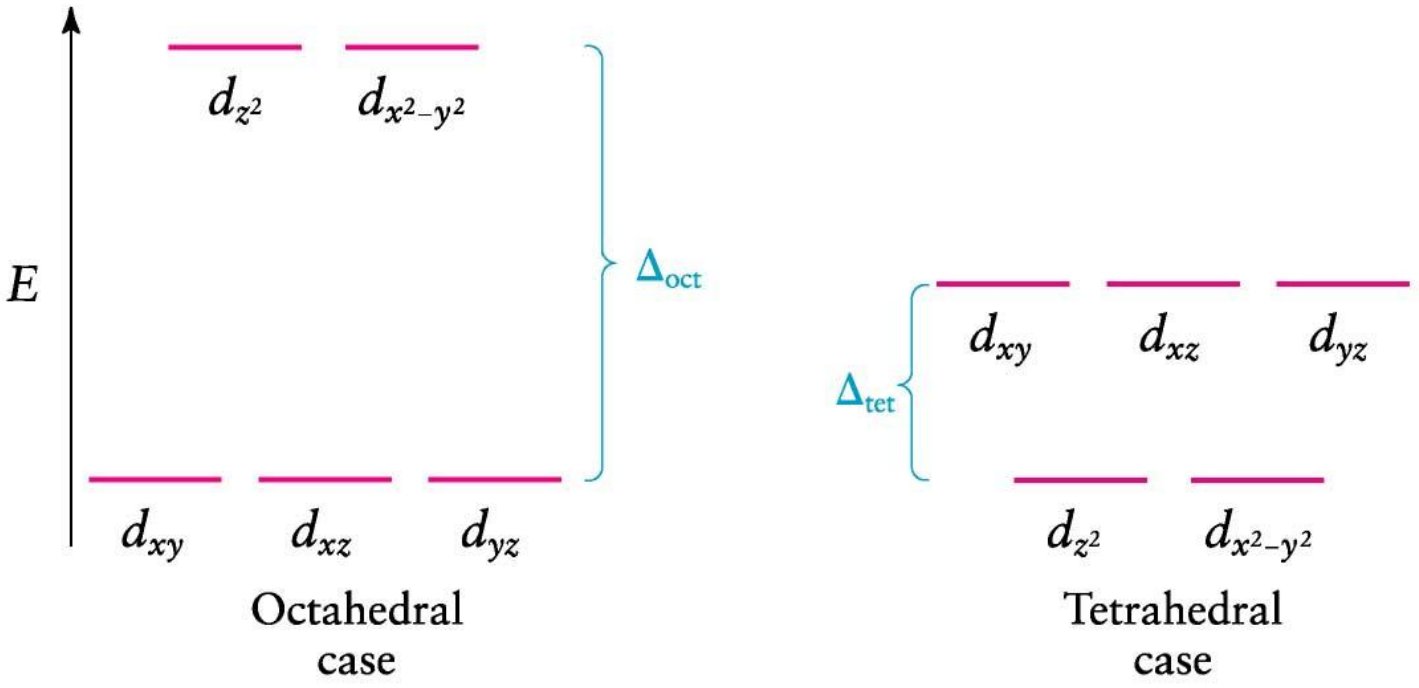


free ion | cubic | tetragonal

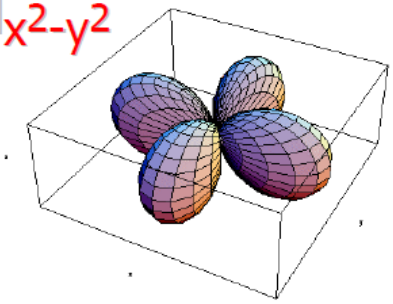


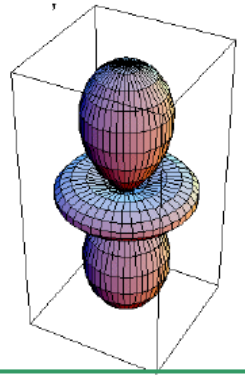
crystal field splitting

Lower symmetry ⟶


E
d_{z^2}
$d_{x^2-y^2}$
Δ_{oct}
d_{xy}
d_{xz}
d_{yz}
Octahedral case
Δ_{tet}
d_{xy}
d_{xz}
d_{yz}
d_{z^2}
$d_{x^2-y^2}$
Tetrahedral case

