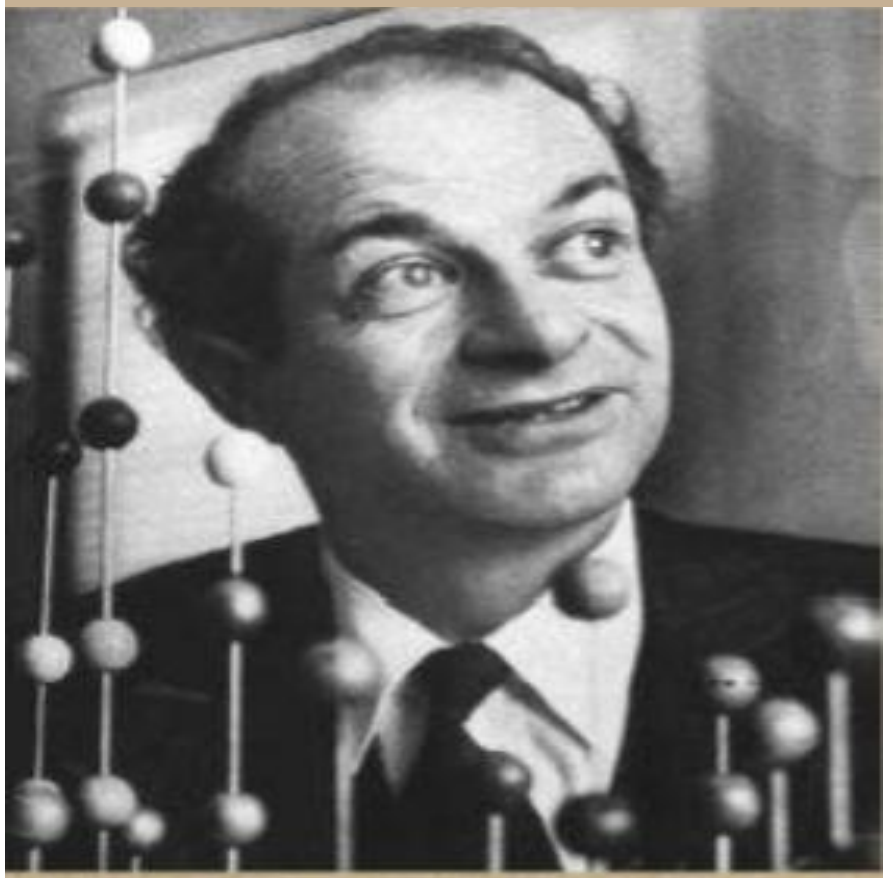
Pauli's Exclusion Principal

by Quantum Mechanical Approach



LINUS CARL PAULING

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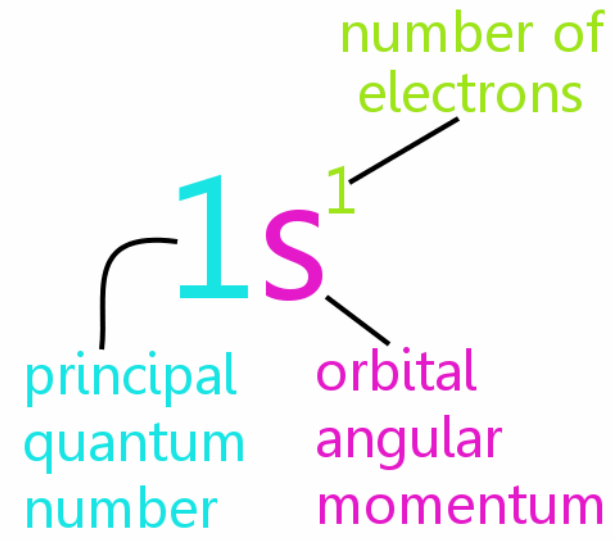
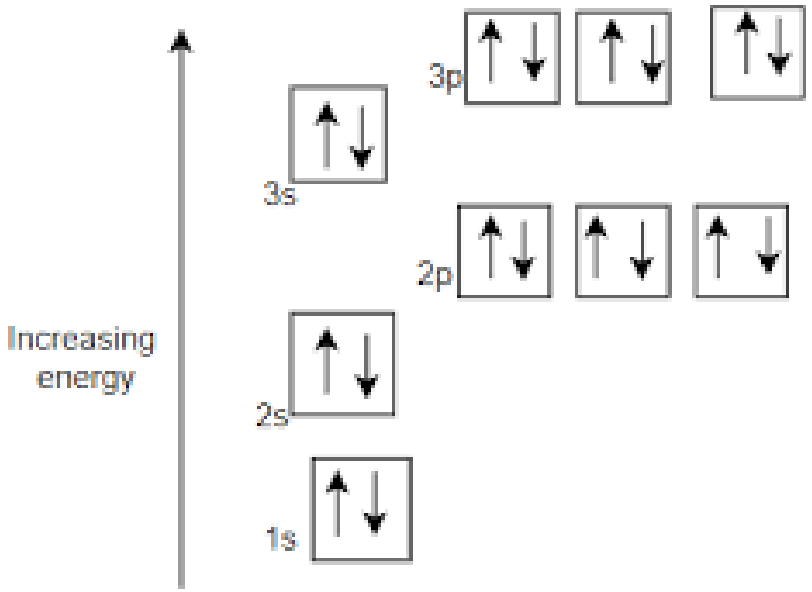
Pauli's Exclusion Principal

