B.Sc. Semester-IV
Core Course-VIII (CC-VIII)
Inorganic Chemistry

I. Coordination Chemistry
18. Qualitative Aspects of Ligand Field and MO Theory

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I. Coordination Chemistry: 20 Lectures

Werner's theory, valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding. Crystal field theory, measurement of 10 Dq (Δo), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of 10 Dq (Δo, Δt). Octahedral vs. tetrahedral coordination, tetragonal distortions from octahedral geometry Jahn-Teller theorem, square planar geometry. Qualitative aspect of Ligand field and MO Theory.

IUPAC nomenclature of coordination compounds, isomerism in coordination compounds. Stereochemistry of complexes with 4 and 6 coordination numbers. Chelate effect, polynuclear complexes, Labile and inert complexes.

Coverage:
1. Qualitative Aspects of Ligand Field and MO Theory

Ligand Field Theory

I. Octahedral Complexes

  A. History

    1) Crystal Field Theory only includes ionic interactions in the solid state

    2) MO Theory developed and applied only to non-metal compounds

    3) Ligand Field Theory combines both for transition metal coordination compounds

  B. MO's for O_h complexes

    1) Donor atom = atom in the ligand with a p-orbital or hybrid orbital directly approaching the metal ion to form a σ-bond

    2) The d_{xy}, d_{xz}, d_{yz} orbitals are not of correct symmetry to σ-bond with ligands

    3) The d_{x2-y2}, d_{z2}, p_x, p_y, p_z, and s orbitals all have correct symmetry for interaction with ligands

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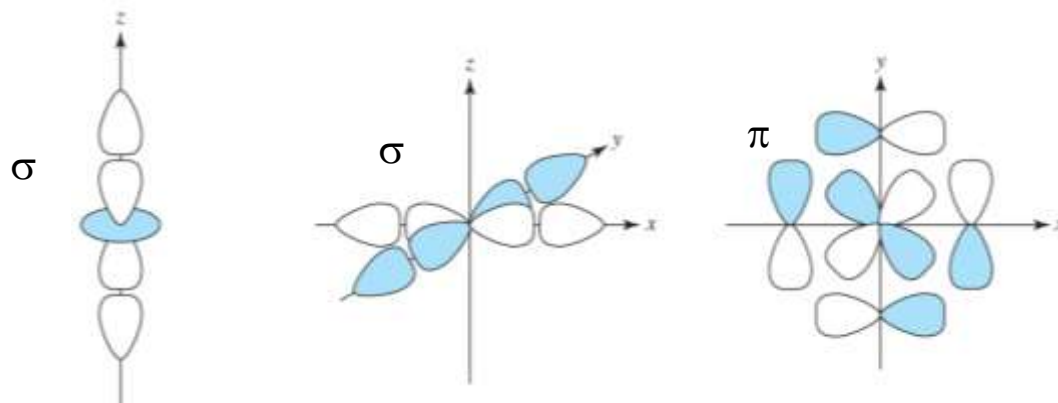
4) Use the Group Theory Approach to find Molecular Orbitals

    a) The six ligand orbitals generate the group orbitals to combine with metal Atomic Orbitals

TABLE 10.4 Character Table for O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4{}^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		
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		(xy, xz, yz)
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		

    b) The reducible representation: $\Gamma = A_{1g} + T_{1u} + E_g$

    c) Nondbonding metal orbitals: d_{xy}, d_{xz}, d_{yz} orbitals have T_{2g} symmetry

    d) Bonding metal orbitals: s orbital has A_{1g} symmetry; p_x, p_y, p_z have T_{1u} symmetry, and d_{x2-y2}, d_{z2}, have E_g symmetry

e) The 6 metal AO's of proper symmetry combine with the six ligand group orbitals

