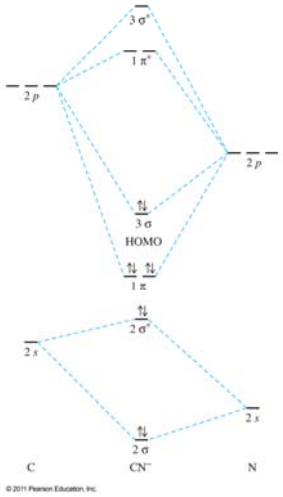
10.3 Ligand Field Theory

- Fig.10.9: CN^- MO

: both σ- & π-interaction



- HOMO of CN^-: donor orbital σ bonding to form

- LUMO of CN^-: two empty π^* orbitals → π-bonding

10.3 Ligand Field Theory

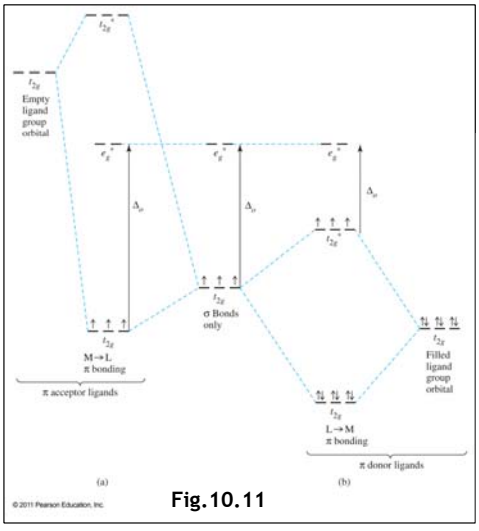


Fig.10.11

- (a): E (ligand π^* orbitals) > E (M's t_{2g})

↳ forming → t_{2g}^* (anti-) → higher than e_g^*

→ t_{2g} (bonding) → lower than the initial M's t_{2g}

↳ M's d e^- → occupy the bonding orbitals (HOMO)

↓

Δ_o ↑, bonding strength ↑

↓

This is <u>metal-to-ligand (M-L) π bonding</u>

(= π back-bonding)

↳ e^-: from M's d → to <u>ligands</u>

(π acceptor)

10.3 Ligand Field Theory

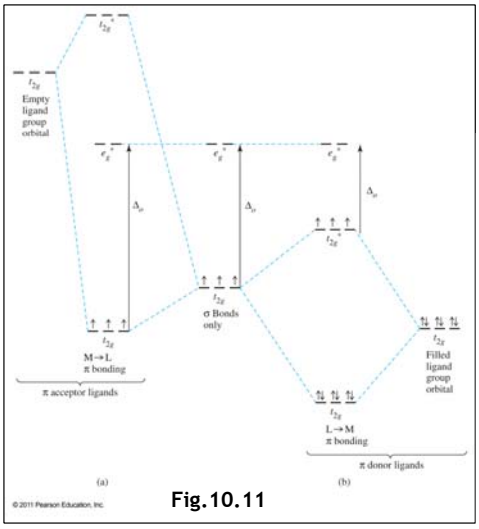


Fig.10.11

- (b): ligands w/ e^- in *p* orbitals (e.g. F^-, Cl^-)
  - ↳ bonding molecular π orbitals: occupied by these e^-

↓

1) t_{2g} bonding orbital: strengthen the ligand-M bond

2) t_{2g}^* (primarily derived from M): *E* ↑
   : become antibonding

↓

Δ_o↓, e^- : derived from M's *d* → to ligand t_{2g}^*

↳ this is ligand-to-metal (L →M) π bonding

- combined σ & π donations from ligands

↓

more '-' charge on M

↓

decrease attraction b/w M & L

↓

∴ less favorable bonding !!

10.3 Ligand Field Theory

filled π or *p* orbitals on ligands w/ lower *E*
- ↳ L → M π-bonding, Δ_o ↓ ➡ **(b) case**
  - ↳ stability ↓, favors high-spin

empty π or *d* orbitals on ligands w/ higher *E*
- ↳ M → L π-bonding, Δ_o ↑ ➡ **(a) case**
  - ↳ stability ↑, favors low-spin

10.3.2 Orbital Splitting and Electron Spin

- in octahedral coordination complexes,
  - e^- from the ligands → all six bonding MO
  - e^- from M ion → t_{2g} & e_g^*

- strong-field ligands: strong interaction b/w ligands & M ions
  : large t_{2g} & e_g^* split
  : Δ_o large

