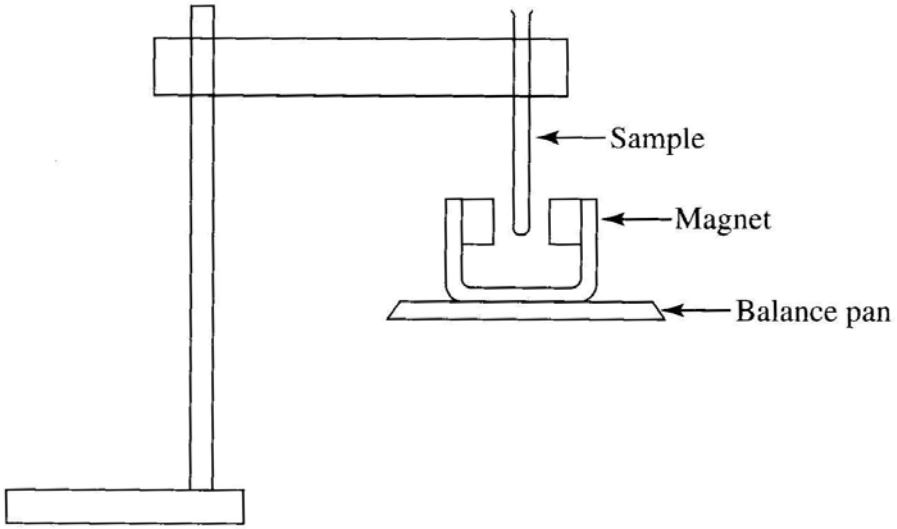
Bonding in Transition Metal Complexes :

Valence Bond Theory, Crystal Field Theory and Ligand Field Theory

Magnetic Susceptibility Measurement



$\mu = 2.828\ (\chi T)^{\frac{1}{2}}$ (T = Kelvin temperature) The unit of magnetic moment is the Bohr magneton, with $1\ \mu_B = 9.27 \times 10^{-24}\ \text{J T}^{-1}$ (joules/tesla).

Equation for Magnetic Moment

$$\mu_{S+L} = g\sqrt{[S(S+1)] + [\tfrac{1}{4}L(L+1)]}$$

When orbital contribution is small

$$\mu_S = g\sqrt{S(S+1)}$$

TABLE 10-3
Calculated and Experimental Magnetic Moments

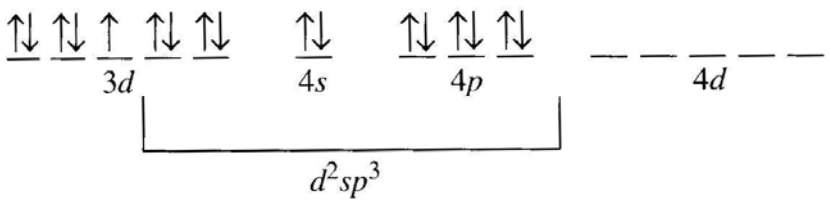
Ion	*n*	*S*	*L*	μ_S	μ_{S+L}	*Observed*
V^{4+}	1	$\frac{1}{2}$	2	1.73	3.00	1.7–1.8
Cu^{2+}	1	$\frac{1}{2}$	2	1.73	3.00	1.7–2.2
V^{3+}	2	1	3	2.83	4.47	2.6–2.8
Ni^{2+}	2	1	3	2.83	4.47	2.8–4.0
Cr^{3+}	3	$\frac{3}{2}$	3	3.87	5.20	~3.8
Co^{2+}	3	$\frac{3}{2}$	3	3.87	5.20	4.1–5.2
Fe^{2+}	4	2	2	4.90	5.48	5.1–5.5
Co^{3+}	4	2	2	4.90	5.48	~5.4
Mn^{2+}	5	$\frac{5}{2}$	0	5.92	5.92	~5.9
Fe^{3+}	5	$\frac{5}{2}$	0	5.92	5.92	~5.9

SOURCE: F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, New York, 1980, pp. 627–628.

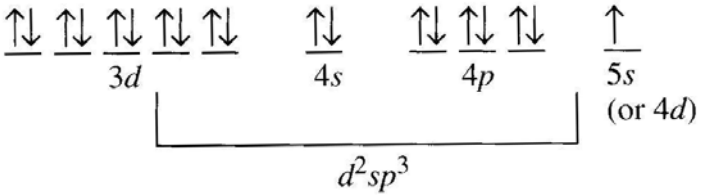
NOTE: All moments are given in Bohr magnetons.

Valence Bond Theory : Proposed by Pauling in 1930's using the hybridization idea.

