

Molecular Orbital Theory (MOT)

Ψ – represents an atomic or molecular orbital wavefunction

N- normalization constant

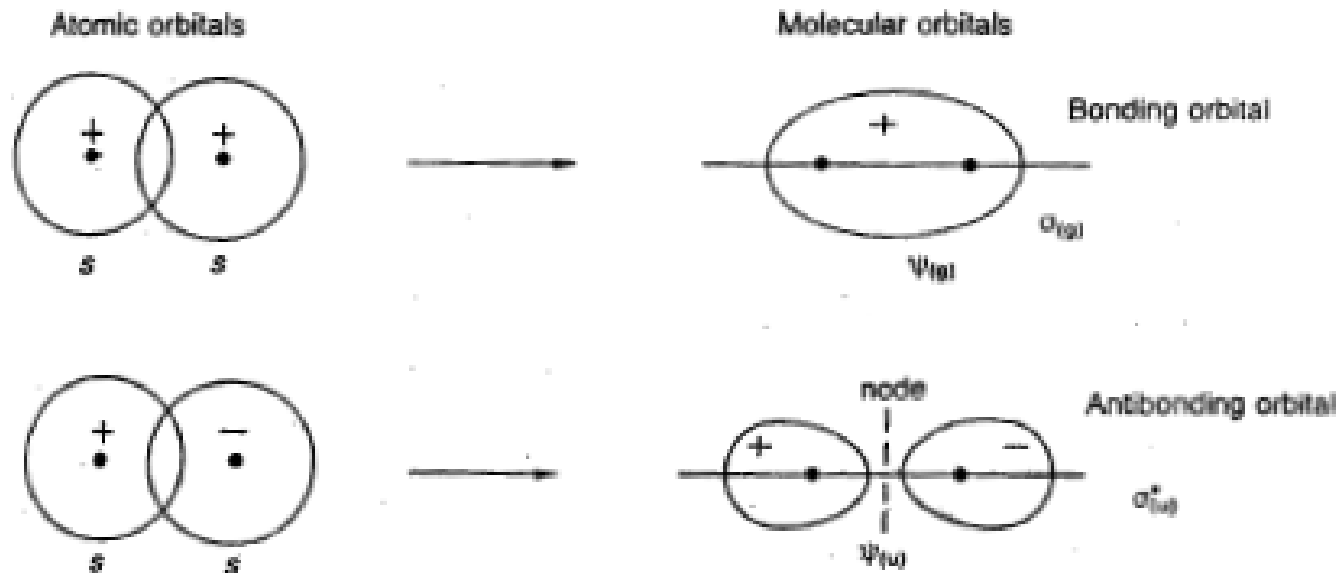
c – coefficient of wavefunction

$$\Psi_{(AB)} = (c_1\Psi_{(A)} + c_2\Psi_{(B)})$$

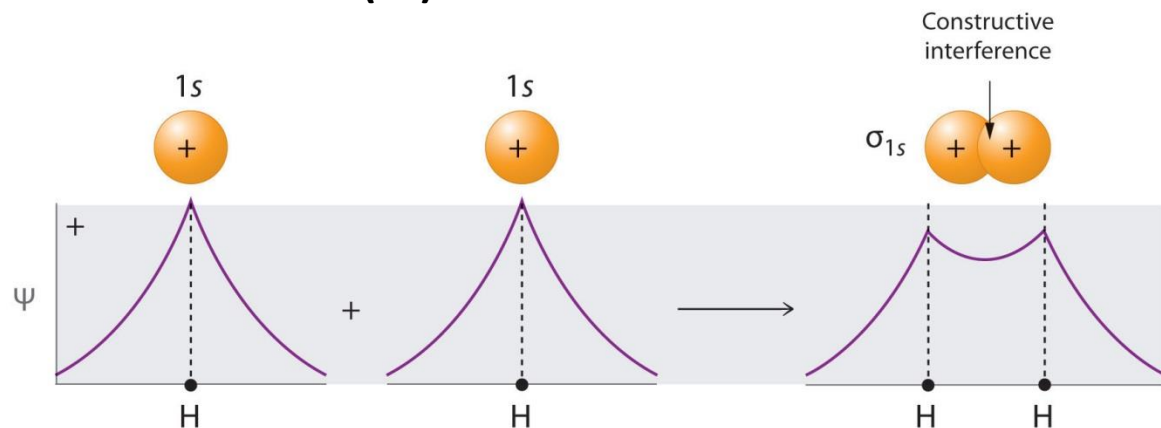
$$\Psi_{(AB)}^2 = (c_1^2\Psi_{(A)}^2 + 2c_1c_2\Psi_{(A)}\Psi_{(B)} + c_2^2\Psi_{(B)}^2)$$

Overlap of atomic orbitals

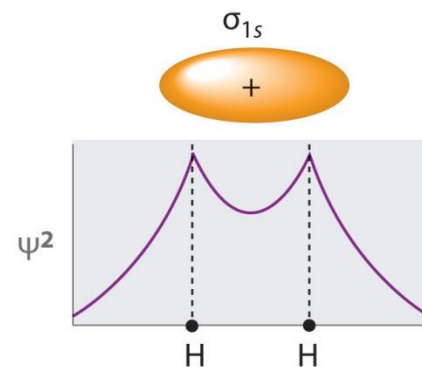
s-s overlap



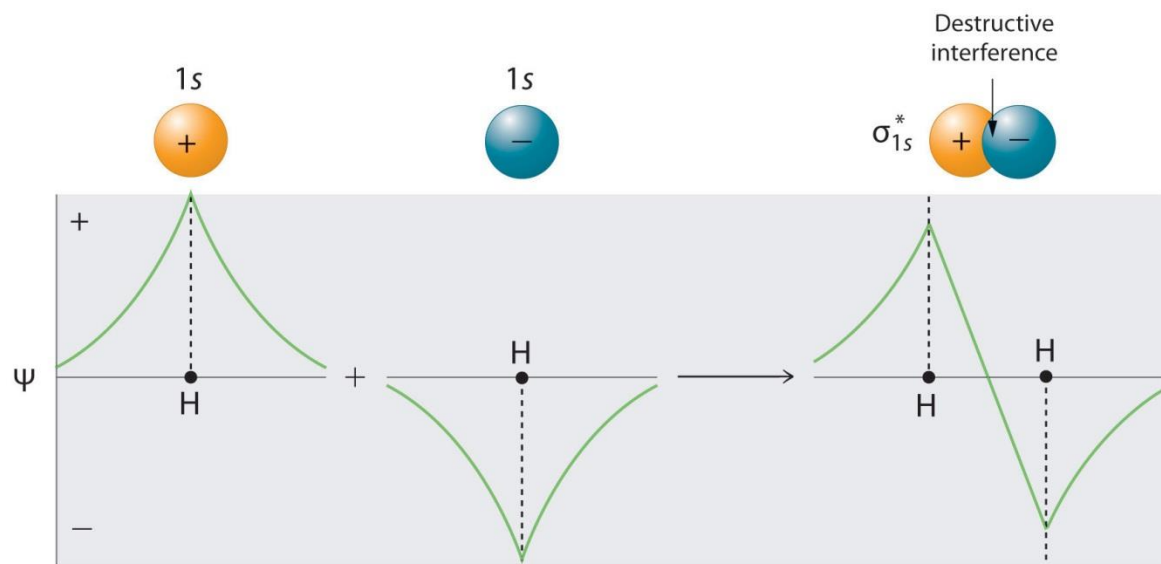
View of overlap of the wavefunctions of the valence AO (1s)