f) 6 bonding MO's are filled by ligand electron pairs

g) The metal t_{2g} Atomic Orbitals are nonbonding (d_{xy}, d_{xz}, d_{yz})
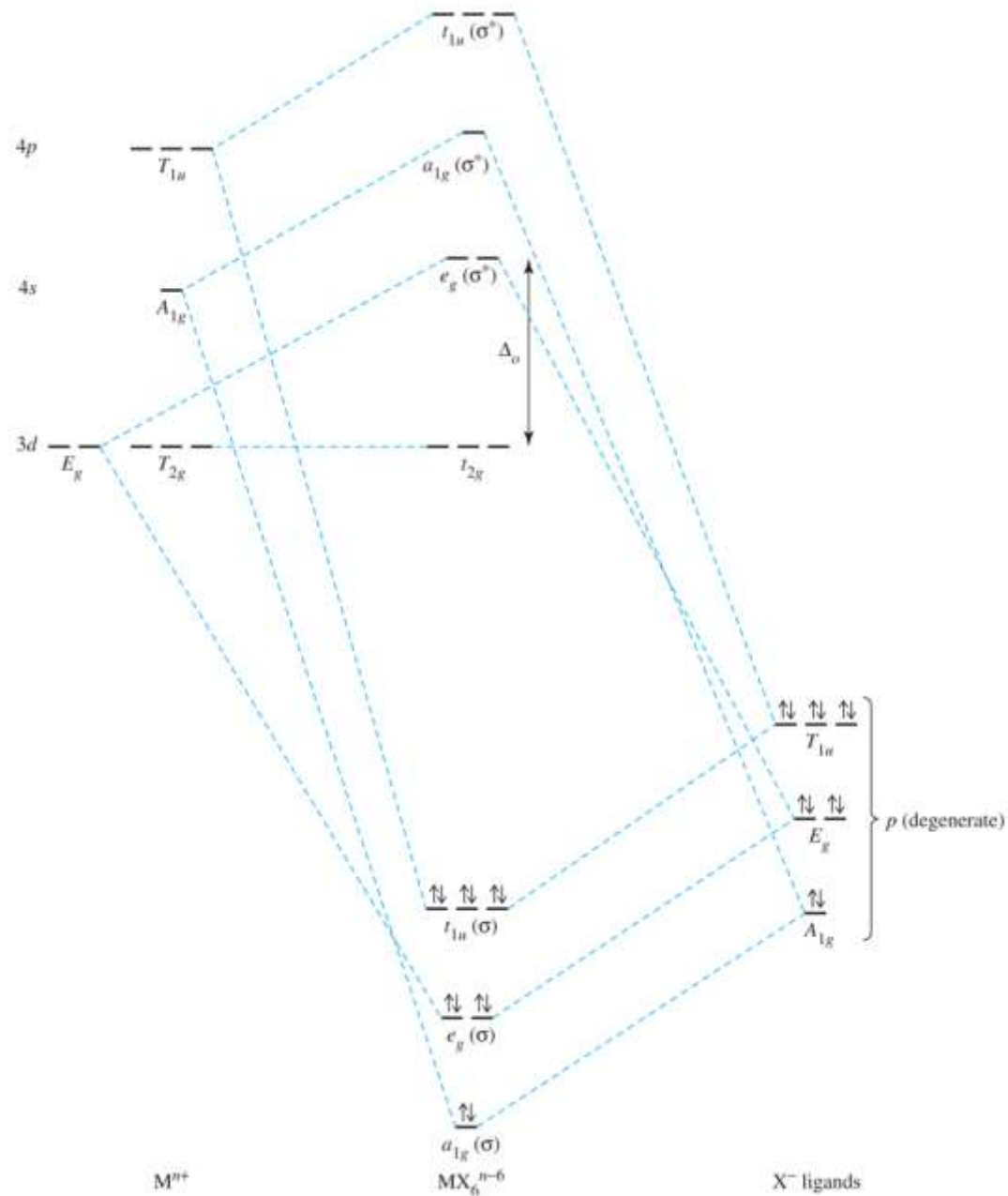
I. 6 antibonding orbitals are formed with the same symmetries as the bonding orbitals

II. The 2 e_g^* antibonding orbitals are the lowest energy antibonding orbitals available

III. The d-electrons from the metal ion will fill in the t_{2g} and e_g^* MO's

5) All octahedral metal complexes will have the exact same MO diagram, only the number of d-electrons will change

6) The 6 bonding MO's, with lowered energy for their electron pairs is what holds the metal complex together

7) The d-electrons in the t_{2g} and e_g* MO's
   a) Determine the "Ligand Field"
   b) Determine the geometry and many characteristics of the metal complex

C. Orbital Splitting and Electron Spin
   1) The energy difference between the t_{2g} and e_g* MO's $= \Delta_o =$ **"delta octahedral"**

   2) **Strong-Field Ligands** = ligands whose orbitals interact strongly with metal ion
   a) e_g* is raised in energy
   b) Δ_o is large

   3) **Weak-Field Ligands** = ligands whose orbitals interact weakly with metal ion
   a) e_g* is raised only slightly in energy
   b) Δ_o is small

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4) **Electron Spin**

a) d^0 – d^3 and d^8 – d^{10} octahedral complexes have only one possible arrangement of electrons in the t_{2g} and e_g^* MO's

b) d^4 – d^7 octahedral complexes have two possible electronic arrangements

  i. **Low Spin** = least number of unpaired electrons; favored by strong field ligands with large Δ_o

  ii. **High Spin** = maximum number of unpaired electrons; favored by weak field ligands with small Δ_o
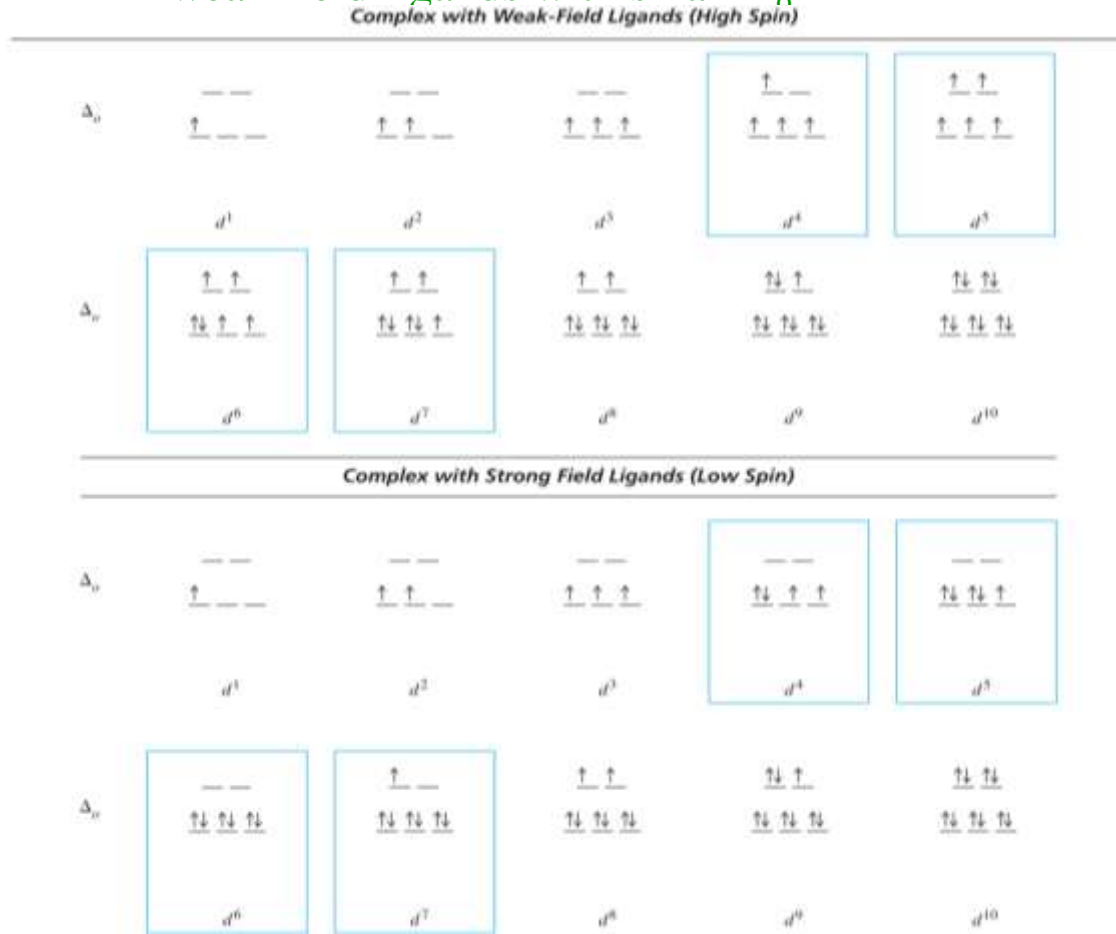
5) Explanation for low/high spin complexes

