

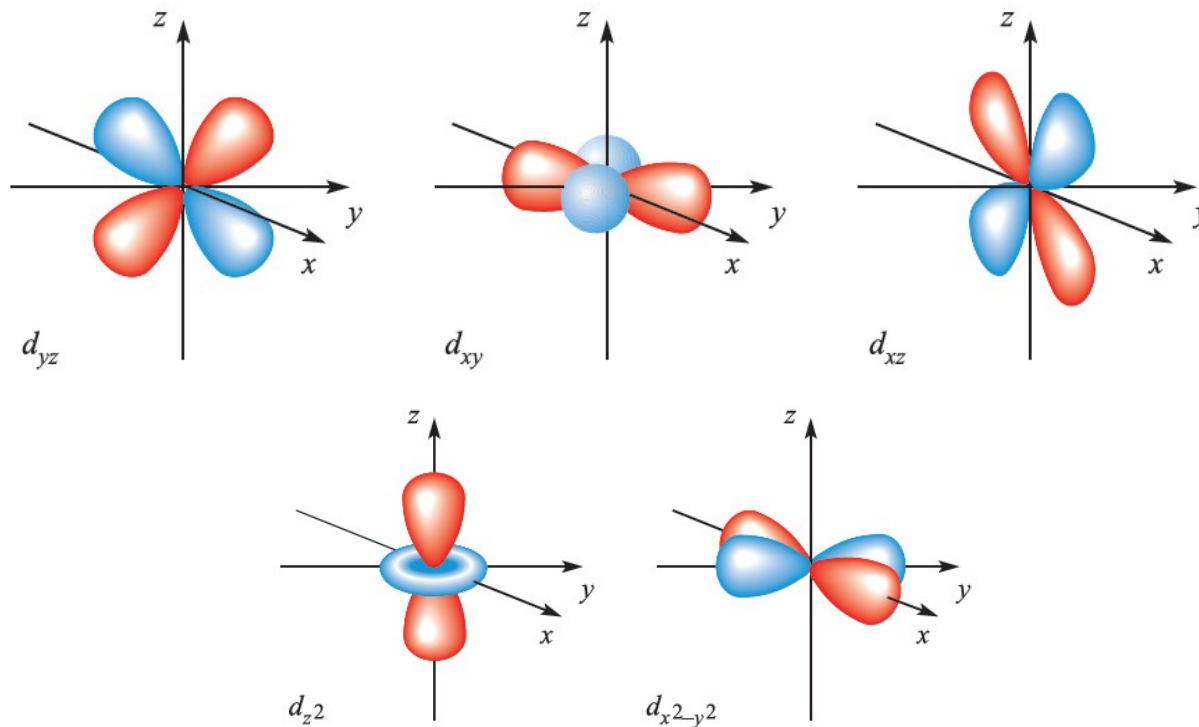
CH103: Introductory Chemistry



Coordination chemistry:

Valence bond, crystal field and molecular orbital theories.

Spatial orientation of d-orbitals

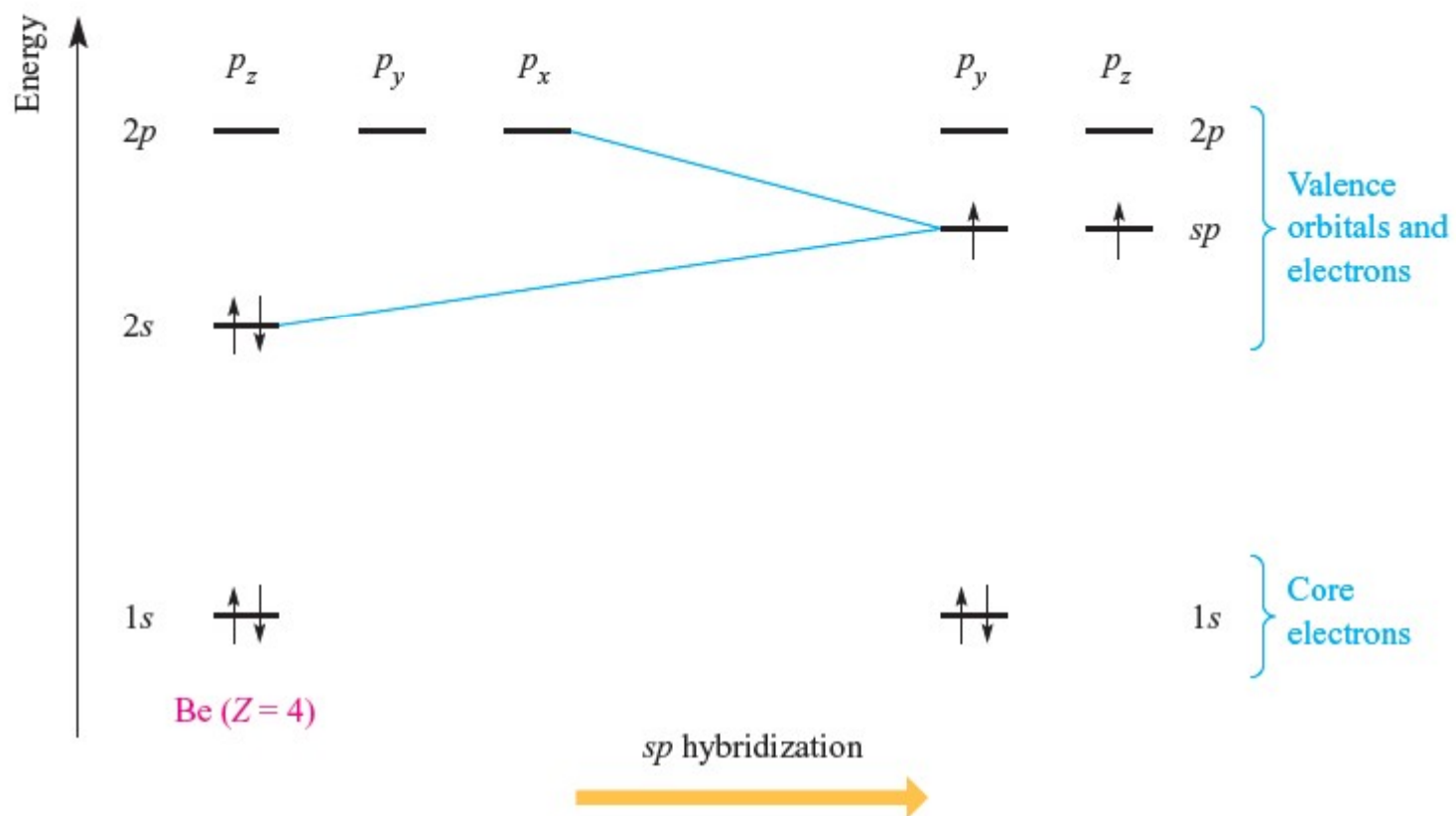


consequence of this difference: the d orbitals in the presence of ligands are **split into groups of different energies**, the type of splitting and the magnitude of the energy differences depending on the **arrangement and nature of the ligands**.

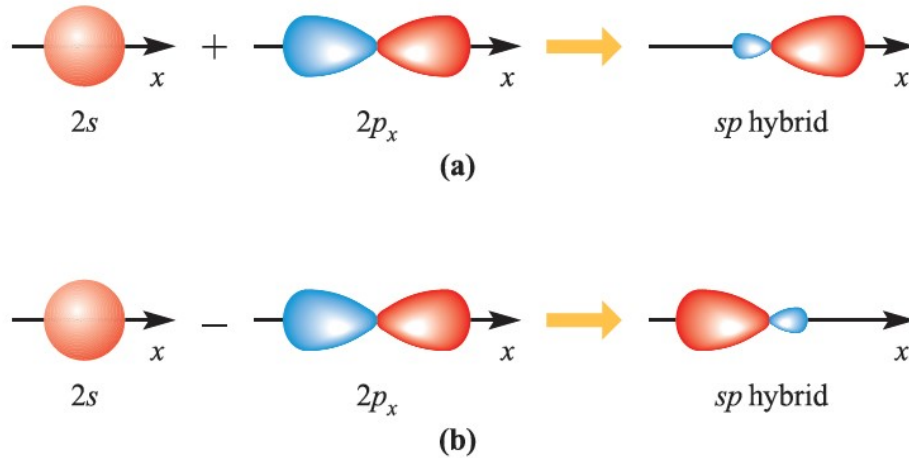
Valence bond theory

- **Hybridization** of atomic orbitals
- 'hybridization' means '**mixing**'
- Hybrid orbitals may be formed by mixing the characters of atomic orbitals that are close in energy
- The **labels** given to hybrid orbitals reflect the contributing atomic orbitals: sp , sp^2 , sp^3 , *etc.*
- The character of a hybrid orbital depends on the atomic orbitals involved and their percentage contributions.

sp hybridization: BeCl_2

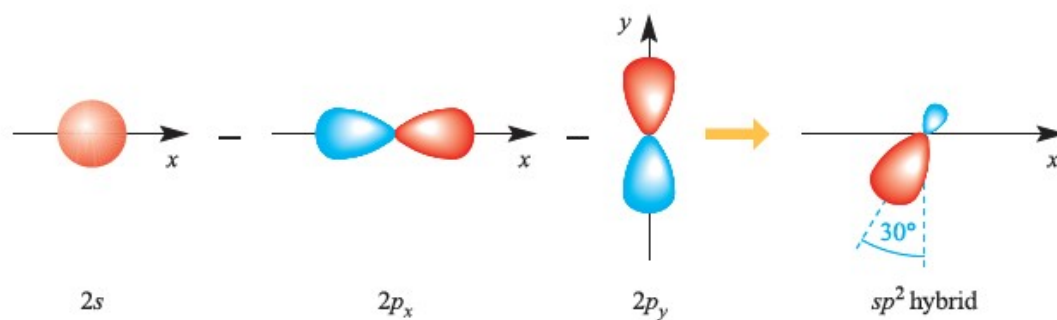
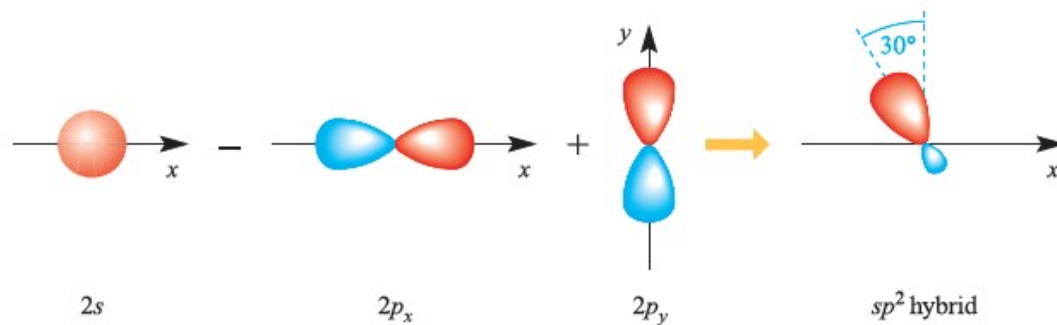
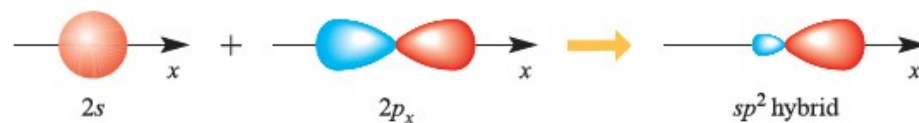


sp hybridization

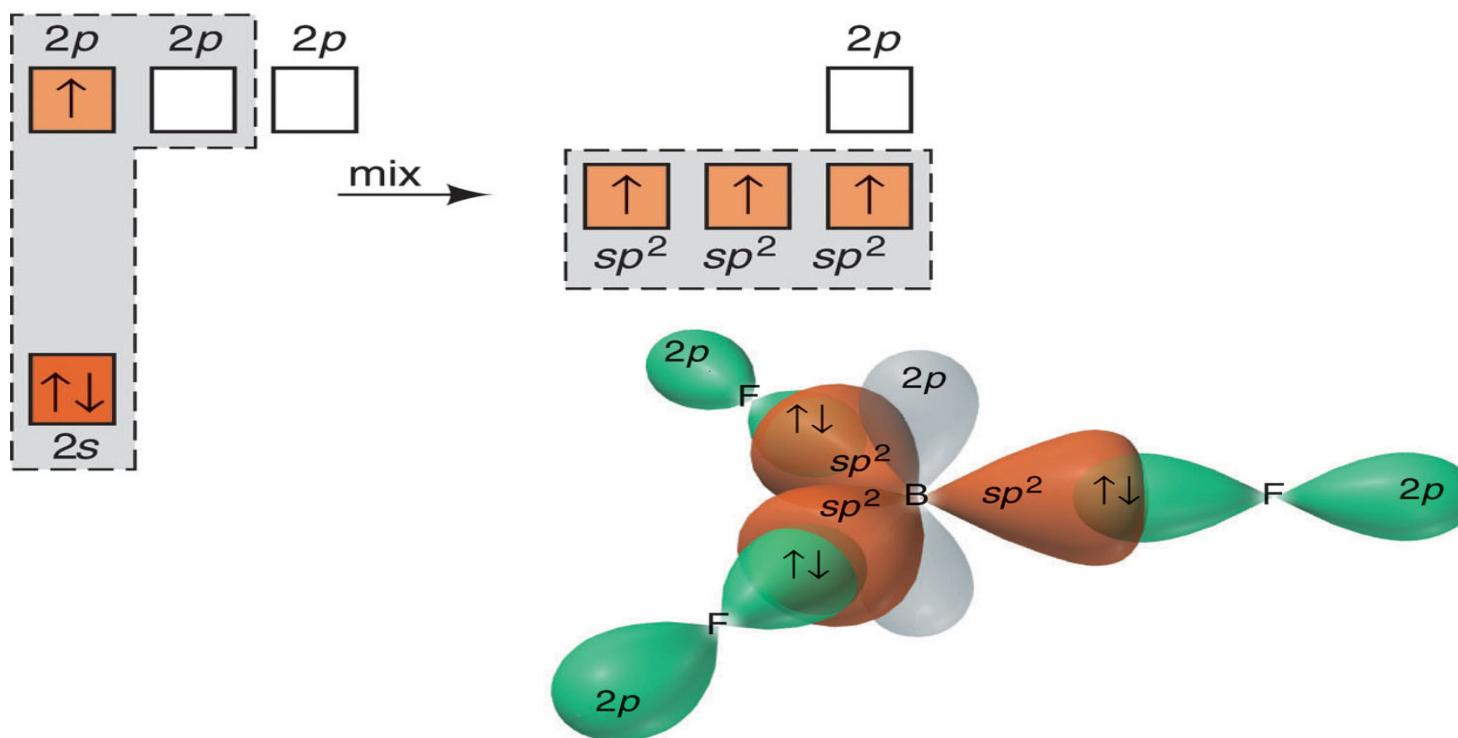


- *if we begin with n atomic orbitals, we must end up with n orbitals after hybridization.*
- Be-Cl bonds are of equal length
- BeCl₂ linear molecule