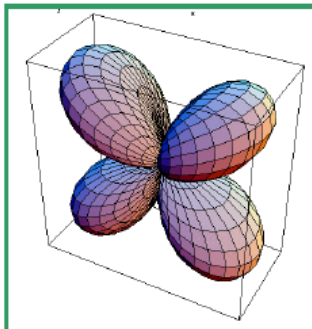
$3d_{x^2-y^2}$

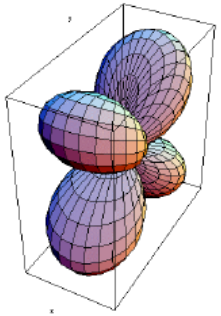


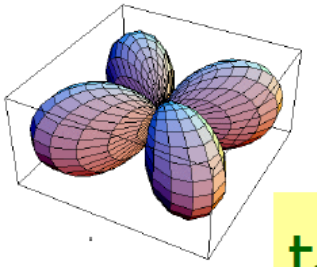


$3d_{z^2-r^2}$

e_g





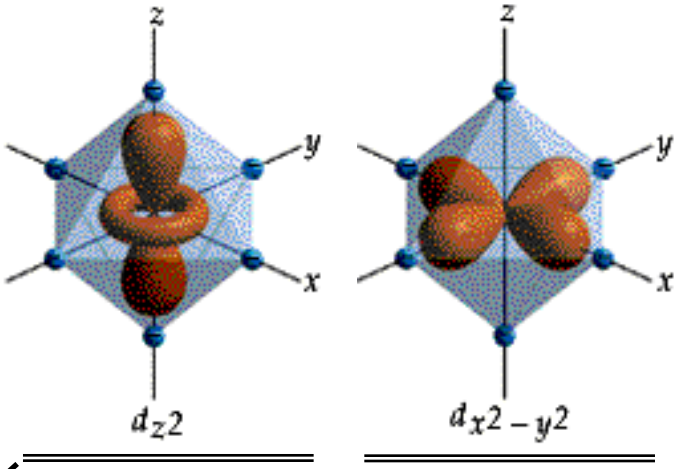


t_{2g}

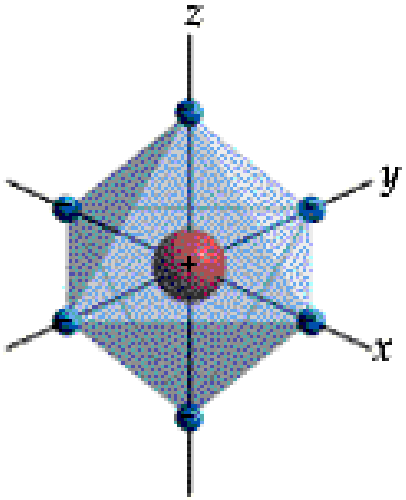
$3d_{xz}$ $3d_{yz}$ $3d_{xy}$

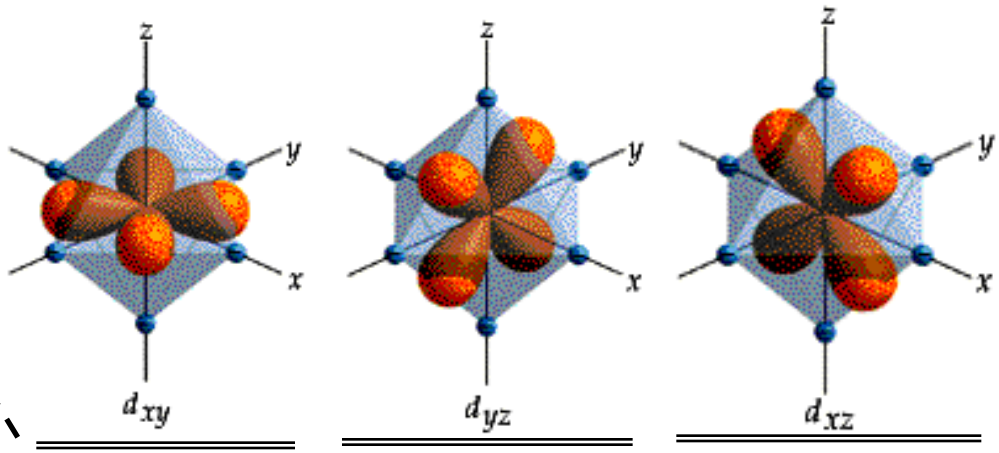
3d-orbitals occupation and ligand interaction

(Octahedral Field)



d-orbitals pointing directly at axis are affected most by electrostatic interaction





d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

Hund's coupling energy

Hund*'s *rules?