    a) Pairing Energy = Π = energy it costs to pair 2 e- in an orbital

    b) Delta Octahedral = Δ_o = energy gained by having e- in t_{2g} not e_g^*

    c) Strong-Field ligands have large Δ_o favors pairing up in t_{2g} MO ($\Delta_o > \Pi$)

    d) Weak-Field ligands have small Δ_o favor keeping e- unpaired ($\Delta_o < \Pi$)

6) Aqua complexes

Ion	Δ_o	Π	Ion	Δ_o	Π
d^1			Ti^{3+}	18,800	
d^2			V^{3+}	18,400	
d^3	V^{2+}	12,300		Cr^{3+}	17,400	
d^4	Cr^{2+}	9,250	23,500	Mn^{3+}	15,800	28,000
d^5	Mn^{2+}	7,850b	25,500	Fe^{3+}	14,000	30,000
d^6	Fe^{2+}	9,350	17,600	Co^{3+}	16,750	21,000
d^7	Co^{2+}	8,400	22,500	Ni^{3+}		27,000
d^8	Ni^{2+}	8,600				
d^9	Cu^{2+}	7,850				
d^{10}	Zn^{2+}	0				

7) Trends in Δ_o

    a) 3^+ ion > 2^+ ion (greater interaction with ligand electrons)

    b) 3rd row metal > 2nd row metal > 1st row metal

       i. Greater overlap between 4d/5d and ligand orbitals

       ii. Decrease in Π as volume of the orbitals increases

D. Ligand Field Stabilization Energy = LFSE

1) LFSE = energetic stabilization of the d-electrons due to orbital splitting (measured in units of Δ_o)

2) Essentially equivalent to CFSE, although the theoretical approach is different

3) Treat electrons in t_{2g} orbitals as stabilized by $-2/5\ \Delta_o$ and electrons in e_g* orbitals as destabilized by $+3/5\ \Delta_o$
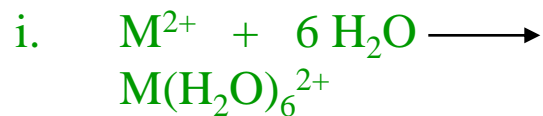
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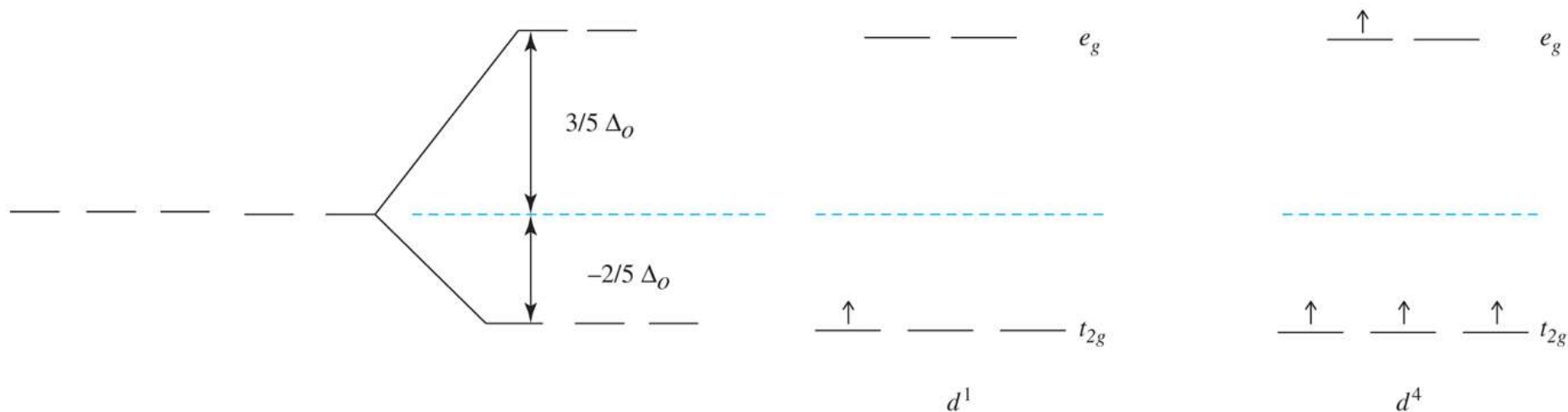
Number of d Electrons	Weak-Field Arrangement t_{2g}			e_g		LFSE (Δ_o)
1	↑					$-\frac{2}{5}$
2	↑	↑				$-\frac{4}{5}$
3	↑	↑	↑			$-\frac{6}{5}$
4	↑	↑	↑	↑		$-\frac{3}{5}$
5	↑	↑	↑	↑	↑	0
6	↑↓	↑	↑	↑	↑	$-\frac{2}{5}$
7	↑↓	↑↓	↑	↑	↑	$-\frac{4}{5}$
8	↑↓	↑↓	↑↓	↑	↑	$-\frac{6}{5}$
9	↑↓	↑↓	↑↓	↑↓	↑	$-\frac{3}{5}$
10	↑↓	↑↓	↑↓	↑↓	↑↓	0

