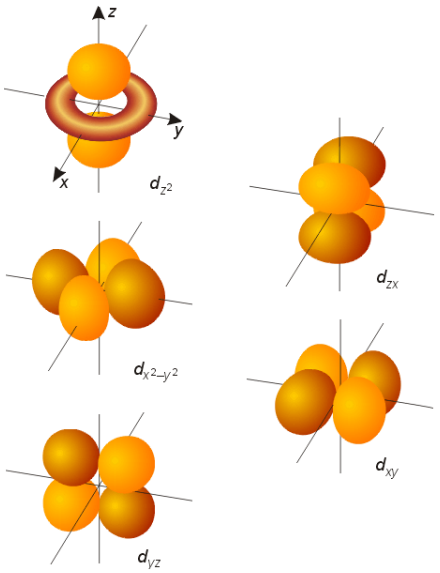
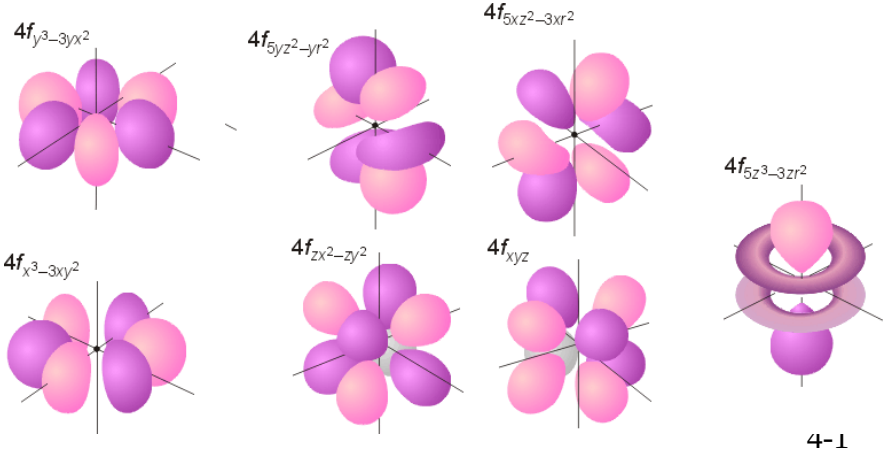
RDCH 702 Lecture 4: Orbitals and energetics

- Molecular symmetry
- Bonding and structure
- Molecular orbital theory
- Crystal field theory
- Ligand field theory

Provide fundamental understanding of chemistry dictating radionuclide complexes



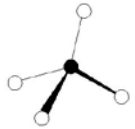
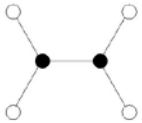
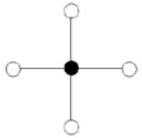
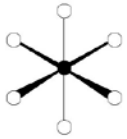
- Structure based on bonding
  - Coordination important in defining structure
    - → Structure related to spectroscopic behavior
    - → Electron configuration important in structure
      - * d^8 are square planar
      - * d^0 and d^{10} tetrahedral



Molecular symmetry

- Evaluation of point groups
  - Description of symmetry present in molecules
    - → Axis
    - → Planes
    - → Inversion
    - → Rotation
- Use with group theory to determine spectroscopic properties

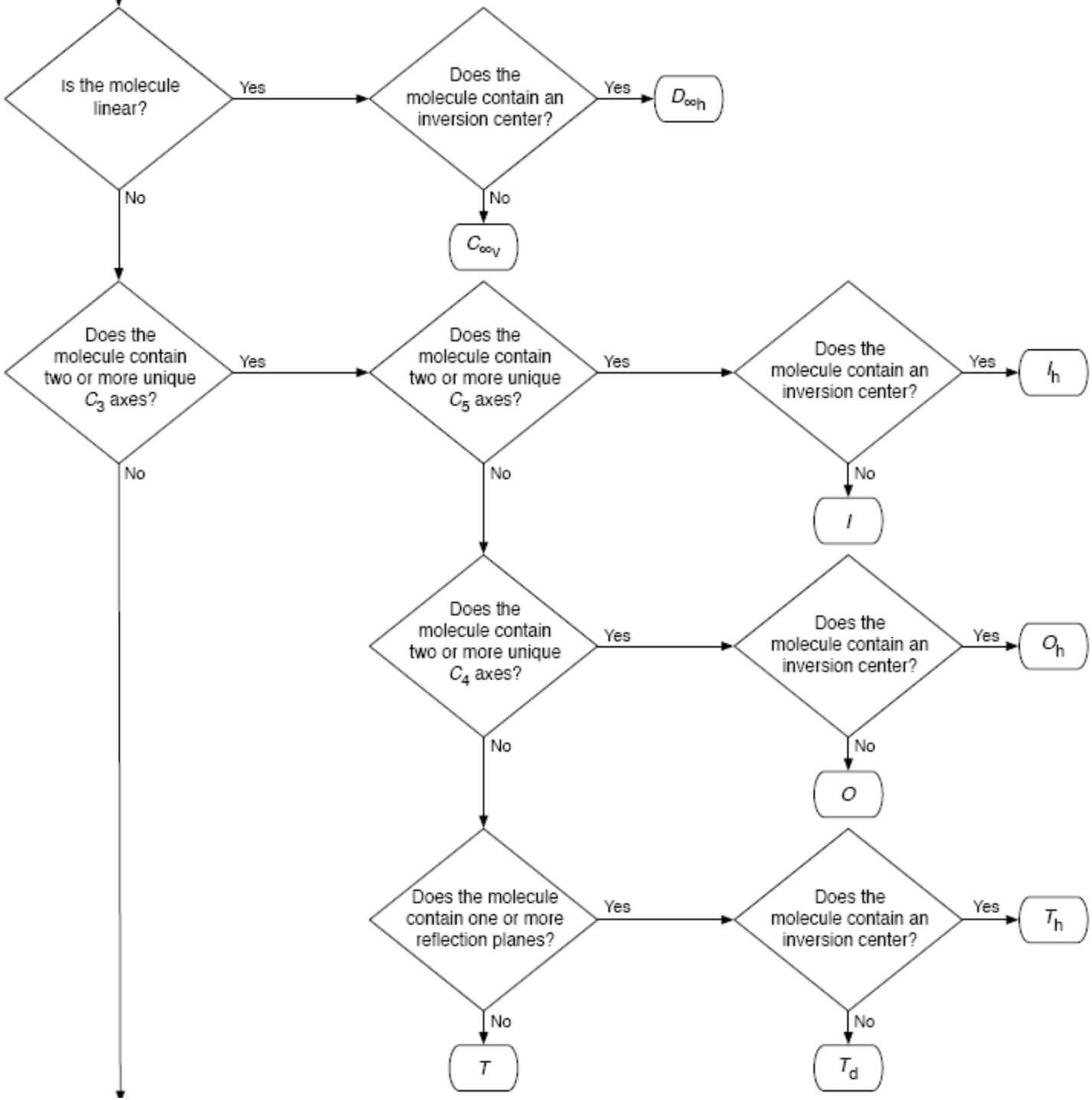
Table 4.2 The composition of some common groups*

Point group	Symmetry elements	Shape	Examples
C_1	E		SiBrClFI
C_2	E, C_2		H_2O_2
C_s	E, σ		NHF_2
C_{2v}	$E, C_2, \sigma_v, \sigma_v$		H_2O, SO_2Cl_2
C_{3v}	$E, 2C_3, 3\sigma_v$		NH_3, PCl_3, $POCl_3$
$C_{\infty v}$	$E, C_2, 2C_\phi, \ldots \infty\sigma_v$		CO, HCl, OCS
D_{2h}	$E, C_2(x,y,z), \sigma(xy,yz,zx), i$		N_2O_4, B_2H_6
D_{3h}	$E, C_3, 3C_2, 3\sigma_v, \sigma_h, S_3$		BF_3, PCl_5
D_{4h}	$E, C_4, C_2, 2C_2', 2C_2'', i, S_4, \sigma_h, 2\sigma_v, 2\sigma_d$		XeF_4, *trans*-MA_4B_2
$D_{\infty h}$	$E, C_\infty, \ldots, \infty\sigma_v, i, S_\infty, \ldots, \infty C_2$		H_2, CO_2, C_2H_2
T_d	$E, 3C_2, 4C_3, 6\sigma_d, 4S_4$		CH_4, $SiCl_4$
O_h	$E, 6C_2, 4C_3, 3C_4, 4S_6, 3S_4, i, 3\sigma_h, 6\sigma_d$		SF_6

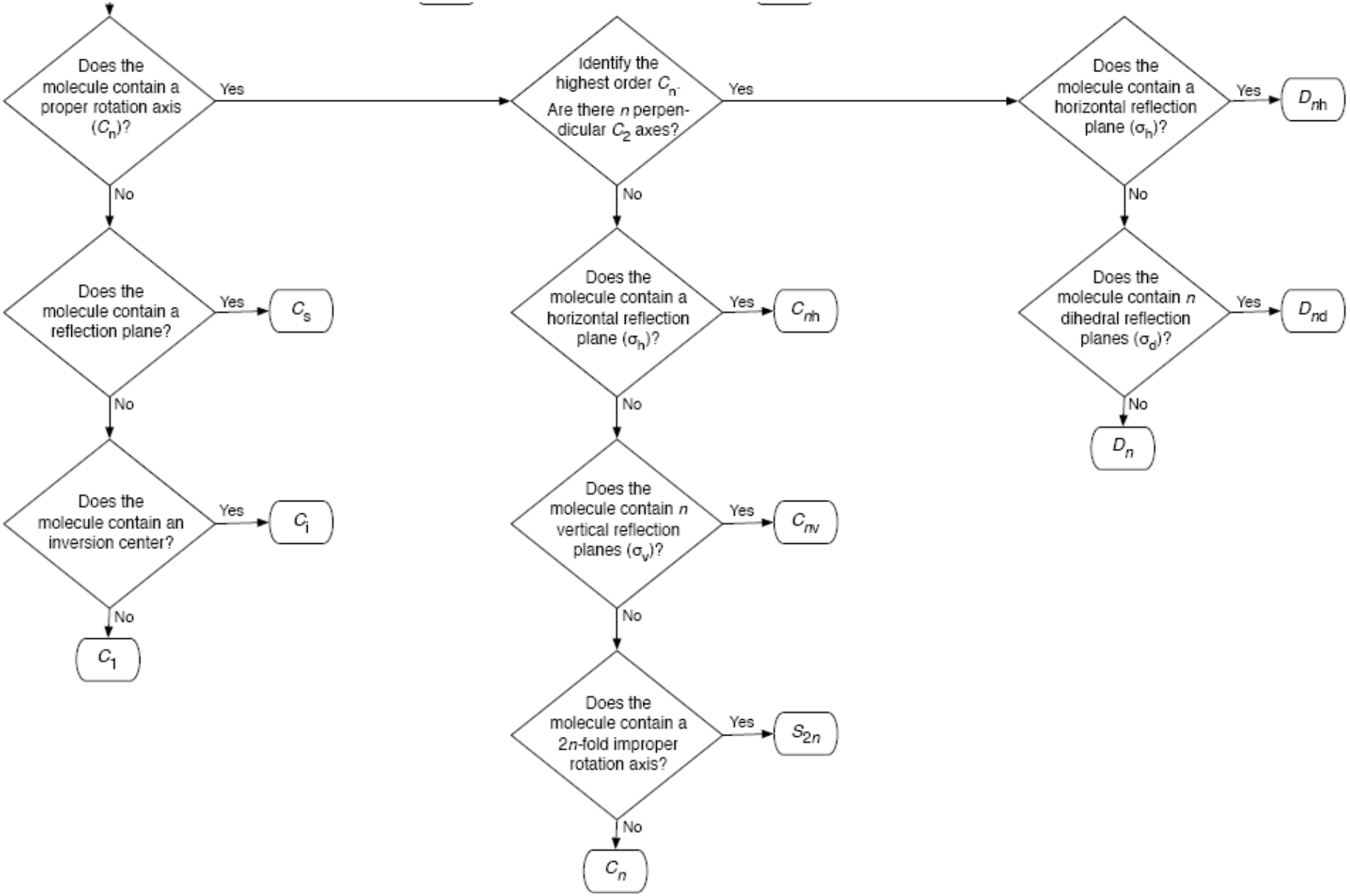
* Not all the elements of each group are listed, but enough are listed for unambiguous assignments to be made.