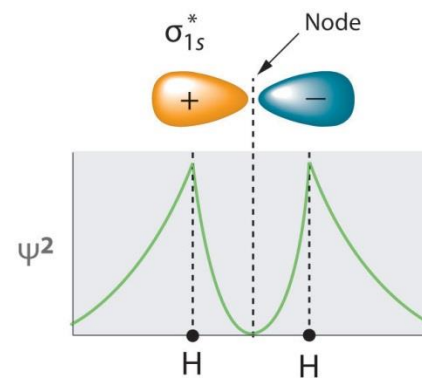
(a) Wave functions combined for σ_{1s}



(b) Bonding probability density

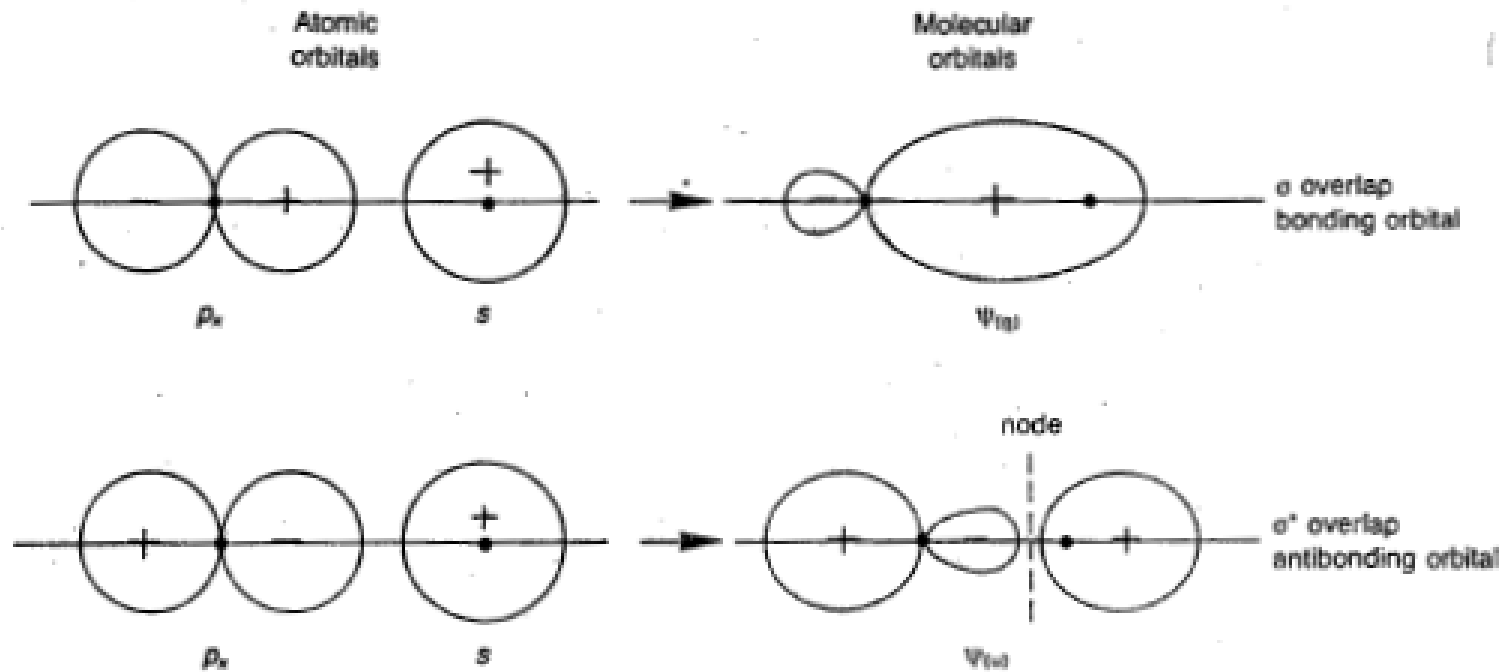


(c) Wave functions combined for σ_{1s}^*

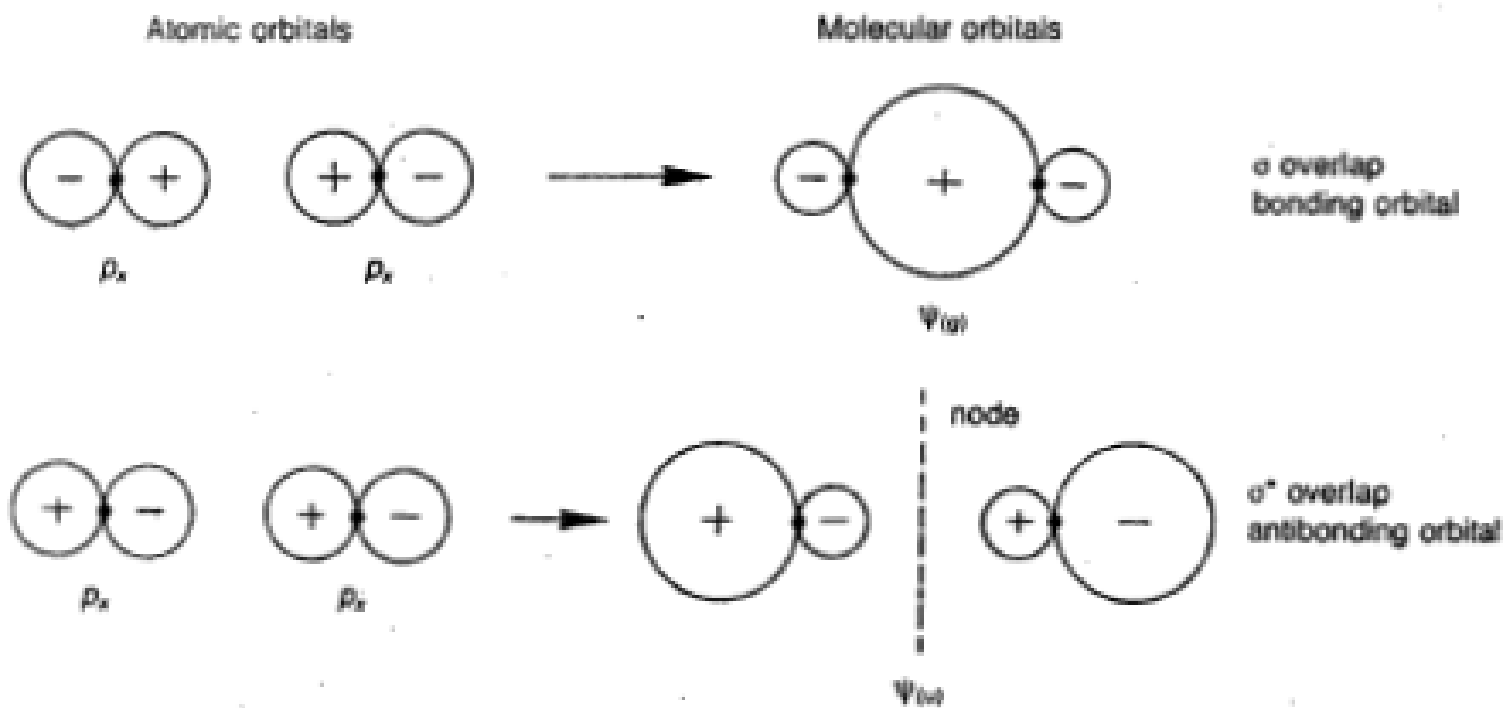


(d) Antibonding probability density

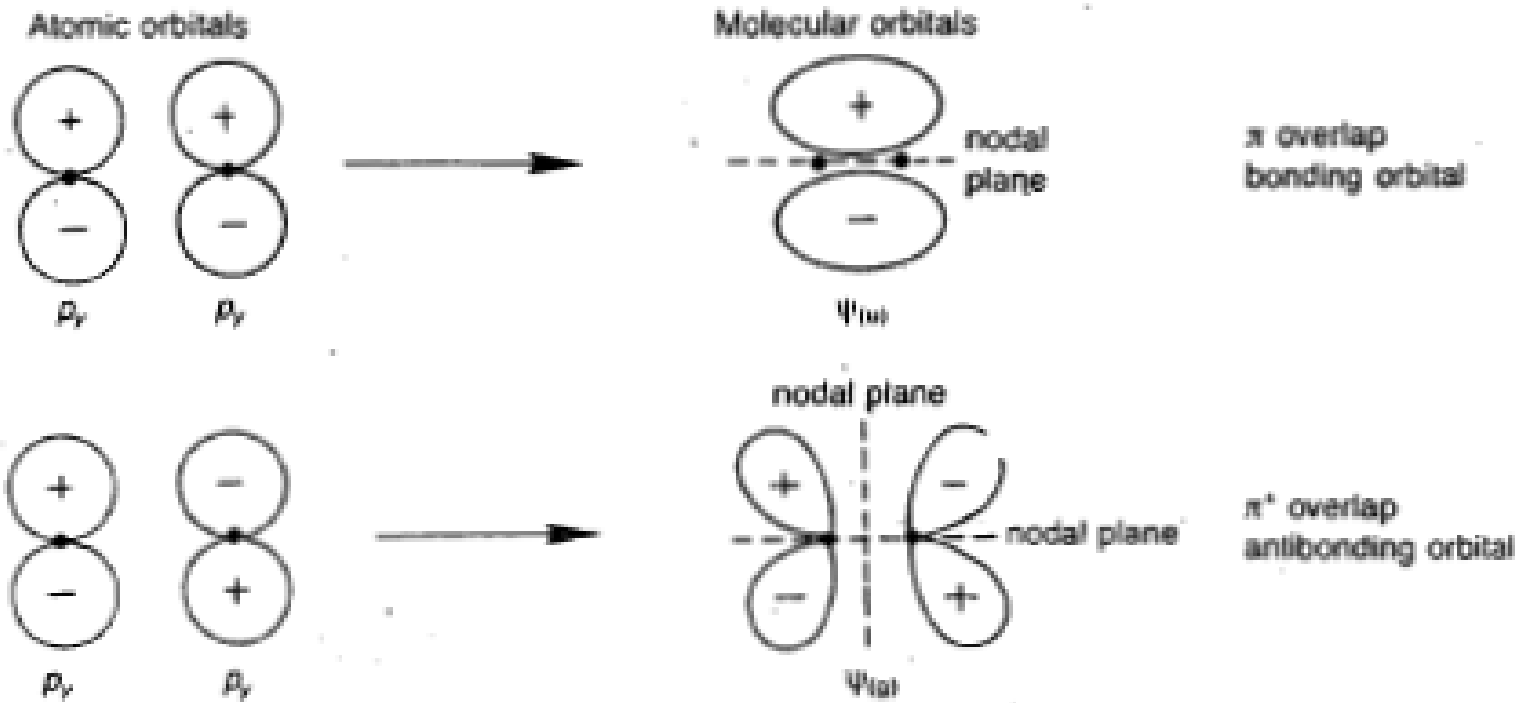
s-p mixing



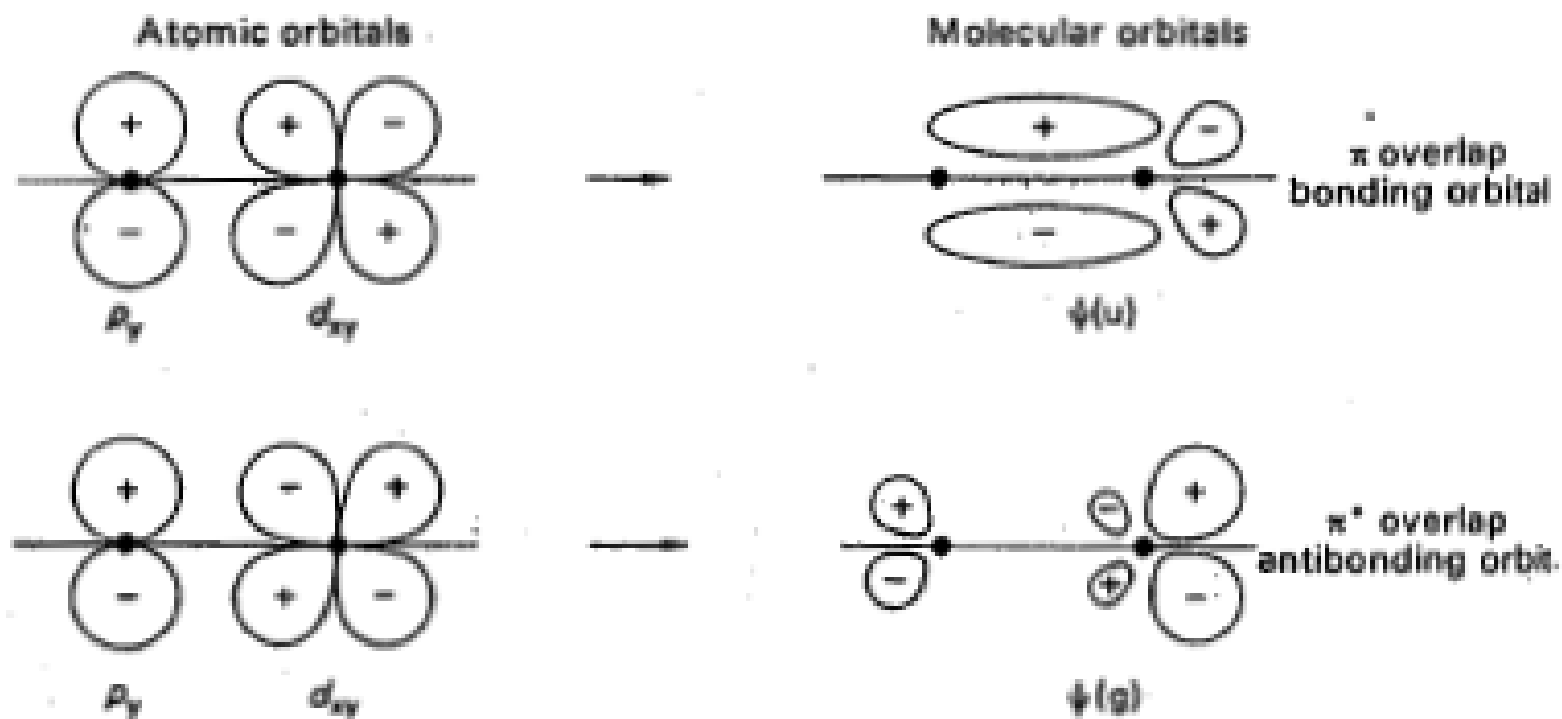
p-p head-on overlap



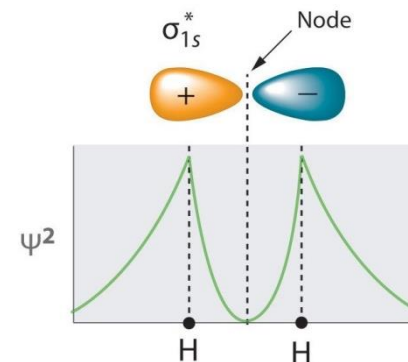
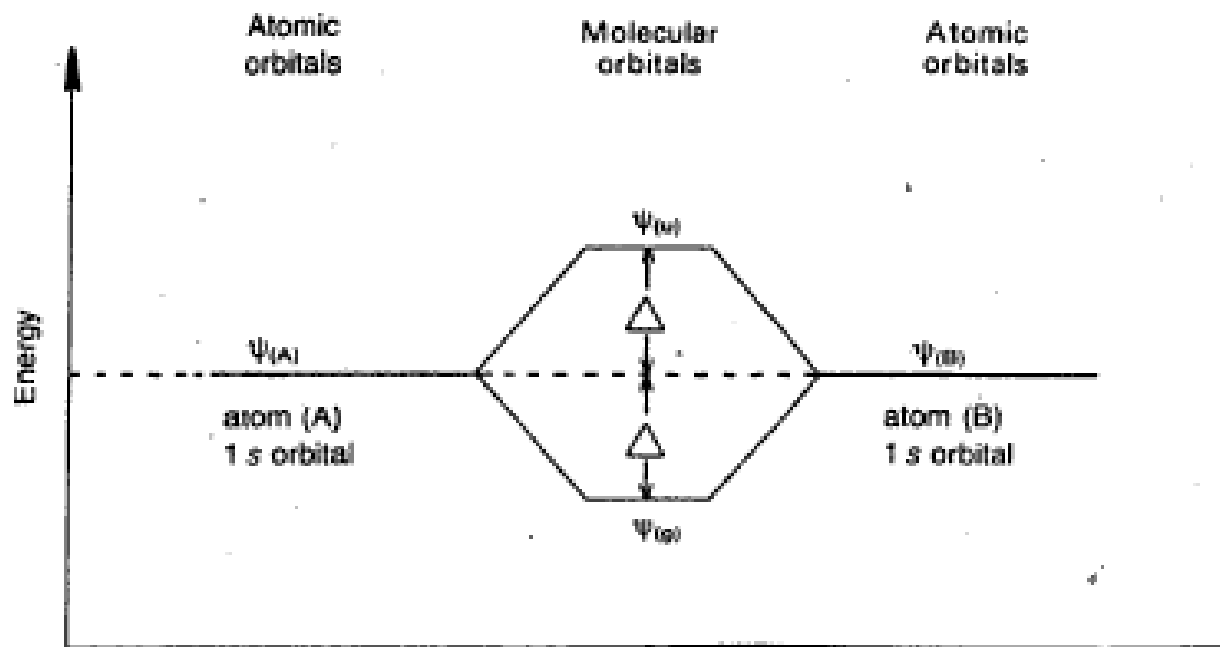
p-p lateral overlap