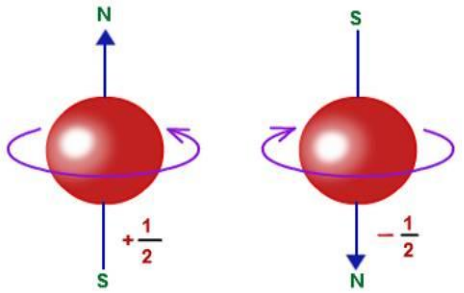
In an atom or molecule, no two electrons can have the same 4 quantum numbers.

Maximum only 3 Q.N. are same.

n; l; m; s

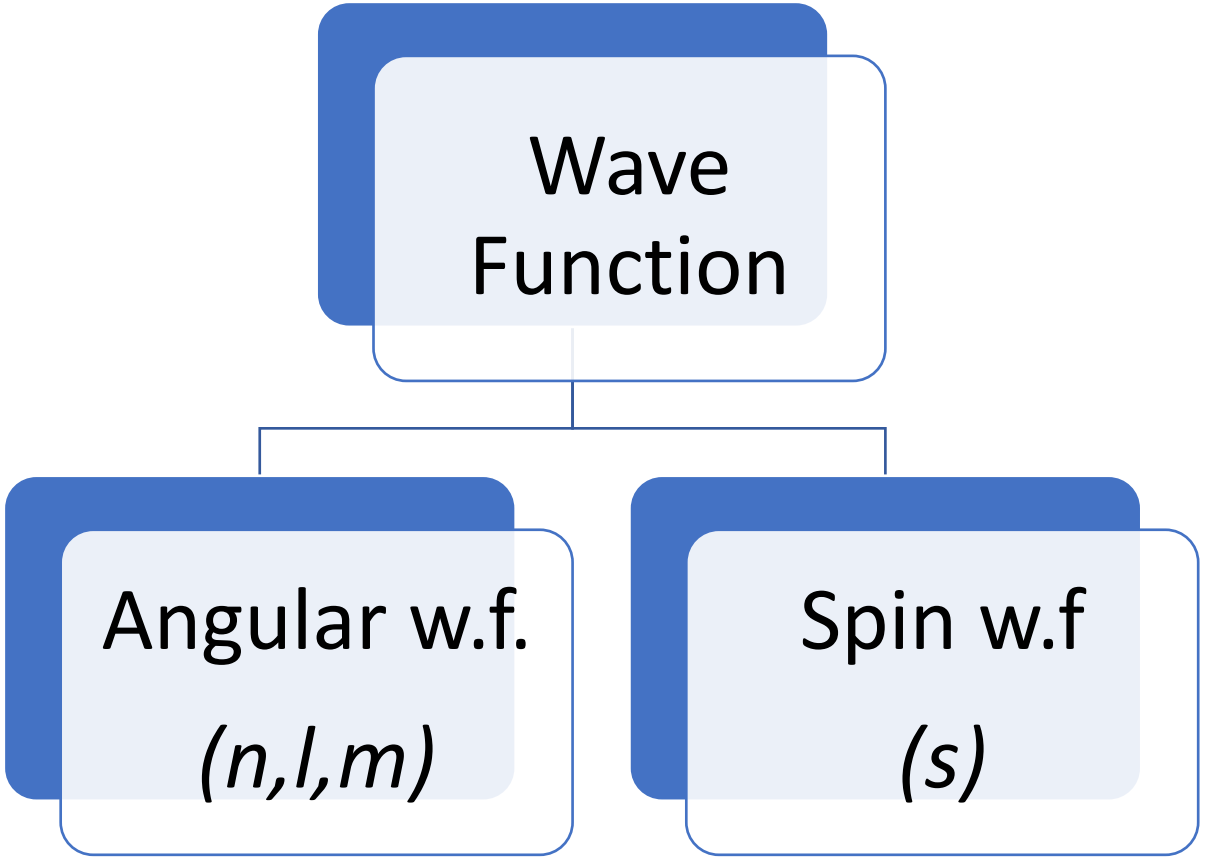






Pauli's Exclusion Principal-
by Quantum Mechanical Approach

[1] Wave function dependent on angular and spin Q.N. (n,l,m,s)