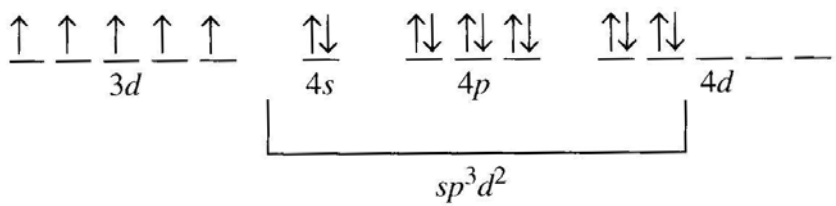
For a d^5 metal ion:
Inner orbital



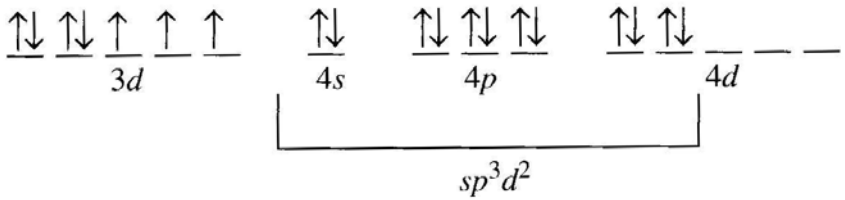
For a d^7 metal ion:
Inner orbital



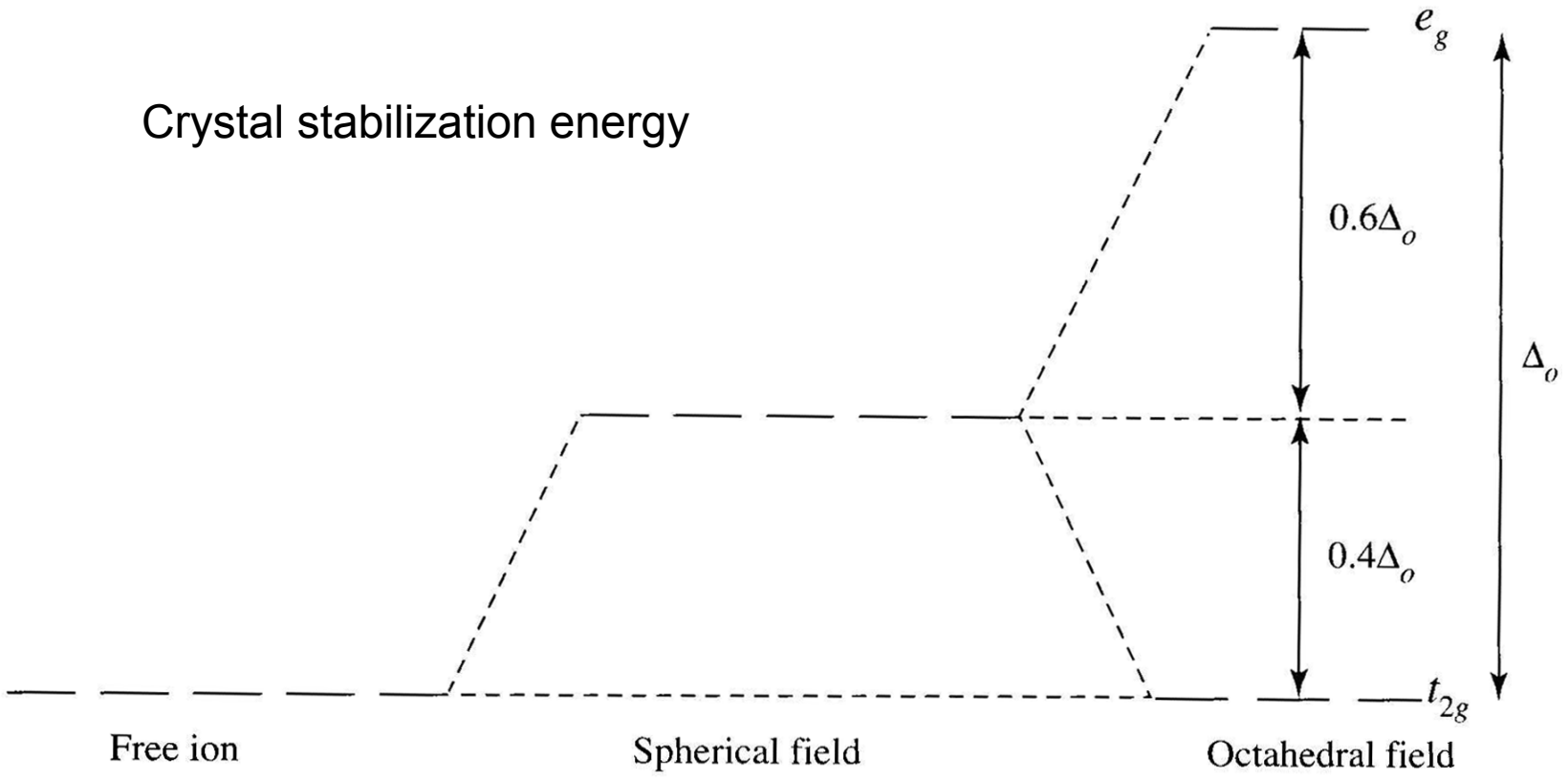
For a d^5 metal ion:
Outer orbital



For a d^7 metal ion:
Outer orbital

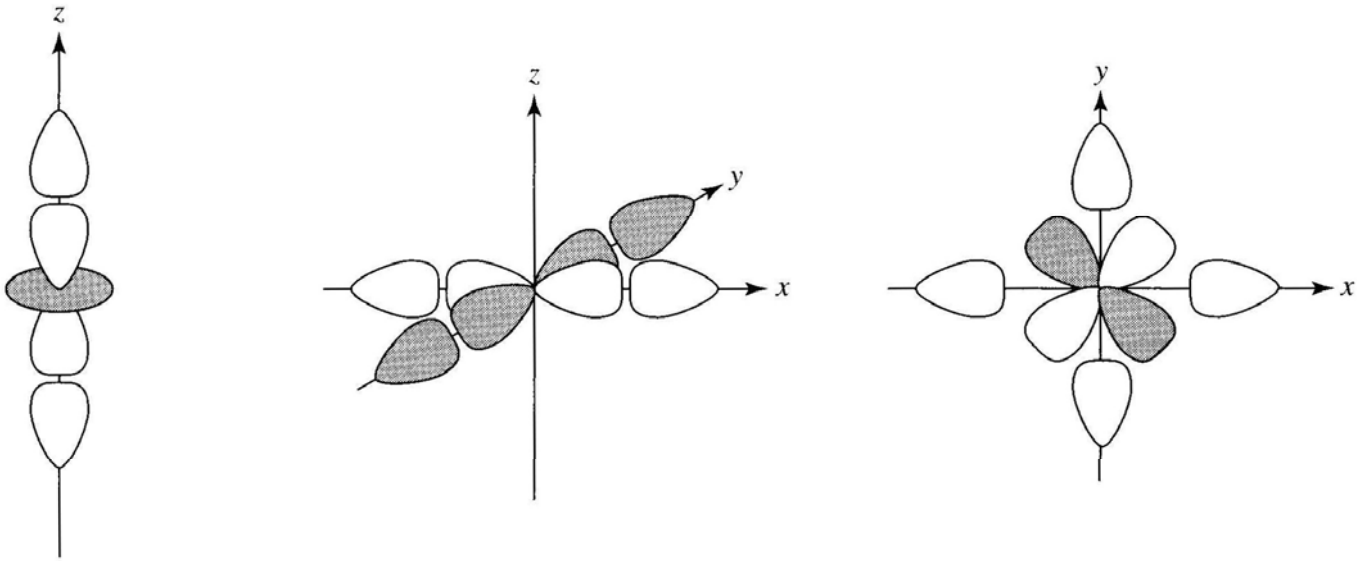


Crystal Field Theory : Original develop for description of the electronic structure of metal ions in ionic crystals.



Ligand Field Theory : The electrostatic crystal field theory and the molecular orbital theory were combined into a more complete theory.

Octahedral complex



Bonding interaction between two ligand orbitals and metal d_{z^2} orbital

Bonding interaction between four ligand orbitals and metal $d_{x^2-y^2}$ orbital

Nonbonding (no interaction) four ligand orbitals and metal d_{xy} orbital

Octahedral Complexes

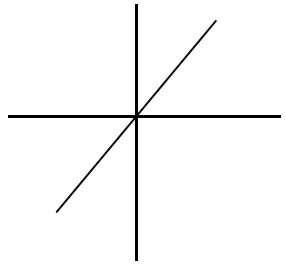


TABLE 10-4
Character table for O_h

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		
Γ	6	0	0	2	2	0	0	0	4	2		$x^2 + y^2 + z^2$
A_{1g}	1	1	1	1	1	1	1	1	1	1		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2,\ x^2 - y^2)$

Molecular Orbitals of Octahedral Complex MX_6

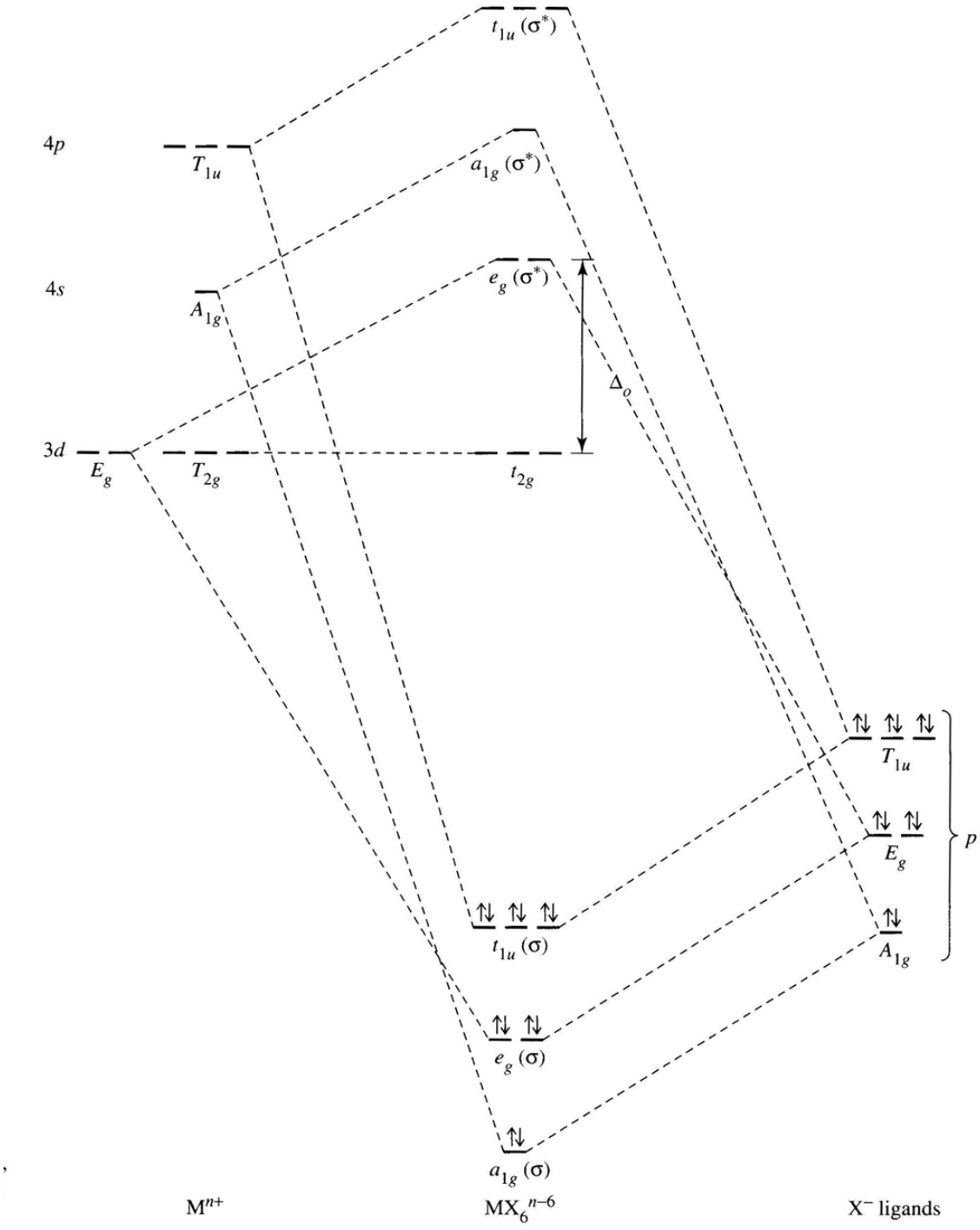
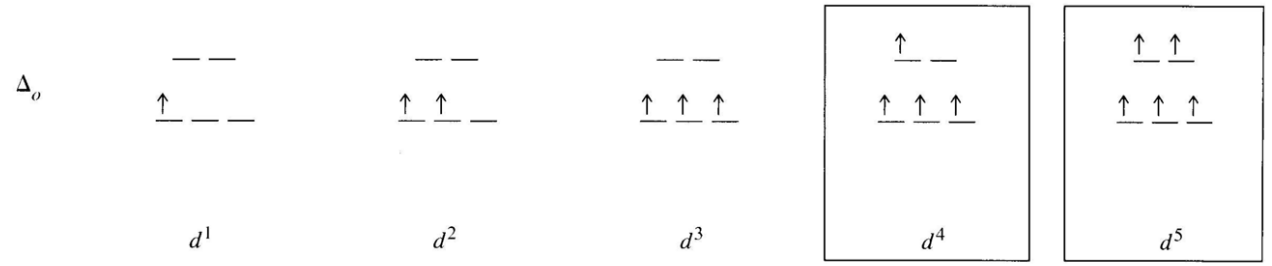
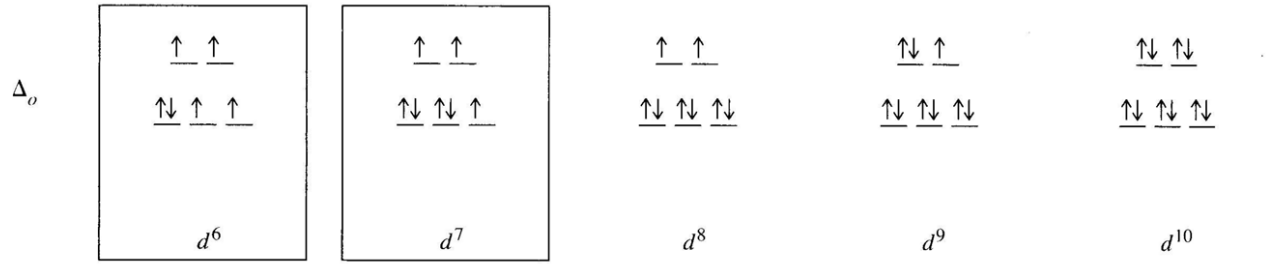