sp^2 hybridization

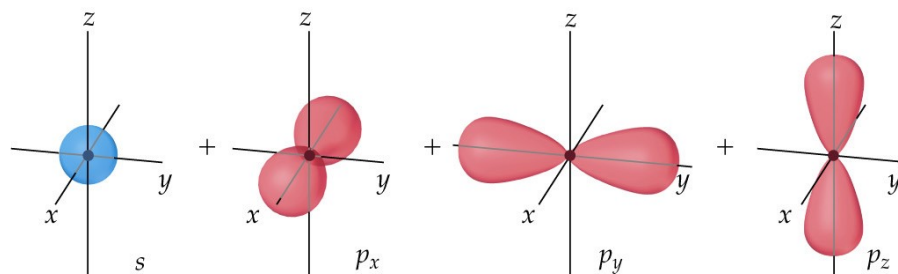


sp^2 hybridization: BF_3

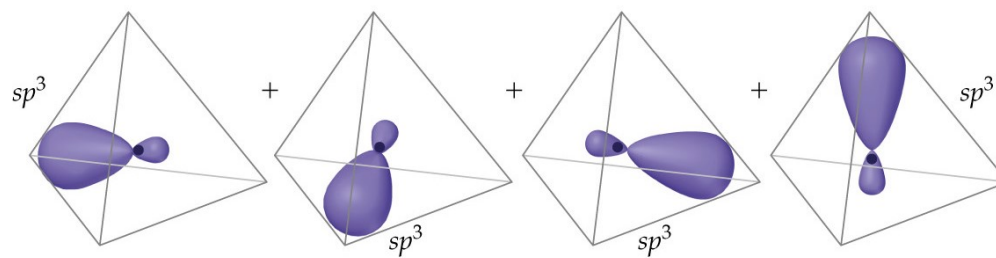


Trigonal planar species

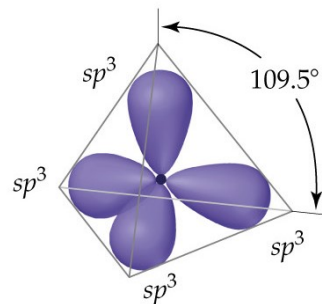
sp^3 hybridization



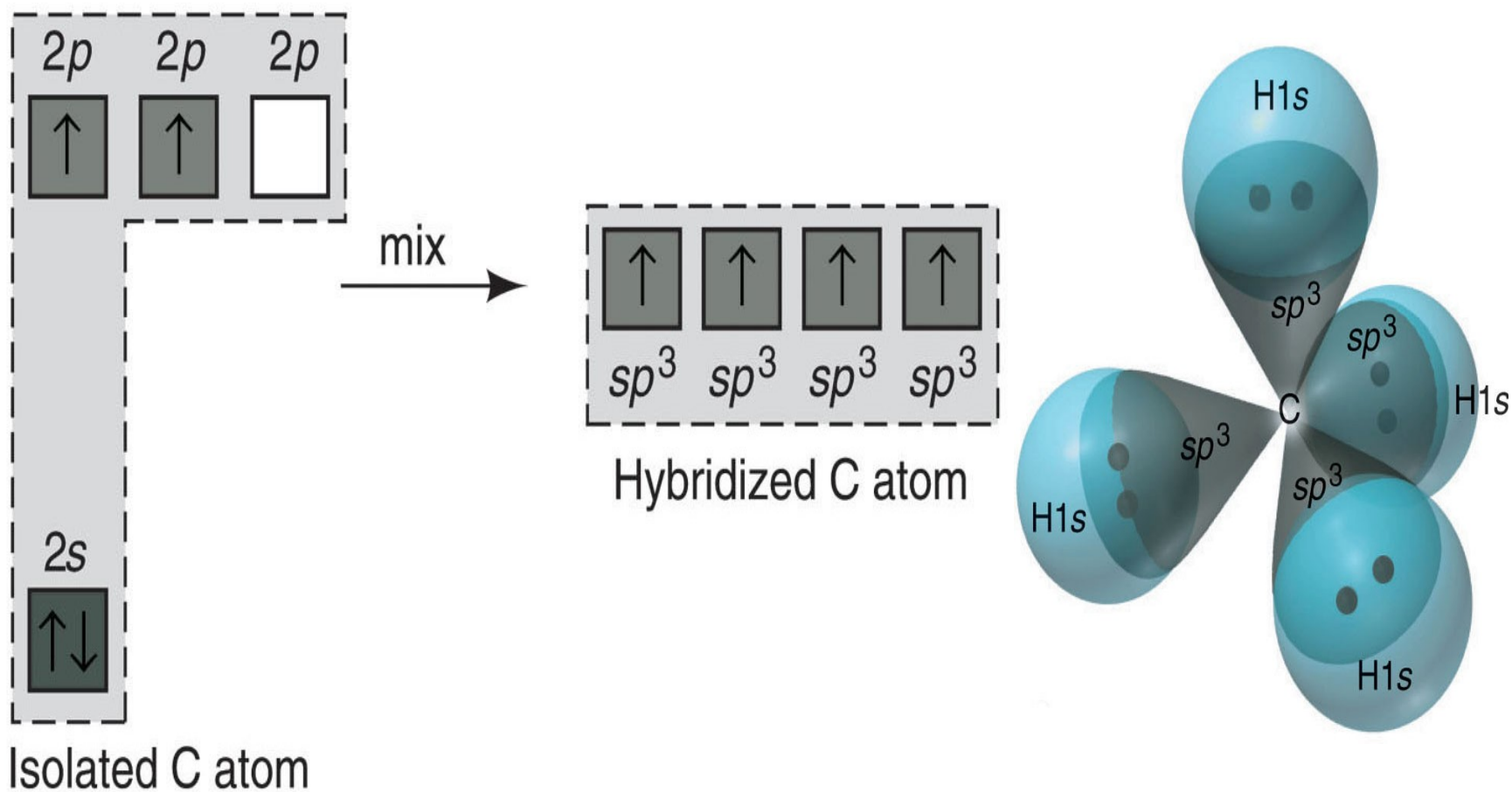
Hybridize to form four sp^3 hybrid orbitals



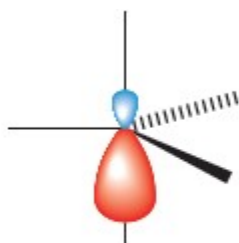
Shown together (large lobes only)



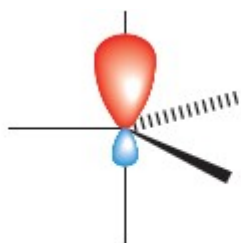
sp^3 hybridization: Methane



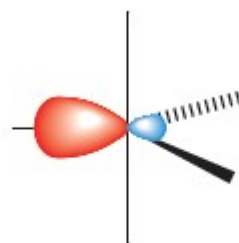
sp^3d hybridization



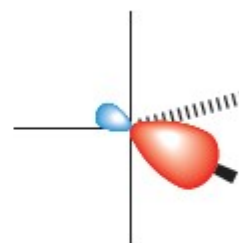
Axial



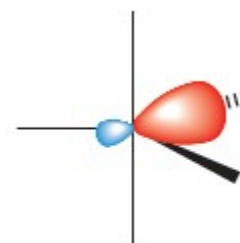
Axial



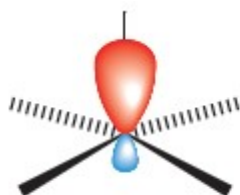
Equatorial



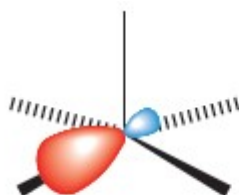
Equatorial



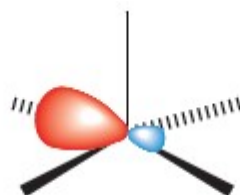
Equatorial



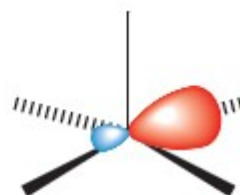
Axial



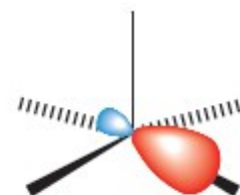
Basal



Basal

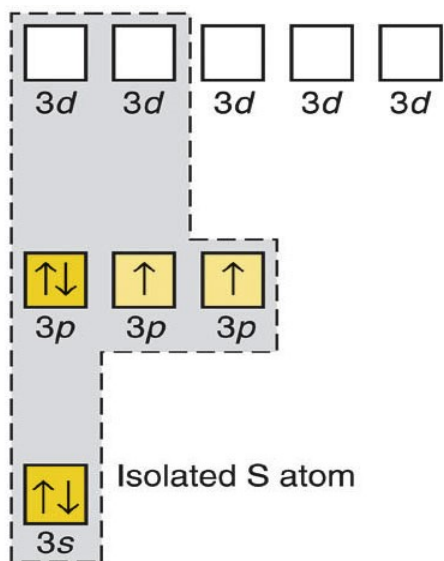


Basal

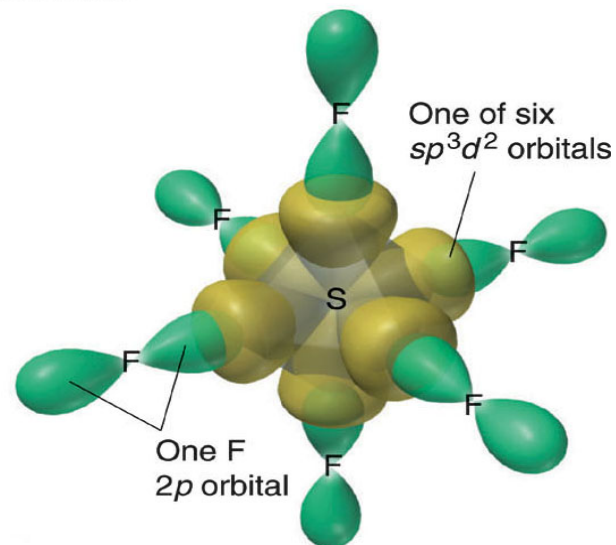
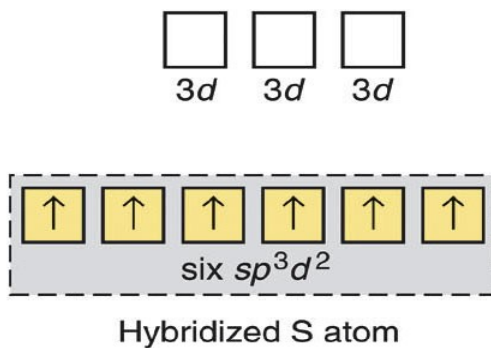


Basal

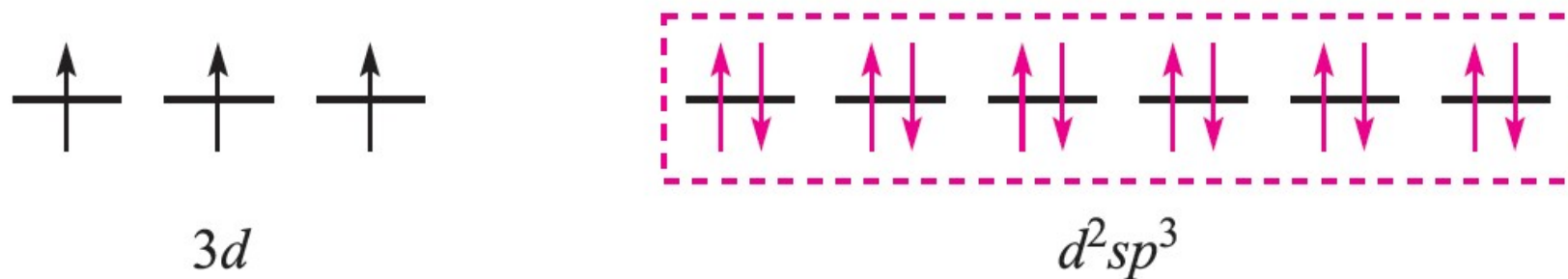
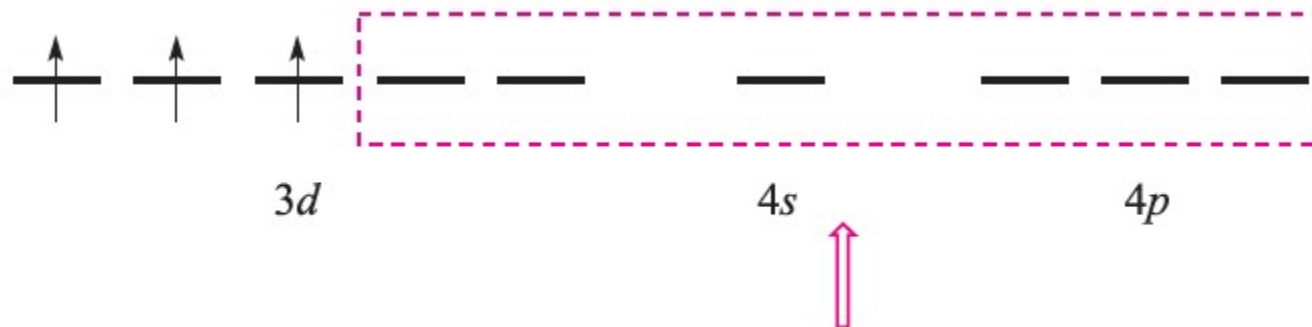
sp^3d^2 hybrid orbitals in SF_6



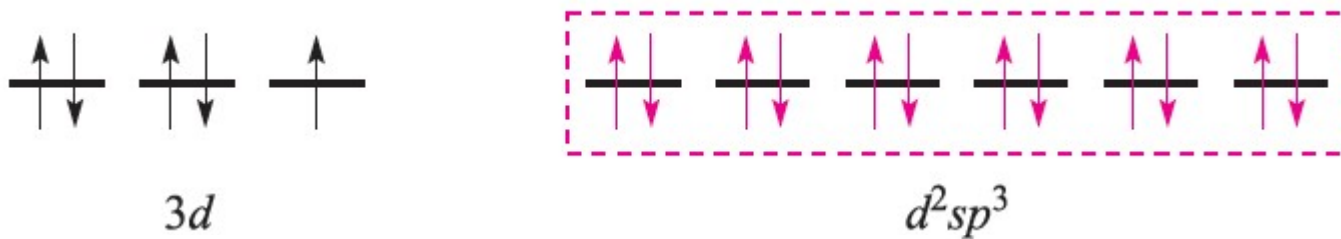
mix →



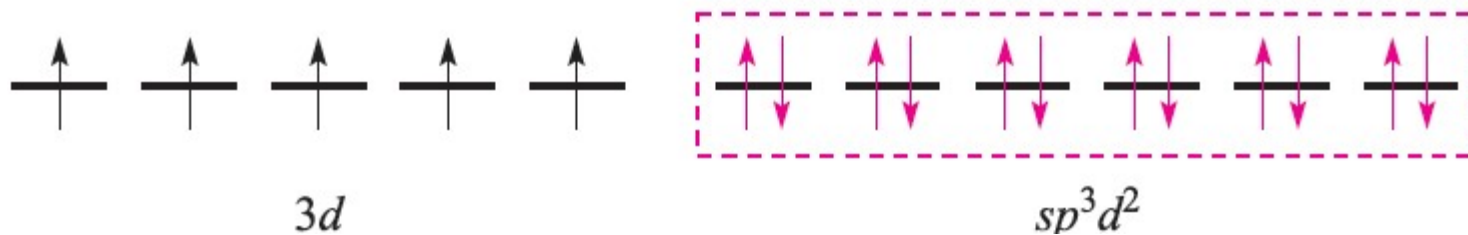
Chromium (III): Octahedral



Fe³⁺ ion: Octahedral



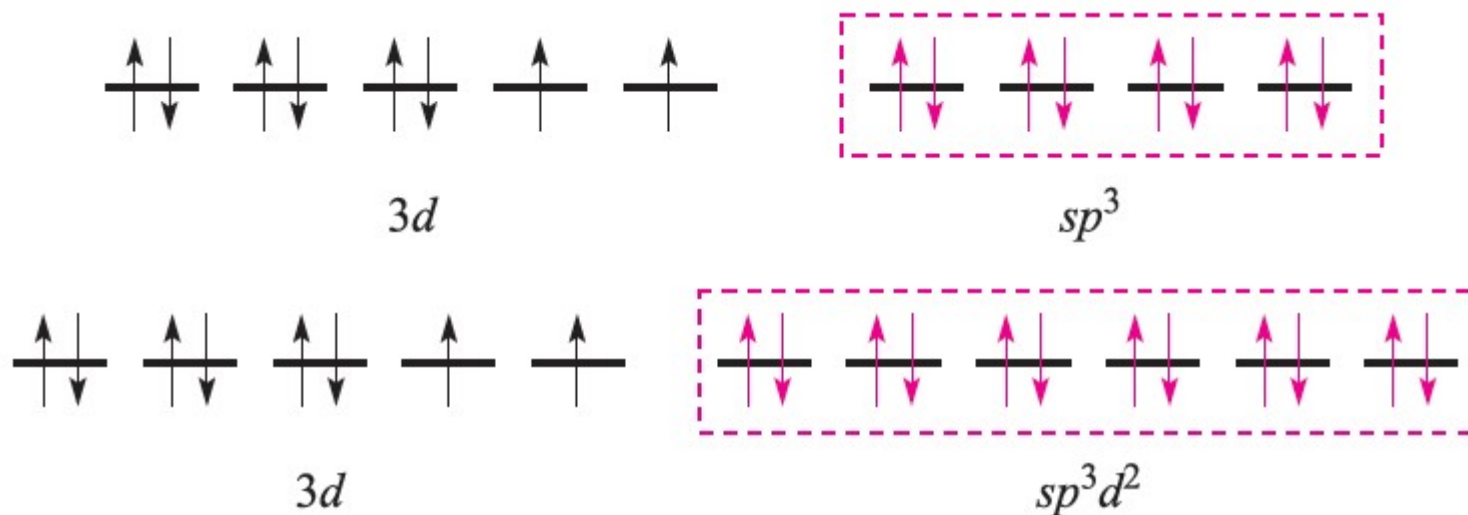
Low spin: paramagnetic



High spin: paramagnetic

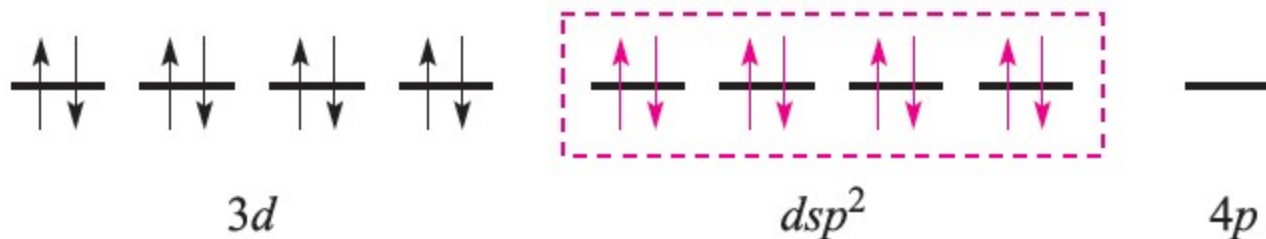
Ni²⁺ ion: Octahedral vs Tetrahedral

- Nickel(II) (d⁸) forms **paramagnetic tetrahedral and octahedral complexes.**



Ni²⁺ ion: Square Planar

- Nickel(II) (d⁸) forms **diamagnetic square planar complexes**.