Method for determining molecular symmetry and point group

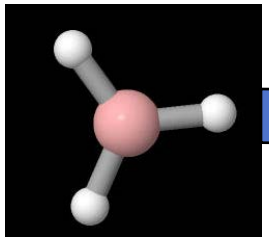
Use molecular geometry to follow chain



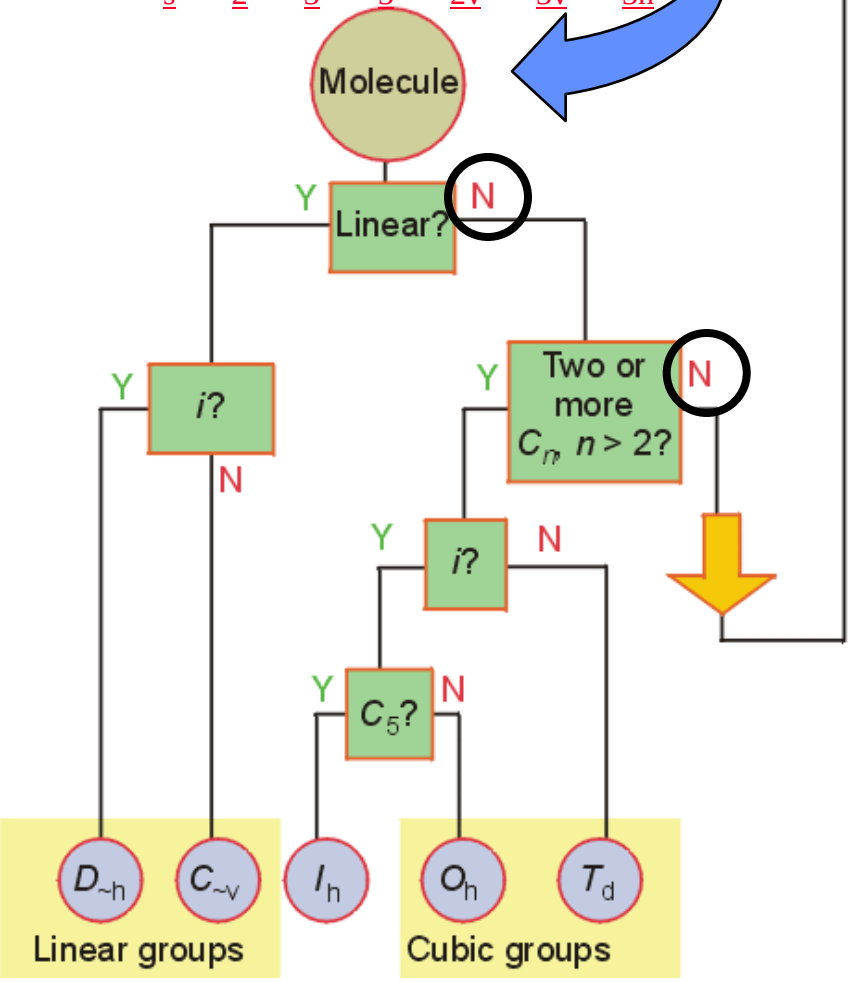
Non-linear, less than 2 unique C_3 axis

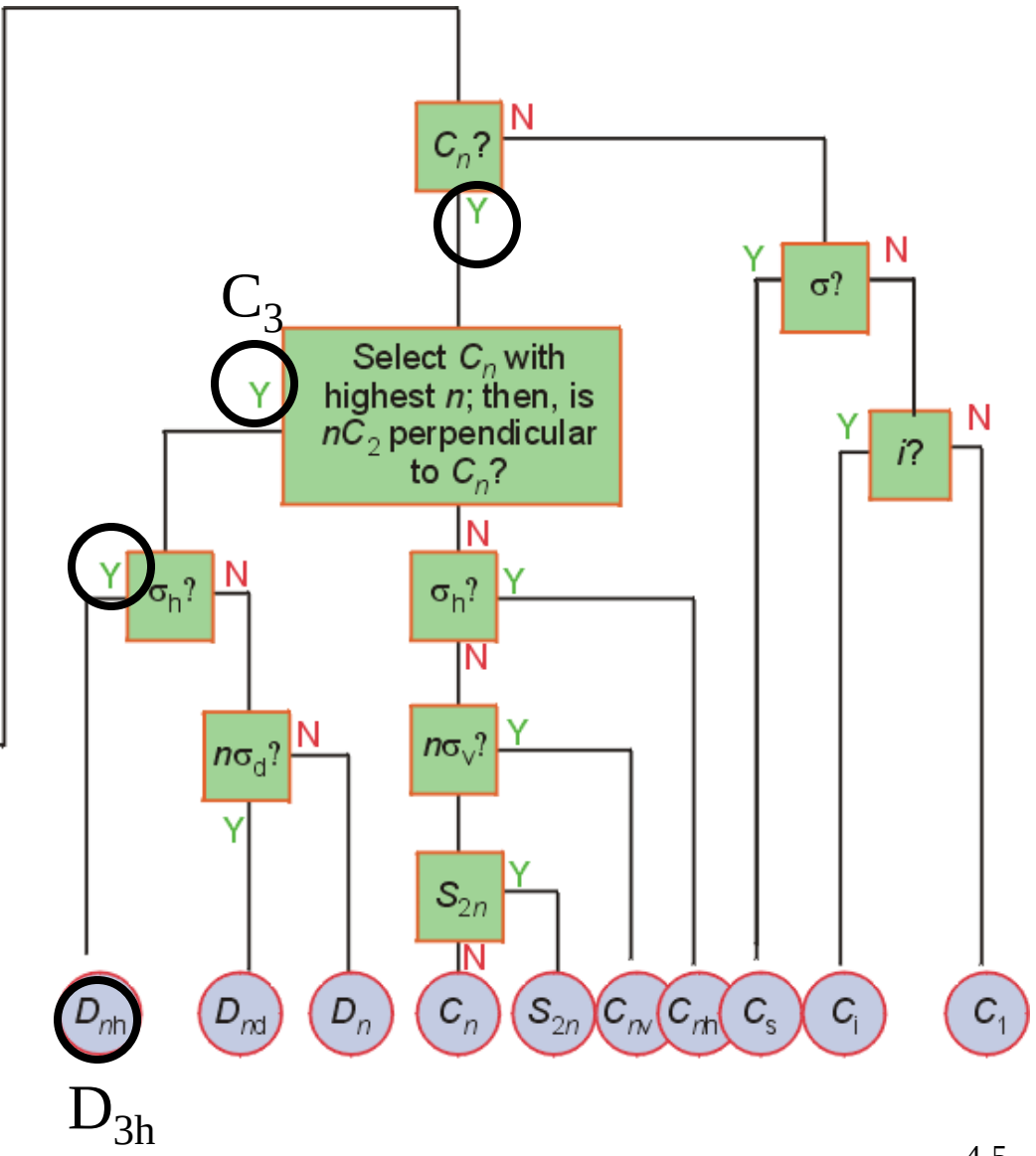


Identifying Point Group



C_s, C_2, C_3, D_3, C_{2v}, C_{3v}, C_{3h}



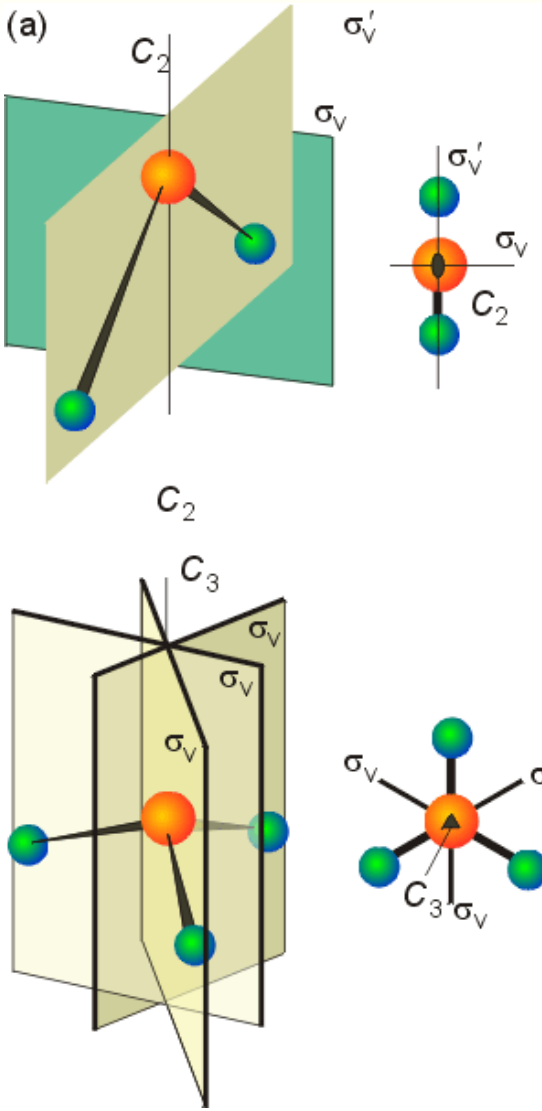


C_3

D_{3h}

Point Groups

- H_2O point group
  - C_{2v} symmetry
  - Symmetry elements
    - → E, C_2 (180° rotation), 2 vertical mirror planes (σ_v)
      - * E, C_2, σ_v, σ_v'
- NH_3 point group
  - C_{3v} point group
  - Elements
    - → E, C_3 (each N-H), three vertical mirror plane through each N-H ($3\sigma_v$)
      - * E, C_3, $3\sigma_v$
- Apply to identification tree



