

**Unit 3 – Deck 5**

# Inorganic

**Orbitals interactions in metals: Crystal Field Theory**



# Last Time

- Equilibrium Constants of Coordination Complexes
- Chelate Effect
- Polydentate Ligands
- Ionic Size and Charge
- Hard and Soft Acid Base Theory

# Lecture Topics

- Valence Bond Theory (atomic orbital hybridization schemes)
- Crystal Field Theory
- High-Spin States & Low-Spin
- Octahedral Field Splitting
- Crystal Field Stabilization Energy

# Common Models of Bonding in Molecules

**VSEPR** – Predict 3-D shapes by counting valence and bonding electrons

**HSAB** – Predict favorability of interaction between Lewis acids and bases based on charge density, electronegativity, and polarizability.

**Valence Bond Theory** – Model for bonding between atoms. Predicts magnetic properties and sometimes coordination geometry.

**Molecular Orbital Theory** – Model for bonding throughout a molecule

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**Crystal Field Theory** – Predict electronic spectra and magnetic properties and stability trends by pretending ligands are point charges that destabilize *d*-orbitals

**Ligand Field Theory** – MO theory (called ligand field theory when discussing metal ligand bonding interactions)

# Valence Bond Theory

Describes one way of picturing \*how\* the bonding occurs

Describes the geometry predicted by VSEPR

The atoms combine their “pure” valence shell atomic orbitals ( $s$ ,  $p$ ,  $d$ , and  $f$ ) to form a new set of orbitals to use in bonding.

- The process is called hybridization
- The resulting orbitals are called hybrid orbitals

*Hybridization is a fiction that provides a reasonable approximation of the molecule's wavefunction near an atom. Using this approach valence bond theory over emphasizes electron localization.*

# Can We Apply VB Theory?

An empty hybrid orbital on the metal center can accept a pair of electrons from a ligand to form a  $\sigma$ -bond.

The hybridization of the  $p$  or  $d$  orbitals depends on the orientation of the orbitals within the molecule.

# VBT for different molecular geometries

Coordination number	Geometry	Orbitals involved	Hybrid name	Example
2	Linear	$s, p_z$	$sp$	$[Ag(NH_3)_2]^+$
3	Trigonal planar	$s, p_x, p_y$	$sp^2$	$[HgI_3]^-$
4	Tetrahedral	$s, p_x, p_y, p_z$	$sp^3$	$[FeBr_4]^{2-}$
4	Square planar	$s, p_x, p_y, d_{x^2-y^2}$	$sp^2d$	$[Ni(CN)_4]^{2-}$
5	Trigonal bipyramid	$s, p_x, p_y, p_z, d_{z^2}$	$sp^3d$	$[CuCl_5]^{3-}$
5	Square pyramid	$s, p_x, p_y, p_z, d_{x^2-y^2}$	$sp^3d$	$[Ni(CN)_5]^{3-}$
6	Octahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$	$sp^3d^2$	$[Co(NH_3)_6]^{3+}$
6	Trigonal prism	$s, d_{xy}, d_{yz}, d_{xz}, d_{z^2}, d_{x^2-y^2}$ or $s, p_x, p_y, p_z, d_{xz}, d_{yx}$	$sd^5$ or $sp^2d^2$	$[Zr(CH_3)_6]^{2-}$
7	Pentagonal bipyramid	$s, p_x, p_y, p_z, d_{xy}, d_{x^2-y^2}, d_{z^2}$	$sp^3d^3$	$[V(CN)_7]^{4-}$
7	Capped trigonal prism	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{z^2}$	$sp^3d^3$	$[NbF_7]^{2-}$
8	Cubic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, f_{xyz}$	$sp^2d^3f$	$[PaF_8]^{3-}$
8	Dodecahedral	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{z^2}$	$sp^2d^4$	$[Mo(CN)_8]^{4-}$
8	Square antiprism	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$	$sp^2d^4$	$[TaF_8]^{3-}$
9	Tricapped trigonal prism	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{z^2}, d_{x^2-y^2}$	$sp^2d^5$	$[ReH_9]^{2-}$

# Example

Assign the hybridization state for each atom in propylene.



