

Crystal field theory

Chemistry of the elements

Lecture 6



Aalto-universitetet
Högskolan för
kemiteknik

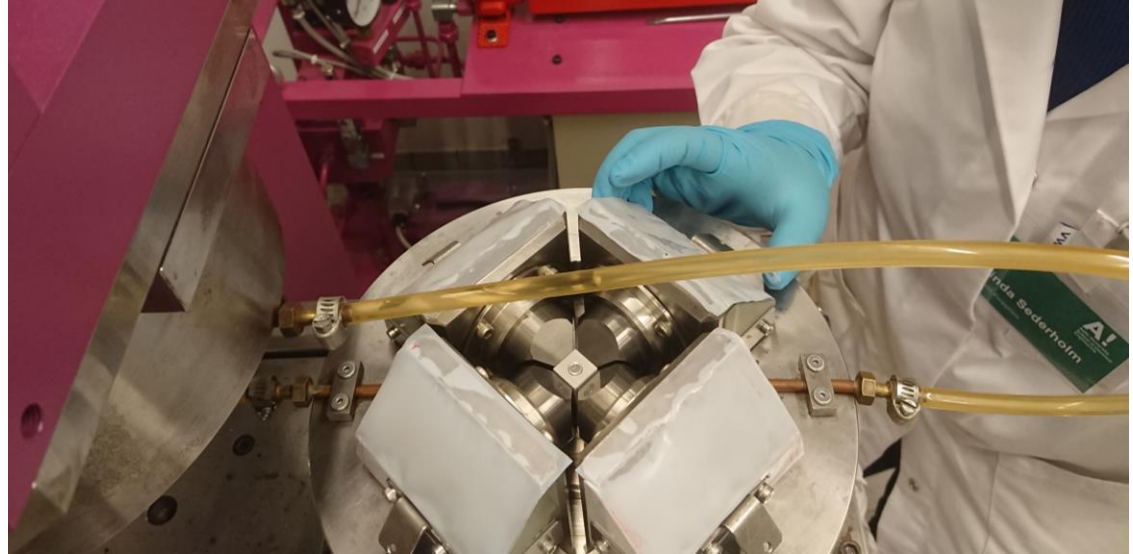
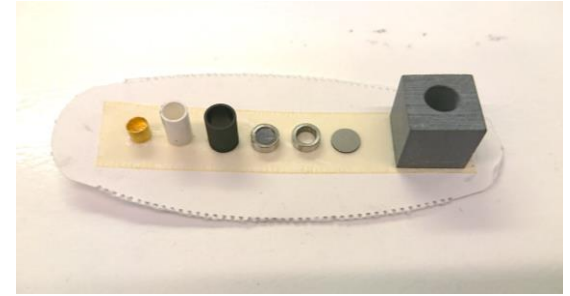
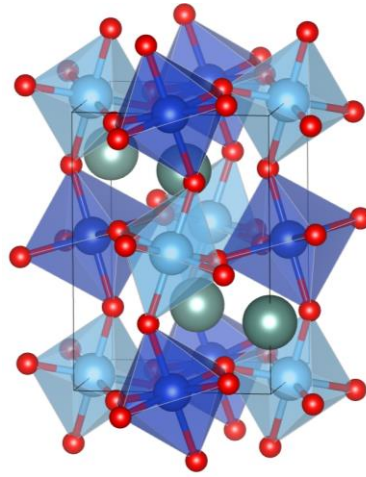
Linda Sederholm

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18.9.2023


Who am I?

- **Doctoral researcher**
- **High-pressure synthesis**
- **Perovskites**
- **Magnetism and superconductivity**
- **Welcome to ask questions via e-mail!**



LECTURE SCHEDULE

Mon (Ke3) 12.15 – 14.00
Wed (Ke2) 10.15 – 12.00
Fri (Ke5) 10.15 – 12.00



	Date	Topic
1.	Wed 06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri 08.09.	Short Survey of Main Group Elements
3.	Mon 11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed 13.09.	Transition Metals: General Aspects & Pigments
5.	Fri 15.09.	Redox Chemistry
6.	Mon 18.09.	Crystal Field Theory (Linda Sederholm)
7.	Wed 20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon 25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed 27.09.	Mn, Fe, Co, Ni, Cu
10.	Fri 29.09.	Cu & Magnetism & Superconductivity
11.	Mon 02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed 04.10.	Lanthanoids + Actinoids & Luminescence
13.	Fri 06.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri 13.10.	Inorganic Materials Chemistry Research

EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2

Contents

- **Spatial distribution of d -orbitals**
- **Octahedral and tetrahedral environment**
- **Orbital electron occupation: effect on energy**
- **Visible and measurable effects**

QUESTIONS: Lecture 6

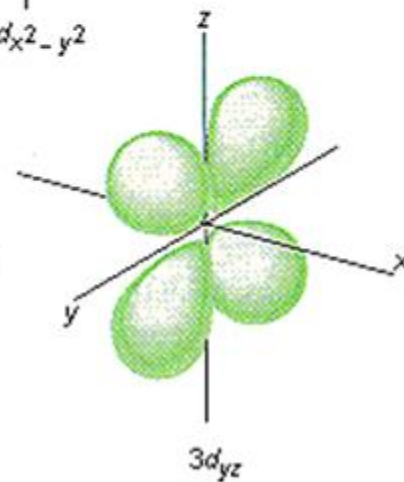
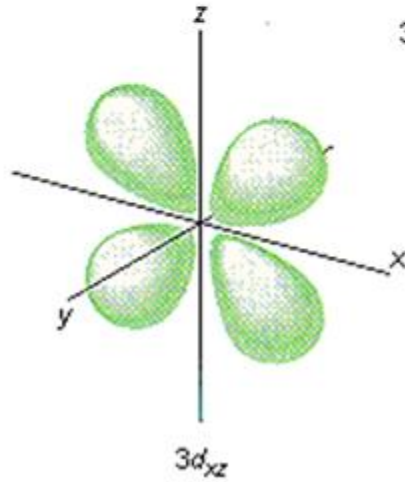
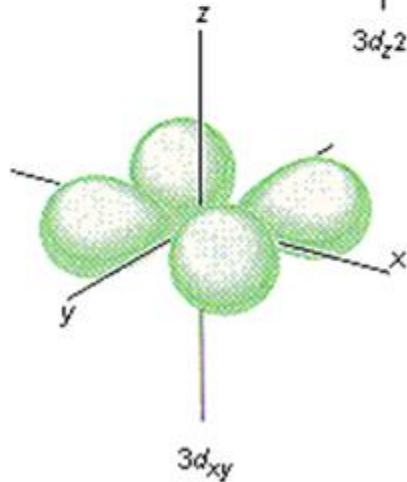
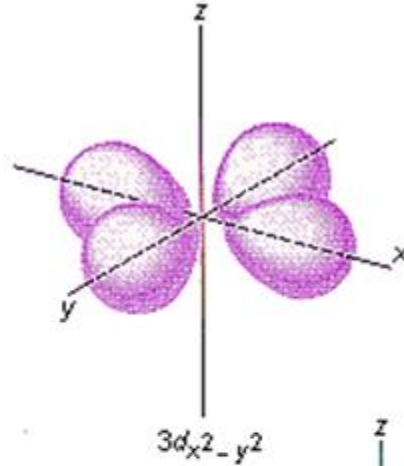
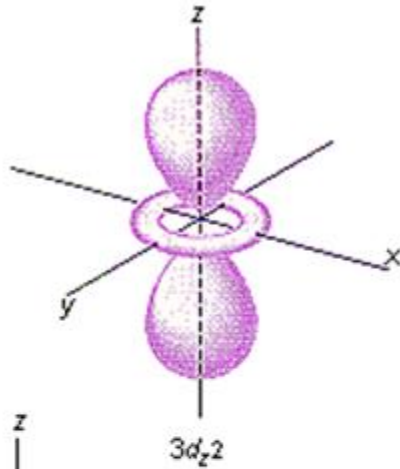
- In octahedral crystal field, transition metal cations with the electron configurations of d^4 , d^5 , d^6 and d^7 have the choice of showing two different spin states, high-spin state or low-spin state. Give the electron configurations for which the same applies in tetrahedral crystal field.
- How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

