

Coordination Chemistry: Bonding Theories

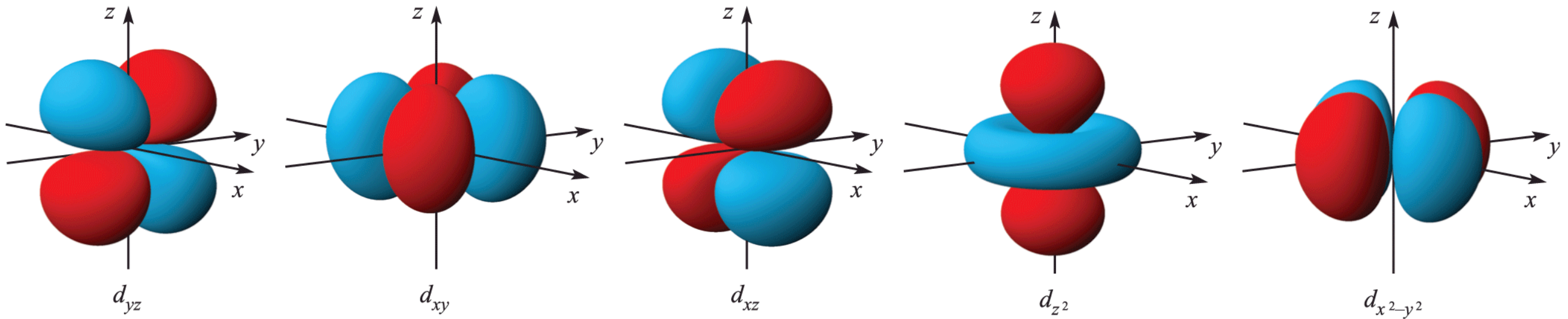
Crystal Field Theory

Chapter 20

Review of the Previous Lecture

1. We discussed different types of isomerism in coordination chemistry
 - **Structural or constitutional isomers**-Bonds not between the same atoms
 - **Stereo or configurational isomers**-Bonds between the same atoms
2. We then focused on the relationship between coordination number and structures in coordination compounds
3. We discussed the factors that favor low and high coordination numbers

1. Chemistry of the d-orbitals



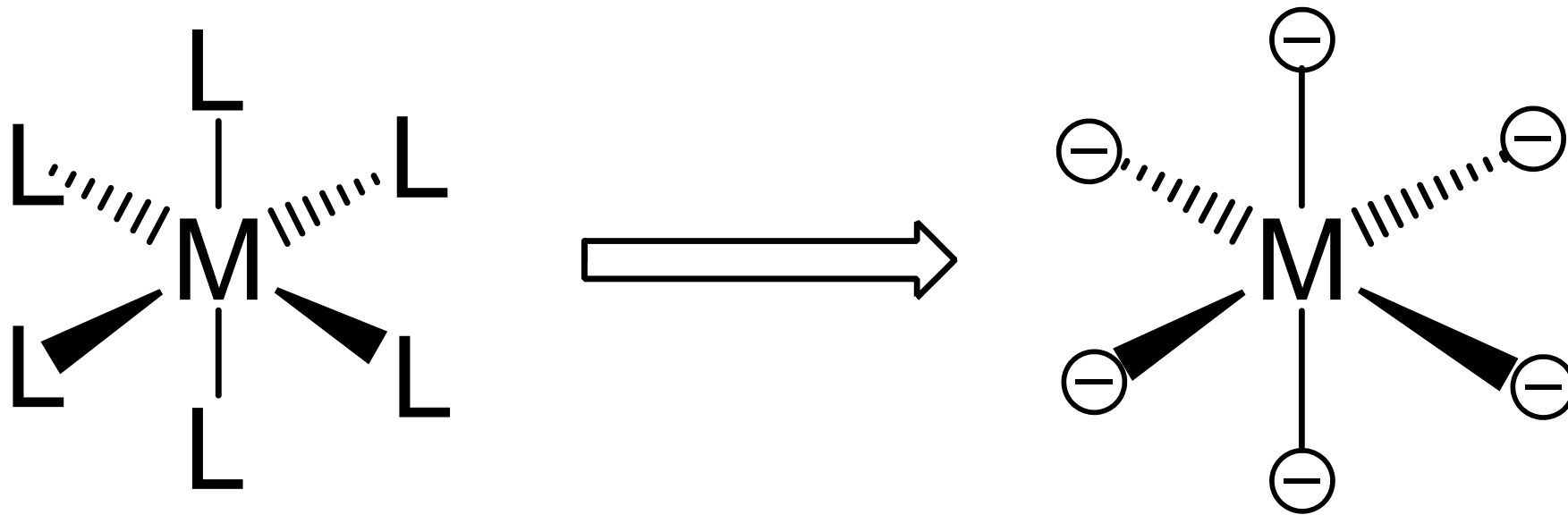
For transition metals in row n of the periodic table, we consider the effect of ligand interactions with the $n-1$ d-orbitals.

- If in $n = 4$, then we focus on the five 3d orbitals.
- If in $n = 5$, then we focus on the five 4d orbitals.

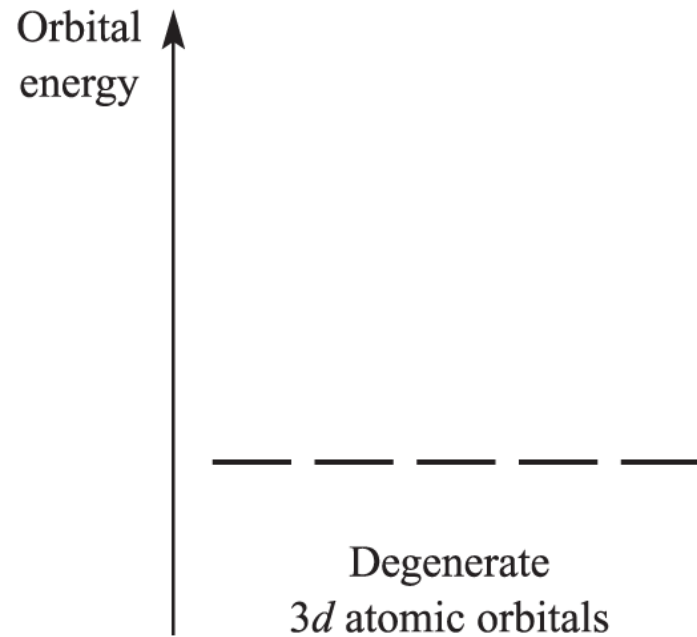
2. Crystal Field Theory

A purely electrostatic consideration

- Ligand electrons create an electric field around the metal center
- Ligands are point charges and we do not take their orbitals into consideration
- No metal-ligand covalent interactions



3. Energy of the d-orbitals



M

The energy of the five d orbitals of the transition metals is equal in the absence of ligands.