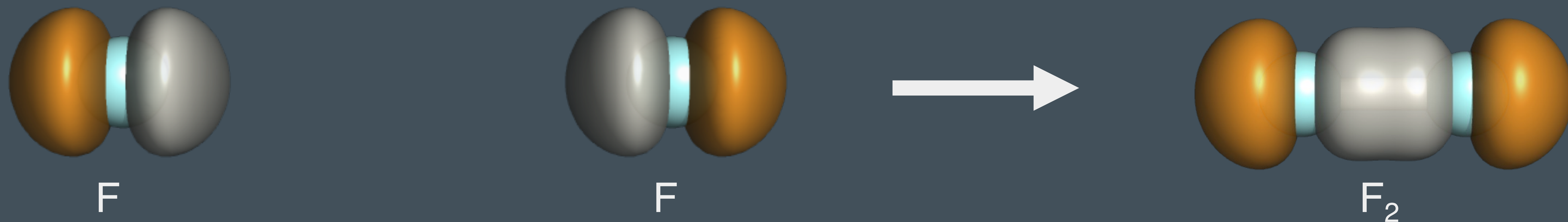
# Molecular Orbital Theory

Wave functions are calculated to predict bonding in MO Theory

**Atomic Orbitals** are combined to form **Molecular Orbitals**

Methods include: LCAO & Tight Binding

Electrons are delocalized in orbitals across multiple atoms



# VBT vs. MOT

VBT and MOT are quantitatively equivalent descriptions of electronic structure

VB: number of orbitals is conserved

MO: number of orbitals is conserved

VB: Atomic orbitals form hybridized orbitals that interact with neighboring atoms that are also hybridized.

MO: Molecular orbitals are composed across multiple atoms

# VBT vs. MOT

VB: electron's correlation/localization is emphasized (on central atom)

MO: electrons delocalization is emphasize, electron correlation is deemphasized

VB: predicts  $\sigma$  and  $\pi$  bonds

MO: predicts  $\sigma$  and  $\pi$  bonds

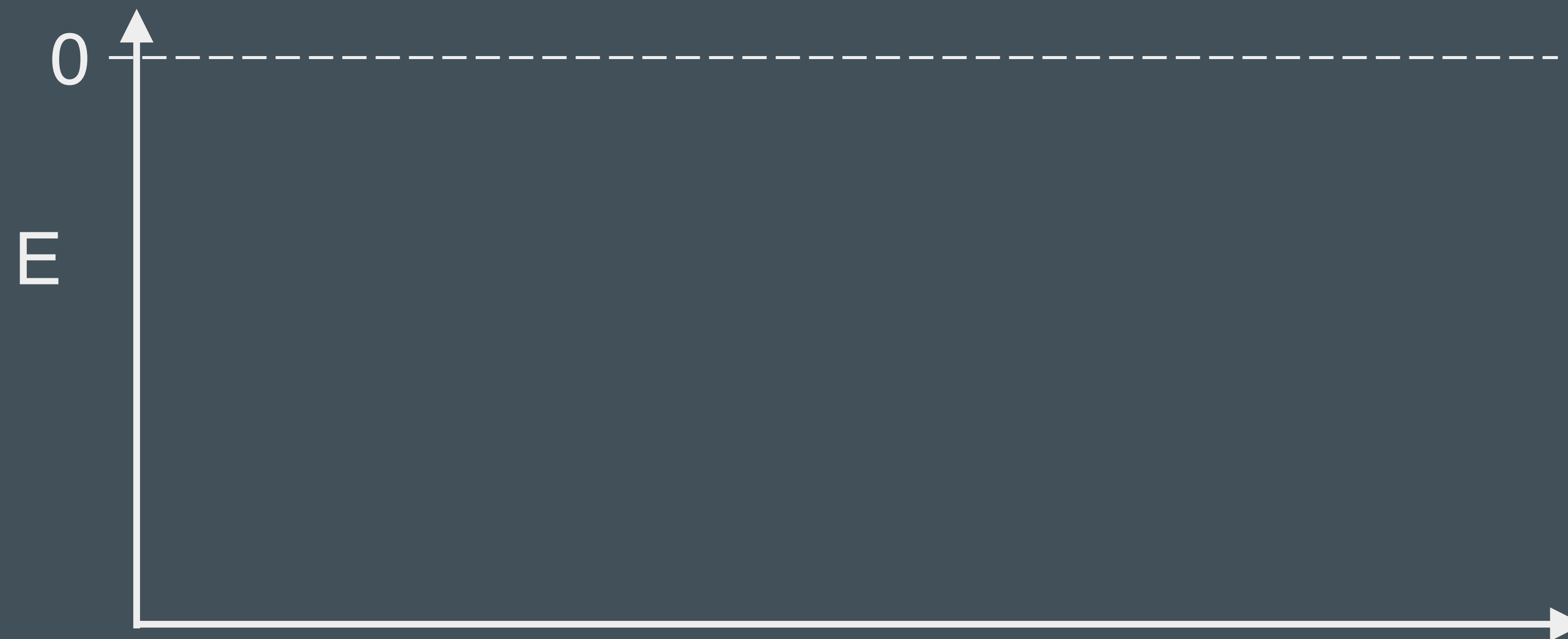
MO: Qualitative mental models tend to provide reasonable predictions of electronic structures and electronic transitions more readily.