Number of d Electrons	Strong-Field Arrangement t_{2g}			e_g		LFSE (Δ_o)
1	↑					$-\frac{2}{5}$
2	↑	↑				$-\frac{4}{5}$
3	↑	↑	↑			$-\frac{6}{5}$
4	↑↓	↑	↑			$-\frac{8}{5}$
5	↑↓	↑↓	↑			$-\frac{10}{5}$
6	↑↓	↑↓	↑↓			$-\frac{12}{5}$
7	↑↓	↑↓	↑↓	↑		$-\frac{9}{5}$
8	↑↓	↑↓	↑↓	↑	↑	$-\frac{6}{5}$
9	↑↓	↑↓	↑↓	↑↓	↑	$-\frac{3}{5}$
10	↑↓	↑↓	↑↓	↑↓	↑↓	0

Only $d^4 - d^7$ metals have differences between high and low spin

4) Importance of LFSE

a) Hydration of M^{2+} first row ions

    i. $M^{2+} + 6 H_2O \longrightarrow M(H_2O)_6^{2+}$
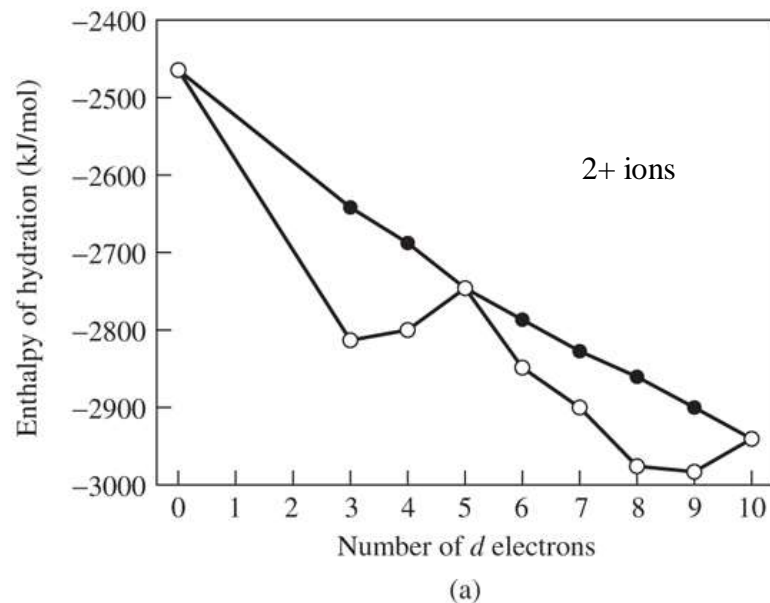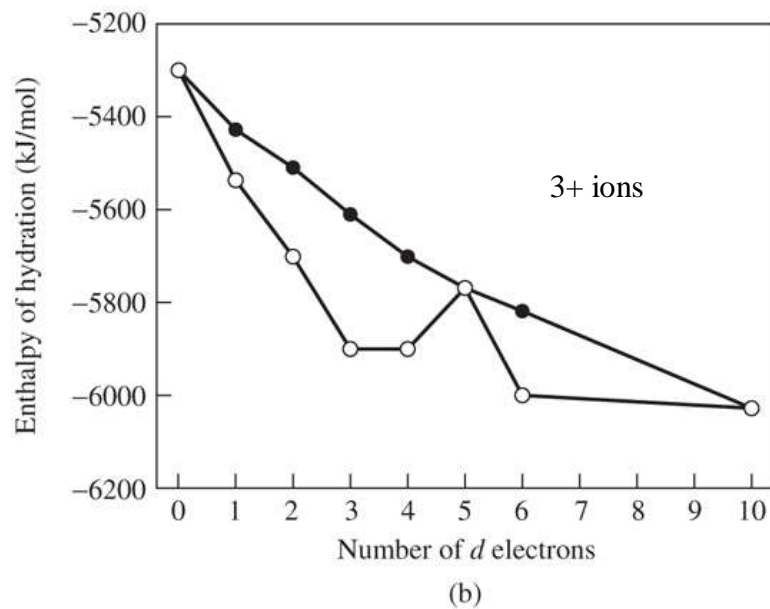
    ii.   Enthalpy ($-\Delta H$) becomes more favorable left to right on period table

    iii. Predict a smooth change as nuclear charge increases and size decreases

    iv. The observed pattern has a "double hump" that parallels LFSE

(a)