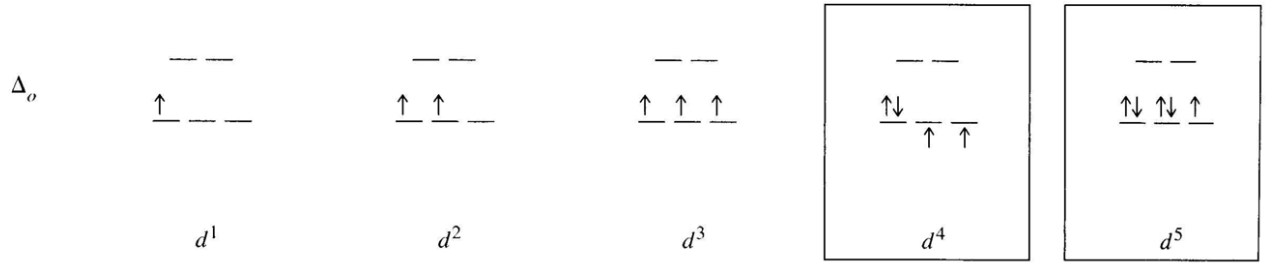
TABLE 10-5
Spin States and Ligand Field Strength

Complex with Weak Field Ligands (High Spin)





Complex with Strong Field Ligands (Low Spin)



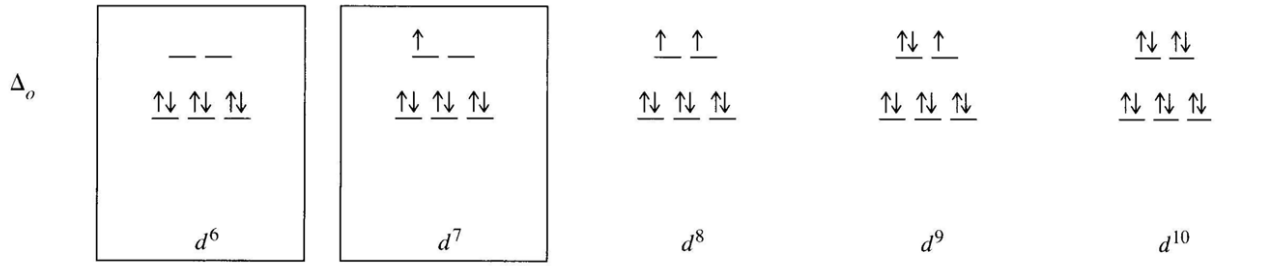


TABLE 10-6
Orbital Splitting (Δ_o) and Mean Pairing Energy (Π) for Aqueous Ions[a]

	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.

Ligand Field Stabilization Energy

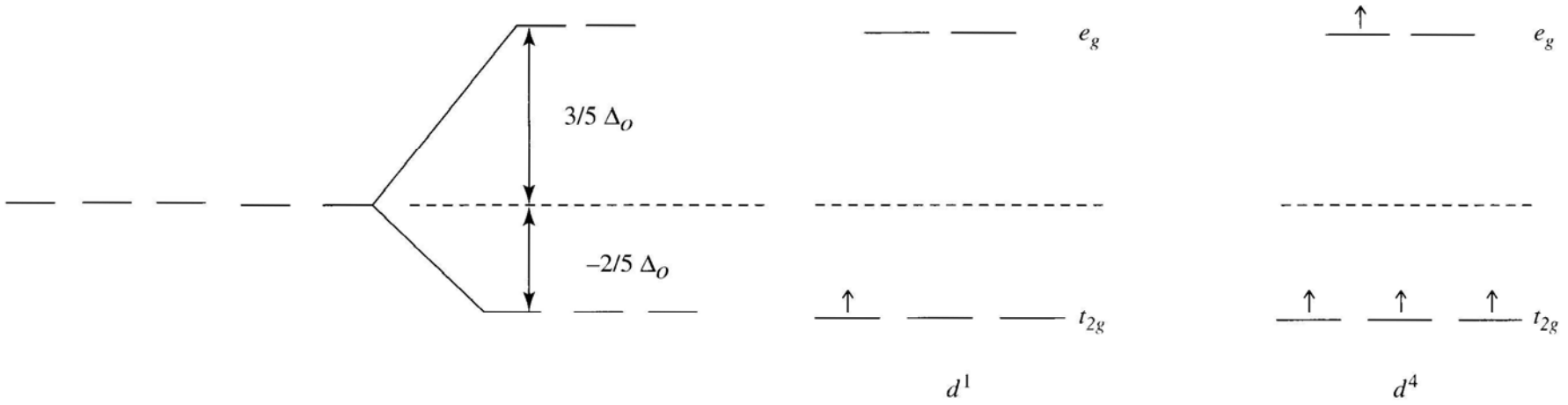


FIGURE 10-6 Splitting of Orbital Energies in a Ligand Field.

TABLE 10-7
Ligand Field Stabilization Energies

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

Number of d Electrons	*Strong-Field Arrangement*					*LFSE* (Δ_o)	*Coulombic Energy*	*Exchange Energy*	*Strong Field − Weak Field*
	t_{2g}			e_g					
1	↑					$-\frac{2}{5}$			0
2	↑	↑				$-\frac{4}{5}$		Π_e	0
3	↑	↑	↑			$-\frac{6}{5}$		$3\Pi_e$	0
4	↑↓	↑	↑			$-\frac{8}{5}$	Π_c	$3\Pi_e$	$-\Delta_o + \Pi_c$
5	↑↓	↑↓	↑			$-\frac{10}{5}$	$2\Pi_c$	$4\Pi_e$	$-2\Delta_o + 2\Pi_c$
6	↑↓	↑↓	↑↓			$-\frac{12}{5}$	$3\Pi_c$	$6\Pi_e$	$-2\Delta_o + 2\Pi_c + 2\Pi_e$
7	↑↓	↑↓	↑↓	↑		$-\frac{9}{5}$	$3\Pi_c$	$6\Pi_e$	$-\Delta_o + \Pi_c + \Pi_e$
8	↑↓	↑↓	↑↓	↑	↑	$-\frac{6}{5}$	$3\Pi_c$	$7\Pi_e$	0
9	↑↓	↑↓	↑↓	↑↓	↑	$-\frac{3}{5}$	$4\Pi_c$	$7\Pi_e$	0
10	↑↓	↑↓	↑↓	↑↓	↑↓	0	$5\Pi_c$	$8\Pi_e$	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^5 or when $\Delta_o > \Pi_c + \Pi_e$ for d^6 or d^7, the strong-field arrangement (low spin) is favored.

Enthalpies of Hydration of Transition Metal Ions

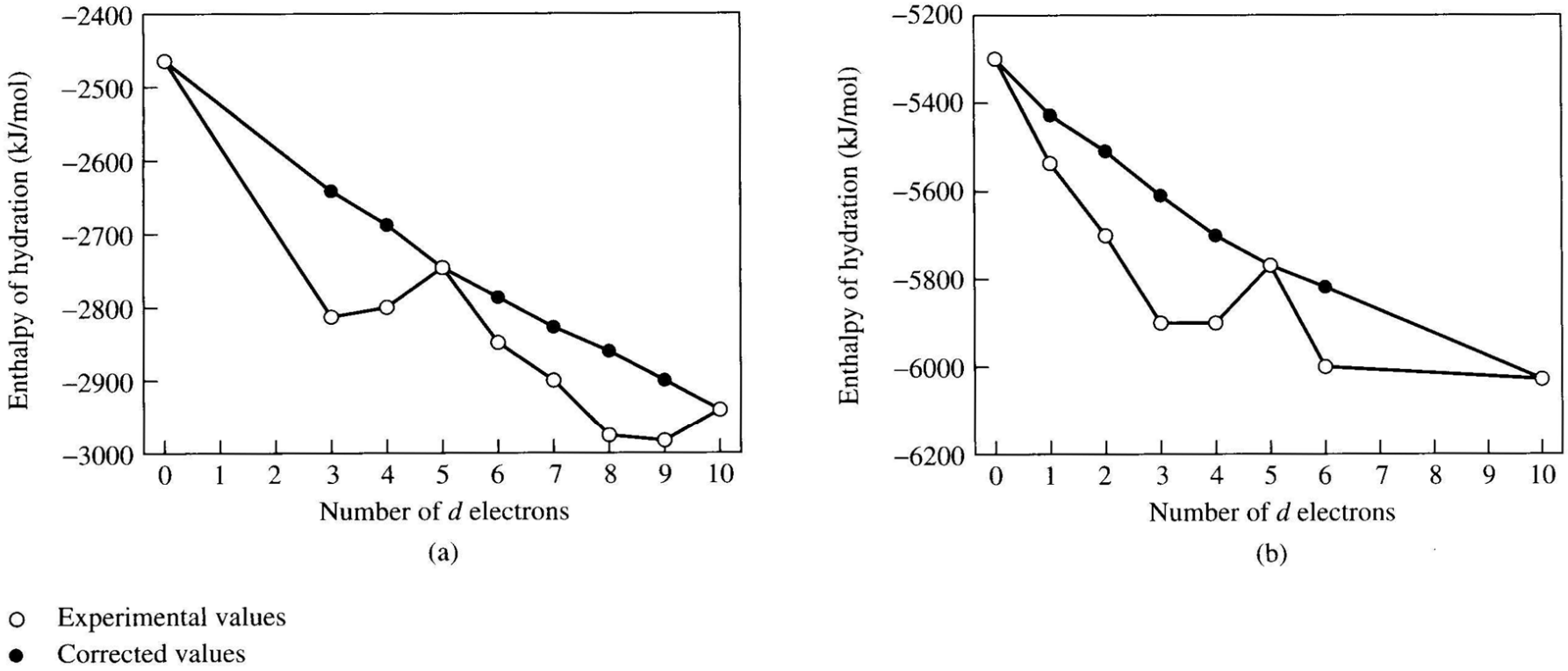


FIGURE 10-7 Enthalpies of Hydration of Transition Metal Ions. The lower curves show experimental values; the upper curves result when contributions from spin-orbit splitting, a relaxation effect from contraction of the metal-ligand distance, and interelectronic repulsion energy are subtracted. (a) 2+ ions. (b) 3+ ions. (Reproduced with permission from D. A. Johnson and P. G. Nelson, *Inorg. Chem.*, **1995**, *34*, 5666 (M^{2+} data); and D. A. Johnson and P. G. Nelson, *Inorg. Chem.*, **1999**, 4949 (M^{3+} data). © 1995, 1999, American Chemical Society.)

