

# **Coordination Chemistry II: Theories of Electronic Structure**

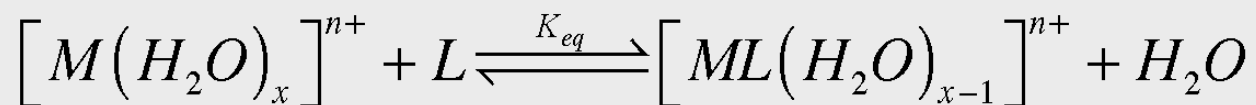
Chapter 10

Friday, November 20, 2015

# Experimental Evidence for Electronic Structure

**Electronic structure models seek to explain (and predict) the trends in experimental data that are observed for coordination complexes**

- Thermodynamic data – formation constants reflect relative M–L bond strengths



- Magnetic moment – coordination complexes often have unpaired electrons, which lead to measurable magnetic moments

$$\mu_{eff} = 2.828\sqrt{\chi T} = g\sqrt{\left[ S(S+1) \right] + \frac{1}{4}\left[ L(L+1) \right]} = \mu_{S+L}$$

$$\cong g\sqrt{\left[ S(S+1) \right]} = \mu_s \quad \boxed{\text{spin-only magnetic moment}}$$

- Electronic spectra – **UV-Vis spectroscopy probes electronic transitions between electronic states of different energy**
- Coordination number and geometry – **in coordination complexes the observed geometries are often strongly influenced by subtle electronic structural considerations in addition to sterics and the number of non-bonding electron pairs (VSEPR considerations)**

# Theories of Electronic Structure

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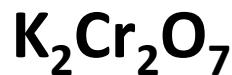
Over the years electronic structural theories have become more and more sophisticated.

- Valence Bond Theory – uses hybrid orbitals, Lewis dot structures, and VSEPR to understand and predict the electronic structure of simple molecules
- Molecular Orbital Theory – assumes that the valence electrons of a molecule are shared by all nuclei in the molecule, forming molecular orbitals analogous to the atomic orbitals of individual atoms
- **Crystal Field Theory** – an electrostatic approach to understanding the electronic spectroscopy of crystals – metal valence electrons are perturbed by negative point charges arranged in a regular coordination geometry – no description of M–L bonding
- **Ligand Field Theory** – combines ideas of crystal field theory and molecular orbital theory to describe the interactions of metal valence orbitals with frontier MOs of the ligands
- **Angular Overlap Method** – an empirical method for estimating the relative frontier orbital energies in LFT calculations by accounting for the relative orientation of the metal and ligand orbitals

# Electronic Structure of Complexes

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Metal complexes are often brilliantly colored and/or paramagnetic. These properties result from the electronic structure of the complexes.



- Crystal Field Theory (simple electrostatic model)
- Ligand Field Theory (more accurate MO model)

# Transition Metals

Group #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
			* Lanthanoids	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			** Actinoids	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

- The **transition elements** are those elements with partially filled  $d$ -orbitals. Groups 3 through 11.
- These elements are all metals → **transition metals**.
- Partially filled  $d$ -orbitals responsible for color and magnetism.