○ Experimental values
● Corrected values

(b)

b) Uses of LFSE

    i.   Prediction of high spin or low spin based on ligand type

    ii.   Explanation of electronic spectra (UV-Vis spectra)

    iii. Explanation of magnetic behavior

E.   π-Bonding

1)   Our previous treatment of bonding only looked at σ interactions

2)   Other orbitals of the ligand can be involved with π-bonding to the metal

    a)   Other p or hybrid orbitals

    b)   MO's from molecular ligands that have π symmetry

3)   Group orbital approach to π-bonding

    a)   Choose x,y,z axes so that y points directly at metal (σ)

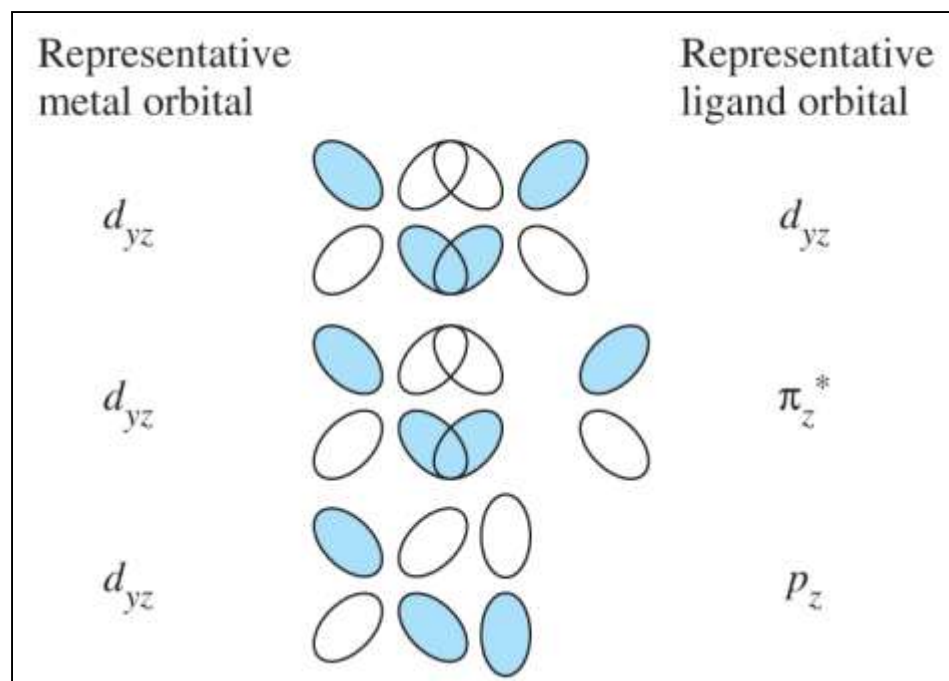   b)   Find the reducible representation of the 12 p_x and p_z orbitals

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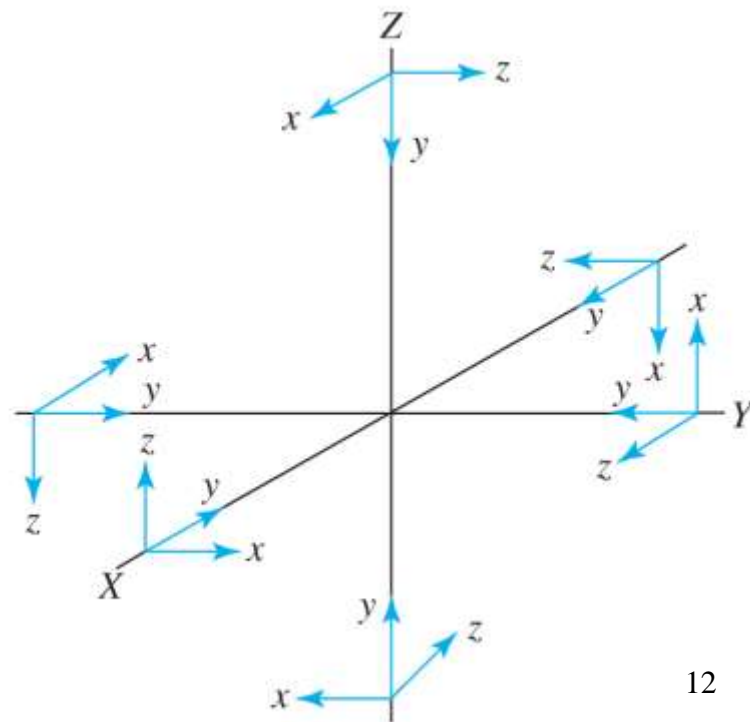
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4{}^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
Γ_π	12	0	0	0	−4	0	0	0	0	0	
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1	(xy, xz, yz)
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1	

c) $\Gamma = T_{1g} + T_{2g} + T_{1u} + T_{2u}$

d) T_{1g} and T_{2u} have no matching metal orbitals to overlap with

e) T_{2g} matches metal d_{xy}, d_{xz}, d_{yz} orbitals for π-bonding

f) T_{1u} matches metal p_x, p_y, p_z orbitals for π-bonding, but are already used in σ-bonding and are poor size matches for ligand π-MO's