Name your file Exe-6-Familyname; Return by noon tomorrow into MyCourses drop-box

Crystal (ligand) field theory

- Electron configuration of n-period transition metal (T): $ns^2(n-1)d^x$
- For a free atom T, all d-orbitals are degenerate (= have the same energy)
- For T surrounded by neighbours (crystal, molecule or solution), the ns^2 electrons and possibly also a portion of the d-electrons (y) participate in the formation of the chemical bond
 - $T^{(2+y)+} : d^{(x-y)}$
- Portion of d-electrons (x-y) remain non-bonded
- These remaining d-electrons are the source of exciting properties

Geometry of d -orbitals



In an isolated atom
the different d -orbitals
of the same shell
all have the **same energy**
(but different shapes &
orientations)

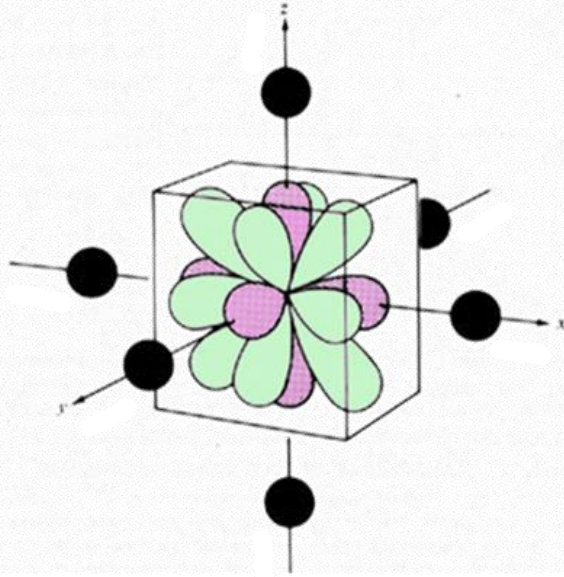
= **degenerate** states

Bonded T-atom

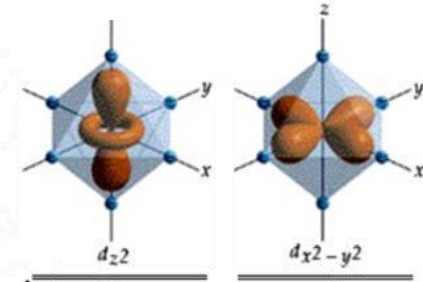
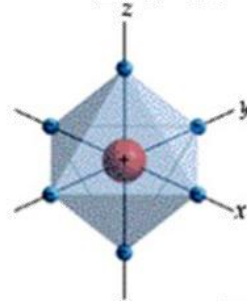
- Each **T** atom (cation) likes simultaneously to:
 1. **get the nearest-neighbour anions (e.g. O^{2-}) as close as possible**
(such that the bond can form)
 2. **keep the non-bonded d-electrons away from the nearest-neighbour anions**
(to minimize electron-anion repulsion)

→ 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 so have the **highest energy**, while those that are **farther** have a **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)

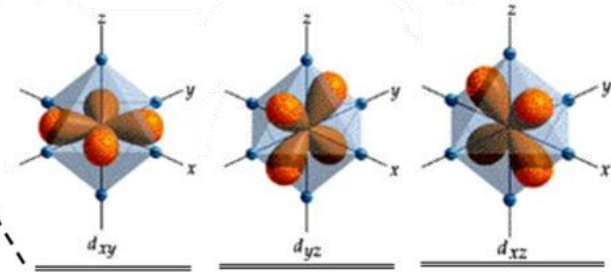
Octahedral ligand field



Ligands approach metal



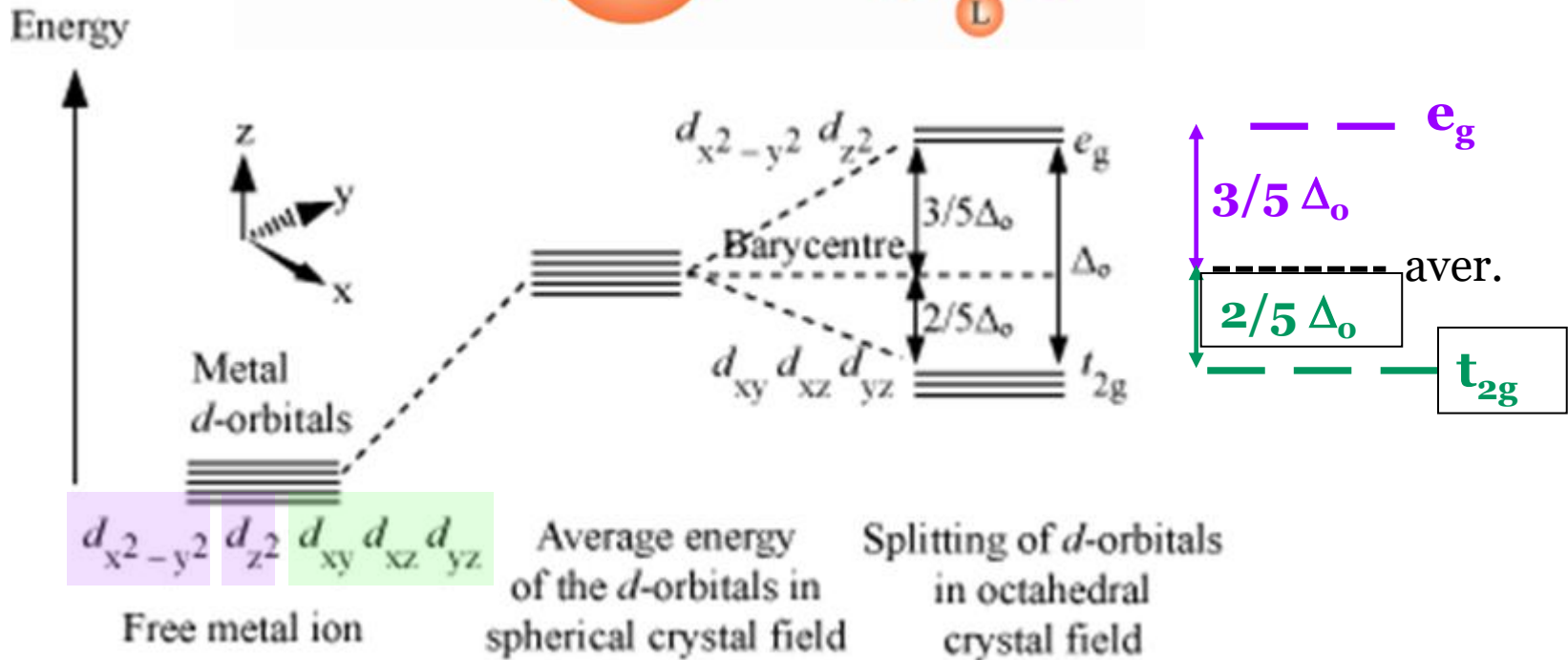
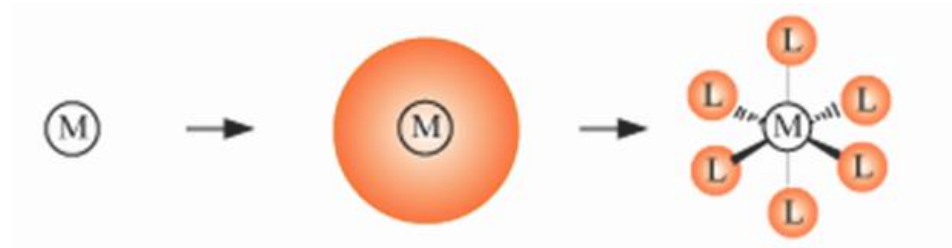
d-orbitals pointing directly at axis are affected most by electrostatic interaction