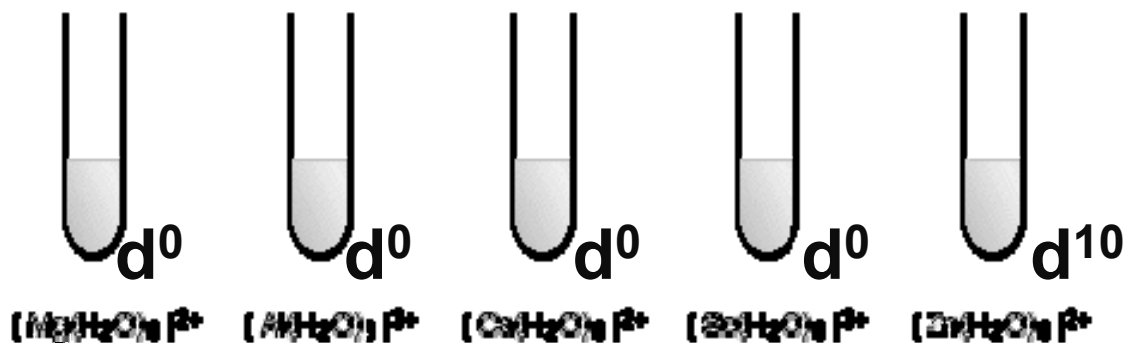
# Origin of Color in Complexes

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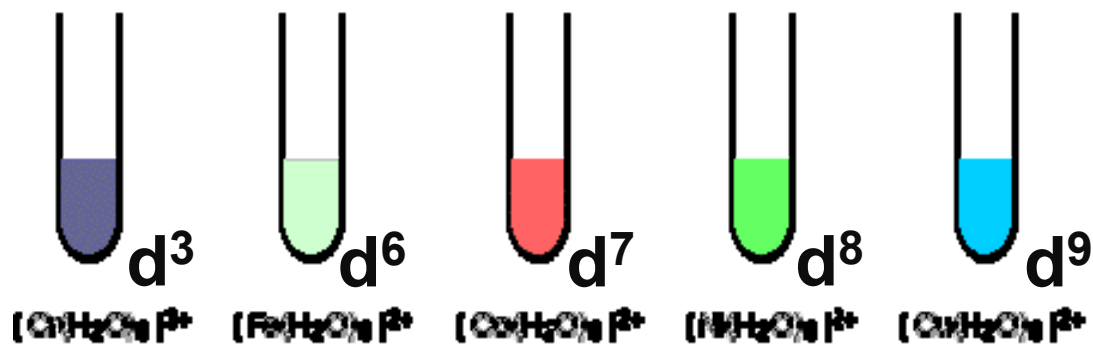
**Color arises from electronic transitions involving *d*-orbitals.**

- color depends on metal and ligand(s) combination.

Metals with totally empty/full *d*-orbitals are colorless.

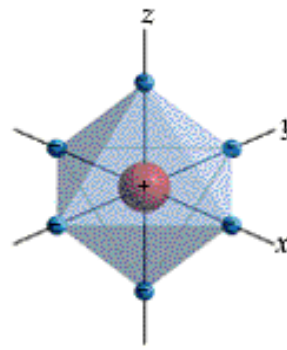


Transition metals with partially filled *d*-orbitals have color.

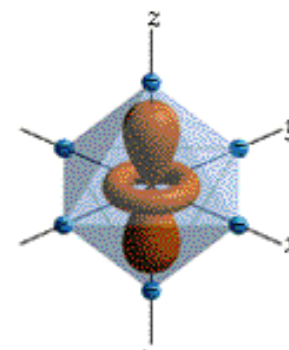


# Crystal Field Theory

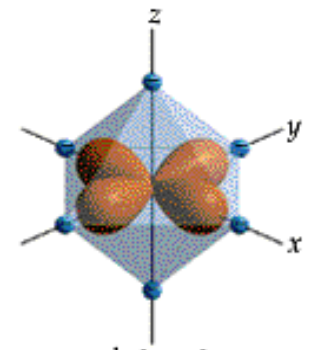
Simple electrostatic theory to explain the color and magnetism of transition metal complexes.



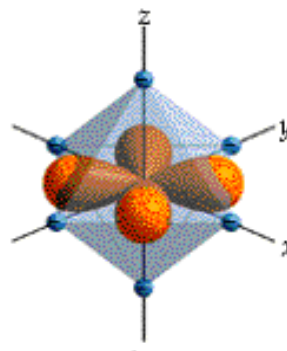
(a)



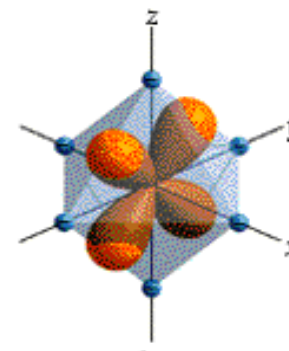
$d_{z^2}$   
(b)