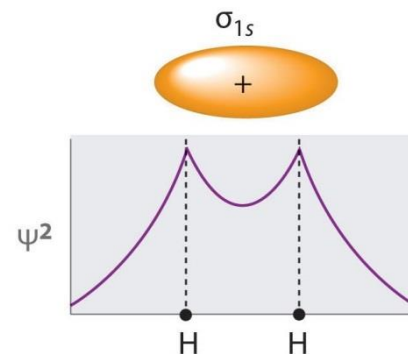
p-d mixing



S-S overlap to form BMO and ABMO

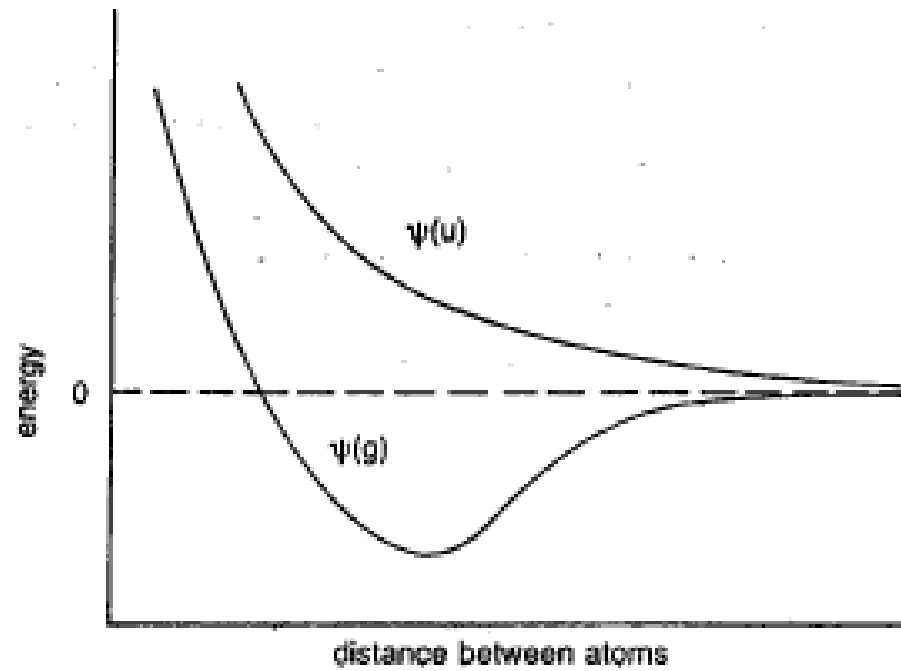


(d) Antibonding probability density

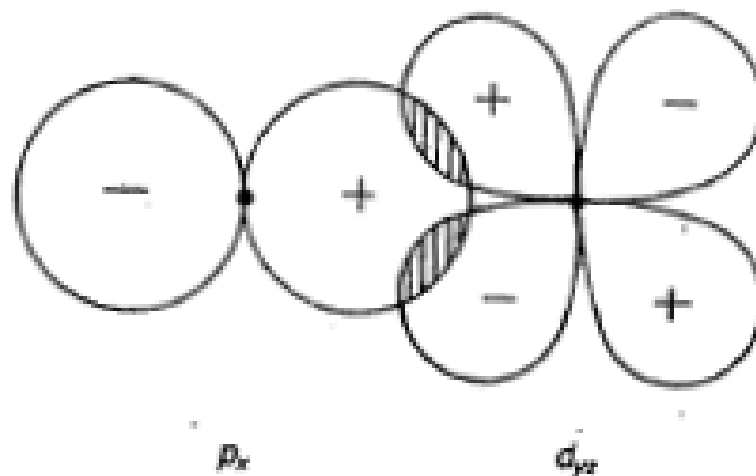
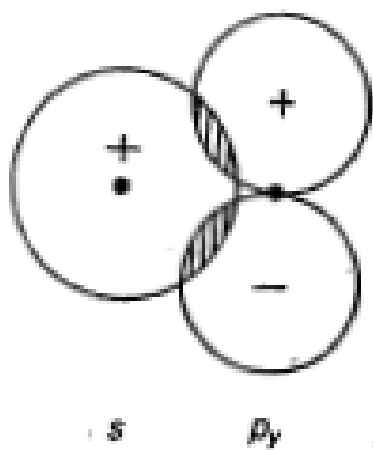


(b) Bonding probability density

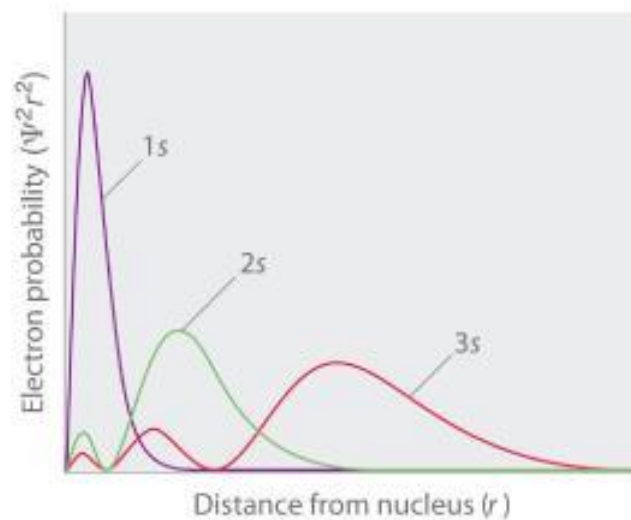
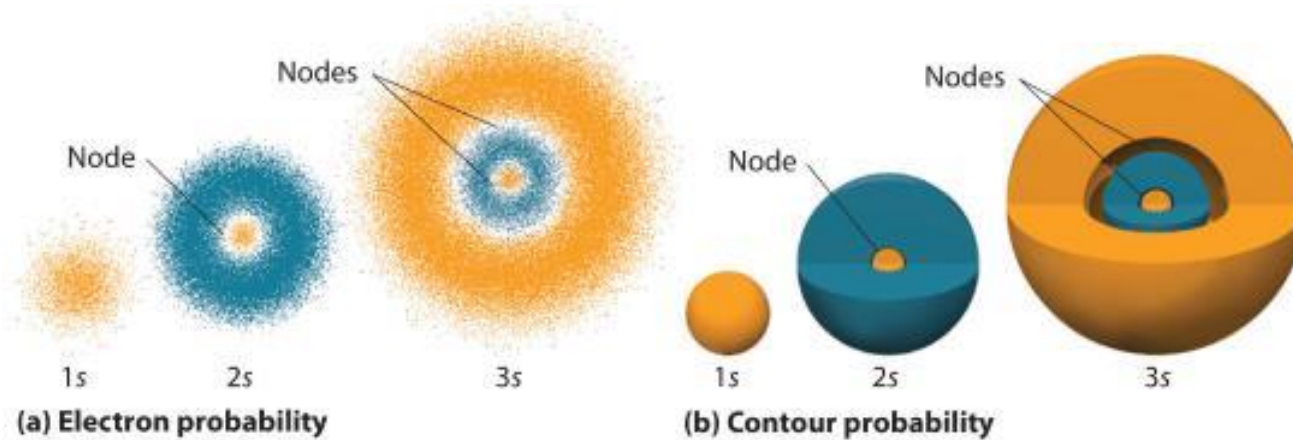
Energy profile of the BMO and ABMO



Some of the restricted (or) forbidden overlap



Radial distribution function (RDF) of 1s, 2s and 3s electrons

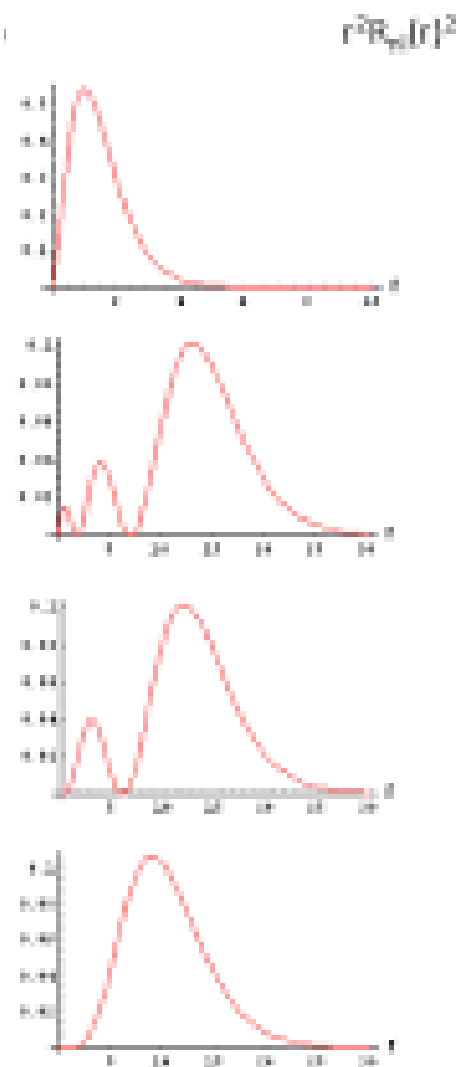
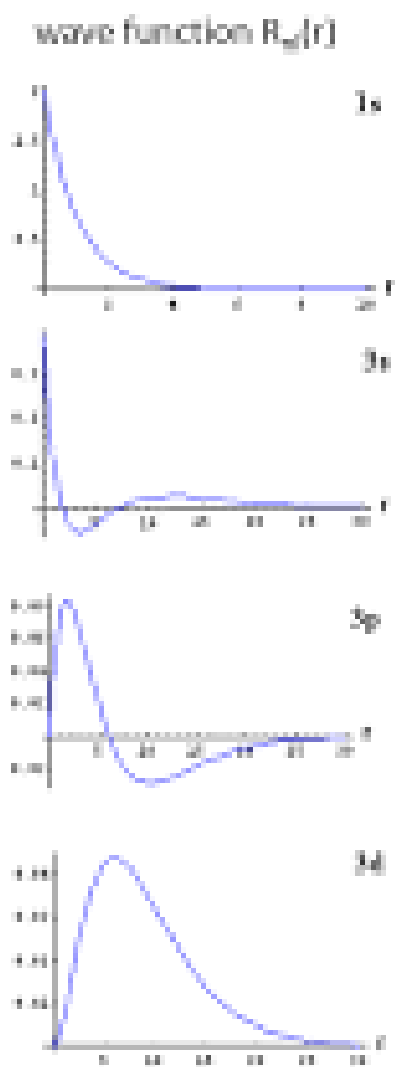