# Spherically symmetric electronic environments

Last semester, we told you that the five  $d$ -orbitals were degenerate for an atom in vacuum.

This is also true for a  $ML_6$  complexes with infinitely long bonds.

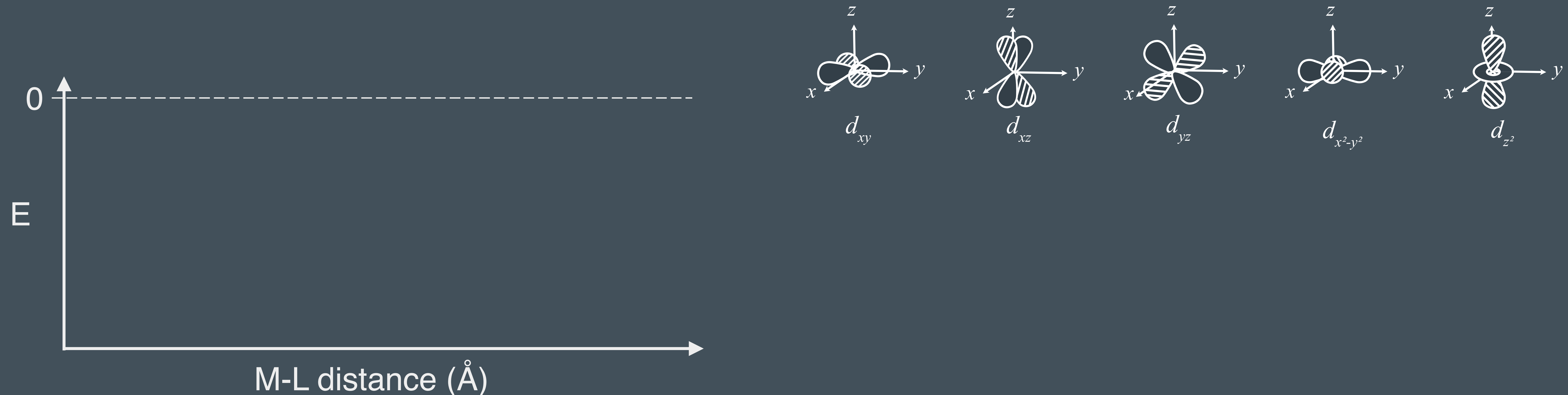
If an electrostatic field is spherically symmetric, the degenerate  $d$ -orbitals will be destabilized (raised).



# Octahedrally shaped charge fields

As the bond distance of an  $ML_6$  complex decrease, the  $d$ -orbitals of the metal ion are destabilized by the ligands' electrons. Ligand electrons are stabilized.