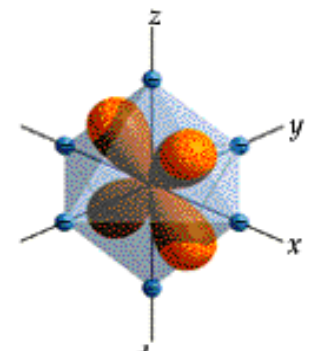
$d_{x^2 - y^2}$   
(c)



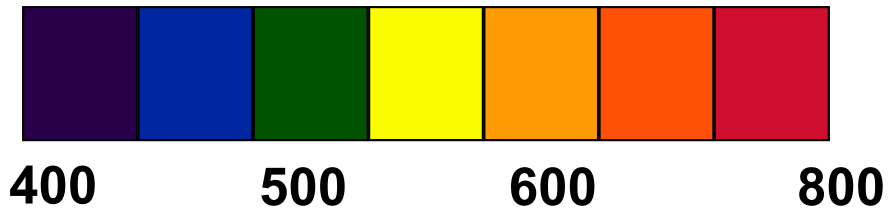
$d_{xy}$   
(d)



$d_{yz}$   
(e)



$d_{xz}$   
(f)



# Transition Metal Gems

Many gemstones owe their color to transition metal ions



Corundum ( $\text{Al}_2\text{O}_3$ ): Colorless

**Cr** → **Al** : **Ruby**

**Mn** → **Al**: **Amethyst**

**Fe** → **Al**: **Topaz**

**Ti & Co** → **Al**: **Sapphire**

Beryl ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ): Colorless

**Cr** → **Al**: **Emerald**

**Fe** → **Al**: **Aquamarine**

CFT was originally developed to explain the colors of these crystals.

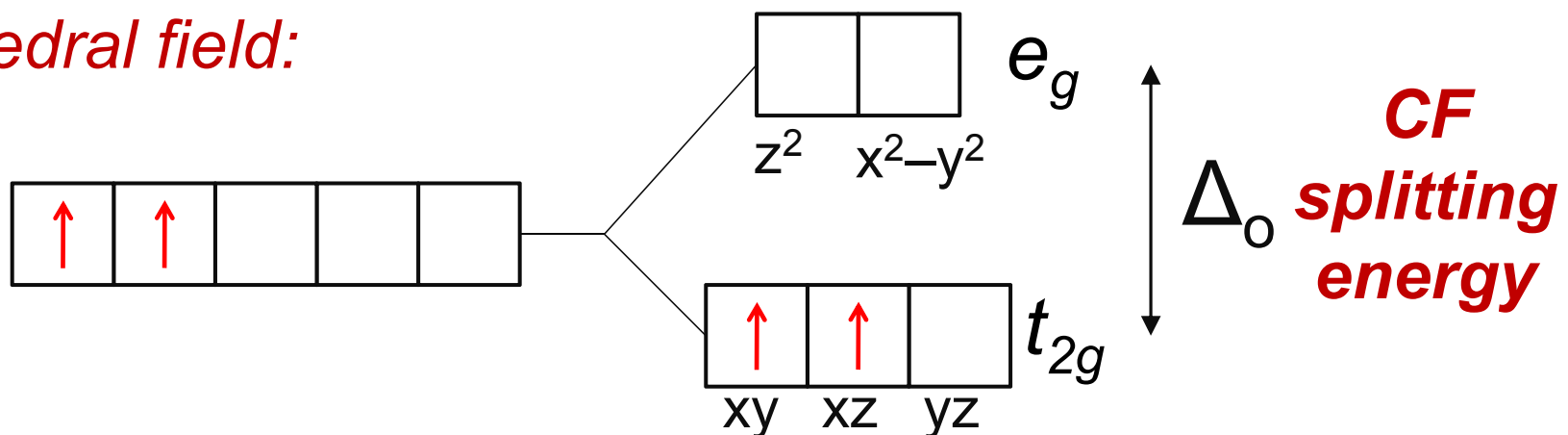


# Crystal Field Theory

- *Basic idea*: ligands act as point negative charges, and the energy of electrons in the metal orbitals depends on the amount of electrostatic repulsion with ligands.
- *Factor #1*: Metal (usually positive) is stabilized by bonding to negative ligands to form complex.
- *Factor #2*: The *d*-orbitals have different shapes. Electrons in the *d*-orbitals are repelled to different degrees by the ligands.