(c) Radial probability

Wave functions of 1s, 3s, 3p and 3d orbitals or electrons

RDF

Radial Nodes



nodes = $n - l - 1$

nodes = 0

nodes = 2

nodes = 1

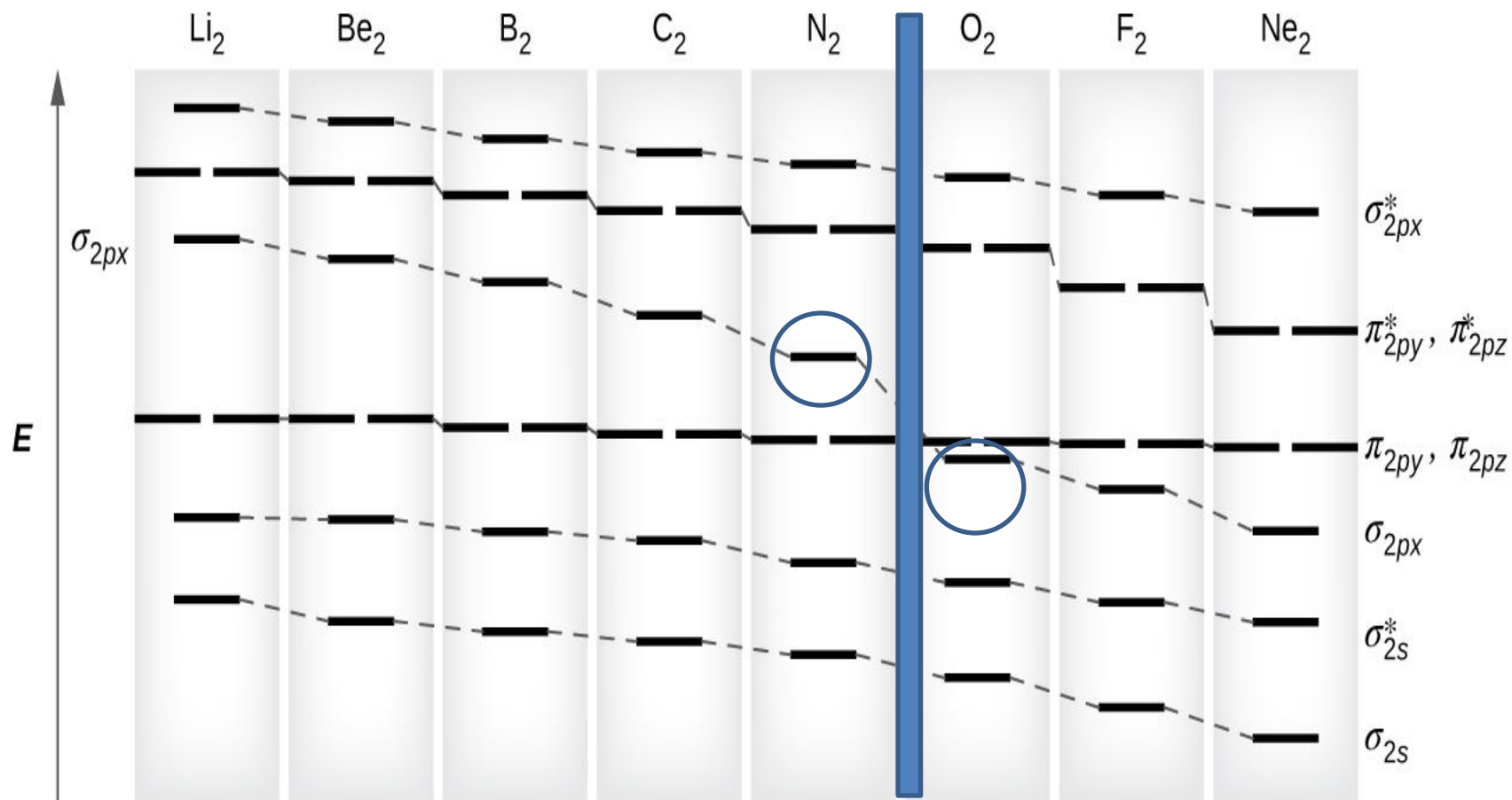
nodes = 0

Construction of MO

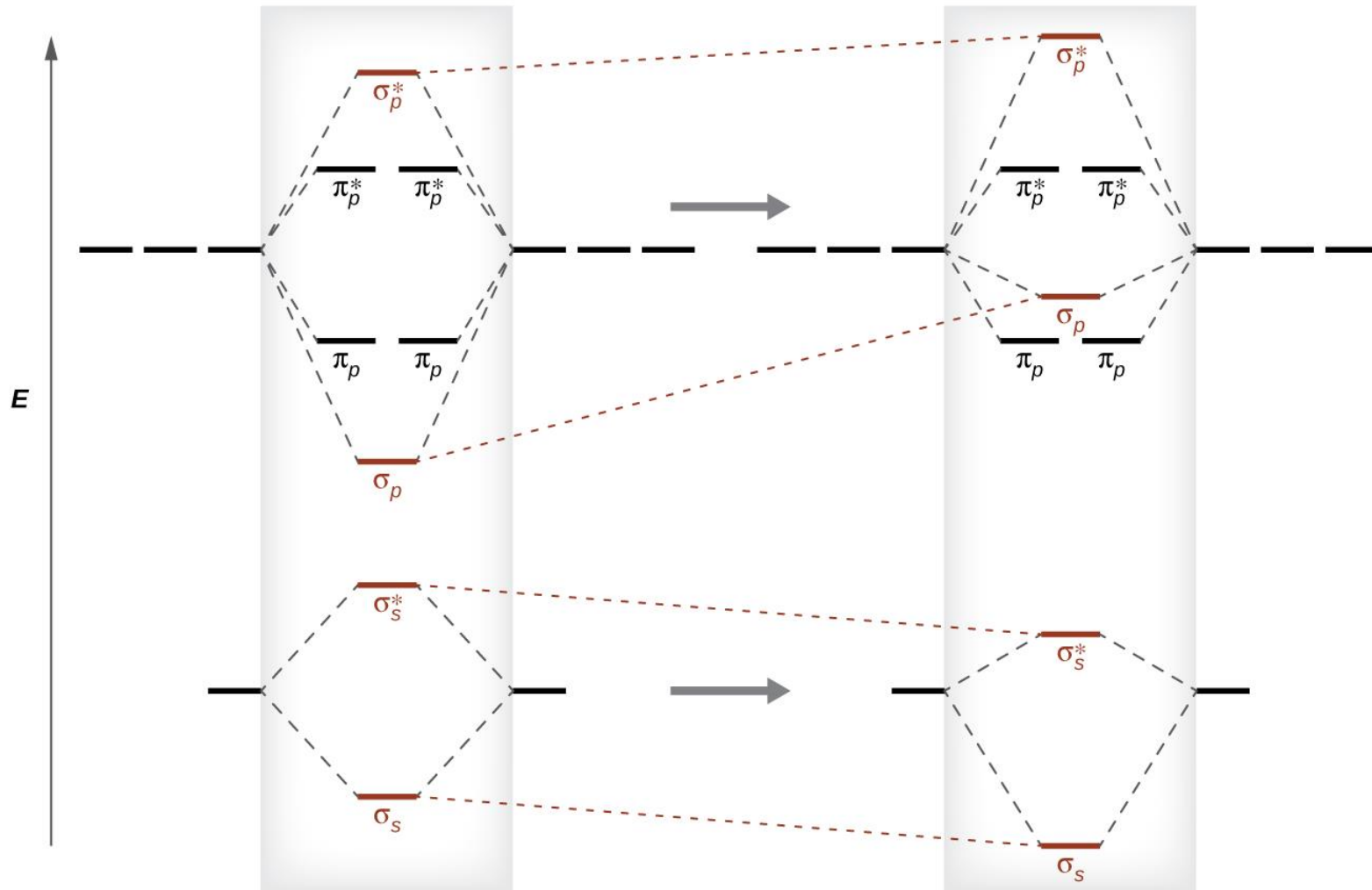
No. of AO combined = No. of MO formed

The MO will have the AO character which is close in energy to that MO

MO of homonuclear diatomic molecules of 2nd row elements

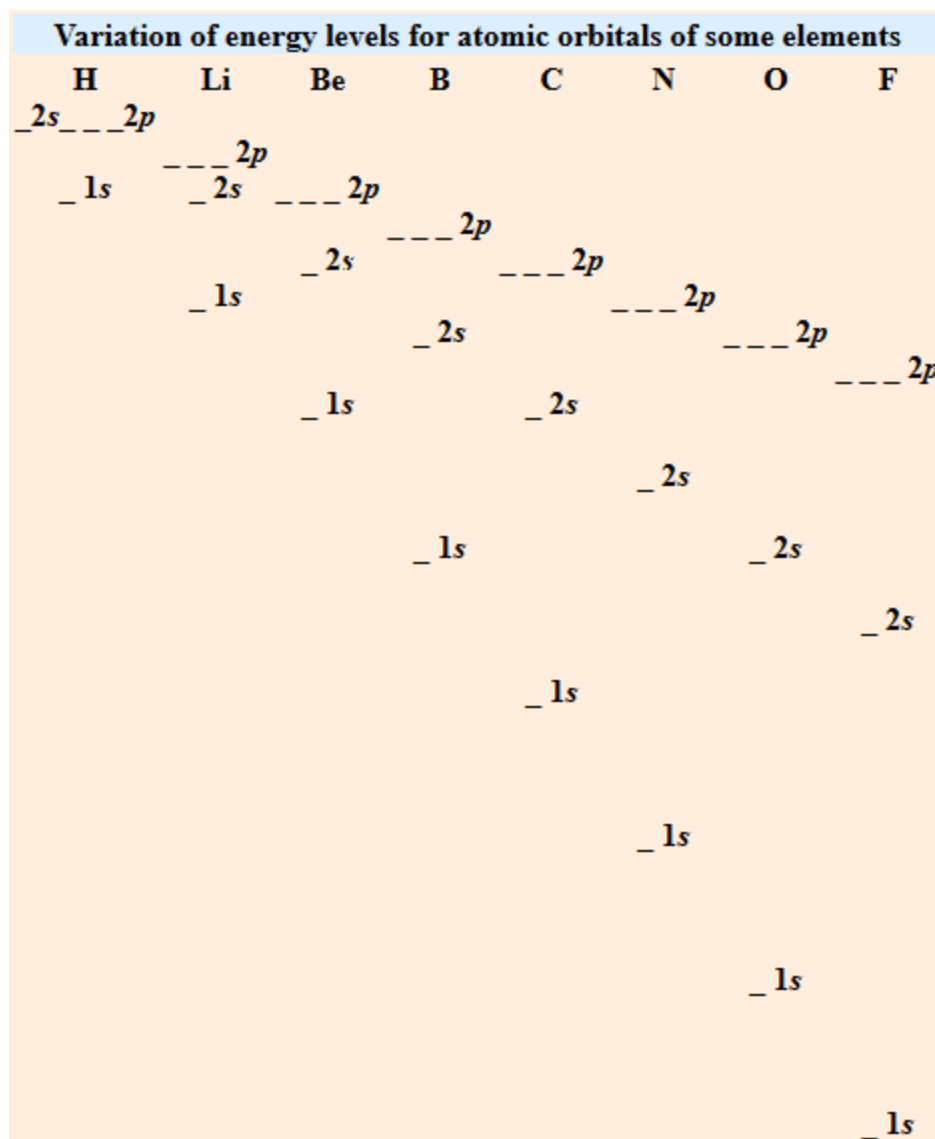


Effect of s-p mixing



2nd row elements

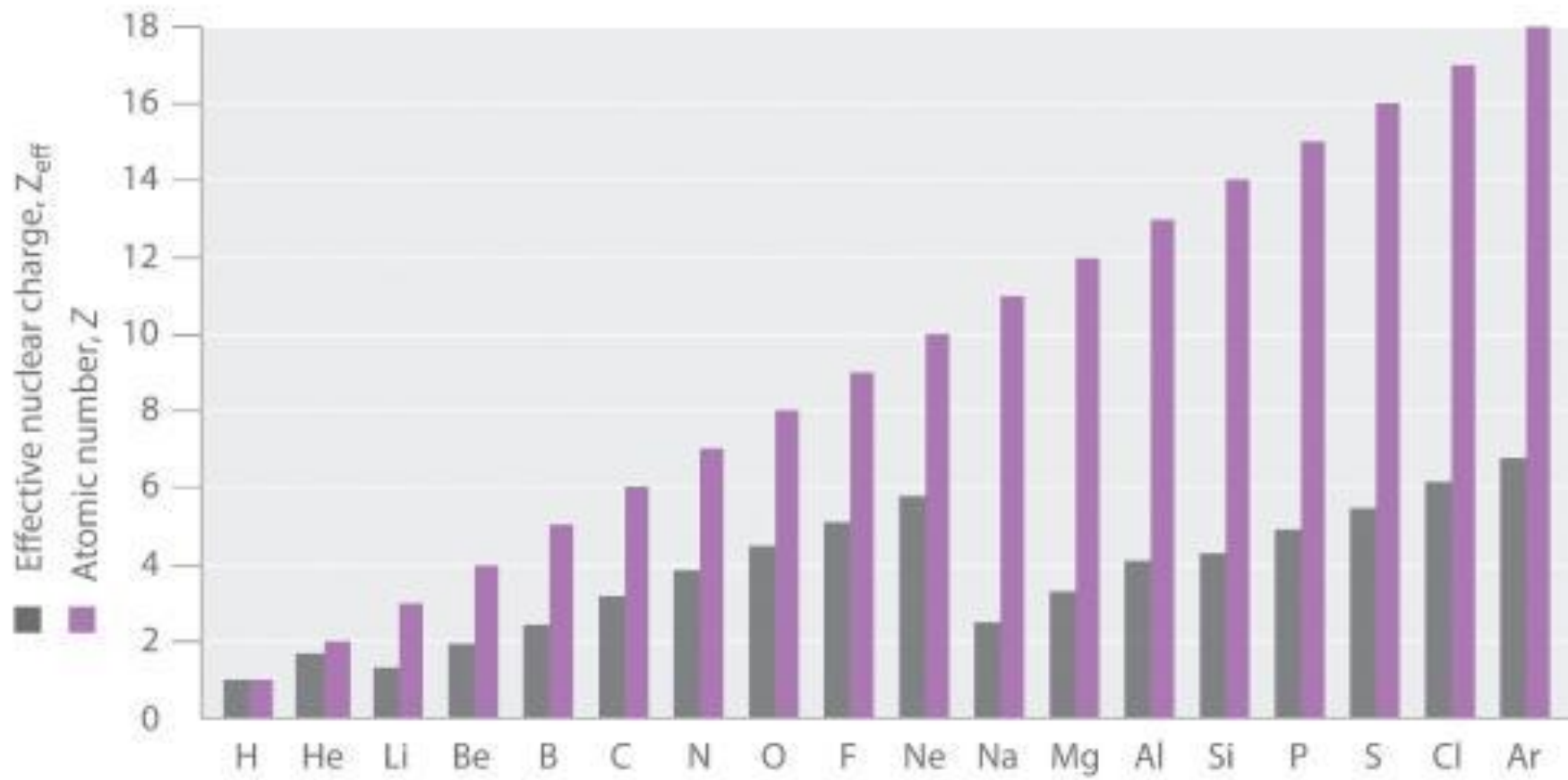
E



Atomic energy levels E in kJ mol^{-1} of second group elements

Element	E_{2s}	E_{2p}	$E_{2p}-E_{2s}$
Li	-521		
Be	-897		
B	-1350	-801	549
C	-1871	-1022	849
N	-2470	-1274	1196
O	-3116	-1524	1592
F	-3879	-1795	2084
Ne	-4680	-2084	2596