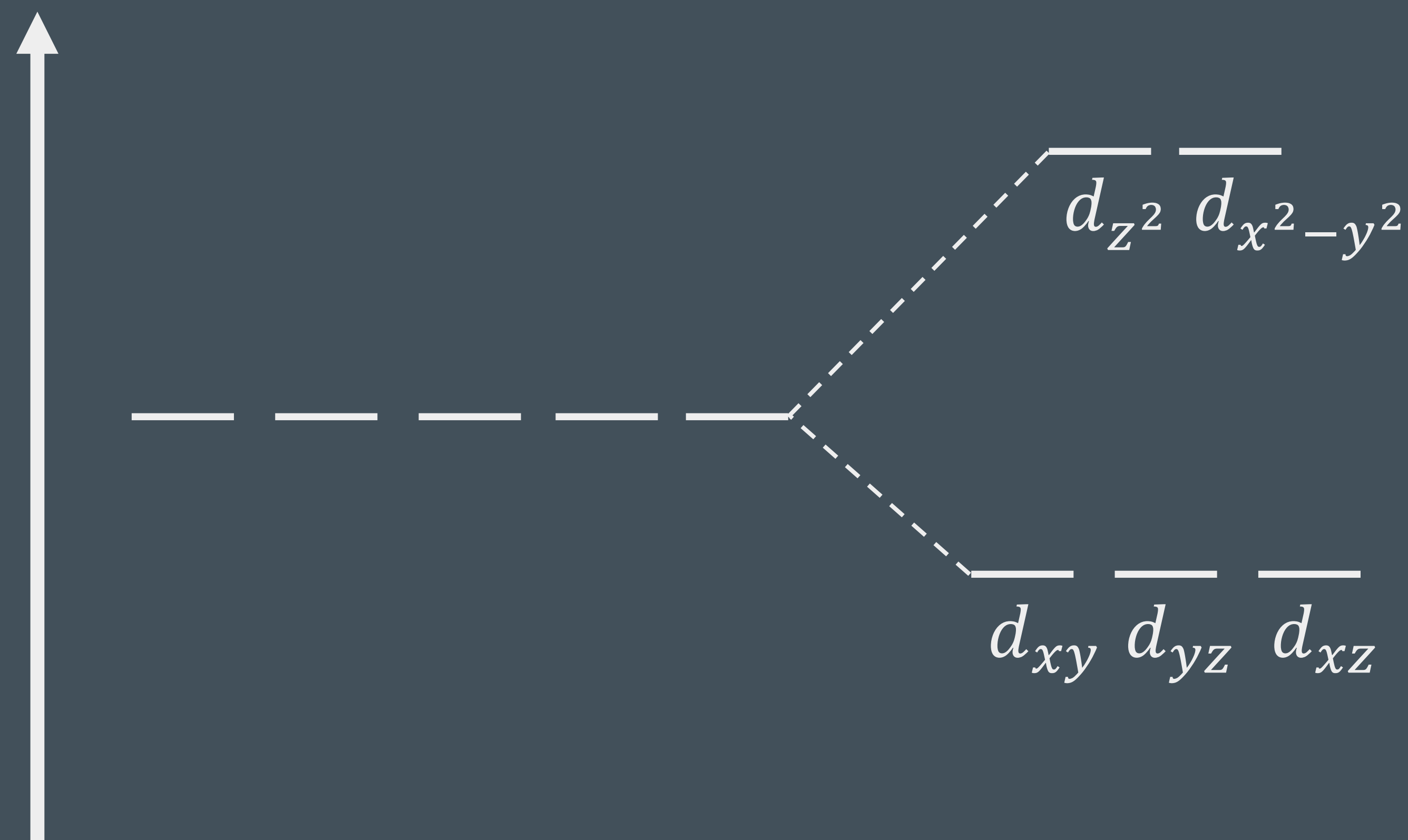
In octahedral molecular geometry, the  $d_{z^2}$  and  $d_{x^2-y^2}$  atomic orbitals for the metal ion point directly at the ligands.



# Orbital Overlap - Octahedral

When there is orbital overlap, the atomic orbitals on the metal ion are destabilized. This is due to the electron-electron repulsions.

When the atomic orbitals on the metal center point between the ligands, the atomic orbitals are stabilized.



# Summary (Orbital Notation) – Octahedral Field

The  $d_{z^2}$  and  $d_{x^2-y^2}$  atomic orbitals are destabilized because they point directly at the ligands.

The  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals are stabilized to in balance with the destabilization of  $d_{z^2}$  and  $d_{x^2-y^2}$  .