Symmetry and spectroscopy

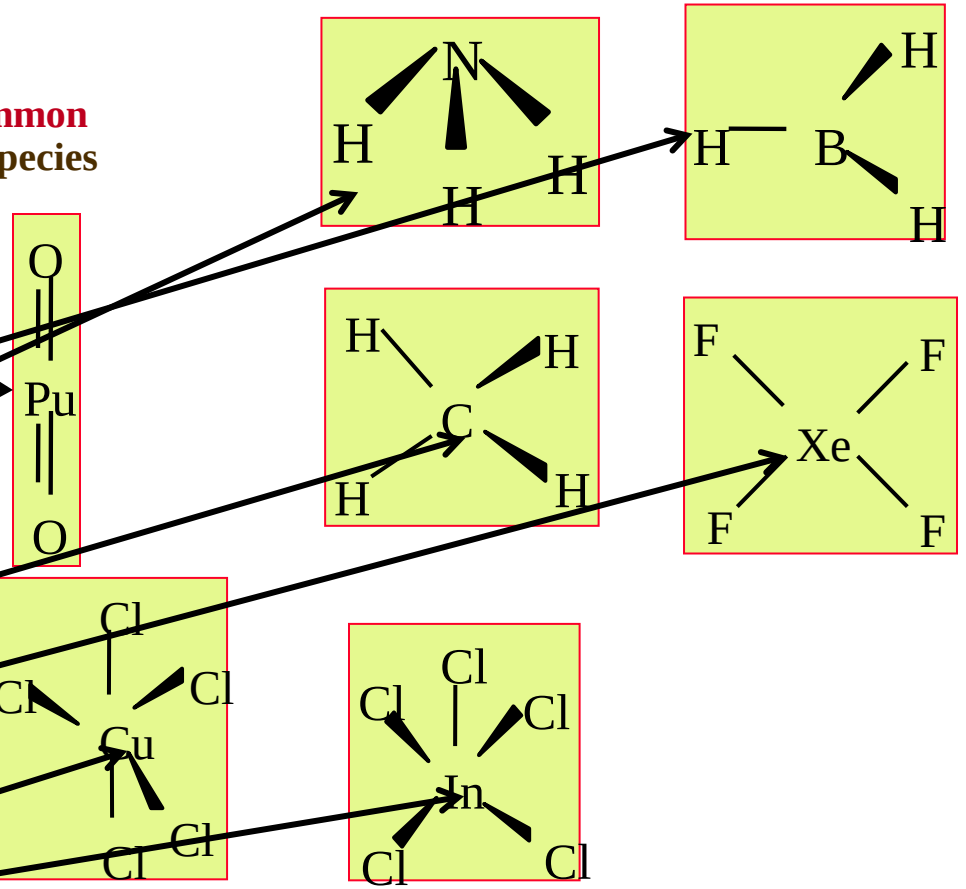
C_{2v}	E	C_2	σ_v (xz)	σ_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

- a_1 vibration generates a changing dipole moment in the z-direction
- b_1 vibration generates a changing dipole moment in the x-direction
- b_2 vibration generates a changing dipole moment in the y-direction
- a_2 vibration does not generate a changing dipole moment in any direction (no 'x', 'y' or 'z' in the a2 row).
  - **a_1, b_1 and b_2 vibrations provide changes dipole moments and are IR active**
  - **a_2 vibrations have no dipole moments**
    → **IR inactive**

Coordination number

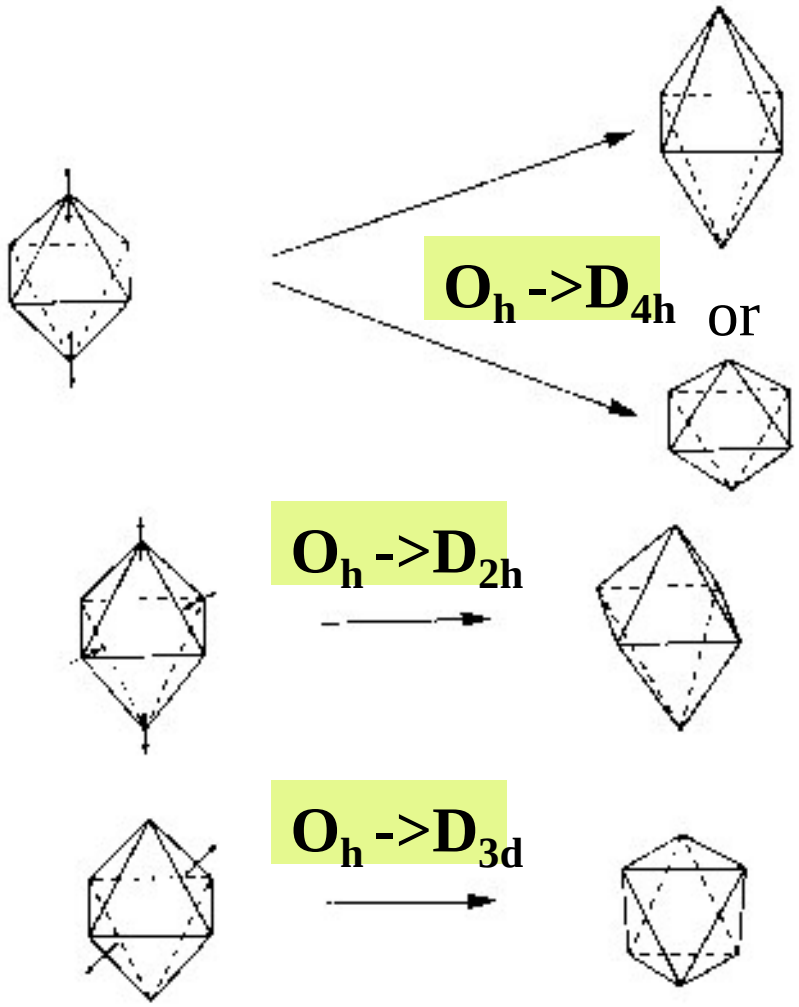
- **Geometry strongly influence by coordination number**
  - **Can assess information on potential structure and geometry from coordination number (CN)**
- **CN=5**
- **Interconvertibility between geometries**
  - **Compounds can vary between shapes**
  - **Trigonal bipyramid seems to be more common**
    - → **Common with metal pentachloride species**

CN	Geometries
2	Linear ($D_{\infty h}$) Bent (C_{2v})
3	Planar (D_{3h}) Pyramidal (C_{3v}) Some T-shaped forms (C_{2v})
4	Tetrahedral (T_d) Square geometry (C_{4h}) One lone pair (C_{2v})
5	Trigonal bipyramid (D_{3h}) Square pyramid (C_{4v})

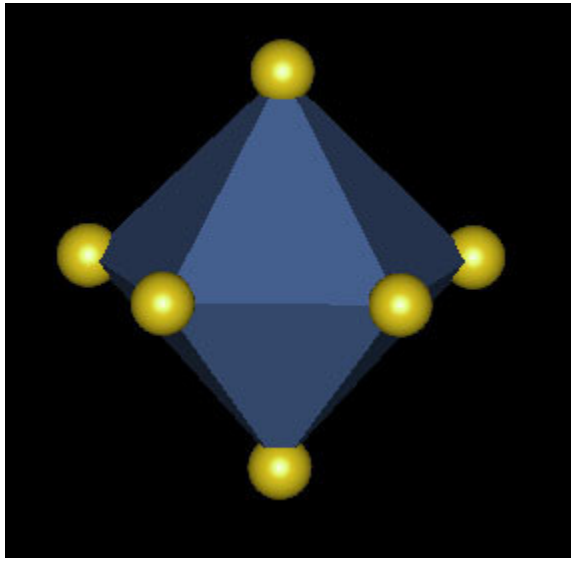


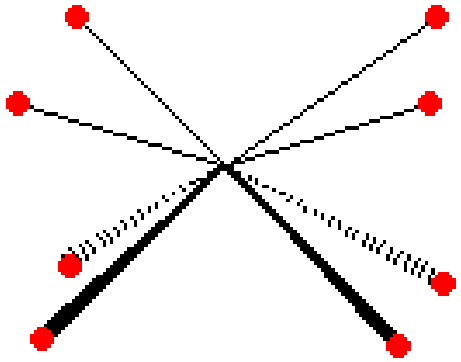
Coordination Number

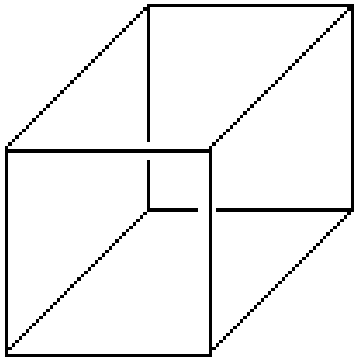
- Coordination number 6
- Very common coordination number
  - Ligands at vertices of octahedron or distorted octahedron
    - →Octahedron (O_h)
    - →Tetragonal octahedron (D_{4h})
      - * Elongated or contracted long z axis
    - →Rhombic (D_{2h})
      - * Changes along 2 axis
    - →Trigonal distortion (D_{3d})



Higher coordination: Relevant for actinides





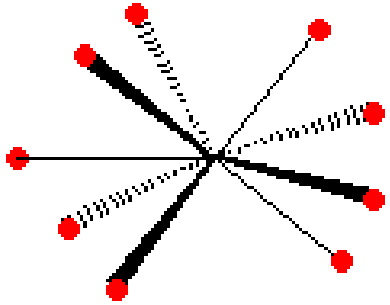


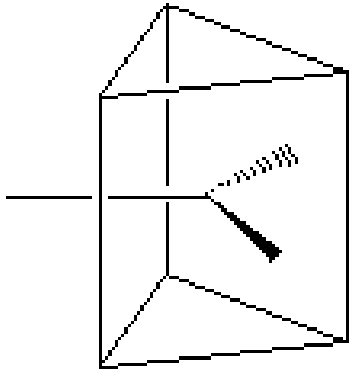
8 coordination: Cubic structure, the Square Antiprism, Dodecahedron

7 coordination

Pentagonal Bipyramidal, Capped Trigonal Prismatic and Capped

Octahedral.





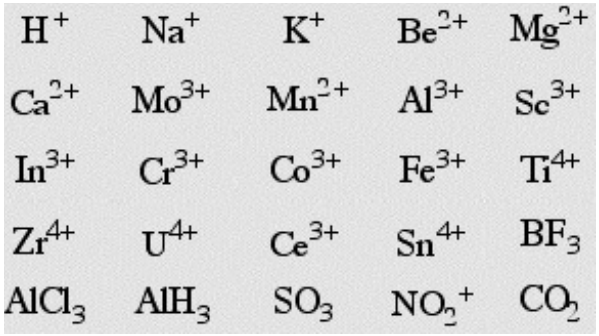
9 coordination: Tricapped trigonal prismatic

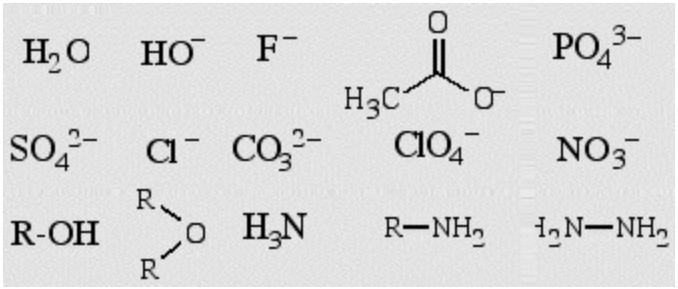
http://www.d.umn.edu/~pkiprof/ChemWebV2/Coordination/CN8.html

Hard and soft metals and ligands

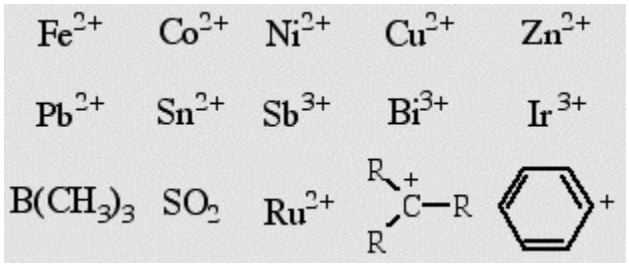
- Based on Lewis acid definition
  - Ligand acts as base
    - → donates electron pair to metal ion
- Hard metal ion interact with hard bases
  - Hard ligands N, O, F
  - Soft ligands P, S, Cl
    - → Ligand hardness decreases down a group
- Hard metals
  - High positive charges
  - Small radii
  - Closed shells or half filled configurations
- Soft metals
  - Low positive charges
  - Large ionic radius
  - Non-closed shell configurations
    - → Tend to be on right side of transition series
- Lanthanides and actinides are hard
  - Actinides are softer than lanthanides
    - → Ligands with soft groups can be used for actinide/lanthanide separations