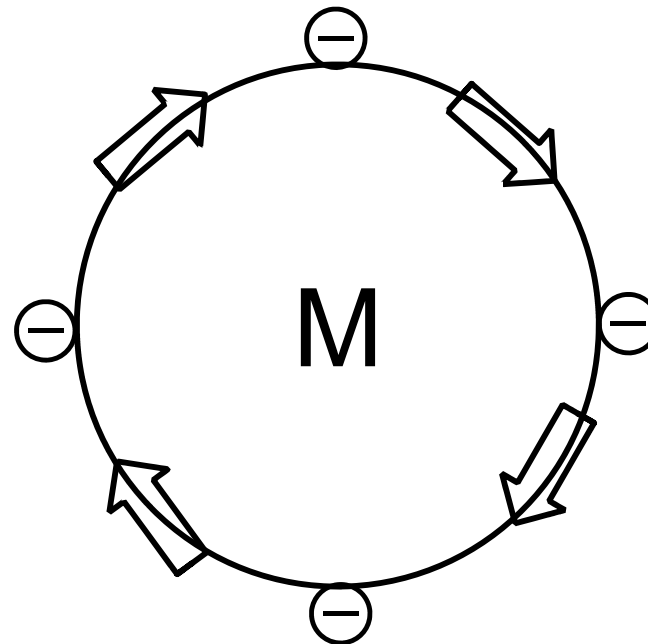
3. Energy of the d-orbitals

Orbital energy ↑

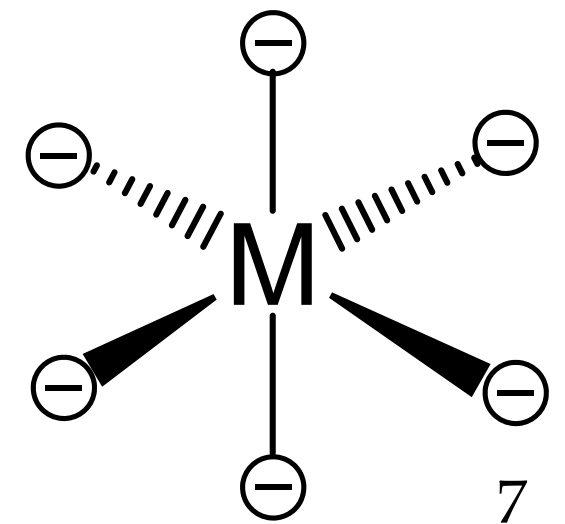
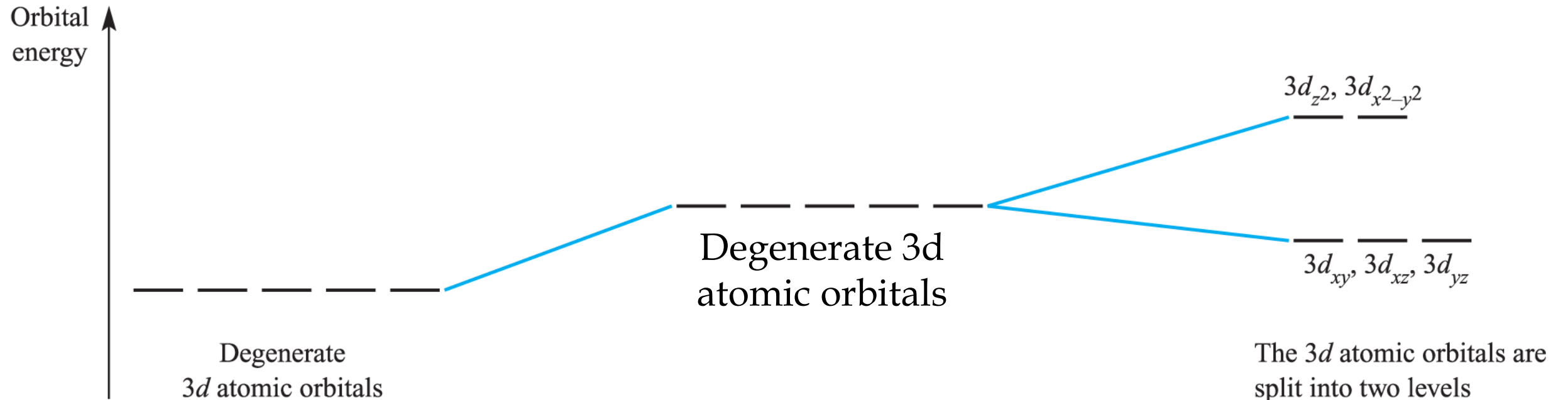
A spherical distribution of ligand electrons equally destabilizes the energy of the d orbital electrons.



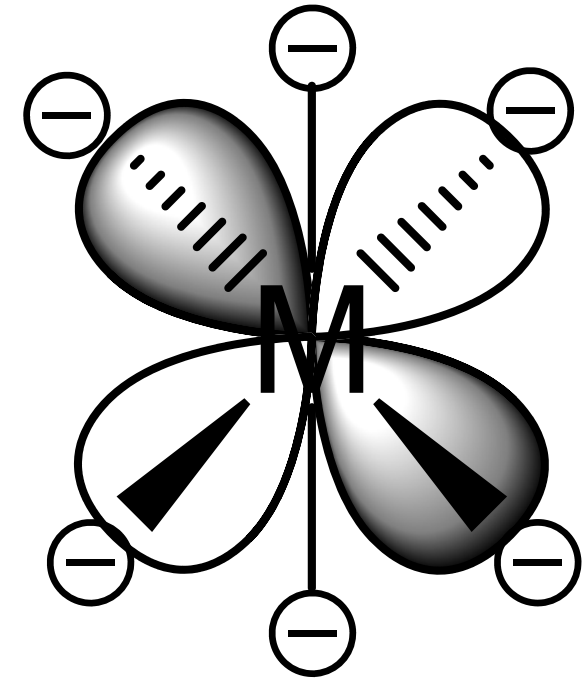
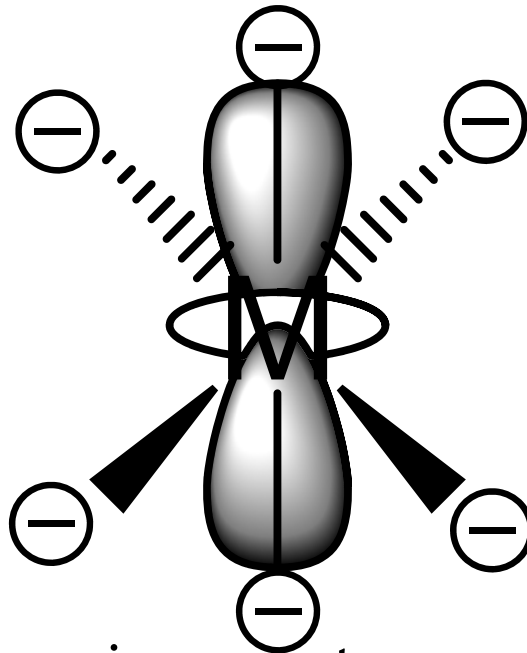
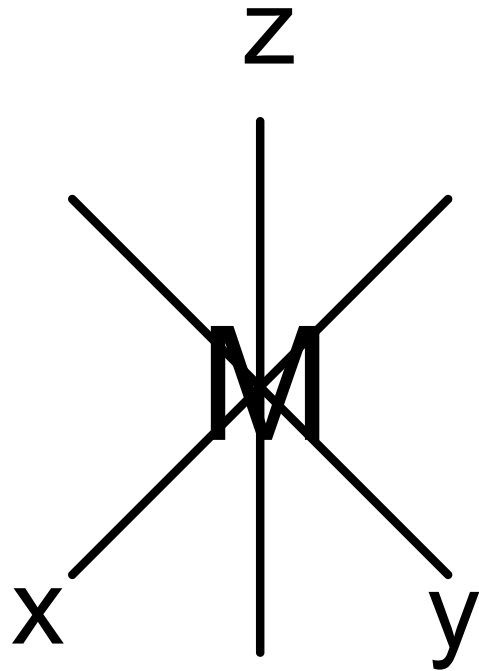
Degenerate 3d atomic orbitals