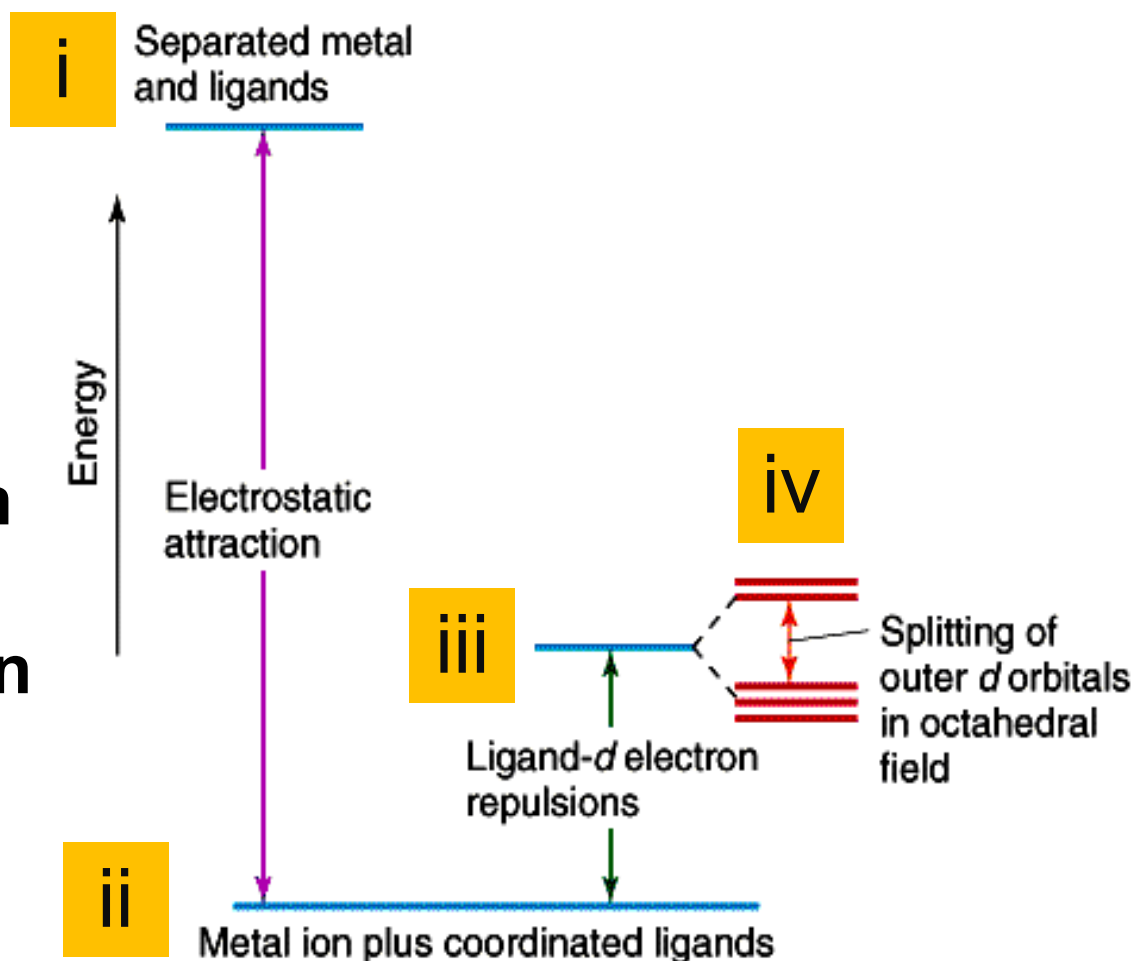
➔ The five *d*-orbitals will ***split in the crystal field***.