Z_{eff} of 2nd and 3rd row elements



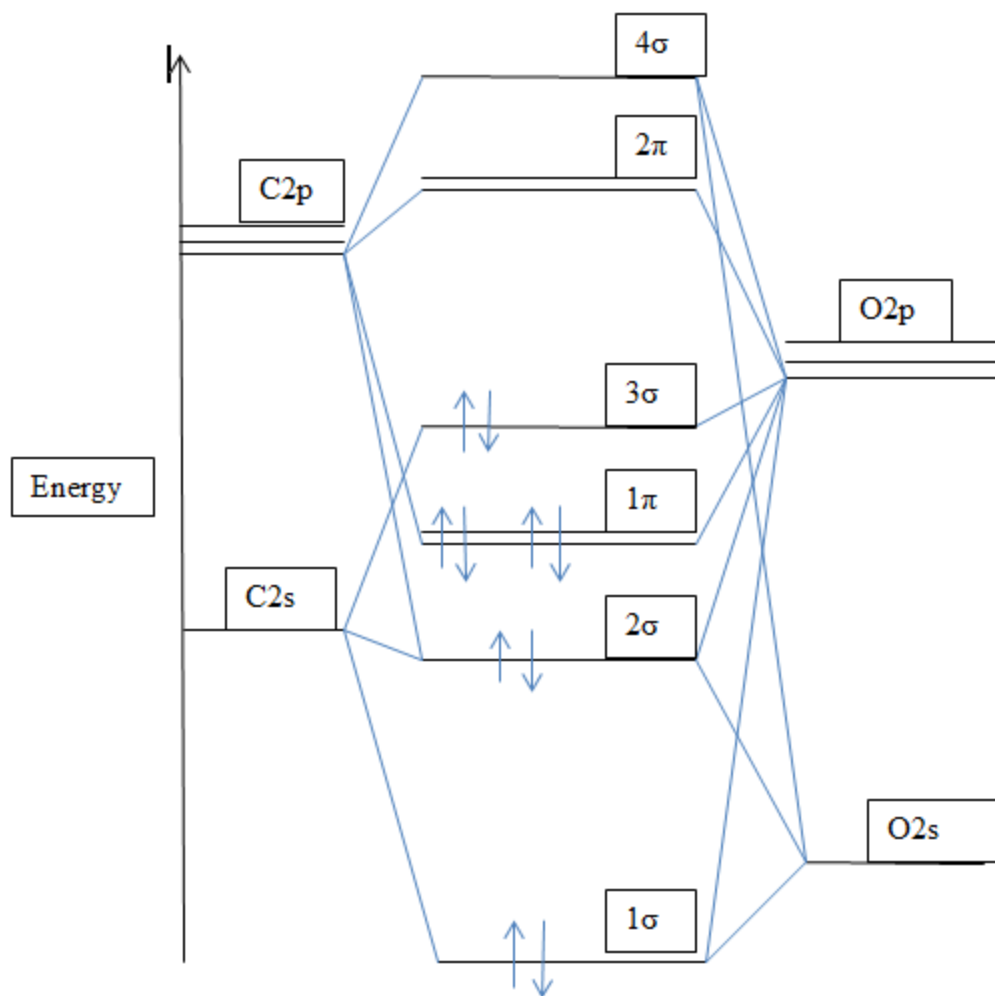
**Heteronuclear
diatomic molecules**

**CO, NO,
HF**

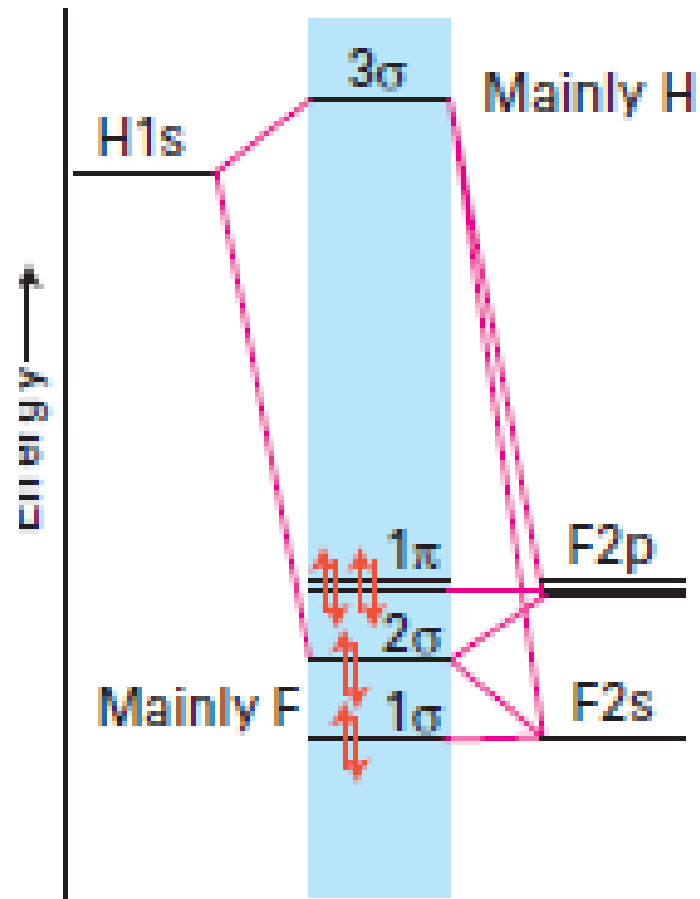
No. of AO combined = No. of MO formed

The MO will have the AO character which is
close in energy to that MO

CO



HF



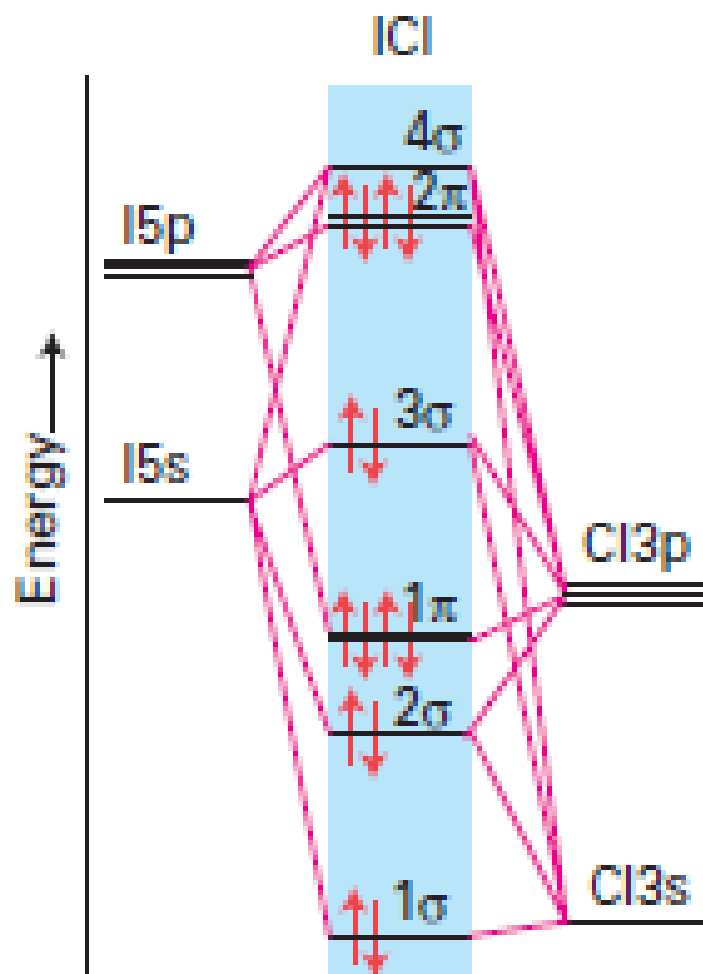


Fig. 2.24 A schematic illustration of the energies of the molecular orbitals of ICl.

Coordination Chemistry

Topics of Discussion

- Coordination number and geometry
- Isomerism in coordination complexes
- Crystal field theory (CFT) and Magnetism

Co. No. and Geometries

Table 19.4 Coordination geometries; each describes the arrangement of the donor atoms that surround the metal centre. Note that for some coordination numbers, more than one possible arrangement of donor atoms exists.

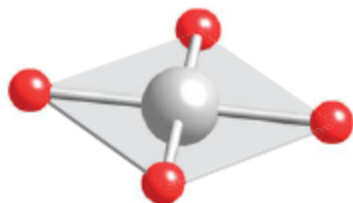
Coordination number	Arrangement of donor atoms around metal centre	Less common arrangements
2	Linear	
3	Trigonal planar	Trigonal pyramidal
4	Tetrahedral; square planar	
5	Trigonal bipyramidal; square-based pyramidal	
6	Octahedral	Trigonal prismatic
7	Pentagonal bipyramidal	Monocapped trigonal prismatic; monocapped octahedral
8	Dodecahedral; square antiprismatic; hexagonal bipyramidal	Cube; bicapped trigonal prismatic
9	Tricapped trigonal prismatic	

CO. No. 4



14 Tetrahedral complex (T_d)

$[\text{VO}_4]^{3-}$, $[\text{CrO}_4]^{2-}$, $[\text{MnO}_4]^-$, $[\text{FeCl}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$, $[\text{NiBr}_4]^{2-}$, and $[\text{CuBr}_4]^{2-}$

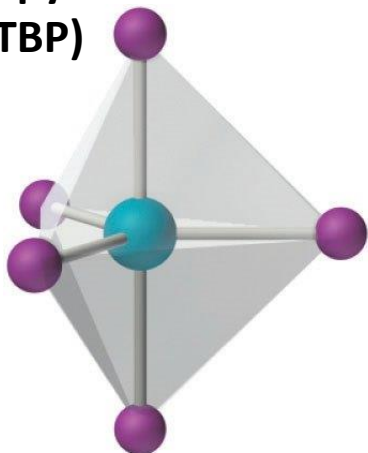


15 Square-planar complex (D_{4h})

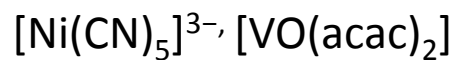
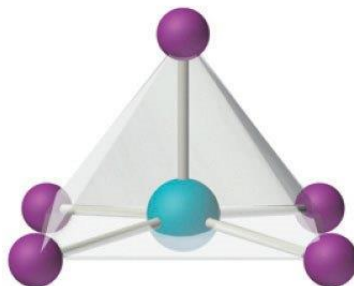
$[\text{RhCl}(\text{PPh}_3)_3]$,

$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PdCl}_4]^{2-}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$, and $[\text{AuCl}_4]^-$.

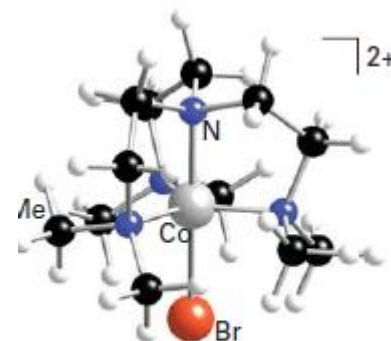
**Trigonal
Bipyramidal
(TBP)**



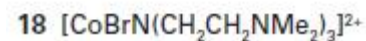
**Square
Planar (SP)**



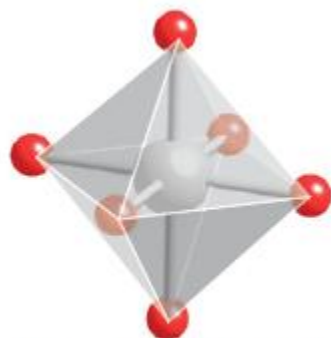
CO. No. 5



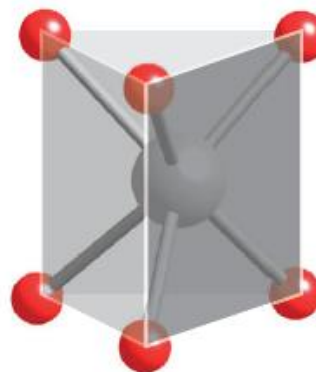
TBP



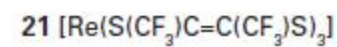
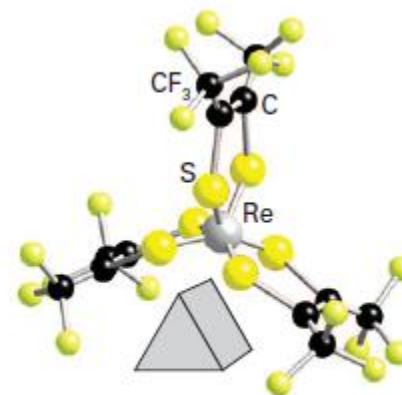
CO. No. 6