3. Energy of the d-orbitals



3. Energy of the d-orbitals



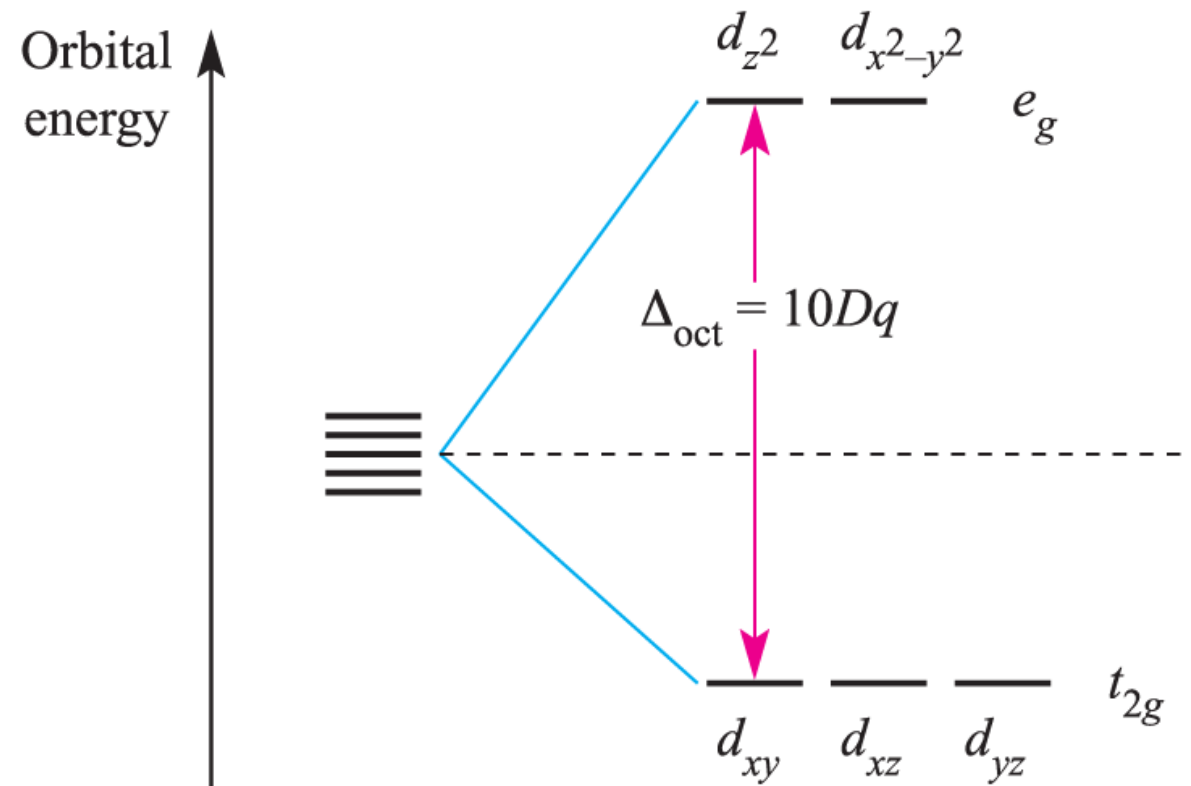
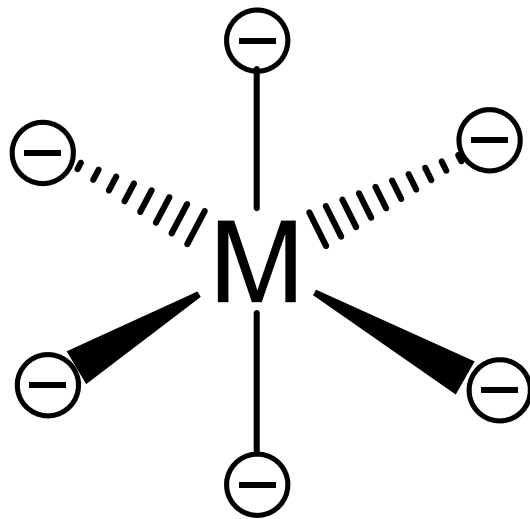
In an octahedral coordination environment:

- The axial ligands interact directly with the two lobes of the d_{z^2} orbital while the equatorial ligands interact with the toroid lobe
- The equatorial ligands interact directly with the four lobes of the $d_{x^2-y^2}$ orbital
- The d_{z^2} and $d_{x^2-y^2}$ orbitals are destabilized whereas the d_{xy} , d_{xz} , and d_{yz} are stabilized

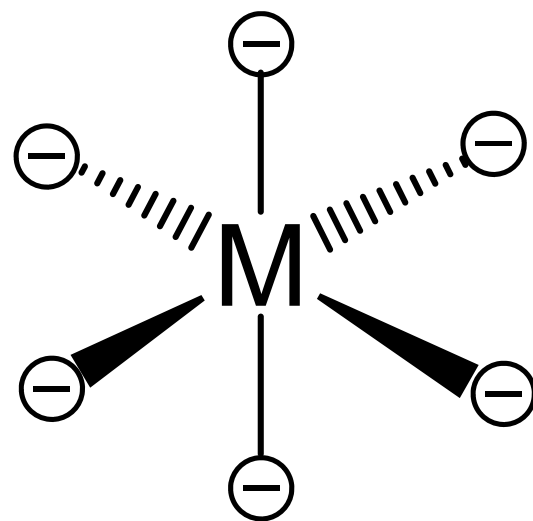
4. The Octahedral Crystal Field

Octahedral coordination environment:

- Point Group: O_h
- d_{z^2} and $d_{x^2-y^2}$ orbitals: e_g symmetry
- d_{xy} , d_{xz} , and d_{yz} : t_{2g} symmetry



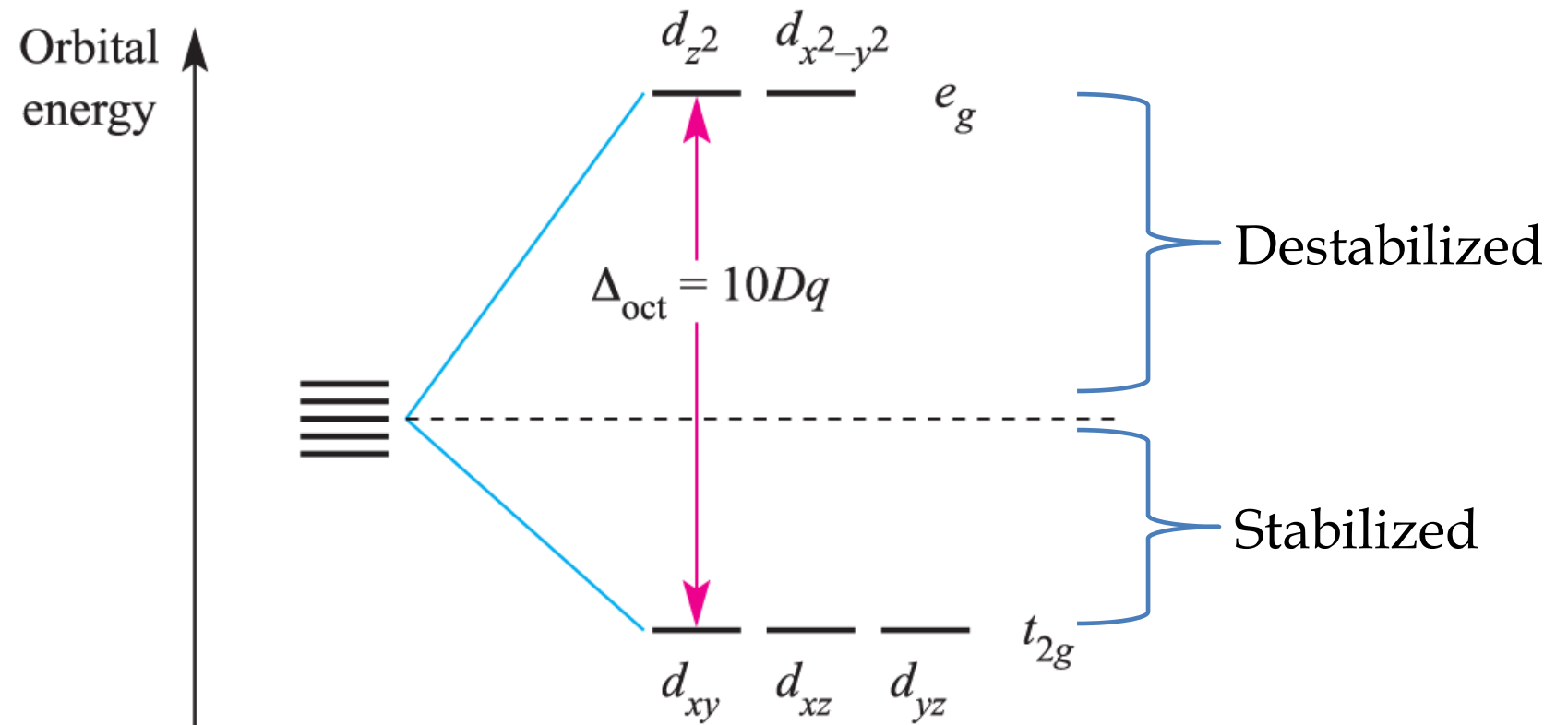
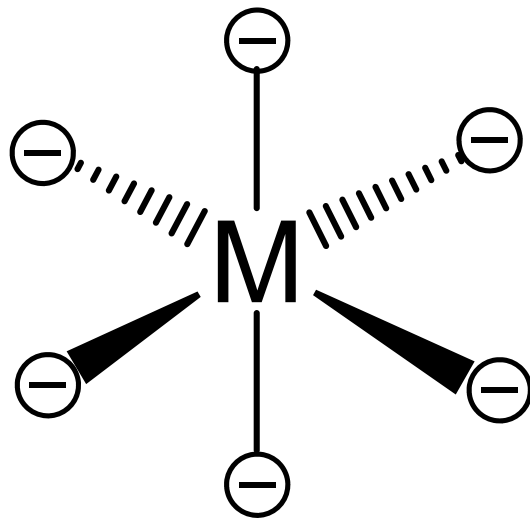
O_h	E	8 C_3	6 C_2	6 C_4	3 $C_2 (= C_4^2)$	i	6 S_4	8 S_6	3 σ_h	6 σ_d		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		