# Crystal Field Theory (CFT)

Invented to explain the colors and emissive properties of crystals

CFT is sort of an **electrostatic** model. “Ligand electrons create an electric field around the metal center.”

Ligands simplified as point charges. **No metal-ligand covalent interactions and no charge transfer.**

The pattern of the splitting of the *d*-orbitals depends on the crystal field, which is determined by the arrangement and type of ligands.



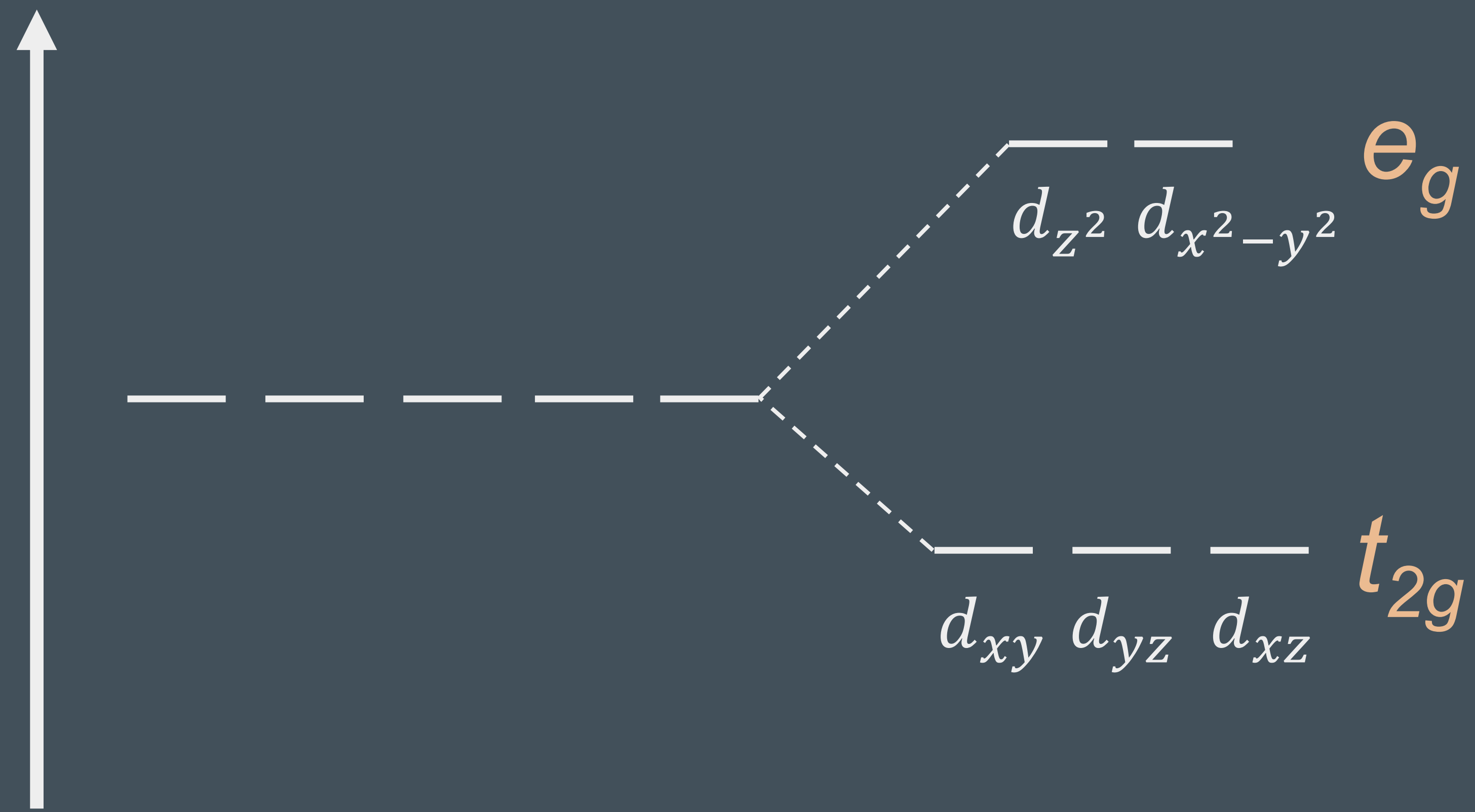
# The Crystal Field

In chemistry, we use the term “**the crystal field**” to describe the electric field that exists around a metal ion in a complex.