Valence bond theory

Coordination number	Arrangement of donor atoms	Orbitals hybridized	Hybrid orbital description	Example
2	Linear	s, p_z	sp	$[\text{Ag}(\text{NH}_3)_2]^+$
3	Trigonal planar	s, p_x, p_y	sp^2	$[\text{HgI}_3]^-$
4	Tetrahedral	s, p_x, p_y, p_z	sp^3	$[\text{FeBr}_4]^{2-}$
4	Square planar	$s, p_x, p_y, d_{x^2-y^2}$	sp^2d	$[\text{Ni}(\text{CN})_4]^{2-}$
5	Trigonal bipyramidal	$s, p_x, p_y, p_z, d_{z^2}$	sp^3d	$[\text{CuCl}_5]^{3-}$
5	Square-based pyramidal	$s, p_x, p_y, p_z, d_{x^2-y^2}$	sp^3d	$[\text{Ni}(\text{CN})_5]^{3-}$
6	Octahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$	sp^3d^2	$[\text{Co}(\text{NH}_3)_6]^{3+}$
6	Trigonal prismatic	$s, d_{xy}, d_{yz}, d_{xz}, d_{z^2}, d_{x^2-y^2}$ or $s, p_x, p_y, p_z, d_{xz}, d_{yz}$	sd^5 or sp^3d^2	$[\text{ZrMe}_6]^{2-}$
7	Pentagonal bipyramidal	$s, p_x, p_y, p_z, d_{xy}, d_{x^2-y^2}, d_{z^2}$	sp^3d^3	$[\text{V}(\text{CN})_7]^{4-}$
7	Monocapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{z^2}$	sp^3d^3	$[\text{NbF}_7]^{2-}$
8	Cubic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, f_{xyz}$	sp^3d^3f	$[\text{PaF}_8]^{3-}$
8	Dodecahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{xy}, d_{xz}, d_{yz}$	sp^3d^4	$[\text{Mo}(\text{CN})_8]^{4-}$
8	Square antiprismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$	sp^3d^4	$[\text{TaF}_8]^{3-}$
9	Tricapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{z^2}, d_{x^2-y^2}$	sp^3d^5	$[\text{ReH}_9]^{2-}$

Bent's rule

- Hybrid orbitals may or may not be equivalent.
- Depends on the substituents.

— BeCl_2 and BeClBr

— The more electronegative substituent will prefer hybrid orbitals having less s-character.

— Shape PCl_3F_2

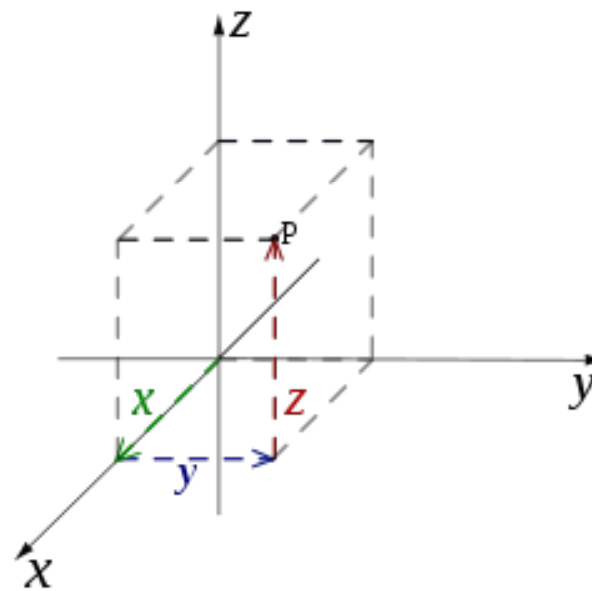
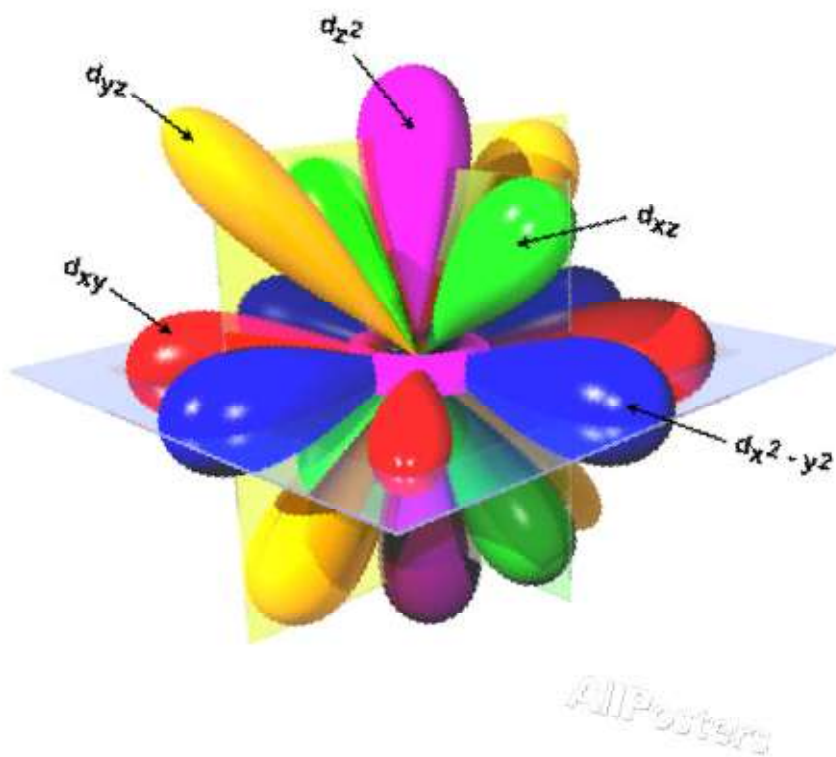
Limitations

- It can say nothing about **electronic spectroscopic properties** .
- **Chemical reactivity** can't be predicted
 - kinetic inertness that is a characteristic of the low-spin d 6 configuration.
- Furthermore, the model implies a **distinction between high- and low-spin complexes** that is actually **misleading**.
- Finally, it cannot tell us why certain ligands are associated with the **formation of high- (or low-)spin complexes**.

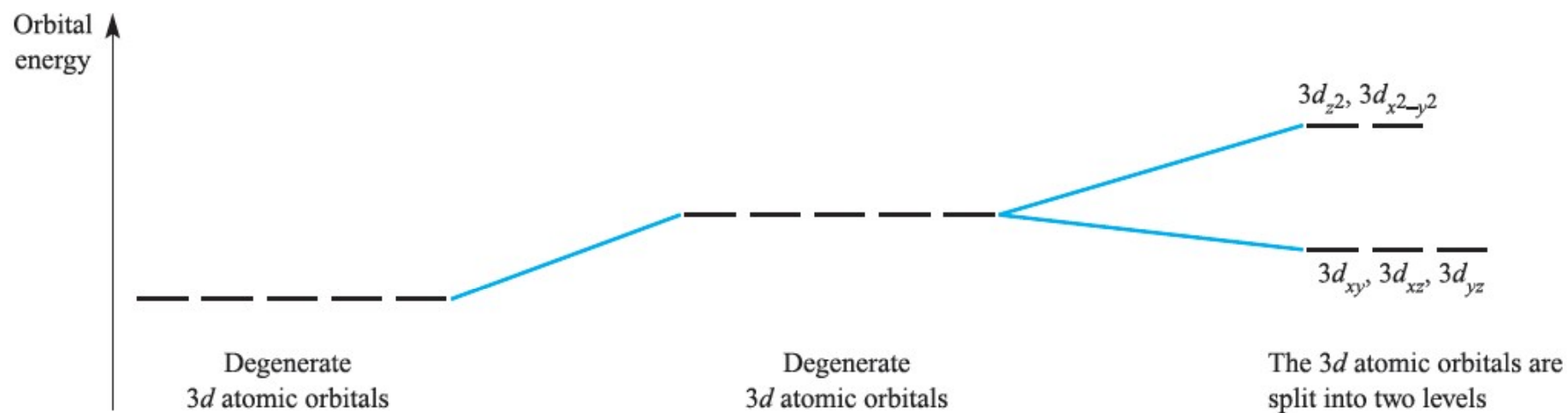
Crystal field theory (CFT)

- This is an **electrostatic model** and simply uses the ligand electrons to create an electric field around the metal centre.
- **Ligands** are considered as **point charges** and there are no metal–ligand covalent interaction.
- Predicts that the **d orbitals** in a metal complex are **not degenerate**.
- **Pattern of splitting of the d orbitals** depends on the crystal field, this being determined by the arrangement and **type of ligands**

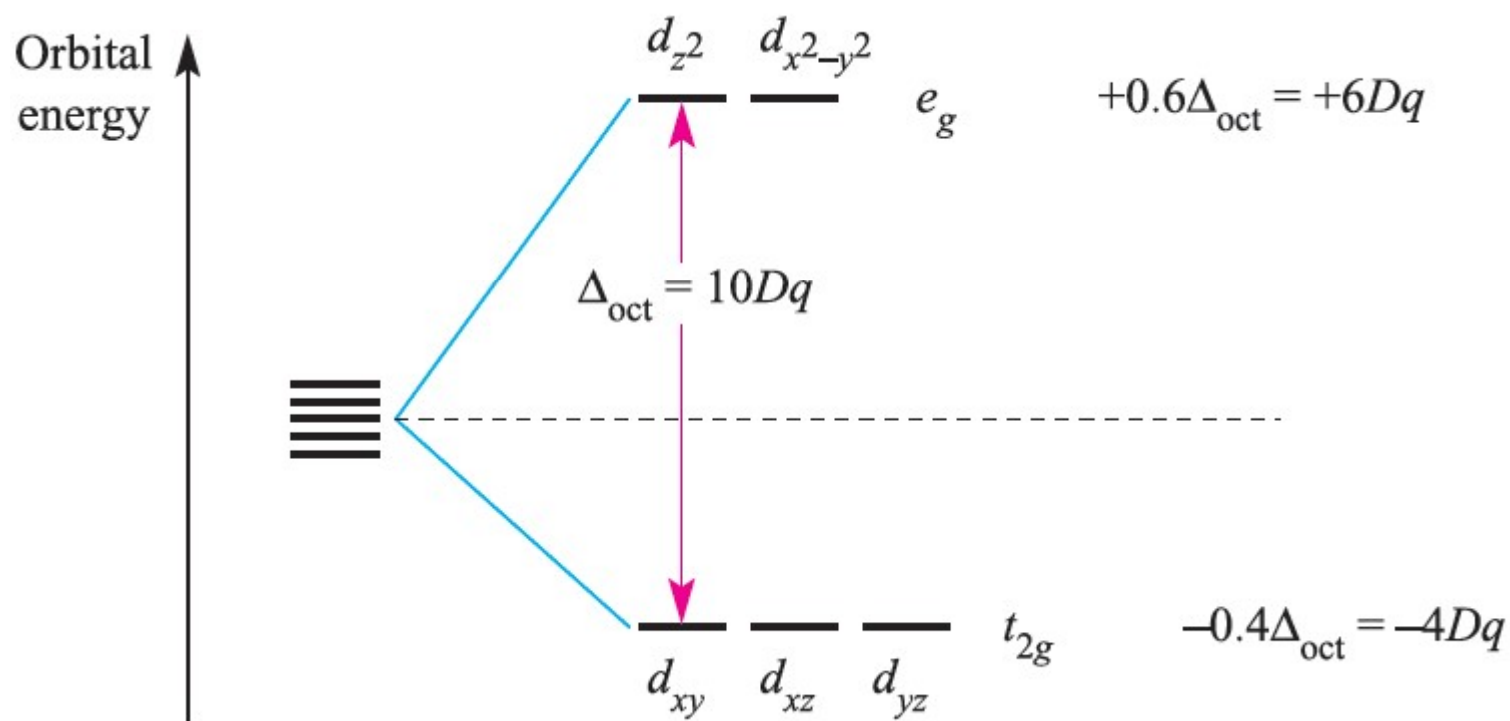
Crystal field theory (CFT)



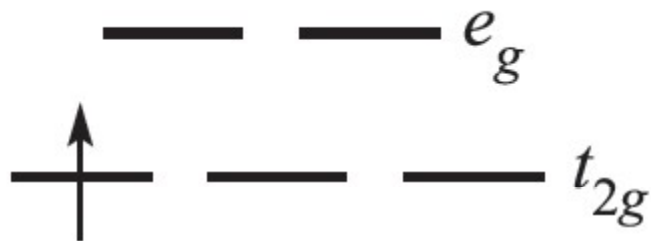
Octahedral crystal field



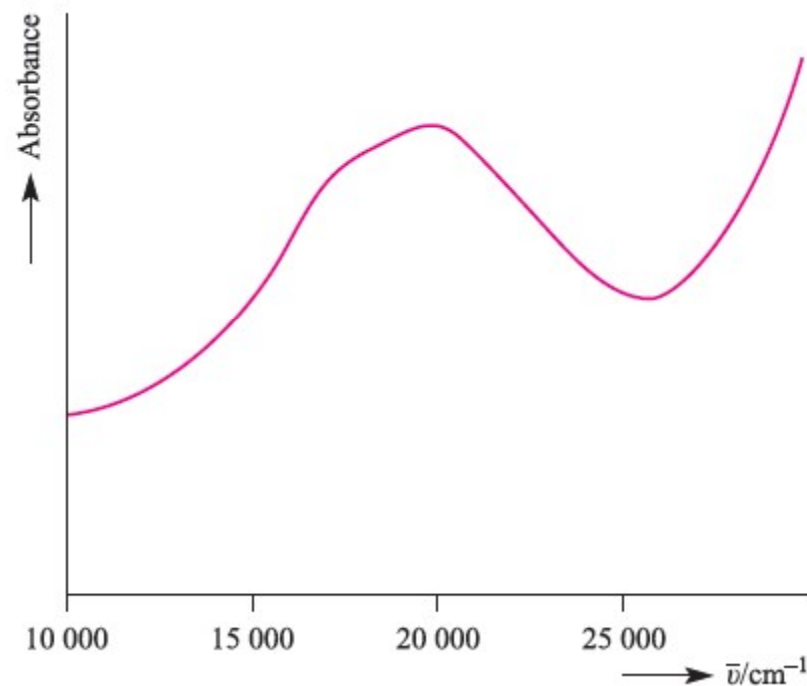
Splitting of the d orbitals in an octahedral crystal field



Electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.