4. The Octahedral Crystal Field

Octahedral coordination environment:

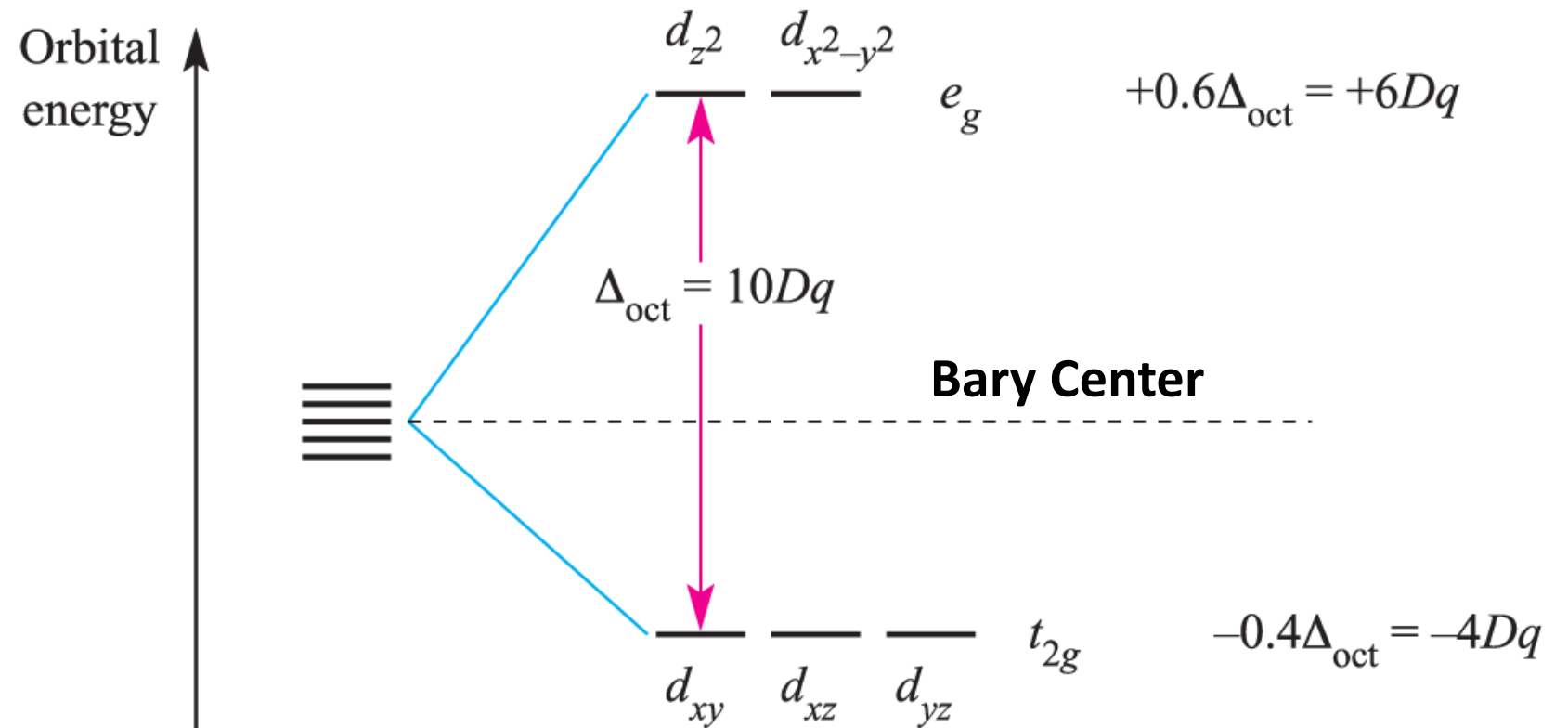
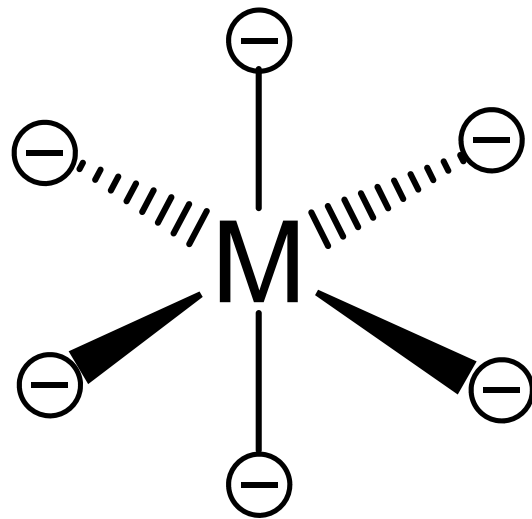
- Point Group: O_h
- d_{z^2} and $d_{x^2-y^2}$ orbitals: e_g symmetry
- d_{xy} , d_{xz} , and d_{yz} : t_{2g} symmetry



4. The Octahedral Crystal Field

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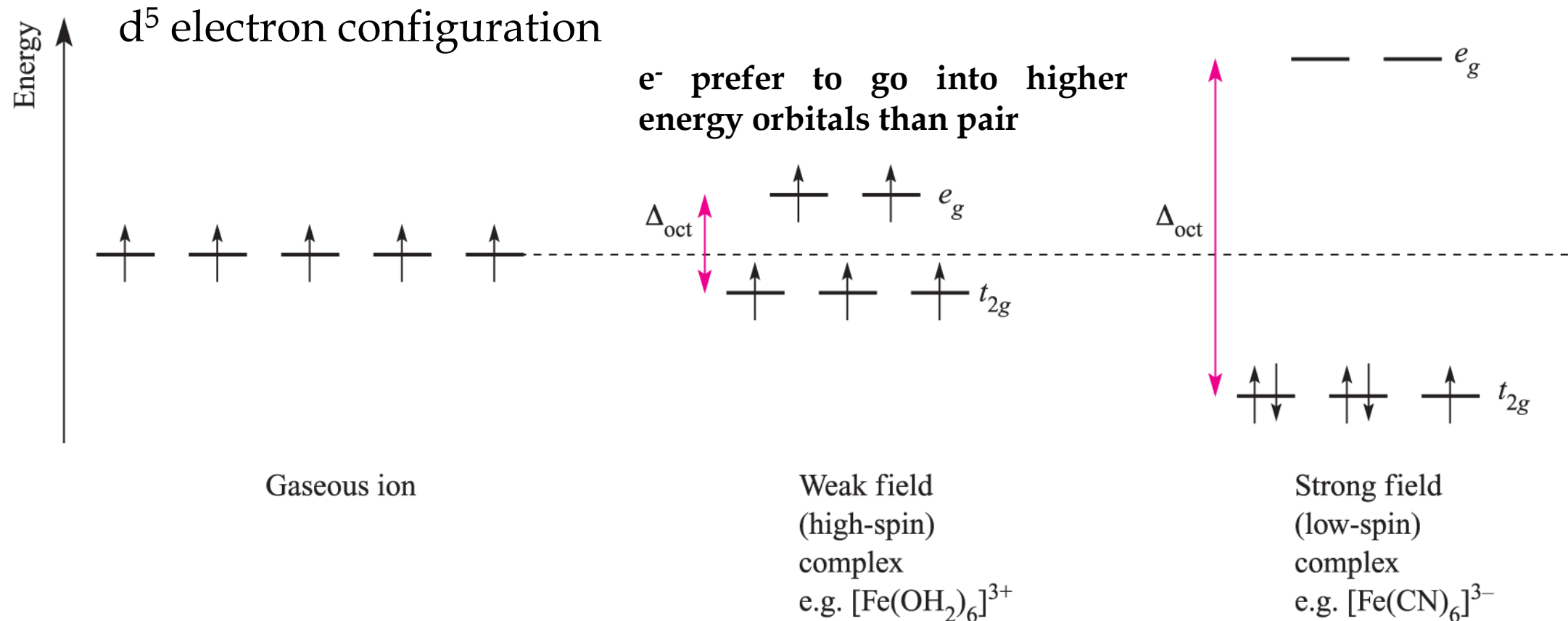


