Crystal field theory

Chemistry of the elements

Lecture 7

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kemiteknik

Who am I?

- **Doctoral researcher**

- **High-pressure synthesis**

- **Perovskites**

- **Magnetism and superconductivity**

- **Welcome to ask questions via e-mail!**
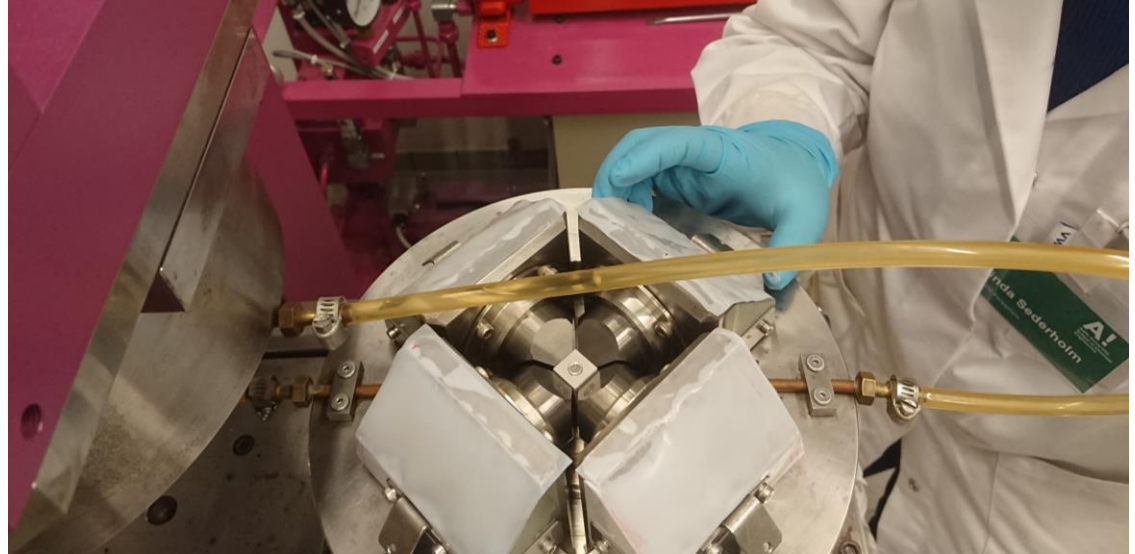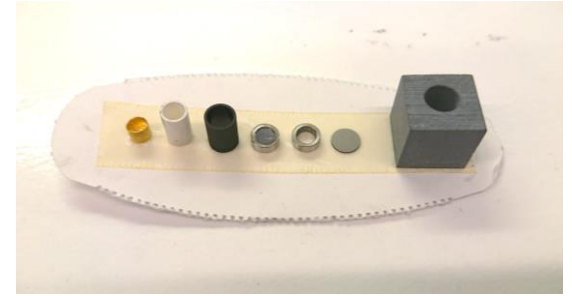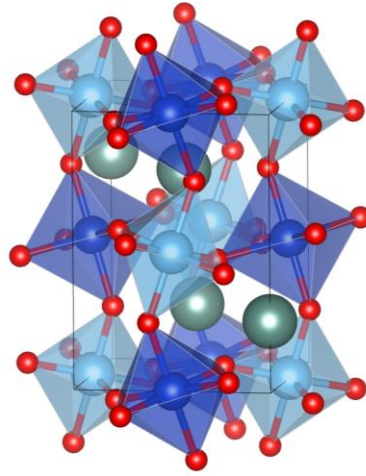
TENTATIVE LECTURE SCHEDULE

	Date	Topic

1. **Wed** 07.09. **Course Introduction & Short Review of the Elements**

2. **Fri 09.09. Periodic Properties & Periodic Table & Main Group Elements (starts)**

3. **Mon** 12.09. **Short Survey of the Chemistry of Main Group Elements (continues)**

4. **Fri 16.09. Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)**

5. **Mon** 19.09. **Transition Metals: General Aspects & Pigments**

6. **Wed** 21.09. **Redox Chemistry**

7. **Fri 23.09. Crystal Field Theory (Linda Sederholm)**

8. **Mon** 26.09. **V, Nb, Ta & Metal Complexes & MOFs**

9. **Wed** 28.09. **Cr, Mo, W & 2D materials**

10. **Fri 30.09. Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity**

10. **Mon 03.10. Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)**

11. **Fri 07.10. Lanthanoids + Actinoids & Luminescence**

12. **Mon 10.10. EXTRA**

14. **Wed** 12.10. **Resources of Elements & Rare/Critical Elements & Element Substitutions**

15. **Fri 14.10. Inorganic Materials Chemistry Research**

EXAM: Oct. 18, 9:00-12:00

Contents

- **Spatial distribution of _d_-orbitals**

- **Octahedral and tetrahedral environment**

- **Orbital electron occupation: effect on energy**

- **Visible and measurable effects**

QUESTIONS: Lecture 7

- In octahedral crystal field, transition metal cations with the electron configurations of d^4, d^5, d^6 and d^7 have the choice of showing two different spin states, high-spin state or low-spin state. Give the electron configurations for which the same applies in tetrahedral crystal field.

- How many unpaired electrons the following ions have in high-spin state in (a) octahedral, and (b) tetrahedral crystal fields: Cr^{3+}, Mn^{2+}, Fe^{2+} and Co^{+2}?

- For which of the following ions (assume high-spin) would you expect to see (strong) Jahn-Teller distortion: Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Cu^{2+}. **Explain why!**

Crystal (ligand) field theory

- **Electron configuration of n-period transition metal (T) : $ns^2 (n-1)d^x$**

- **For free T atom: all d-orbitals degenerated (= have the same energy)**

- **For T surrounded by neighbours (crystal, molecule or solution):**

- **ns^2 electrons and possibly also a portion of the d-electrons (y) participate in the formation of the chemical bond**

    $\rightarrow$ **$T^{(2+y)+} : d^{x-y}$**

- **Portion of d-electrons (x-y) remain non-bonded**

- **These remaining d-electrons are the source of exciting properties**

Geometry of *d*-orbitals

$3d_z2$

$3d_x2-y2$

$3d_{xy}$

$3d_{xz}$

$3d_{yz}$
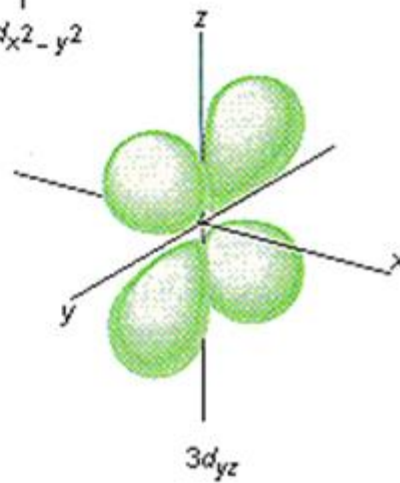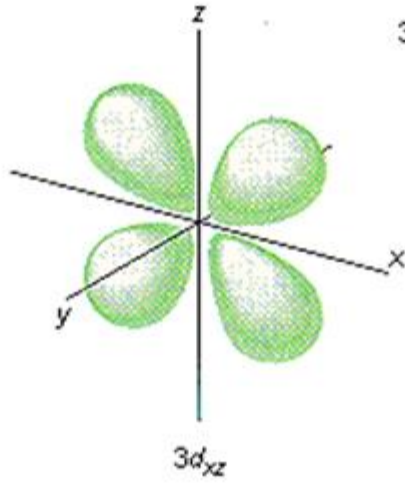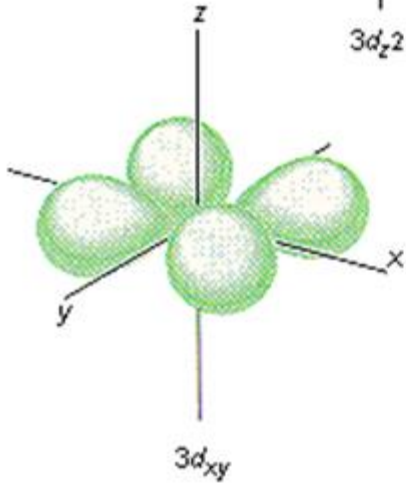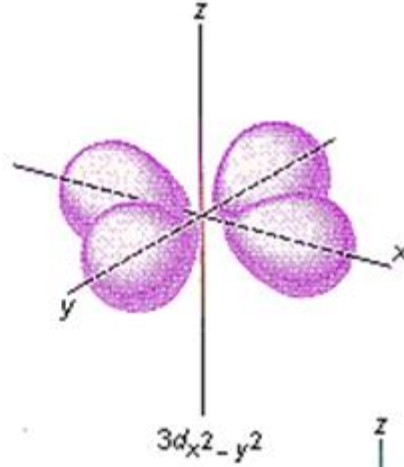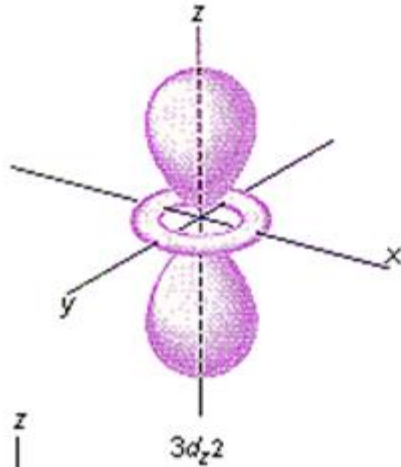
In an isolated atom the different *d*-orbitals of the same shell all have the same energy (but different shapes & orientations)