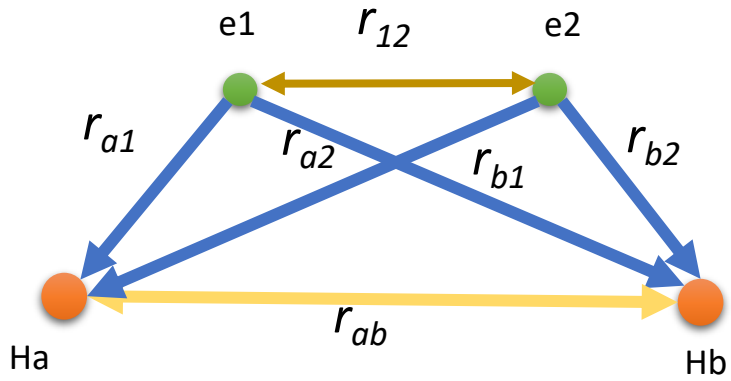
Angular w.f.
(n,l,m)

Molecule's possible structure & wave function

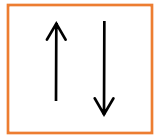
$$H_{A(1)}H_{B(2)} = \varphi_{a(1)}\varphi_{b(2)} = \varphi_1$$
$$H_{A(2)}H_{B(1)} = \varphi_{a(2)}\varphi_{b(1)} = \varphi_2$$

$$\phi_s = \phi_1 + \phi_2$$
$$\phi_A = \phi_1 - \phi_2$$

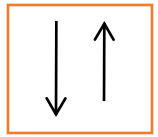
$$\varphi_s = \varphi_{a(1)}\varphi_{b(2)} + \varphi_{a(2)}\varphi_{b(1)}$$
$$\varphi_A = \varphi_{a(1)}\varphi_{b(2)} - \varphi_{a(2)}\varphi_{b(1)}$$



Spin w.f
(s)



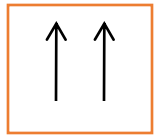
$$\varphi_1^s = \alpha_{(1)}\beta_{(2)}$$



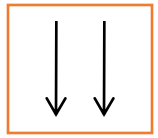
$$\varphi_2^s = \alpha_{(2)}\beta_{(1)}$$

$$\varphi_S^s = \alpha_{(1)}\beta_{(2)} + \alpha_{(2)}\beta_{(1)}$$

$$\varphi_A^s = \alpha_{(1)}\beta_{(2)} - \alpha_{(2)}\beta_{(1)}$$



$$\varphi_3^s = \alpha_{(1)}\alpha_{(2)}$$



$$\varphi_4^s = \beta_{(1)}\beta_{(2)}$$

[1] Wave function dependent on angular and spin Q.N. (n,l,m,s)

$$\varphi_T = AngularWF \times SpinWF$$

$$\varphi_s = \varphi_{a(1)}\varphi_{b(2)} + \varphi_{a(2)}\varphi_{b(1)}$$

$$\varphi_A = \varphi_{a(1)}\varphi_{b(2)} - \varphi_{a(2)}\varphi_{b(1)}$$

$$\varphi_S^s = \alpha_{(1)}\beta_{(2)} + \alpha_{(2)}\beta_{(1)}$$

$$\varphi_A^s = \alpha_{(1)}\beta_{(2)} - \alpha_{(2)}\beta_{(1)}$$

$$\varphi_3^s = \alpha_{(1)}\alpha_{(2)}$$

$$\varphi_4^s = \beta_{(1)}\beta_{(2)}$$

$$\varphi_{T(1)} = \varphi_S \times \varphi_S^s \qquad \varphi_{T(5)} = \varphi_A \times \varphi_S^s$$

$$\varphi_{T(2)} = \varphi_S \times \varphi_A^s \qquad \varphi_{T(6)} = \varphi_A \times \varphi_A^s$$

$$\varphi_{T(3)} = \varphi_S \times \varphi_3^s \qquad \varphi_{T(7)} = \varphi_A \times \varphi_3^s$$

$$\varphi_{T(4)} = \varphi_S \times \varphi_4^s \qquad \varphi_{T(8)} = \varphi_A \times \varphi_4^s$$