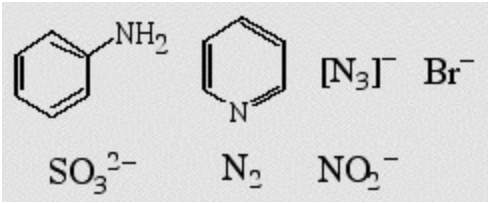
Hard



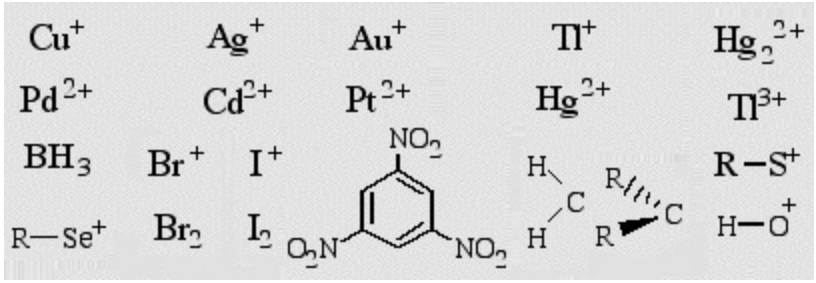


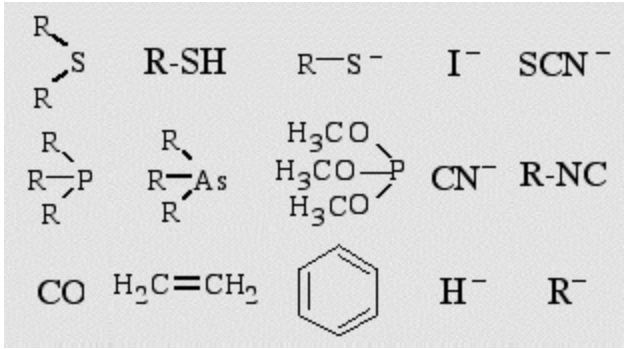
Intermediate





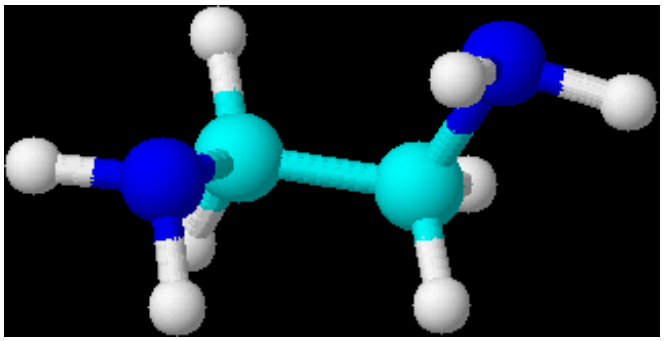
Soft

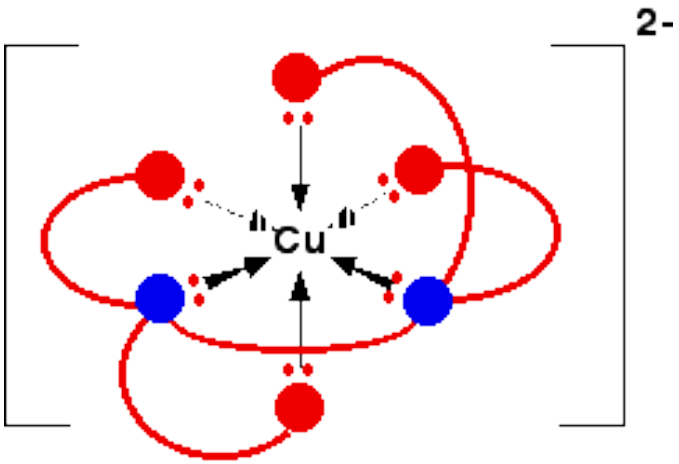




Chelation and stability

- **Ligands with more than 1 complexing functional group**
  - **Carbonate, ethylenediamine**
  - **Enhanced stability through chelation effect**
  - **ethylenediamine binding stronger than 2 ammonia groups**
    - **→Bidentate**
    - **→Tridentate**
  - **Ligands can wrap around metal ion forming stronger complex**





the $[Cu(EDTA)]^{2-}$ ion

Effective atomic number

- **Metal bonding can be described with effective atomic number**
  - **Number of electrons surrounding metal is effective atomic number**

    →Transitions metal have 9 possible bonds

    *** 5 d, 3p, 1 s**

    ⌘ 18 electrons
  - **Possible to have effective atomic number different than 18**

    →Few d electrons

    →Electronegative ligands

Effective atomic number

- 16 electron
  - Square planar
  - d^8 configuration (Au, Pt)
- Greater than 18 electron
  - 8-10 d electrons
- Expand metal-ligand interactions to exploit bonding and geometry
  - Molecular orbital theory
  - Crystal field theory
  - Ligand field theory

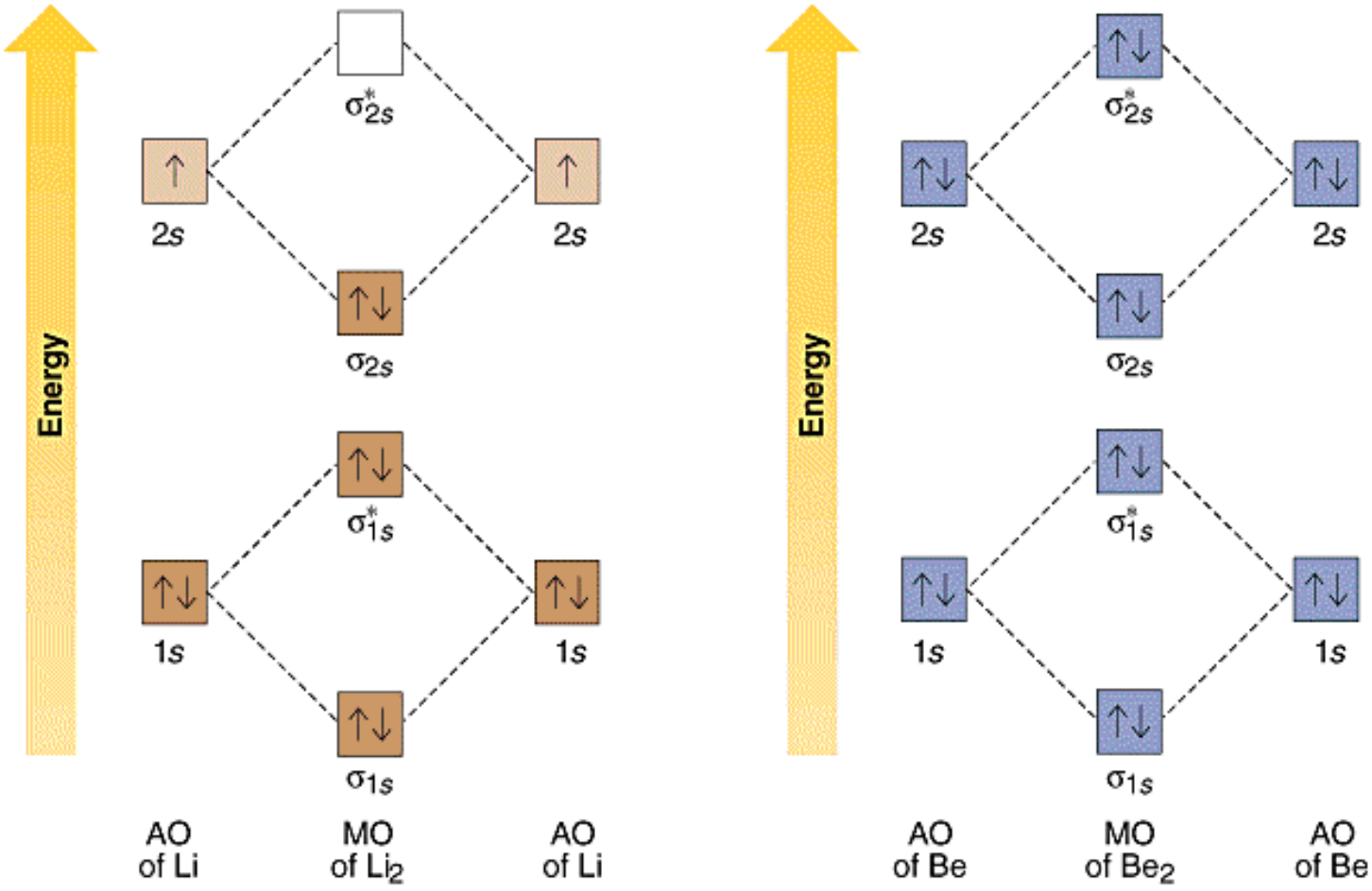
TABLE 6-3. EAN VALUES FOR SEVERAL TRANSITION-METAL COMPLEXES

Complex	Metal Electrons	Ligand-donor Electrons	EAN
VCl_4	1	8	9
TaF_7^{2-}	0	14	14
ZrF_7^{3-}	0	14	14
$Ni(CN)_4^{2-}$	8	8	16
$Pt(NH_3)_2Cl_2$	8	8	16
$Au(NO_3)_4^-$	8	8	16
MnF_6^{4-}	5	12	17
$Fe(CN)_6^{3-}$	5	12	17
$Co(NH_3)_6^{3+}$	6	12	18
$Cr(CO)_6$	6	12	18
$Fe(CO)_5$	8	10	18
$Ni(CO)_4$	10	8	18
$Co(NO_3)_3$	6	12	18
$Re(CO)_5NO_3$	6	12	18
$Ni(H_2O)_6^{2+}$	8	12	20
NiF_6^{4-}	8	12	20

Molecular orbital theory

- Molecular orbitals are comprised from the overlap of atomic orbitals
- Number of molecular orbitals equals the number of combined atomic orbitals
- Different type of molecular orbitals
  - bonding orbital (lower energy)
  - Non-bonding (same energy as atomic orbitals)
  - Anti-bonding orbital (higher energy)
- Electrons enter the lowest orbital available
  - maximum number of electrons in an orbital is 2 (Pauli Exclusion Principle)
  - Electrons spread out before pairing up (Hund's Rule)