= degenerate states

Bonded T-atom

- Each T atom (cation) likes simultaneously to:

   1. get the nearest-neighbour anions (e.g. O^{2-}) as close as possible

      (such that the bond can form)

   2. keep the non-bonded d-electrons away from the nearest-neighbour anions

      (to minimize electron-anion repulsion)

      → this repulsion determines the orientation of the d-orbitals related to the nearest-neighbour anions

- All the five d-orbitals feel the repulsion → energy increased *compared to the energy level in free T atom*

- d-orbitals that are closest to the nearest-neighbour anions feel the strongest repulsion and are with the highest energy, while those that are farther are with the lower energy

- d-orbitals have different shapes and spatial orientations

   → energies of the orbitals split (Δ) when the T cation is surrounded by anions (i.e. degeneration of the d orbitals disappears)
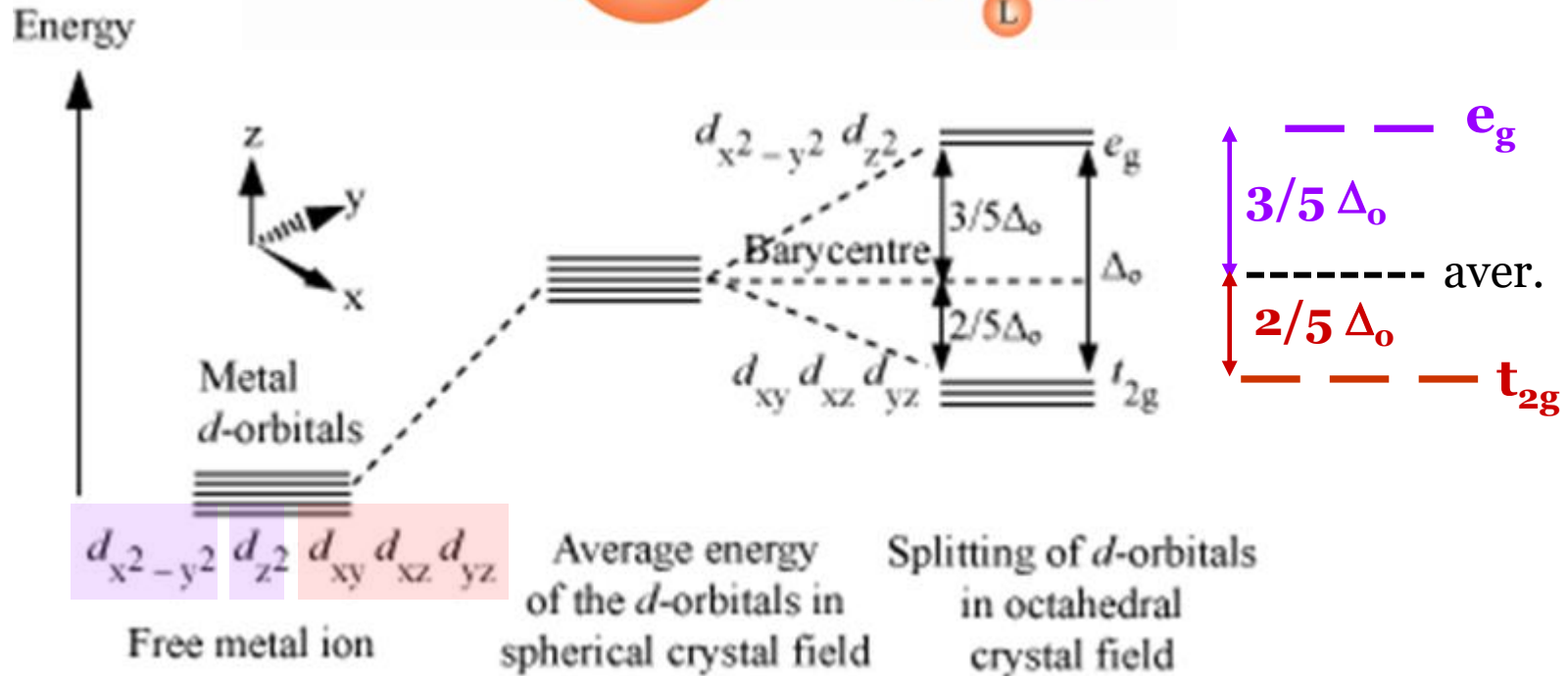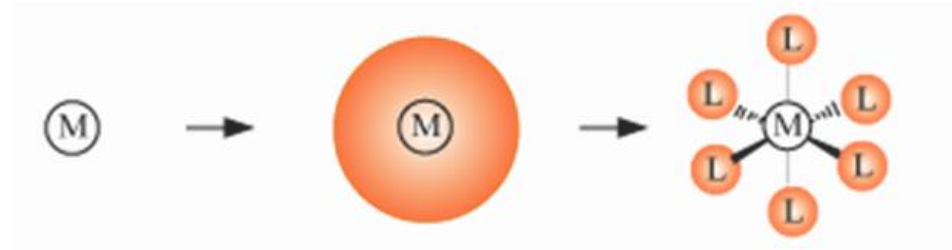
Octahedral ligand field

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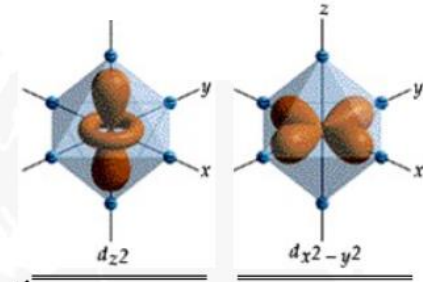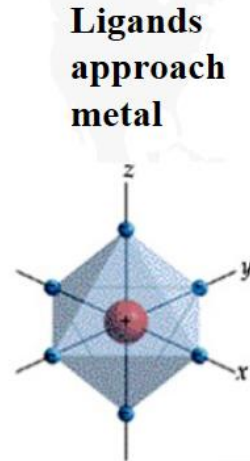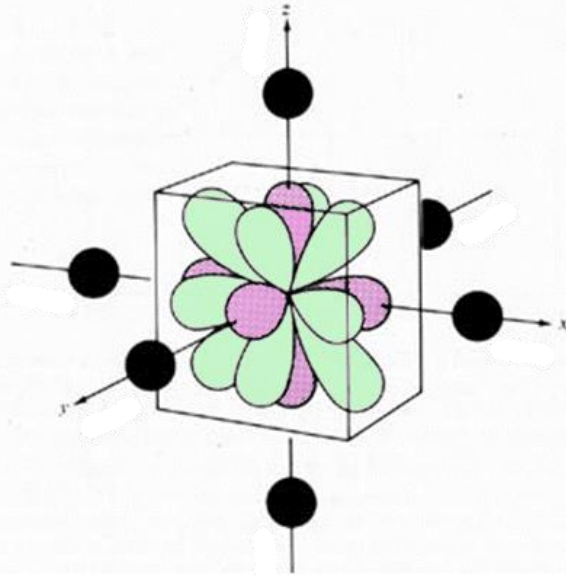
d-orbitals pointing directly at axis are affected most by electrostatic interaction

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

d_{xy} d_{yz} d_{xz}
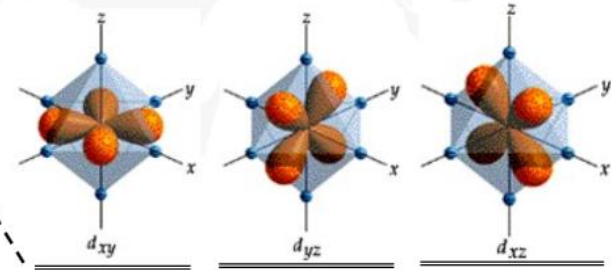
d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

- **three d orbitals (d_{xy}, d_{yz} ja d_{zx}) orient towards the empty spaces between the anions**
  - → **lower energy (2/5 Δo) t_{2g} orbitals**
- **two d-orbitals (d_{z^2} and $d_{x^2-y^2}$) orient towards the anions**
  - → **higher energy (3/5 Δo) e_g orbitals**