Octahedral Complex with π Interactions

TABLE 10-8
Representations of Octahedral π Orbitals

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	(d_{xy}, d_{xz}, d_{yz})
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(p_x, p_y, p_z)
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1	

$$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$

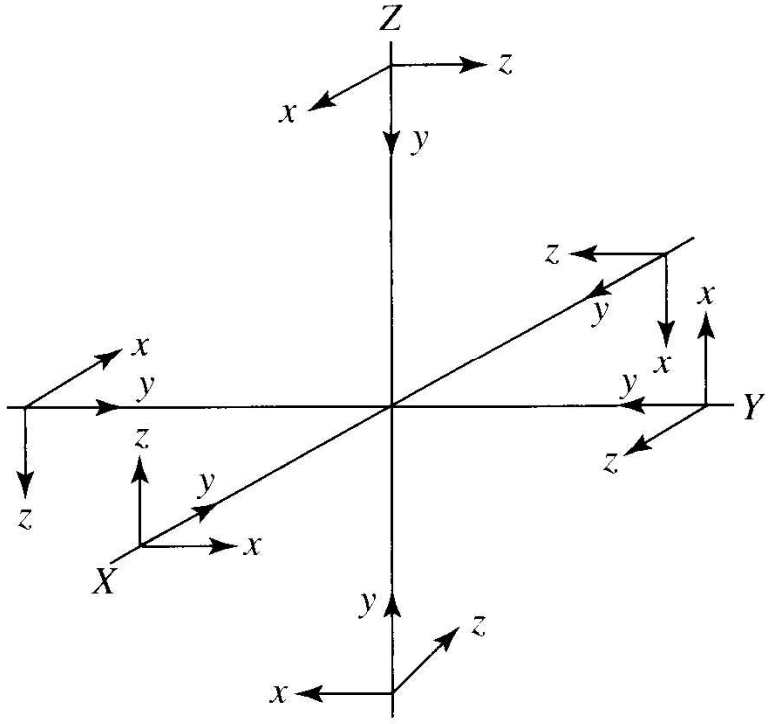
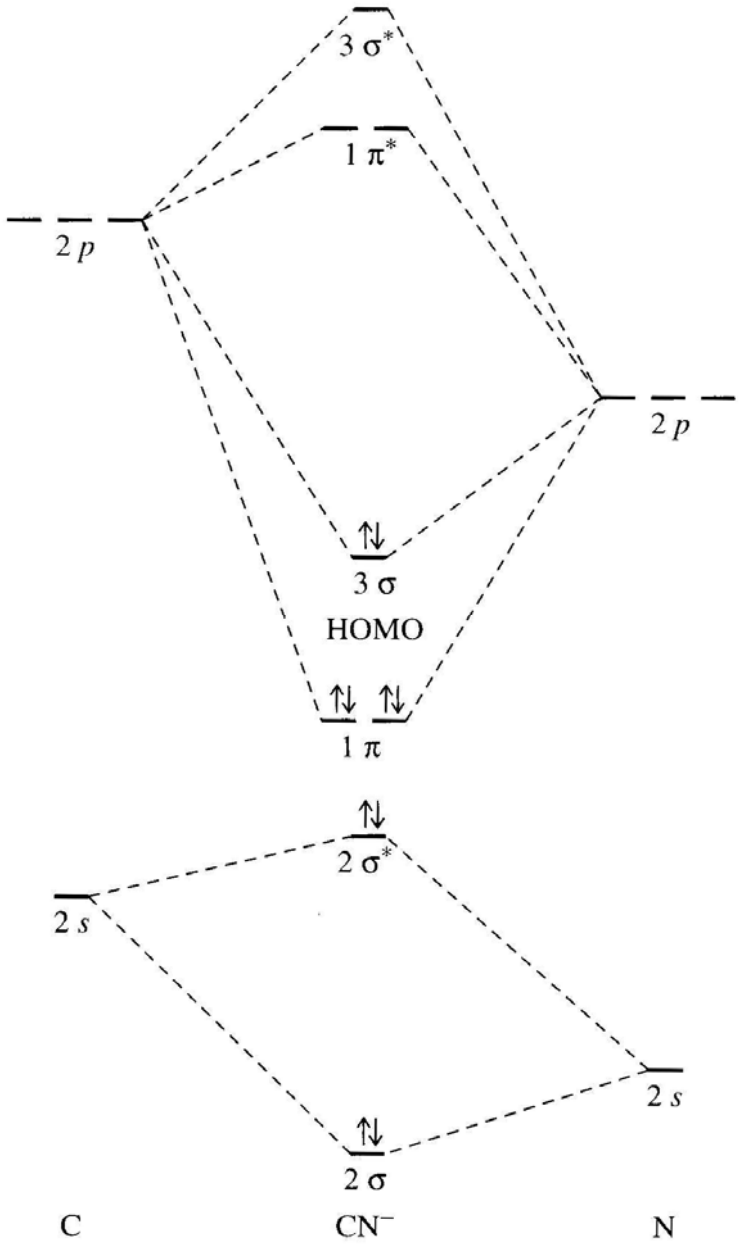
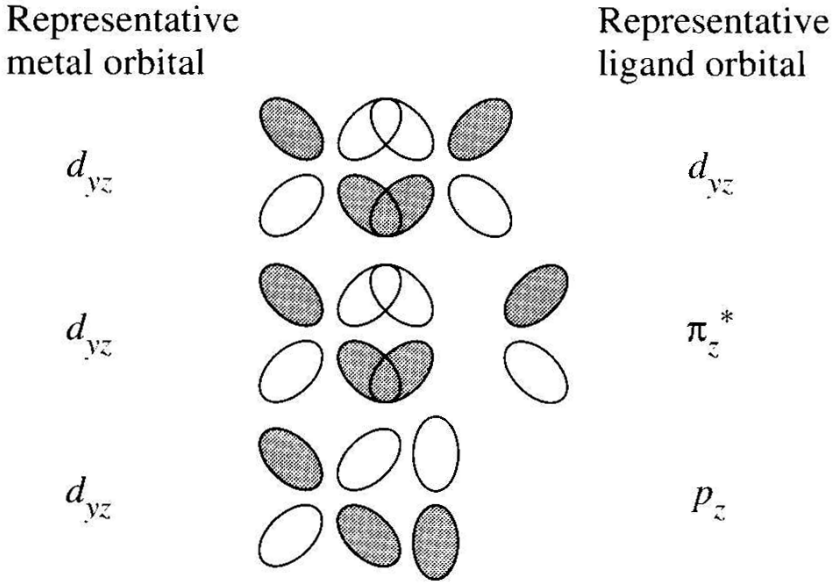