Representative metal orbital — Representative ligand orbital

d_{yz} — d_{yz}

d_{yz} — $\pi_z{}^*$

d_{yz} — p_z

3) CN⁻ Example:

a) HOMO = σ-bonding electron pair donor to metal ion

b) LUMO = π-bonding electron pair acceptor from metal ion

c) The π* orbitals are higher in energy than the metal t_{2g} orbitals having the correct symmetry to overlap with

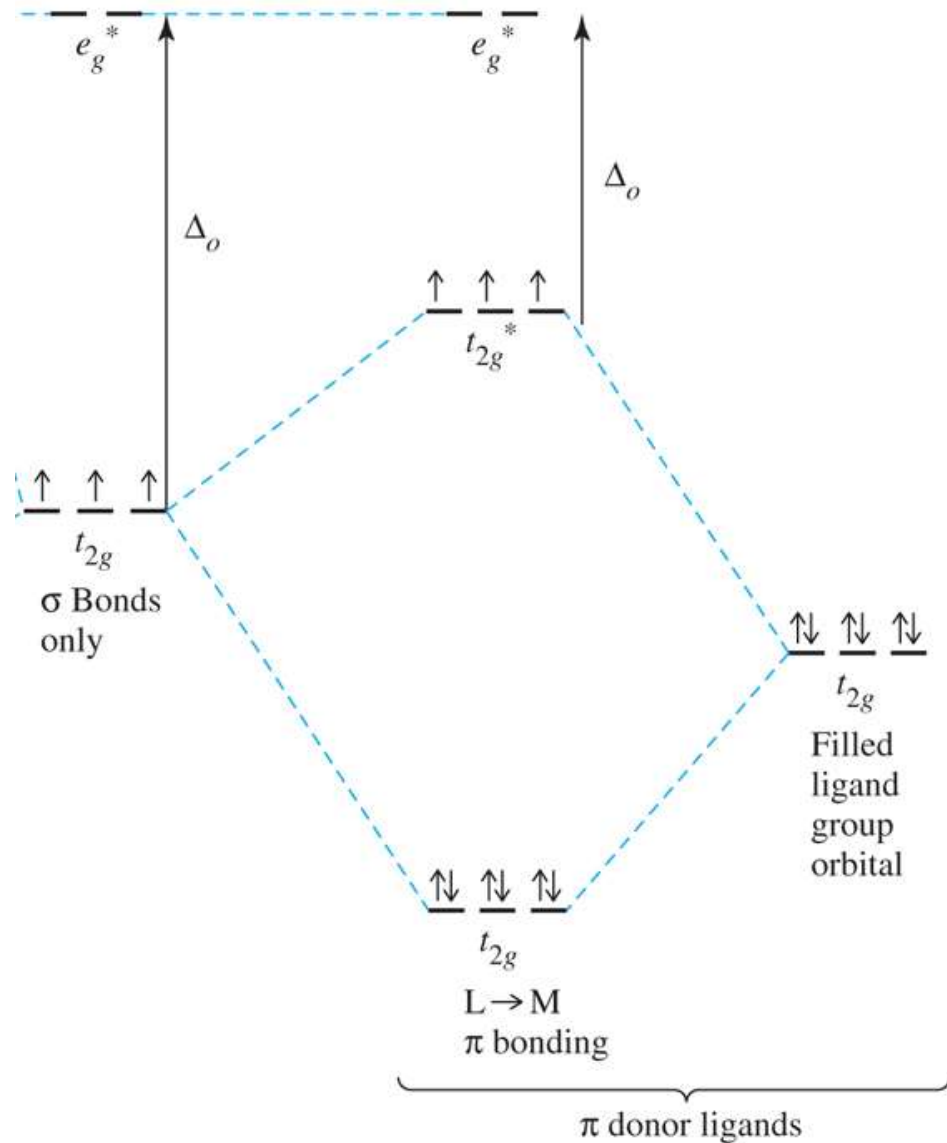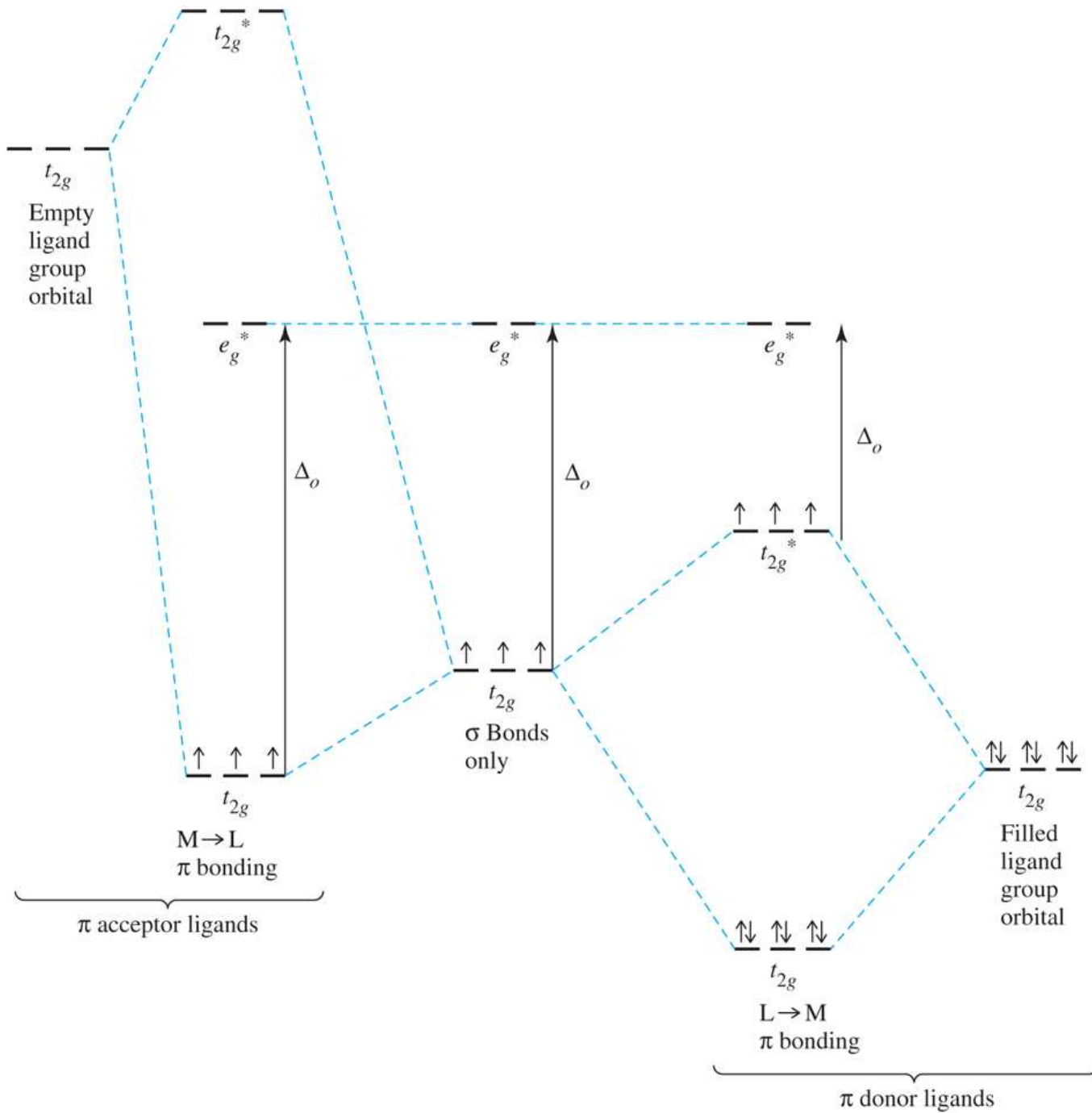d) The energy match is good enough for overlap to occur