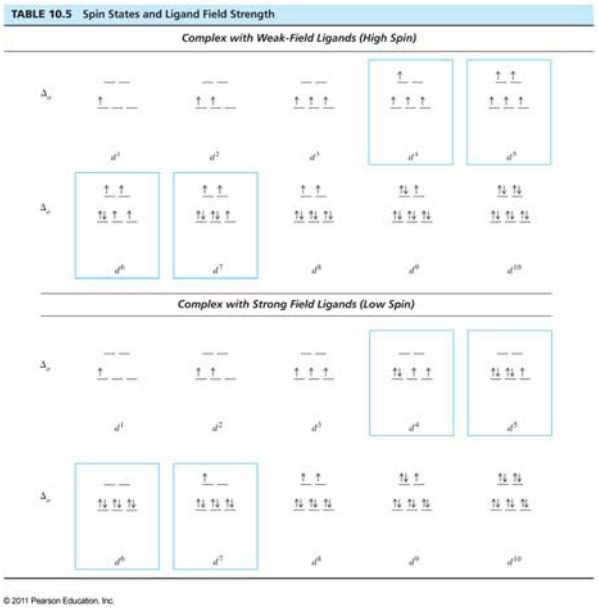
- weak-field ligands: weak interaction b/w ligands & M ions
  : smaller t_{2g} & e_g^* split
  : Δ_o small

- (d^0-d^3 / d^8-d^{10}) : only one e^- configuration is possible

- d^4-d^7: (high-spin & low-spin states) ➡ **in summary:** (**Strong ligand field → large Δ_o → low spin** / **Weak ligand field → small Δ_o → high spin**)

10.3.2 Orbital Splitting and Electron Spin

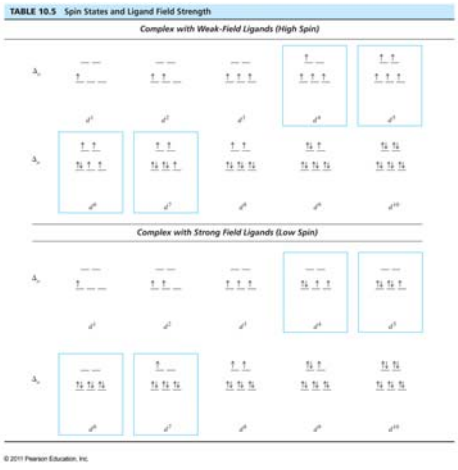
TABLE 10.5 Spin States and Ligand Field Strength



10.3.2 Orbital Splitting and Electron Spin

- *E* of pairing 2 e^-: (Coulombic *E* of repulsion, Π_c + quantum mechanical exchange *E*, Π_e) + Δ_o ➡ determines the orbital configuration of the e^-!!!

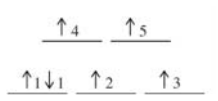
- Ground state: the lower total *E* orbital configuration
  - ↳ if there are more, Π_c → positive *E* → less stability
    Π_e → negative *E* → more stability



10.3.2 Orbital Splitting and Electron Spin

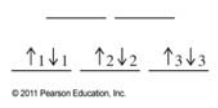
Example on p.379) Determine exchange *E* of d^6 high-spin vs. low-spin

1) high-spin:



↳ exchangeable pairs
1-2, 1-3, 2-3, 4-5
↳ 4 Π_e

2) low-spin:



↳ exchangeable pairs
(1-2, 1-3, 2-3) X 2 = 6
↳ 6 Π_e

⬇

The difference b/w high- & low-spin → $2\Pi_e$

10.3.2 Orbital Splitting and Electron Spin

- Δ_o : strong dependent to ligands & M
- Table 10.6: values of Δ_o for aqueous ions
  - ↳ weak field ligand (small Δ_o)
- # unpaired e^- → depends on the balance b/w Δ_o & Π
  - 1) If Δ_o > Π : pairing e^- → in the lower levels
    - ↳ net loss in *E*
    - ↳ low-spin
  - 2) If Δ_o < Π : more unpaired e^- → lower total *E*
    - ↳ high-spin

Co^{3+} → Δ_o near the size of Π
↳ $[Co(H_2O)_6]^{3+}$: only low-spin complex

TABLE 10.6 Orbital Splitting (Δ_o) and Mean Pairing Energy (Π) for Aqueous Ions[a]

	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+}	7,850[b]	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				

Sources: For Δ_o: M^{2+} data from D. A. Johnson and P. G. Nelson, *Inorg. Chem.*, **1995**, *34*, 5666; M^{3+} data from D. A. Johnson and P. G. Nelson, *Inorg. Chem.*, **1999**, *38*, 4949. For Π: Data from D. S. McClure, The Effects of Inner-orbitals on Thermodynamic Properties, in T. M. Dunn, D. S. McClure, and R. G. Pearson, *Some Aspects of Crystal Field Theory*, Harper & Row, New York, 1965, p. 82.