Short reminder!

Hund's rules

Atoms with not completely filled subshells can exist in several *atomic states*. **Hund's rules define the *lowest energy atomic state* for each given *electronic configuration*.**

The specification of a quantum state of an atom :

Quantum numbers (QN) n, ℓ, m_ℓ, m_s

The implication of **Pauli exclusion principle** is that there should be no two electrons have exactly the same set of quantum numbers at the same time

Hund's rules (Empirical)

Hund's 1st rule: S ! Max has lowest energy

Hund's 2nd rule: if S maximum, L ! Max has lowest energy

Arguments:

(1) Same spin & Pauli principle → electrons further apart → lower Coulomb repulsion

(2) Large L → electrons "move in same direction" → lower Coulomb repulsion

Calculation of the total angular Momentum

$$L = \sum_{occupied} m_\ell$$ Orbital angular momentum (of the whole atom):

$$S = \sum_{occupied} m_s$$ Spin angular momentum

The magnetic property of an atom is due to the angular momentum of the whole atom J

$$\vec{J} = \vec{L} + \vec{S}$$

$J = |L - S|$ If less than one-half of the ℓ subshell is filled.

$J = L + S$ If more than one-half of the ℓ subshell is filled.

Spectroscopic notation

Electronic configuration

$^{2S+1}L_J$

L=	0	1	2	3	4	5
	S	**P**	**D**	**F**	**G**	**H**

Magnetic moment of an ion

The magnitude of dipole moment of an ion/atom is given by:

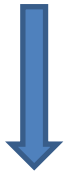
$$\mu_m = g_J \sqrt{J(J+1)}\,\mu_B = p_{eff}\,\mu_B$$

It is more convenient to express in terms of effective magnetron number $p_{eff} \quad = g_J \sqrt{J(J+1)}$

Where g_J is called **Lande g-factor**

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

competition between Hund's coupling energy and strength of the crystal electric field

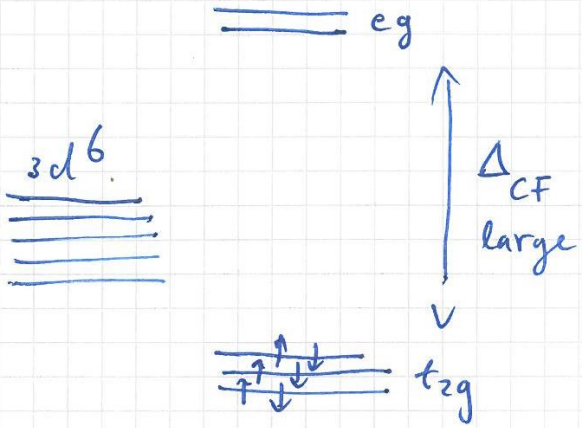


Spin State transitions  **Spin degree of freedom**

See Board, example: $La\mathbf{Co}^{3+}O_3$

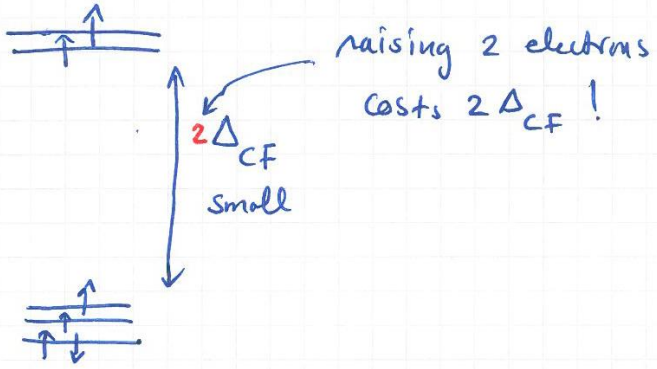
Crystal field energy versus Hund's coupling energy (J_H)

e.g.: Co^{3+} & Fe^{2+} ($3d^6$ electrons)