e) π-bonding results

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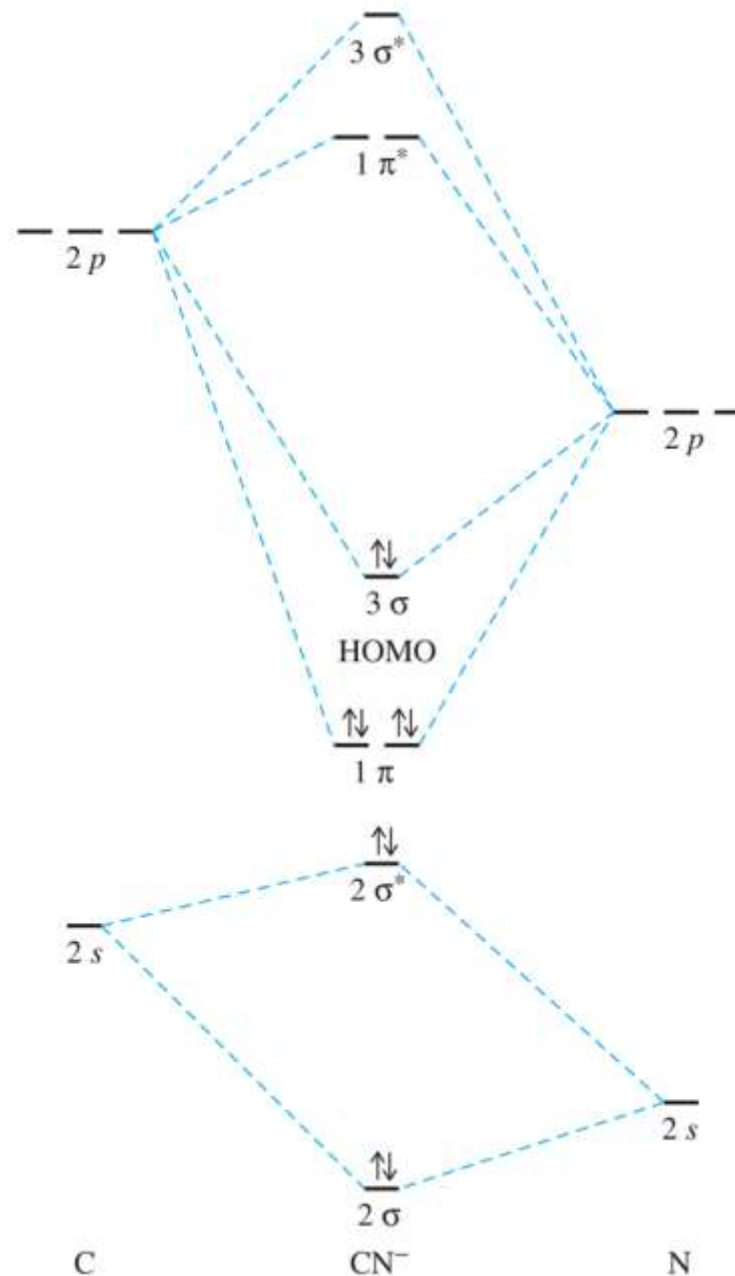
i.   3 new bonding t_{2g} MO's receive the d-electrons

ii. 3 new antibonding $t_{2g}*$ MO's formed

iii.   The e_g* MO's from the σ-bond MO treatment are nonbonding

iv.   Ligands like this increase Δ_o by lowering the energy of t_{2g} MO's favoring low spin complexes

v. CN^- is a strong field ligand

vi.   Metal to Ligand (M→L) or π-back bonding to π-acceptor ligand

vii.   Transfer of electron density away from M^+ stabilizes the complex over σ-bonding only