Octahedral ligand field

Tetrahedral ligand field
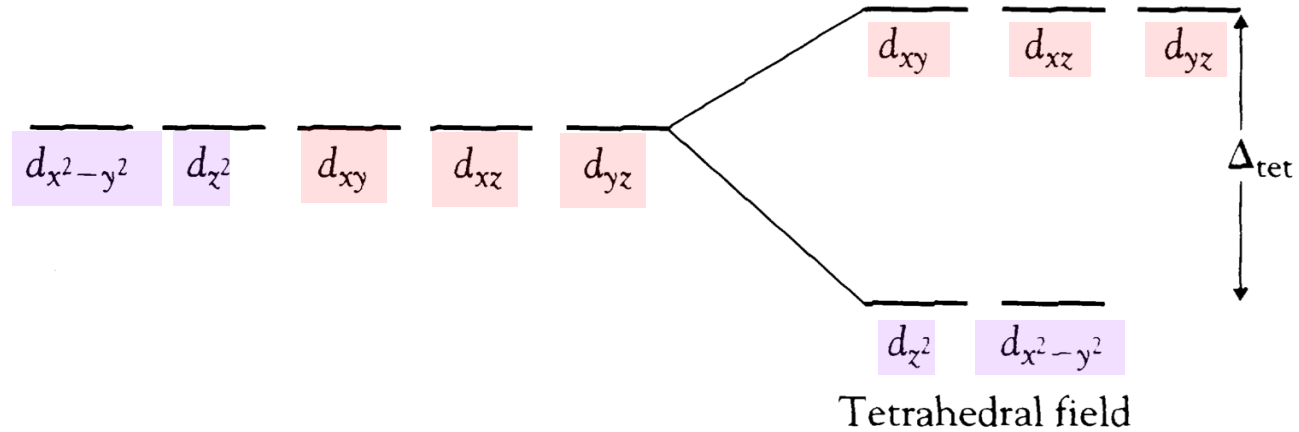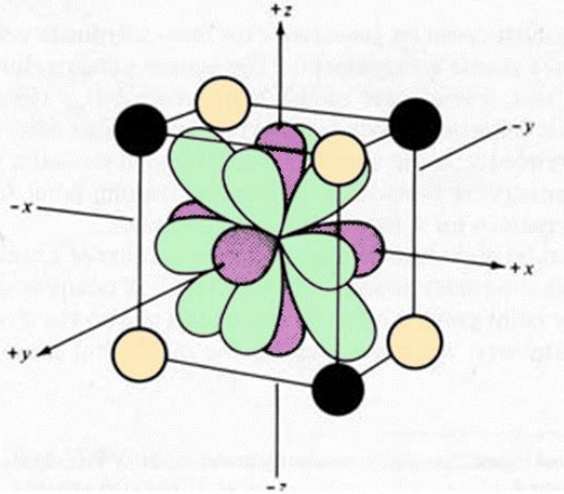
Tetrahedral field

- **4 anions/ligands around transition metal T cation**
- **compared to octahedral case, splitting is less:**
  - **typically Δ_{tet} = 4/9 Δ_{oct} for the same metal/anion pair**

Low and high field splitting

Low field splitting

$0.6\ \Delta_o$

Δ_o

$0.4\ \Delta_o$

$d_{xy}\ d_{zy}\ d_{xz}$

High field splitting

$0.6\ \Delta_o$

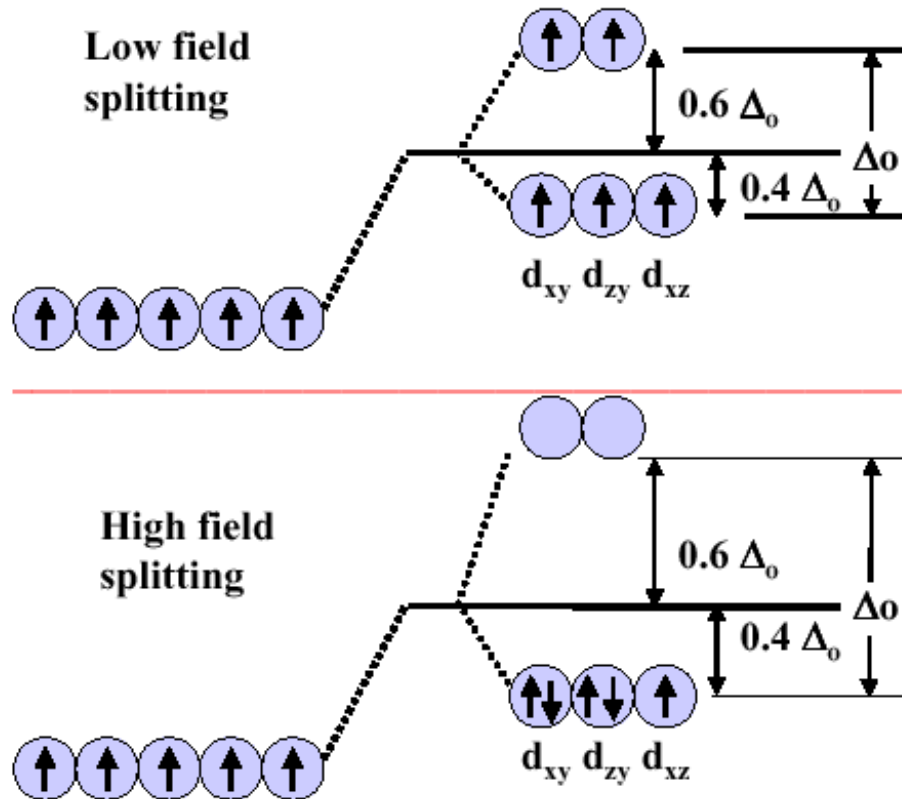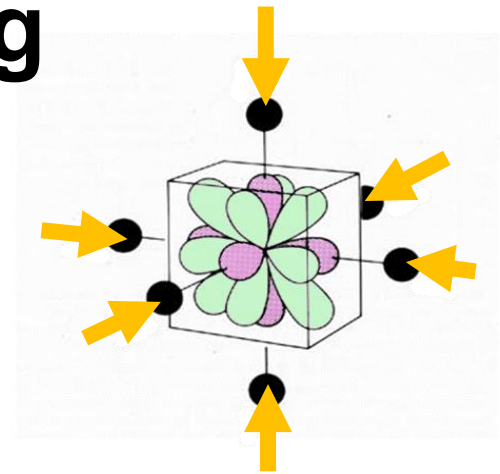Δ_o

$0.4\ \Delta_o$

$d_{xy}\ d_{zy}\ d_{xz}$

Figure 5. The two cases of crystal field splitting for the octahedral geometry.

Geometric distribution of surrounding atoms changes the orbital energies
→ Splitting of d-orbital energies

Also f-orbital energies can split.
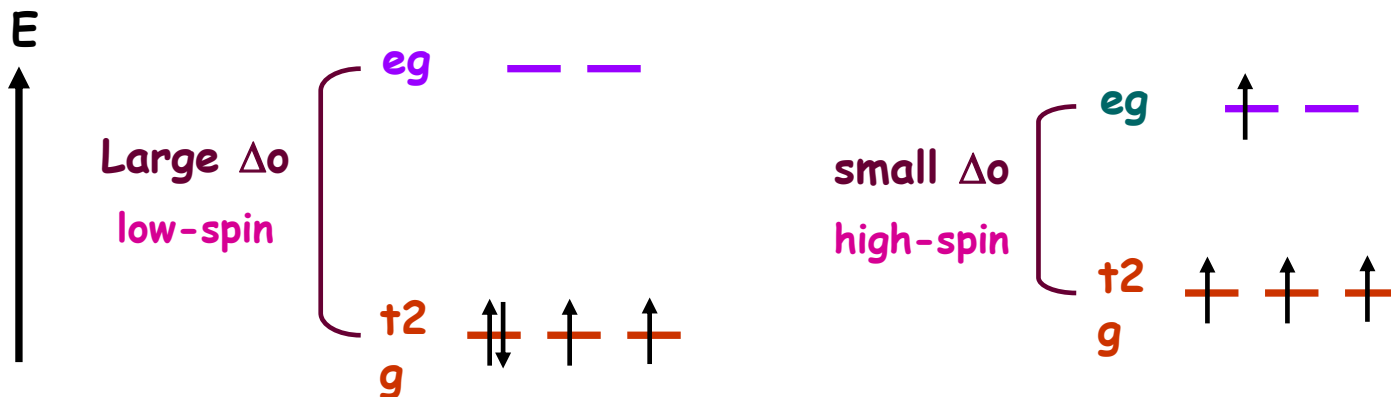
Electron distribution

How do the d-electrons occupy split orbitals?