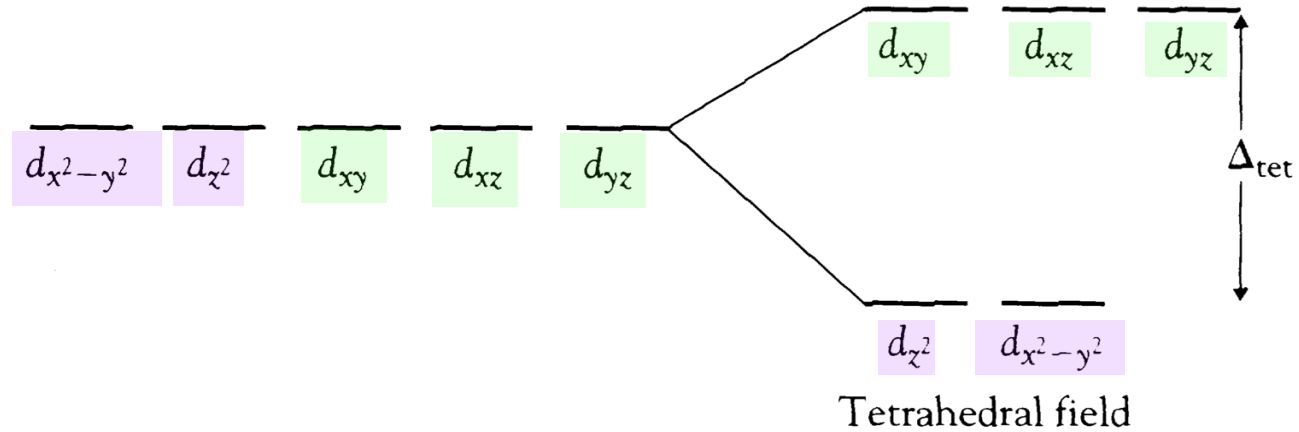
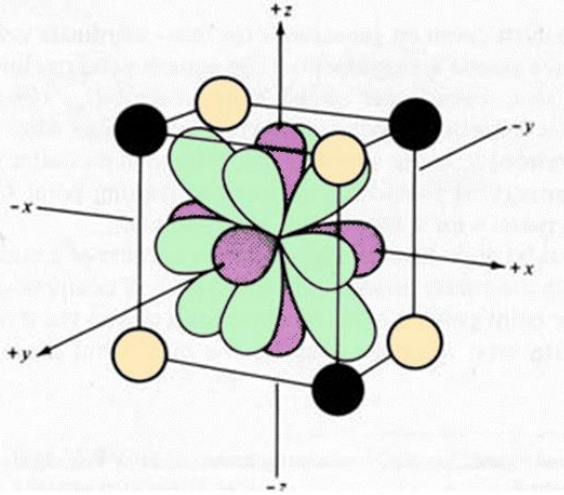
d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

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

Octahedral ligand field



Tetrahedral ligand field



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

Low and high field splitting

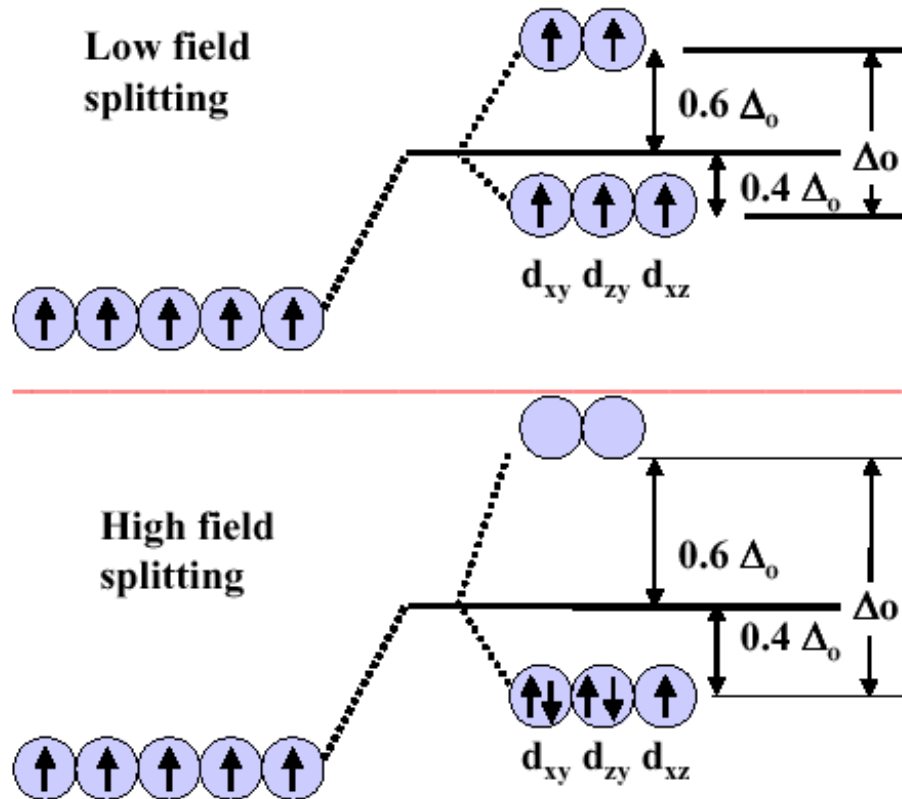
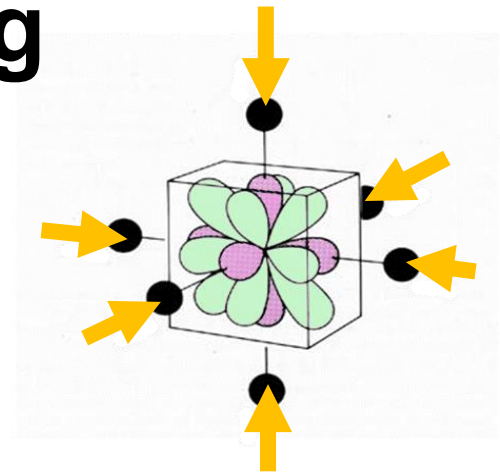


Figure 5. The two cases of crystal field splitting for the octahedral geometry.



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

Also f-orbital energies can split.

Electron distribution

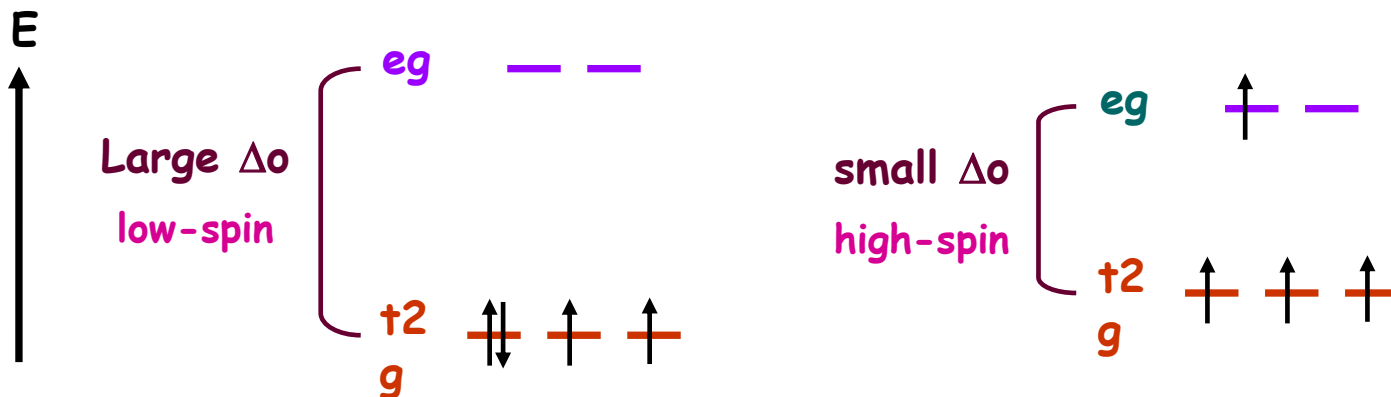
How do the d-electrons occupy split orbitals?

Two contradictory goals:

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

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

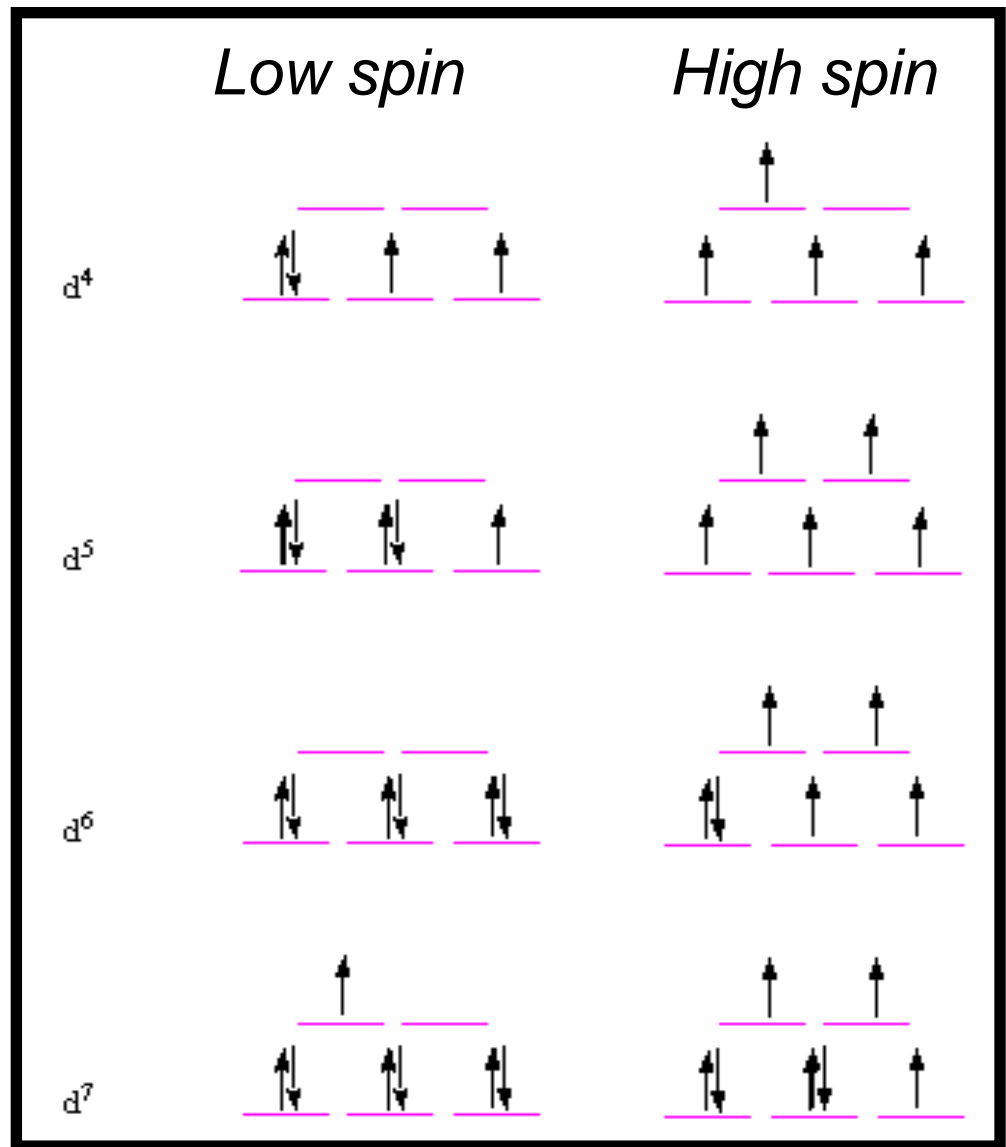
As $\Delta_{\text{tet}} = 4/9 \Delta_{\text{oct}}$, tetrahedral case almost always high-spin



Octahedral
ligand field

Spin state

Let's consider
the OCTAHEDRAL case
(in your lecture exercise
you will consider
the tetrahedral case)



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 and d^{10}) are colourless
- ions with half-filled orbitals (d^5) are colourless or faintly coloured



CFSE: Crystal Field Stabilization Energy

Crystal field stabilization energy

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

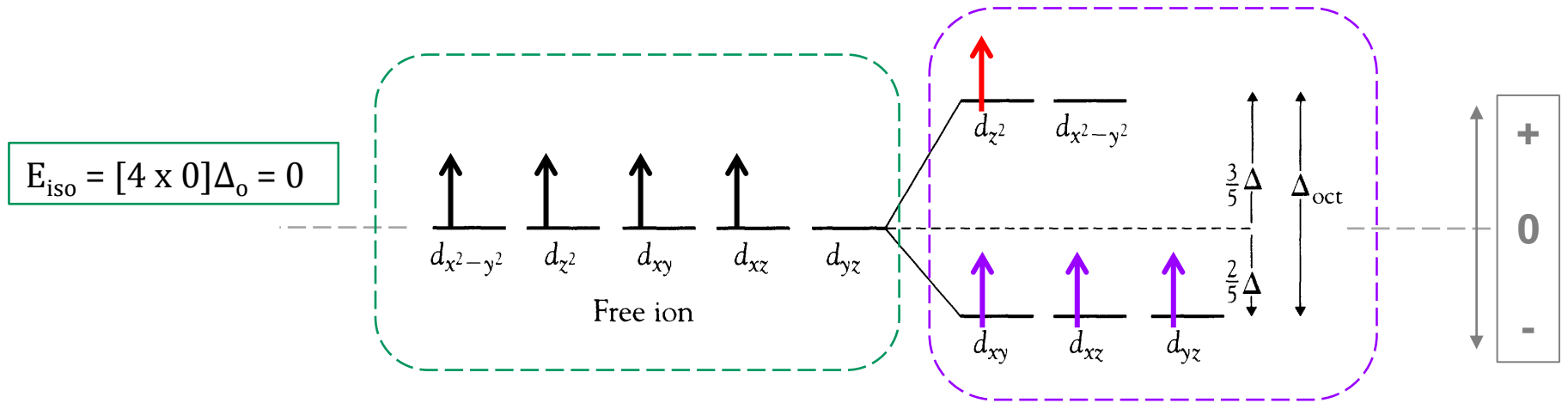
$$CFSE = \Delta E = E_{crystal\ field} - E_{isotropic\ field}$$

- **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

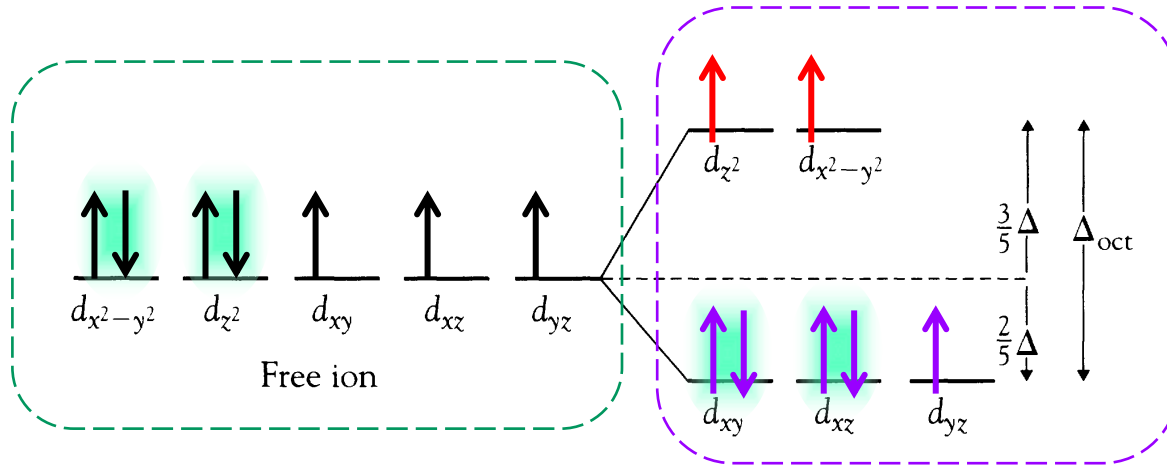


$$CFSE = E_{CF} = [3 \times (-2/5) + 1 \times (3/5)] \Delta_o = -3/5 \Delta_o$$

Calculation example 2: high spin

Octahedral crystal field

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



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

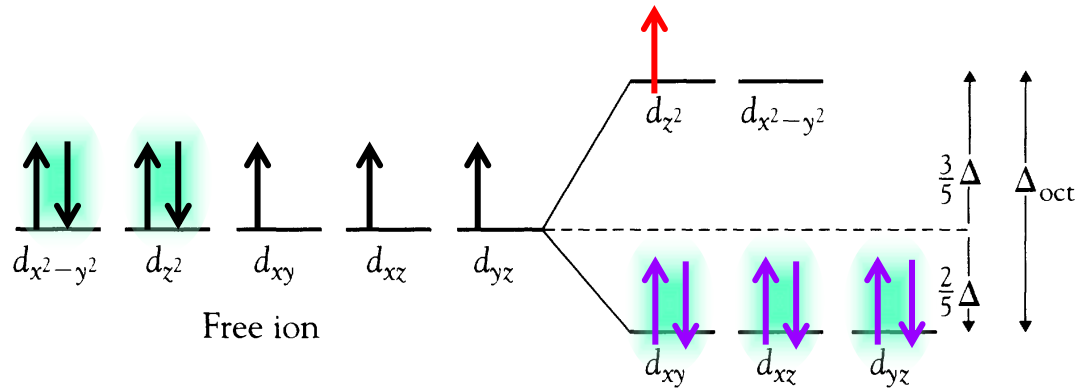
$$E_{\text{CF}} = [5 \times (-2/5) + 2 \times (3/5)] \Delta_o + 2P = -4/5 \Delta_o + 2P$$