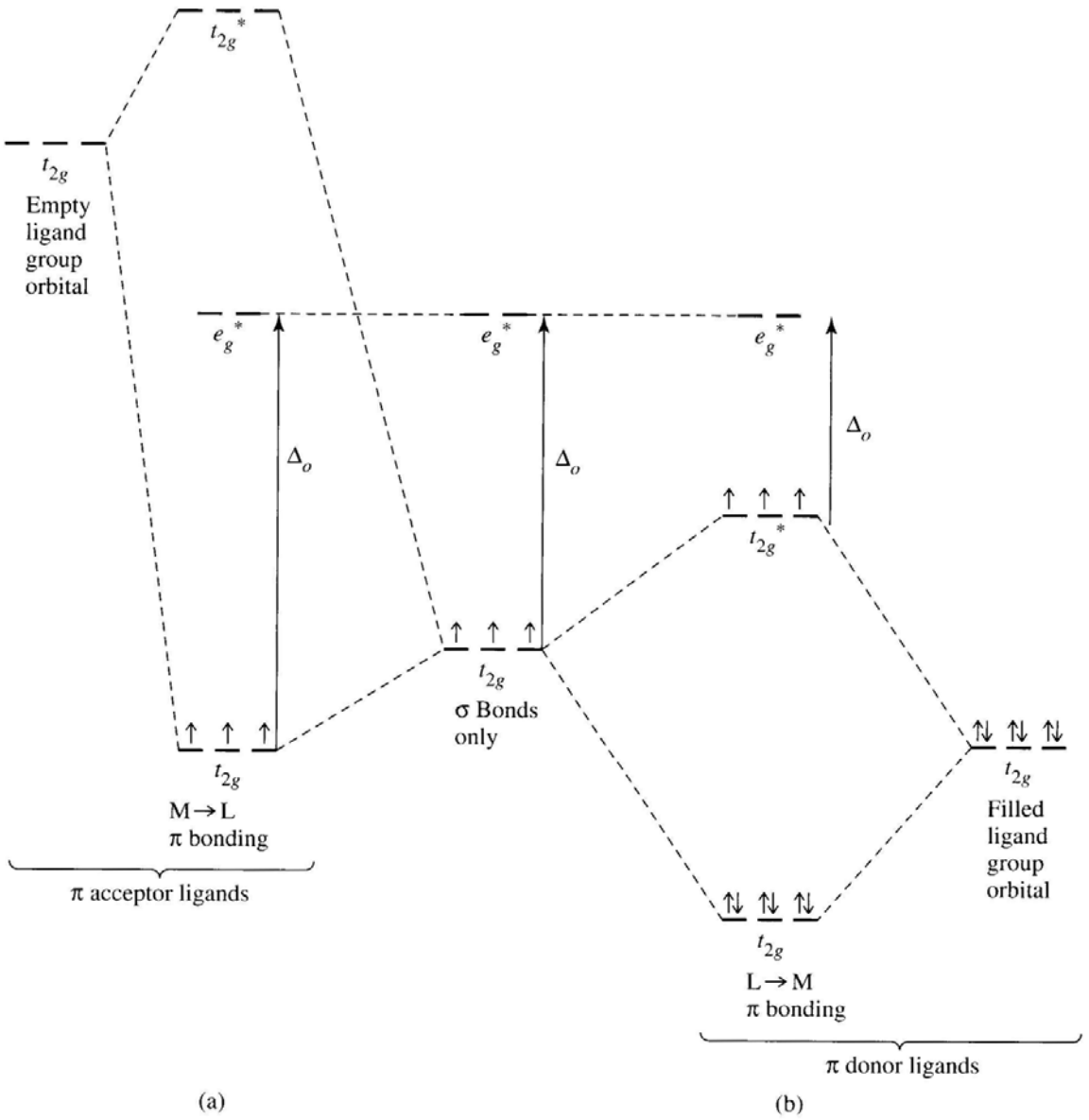
FIGURE 10-8 Coordinate System for Octahedral π Orbitals.

CN^- πAcceptor Ligand and Metal d-Orbital Interaction





Interaction of π Acceptor and π Donor Ligand with Metal Ions



Square Planar Complex

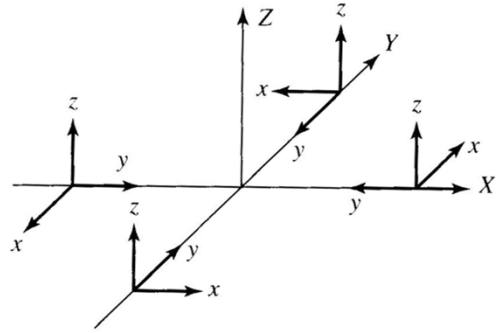


FIGURE 10-12 Coordinate System for Square-Planar Orbitals.

TABLE 10-9
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		$x^2 + y^2, z^2$
A_{2g}	1	1	1	−1		1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1		1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1		1	−1	1	−1	1		xy
E_g	2	0	−2	0		2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1		−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1		−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1		−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1		−1	1	−1	1	−1		
E_u	2	0	−2	0		−2	0	2	0	0	(x, y)	

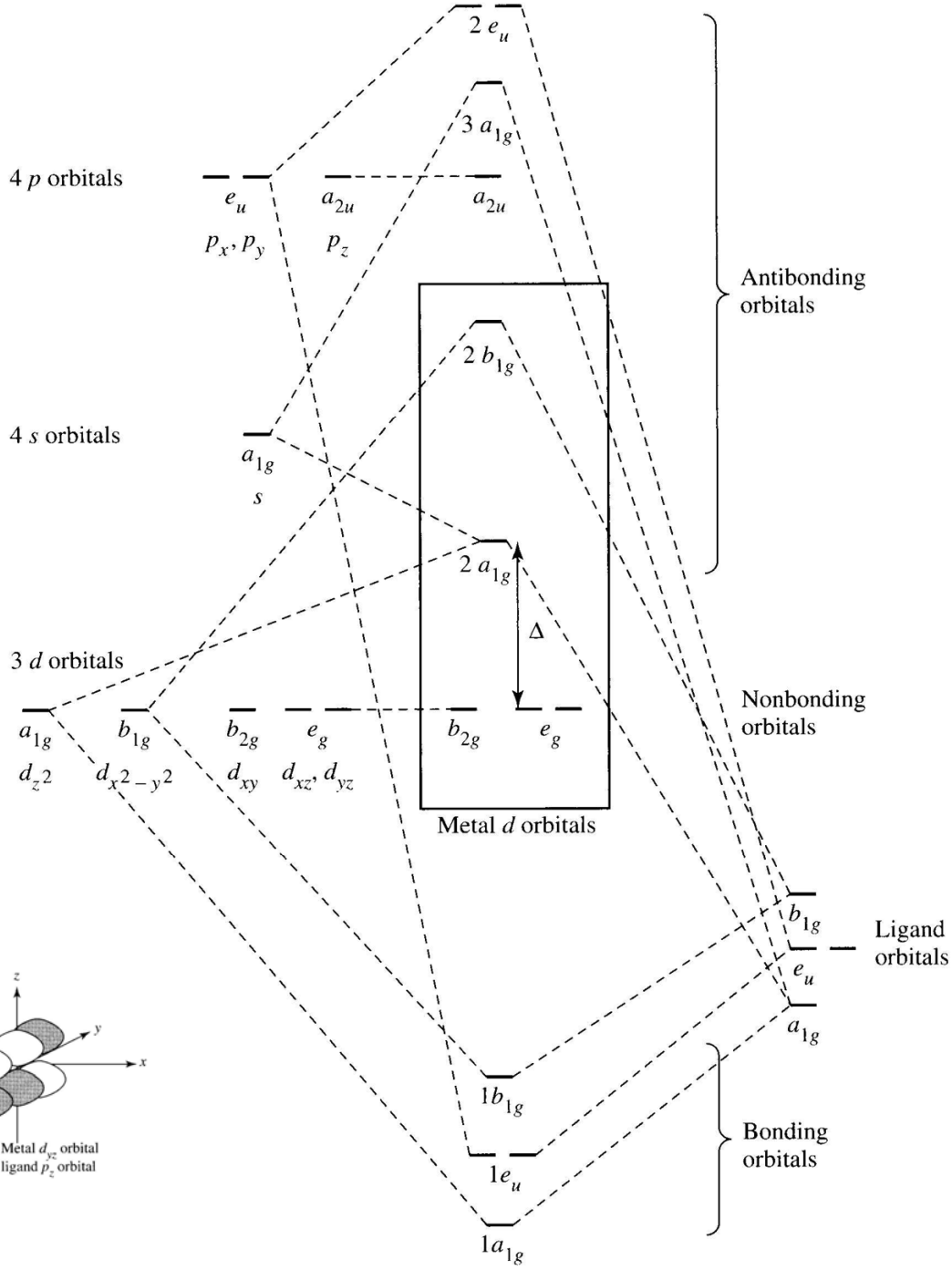
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
Γ_{p_x}	4	0	0	−2		0	0	4	−2	0	$p_\parallel$
Γ_{p_y}	4	0	0	2		0	0	4	2	0	p_σ
Γ_{p_z}	4	0	0	−2		0	0	−4	2	0	$p_\perp$

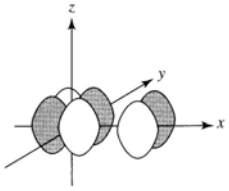
$\Gamma_{p_y} = A_{1g} + B_{1g} + E_u$ (σ) Matching orbitals on the central atom: $s, d_{z^2}, d_{x^2-y^2}, (p_x, p_y)$

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

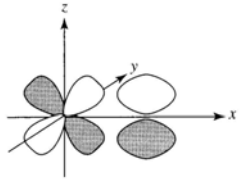
$\Gamma_{p_z} = A_{2u} + B_{2u} + E_g$ ($\perp$) Matching orbitals on the central atom: $p_z, (d_{xz}, d_{yz})$