19 Octahedral complex (O_h)

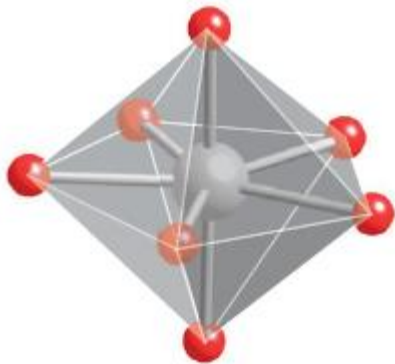


20 Trigonal prism (D_{3h})

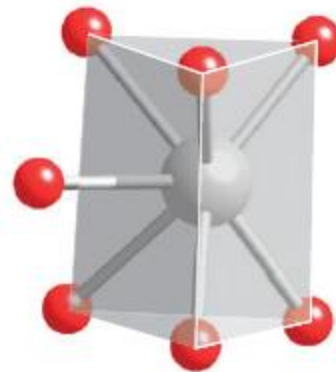


CO. No. 7

More common

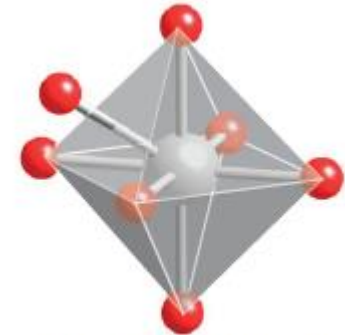


22 Pentagonal bipyramid (D_{5h})



24 Capped trigonal prism

Less common



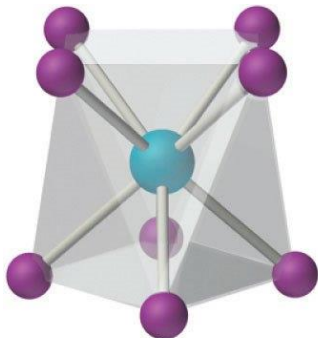
23 Capped octahedron



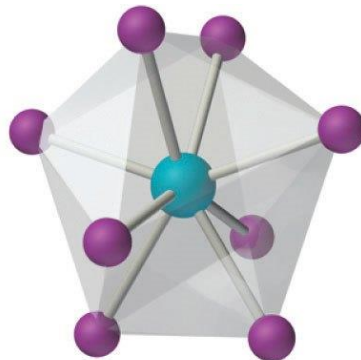
More common

CO. No. 8

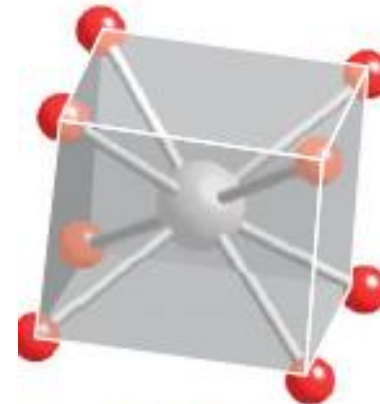
Less common



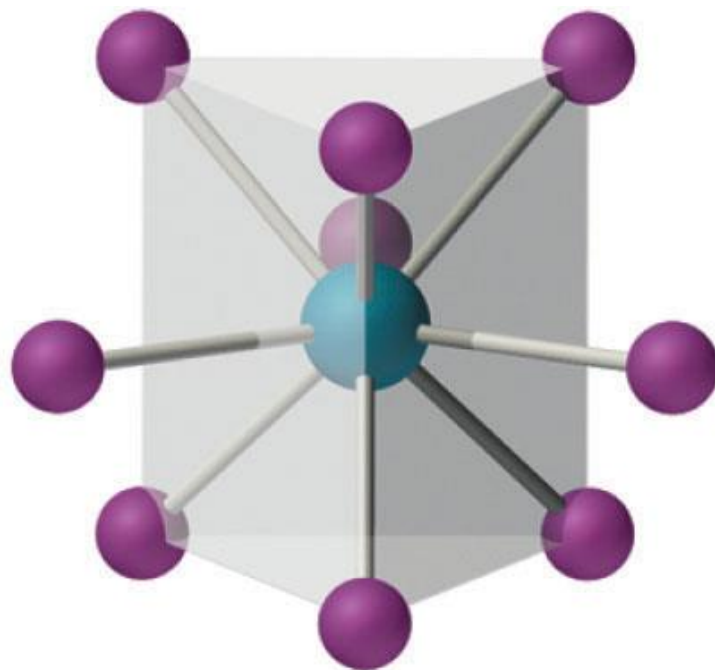
Square antiprismatic



Trigonal dodecahedral



30 Cube (O_h)



Tricapped trigonal prismatic ML_9

Isomerism in coordination complexes

```
graph TD; A[Isomerism in coordination complexes] --> B[Structural isomerism]; A --> C[Stereoisomerism]; B --> D[Ionization isomerism]; B --> E[Hydration isomerism]; B --> F[Coordination isomerism]; B --> G[Linkage isomerism]; C --> H[Diastereoisomers]; C --> I[Enantiomers];
```

Structural isomerism

Ionization isomerism
Hydration isomerism
Coordination isomerism
Linkage isomerism

Stereoisomerism

Diastereoisomers
Enantiomers

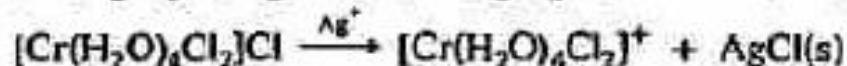
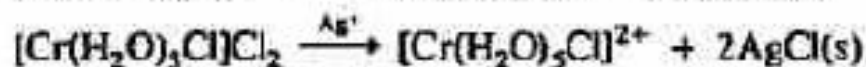
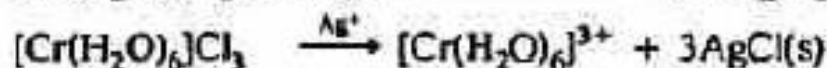
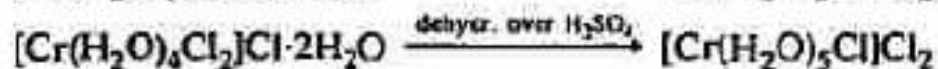
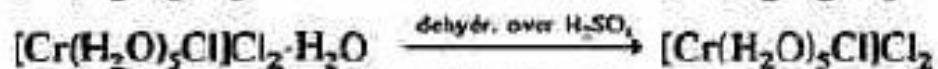
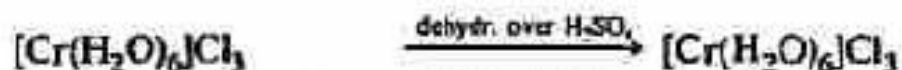
Structural isomerism in coordination complexes

Structural isomers have same molecular formula but the connectivities between the atoms in a molecule are different

Ionization isomerism



Solvate isomerism



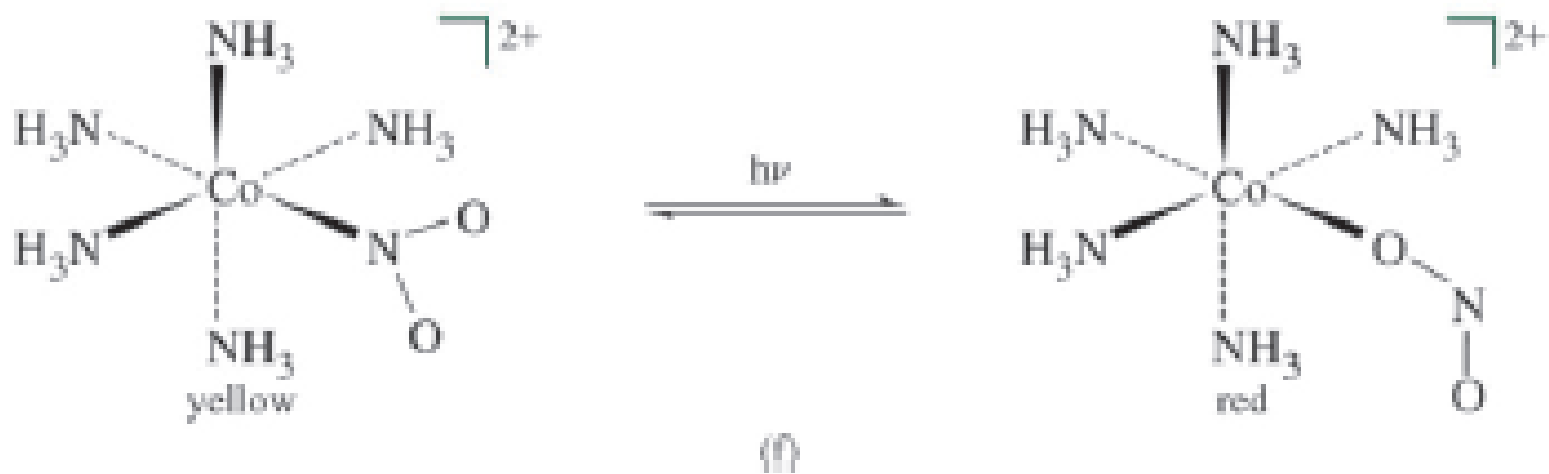
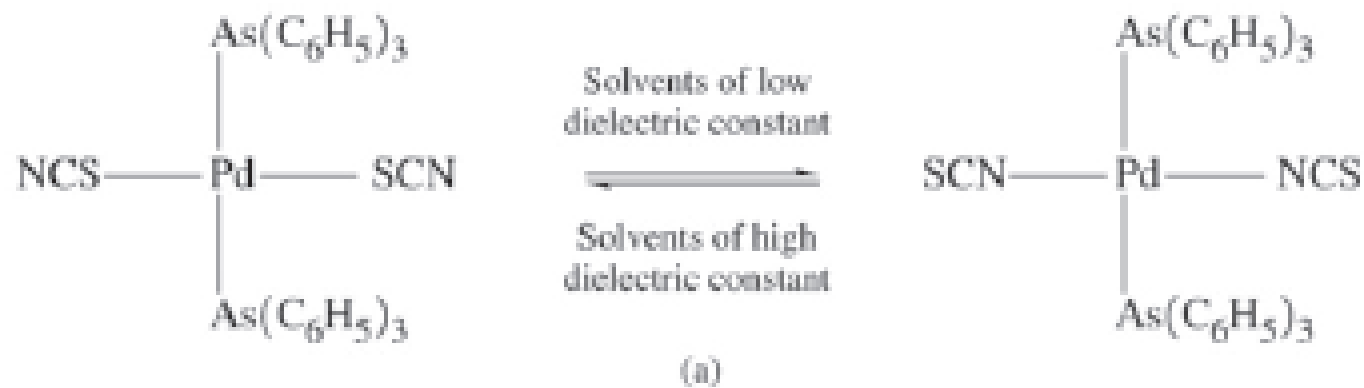
Coordination isomerism



Pt(II) Pt(IV)

Pt(IV) Pt(II)

Linkage isomerism



Stereoisomerism

Stereoisomers have

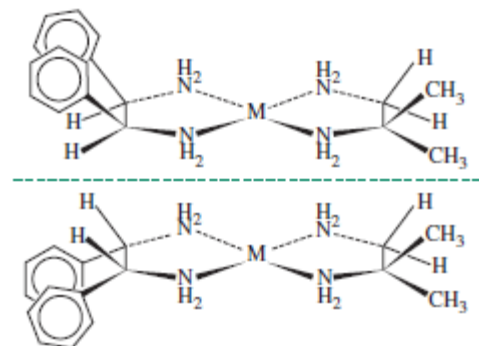
- Same molecular formula
- Connectivity or bonding between the atoms in a molecule are same
- Different spatial orientations of atoms or group of atoms in a molecule

They are classified into chiral and achiral stereoisomers

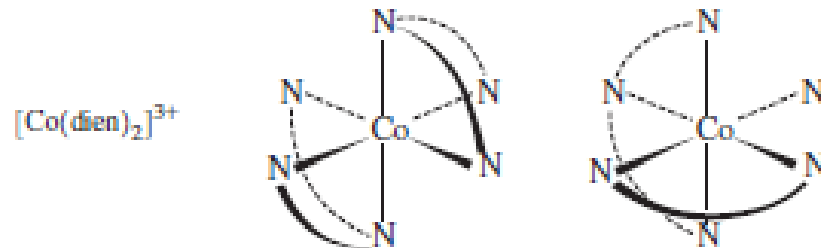
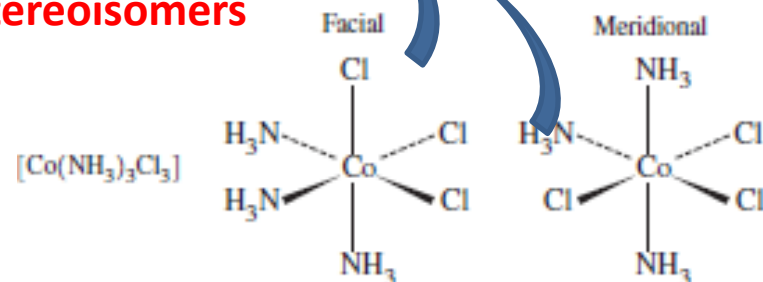
- Chiral isomers are optically active
- Achiral isomers are optically inactive

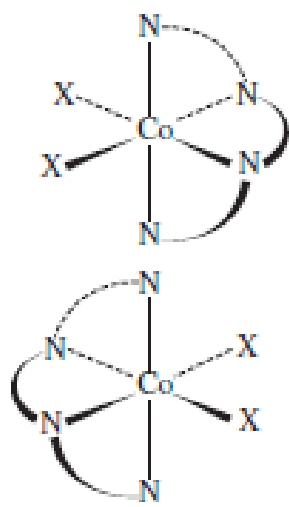
Conditions for a molecule to be chiral

- It should not have plane of symmetry
- It can have molecular plane of symmetry
- It should not have inversion symmetry, i ($S_2 = C_2\sigma_h = i$) and also any other S_n axis of symmetry