Low Spin (LS) $\Rightarrow S = 0$

$E_{LS} = -6J_H$



High Spin (HS) $\Rightarrow S = 2$

$E_{HS} = 2\Delta_{CF} - 10J_H$

Energy balance: $E_{LS} - E_{HS} = -6J_H - (2\Delta_{CF} - 10J_H) = 0$

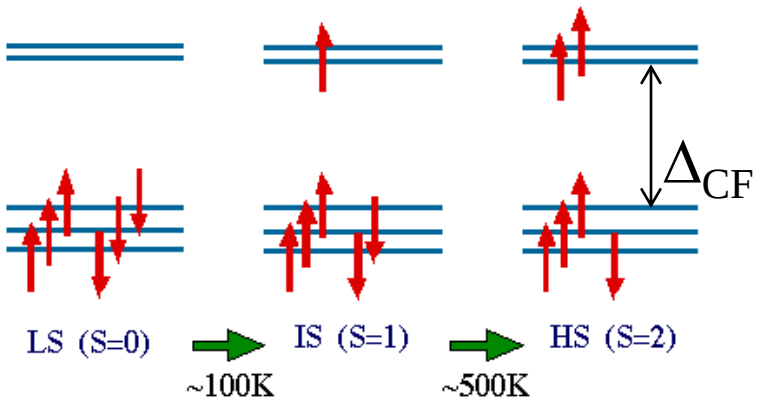
$\Rightarrow 2\Delta_{CF} = 4J_H$ or $\boxed{\Delta_{CF} = 2J_H}$

balance determines HS or LS state!

$La_{1-x}Sr_xCoO_3$ rhombohedral distorted perovskite structure

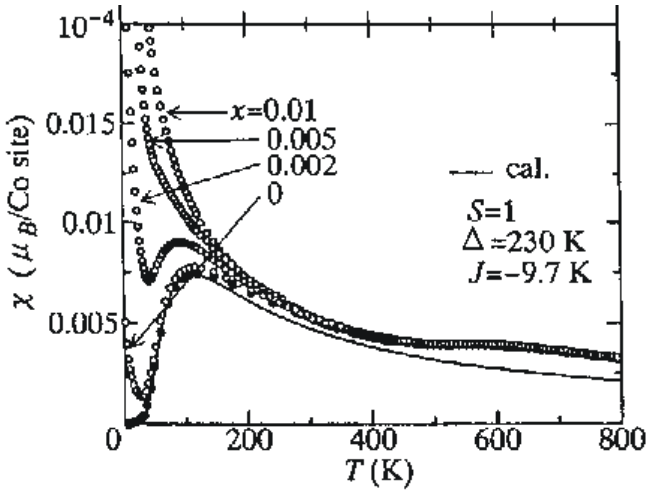
$LaCoO_3$: (undoped)

- Co^{3+}, $3d^6$, Low-Spin (LS) state ($S = 0$)
- ground state: nonmagnetic, insulator
- temperature-induced spin transition (T ~ 100K)
- temperature-induced insulator-metal transition (T ~ 500K)



$La_{1-x}Sr_xCoO_3$: (doped)