$$\lambda_{\text{max}} = 20\,300\text{ cm}^{-1}$$

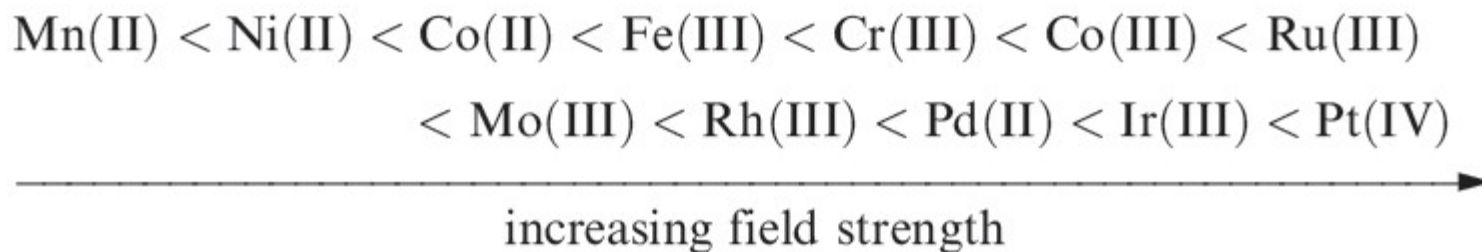
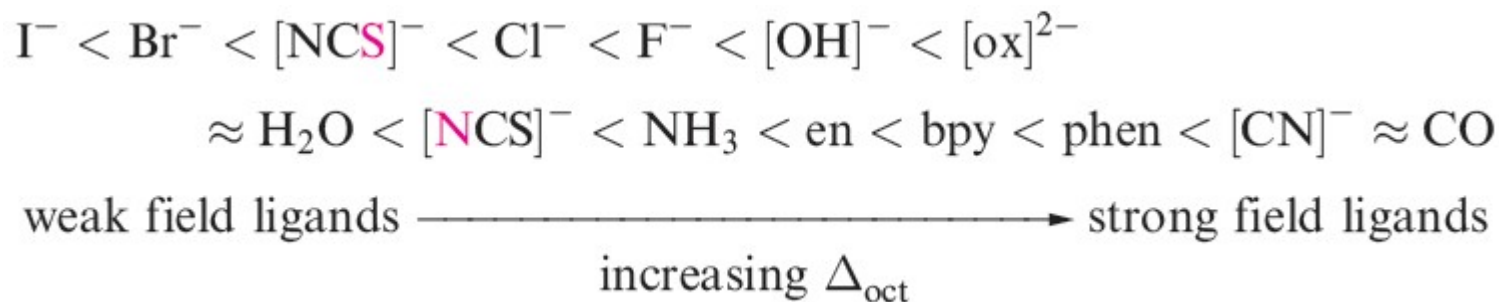


$$\Delta_{\text{oct}} = 243\text{ kJ mol}^{-1}$$

Spectrochemical Series

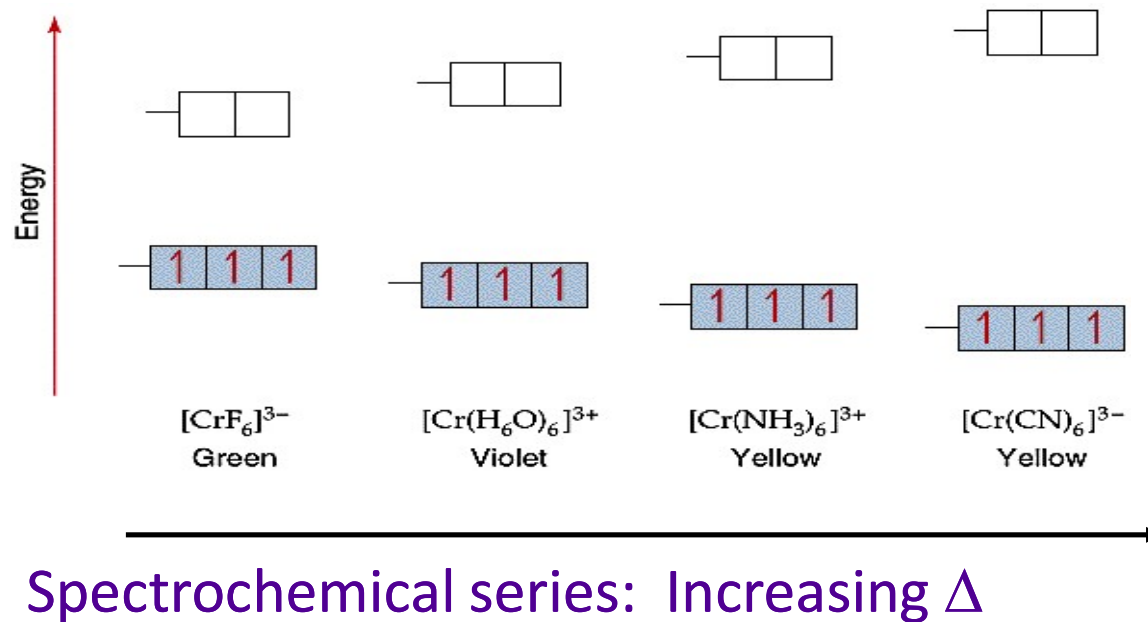
Weak and Strong field

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



Magnitude of CF Splitting (Δ or $10Dq$)

- Color of the Complex depends on magnitude of $10Dq$
- **Weak field Ligand:** Low electrostatic interaction: small CF splitting.
- **High field Ligand:** High electrostatic interaction: large CF splitting.



Pairing Energy and Δ_{oct} :



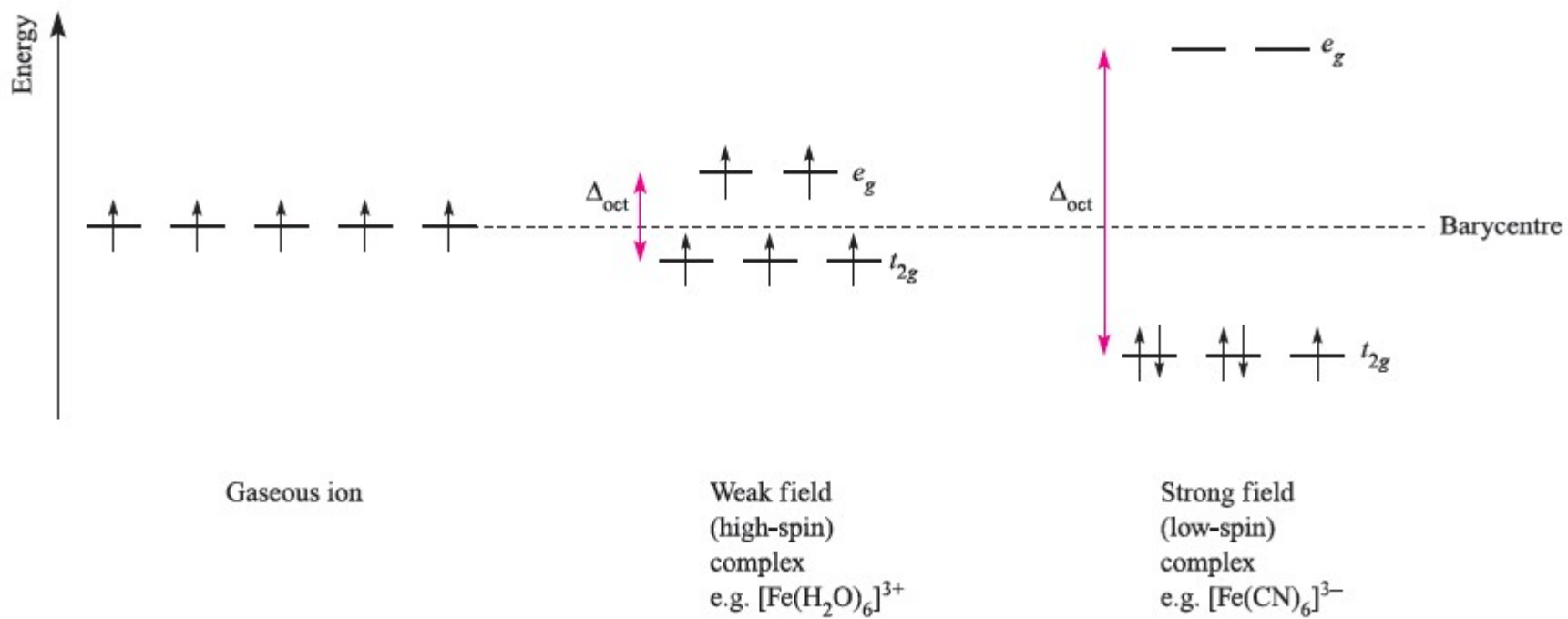
For high-spin: $\Delta_{\text{oct}} < P$

For low-spin: $\Delta_{\text{oct}} > P$

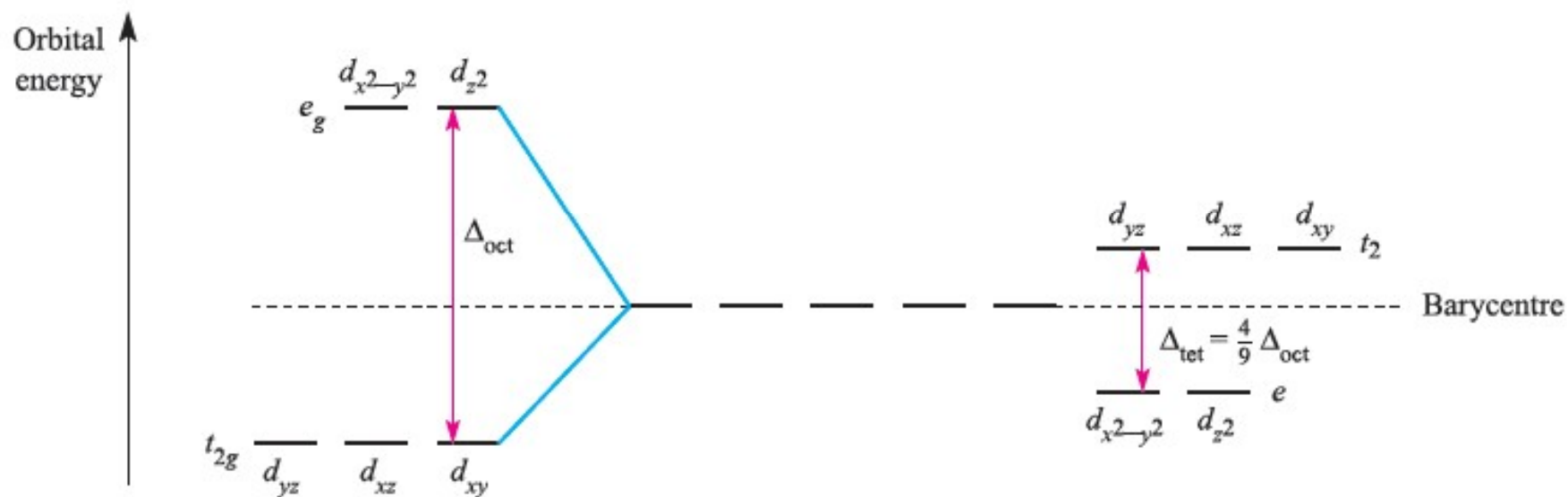
High Spin and Low Spin

d^n	High-spin = weak field		Low-spin = strong field	
	Electronic configuration	CFSE	Electronic configuration	CFSE
d^1	$t_{2g}^1 e_g^0$	$-0.4\Delta_{\text{oct}}$		
d^2	$t_{2g}^2 e_g^0$	$-0.8\Delta_{\text{oct}}$		
d^3	$t_{2g}^3 e_g^0$	$-1.2\Delta_{\text{oct}}$		
d^4	$t_{2g}^3 e_g^1$	$-0.6\Delta_{\text{oct}}$	$t_{2g}^4 e_g^0$	$-1.6\Delta_{\text{oct}} + P$
d^5	$t_{2g}^3 e_g^2$	0	$t_{2g}^5 e_g^0$	$-2.0\Delta_{\text{oct}} + 2P$
d^6	$t_{2g}^4 e_g^2$	$-0.4\Delta_{\text{oct}}$	$t_{2g}^6 e_g^0$	$-2.4\Delta_{\text{oct}} + 2P$
d^7	$t_{2g}^5 e_g^2$	$-0.8\Delta_{\text{oct}}$	$t_{2g}^6 e_g^1$	$-1.8\Delta_{\text{oct}} + P$
d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_{\text{oct}}$		
d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_{\text{oct}}$		
d^{10}	$t_{2g}^6 e_g^4$	0		

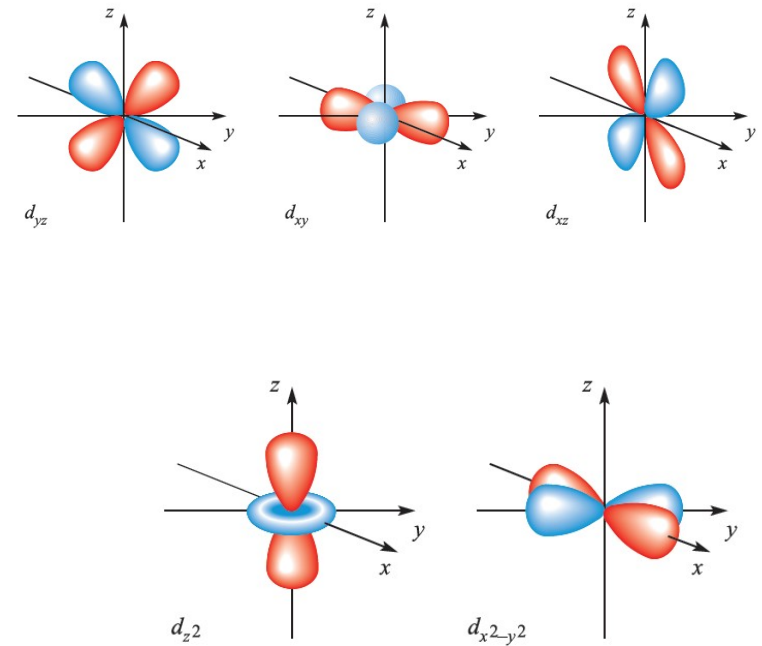
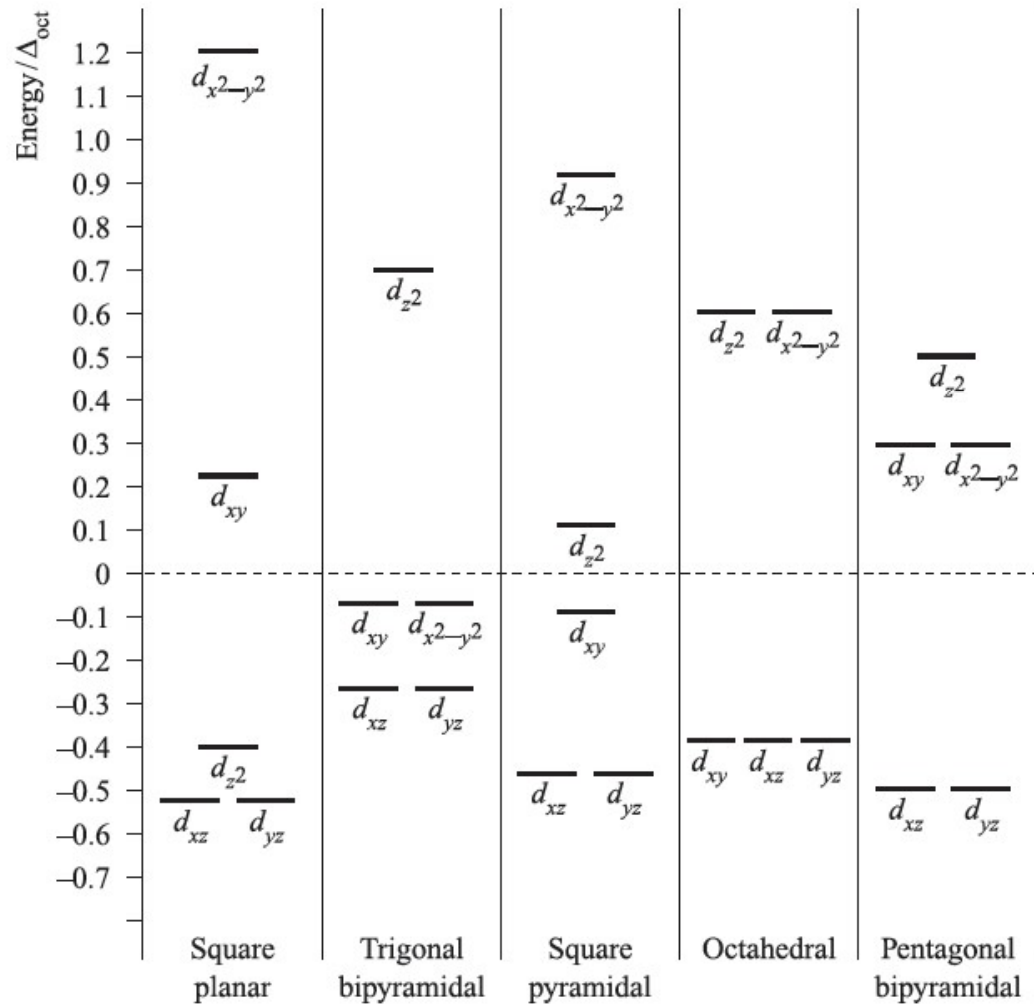
High Spin and Low Spin



Octahedral vs Tetrahedral



Crystal Field Splittings



Crystal field theory: uses and limitations

- Crystal field theory can bring together structures, magnetic properties and electronic properties
- Trends in CFSEs provide some understanding of thermodynamic and kinetic aspects of d-block metal complexes
- crystal field theory provides no explanation as to why particular ligands are placed in the spectrochemical series.

Molecular Orbital Theory (MOT)

- Considers **covalent interactions** between the metal centre and ligands. Electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei
- In molecular orbital (MO) theory, we begin by placing the nuclei of a given molecule in their equilibrium positions and then calculate the molecular orbitals (i.e. regions of space spread over the entire molecule) that a single electron might occupy.
- Each MO arises from interactions between orbitals of atomic centres in the molecule, and such interactions are:
 - **allowed** if the symmetries of the atomic orbitals are compatible with one another;
 - **efficient** if the region of overlap between the two atomic orbitals is significant;
 - **efficient** if the atomic orbitals are relatively close in energy.