A. The Magnitude of Δ_{oct}

Determined by the strength of the crystal field:

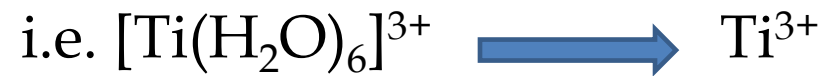
- Weak field
- Strong field

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

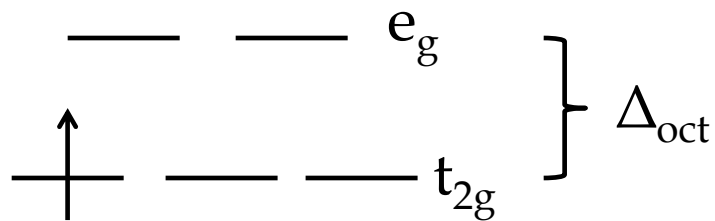


B. Crystal Field Stabilization Energy (CFSE)

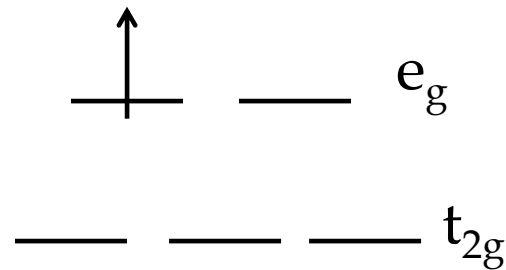
Consider a d^1 electron configuration:



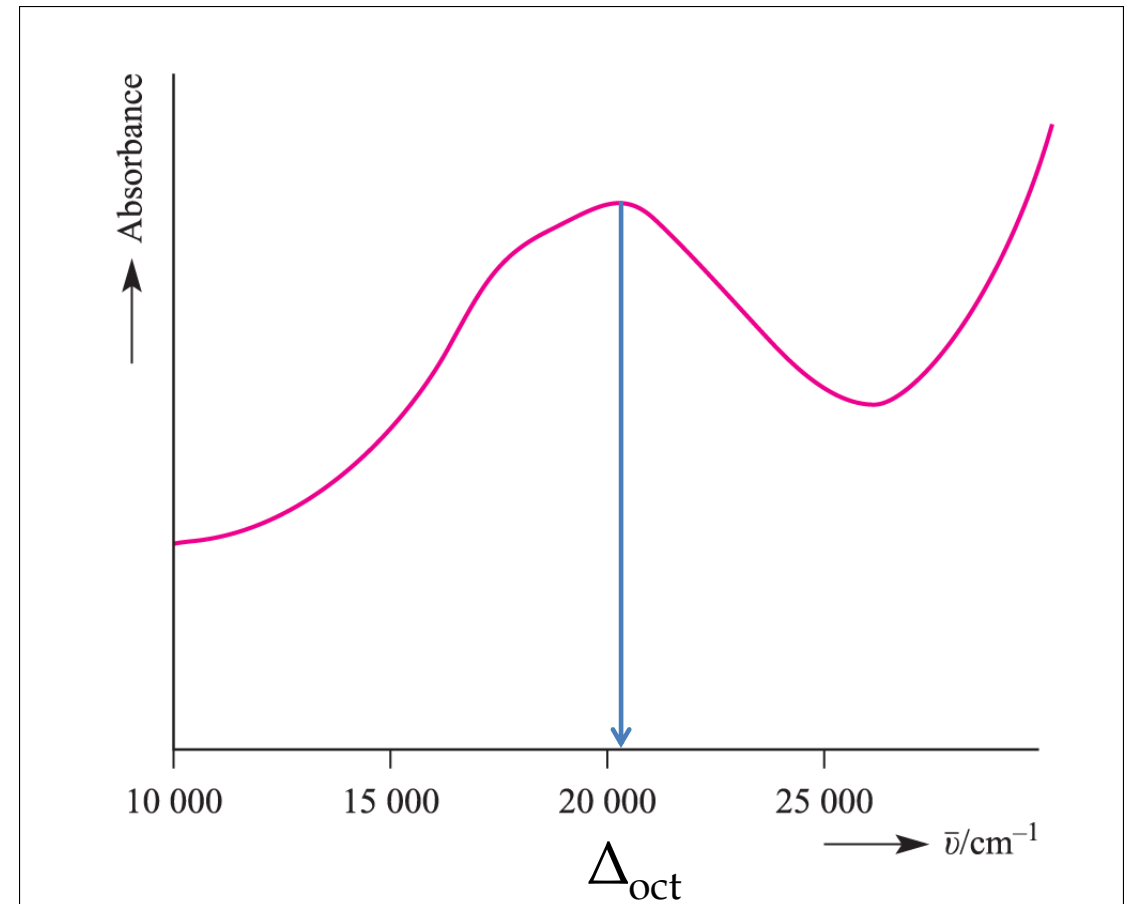
Ground State



Electronic absorbance

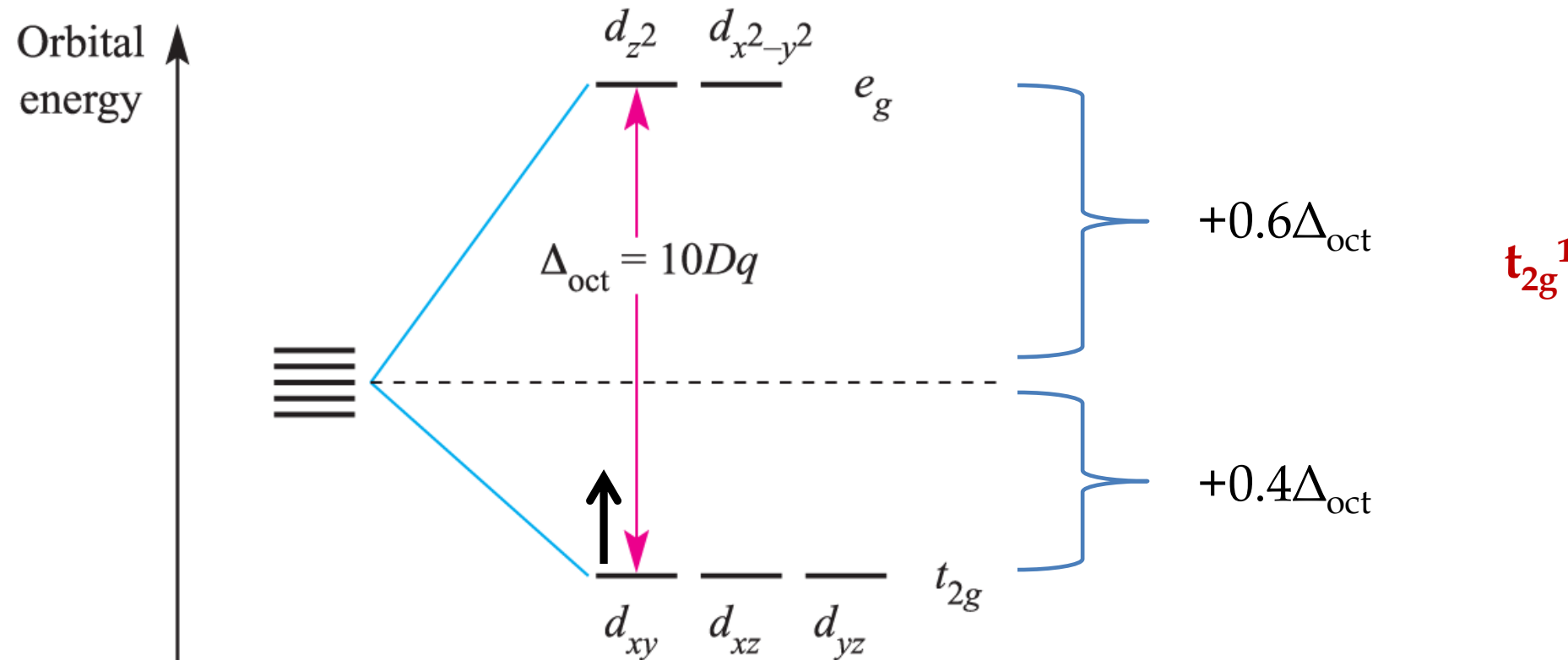


- The single electron will be in less energetic ground state.