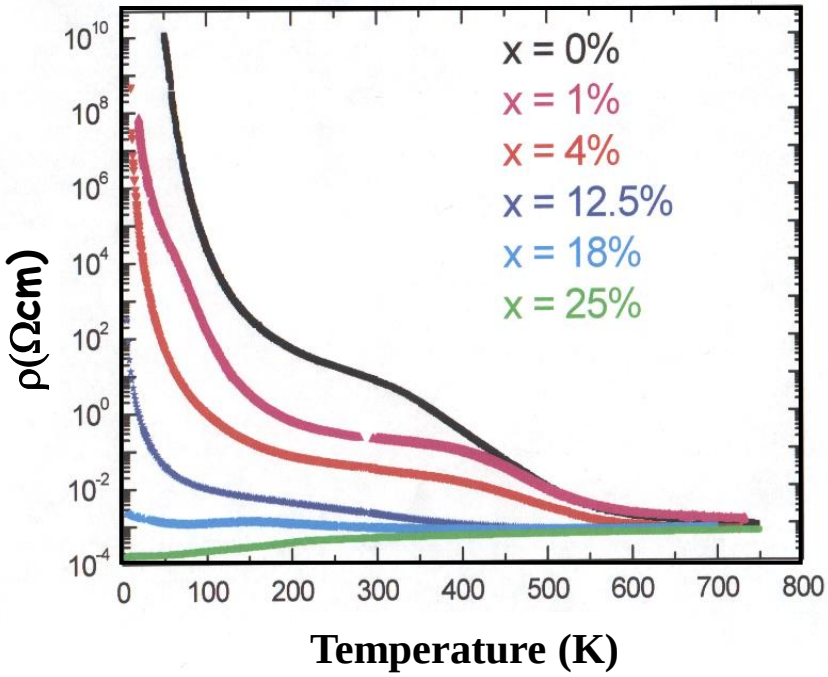
- $Co^{3+} \rightarrow Co^{4+}$ ($3d^5$) increasing valence due to Sr^{2+} (hole-) doping
- ground state: LS-state is suppressed: nonmagnetic $\rightarrow$ spin glass $\rightarrow$ $x \geq 0.18$ ferromagnetic
- $x \geq 0.18$ insulator-metal transition
- rhombohedral distortion decreases with x and $\rightarrow$ cubic for x ~ 0.50



Electrical and magnetical properties of $La_{1-x}Sr_xCoO_3$

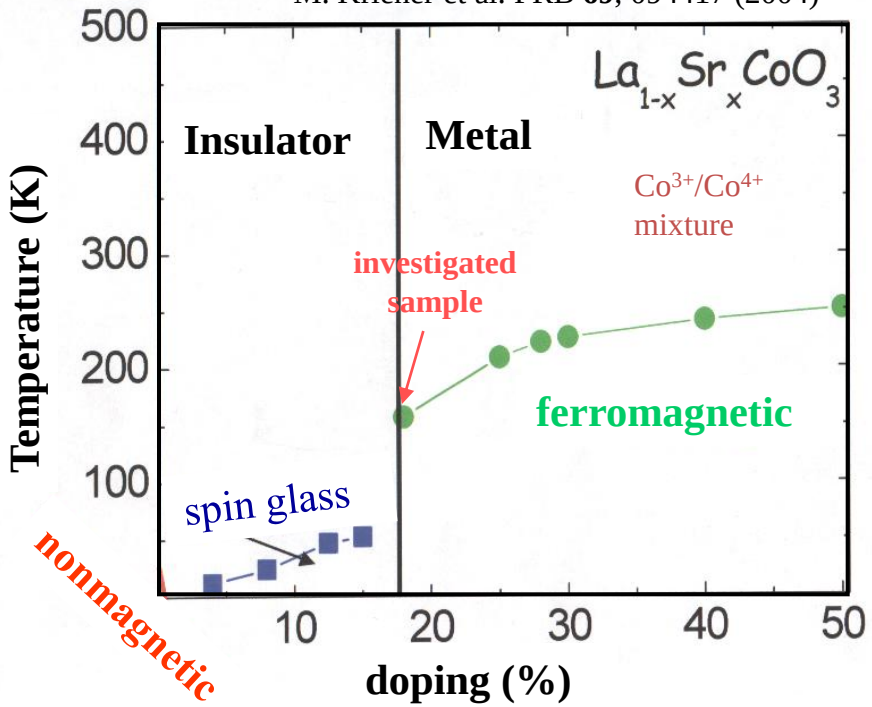
electrical resistivity

Ch. Zobel et al. PRB **66,** 020402 (2002)



magnetic phase diagram

M. Kriener et al. PRB **69**, 094417 (2004)



⇒ insulator-metal transition

at x ≥ 0.18

⇒ onset of ferromagnetic

ordering at x ≥ 0.18

Open questions

- **whether and to what extent the spin degree of freedom (spin transitions) affects the insulator-metal transition?**

→ **better understanding of the connection between the metal-insulator transition and onset of ferromagnetic ordering.**

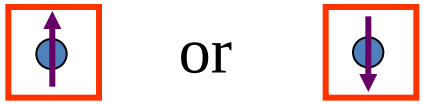
More in the comming lectures!