*in an octahedral field:*



# CFT Energetics

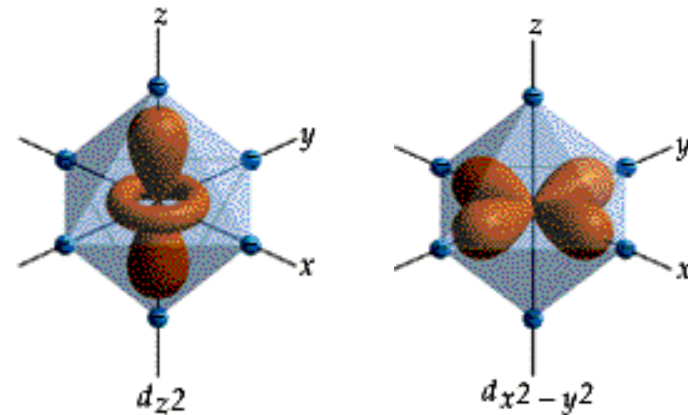
- i) Separated metal and ligands → high energy**
- ii) Coordinated metal complex → stabilized**
- iii) Include ligand-*d* electron repulsion → isotropic destabilization**
- iv) Include orbital shapes → degeneracy lifted**



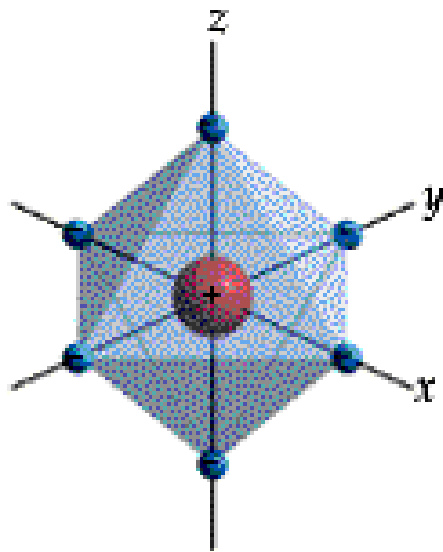
# Field Splitting of d-Orbitals

## octahedral field

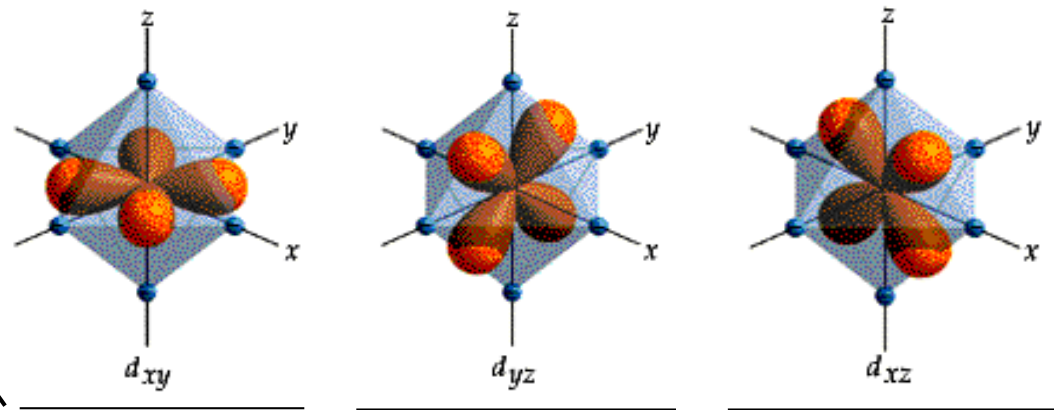
The **degeneracy** of the d-orbitals is lifted.



$e_g$   
d-orbitals pointing directly at ligands experience more electrostatic repulsion and are **destabilized** (higher energy)