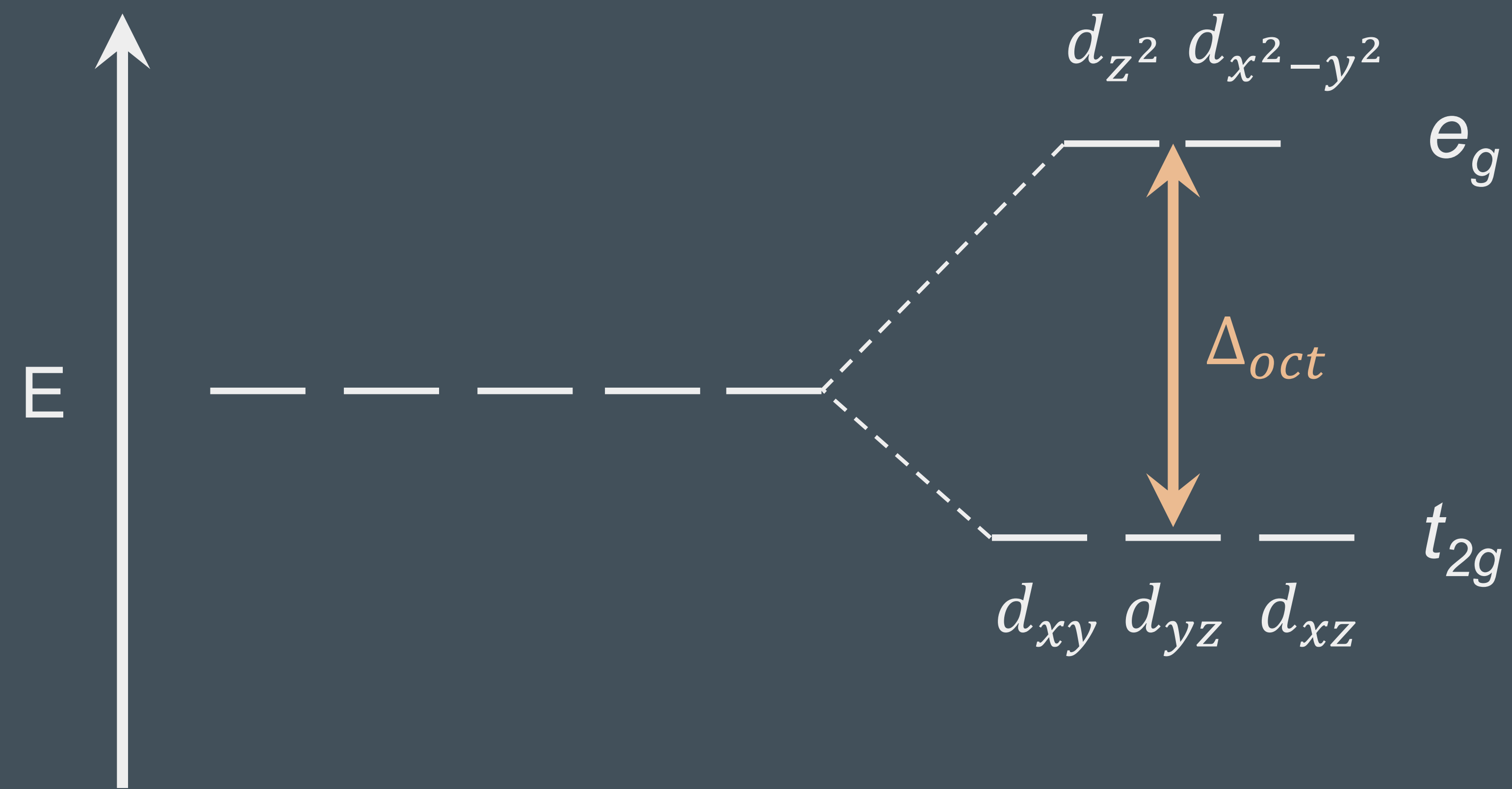
It has two extremes: weak field and strong field

$$\Delta_{\text{oct}} (\text{weak field}) < \Delta_{\text{oct}} (\text{strong field})$$

# Octahedral Crystal Field ( $O_h$ ) – Symmetry



# Octahedral Crystal Field ( $O_h$ )



The magnitude of  $\Delta_{oct}$  is determined by the strength of the crystal field.