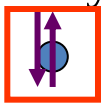
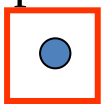
Spin degree of freedom

Mott-Insulator with half filling (only one Band/ Orbital):

In the ground state each site is occupied with **one electron /spin**

⟹ **spin degree of freedom**, i.e. **two possible spin orientations**:



In conventional Band insulator bands are completely full or completely empty i.e. each orbital is either double occupied  or empty 

total spin = 0, ***no degeneracy*** ⟹ **no spin degree of freedom!**

Spin degree of freedom

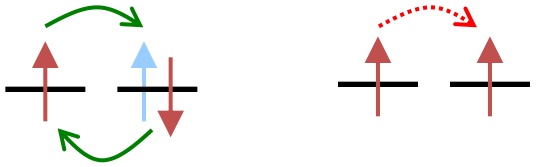
Magnetic ordering in Mott insulators

Mott insulator: spin degeneracy is lifted by exchange interaction through electron hopping between neighbor sites.

Compromise between Coulomb- & kinetic energy

large U prevents double occupation, but restricts electrons on one site, leading to a large increase of kinetic energy ($\Delta x \Delta p \geq \hbar$)

Kinetic Energy is optimized by virtual hopping to next neighbors



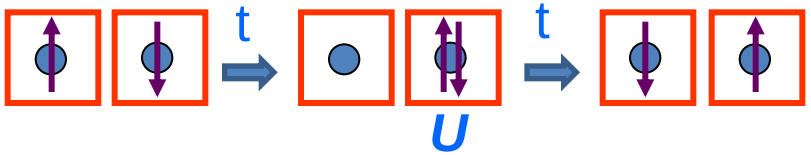
Pauli principle: allowed forbidden

$$H_0 = U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$$H' = \sum_{\langle i,j \rangle, \sigma} t \; c^+_{i\sigma} c_{j\sigma}$$

Hopping as small perturbation, using 2nd order perturbation theory

➡ **energy gain associated with virtual hopping:**

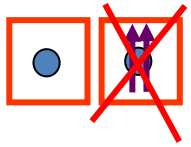


$$E_0^{(2)} = \sum_n \frac{\langle 0|H'|n\rangle\langle n|H'|0\rangle}{E_0 - E_n} \sim -\frac{t^2}{U}$$

Exchange interaction, Heisenberg-Hamiltonian

Example: one band model with direct overlap between orbitals

Pauli-Principle: exchange forbidden for parallel spins

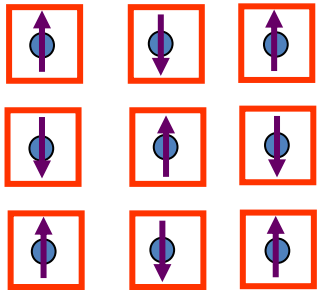


➡ for neighboring spins:

singlet state is favorable against triplet state by:

$$E_0^{(2)} = J = \frac{4t^2}{U}$$

antiferromagnetic ground state



J is the exchange coupling constat

Low energy physics (J << U) in Mott-Insulator is determined by the spins.

Effective low energy –Hamiltonian describes exchange interaction:

Heisenberg-Model

$$H = J \sum_{<i,j>} \vec{S}_i \vec{S}_j = J \sum_{<i,j>} S_i^x S_j^x + S_i^y S_j^y + S_i^z S_j^z$$

$$= J \sum_{<i,j>} \tfrac{1}{2}\left(S_i^+ S_j^- + S_i^- S_j^+ \right) + S_i^z S_j^z$$

S^+, S^- spin operators

$$(S_i^+ = c_{i\uparrow}^+ c_{i\downarrow}; \quad S_i^- = c_{i\downarrow}^+ c_{i\uparrow})$$

$$E_{Singulett} = -\tfrac{3}{4} J$$

$$E_{Triplett} = +\tfrac{1}{4} J$$

for detailed calculations an comments , see board

Exchange interaction, Heisenberg Hamiltonian

Comparison between Triplet ($\uparrow\uparrow$) and singlet ($\uparrow\downarrow$) states.