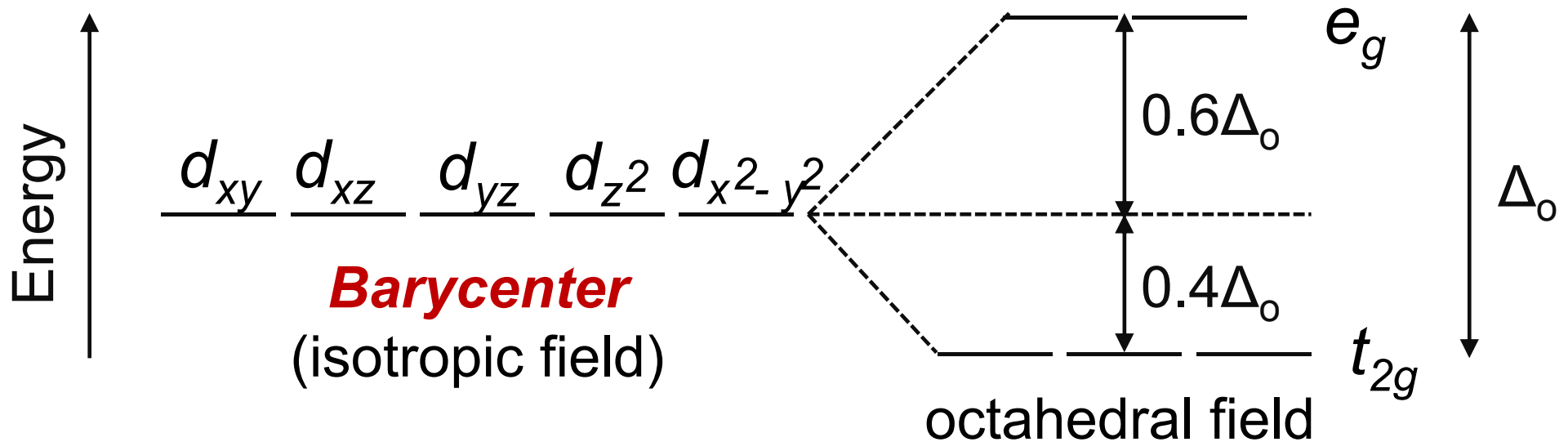
energy (including electron-ligand repulsions) before accounting for orbital shapes



$t_{2g}$   
d-orbitals pointing between the ligands experience less electrostatic repulsion and are **stabilized** (lower energy)