NOTE [a]Values given are in cm^{-1}.

[b] Estimated value

10.3.2 Orbital Splitting and Electron Spin

- for greater ligand-metal interactions,,
  - ↳ metal w/ higher charges
    - ex) Δ_o (3+) > Δ_o (2+)
      - values (d^5) < values (d^4, d^6)

- 2nd, 3rd row TM: forms low-spin complexes
  - ↳ ∵ 1) greater overlap b/w larger 4*d* & 5*d* and ligands orbital
    - 2) decrease of pairing *E* due to the larger volume available for e^- in the 4*d* & 5*d* than 3*d*

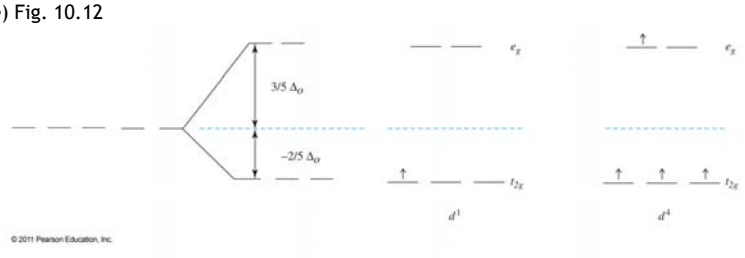
10.3.3 Ligand Field Stabilization Energy

- ligand field stabilization *E* (LFSE): difference b/w
  - 1) total *E* of a coordination complex from ligand field splitting of the orbitals
  - 2) orbital *E* for the same complex b/w all *d* orbitals are equally populated

: represent the stabilization of the *d* e^- due to the M-ligand environment

10.3.3 Ligand Field Stabilization Energy

- example) Fig. 10.12



- Insertion of *d* orbitals w/ ligands orbitals
  - splitting of orbitals *E*
    - t_{2g} sets: lowered *E* by $-2/5\ \Delta_o$
    - e_g sets: increased *E* by $3/5\ \Delta_o$

ex) d^1 system: $-2/5\ \Delta_o$

d^4 system (high spin): $3/5\ \Delta_o + 3(-2/5\ \Delta_o) = -3/5\ \Delta_o$

10.3.3 Ligand Field Stabilization Energy

- Table 10.7) LFSE values for σ-bonded octahedral complexes w/ 1-10 e^- in both hi-/lo-spin
  - (1 → 3 e^- / 8 → 10 e^-) → no diff. in *E* of unpaired e^- or the LFSE
  - 4 → 7 e^- → significant *E*. diff. in both

TABLE 10.7 Ligand Field Stabilization Energies

Number of d Electrons	Weak-Field Arrangement t_{2g}	Weak-Field Arrangement e_g	LFSE (Δ_o)	Coulombic Energy	Exchange Energy
1	↑		$-\frac{4}{10}$		
2	↑ ↑		$-\frac{8}{10}$		Π_c
3	↑ ↑ ↑		$-\frac{12}{10}$		$3\Pi_c$
4	↑ ↑ ↑ ↑		$-\frac{6}{10}$		$3\Pi_c$
5	↑ ↑ ↑ ↑ ↑		0		$4\Pi_c$
6	↑↓ ↑ ↑ ↑ ↑		$-\frac{4}{10}$	Π_c	$4\Pi_c$
7	↑↓ ↑↓ ↑ ↑ ↑		$-\frac{8}{10}$	$2\Pi_c$	$5\Pi_c$
8	↑↓ ↑↓ ↑↓ ↑ ↑		$-\frac{12}{10}$	$3\Pi_c$	$7\Pi_c$
9	↑↓ ↑↓ ↑↓ ↑↓ ↑		$-\frac{6}{10}$	$4\Pi_c$	$7\Pi_c$
10	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		0	$5\Pi c$	$8\Pi_c$

Number of d Electrons	Strong-Field Arrangement t_{2g}	Strong-Field Arrangement e_g	LFSE (Δ_o)	Coulombic Energy	Exchange Energy	Strong Field – Weak Field
1	↑		$-\frac{4}{10}$			0
2	↑ ↑		$-\frac{8}{10}$		Π_c	0
3	↑ ↑ ↑		$-\frac{12}{10}$		$3\Pi_c$	0
4	↑↓ ↑ ↑		$-\frac{8}{10}$	Π_c	$3\Pi_c$	$-\Delta_o + \Pi_c$
5	↑↓ ↑↓ ↑		$-\frac{12}{10}$	$2\Pi_c$	$4\Pi_c$	$-2\Delta_o + 2\Pi_c$
6	↑↓ ↑↓ ↑↓		$-\frac{24}{10}$	$3\Pi_c$	$6\Pi_c$	$-2\Delta_o + 2\Pi_c + 2\Pi_c$
7	↑↓ ↑↓ ↑↓ ↑		$-\frac{18}{10}$	$3\Pi_c$	$6\Pi_c$	$-\Delta_o + \Pi_c + \Pi_c$
8	↑↓ ↑↓ ↑↓ ↑ ↑		$-\frac{12}{10}$	$3\Pi_c$	$7\Pi_c$	0
9	↑↓ ↑↓ ↑↓ ↑↓ ↑		$-\frac{6}{10}$	$4\Pi_c$	$7\Pi_c$	0
10	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		0	$5\Pi_c$	$8\Pi_c$	0