$\hat{\phi}\,\hat{\phi}$ Pauli forbidden! $\Rightarrow E_{\uparrow\uparrow} = 0$

$\hat{\phi}\,\phi_{\downarrow}$

(i) $\hat{\phi}\,\phi_{\downarrow} \rightarrow \bullet\,\phi_{\downarrow}\,\phi_{\downarrow} \rightarrow \hat{\phi}\,\phi_{\downarrow}\,\phi_{\downarrow} \Rightarrow \frac{-t^2}{U}$

(ii) $\hat{\phi}\,\phi_{\downarrow} \rightarrow \phi_{\downarrow}\,\phi_{\downarrow}\,\bullet \rightarrow \hat{\phi}\,\phi_{\downarrow}\,\phi_{\downarrow} \Rightarrow \frac{-t^2}{U}$

$\Rightarrow$ Energy gain $= -\frac{2t^2}{U}$

$$\boxed{E_{\uparrow\uparrow} - E_{\uparrow\downarrow} = \frac{2t^2}{U}}$$

Description of the A.F state by the effective Hamiltonian – Heisberg Model

Heisenberg model (mean field) : $\mathcal{H} = J \sum_{\langle i,j \rangle} \vec{S}_i \vec{S}_j$

$\nearrow E_{\uparrow\uparrow} = J \cdot \frac{1}{4}$

$\searrow E_{\uparrow\downarrow} = -J \cdot \frac{1}{4}$

$$\Rightarrow \quad E_{\uparrow\uparrow} - E_{\uparrow\downarrow} = J\left(+\tfrac{1}{4}\right) - J\left(-\tfrac{1}{4}\right) = \tfrac{1}{2}J = \frac{2t^2}{U}$$

$$\Rightarrow \boxed{J = \frac{4t^2}{U}}$$

<u>sign of J</u> :

$$\mathcal{H} = J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j \ .$$

for $\uparrow\uparrow$ (FM) ; $\vec{S}_i \cdot \vec{S}_j > 0 \Rightarrow J < 0 \Rightarrow$ stable state

for $\uparrow\downarrow$ (AF) ; $\vec{S}_i \cdot \vec{S}_j < 0 \Rightarrow J > 0 \Rightarrow$ stable state

Calculation of $\sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j$

$$\left(\vec{S}_i \cdot \vec{S}_j\right) = S_i^x S_j^x + S_i^y S_j^y + S_i^z S_j^z$$

$$\text{singlet} \quad = -\frac{1}{4} \quad + -\frac{1}{4} \quad - \frac{1}{4}$$

$$\left(S_i\ S_j\right)_{\text{triplet}} \Longrightarrow \begin{cases} \left(\vec{S}_i + \vec{S}_j\right)^2 = S_{\text{total}}^2 & \left\{ \begin{array}{l} S_{\text{total}} = 1 \text{ for triplet} \\ \quad\ = 0 \text{ for singlet} \end{array} \right\} \\ \Rightarrow S_i^2 + S_j^2 + 2\,\vec{S}_i \vec{S}_j = S_i(S_i+1) + S_j(S_j+1) + 2\,\vec{S}_i \vec{S}_j \\ \Rightarrow \vec{S}_i \vec{S}_j = \dfrac{S_{\text{total}}^2 - S_i^2 - S_j^2}{2} \\ \Rightarrow \vec{S}_i \vec{S}_j = \dfrac{S_{\text{total}}(S_{\text{total}}+1) - S_i(S+1) - S_j(S_j+1)}{2} \end{cases}$$

$\Longrightarrow$

$$\vec{S}_i \cdot \vec{S}_j = -3/2 \text{ for singlet } (S=0)$$
$$= +1/4 \text{ for triplet } (S=1)$$

Super exchange interaction

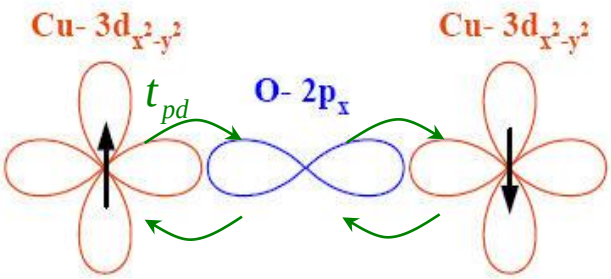
The exchange interaction between the spins of transition metals in **TMO** is mediated by the **ligand** of the oxygen ions ⟶ **super exchange**