Molecular Orbital Theory (MOT)

Bonding and Antibonding molecular orbital

$$\psi_b = \psi_A + \psi_B$$

$$\psi_a = \psi_A - \psi_B$$

H₂⁺ molecule

$$\psi = \psi_{b(1)} = \psi_{A(1)} + \psi_{B(1)}$$

H₂ molecule

$$\psi = \psi_{b(1)}\psi_{b(2)} = [\psi_{A(1)} + \psi_{B(1)}][\psi_{A(2)} + \psi_{B(2)}]$$

$$\psi = \psi_{A(1)}\psi_{A(2)} + \psi_{B(1)}\psi_{B(2)} + \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)}$$

Electronic distribution

$$\psi_b^2 = \psi_A^2 + 2\psi_A\psi_B + \psi_B^2$$

$$\psi_a^2 = \psi_A^2 - 2\psi_A\psi_B + \psi_B^2$$

Molecular Orbital Theory (MOT)

$$\int N_b^2 \psi_b^2 d\tau = N_b^2 \left[\int \psi_A^2 d\tau + \int \psi_B^2 d\tau + 2 \int \psi_A \psi_B d\tau \right] = 1 \quad (5.33)$$

where N_b is the *normalizing constant*. If we let S be the overlap integral, $\int \psi_A \psi_B d\tau$, we have

$$\int \psi_b^2 d\tau = \left[\int \psi_A^2 d\tau + \int \psi_B^2 d\tau + 2S \right] \quad (5.34)$$

Now since the atomic wave functions ψ_A and ψ_B were previously normalized, $\int \psi_A^2 d\tau$ and $\int \psi_B^2 d\tau$ each equal one. Hence

$$N_b^2 = \frac{1}{2 + 2S} \quad (5.35)$$

$$N_b = \sqrt{\frac{1}{2 + 2S}} \quad (5.36)$$

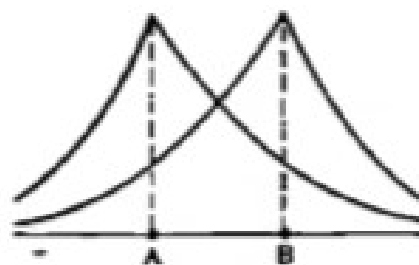
and

$$N_a = \sqrt{\frac{1}{2 - 2S}} \quad (5.37)$$

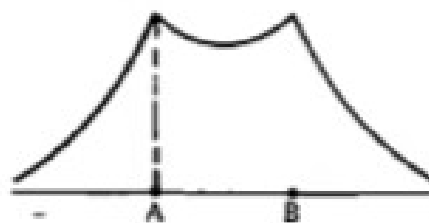
$$\psi_b = \sqrt{\frac{1}{2}} (\psi_A + \psi_B)$$

$$\psi_a = \sqrt{\frac{1}{2}} (\psi_A - \psi_B)$$

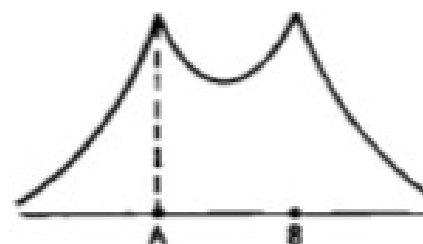
Molecular Orbital Theory (MOT)



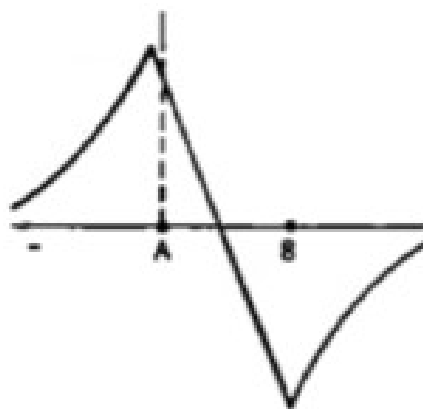
(a)



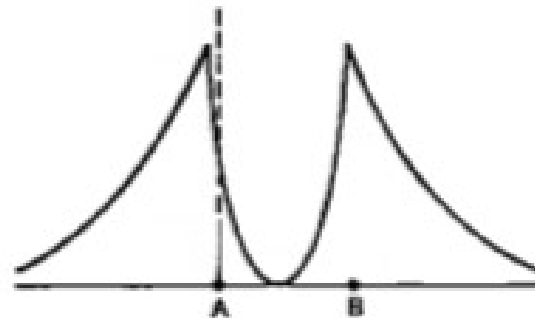
(b)



(c)



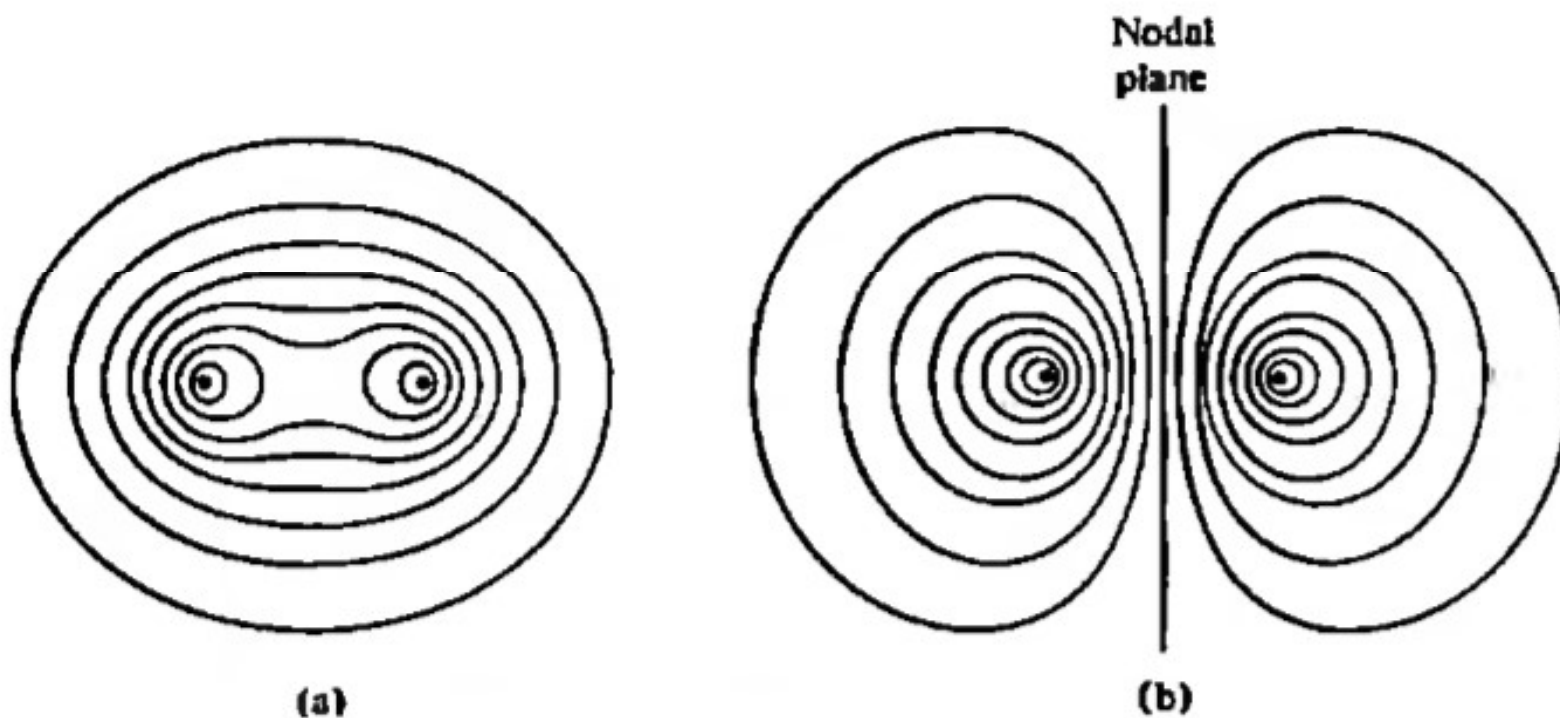
(d)



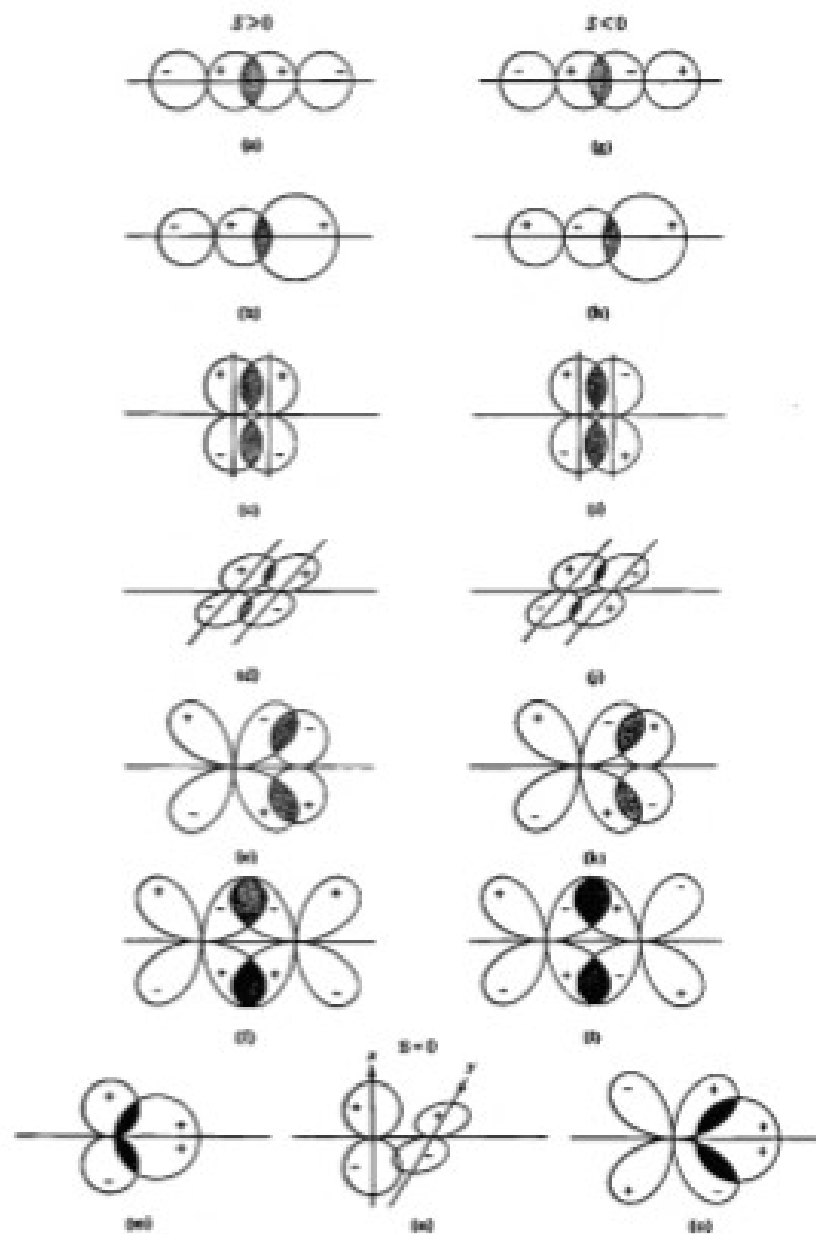
(e)

Molecular Orbital Theory (MOT)

H_2^+ molecule bonding and antibonding orbital

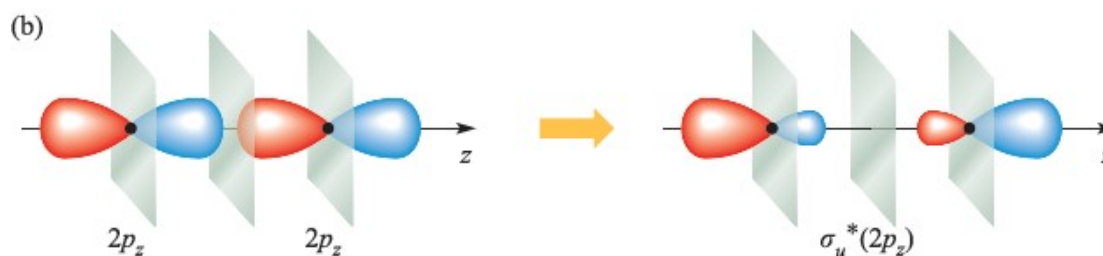
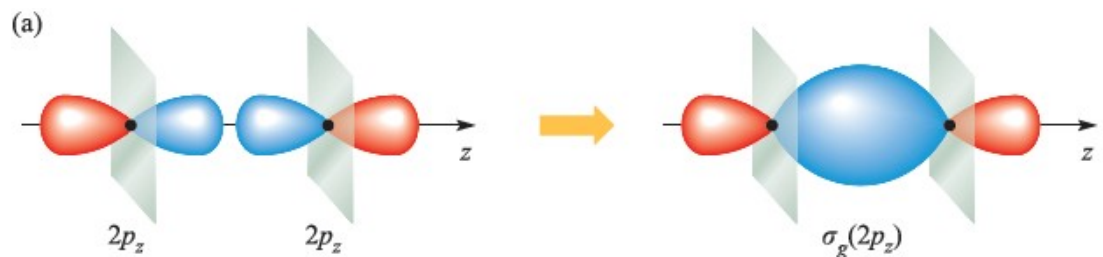
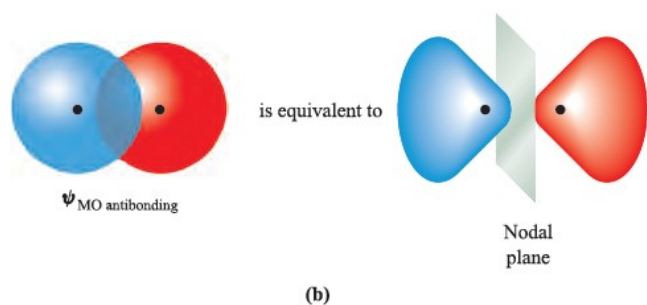
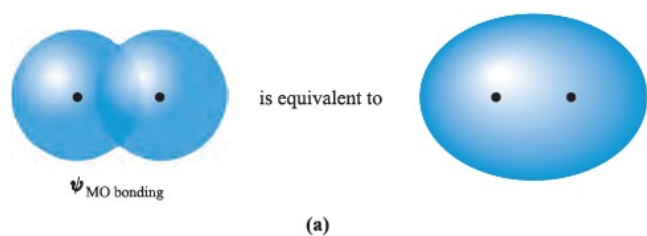


Molecular Orbital Theory (MOT)



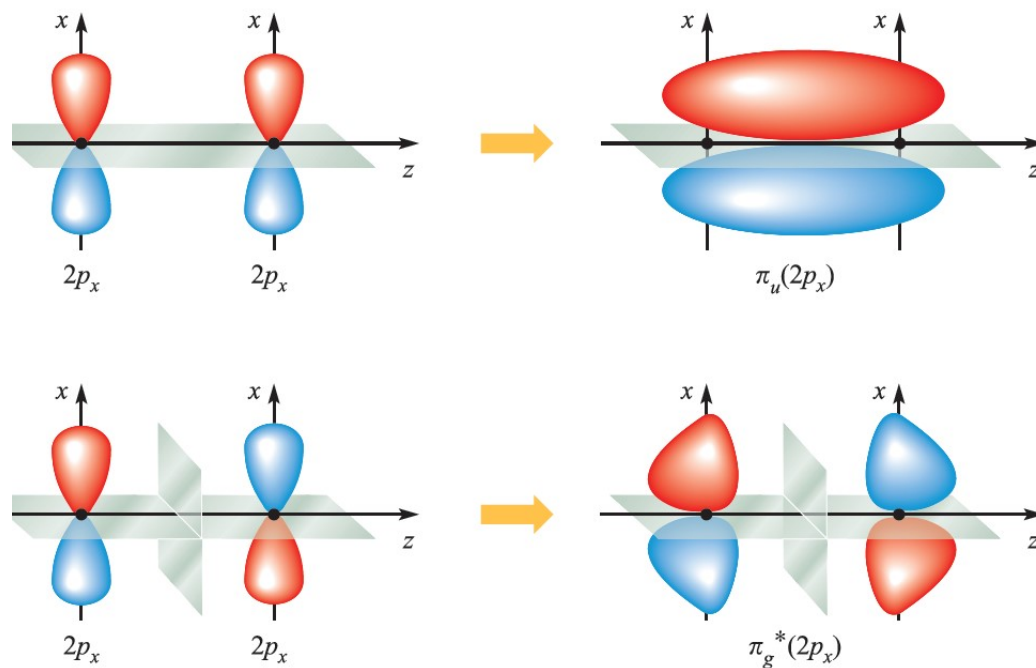
Molecular Orbital Theory (MOT)

- The σ label means that rotation of the orbital about the internuclear axis generates no phase change, and
- the $*$ label means that there is a nodal plane between the nuclei, and this plane is orthogonal to the internuclear axis.