Molecular orbital



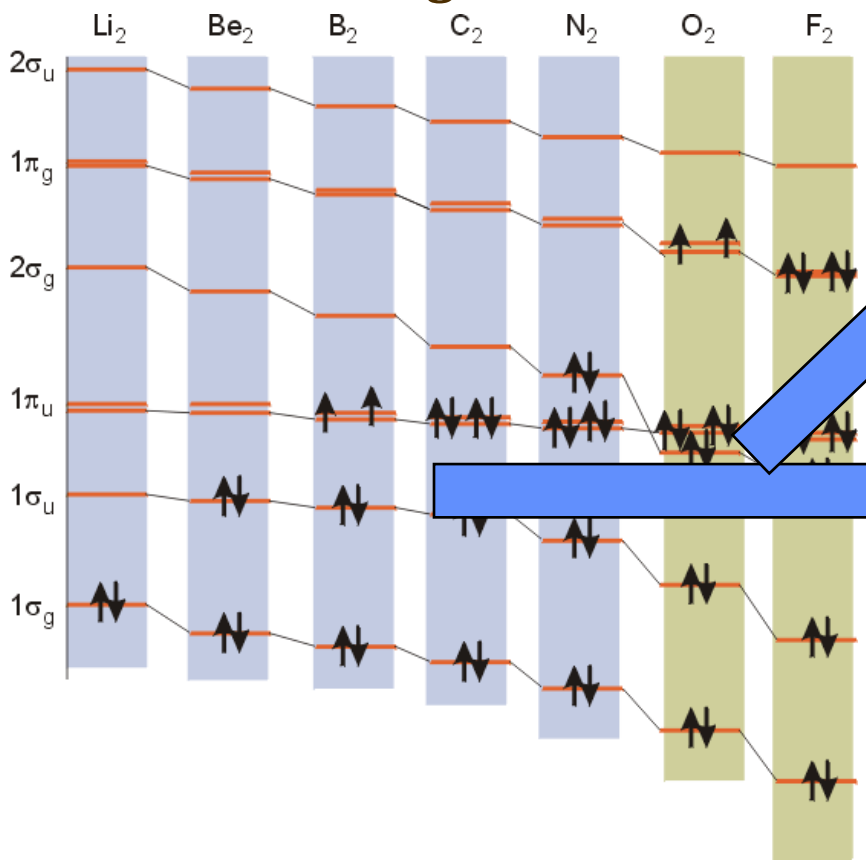
A Li_2 bond order = 1

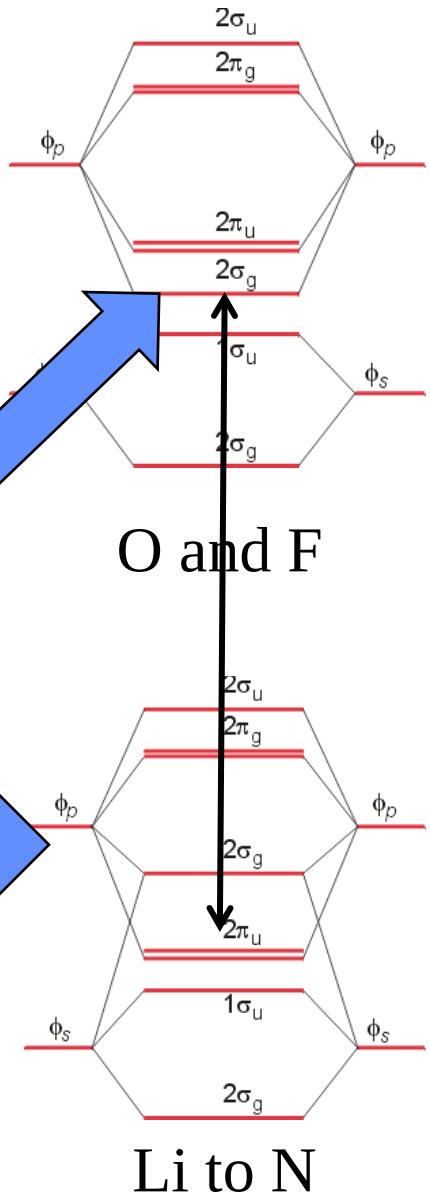
B Be_2 bond order = 0

Molecular orbitals

- Sigma, Pi, delta
  - Gerade and ungerade
- N molecular orbitals from N atomic orbitals
  - N=8 in period 2
  - 4 sigma, 4 Pi

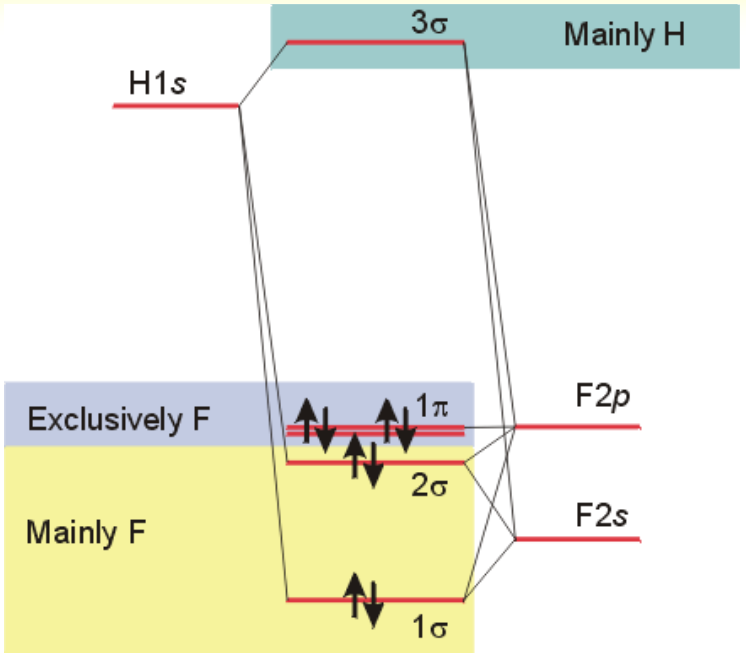
→ Pi degenerate bonding and antibonding

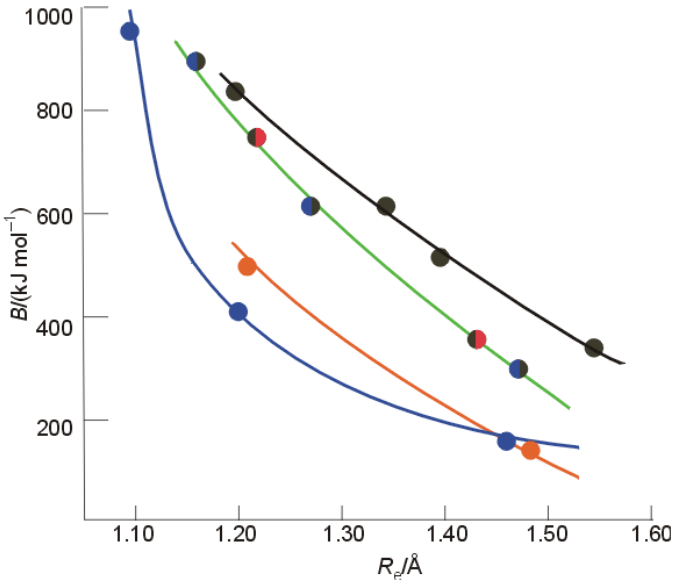




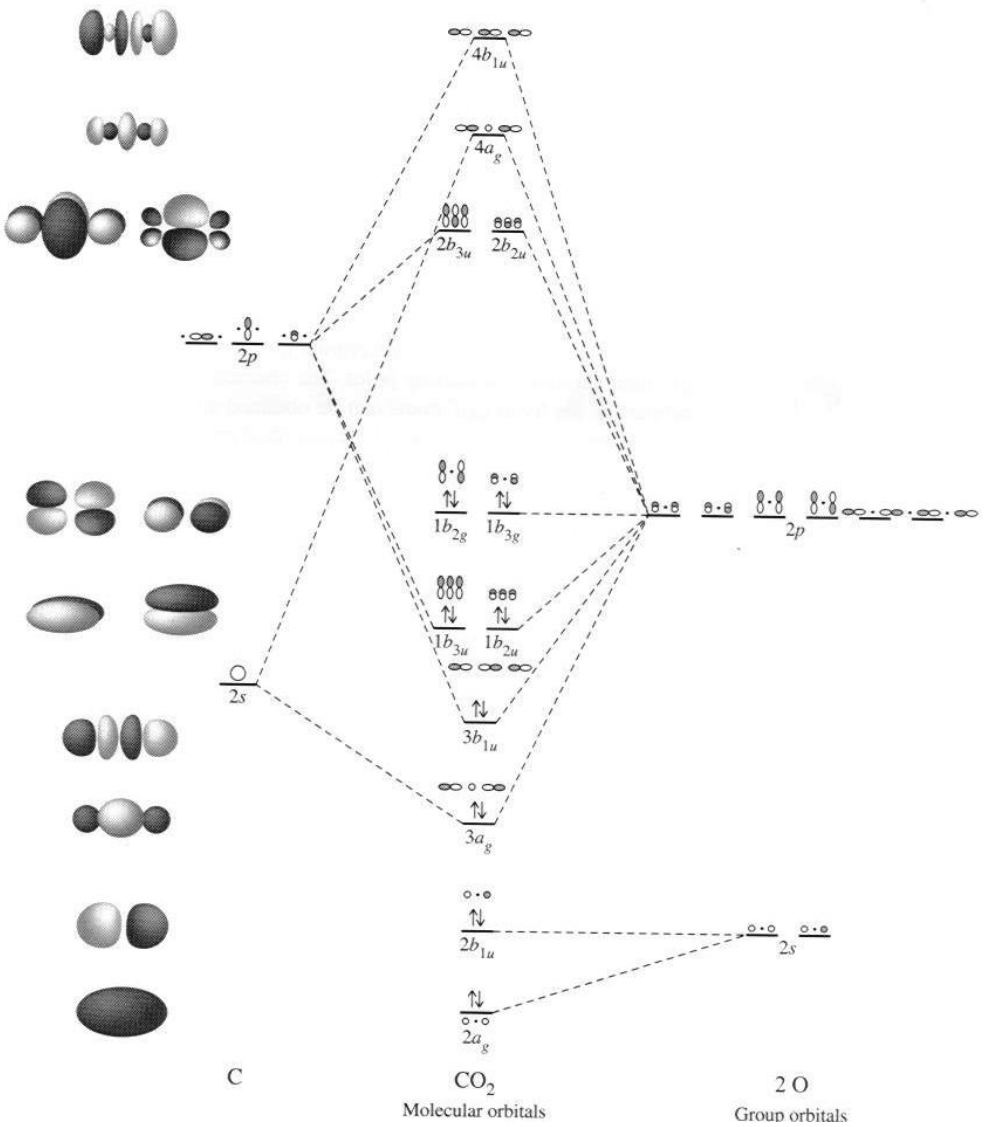
Molecular orbitals

- Mixture of different atoms
  - Some bonding characteristics dominate
  - Nonbonding orbitals
    - → No Pi from H
- High occupied electron orbital
- Lowest unoccupied electron orbital
- Bond order
  - Overall shared electron
  - B=0.5(n-n*)





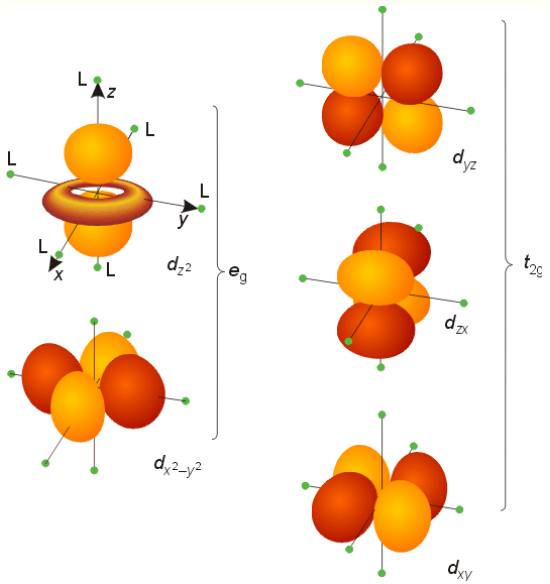
Symmetry adapted orbitals

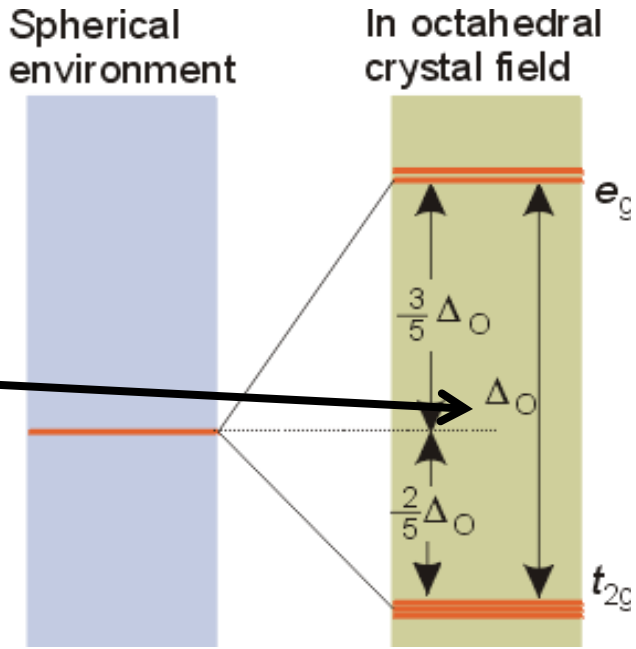


- Combination of orbitals with symmetry considerations
- If molecule has symmetry degenerate atomic orbitals with similar atomic energy can be grouped in linear combinations
  - groups are known as symmetry-adapted linear combinations