B. Crystal Field Stabilization Energy (CFSE)

Calculate the magnitude by which the single electron is stabilized



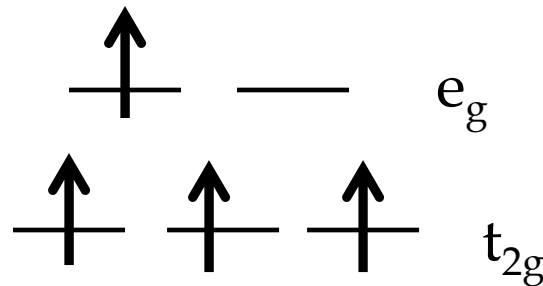
$$\text{CFSE} = -[(\# \text{ electrons in } t_{2g}) \times 0.4\Delta_{\text{oct}}] + [(\# \text{ electrons in } e_g) \times 0.6\Delta_{\text{oct}}]$$

$$= -[1 \times 0.4\Delta_{\text{oct}}] + [0] = -0.4\Delta_{\text{oct}} \text{ Relative to the Bary center}$$

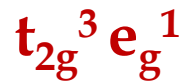
C. CFSE and High vs Low Spin

Consider a d^4 electron configuration (Cr^{2+}):

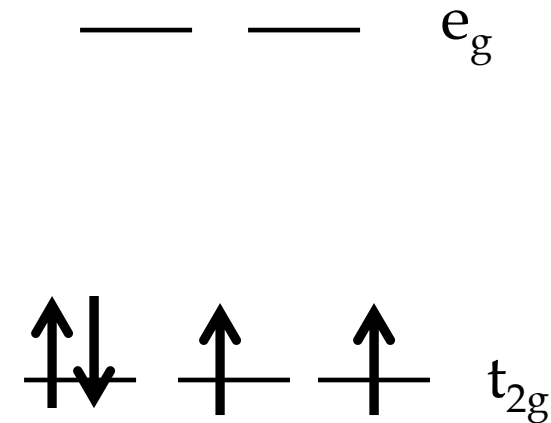
- Depending on the field, pairing may be invoked



$\Delta_{\text{oct}} < p$ (pairing energy)
Weak Field, High spin



$$\text{CFSE} = -[3 \times 0.4\Delta_{\text{oct}}] + [1 \times 0.6\Delta_{\text{oct}}] = -0.6\Delta_{\text{oct}}$$



$\Delta_{\text{oct}} > p$
Strong Field, Low spin



$$\text{CFSE} = -[4 \times 0.4\Delta_{\text{oct}}] = -1.6\Delta_{\text{oct}} + 1 p$$

I. What determines p ?

i. Inherent coulombic repulsion \downarrow with $\uparrow n$

- The more diffuse the orbital, the more able to have two electrons

ii. Loss of exchange energy as e^- pair

II. What determines Δ ?

i. Oxidation state of the metal ion
▪ $\uparrow \Delta$ with \uparrow ionic charge

ii. Nature of M
 $3d < 4d < 5d$



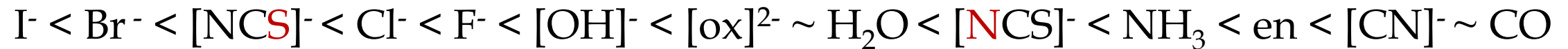
Really big Δ , normally low spin (As you go down the periodic table, $\uparrow \Delta$)

iii. Number and geometry of ligands
 $\Delta_{\text{tetrahedral}}$ only $\sim 50\%$ of $\Delta_{\text{octahedral}}$

II. What determines Δ ?

iv. Nature of ligands

- Spectrochemical series (partial)

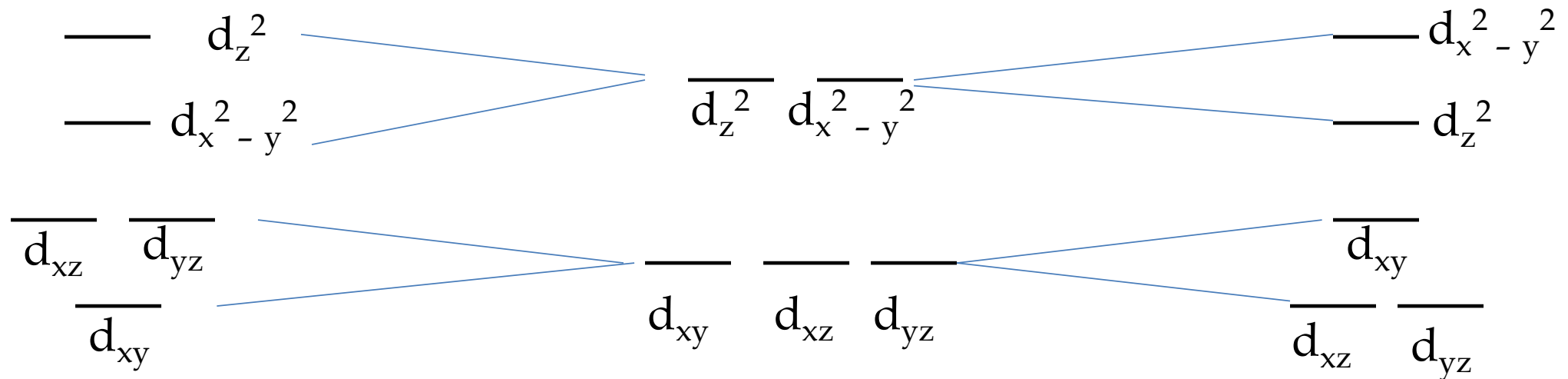
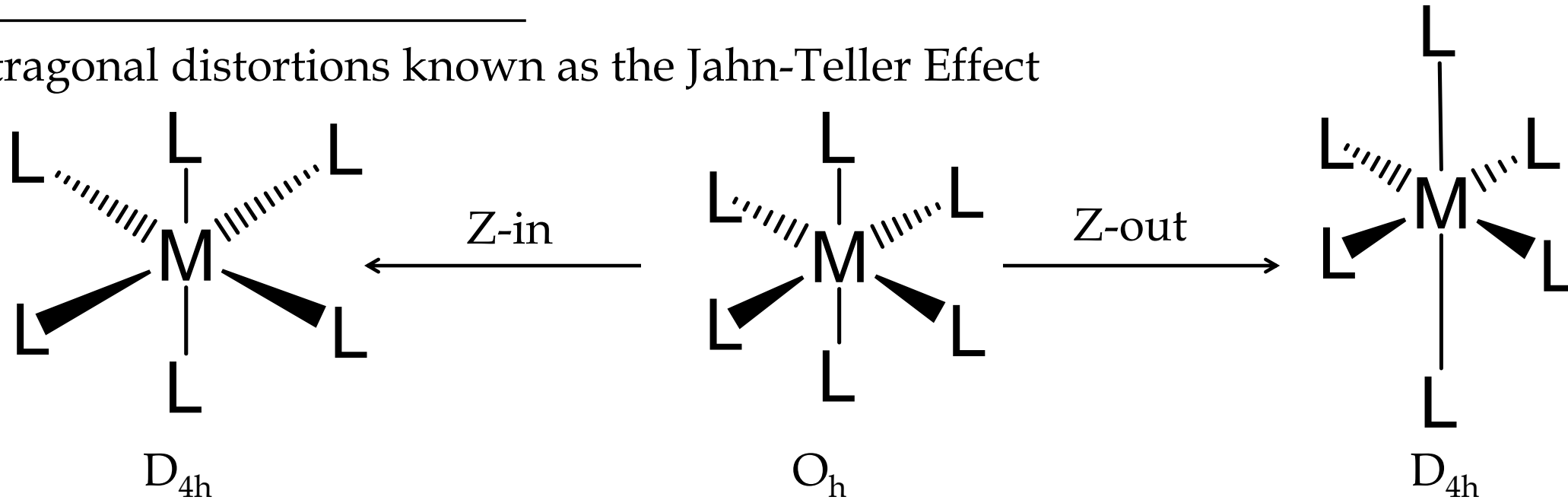