Molecular Orbital Theory (MOT)

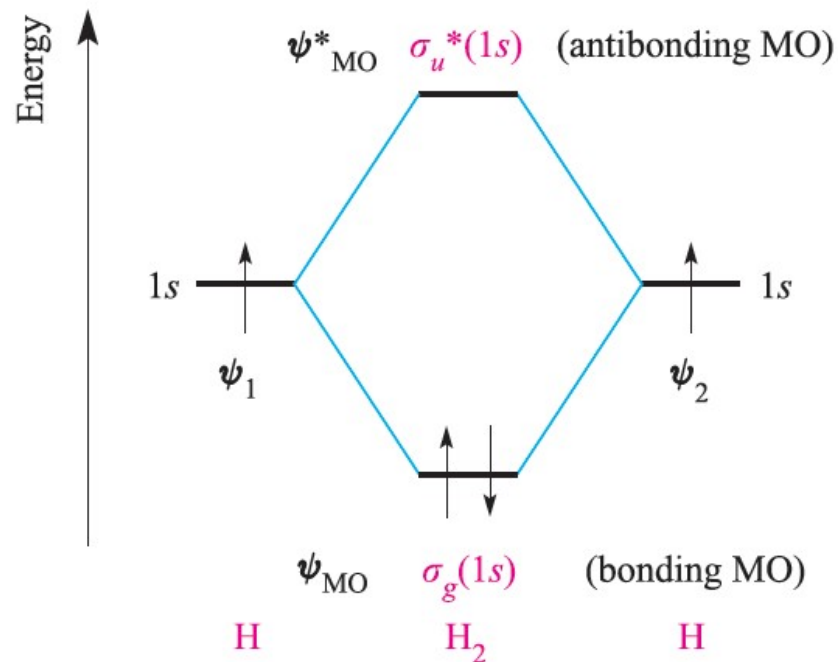
- The π label means that rotation of the orbital about the internuclear axis generates a phase change, and
- The $*$ label means that there must be a nodal plane between the nuclei.



Molecular Orbital Theory (MOT)

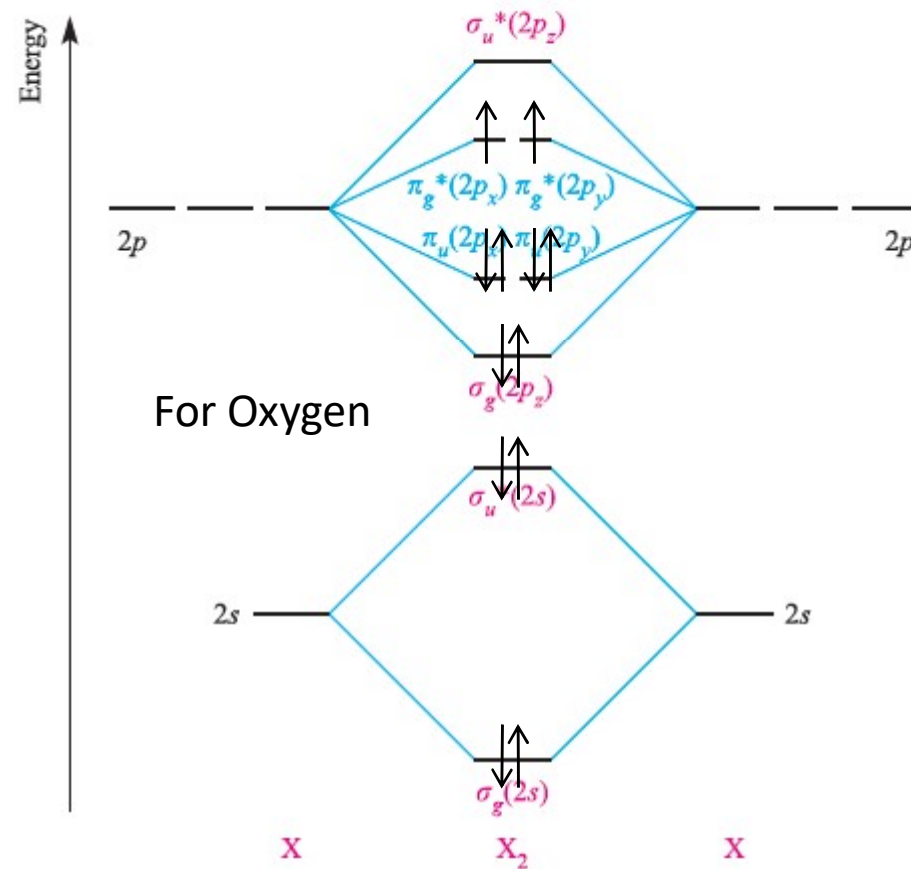
$$\text{Bond order} = \frac{1}{2} [(\text{Number of bonding electrons}) \\ - (\text{Number of antibonding electrons})]$$

- The number of MOs that can be formed must equal the number of atomic orbitals of the constituent atoms.
- Construct the orbital interaction diagram first and then put in the electrons according to the aufbau principle.



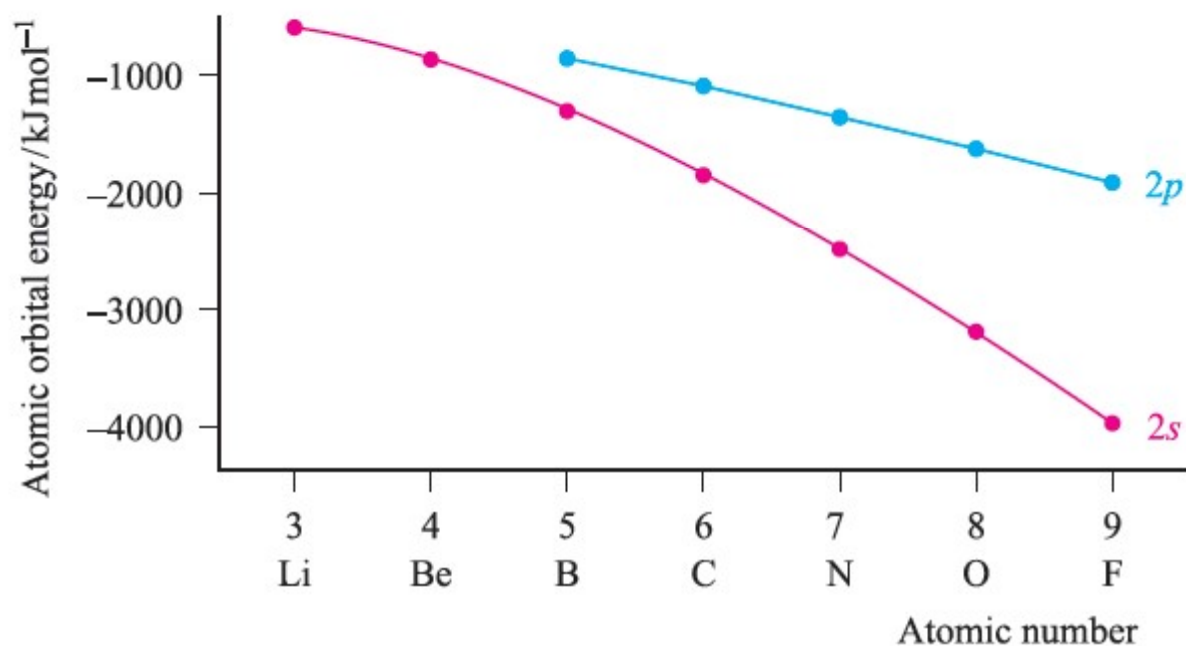
Molecular Orbital (MO) Theory

Homonuclear diatomic molecules



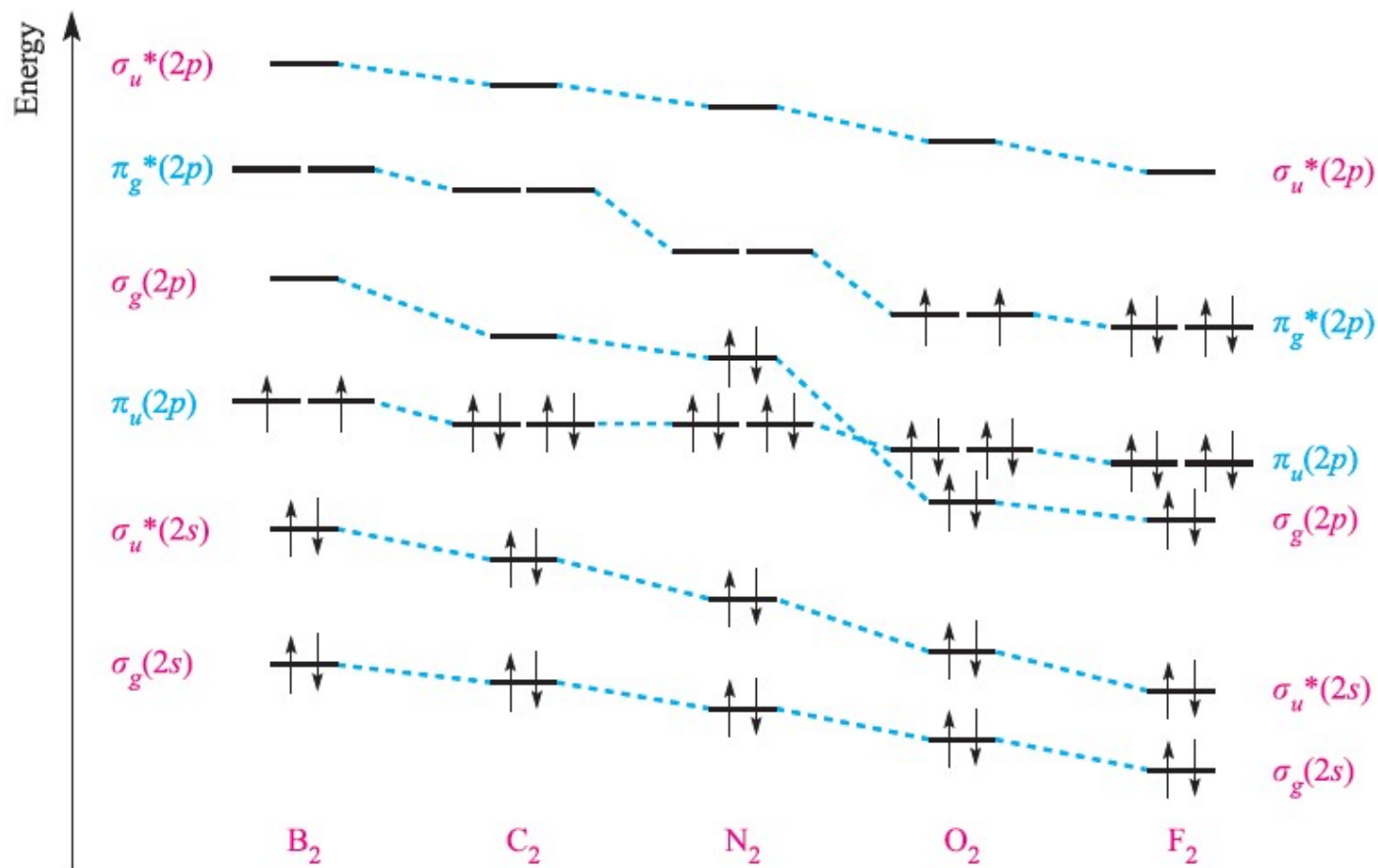
Molecular Orbital (MO) Theory

Homonuclear diatomic molecules



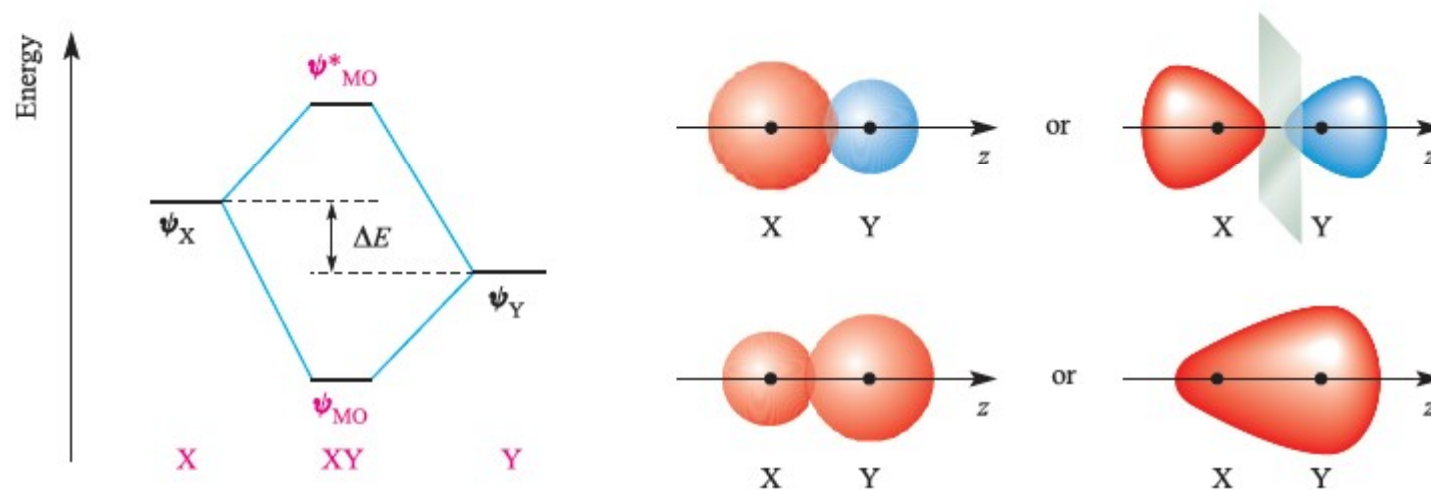
Relative energies of the 2s and 2p atomic orbitals