Two contadictory goals:

(1) Minimum energy → **low spin** (if large Δ)

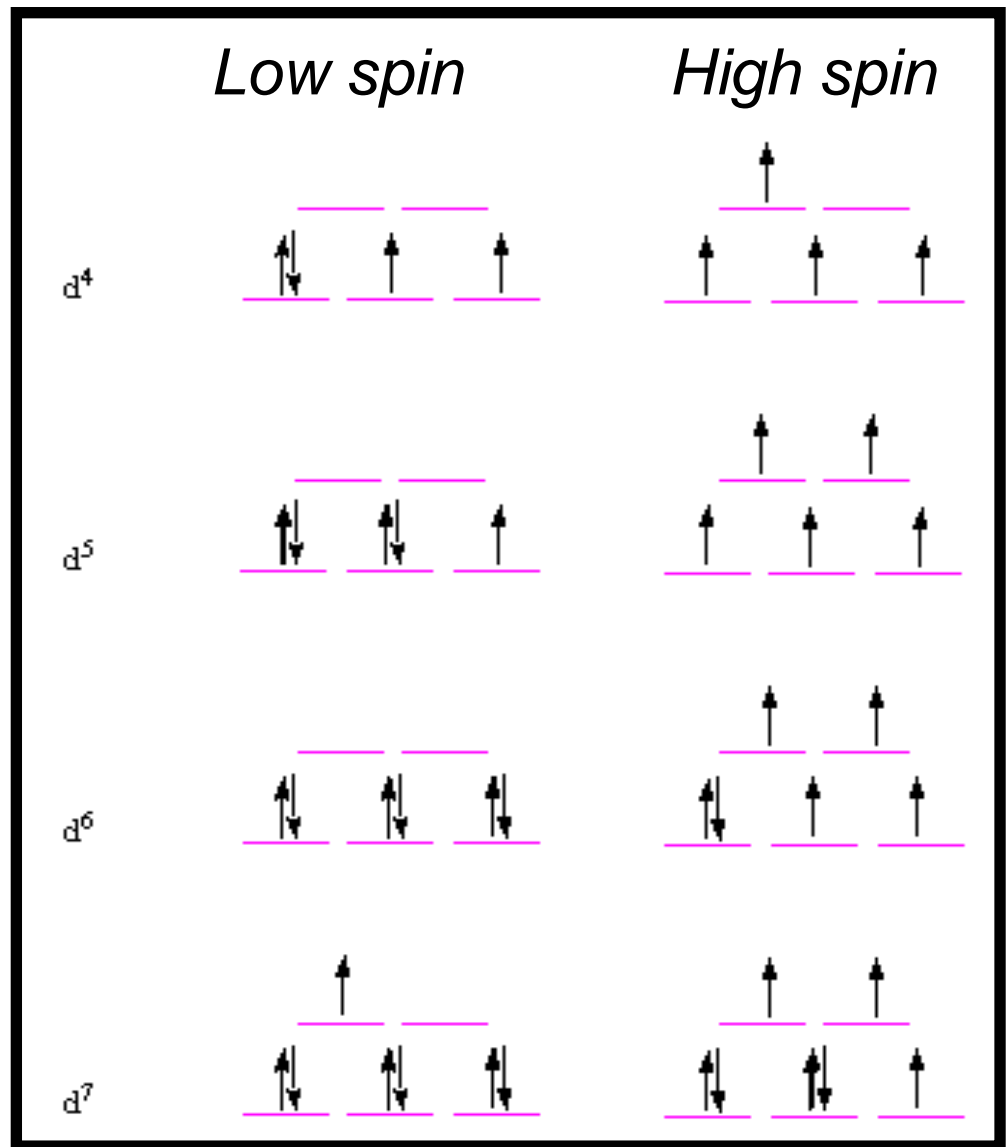(2) Hund's rule (avoid electron pairs) → **high spin** (if small Δ)

As $\Delta_{tet} = 4/9\ \Delta_{oct}$, tetrahedral case almost always high-spin

E

Large Δo

low-spin

eg

t2g

small Δo

high-spin

eg

t2g

Octahedral ligand field

Spin state

Let's consider

the OCTAHEDRAL case

(in your lecture exercise you will consider the tetrahedral case)

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Colours of d-block metal ions

- **partly filled *d*-orbitals**
- **electrons can hop between *d*-orbitals**
- **energy needed for the transfer is small**
- **corresponds to visible light wavelengths**
- **ions absorb certain wavelengths within the visible light spectrum**
- **if an ion absorbs certain colour (e.g. red), the transmitted or reflected light contains relatively more other colours (blue and green)**

    → the ion looks coloured (bluish green)
- **ions with empty or full orbitals (d^0 ja d^{10}) are colourless**
- **ions with half-filled orbitals (d^5) are colourless or faintly coloured**

$[Fe(H_2O)_6]^{3+}$ $[Ni(H_2O)_6]^{2+}$ $[Zn(H_2O)_6]^{2+}$

$[Co(H_2O)_6]^{2+}$ $[Cu(H_2O)_6]^{2+}$

CFSE:
Crystal Field Stabilization Energy

Crystal field stabilization energy

- **How the electron configuration in the split field compares to the non-split field**

$$CFSE = \Delta E = E_{ligand\,field} - E_{isotropic\,field}$$

- **What contributes to the energy change:**
  - Geometry
  - d-shell occupation
  - Spin pairing
  - Ligand character

Calculation example 1

Octahedral crystal field

- **each t_{2g} electron stabilizes** (relatively) **the compound**
- **each e_g electron destabilizes** (relatively) **the compound**

CFSE = [3 x (-2/5) + 1 x (3/5)]Δ_o = - 3/5 Δ_o
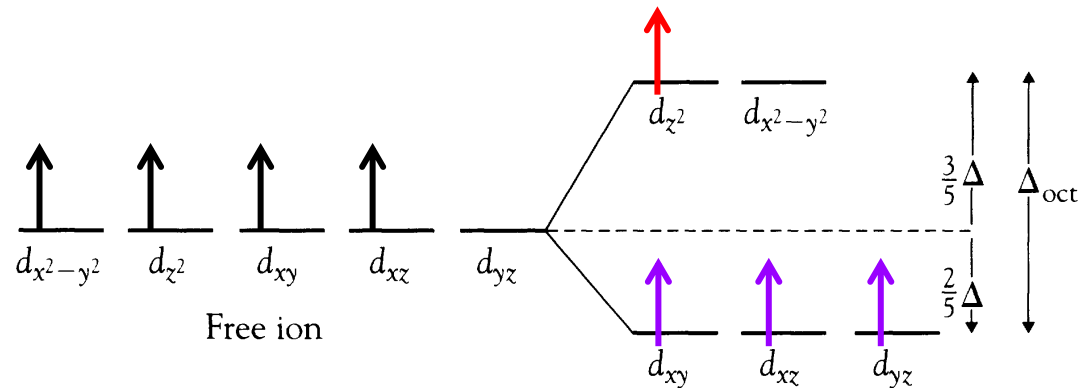
Calculation example 2: high spin

Octahedral crystal field

- **Spin pairing energy to consider! Pairing energy is *P* for each pair**
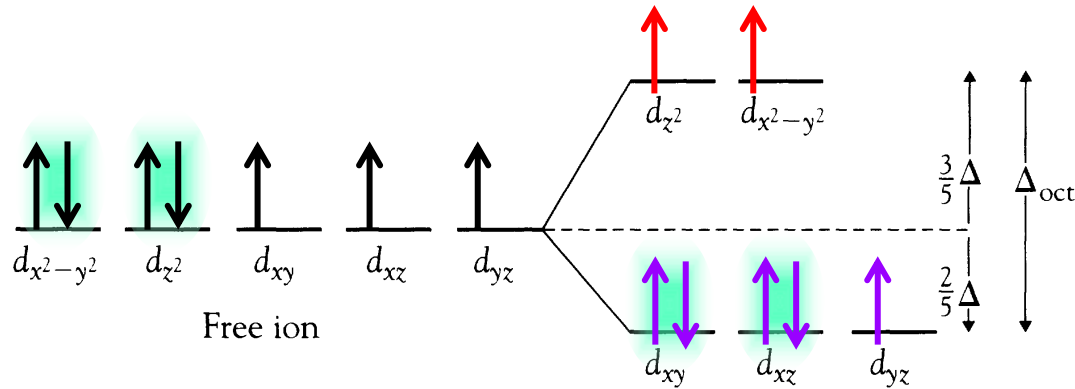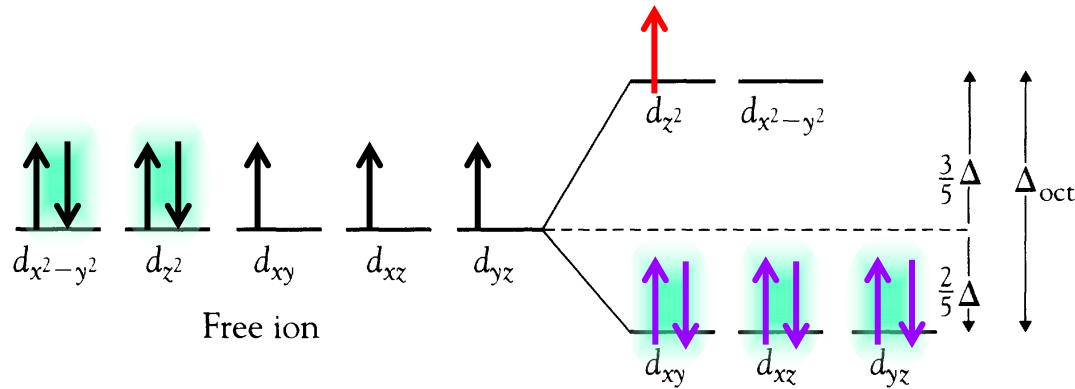