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

Calculation example 2: low spin

Octahedral crystal field

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

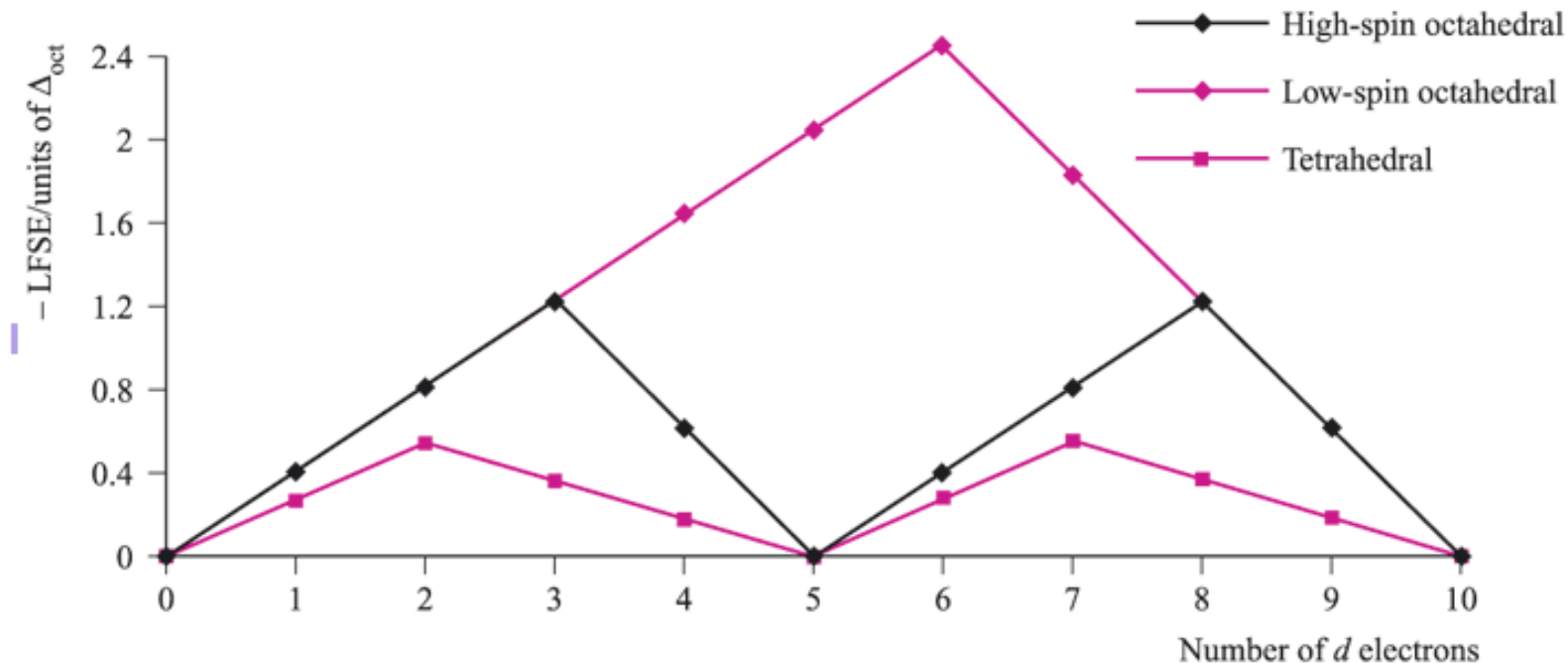


$$E_{\text{iso}} = [7 \times 0]\Delta_o + 2P = 2P$$

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

$$\text{CFSE} = (-9/5 \Delta_o + 3P) - 2P = -9/5 \Delta_o + P$$

General trend of CFSE

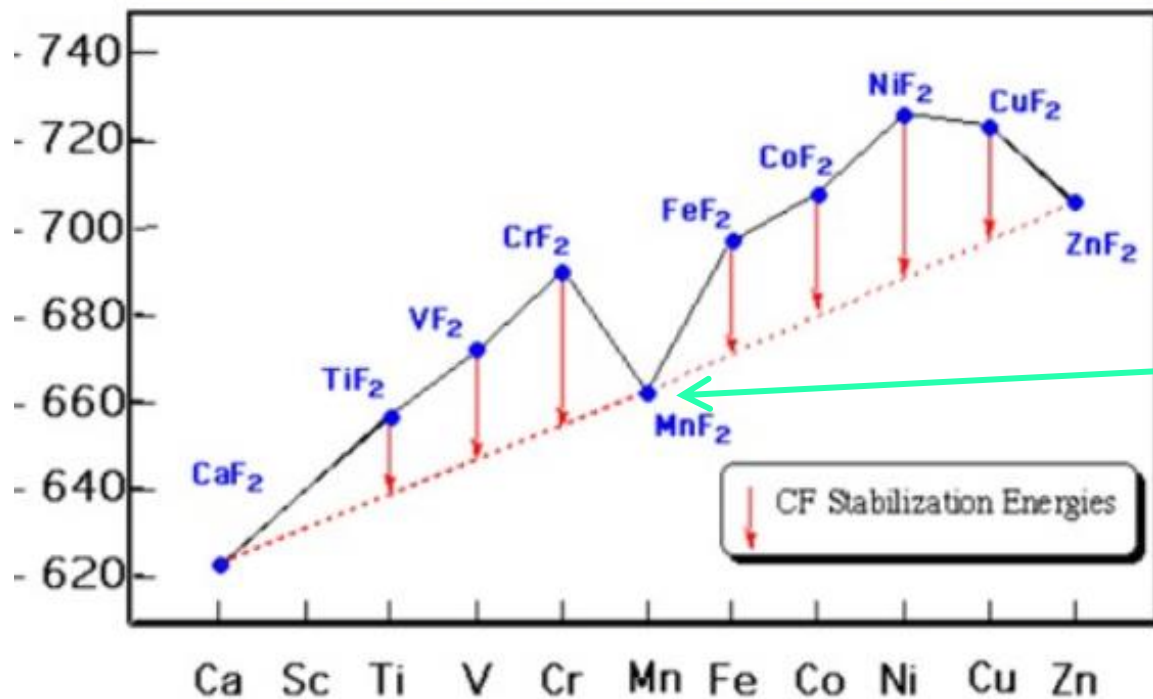


similarities with other thermodynamic energy trends - more info:

https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_%28Inorganic_Chemistry%29/Crystal_Field_Theory/Octahedral_vs._Tetrahedral_Geometries

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.



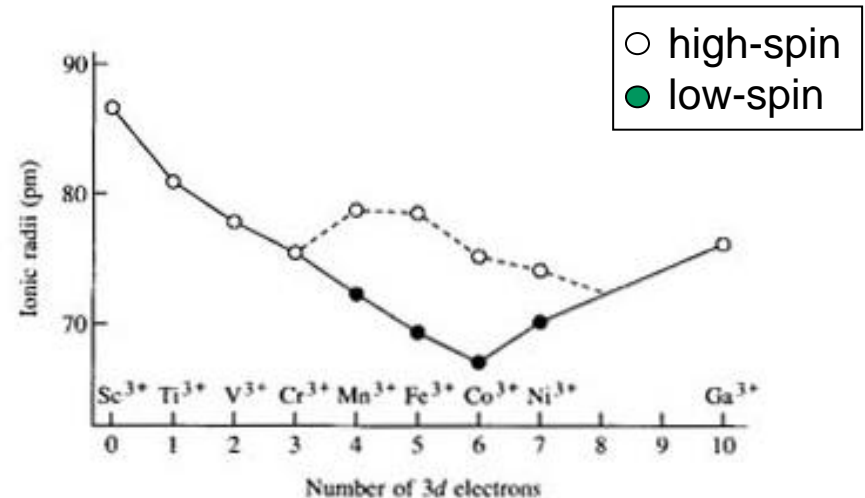
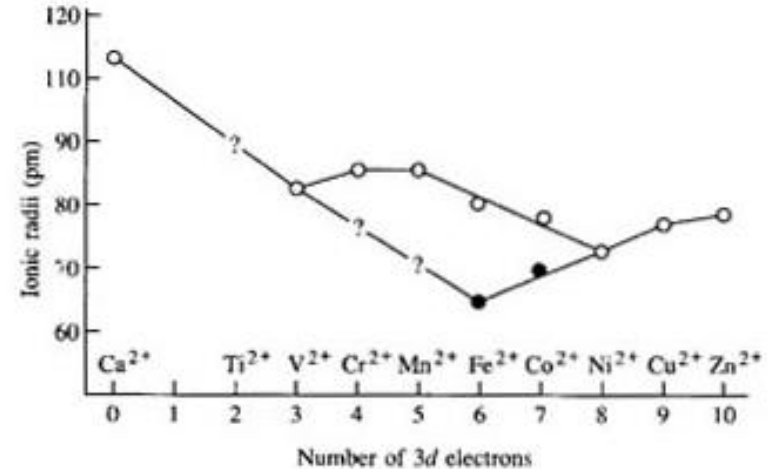
**5 d-electrons
all unpaired**