Molecular Orbital (MO) Theory

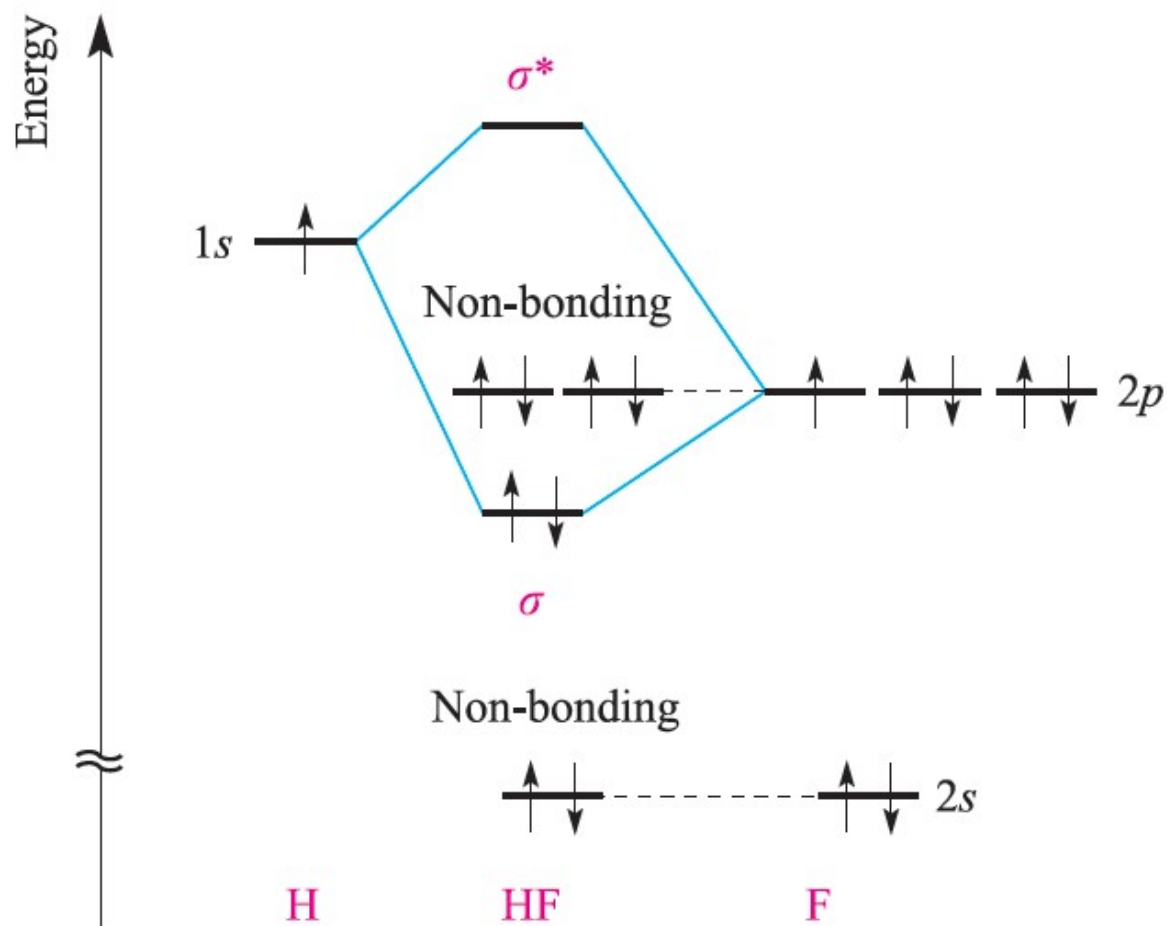


homonuclear diatomic molecules involving first-row p-block elements

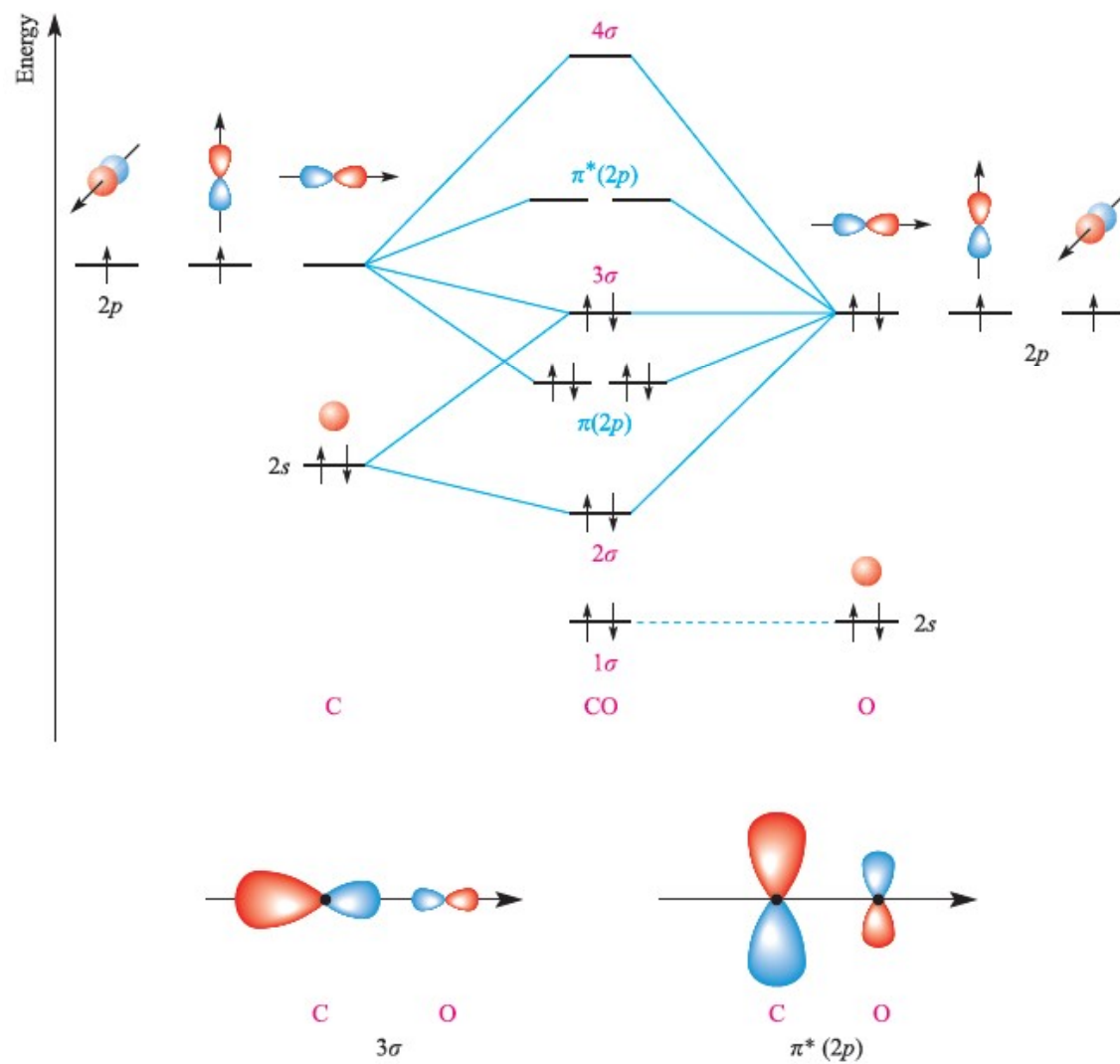
MO theory: heteronuclear diatomic molecules



MO theory: heteronuclear diatomic molecules

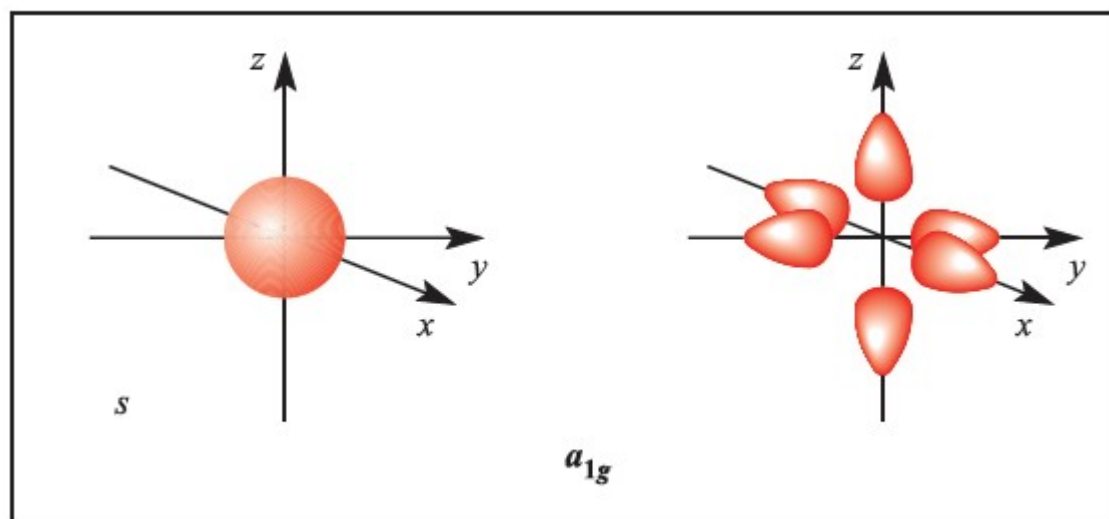


MO theory: heteronuclear diatomic molecules



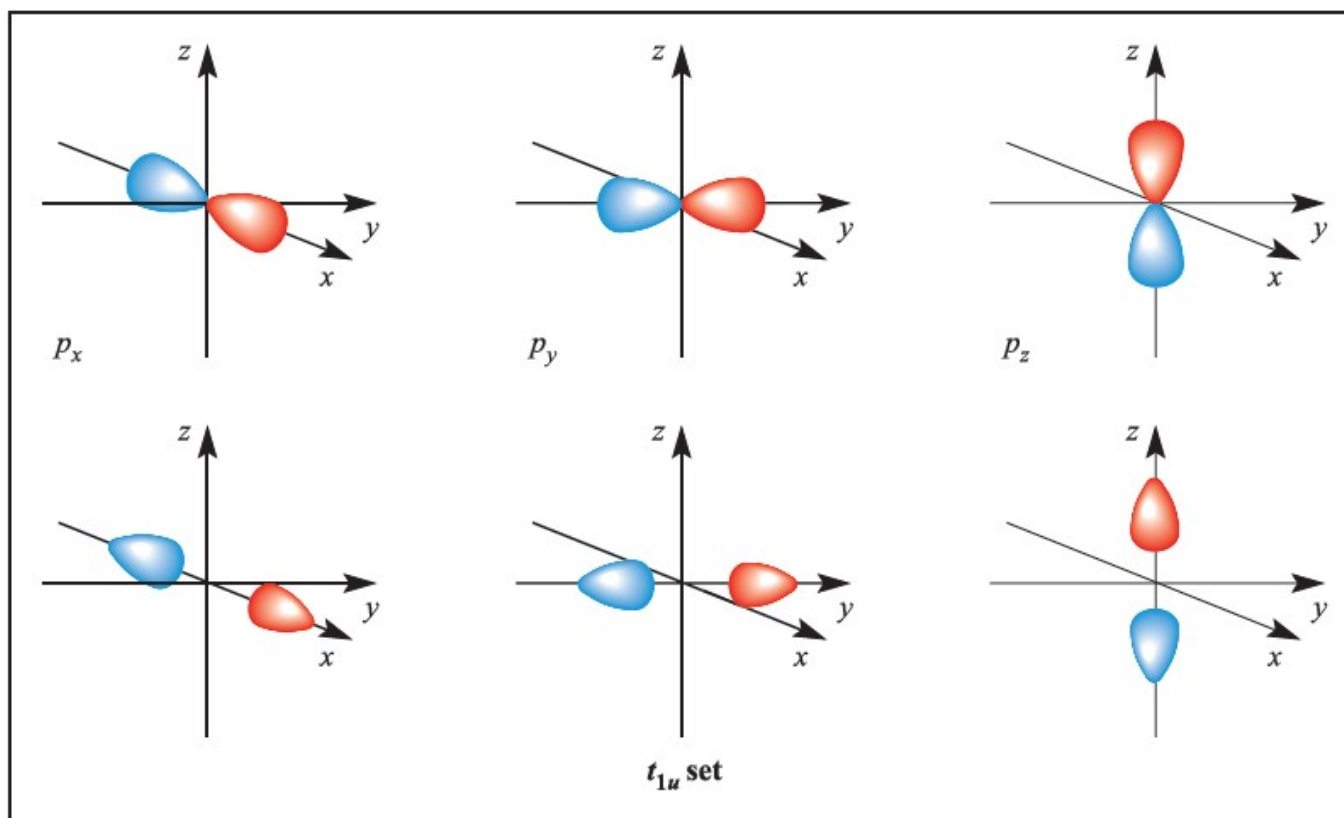
MO diagram : $O_h [ML_6]^{n+}$

- For a first row metal, the valence shell atomic orbitals are 3d, 4s and 4p



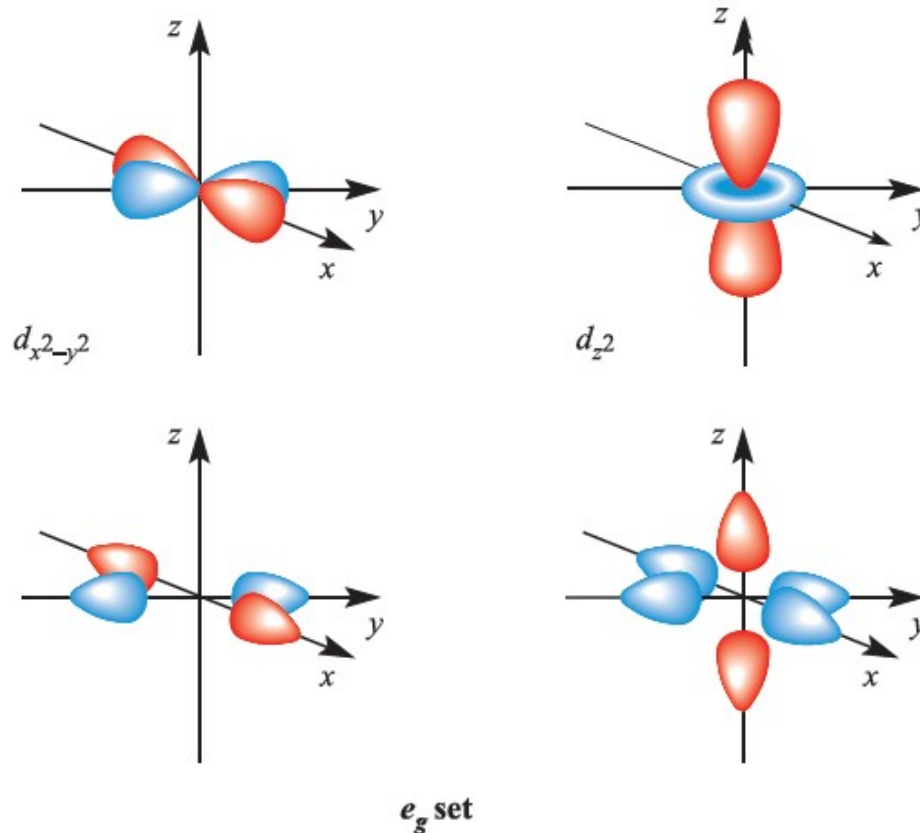
MO diagram : $O_h [ML_6]^{n+}$

- For a first row metal, the valence shell atomic orbitals are 3d, 4s and 4p

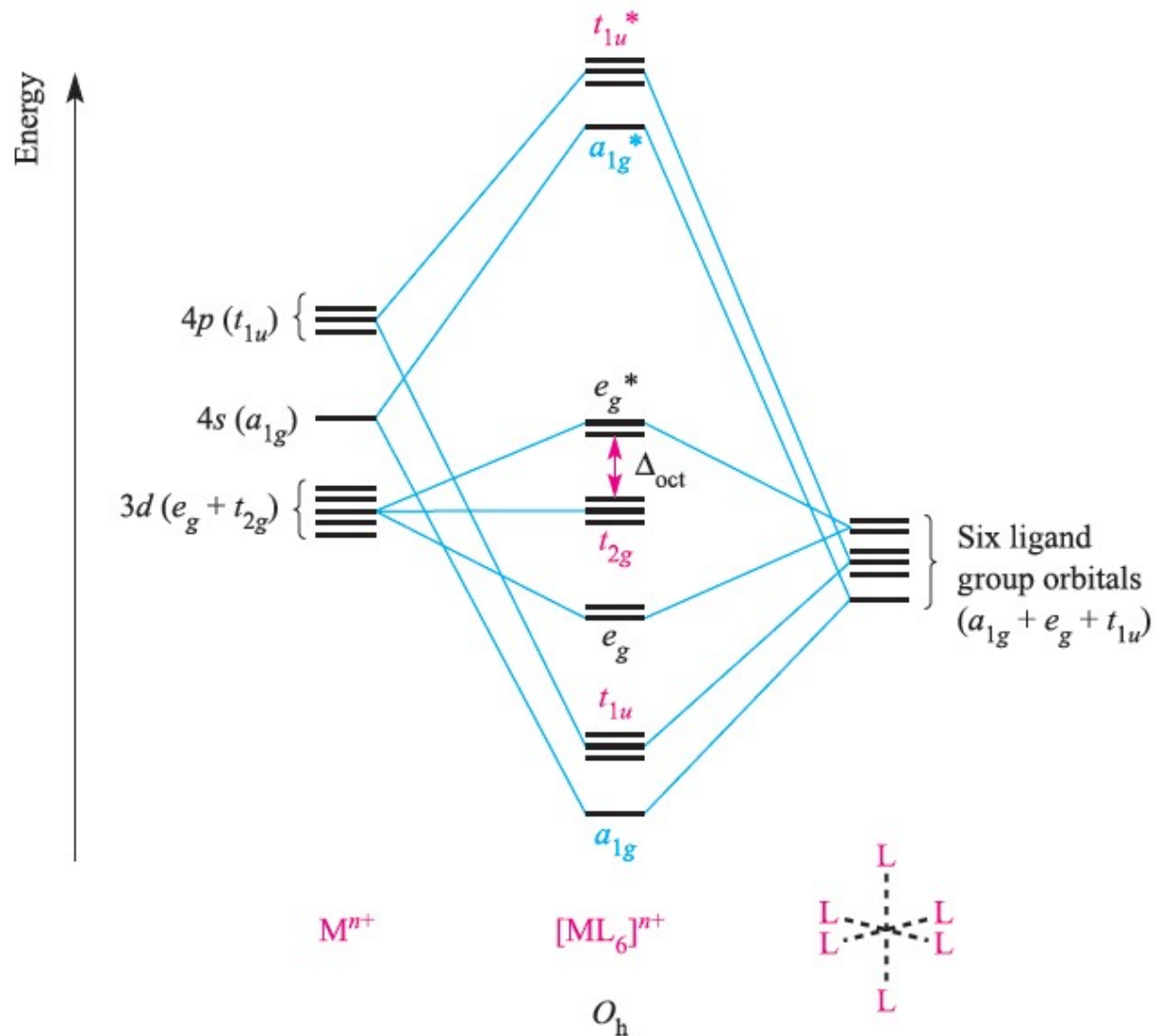


MO diagram : $O_h [ML_6]^{n+}$

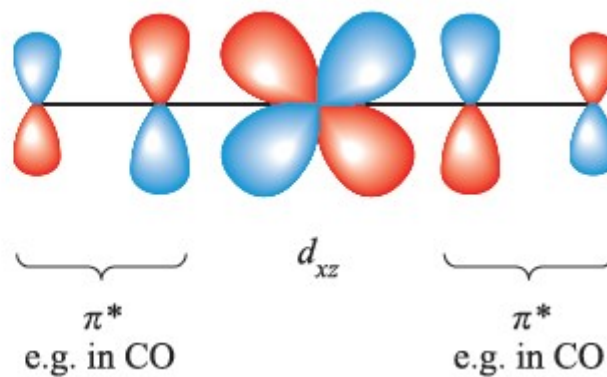
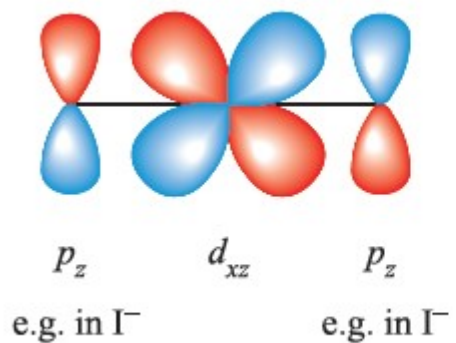
- For a first row metal, the valence shell atomic orbitals are 3d, 4s and 4p