# The Spectrochemical Series - Ligands

$\Delta_{oct}$  increases along spectrochemical series:



Weak Field  
Ligands  
(Smaller  $\Delta_{oct}$ )

Strong Field  
Ligands  
(Larger  $\Delta_{oct}$ )

# The Spectrochemical Series – Metal ions

The spectrochemical series is an empirical generalization that can also be applied to metal ions.

Mn(II) < Ni(II) < Co(II) < Fe(III) < Cr(III) < Co(III) < Ru(III) < Mo(III) < Rh(III) < Pd(II) < Ir(III) < Pt(IV)

Weak Field  
Ligands  
(Smaller  $\Delta_{\text{oct}}$ )

Strong Field  
Ligands  
(Larger  $\Delta_{\text{oct}}$ )

*Most often in conversation “The spectrochemical series” is mentioned in the context of ligands*

# Experimental $\Delta_{\text{oct}}$ Data – Absorption Spectroscopy

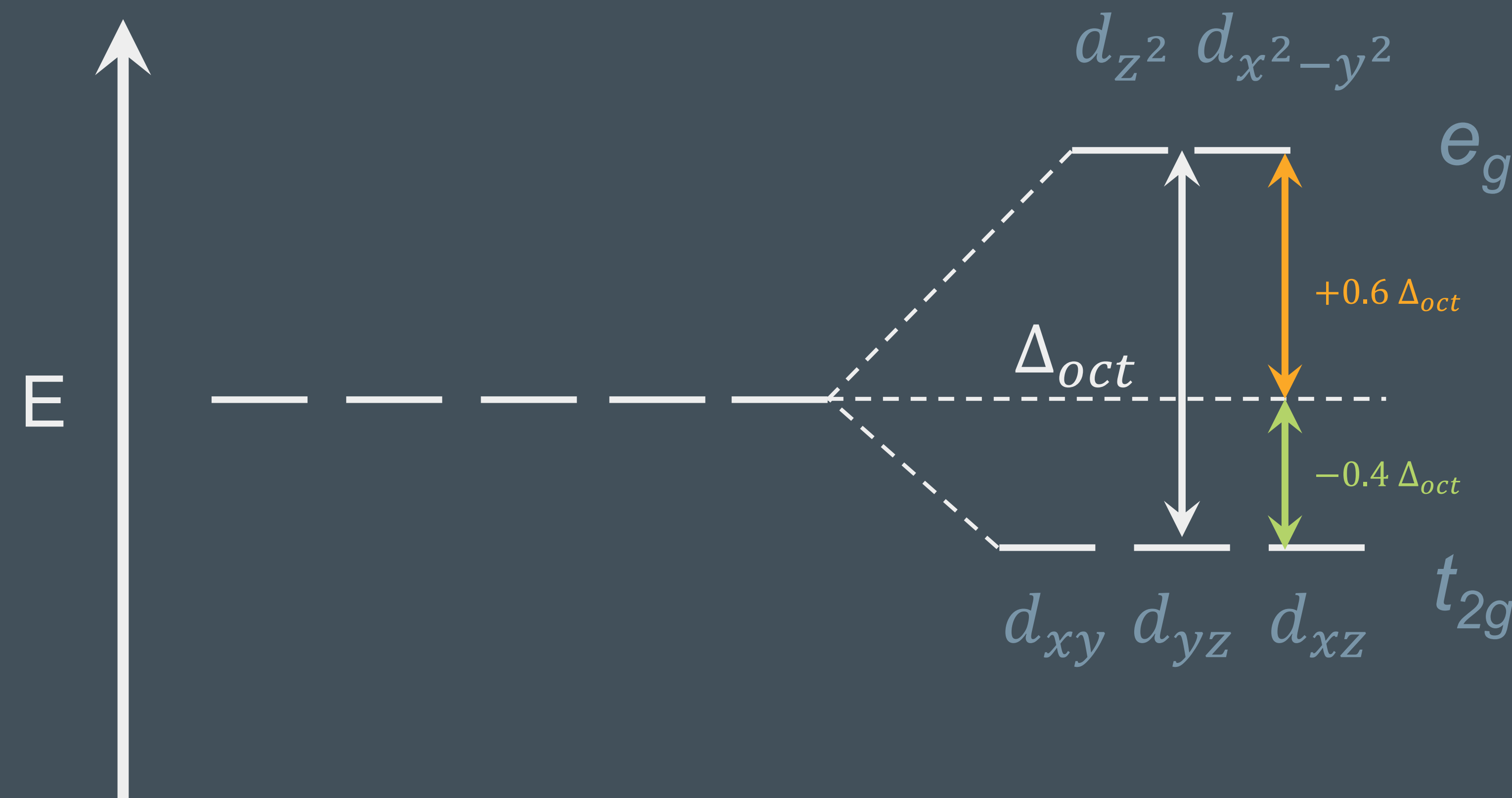
Complex	$\Delta_{\text{oct}} / \text{cm}^{-1}$
$[\text{Fe}(\text{OH}_2)_6]^{3+}$	13,700
$[\text{Fe}(\text{OH}_2)_6]^{2+}$	9,400
$[\text{Fe}(\text{CN})_6]^{3-}$	35,000
$[\text{Fe}(\text{CN})_6]^{4-}$	33,800