Crystal Field Theory

- Behavior of electrons with ligands
  - changes degenerate states
    - → d and f electrons
- Lone pair modeled as point
  - Repels electrons in d or f orbital
  - d orbitals have energy differences due to point
    - → Results in ligand field splitting
      - * About 10 % of metal-ligand interaction
      - * e and t orbitals
    - → Ignores covalent contribution
- Energy difference is ligand field splitting parameter (Δ_o)
  - Can be determined from absorption spectrum
    - → $e_g \leftarrow t_{2g}$ transition





Crystal Field Theory

- $Ti(OH_2)_6^{3+}$
  - Absorbance at 500 nm, 20000 cm^{-1}
  - 1000 cm^{-1} = 11.96 kJ/mol
    - → Δ_0=239.2 kJ/mol
  - Δ_0 found to vary with ligand
    - → For metal ion increases with oxidation state and increases down a group
- $I^- < Br^- < \underline{S}CN^- \sim C^{l-} < F^- < OH^- \sim \underline{O}NO^- < C_2\underline{O}_4^{2-} < H_2O < \underline{N}CS^- < \underline{E}DTA^{4-} < NH_3 \sim pyr \sim en < bipy < phen < CN^- \sim CO$

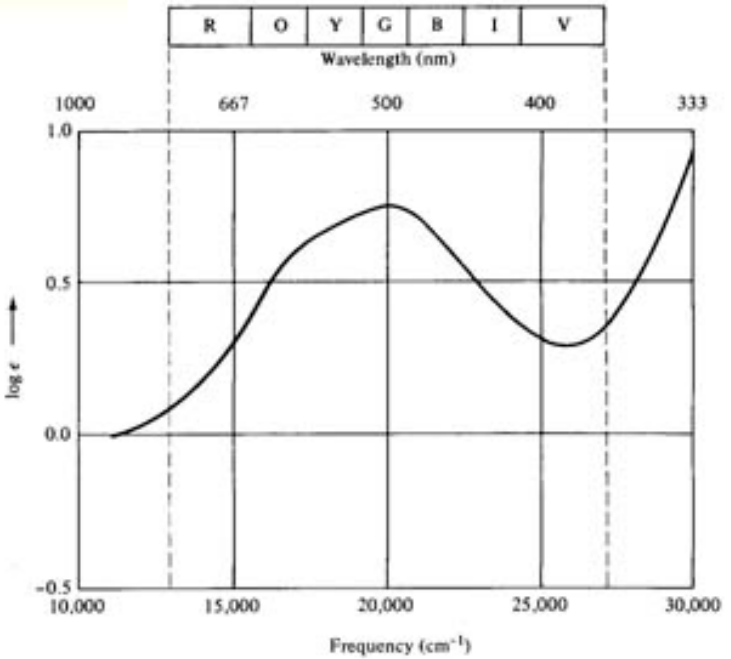


Table 7.3 Ligand-field splitting parameters Δ_O of ML_6 complexes*

	Ions	Ligands				
		Cl^-	H_2O	NH_3	en	CN^-
d^3	Cr^{3+}	13.7	17.4	21.5	21.9	26.6
d^5	Mn^{2+}	7.5	8.5		10.1	30
	Fe^{3+}	11.0	14.3			(35)
d^6	Fe^{2+}		10.4			(32.8)
	Co^{3+}		(20.7)	(22.9)	(23.2)	(34.8)
	Rh^{3+}	(20.4)	(27.0)	(34.0)	(34.6)	(45.5)
d^8	Ni^{2+}	7.5	8.5	10.8	11.5	

*Values are in multiples of 1000 cm^{-1}; entries in parentheses are for low-spin complexes.
Source: H.B. Gray, *Electrons and chemical bonding.* Benjamin, Menlo Park (1965).

Crystal field theory

- **Ligand field stabilization energies**
  - **t_{2g} stabilized (40 % of Δ_o)**
  - **e_g increase energy (60 % of Δ_o)**
    - **→ LFSE=(-0.4 t_{2g} + 0.6 e_g)Δ_o**
    - **→ LFSE few % of energy**

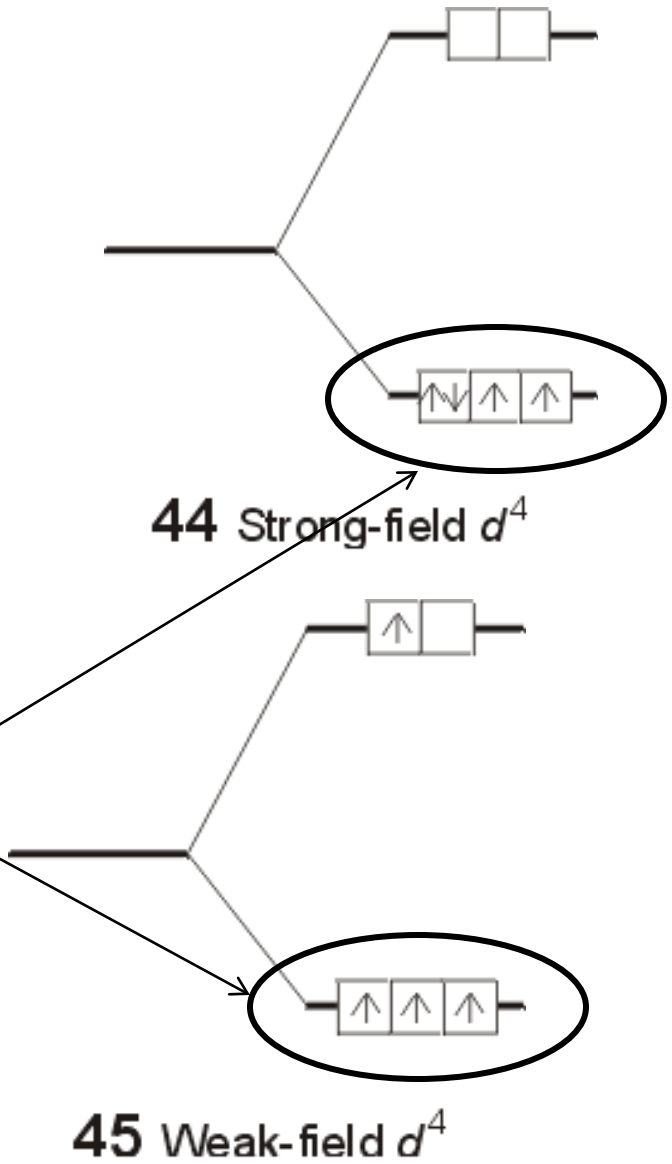
Table 7.4 Ligand-field stabilization energies (absolute values)*

d^n	Example	Octahedral				Tetrahedral	
				N	LFSE	N	LFSE
d^0	Ca^{2+}, Sc^{3+}			0	0	0	0
d^1	Ti^{3+}			1	0.4	1	0.6
d^2	V^{3+}			2	0.8	2	1.2
d^3	Cr^{3+}, V^{2+}			3	1.2	3	0.8
		Strong-field			Weak-field		
d^4	Cr^{2+}, Mn^{3+}	2	1.6		4 0.6	4	0.4
d^5	Mn^{2+}, Fe^{3+}	1	2.0		5 0	5	0
d^6	Fe^{2+}, Co^{3+}	0	2.4		4 0.4	4	0.6
d^7	Co^{2+}	1	1.8		3 0.8	3	1.2
d^8	Ni^{2+}			2	1.2	2	0.8
d^9	Cu^{2+}			1	0.6	1	0.4
d^{10}	Cu^{+}, Zn^{2+}			0	0	0	0

*N is the number of unpaired electrons; LFSE is in units of Δ_O for octahedra or Δ_T for tetrahedra; the calculated relation is $\Delta_T \approx \frac{4}{9}\Delta_O$.

Crystal Field Theory

- **Weak and strong field limits**
  - **Related to location of 4th d^4 electron**
    - → **t_{2g}^4 or $t_{2g}^3 e_g^1$**
      - * **All in t_{2g} has coulombic repulsion (P) but promotion to e_g need Δ_o energy**
    - → **$\Delta_o < P$**
      - * **Lower energy if e_g is occupied**
      - * **Weak field**
        - ⌘ **High spin**
  - **Low spin for ligands high in series with strong field**
- **Δ_o and P related to metal and ligand**
  - **4d and 5d generally have Δ_o greater than 3d**
    - → **typically low spin**



Crystal Field Theory

- **Magnetic properties**
  - **Determination of spin state**
    - → **Diamagnetic**
      - * **Move out of a magnetic field**
    - → **Paramagnetic**
      - * **Move into a magnetic field**
  - **Dipole moment**
    - → **Spin only paramagnetism due to quenching of orbital angular momentum with ligand**
      - * **$\mu=[N(N+2)]^{1/2}\mu_B$; with μ_B= 9.274E-24 JT^{-1} and N number of unpaired electrons**
        - ⌘ **For d^6 N= 4 or 0, depending on spin**
- **Accounts for observations on trends**
  - **Ionic radius**