Molecular Orbital of Square Planar Complex

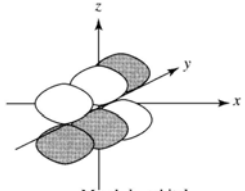




Metal d_{xy} orbital
ligand p_x orbital



Metal d_{xz} orbital
ligand p_z orbital



Metal d_{yz} orbital
ligand p_z orbital

Molecular Orbital of Square Planar Complex

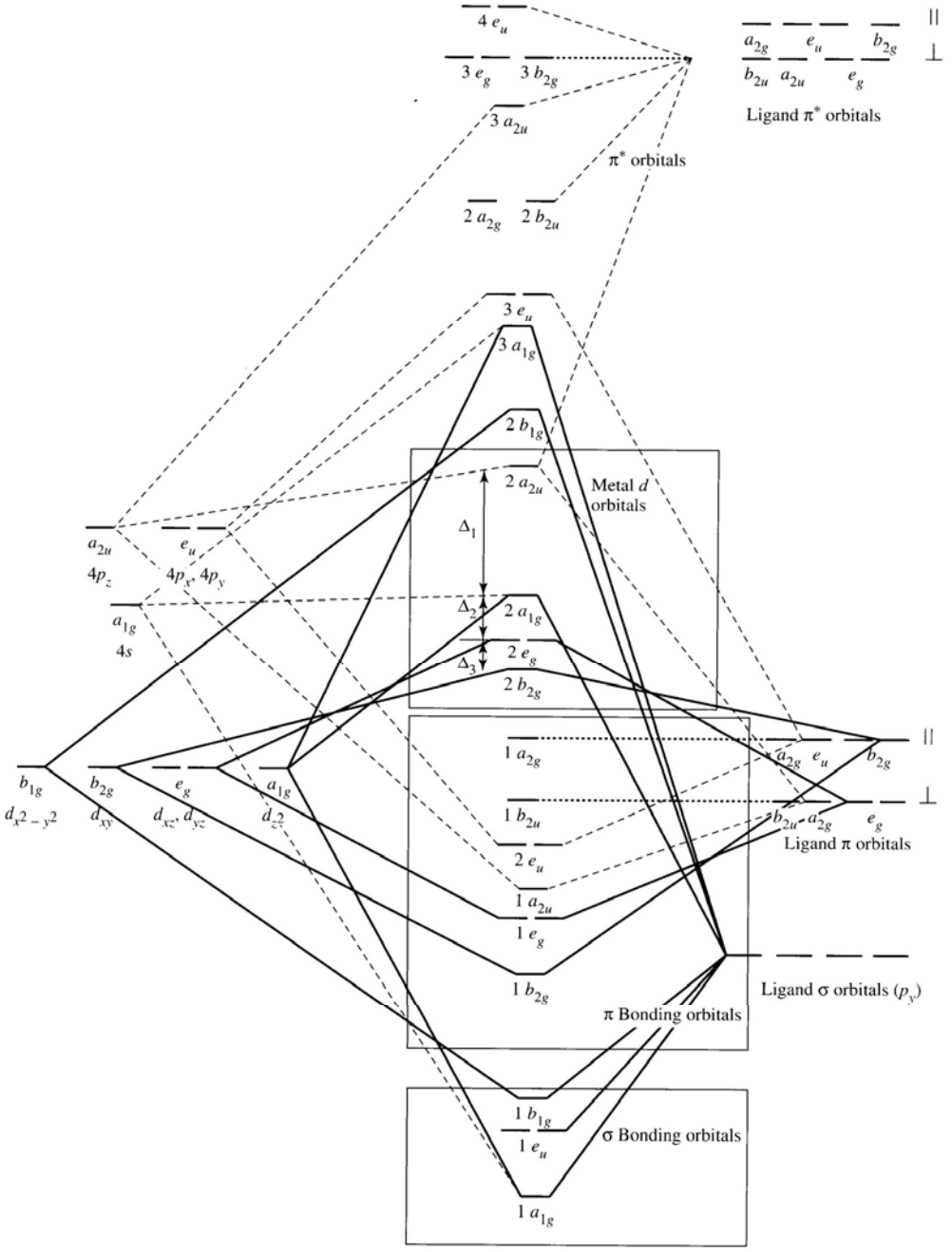


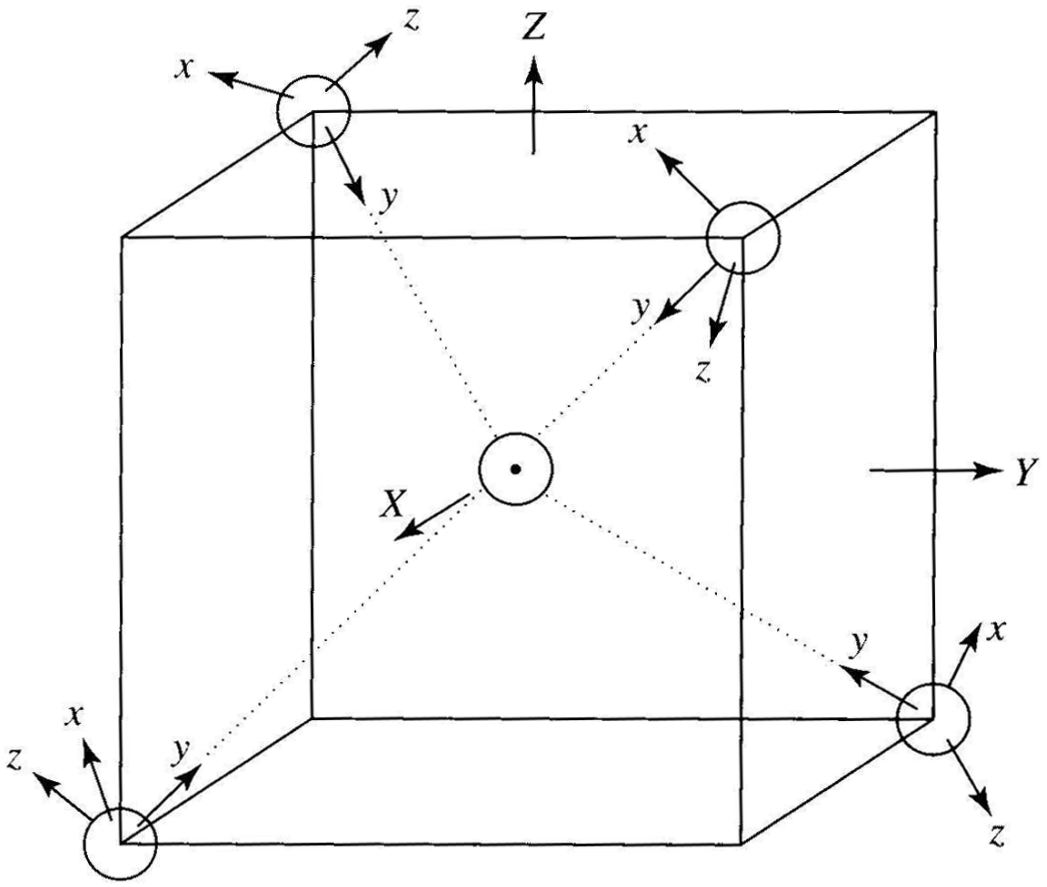
FIGURE 10-15 D_{4h} Molecular Orbitals, Including π Orbitals. Interactions with metal d orbitals are indicated by solid lines, interactions with metal s and p orbitals by dashed lines, and nonbonding orbitals by dotted lines.

Tetrahedral Complex

TABLE 10-10
Representations of Tetrahedral Orbitals

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1			$x^2 + y^2 + z^2$
A_2	1	−1	1	−1			
E	2	−1	2	0			$(2x^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1		(R_x, R_y, R_z)	
T_2	3	0	−1	−1		(x, y, z)	(xy, yz, xz)
Γ_σ	4	1	0	0		$A_1 + T_2$	
Γ_π	8	−1	0	0		$E + T_1 + T_2$	

Geometries and Orbital Splitting in Tetrahedral Complex



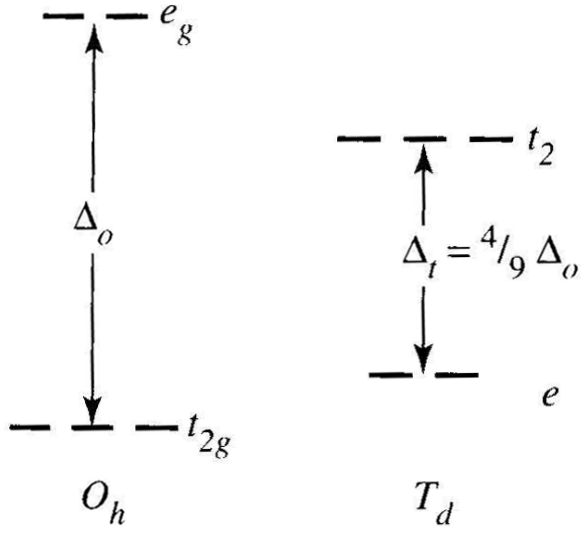
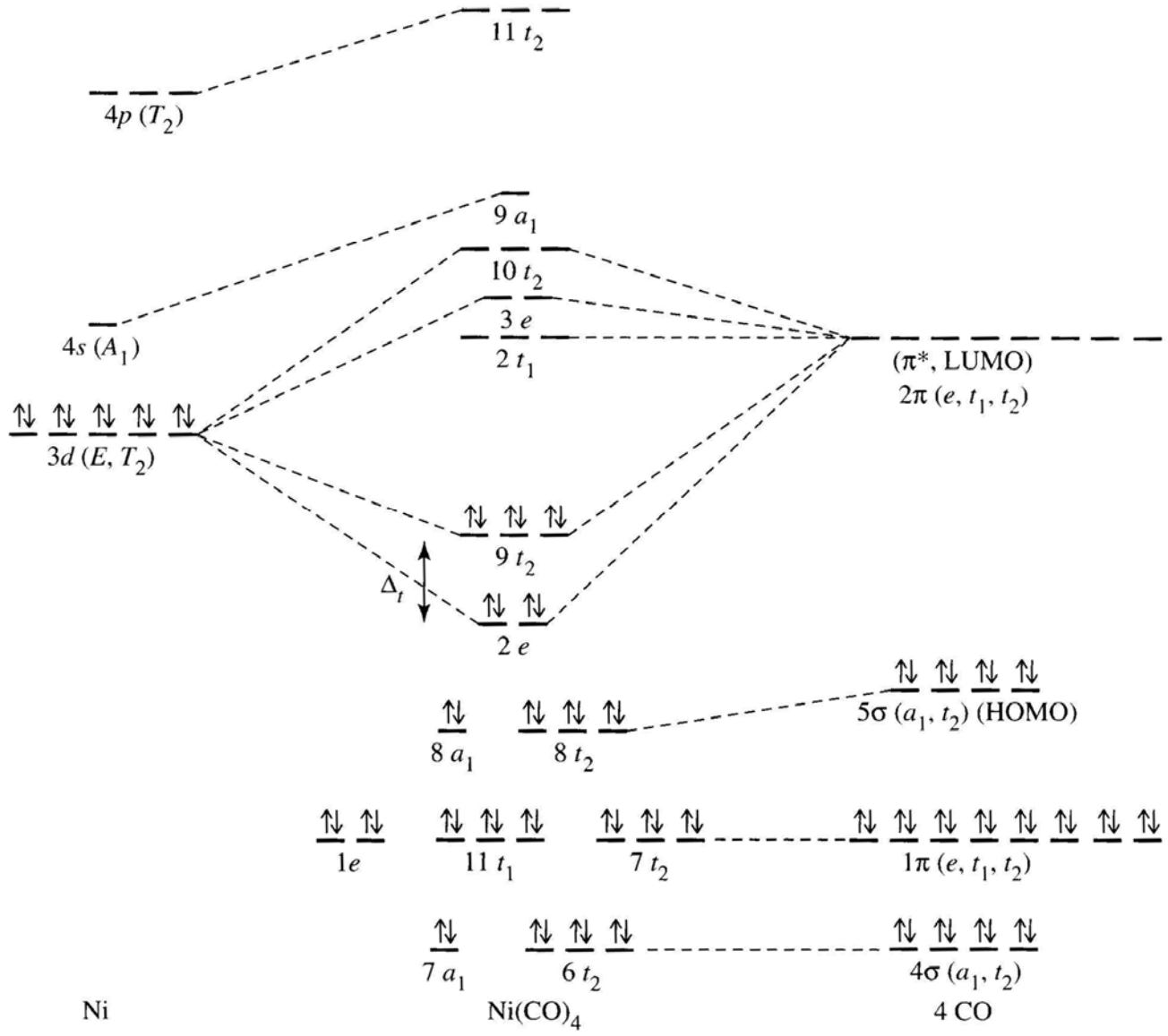