Weak field ligands $\xrightarrow{\text{Ligands increasing } \Delta_{\text{oct}}}$ **Strong field ligands**

YOU CAN NOT UNDERSTAND THIS TREND WITH CRYSTAL FIELD THEORY

5. Octahedral Geometry Distortions

Tetragonal distortions known as the Jahn-Teller Effect



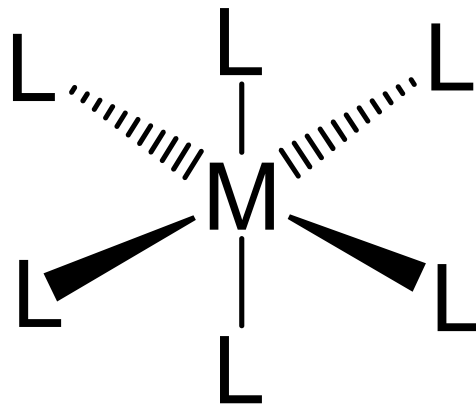
Jahn-Teller Effect

The theorem states that degenerate orbitals cannot be unequally occupied.

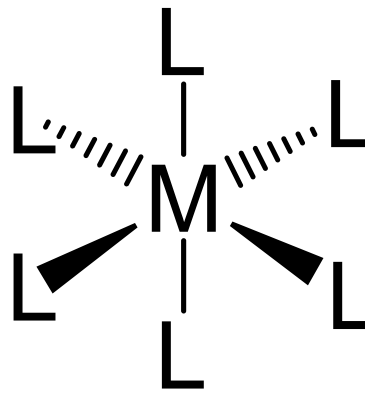
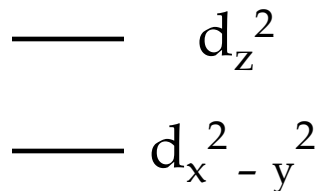
- The molecule distorts by lowering its symmetry to remove the degeneracy
- Quite common for octahedral complexes of d^9 (Cu^{2+}) and high-spin d^4 ions
- For Cu^{2+} complexes, a Z-out ligand arrangement is common.

5. Octahedral Geometry Distortions

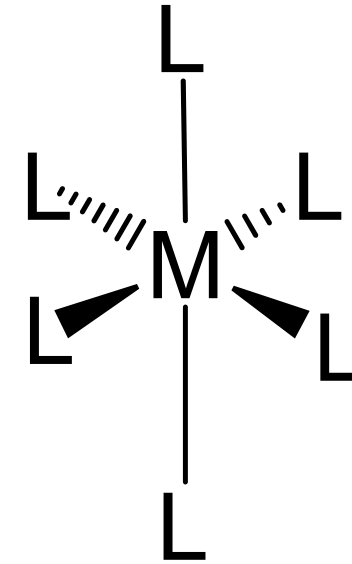
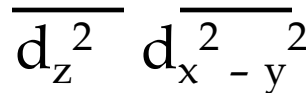
What about a d^1 electron configuration?



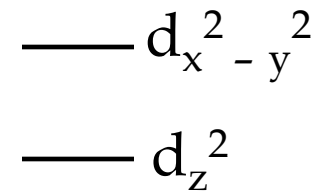
D_{4h}



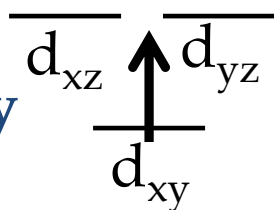
O_h



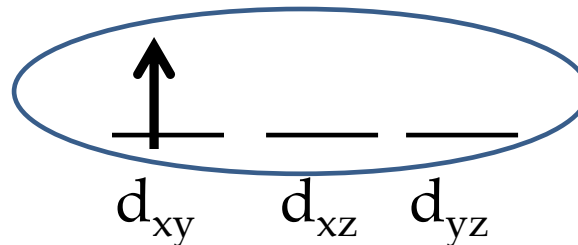
D_{4h}



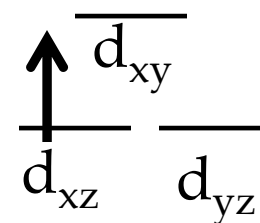
YES!!!
Degeneracy
Removed



No



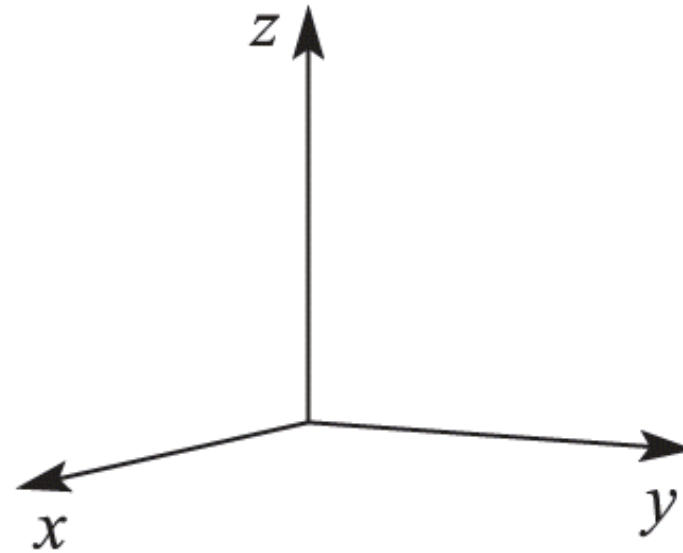
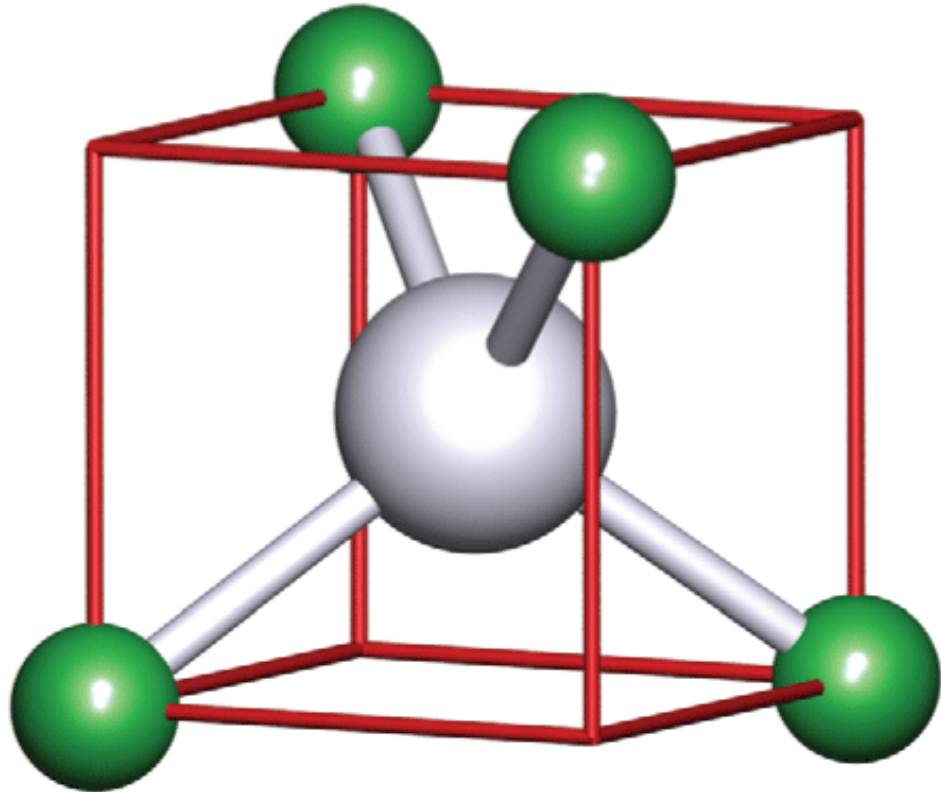
No