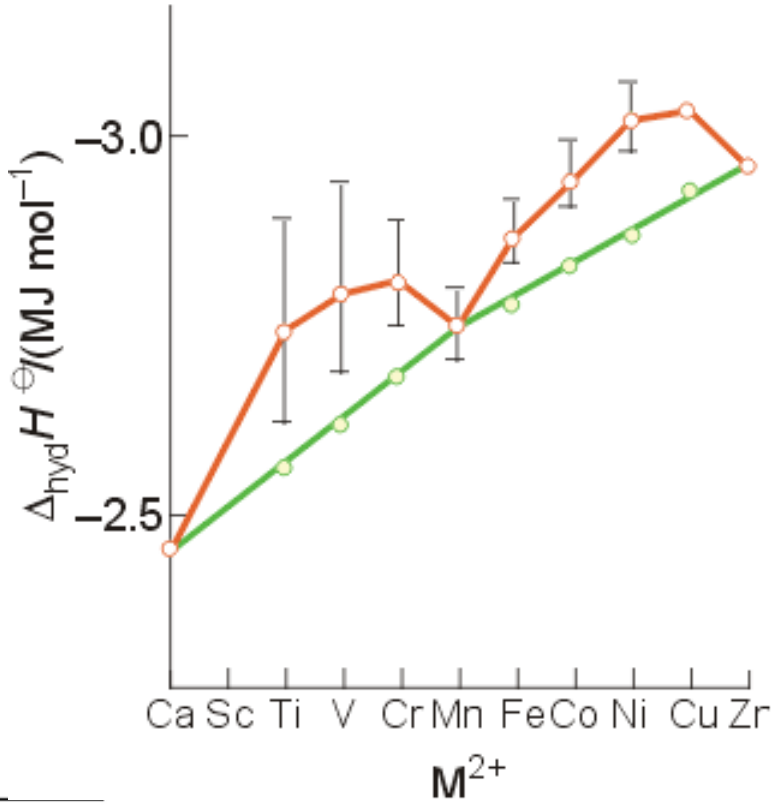
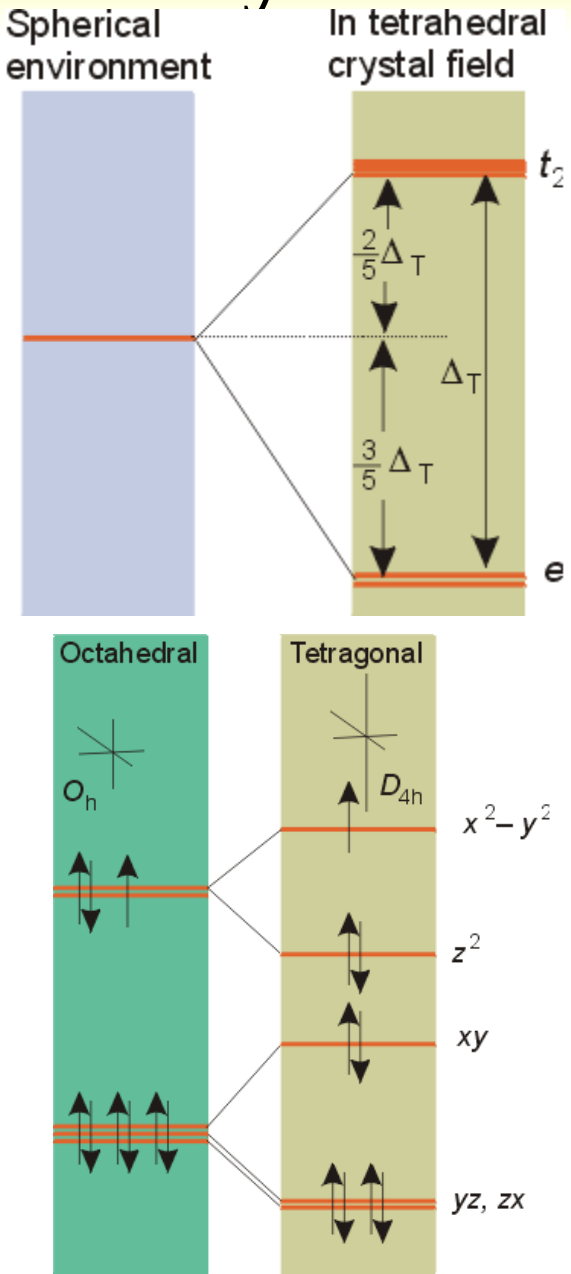


Table 7.5 Calculated spin-only magnetic moments

Ion	N	S	μ/μ_B	
			Calculated	Experiment
Ti^{3+}	1	$\frac{1}{2}$	1.73	1.7–1.8
V^{3+}	2	1	2.83	2.7–2.9
Cr^{3+}	3	$\frac{3}{2}$	3.87	3.8
Mn^{3+}	4	2	4.90	4.8–4.9
Fe^{3+}	5	$\frac{5}{2}$	5.92	5.9

Crystal Field Theory

- T_d
  - Weak field splitting
  - e lower energy than t
    - → Based on orbital spatial distributions
- Tetragonal complex
  - Splitting into 4 levels
  - Can distort into square planar
    - → $4d^8$ and $5d^8$
- Jahn-Teller effect
  - Distortion of geometry to achieve energy stabilization (see previous)
    - → Energy of distorted complex lower

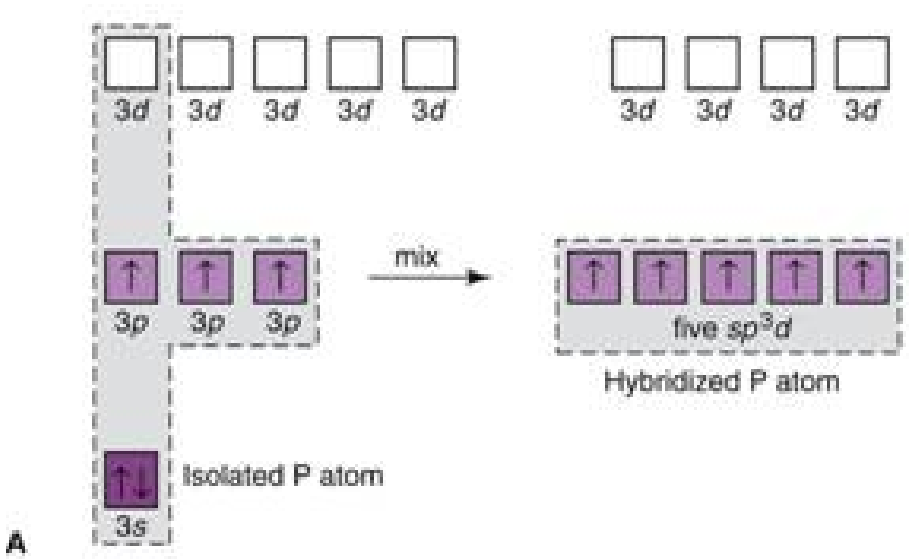


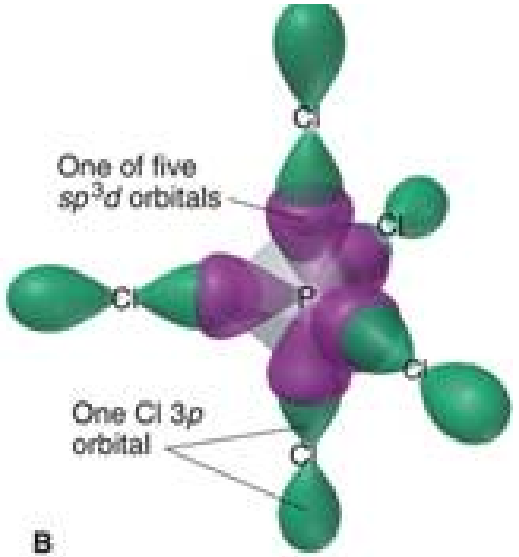
Ligand Field Theory

- **Describes bonding and geometry of coordination complexes**
  - **Use of molecular orbital theory for transition metals**
    - **→Correlated with geometry to identify similar bonds**
    - **→Includes covalent metal-ligand interactions**
      - *** Overlap of ligand and metal orbitals**
      - *** Enhanced understanding of origin of energy separation**

Ligand Field Theory d orbital hybrid

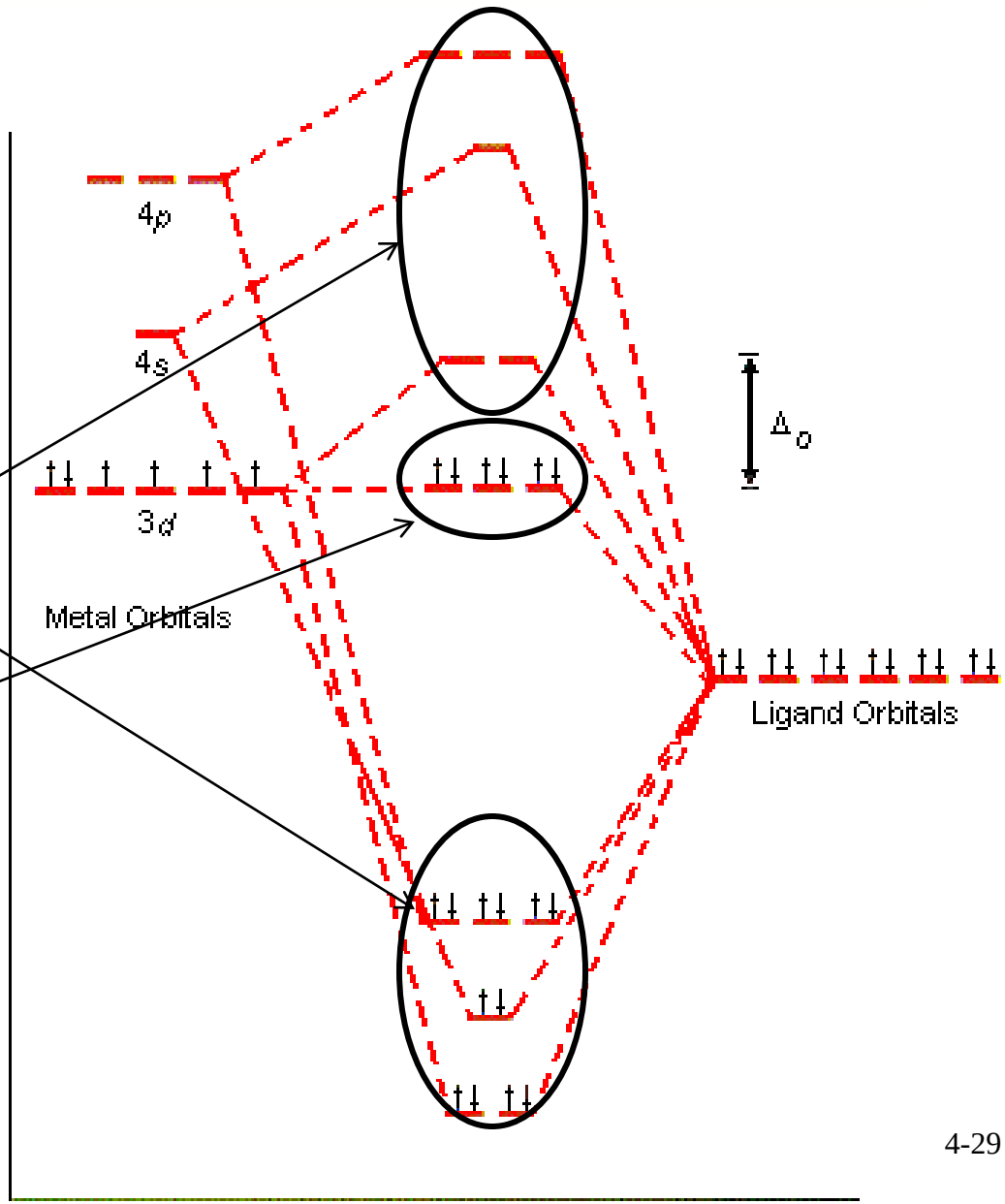
- **O_h complexes**
  - **Six similar bonds, nine valence orbitals**
  - **To make six similar bonds, mixing must occur**
    - → **Hybridization of s, p, and 2 d orbitals**
      - * **d_{x2-y2}, d_{z2}**
        - ⚜ **d^2sp^3 hybrid**
- **Interaction of d orbitals with bonding ligand results in observed properties (magnetic, color)**





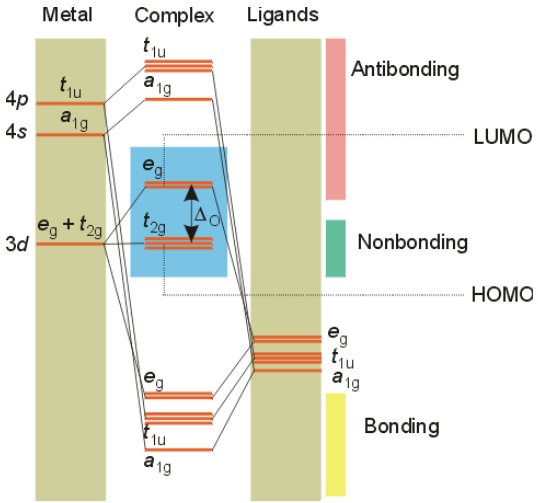
Ligand Field Theory

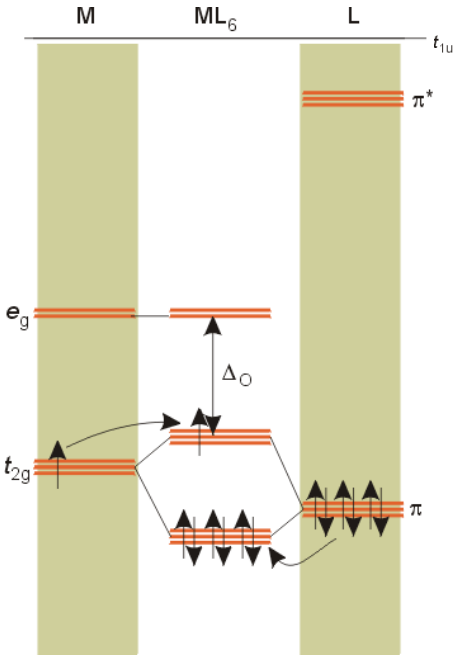
- n*d*, n+1*s*, and n+1*p* orbitals on the metal overlap with one orbital on each of the six ligands
  - forms 15 molecular orbitals
- Six are bonding
  - energies are lower than original atomic orbitals
- Six are antibonding with higher energy
- Three are nonbonding
- Ligand-field theory describes how s,p, and d orbitals on the metal to overlap with orbitals on the ligand