$$3 \times (-2/5) + 2 \times (3/5) = 0$$

CFSE and ionic radius

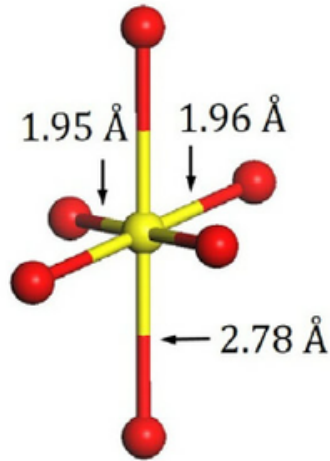
- FOR EXAMPLE: 3d metals in octahedral coordination
- At a fixed oxidation state, ionic radius **decreases** from left to right
- HOWEVER: each electron in e_g orbital **increases** the ionic radii
- Ionic radius depends on spin state !



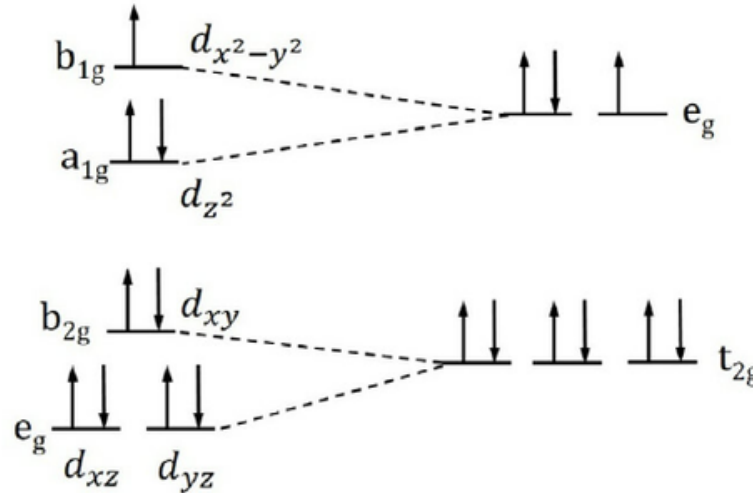
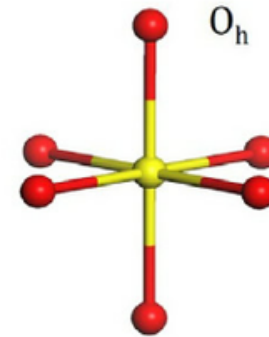
Asymmetric ligand field

Jahn-Teller distortion

Distorted

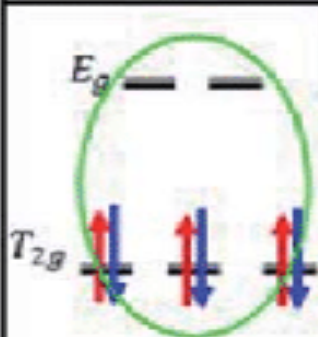
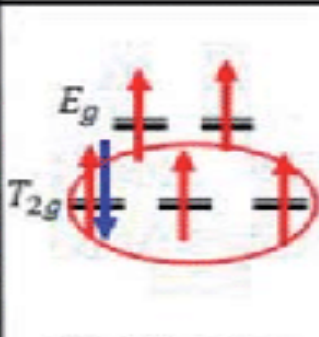
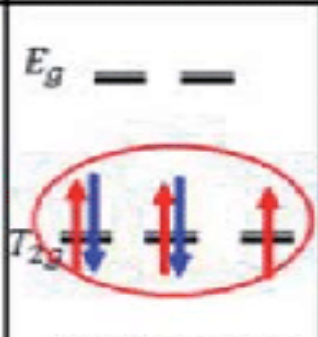
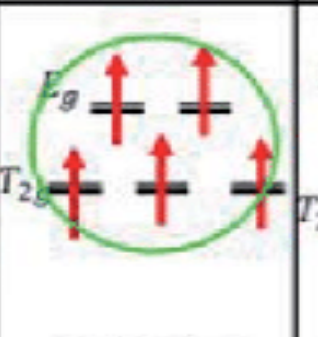
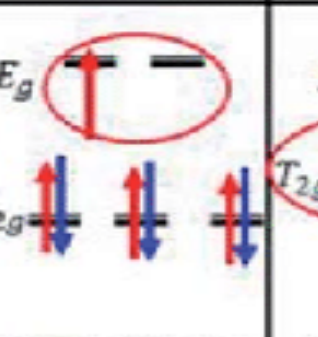
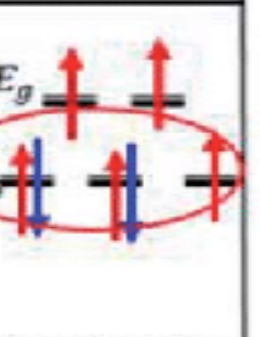
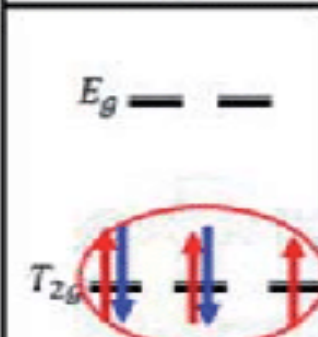
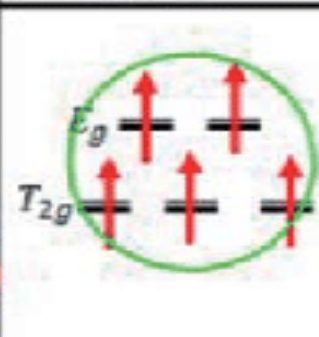
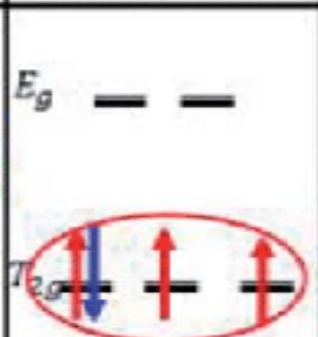
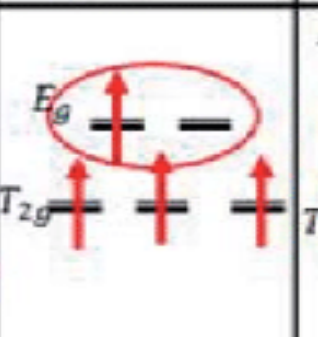
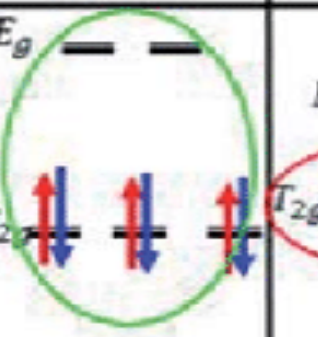
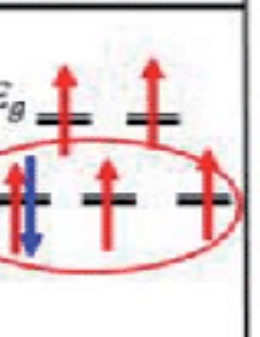