Complex	$\Delta_{\text{oct}} / \text{cm}^{-1}$
$[\text{Co}(\text{NH}_3)_6]^{3+}$	22,900
$[\text{Co}(\text{NH}_3)_6]^{2+}$	10,200
$[\text{Co}(\text{OH}_2)_6]^{3+}$	18,200
$[\text{Co}(\text{OH}_2)_6]^{2+}$	9,300

# Stabilization Energy

Crystal field theory determine the crystal field stabilization energy (CFSE).

The **CFSE** is the difference in energy between the  $d$  electrons in an octahedral crystal field and the  $d$  electrons in a spherical crystal field.



*Explains why CrO is more stable than MnO*

# CFSE Calculations ( $O_h$ )



d<sup>1</sup> system



d<sup>2</sup> system



d<sup>3</sup> system



# CFSE Calculations ( $O_h$ )



$d^4$  system  
Low spin  
(strong field)



$d^4$  system  
high spin  
(weak field)

# Electron-Pairing Energy

The energy required to transform two electrons with parallel spin in different degenerate orbitals into spin-paired electrons in the same orbital.

The energy penalty (electron repulsion + exchange) paid to put 2 electrons in a single orbital

# Electron-Pairing Energy

Pairing Energy depends on two main factors:

1. The loss in the exchange energy which occurs upon pairing the electrons
2. The coulombic repulsion between the spin-paired electrons

# P for Low Spin Complexes ( $O_h$ )



$d^4$  system  
Low spin  
(strong field)

$$\text{CFSE} = -1.6\Delta_{\text{oct}} + P$$



$d^4$  system  
high spin  
(weak field)

$$\text{CFSE} = -0.6\Delta_{\text{oct}}$$

If  $\Delta_{\text{oct}} > P$  low spin configuration is preferred

# Example CFSE Calculations ( $O_h$ )



$d^6$  system  
Low spin  
(strong field)



$d^6$  system  
high spin  
(weak field)

# Example

Predict the spin for the below octahedral complexes. Will they have a large or small  $\Delta_{oct}$ ?



# The Spectrochemical Series - Ligands

$\Delta_{oct}$  increases along spectrochemical series:



Weak Field  
Ligands  
(Smaller  $\Delta_{oct}$ )

Strong Field  
Ligands  
(Larger  $\Delta_{oct}$ )



The spectrochemical series is an empirical generalization that can also be applied to metal ions.

# Next Time

- Ligand Field Theory
- Dative interactions between transition metals and  $\pi$ -donating ligands
- Dative interactions between transition metals and  $\pi$ -accepting ligands (metal  $d\pi$ -backbonding)
- Ligand Field Stabilization Energies (LFSE)
- Demystifying the spectrochemical series
- The Irving-Williams Series