$E_{iso} = [7 \times 0]\Delta_o + 2P = 2P$

$E_{CF} = [5 \times (-2/5) + 2 \times (3/5)]\Delta_o + 2P = -4/5\ \Delta_o + 2P$

$CFSE = (\ -4/5\ \Delta_o + 2P\ ) - 2P = -4/5\ \Delta_o$

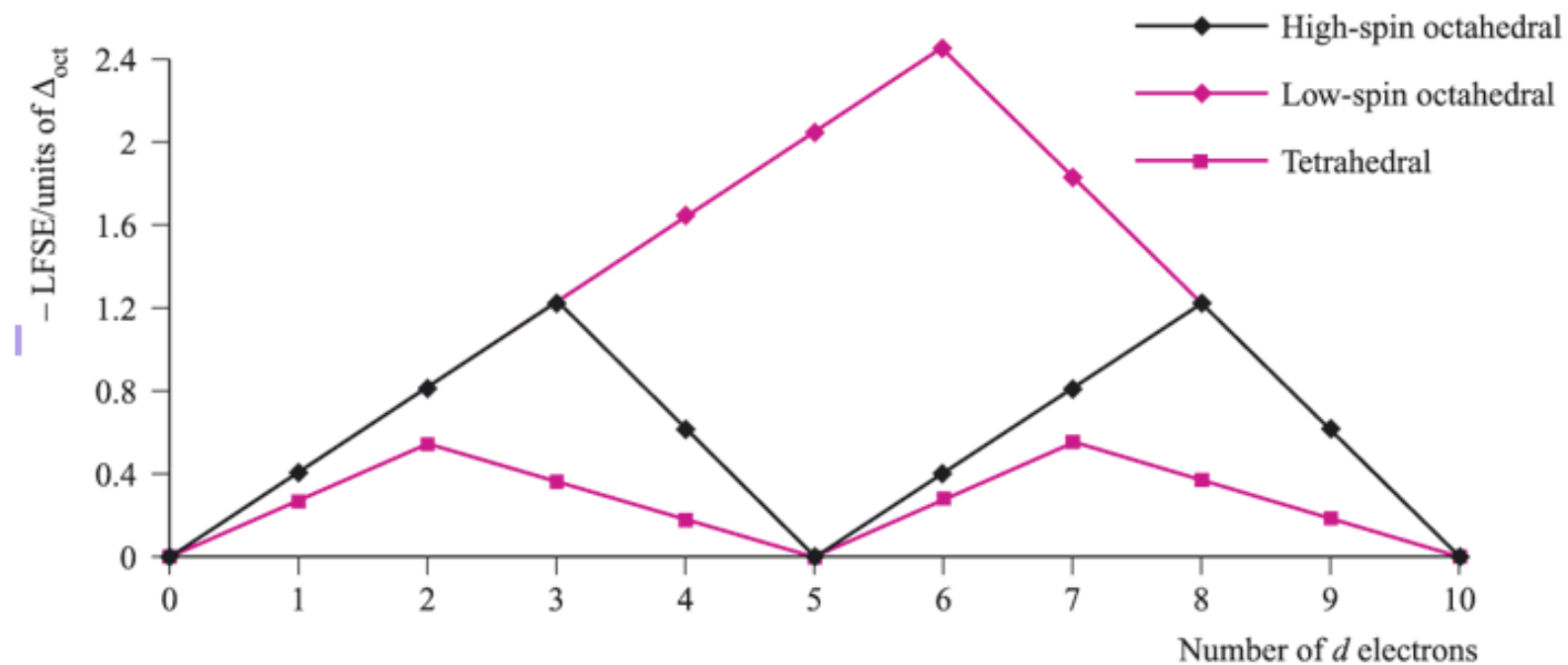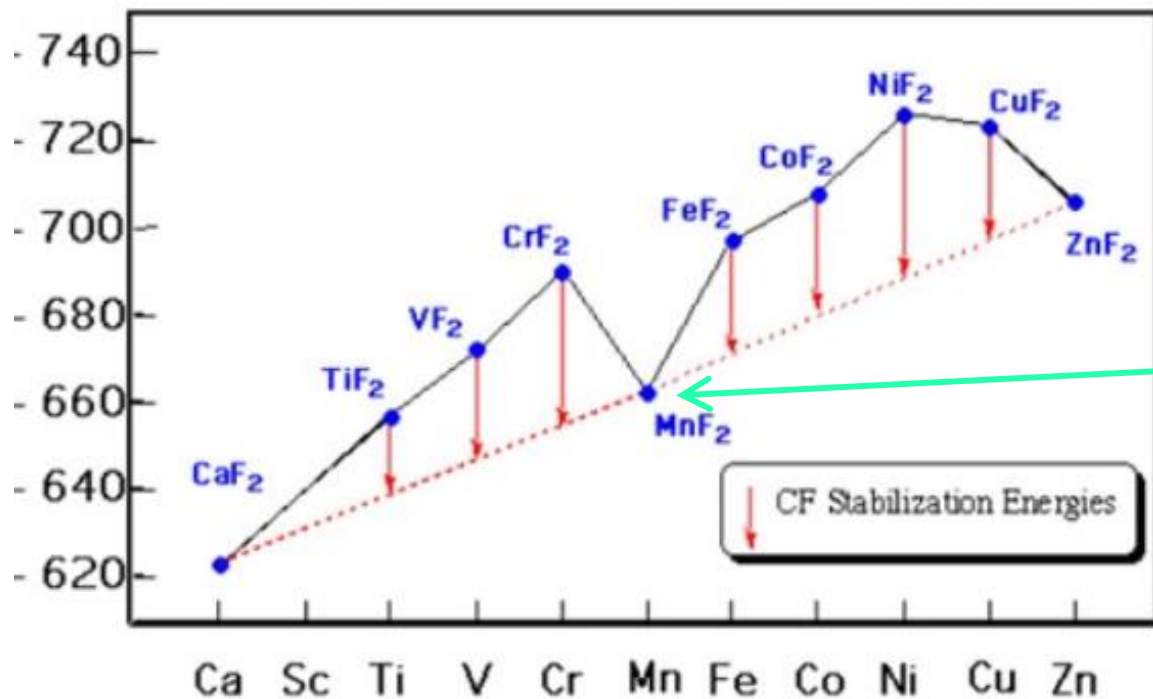# Calculation example 2: low spin

Octahedral crystal field
- **Spin pairing energy to consider! Pairing energy is *P* for each pair**

$E_{iso} = [7 \times 0]\Delta_o + 2\,P = 2\,P$

$E_{CF} = [6 \times (-2/5) + 1 \times (3/5)]\Delta_o + 3\,P = -9/5\,\Delta_o + 3\,P$

$$CFSE = (\, -9/5\,\Delta_o + 3\,P\,) - 2\,P = -9/5\,\Delta_o + P$$

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Transition metal fluorides

Lattice Energy of Transition Metal Fluorides [kcal / mol]