MO diagram: $O_h [ML_6]^{n+}$ no metal-ligand π bonding

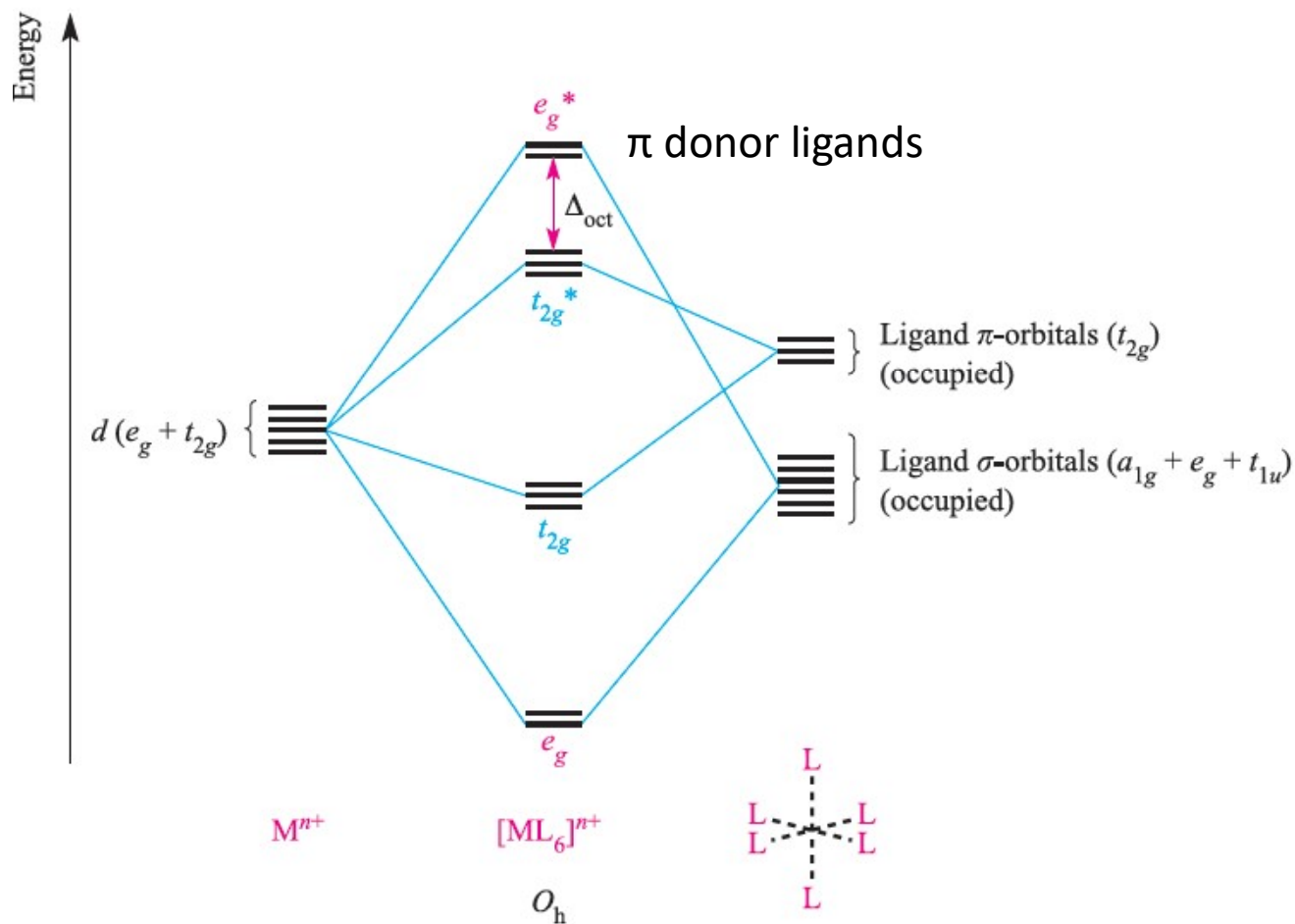


With π donor/acceptor ligands:



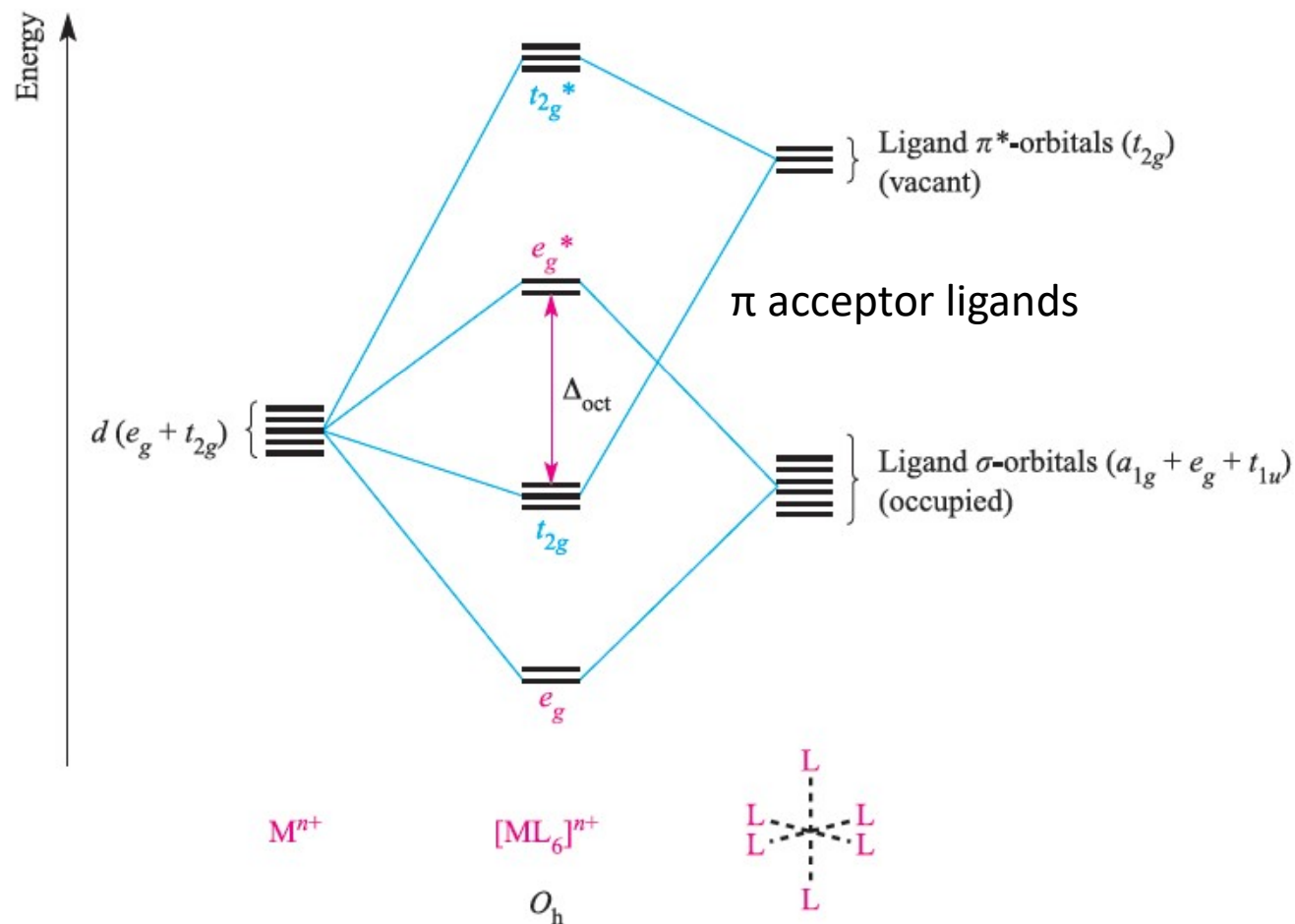
With π donor ligands:

Halide ions

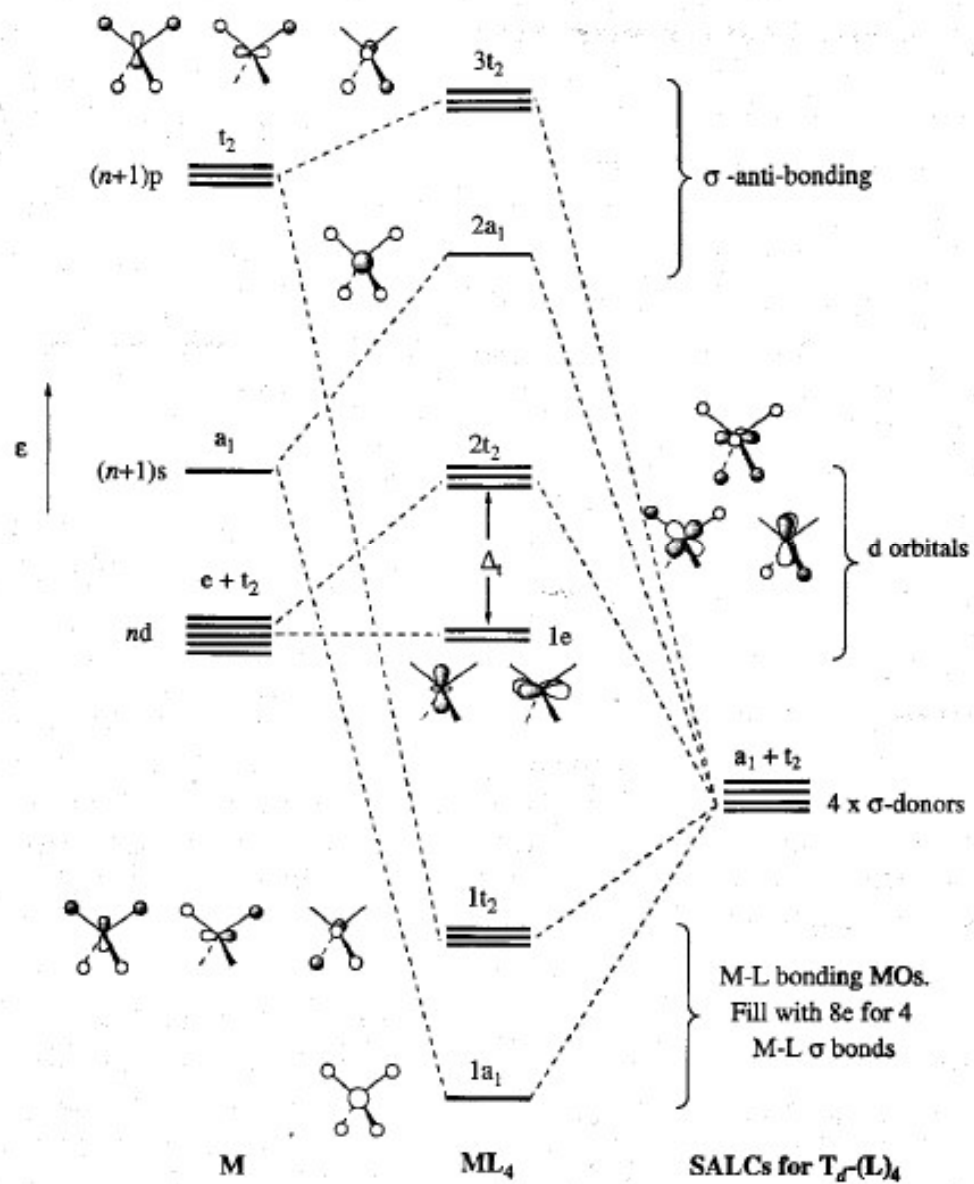


With π acceptor ligands

CO, NO

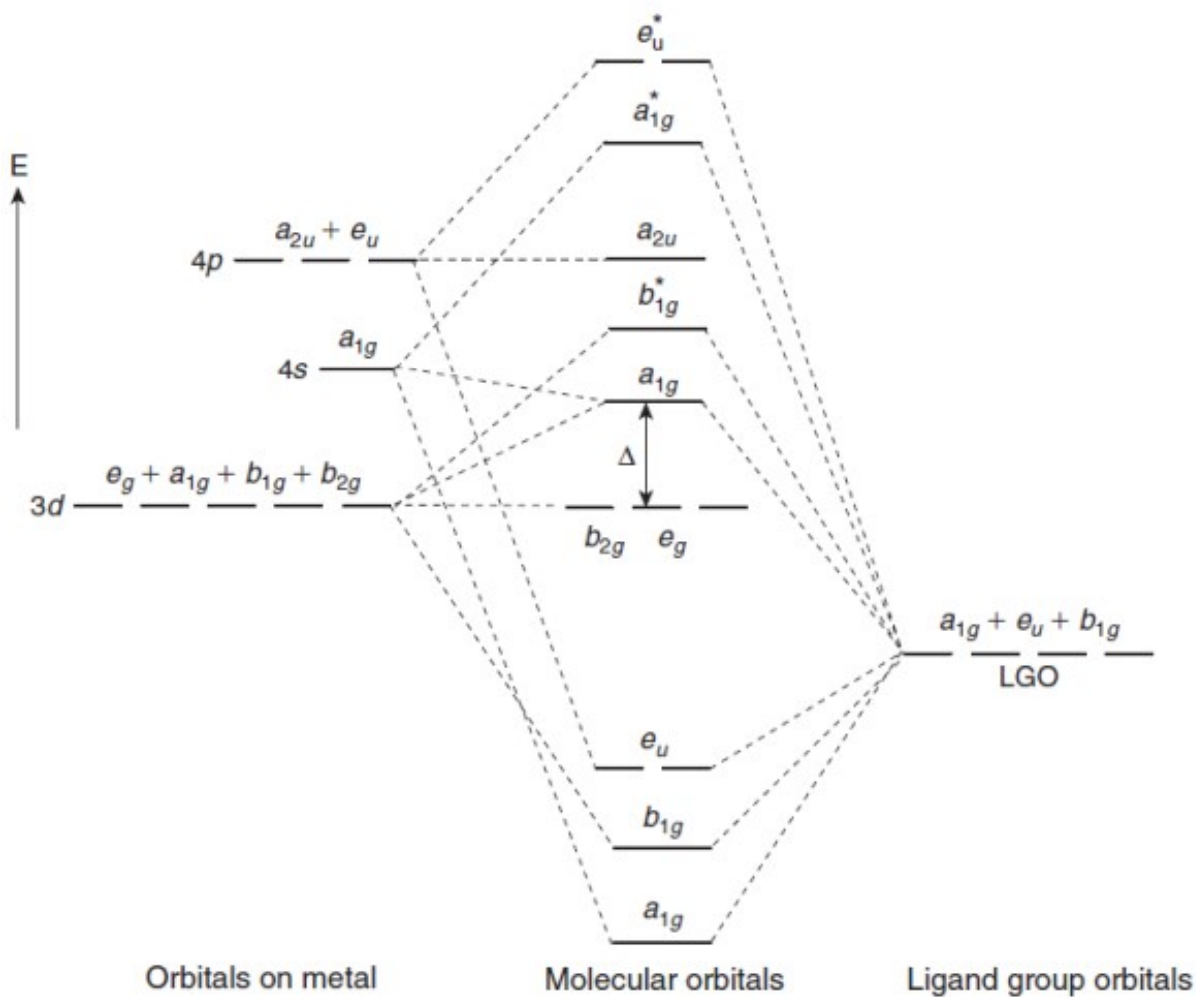


MO diagram: $T_d [ML_4]^{n+}$



Square Planar MO diagram: $[\text{ML}_5]^{n+}$

$b_{1g} (d_{x^2-y^2})$, $b_{2g} (d_{xy})$, $a_{1g} (d_{z^2})$, and $e_g (d_{xz} \text{ and } d_{yz})$



Molecular Orbital Theory (MOT)

- Δ_{oct} decreases in going from a σ -complex to one containing π -donor ligands;
- Δ_{oct} values are relatively large for complexes containing π -acceptor ligands, and such complexes are likely to be low-spin;
- for a complex with π -acceptor ligands, increased π -acceptance stabilizes the t_{2g} level, increasing Δ_{oct} .