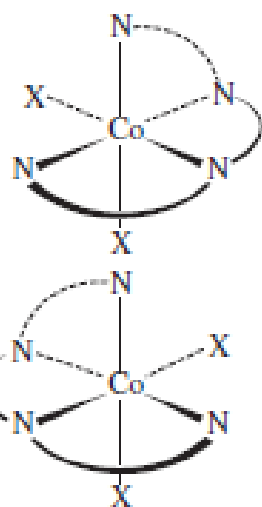


Optically inactive stereoisomers

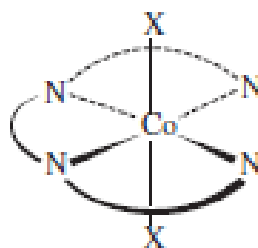




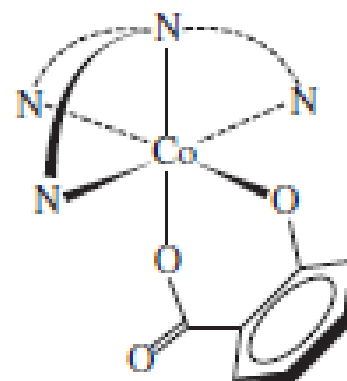
α
No coplanar rings



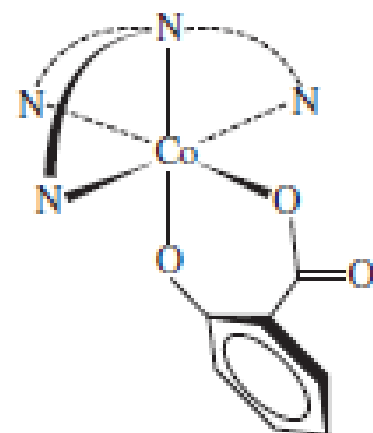
β
Two coplanar rings



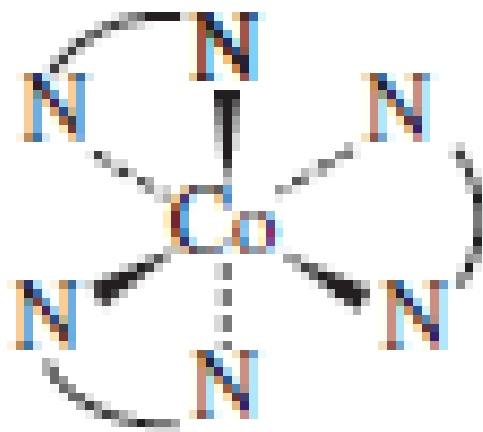
trans
Three coplanar rings



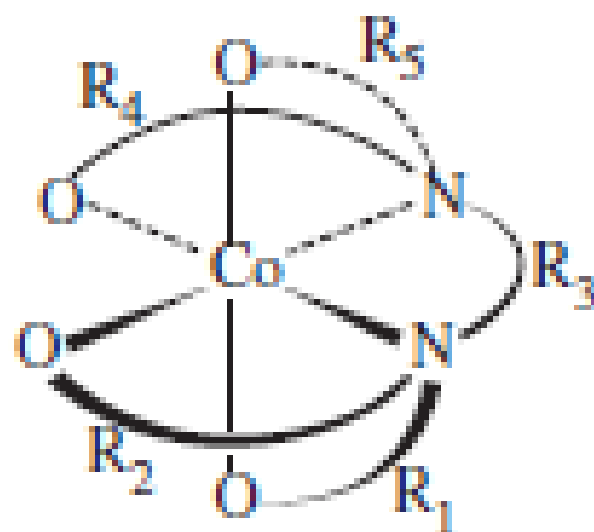
COO⁻ *trans* to tertiary N



COO⁻ *cis* to tertiary N

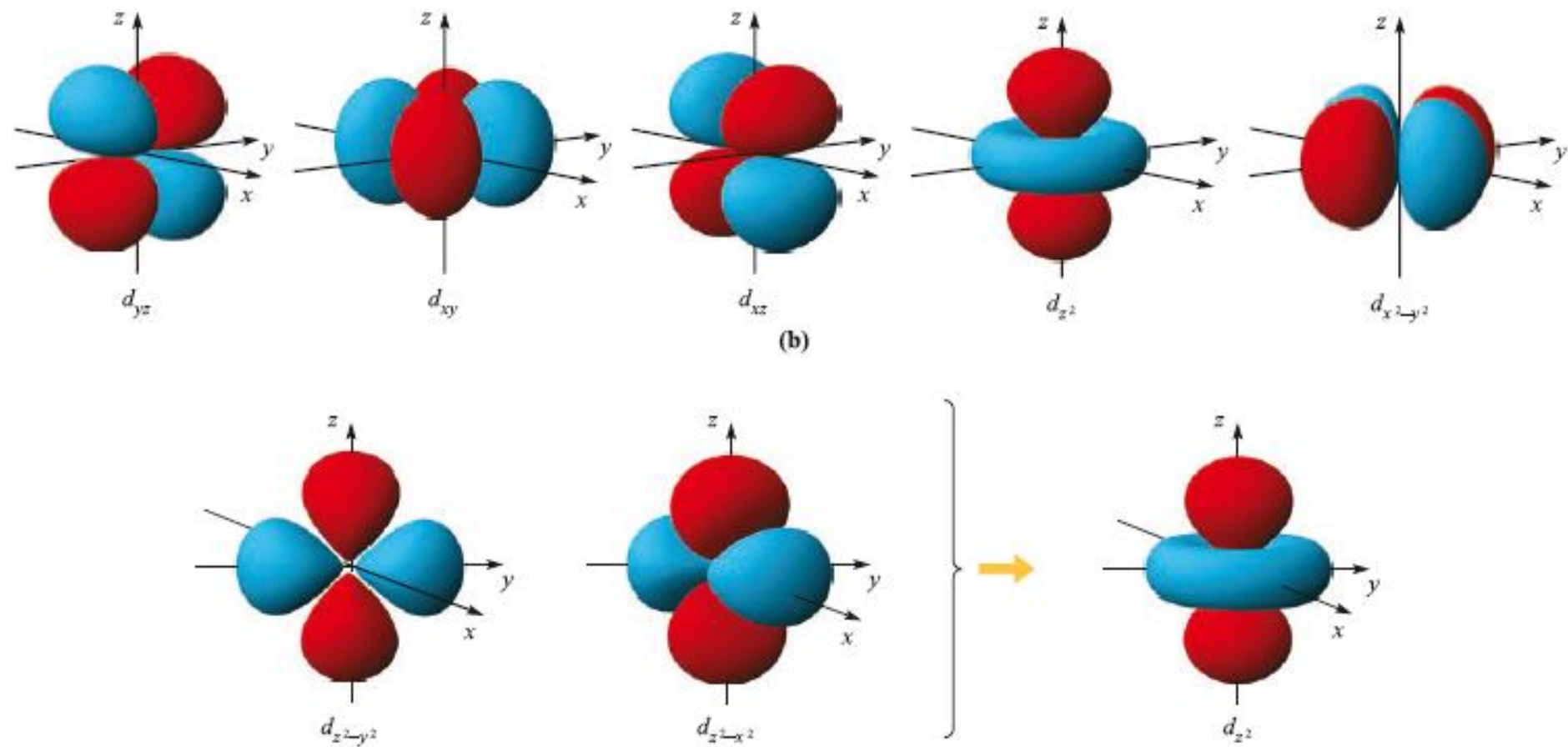


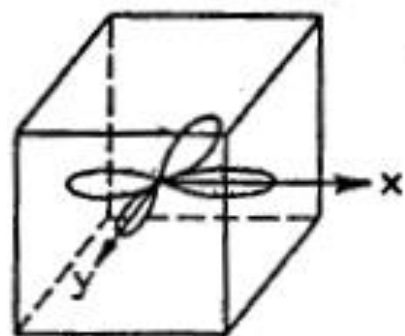
Co(en)₃



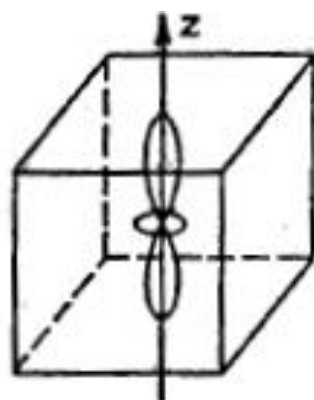
CoEDTA⁻

Spatial orientation of d-orbitals

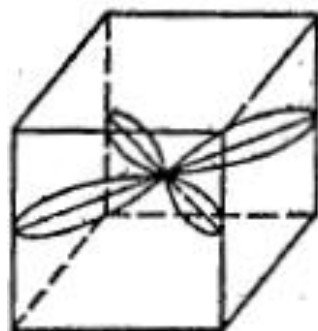




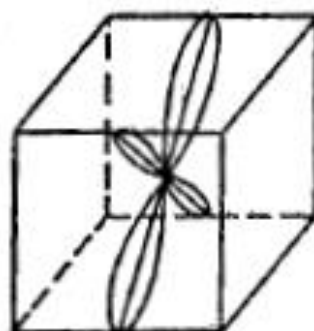
$d_{x^2-y^2}$



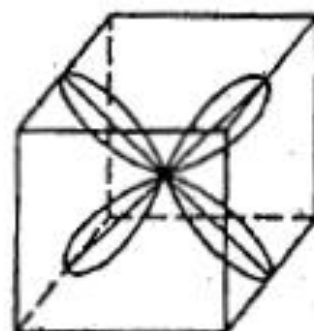
d_{z^2}



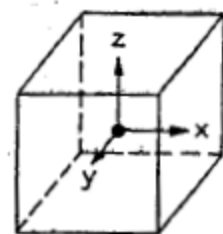
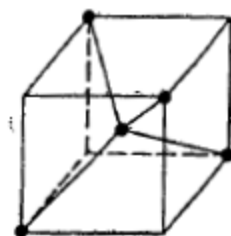
d_{xy}



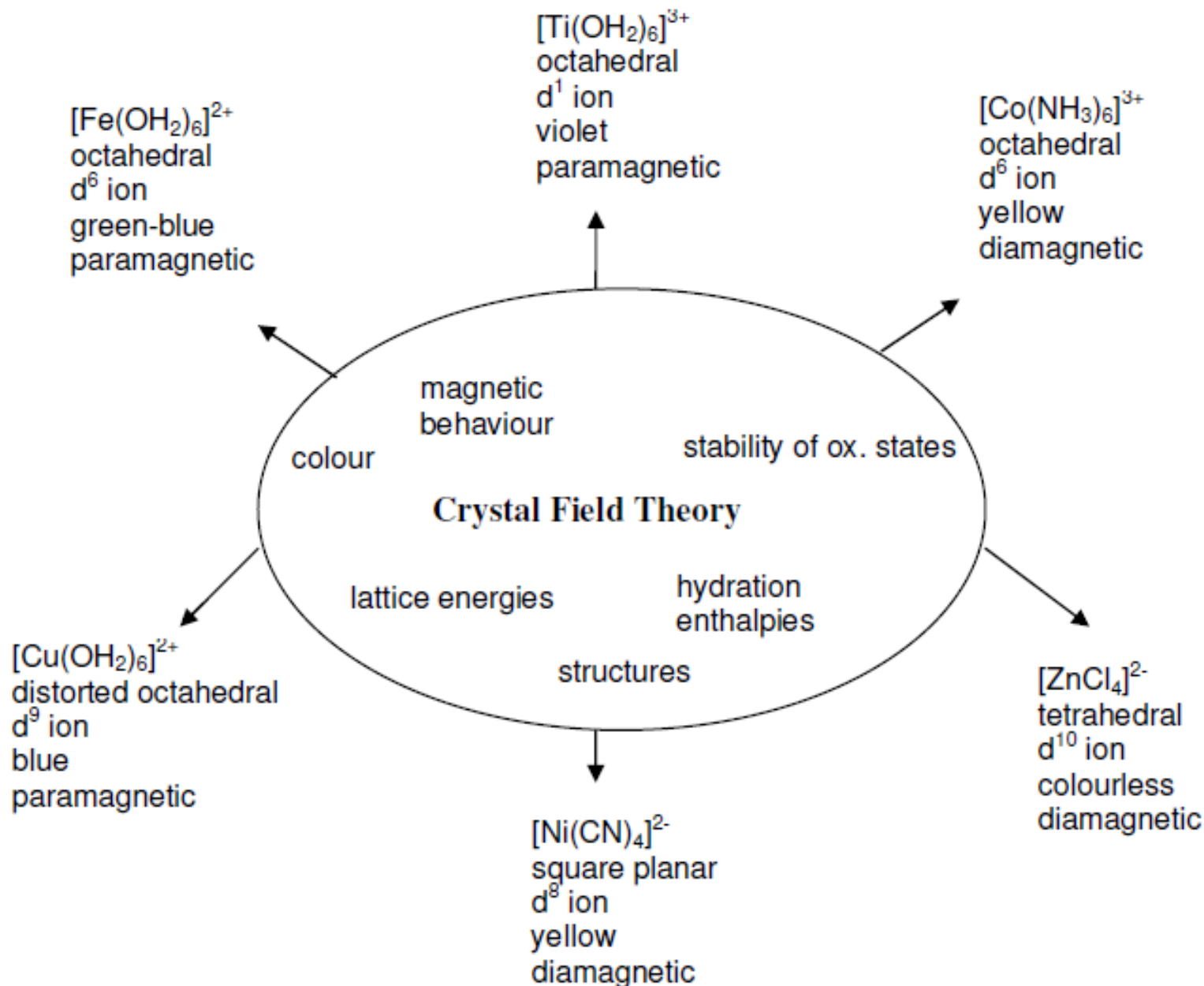
d_{yz}



d_{xz}



CFT- Crystal Field Theory



Assumptions of CFT

- Both the metal atom/ion and the ligands are considered as point charges
- Interaction between the M and L is purely electrostatic