FIGURE 10-17 Orbital Splitting in Octahedral and Tetrahedral Geometries.

Molecular Orbital of Tetrahedral Complex



Angular Overlap Model

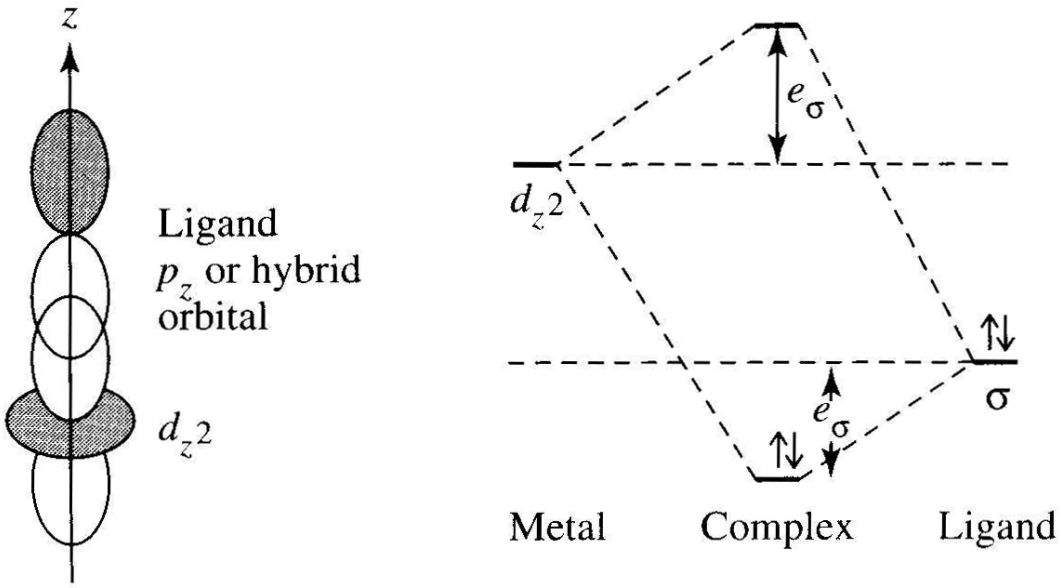
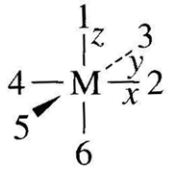
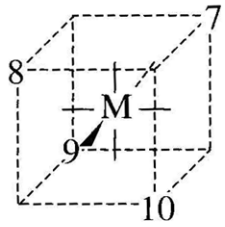


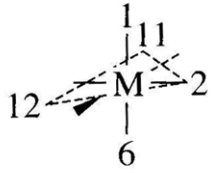
TABLE 10-11
Angular Overlap Parameters: Sigma Interactions



Octahedral positions



Tetrahedral positions



Trigonal-bipyramidal positions

CN	*Shape*	*Positions*
2	Linear	1, 6
3	Trigonal	2, 11, 12
3	T shape	1, 3, 5
4	Tetrahedral	7, 8, 9, 10
4	Square planar	2, 3, 4, 5
5	Trigonal bipyramidal	1, 2, 6, 11, 12
5	Square pyramidal	1, 2, 3, 4, 5
6	Octahedral	1, 2, 3, 4, 5, 6

Sigma Interactions (all in units of e_σ)
Metal d Orbital

Ligand Position	z^2	$x^2 - y^2$	xy	xz	yz
1	1	0	0	0	0
2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
3	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
5	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
6	1	0	0	0	0
7	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
8	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
9	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
10	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
11	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0
12	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0

Angular Overlap Model : σ Interaction for octahedral complex

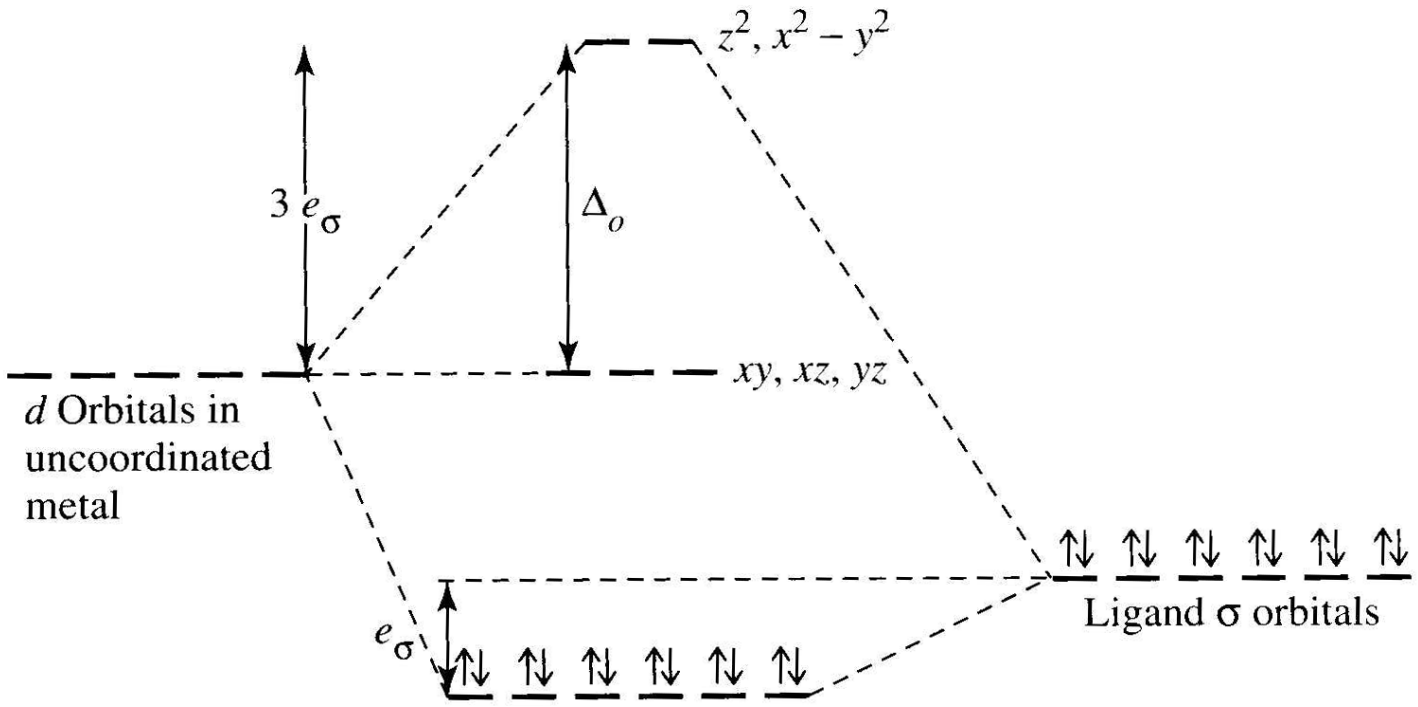
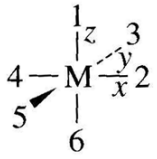
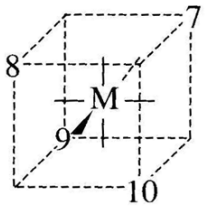


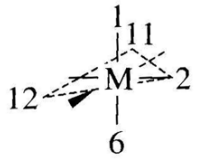
TABLE 10-12
Angular Overlap Parameters: Pi Interactions



Octahedral positions



Tetrahedral positions



Trigonal bipyramidal positions

CN	*Shape*	*Positions*
2	Linear	1, 6
3	Trigonal	2, 11, 12
3	T shape	1, 3, 5
4	Tetrahedral	7, 8, 9, 10
4	Square planar	2, 3, 4, 5
5	Trigonal bipyramidal	1, 2, 6, 11, 12
5	Square pyramidal	1, 2, 3, 4, 5
6	Octahedral	1, 2, 3, 4, 5, 6