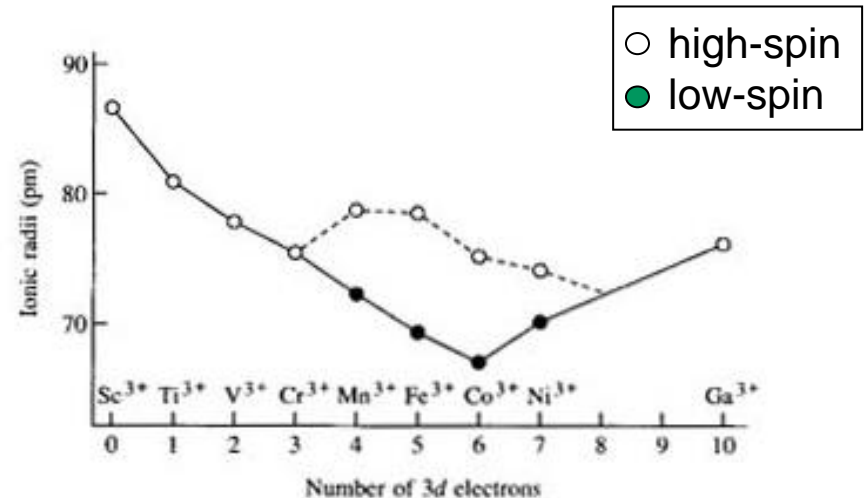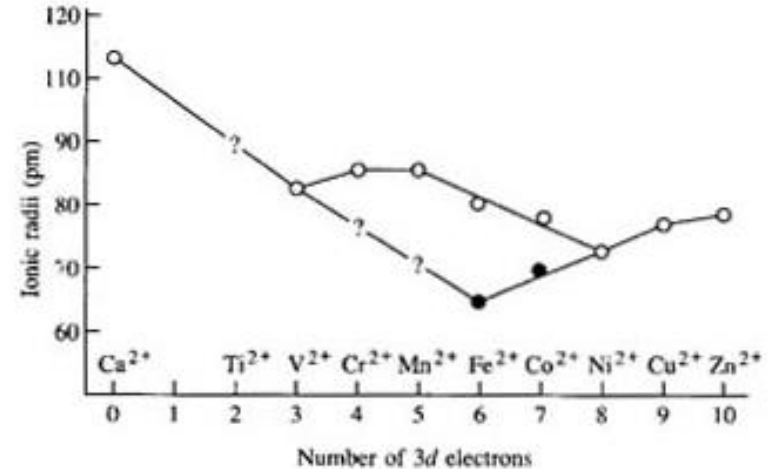C.S.G. Phillips, R. J. P Williams, Inorganic Chemistry, Volume 1, p. 179.

MnF_2
↓
Mn^{2+}
↓
**5 d-electrons
all unpaired**
↓
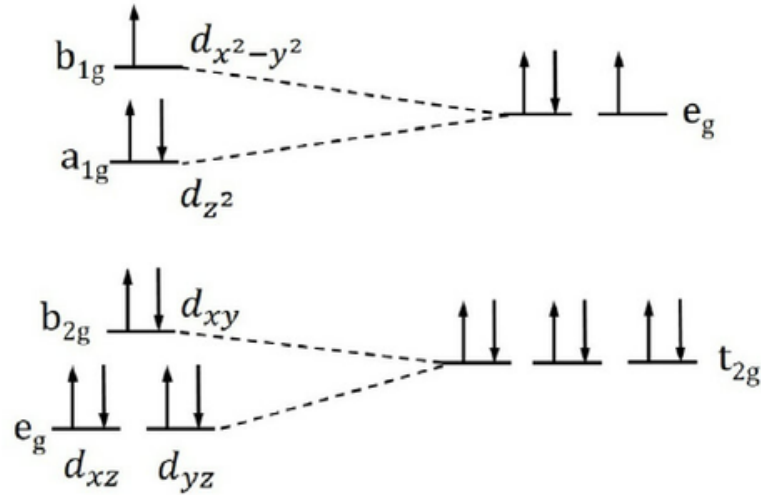$3 \times (-2/5) + 2 \times (3/5) = 0$

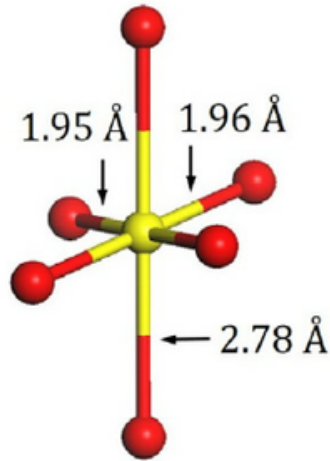# CFSE and ionic radius

- **FOR EXAMPLE: 3d metals in octahedral coordination**

- **At a fixed oxidation state, ionic radius decreases from left to right**

- **HOWEVER: each electron in e_g orbital increases the ionic radii**
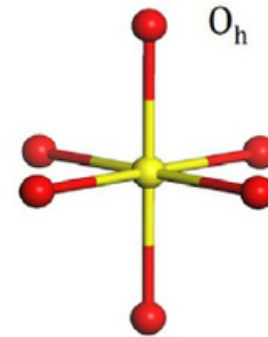
- **Ionic radius depends on spin state !**

○ high-spin
● low-spin

Asymmetric ligand field

Jahn-Teller distortion

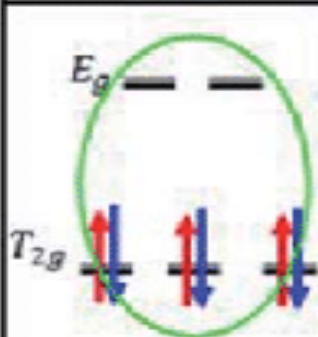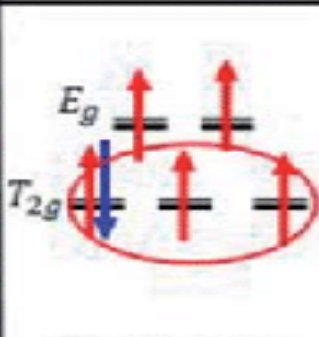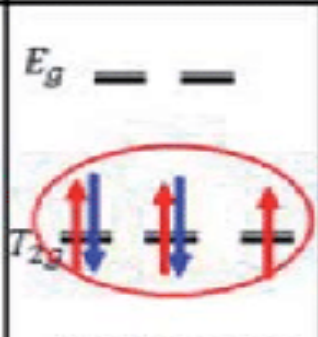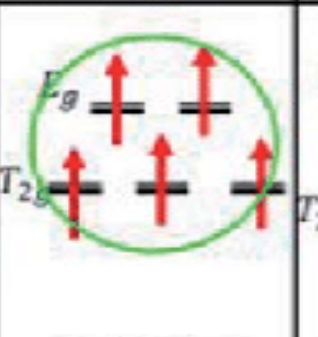**Distorted**   **Regular**

We come back to this when we discuss high-temperature superconducting copper oxides later in this course
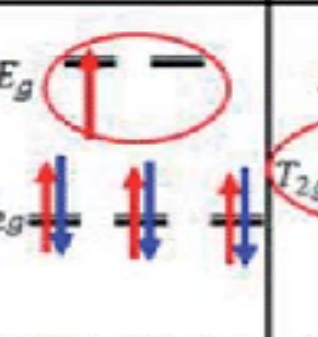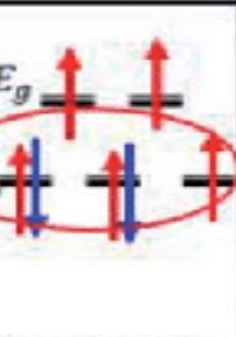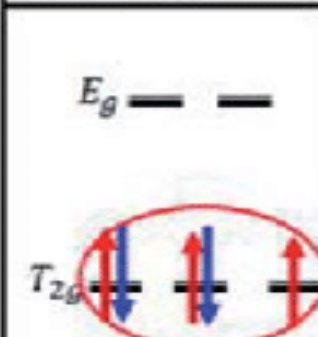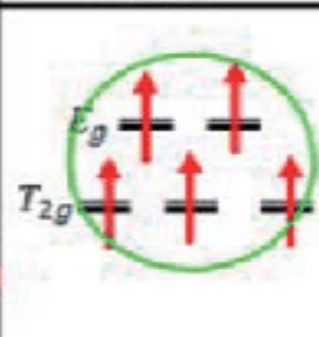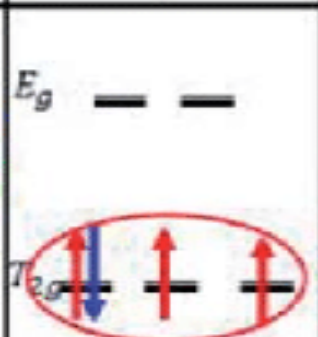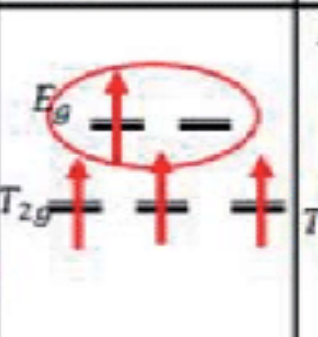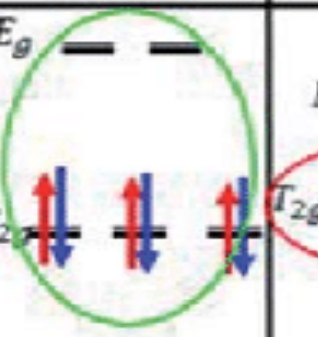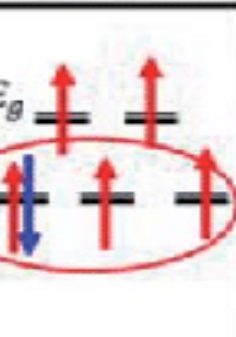
Jahn-Teller distortion