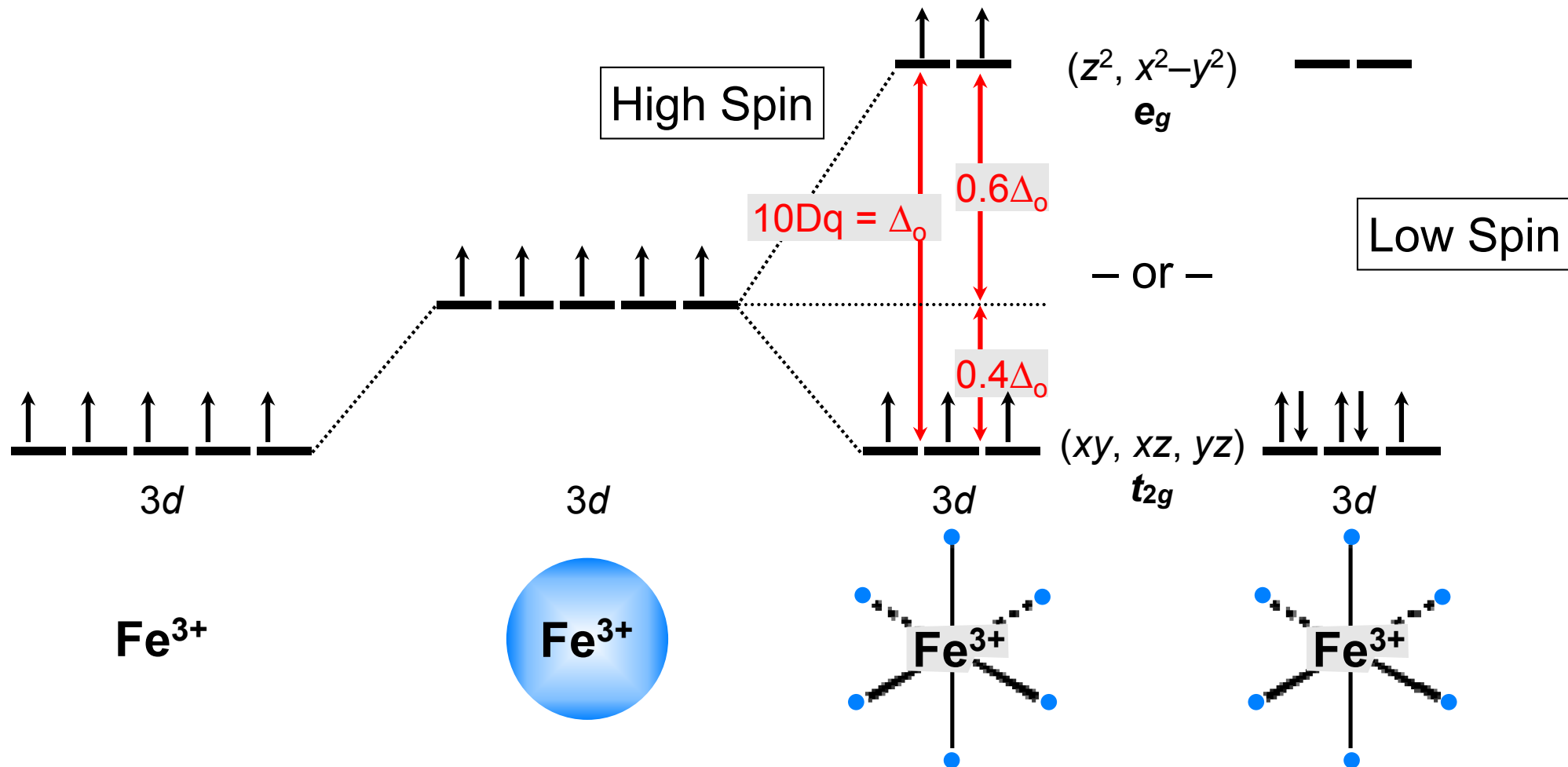
# Field Splitting of d-Orbitals

## octahedral crystal field splitting diagram



- The Barycenter is the average energy of the  $d$ -orbitals.
  - Three orbitals stabilized by  $0.4\Delta_o = -1.2\Delta_o$ .
  - Two orbitals destabilized by  $0.6\Delta_o = 1.2\Delta_o$ .energy conserved
- The energy gap is called  $\Delta_o$  (also “10 Dq”), the crystal field splitting energy.
- The size of  $\Delta_o$  depends on **ligand strength** and metal ion.

# Crystal Field Theory



**Crystal Field Stabilization Energy (CFSE) is the energy difference for the given electron configuration in the crystal field compared to the spherical (isotropic) field:**

$$CFSE = \left( \# e_{t_{2g}} \right) (-0.4\Delta_o) + \left( \# e_{e_g} \right) (0.6\Delta_o)$$

# Calculating CFSE

CFSE is the energy difference for the given electron configuration in the crystal field compared to the spherical (isotropic) field:

$$CFSE = \left( \# e_{t_{2g}} \right) (-0.4\Delta_o) + \left( \# e_{e_g} \right) (0.6\Delta_o)$$

High Spin



$(z^2, x^2-y^2)$   
 $e_g$

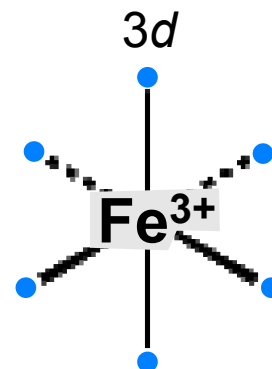
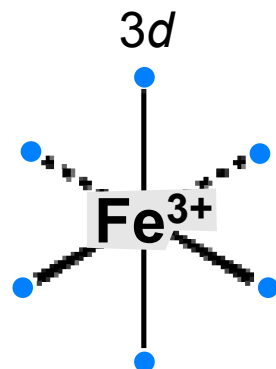
Low Spin



Seems like low spin should always win! It would, except that it costs energy to pair two electrons in a single orbital ( $\Pi_{total}$  see 2.2.3)



$(xy, xz, yz)$   
 $t_{2g}$



$$CFSE(HS) = (3)(-0.4\Delta_o) + (2)(0.6\Delta_o)$$

$$= 0$$

$$CFSE(LS) = (5)(-0.4\Delta_o) + (0)(0.6\Delta_o)$$

$$= -2\Delta_o$$