Pi Interactions (all in units of e_π)
Metal d Orbital

Ligand Position	z^2	$x^2 - y^2$	xy	xz	yz
1	0	0	0	1	1
2	0	0	1	1	0
3	0	0	1	0	1
4	0	0	1	1	0
5	0	0	1	0	1
6	0	0	0	1	1
7	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
8	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
9	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
10	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
11	0	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$
12	0	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$

Angular Overlap Model : π interaction for octahedral complex

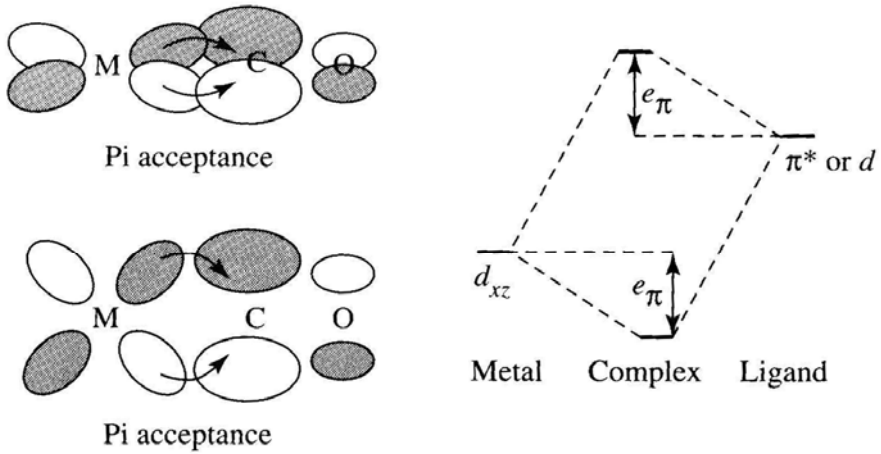


FIGURE 10-21 Pi-Acceptor Interactions.

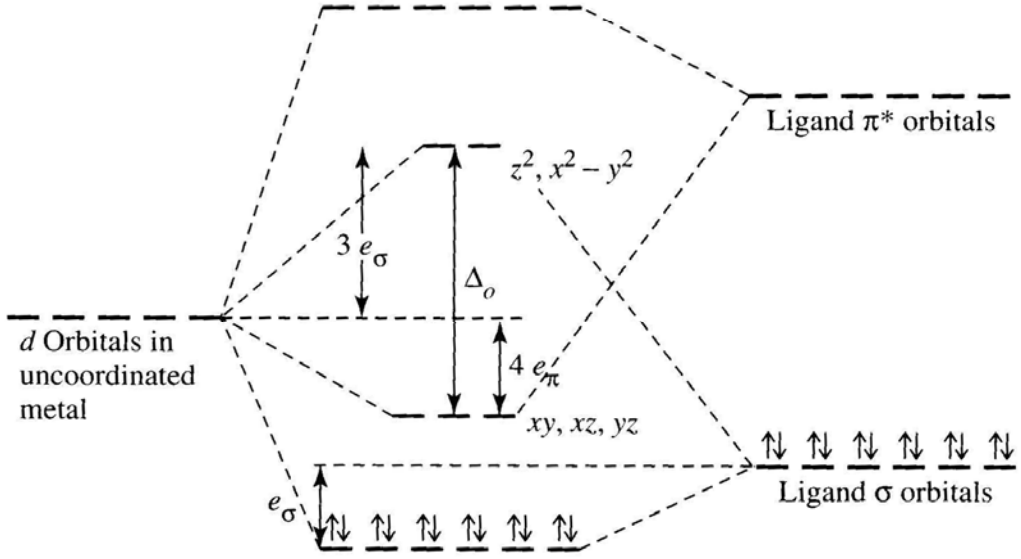


FIGURE 10-22 Energies of *d* Orbitals in Octahedral Complexes: Sigma-Donor and Pi-Acceptor Ligands. $\Delta_o = 3e_\sigma + 4e_\pi$. Metal *s* and *p* orbitals also contribute to the bonding molecular orbitals.

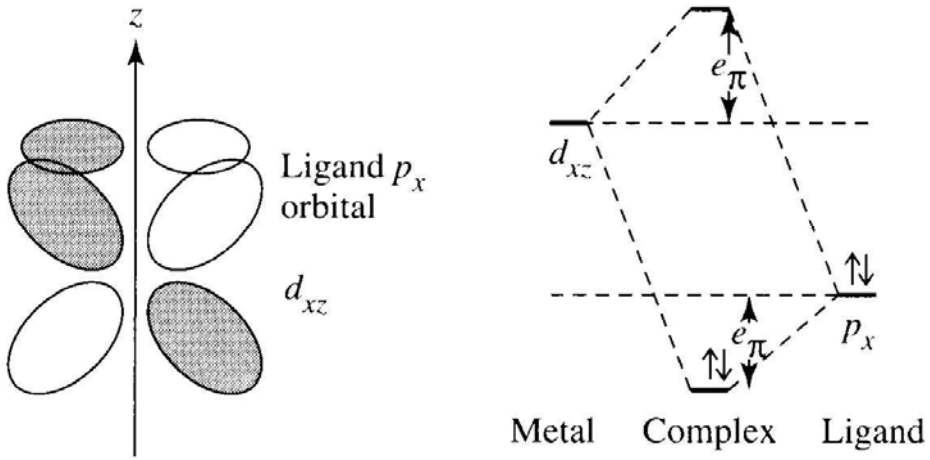


FIGURE 10-23 Pi-Donor Interactions.

Spectrochemical Series

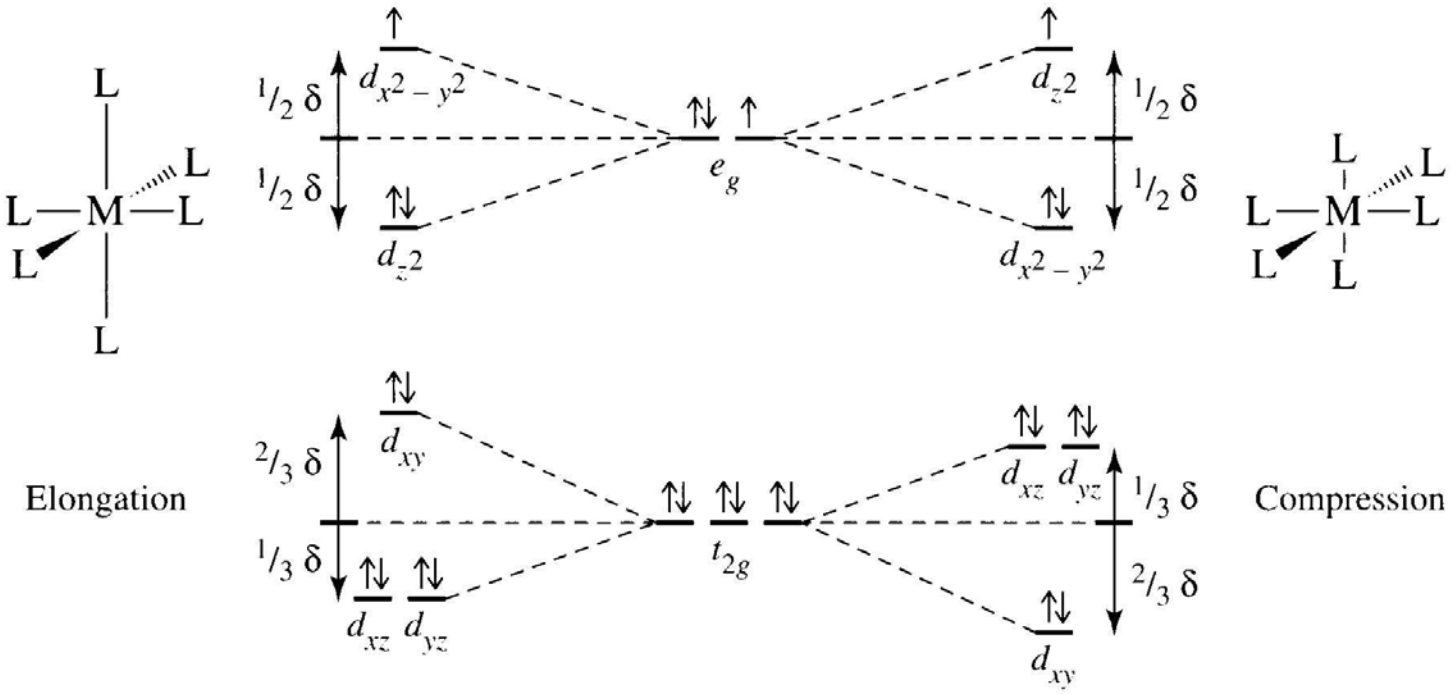
$$en > NH_3$$

$$F^- > Cl^- > Br^- > I^-$$

$$H_2O > F^- > RCO_2^- > OH^- > Cl^- > Br^- > I^-$$

$$CO, CN^- > \text{phenanthroline (phen)} > NO_2^- > NCS^-$$

$$CO, CN^- > phen > NO_2^- > en > NH_3 > NCS^- > H_2O > F^- > RCO_2^- > OH^- > Cl^- > Br^- > I^-$$

Low spin		High spin
Strong field		Weak field
Large Δ		Small Δ
π acceptors	σ donor only	π donors

Jahn-Teller Distortion