Regular

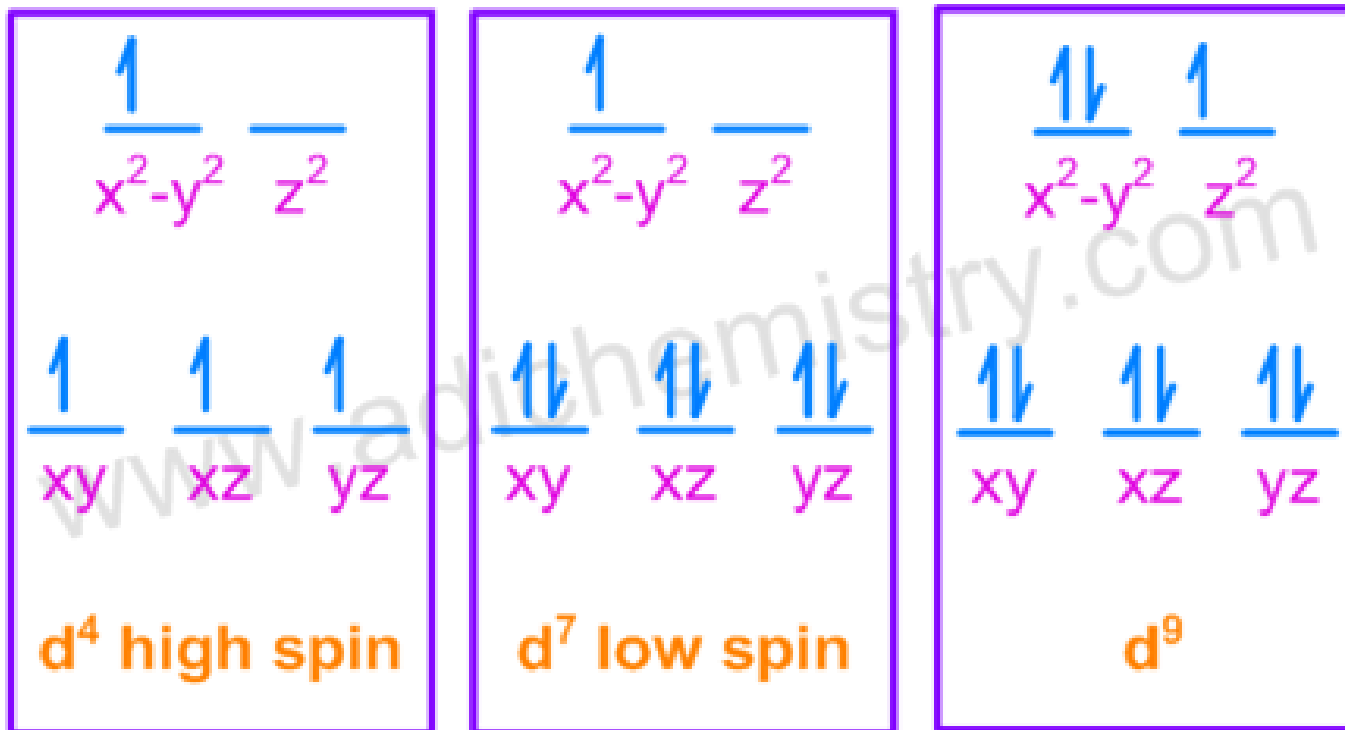


Jahn-Teller distortion

- **1937: Hermann Arthur Jahn & Edward Teller**
- **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 e_g orbitals (as the ligands/anions come closest to these orbitals)**
 - **Distortion (typically elongation) of the octahedron**

Fe(II)		Mn(II)		Co(II)	
Low Spin	High Spin	Low Spin	High Spin	Low Spin	High Spin
 <p><i>No distortion</i></p>	 <p><i>Weak distortion</i></p>	 <p><i>Weak distortion</i></p>	 <p><i>No distortion</i></p>	 <p><i>Strong distortion</i></p>	 <p><i>Weak distortion</i></p>
Fe(III)		Mn(III)		Co(III)	
Low Spin	High Spin	Low Spin	High Spin	Low Spin	High Spin
 <p><i>Weak distortion</i></p>	 <p><i>No distortion</i></p>	 <p><i>Weak distortion</i></p>	 <p><i>Strong distortion</i></p>	 <p><i>No distortion</i></p>	 <p><i>Weak distortion</i></p>

Significant J-T ions



Cr(II)
Mn(III)

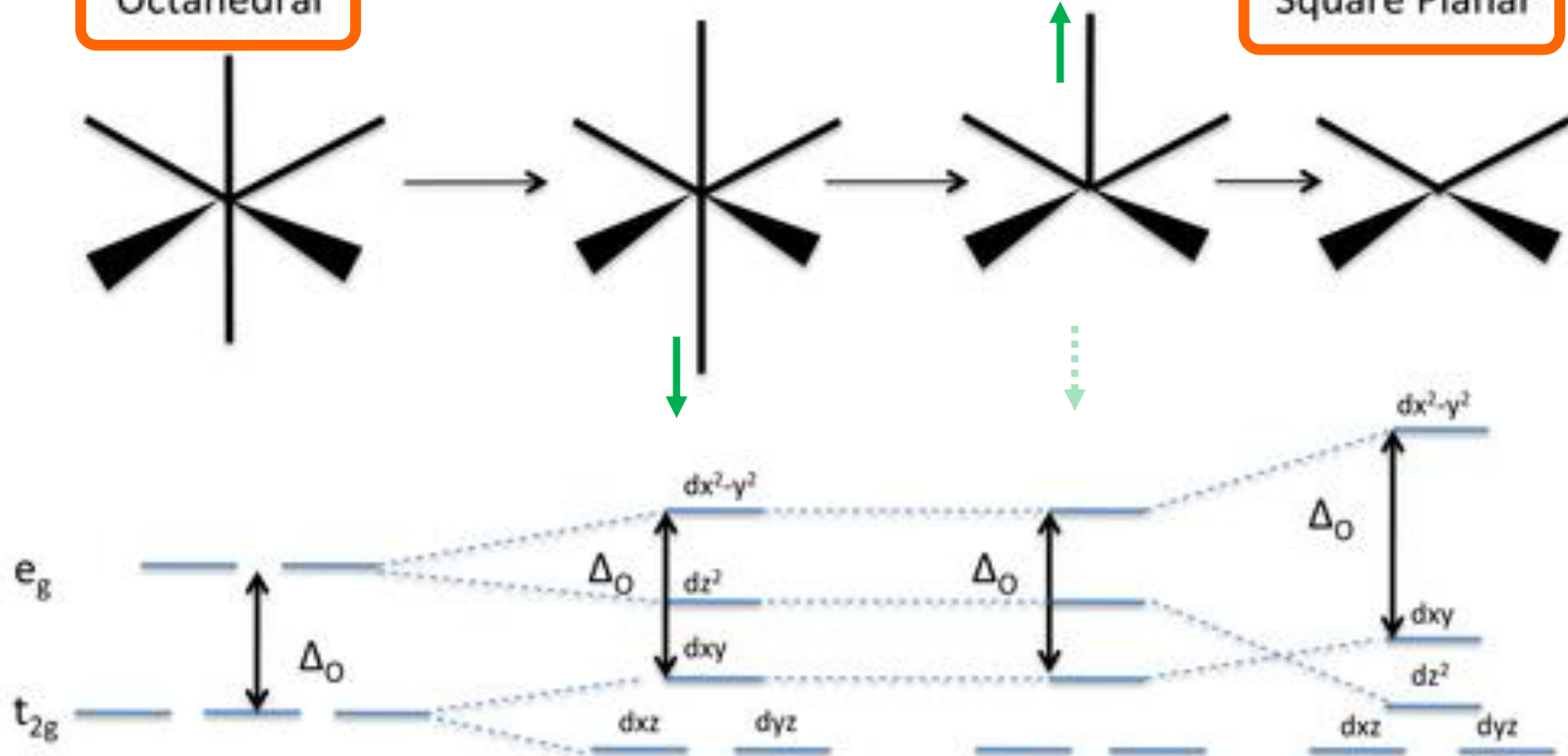
Co(II)
Ni(III)

Cu(II)
Ag(II)