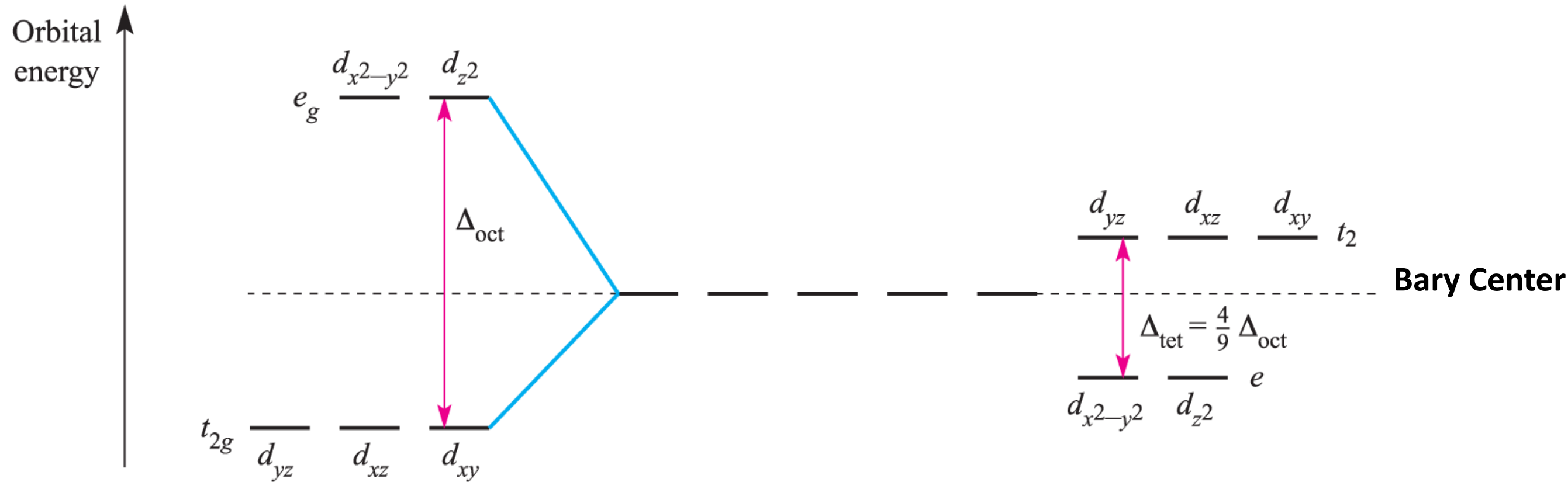
6. The Tetrahedral Crystal Field

Tetrahedral coordination environment:

- Point Group: T_d
- d_{z^2} and $d_{x^2-y^2}$ orbitals: e symmetry; these orbitals are not in direct contact with the ligands
- d_{xy} , d_{xz} , and d_{yz} : t_2 symmetry; these orbitals are in semi contact with the ligands



6. The Tetrahedral Crystal Field



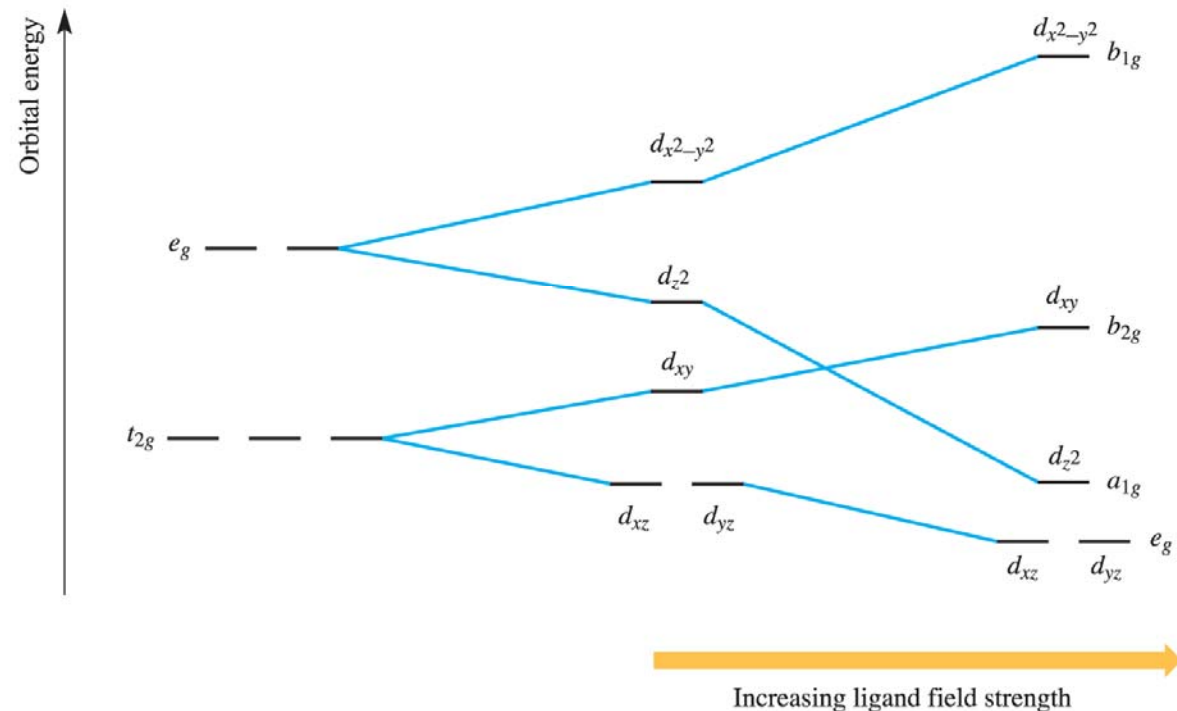
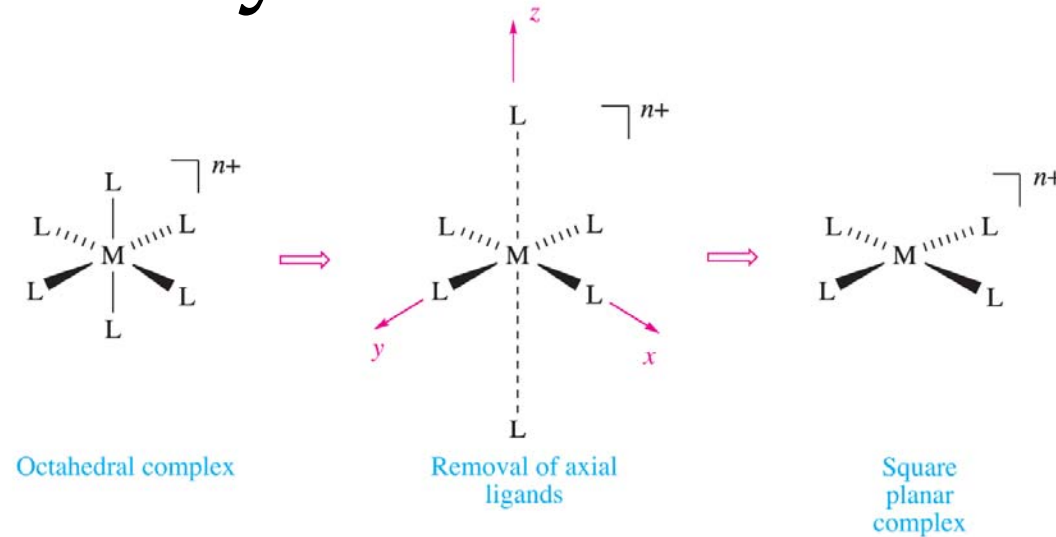
Mostly high spin for these types of complexes.

$$\Delta_{tet} < p$$

7. The Square Planar Crystal Field

Square planar coordination environment:

- Point Group: d_{4h}
- d^8 is diamagnetic vs paramagnetic for tetrahedral



8. Crystal Field Splitting Diagrams for Common Geometric Fields