NOTE: In addition to the LFSE, each pair formed has a positive Coulombic energy, Π_c, and each set of two electrons with the same spin has a negative exchange energy, Π_e. When $\Delta_o > \Pi_c$ for d^4 or d^9, or when $\Delta_o > \Pi_c + \Pi_c$ for d^5 or d^7, the strong-field arrangement (low spin) is favored.

10.3.3 Ligand Field Stabilization Energy

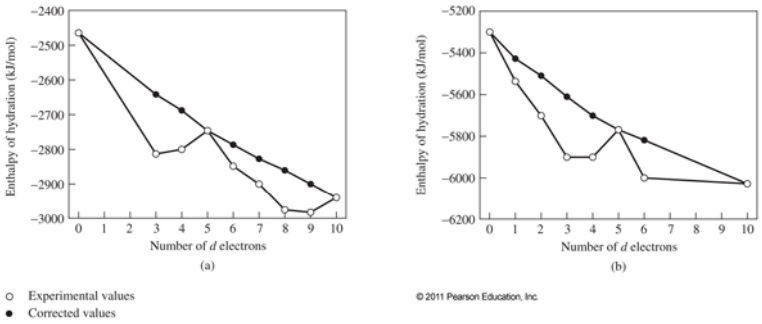
- The most commonly cited example of LFSE in thermodynamic data,,
  - Exothermic enthalpy of hydration of bivalent ions of the 1st TM

$$M^{2+}(g) + 6H_2O(l) \rightarrow [M(H_2O)_6]^{2+}(aq)$$

: for ions w/ spherical symm. → across the TM series
→ radius of ions ↓
→ nuclear charge ↑
→ electrostatic attraction ↑
→ ΔH → exothermic ↑ (more negative)

10.3.3 Ligand Field Stabilization Energy

- Fig.10.13. linear curve of the "corrected" enthalpies
  vs.
  double-humped experimental values
  → difference
  ↓
  LFSE for high-spin



10.3.3 Ligand Field Stabilization Energy

- **Why do we care about LFSE?**

  1) provides a more quantitative approach to the high-/low-spin e^- configuration

     ↳ helping predict which configuration will be more likely

  2) basis of the spectra (Chapter 11)

     ↳ measurement of Δ_o: allow more quantitative understanding of M-ligand interactions

10.3.5 Square-Planar Complexes

▪ **Sigma Bonding**

- $[Ni(CN)_4]^{2-}$, D_{4h}

: y-axis → toward the central atom → σ-bonding (p_y)
x-axis → plane of molecule → $\pi_{\parallel}$ (or p_x)
z-axis → perpendicular to the plane of the molecules → $\pi_{\perp}$ (or p_z)

: Fig.10.14

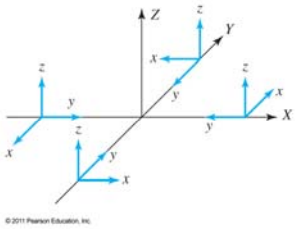


TABLE 10.8 Representations and Orbital Symmetry for Square-Planar Complexes

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
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	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(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	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{σ} (y)	4	0	0	2	0	0	0	4	2	0
$\Gamma_{\parallel}$ (x)	4	0	0	−2	0	0	0	4	−2	0
$\Gamma_{\perp}$ (z)	4	0	0	−2	0	0	0	−4	2	0

$\Gamma_{\sigma} = A_{1g} + B_{1g} + E_u$ (σ) Matching orbitals on the central atom: s, d_{z^2}, $d_{x^2-y^2}$, (p_x, p_y)

$\Gamma_{\parallel} = A_{2g} + B_{2g} + E_u$ ($\parallel$) Matching orbitals on the central atom: d_{xy}, (p_x, p_y)

$\Gamma_{\perp} = A_{2u} + B_{2u} + E_g$ ($\perp$) Matching orbitals on the central atom: p_z, (d_{xz}, d_{yz})