Octahedral elongation

Octahedral

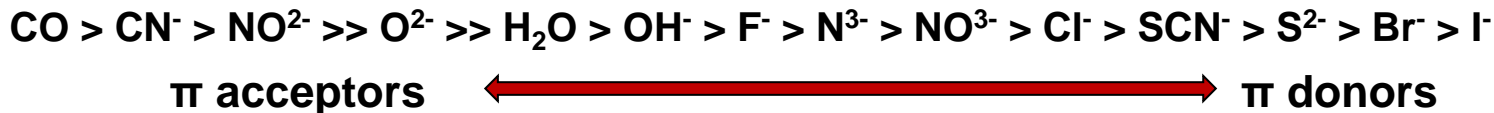
Square Planar



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

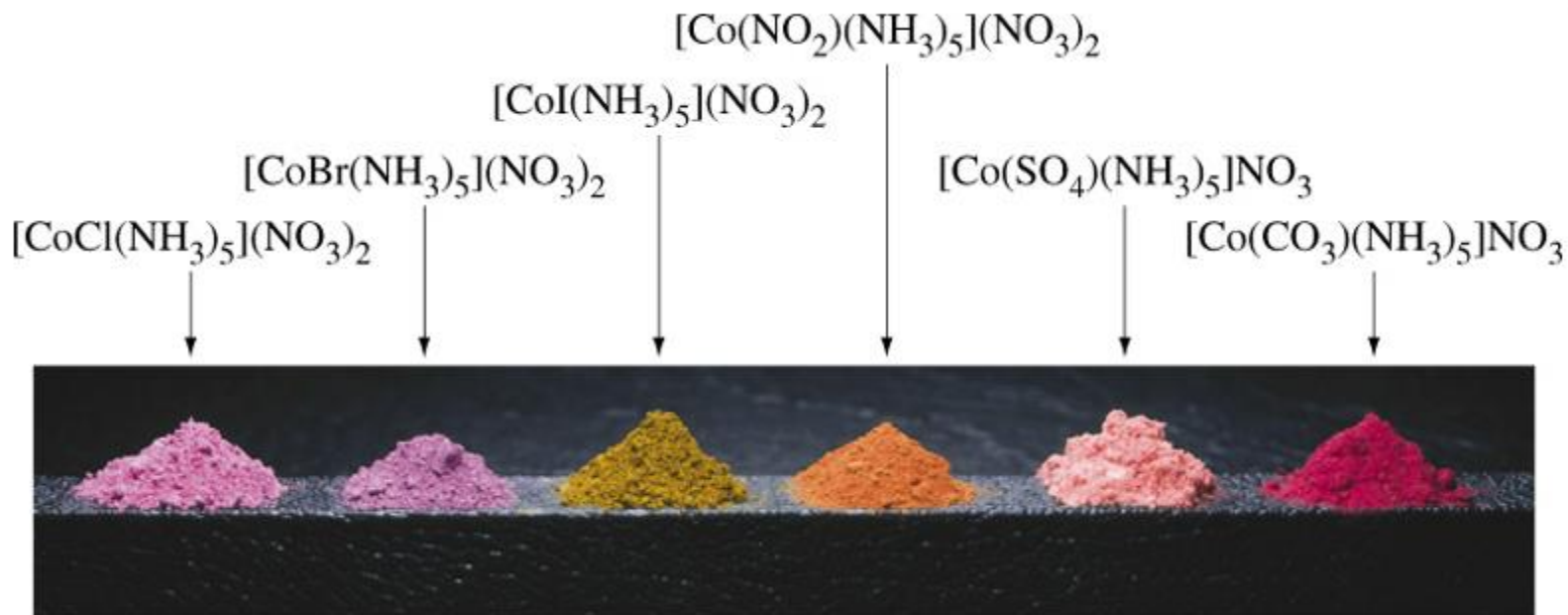


EXAMPLE: For O^{2-} : Δ is still relatively small
→ high-spin configurations common in oxide materials

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

- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$: high-spin → paramagnetic
- $[\text{Fe}(\text{CN})_6]^{4-}$: low-spin → diamagnetic

Ligand change → colour change



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
→ 4d and 5d metals almost always: low-spin

(2) Oxidation state of T

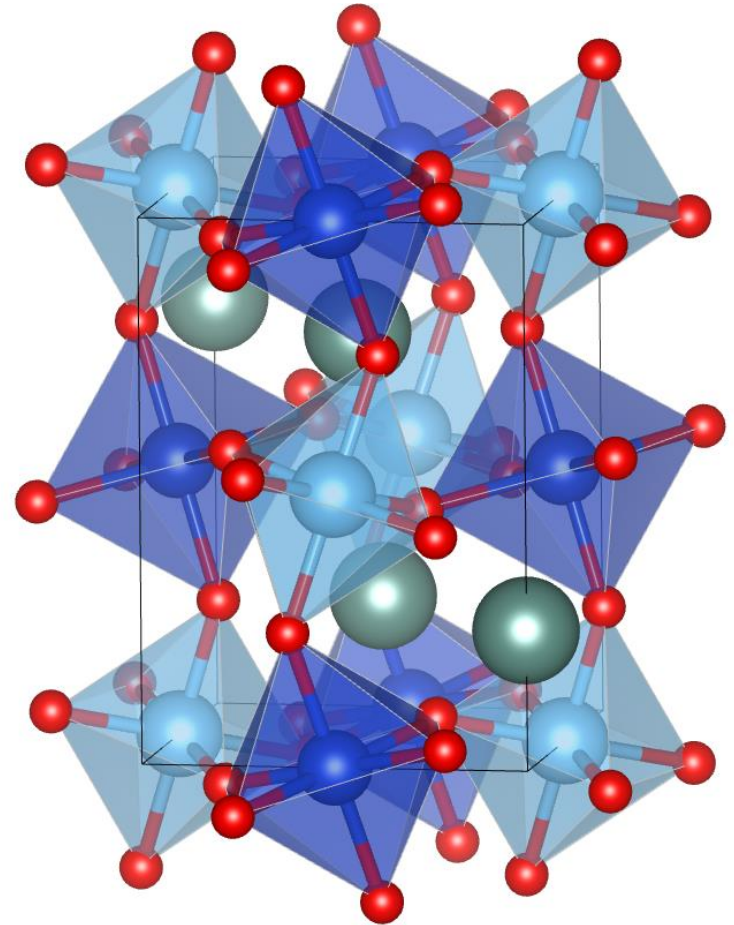
- With increasing oxidation state of T
→ anions become closer
→ larger repulsion between d electrons and anions
→ larger Δ
- 3d metals: when $T^{2+} \rightarrow T^{3+}$, Δ is doubled

(3) Number of anions/ligands

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

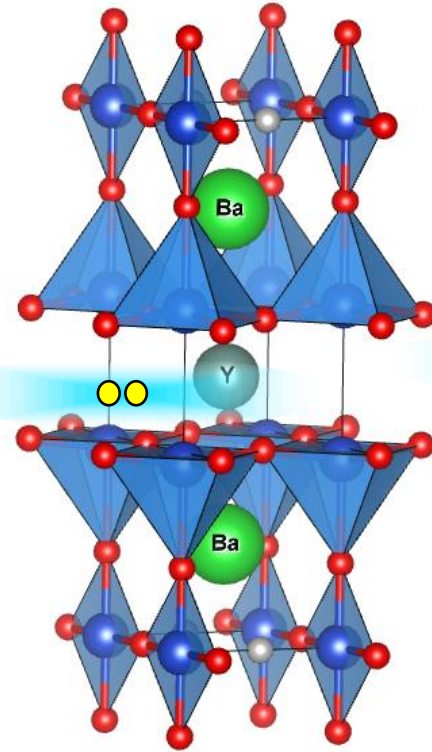
CFT and magnetism

- Perovskite: magnetic **T**-ion in octahedral coordination
- Magnetic interaction depends on orbital connections
- Bonding angle influences orbital overlap geometrically

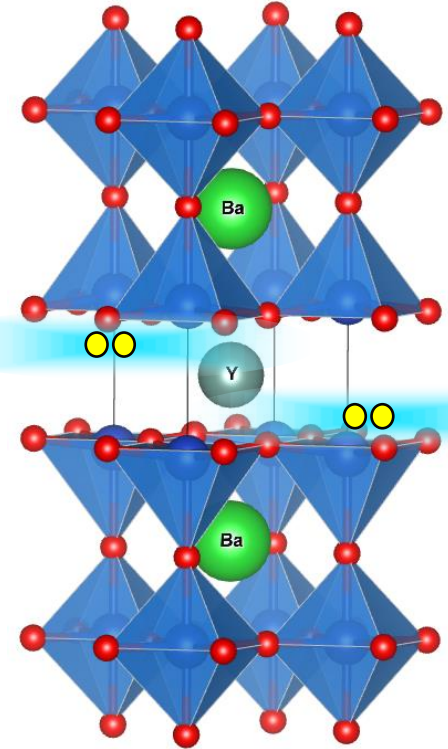


CFT and superconductivity

- Perovskite cousin
- Copper in different coordination environments
- Orbital occupation of copper is key to the formation of Cooper pairs
→ superconduction



$\text{YBa}_2\text{Cu}_3\text{O}_7$



$\text{YBa}_2\text{Cu}_3\text{O}_8$

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
 - \rightarrow orbital identifiers
- When atoms form a bond, the wavefunctions of the atom combine into a new wavefunction \rightarrow the atomic orbitals are replaced by bond orbitals

The solutions to Legendre equation

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

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

A?

Repulsion but no bonding?

An excellent after-class question from last year:

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 Coulomb 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