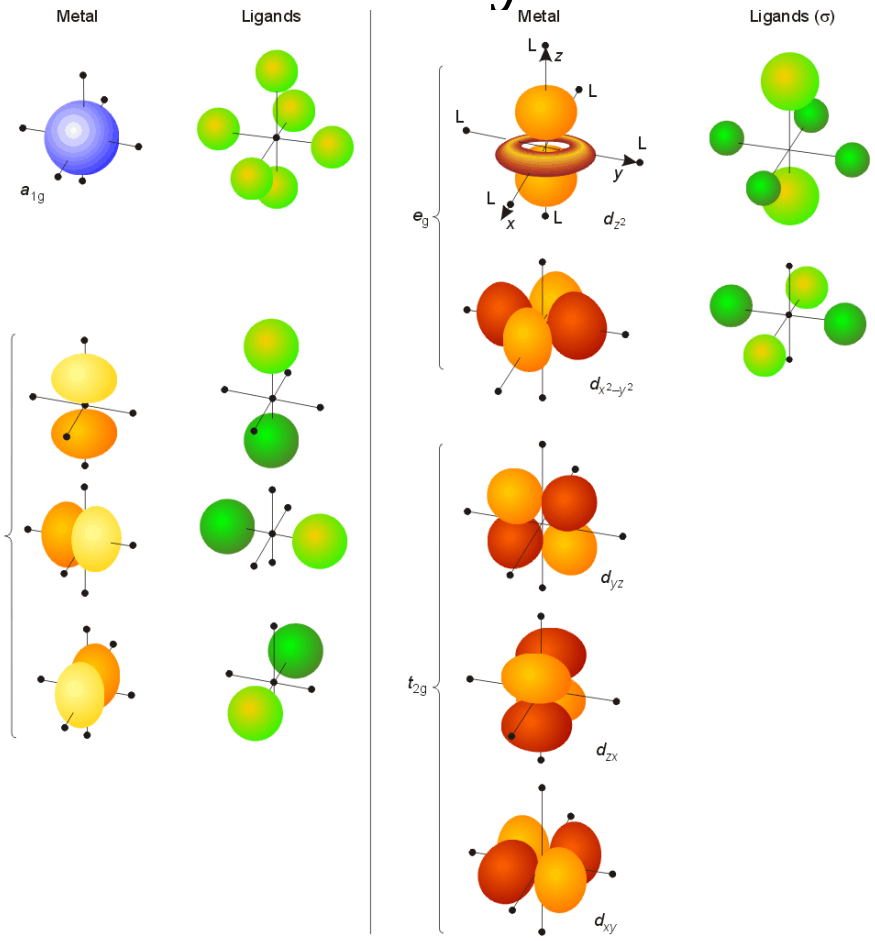


Ligand Field Theory

- Treats overlaps of ligand and metal orbitals
- Stems for SALC
  - Sigma
  - Combine sigma orbitals for each set
    - → t_{2g} has no sigma
  - For molecular orbital combine
    - → $C_M\Psi_M + C_L\Psi_{La1g}$
  - Pi bonding
    - → Donor decrease Δ_o
    - → Acceptor increases
      - * Related to electrochemical series

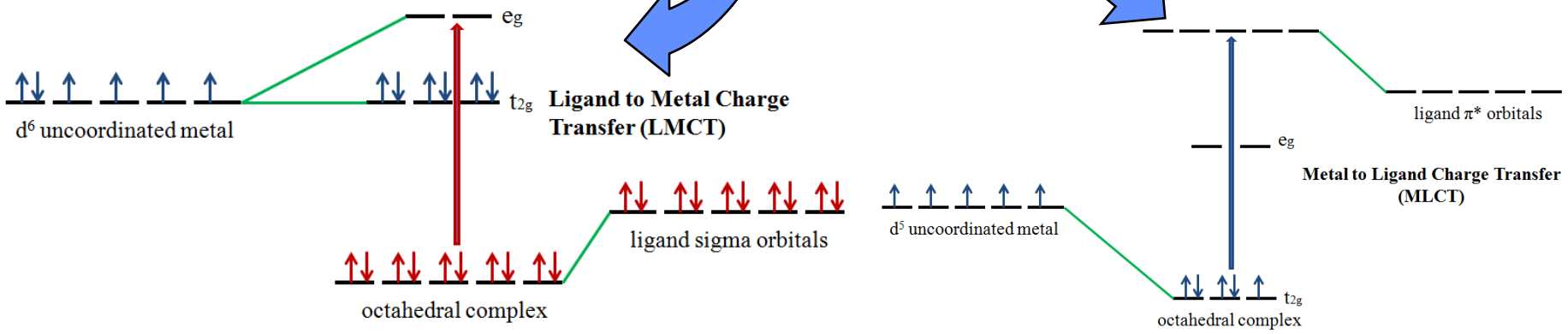






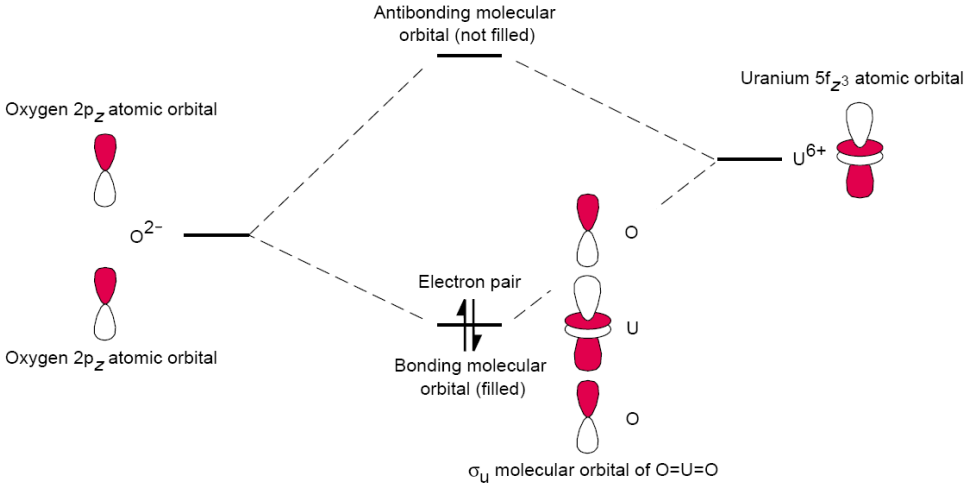
Charge transfer

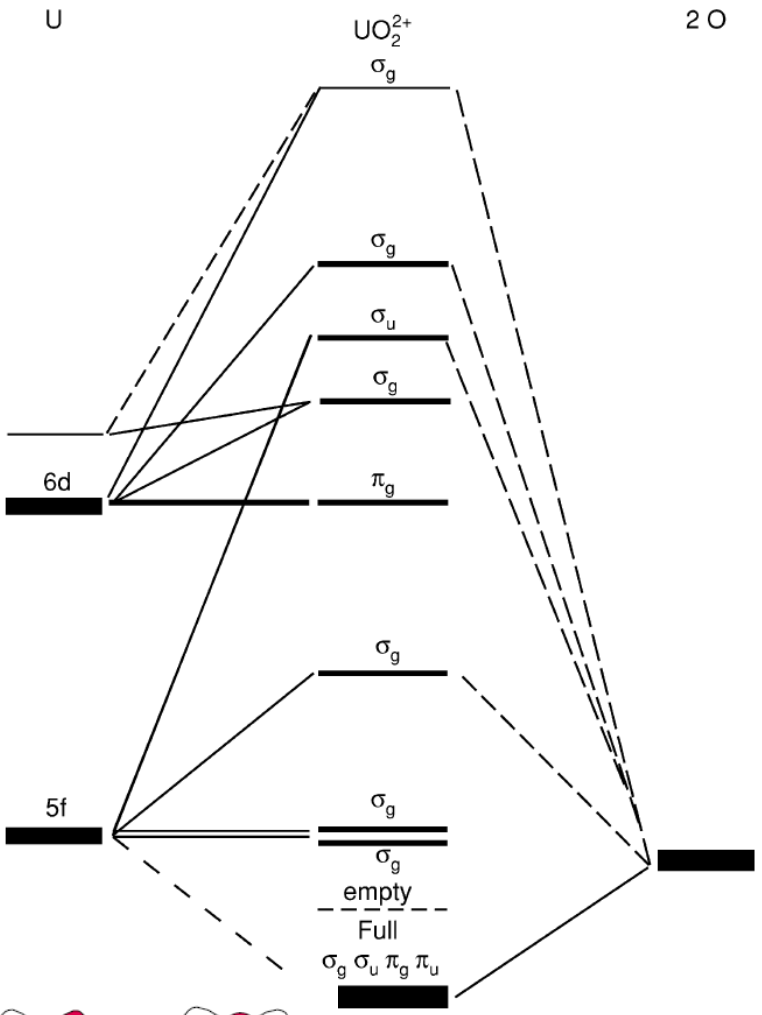
- Allowed transitions in UV-Visible
  - Ligand to metal
  - Metal to ligand
- Related to redox of metals and ligands
  - MnO_4^-
    - → O ligands to Mn metal
- Absorption of radiation involves the transfer of an electron from the donor to an orbital associated with the acceptor.
- Molar absorptivities from charge-transfer absorption are large (greater that 10,000 L mol^{-1} cm^{-1})



Example with UO_2^{2+}

- **Bonding molecular orbitals**
  - $\sigma_g^2 \sigma_u^2 \pi_g^4 \pi_u^4$
    - → Order of HOMO is unclear
      - * $\pi_g < \pi_u < \sigma_g << \sigma_u$ proposed
        - Gap for σ based on 6p orbitals interactions
  - 5fδ and 5fϕ LUMO
  - Bonding orbitals O 2p characteristics
  - Non bonding, antibonding 5f and 6d





Overview

- Bonding and structure relationships
  - Understand how coordination number is related to geometry
- Hard and soft metal interactions
  - First order estimation of interactions
- Modeling of orbitals
  - Molecular orbital theory
  - Charge Transfer
  - Ligand field theory

    →Utility of each concept

    →Exploration of energy difference

Questions

- **What are the possible geometry for a 5 coordinate compound?**
- **Which ligands would be expected to bind strongly with Fe? With Hg?**
- **What is the chelate effect?**
- **What is the relationship between molecular orbital theory, crystal field theory, and ligand field theory?**
- **What does IR and UV-Visible spectroscopy inform about a chemical species?**
- **What accounts for color changes in metal-ligand complexes?**

Questions

- **Comment on blog**
- **Respond to PDF Quiz 4**