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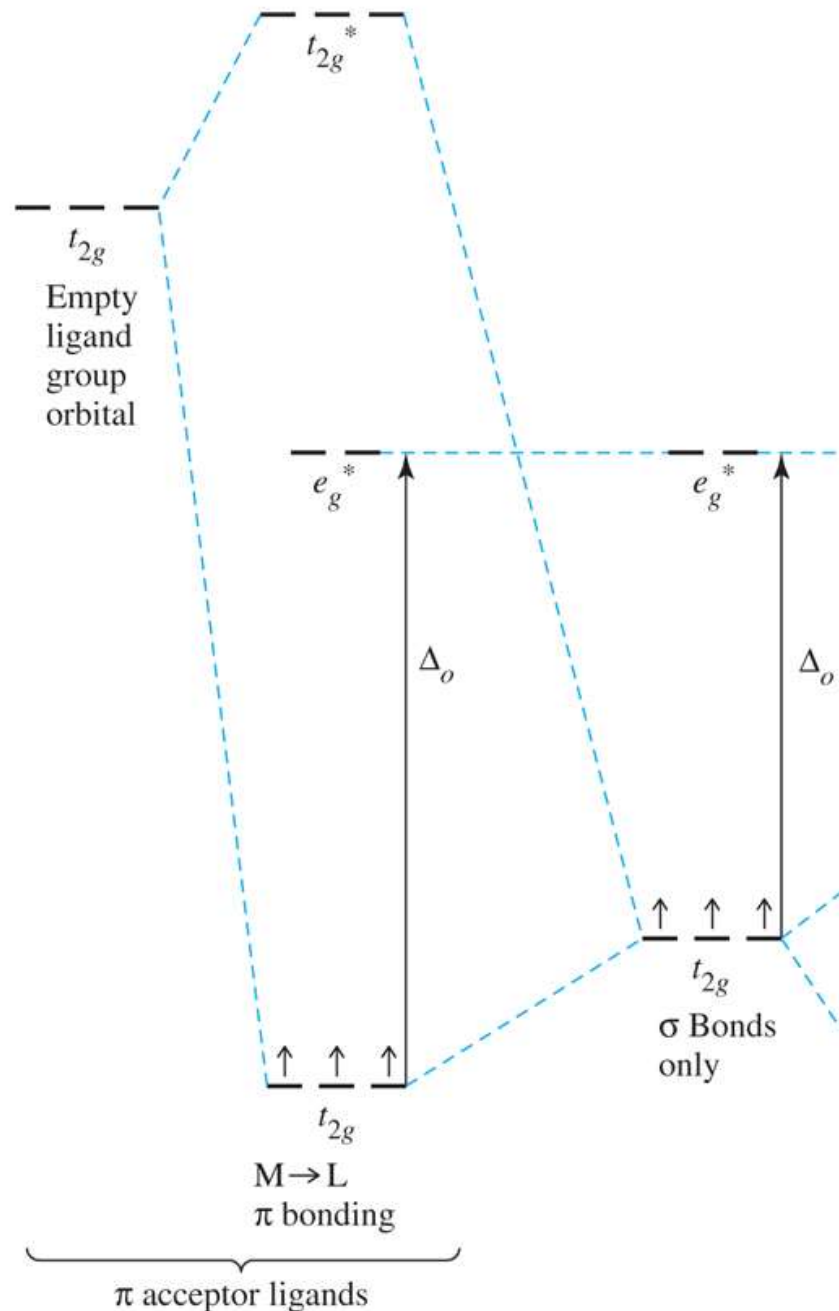
4) F⁻ example

  a) Filled p-orbitals are the only orbitals capable of π-interactions

    i) 1 lone pair used in σ-bonding

    ii) Other lone pairs π-bond

  b) The filled p-orbitals are lower in energy than the metal t_{2g} set

  c) Bonding Interaction

    i. 3 new bonding MO's filled by Fluorine electrons

    ii. 3 new antibonding MO's form $t_{2g}*$ set contain d-electrons

    iii. Δ_o is decreased (weak field)

  d) Ligand to metal (L→M) π-bonding

    i. Weak field, π-donors: F, Cl, H_2O

    ii. Favors high spin complexes

e_g*

e_g*

Δ_o

Δ_o

↑ ↑ ↑
$t_{2g}*$

↑ ↑ ↑
t_{2g}

σ Bonds only

⇅ ⇅ ⇅
t_{2g}
Filled ligand group orbital

⇅ ⇅ ⇅
t_{2g}

L→M
π bonding

π donor ligands

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t_{2g}^*

t_{2g}
Empty
ligand
group
orbital

e_g^* e_g^* e_g^*

Δ_o Δ_o Δ_o

↑ ↑ ↑
t_{2g}^*

↑ ↑ ↑
t_{2g}
σ Bonds
only

↑ ↑ ↑
t_{2g}
M→L
π bonding

⥮ ⥮ ⥮
t_{2g}
Filled
ligand
group
orbital

⥮ ⥮ ⥮
t_{2g}
L→M
π bonding

π acceptor ligands

π donor ligands

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Thank You

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