Goodenough-Kanamori-Anderson-Rules:

1) Finite "overlap" ($t_{dd} \neq 0$)

⟶ **J large & antiferromagnetic**

e.g.: $La_{2-x}Sr_xCuO_2$ J ~ 100 meV



4. order Perturbation theory
O-Cu hopping t_{pd}

$$J \sim \frac{t_{pd}^4}{\Delta^2 U}$$

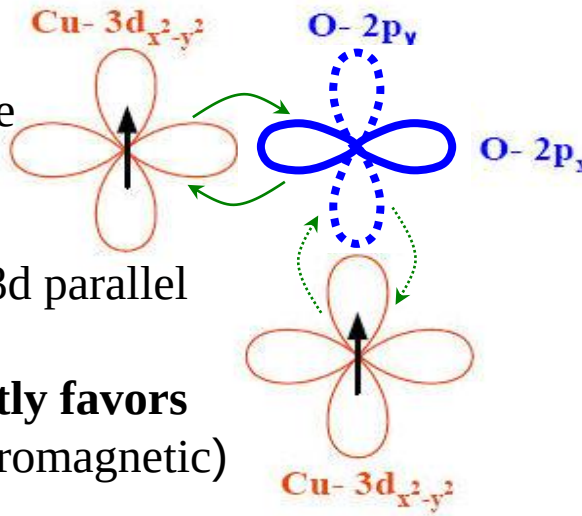
charge transfer energy

$$\Delta = E_{O2p} - E_{Cu3d}$$

Cu 3d^9: spin ½ (spin hole)

2) "overlap" = 0 ($t_{dd} = 0$)

⟶ **J small & ferromagnetic (J < 0)**



In virtually excited state 2 spins (holes) of O-Ion in **orthogonal** 2p-orbitals couple cu-3d parallel Spins.

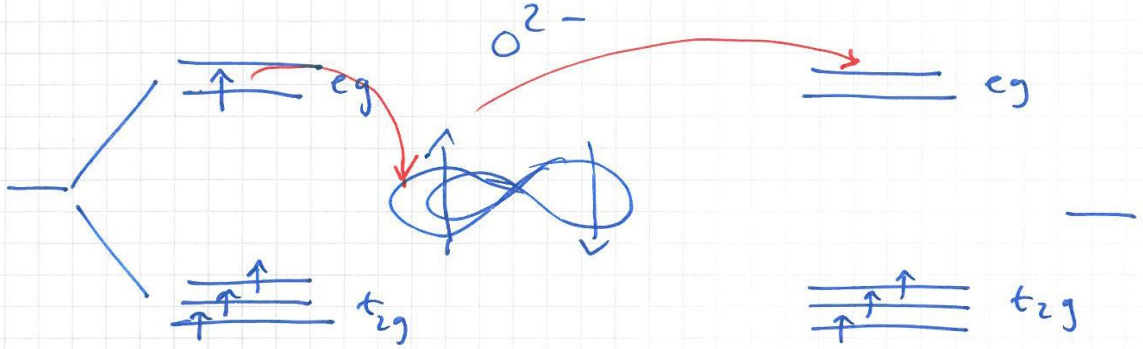
Hund s coupling slightly favors parallel orientation (ferromagnetic)

$$J \sim \frac{t_{pd}^4}{\Delta^2}\left(\frac{1}{U} - \frac{1}{U - J_{Hund}}\right) < 0$$

see board!

Double exchange interaction

e.g.: $La^{3+}_{1-x} Sr_x Mn O_3$ ⇒ mixed valence of Mn: Mn^{3+} and Mn^{4+}



$3d^4 \Rightarrow Mn^{4+}$ $(S=2)$ $\qquad$ $3d^3 \Rightarrow Mn^{3+}$ $(S=3/2)$

simultaneous hopping: $3d^{4+/3+} \leftrightarrow 2p^2 \leftrightarrow 3d^{3+/4+}$

only possible for parallel t_{2g} spin on the two sites (Mn^{4+} and Mn^{3+})

(Hund energy!)