Spectrochemical series

weak field ligands

$I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- < OH^- < EtOH < \text{oxalate} < H_2O$
 $< EDTA < (NH_3 \text{ and pyridine}) < \text{ethylenediamine} < \text{dipyridyl}$
 $< \text{o-phenanthroline} < NO_2^- < CN^- < CO$

strong field ligands

Splitting of d-orbital in octahedral field

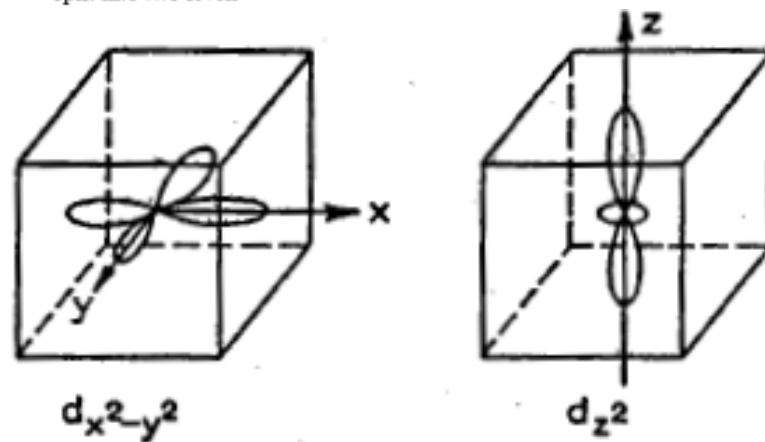
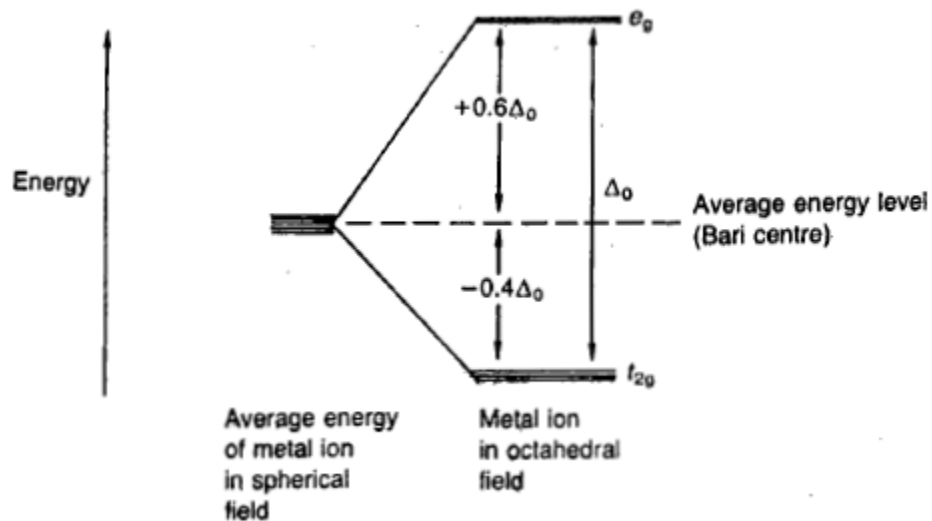
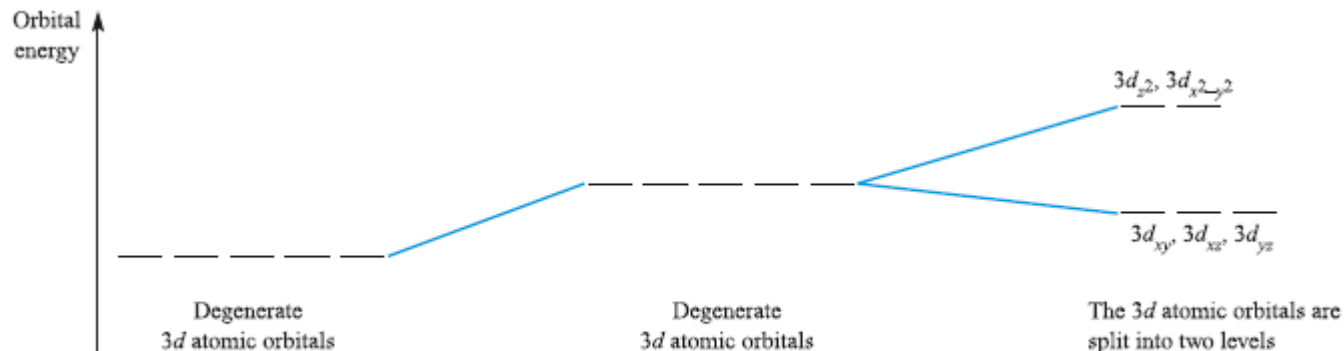
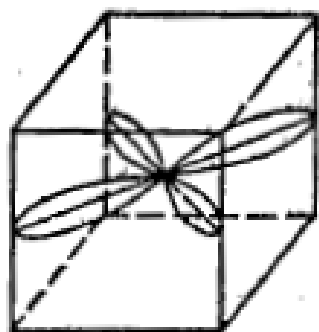


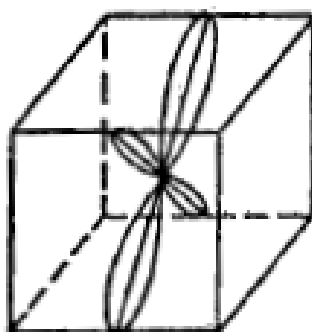
Table 7.8 Crystal field splittings by various ligands

Complex	Absorption peak	
	(cm^{-1})	(kJ mol^{-1})
$[\text{Cr}^{\text{III}}\text{Cl}_6]^{3-}$	13 640	163
$[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$	17 830	213
$[\text{Cr}^{\text{III}}(\text{NH}_3)_6]^{3+}$	21 680	259
$[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$	26 280	314

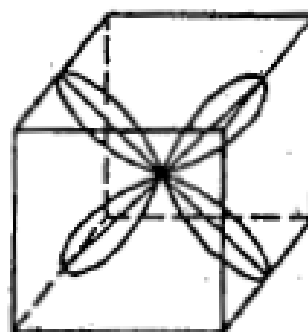
Splitting of d-orbital in tetrahedral field



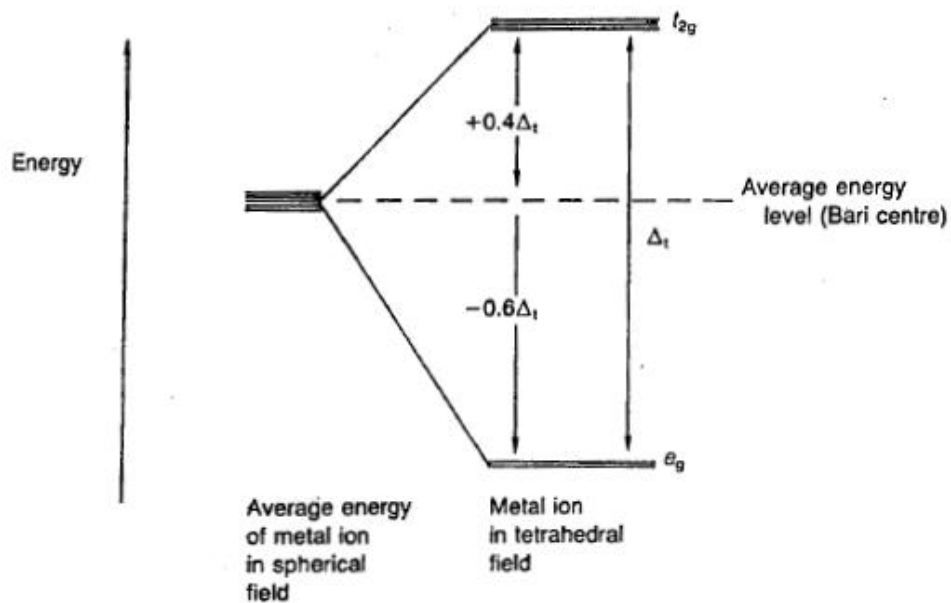
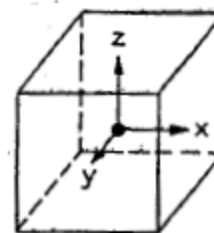
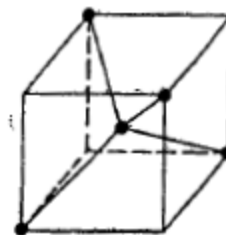
d_{xy}



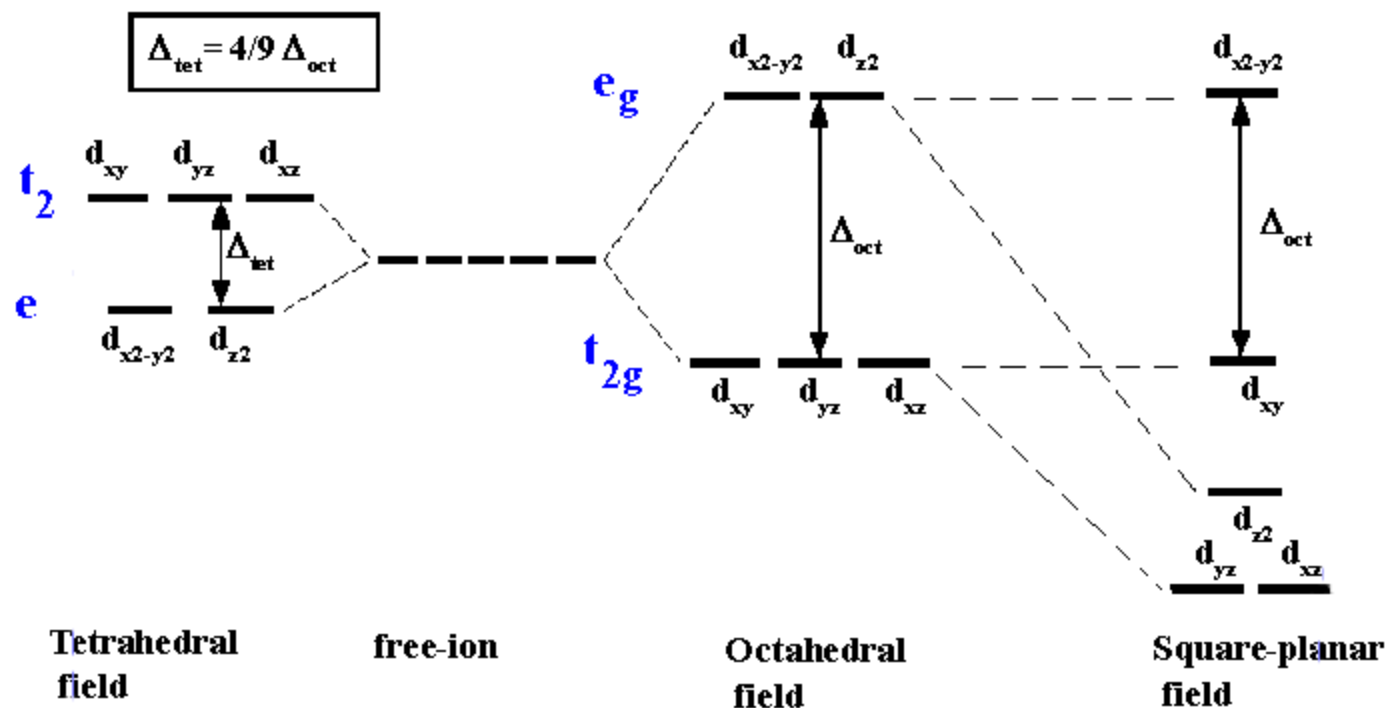
d_{yz}



d_{xz}



Energy levels of the d-orbitals in common stereochemistries



Splitting of d orbitals and their energies in different ligand field geometries

CN.	Structure	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
1	Linear ^c	5.14	-3.14	-3.14	0.57	0.57
2	Linear ^c	10.28	-6.28	-6.28	1.14	1.14
3	Trigonal ^d	-3.21	5.46	5.46	-3.86	-3.86
4	Tetrahedral	-2.67	-2.67	1.78	1.78	1.78
4	Square planar ^d	-4.28	12.28	2.28	-5.14	-5.14
5	Trigonal bipyramidal ^c	7.07	-0.82	-0.82	-2.72	-2.72
5	Square pyramidal ^c	0.86	9.14	-0.86	-4.57	-4.57
6	Octahedral	6.00	6.00	-4.00	-4.00	-4.00
6	Trigonal prismatic	0.96	-5.84	-5.84	5.36	5.36
7	Pentagonal bipyramidal	4.93	2.82	2.82	-5.28	-5.28
8	Cubic	-5.34	-5.34	3.56	3.56	3.56
8	Square antiprismatic	-5.34	-0.89	-0.89	3.56	3.56
9	$[\text{ReH}_9]^{2-}$ structure (see Fig. 12.40)	-2.25	-0.38	-0.38	1.51	1.51
12	Icosahedral	0.00	0.00	0.00	0.00	0.00

Table 7.12 CFSE and electronic arrangements in octahedral complexes

Number of d electrons	Arrangement in weak ligand field				Arrangement in strong ligand field			
	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment $\mu_s(D)$	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment $\mu_s(D)$
d^1	$\uparrow \square \square$	$\square \square$	-0.4	1.73	$\uparrow \square \square$	$\square \square$	-0.4	1.73
d^2	$\uparrow \uparrow \square$	$\square \square$	-0.8	2.83	$\uparrow \uparrow \square$	$\square \square$	-0.8	2.83
d^3	$\uparrow \uparrow \uparrow$	$\square \square$	-1.2	3.87	$\uparrow \uparrow \uparrow$	$\square \square$	-1.2	3.87
d^4	$\uparrow \uparrow \uparrow$	$\uparrow \square$	-1.2 +0.6 = -0.6	4.90	$\uparrow \downarrow \uparrow \uparrow$	$\square \square$	-1.6	2.83
d^5	$\uparrow \uparrow \uparrow$	$\uparrow \uparrow$	-1.2 +1.2 = -0.0	5.92	$\uparrow \downarrow \uparrow \downarrow \uparrow$	$\square \square$	-2.0	1.73
d^6	$\uparrow \downarrow \uparrow \uparrow$	$\uparrow \uparrow$	-1.6 +1.2 = -0.4	4.90	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\square \square$	-2.4	0.00
d^7	$\uparrow \downarrow \uparrow \downarrow \uparrow$	$\uparrow \uparrow$	-2.0 +1.2 = -0.8	3.87	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \square$	-2.4 +0.6 = -1.8	1.73
d^8	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \uparrow$	-2.4 +1.2 = -1.2	2.83	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \uparrow$	-2.4 +1.2 = -1.2	2.83
d^9	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow$	-2.4 +1.8 = -0.6	1.73	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow$	-2.4 +1.8 = -0.6	1.73
d^{10}	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow \downarrow$	-2.4 +2.4 = 0.0	0.00	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow \downarrow$	-2.4 +2.4 = 0.0	0.00

Table 7.10 Δ_o , crystal field splittings in one group

	cm^{-1}	kJ mol^{-1}
$[\text{Co}(\text{NH}_3)_6]^{3+}$	24 800	296
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34 000	406
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41 000	490