- **1937: Hermann Arthur <u>Jahn</u> & Edward <u>Teller</u>**

- **Important in explaining: spectroscopy, stereochemistry, crystal chemistry, solid-state physics and materials science**

- **All is explained by the repulsions between ligands/anions and electrons at outermost orbitals**

- **Crystal field effect: ligands raise the (closer) orbital energy**

- **Jahn-Teller effect: electrons at the higher-energy orbital push the ligand/anion farther**

- **JT effect is most visible in octahedral environment when there is different electron occupancies at the two eg orbitals (as the ligands/anions come closest to these orbitals)**

> **$\rightarrow$ Distortion (typically elongation) of the octahedron**

Significant J-T ions

d^4 high spin

d^7 low spin

d^9

Cr(II)
Mn(III)

Co(II)
Ni(III)

Cu(II)
Ag(II)

Octahedral elongation

Octahedral → Square Planar
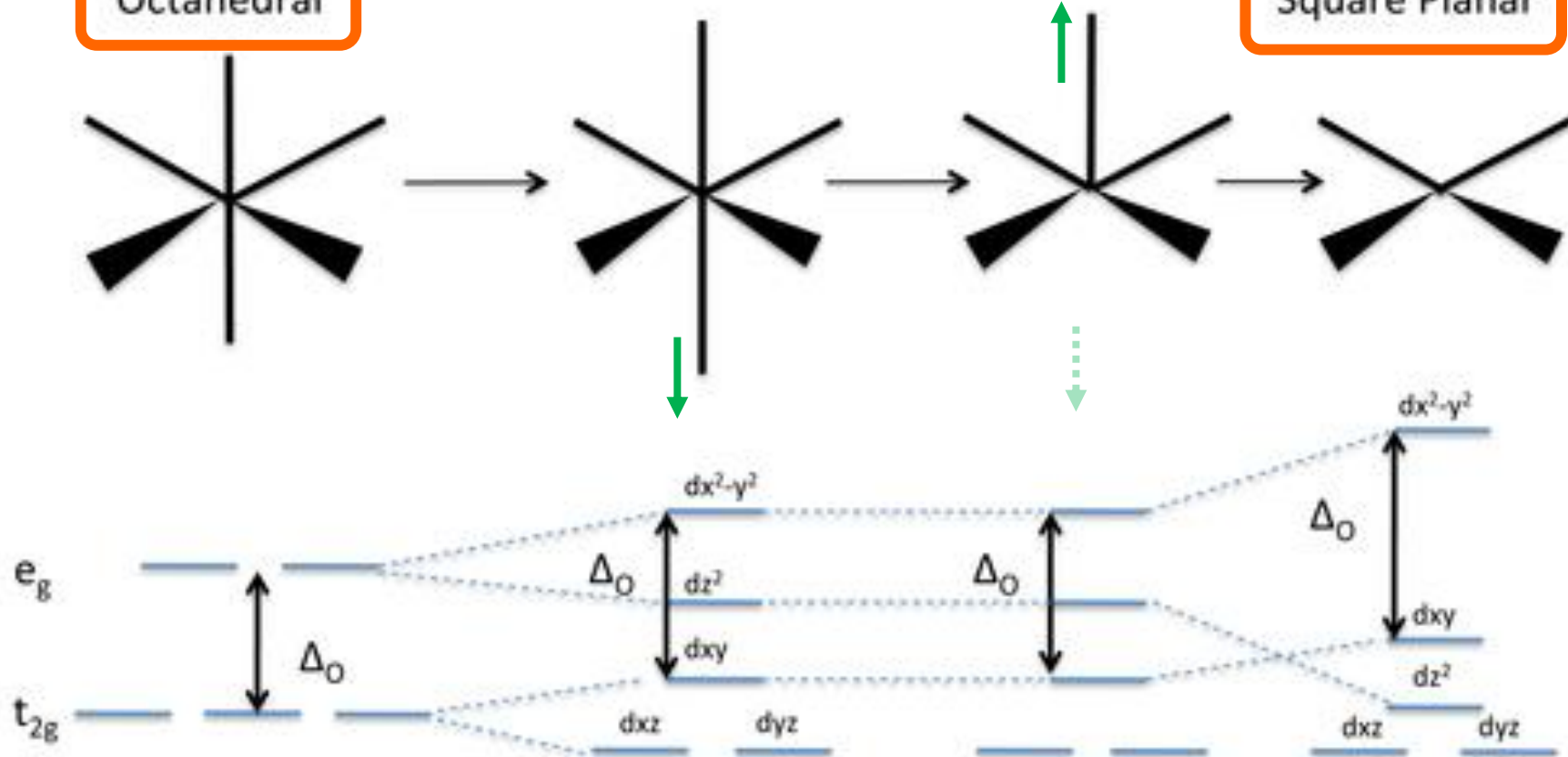
Magnitude of splitting & splitting effects

SPECTROCHEMICAL SERIES

- **Empirically found order for ligands/anions**
- **Ligands in the order of the magnitude of splitting Δ they produce**
- **Below is just part of the series**

$CO > CN^- > NO^{2-} \gg O^{2-} \gg H_2O > OH^- > F^- > N^{3-} > NO^{3-} > Cl^- > SCN^- > S^{2-} > Br^- > I^-$

π **acceptors** $\longleftrightarrow$ π **donors**
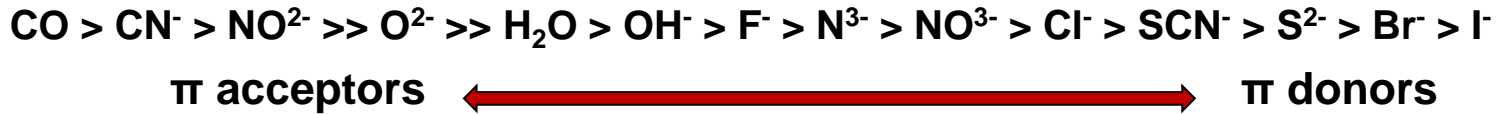
EXAMPLE: For O^{2-} : Δ is still relatively small
$\rightarrow$ high-spin configurations common in oxide materials

EXAMPLE: Fe^{2+}: d^6

- $[Fe(H_2O)_6]^{2+}$: high-spin $\rightarrow$ paramagnetic

- $[Fe(CN)_6]^{4-}$: low-spin $\rightarrow$ diamagnetic

Ligand change → colour change

$[Co(NO_2)(NH_3)_5](NO_3)_2$

$[CoI(NH_3)_5](NO_3)_2$

$[CoBr(NH_3)_5](NO_3)_2$

$[Co(SO_4)(NH_3)_5]NO_3$

$[CoCl(NH_3)_5](NO_3)_2$

$[Co(CO_3)(NH_3)_5]NO_3$
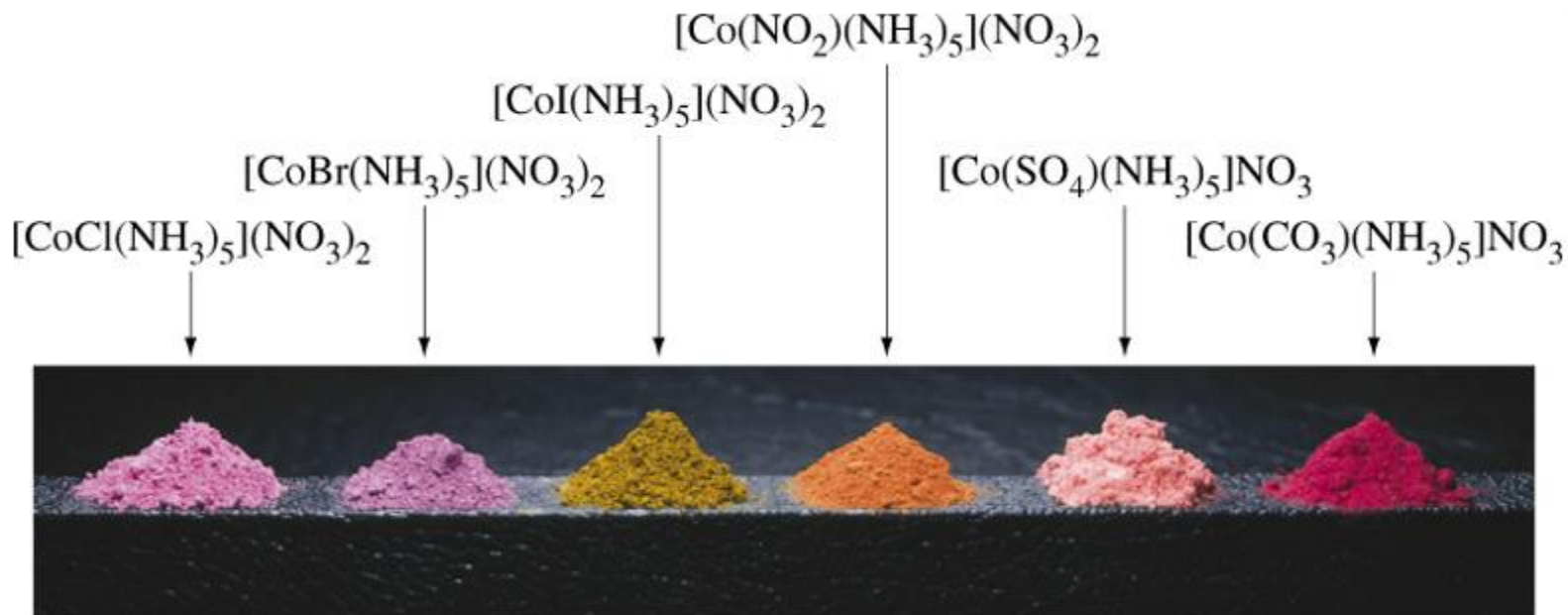
Magnitude of the splitting energy depends also on:

(1) Transition metal T itself

- 50% larger for 4d metals than for 3d metals
- 25% larger for 5d metals than for 4d metals
  $\rightarrow$ 4d and 5d metals almost always: low-spin

(2) Oxidation state of T

- With increasing oxidation state of T
  $\rightarrow$ anions become closer
  $\rightarrow$ larger repulsion between d electrons and anions
  $\rightarrow$ larger Δ

- 3d metals: when $T^{2+} \rightarrow T^{3+}$, Δ is doubled

(3) Number of anions/ligands

- The more ligands the larger Δ : $\Delta_{tet} \approx 4/9 \times \Delta_{oct}$

CFT and magnetism

- **Perovskite: magnetic T-ion in octahedral coordination**

- **Magnetic interaction depends on orbital connections**

- **Bonding angle influences orbital overlap geometrically**
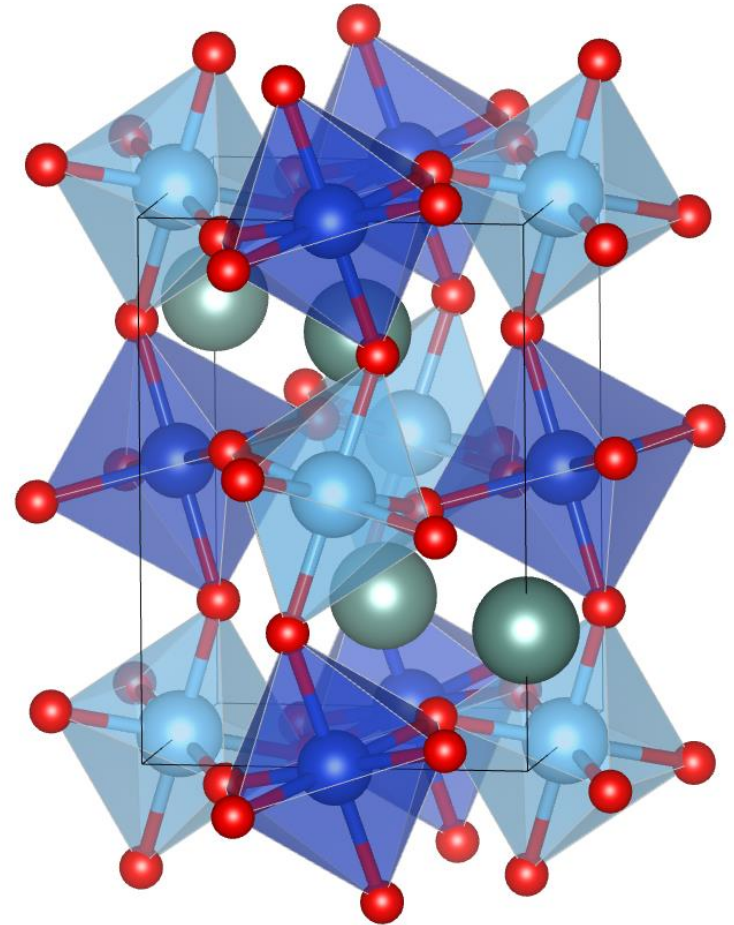
CFT and superconductivity

- **Perovskite cousin**

- **Copper in different coordination environments**

- **Orbital occupation of copper is key to the formation of Cooper pairs**

    → superconduction
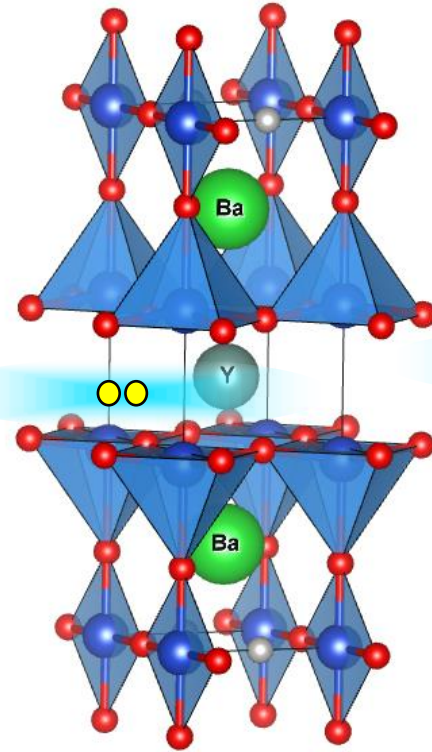
$YBa_2Cu_3O_7$ $YBa_2Cu_3O_8$

Extra material…

Quantum origin of orbitals

- **Solving the Hamiltonian of quantum physics**

- **…leads to the so-called Legendre polynomials**

- **Hamiltonian is split into sub-wavefunctions by quantum numbers l, m, s**
  - → orbital identificators

- **When atoms form a bond, the wavefunctions of the atom combine into a new wavefunction →
the atomic orbitals are replaced by bond orbitals**

The solutions to Legendre equation

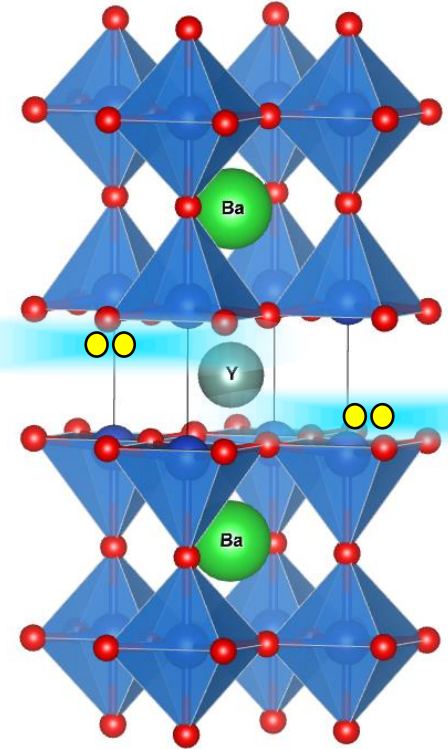$$\left(1-x^2\right)\frac{d^2P(x)}{dx^2} - 2x\frac{dP(x)}{dx} + \left[l(l+1) - \frac{m^2}{1-x^2}\right]P(x) = 0$$

	$l=0$	$l=1$	$l=2$	$l=3$
$m=0$	$P_0^0 = 1$	$P_1^0 = \cos\theta$	$P_2^0 = \frac{1}{2}\left(3\cos^2\theta - 1\right)$	$P_3^0 = \frac{1}{2}\left(5\cos^3\theta - 3\cos\theta\right)$
$m=\pm1$		$P_1^1 = \sin\theta$	$P_2^1 = 3\cos\theta\sin\theta$	$P_3^1 = \frac{3}{2}\left(5\cos^3\theta - 1\right)\sin\theta$
$m=\pm2$			$P_2^2 = 3\sin^2\theta$	$P_3^2 = 15\cos\theta\sin^2\theta$
$m=\pm3$				$P_3^3 = 15\sin^3\theta$

A?

Repulsion but no bonding?

An excellent after-class question:

How can the d-electrons avoid bonding with those same electrons that are 'pushing' on them in the metal-ligand bond?

- **The electrons in an orbital have both particle-properties and wavefunction (orbital) properties**

- **Particle-properties include electric charge and Couloumb repulsion: spatial positions matter**
  - The d-orbitals that are in the same geometrical space as the bond to the ligand, will feel the bonding electrons' charge

- **Orbital properties concern the electrons' quantum mechanical identity, for example wave function: a different 'reality'**
  - The orbital energy of the d-electrons can be very different from the orbital energy of the bond-forming electrons
  - → forbidden from interacting on the wavefunction level

Fe^{3+} *d*-orbital electrons

Far away in the quantum world: no wavefunction interactions and no bonding

Close by physically: feel the Coulomb force

Fe-O bonding orbital electrons (from *s*- and *p*-orbitals of O and Fe)

Quantum mechanical orbital reality

Space-time reality