Acceptable Wave Function

"When change the electron than the W.F. must be change".- Pauli's

$$\varphi_s = \varphi_{a(1)}\varphi_{b(2)} + \varphi_{a(2)}\varphi_{b(1)}$$

$$\varphi_s' = \varphi_{a(2)}\varphi_{b(1)} + \varphi_{a(1)}\varphi_{b(2)}$$

$$\varphi_s' = \varphi_s$$

$$\varphi_A = \varphi_{a(1)}\varphi_{b(2)} - \varphi_{a(2)}\varphi_{b(1)}$$

$$\varphi_A' = \varphi_{a(2)}\varphi_{b(1)} - \varphi_{a(1)}\varphi_{b(2)}$$

$$\varphi_A' = -\varphi_A$$

Anti symmetrical w.f. is Acceptable

$$\varphi_{T(1)} = \varphi_S \times \varphi_S^s$$ Symmetrical

$$\varphi_{T(2)} = \varphi_S \times \varphi_A^s$$ Anti Symmetrical *Acceptable*

$$\varphi_{T(3)} = \varphi_S \times \varphi_3^s$$ Symmetrical

$$\varphi_{T(4)} = \varphi_S \times \varphi_4^s$$ Symmetrical

$$\varphi_{T(5)} = \varphi_A \times \varphi_S^s$$ Anti Symmetrical *Acceptable*

$$\varphi_{T(6)} = \varphi_A \times \varphi_A^s$$ Symmetrical

$$\varphi_{T(7)} = \varphi_A \times \varphi_3^s$$ Anti Symmetrical *Acceptable*

$$\varphi_{T(8)} = \varphi_A \times \varphi_4^s$$ Anti Symmetrical *Acceptable*

Pauli's Exclusion Principal- by Quantum Mechanical Approach

$$\varphi_{T(2)} = \varphi_S \times \varphi_A^s$$

$$\varphi_s = \varphi_{a(1)}\varphi_{b(2)} + \varphi_{a(2)}\varphi_{b(1)}$$

$$\varphi_A^s = \alpha_{(1)}\beta_{(2)} - \alpha_{(2)}\beta_{(1)}$$

$$\varphi_{T(2)} = \left(\varphi_{a(1)}\varphi_{b(2)} + \varphi_{a(2)}\varphi_{b(1)}\right)\times\left(\alpha_{(1)}\beta_{(2)} - \alpha_{(2)}\beta_{(1)}\right)$$

$$\varphi_{T(2)} = \left(\varphi_{a(1)}\varphi_{b(2)}\alpha_{(1)}\beta_{(2)} - \varphi_{a(1)}\varphi_{b(2)}\alpha_{(2)}\beta_{(1)}\right) + \left(\varphi_{a(2)}\varphi_{b(1)}\alpha_{(1)}\beta_{(2)} - \varphi_{a(2)}\varphi_{b(1)}\alpha_{(2)}\beta_{(1)}\right)$$

$$\varphi_T = \begin{vmatrix} \varphi_{a(1)}\alpha_{(1)} & \varphi_{a(1)}\beta_{(1)} \\ \varphi_{b(2)}\alpha_{(2)} & \varphi_{b(2)}\beta_{(2)} \end{vmatrix} + \begin{vmatrix} \varphi_{b(1)}\alpha_{(1)} & \varphi_{b(1)}\beta_{(1)} \\ \varphi_{a(2)}\alpha_{(2)} & \varphi_{a(2)}\beta_{(2)} \end{vmatrix}$$

There are three Q.N. (n,l,m) are same for electron of H2 than $\varphi_a = \varphi_b$

$$\varphi_T = \begin{vmatrix} \varphi_{a(1)}\alpha_{(1)} & \varphi_{a(1)}\beta_{(1)} \\ \varphi_{b(2)}\alpha_{(2)} & \varphi_{b(2)}\beta_{(2)} \end{vmatrix} + \begin{vmatrix} \varphi_{b(1)}\alpha_{(1)} & \varphi_{b(1)}\beta_{(1)} \\ \varphi_{a(2)}\alpha_{(2)} & \varphi_{a(2)}\beta_{(2)} \end{vmatrix}$$

$$\varphi_T = \begin{vmatrix} \varphi_{a(1)}\alpha_{(1)} & \varphi_{a(1)}\beta_{(1)} \\ \varphi_{a(2)}\alpha_{(2)} & \varphi_{a(2)}\beta_{(2)} \end{vmatrix} + \begin{vmatrix} \varphi_{a(1)}\alpha_{(1)} & \varphi_{a(1)}\beta_{(1)} \\ \varphi_{a(2)}\alpha_{(2)} & \varphi_{a(2)}\beta_{(2)} \end{vmatrix}$$

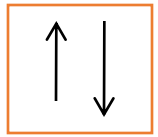
$$\varphi_T = 2\begin{vmatrix} \varphi_{a(1)}\alpha_{(1)} & \varphi_{a(1)}\beta_{(1)} \\ \varphi_{a(2)}\alpha_{(2)} & \varphi_{a(2)}\beta_{(2)} \end{vmatrix}$$

Forth Q.N. (s) is same for two electron of H2

$$\varphi_T = 2\begin{vmatrix} \varphi_{a(1)}\alpha_{(1)} & \varphi_{a(1)}\beta_{(1)} \\ \varphi_{a(2)}\alpha_{(2)} & \varphi_{a(2)}\beta_{(2)} \end{vmatrix}$$

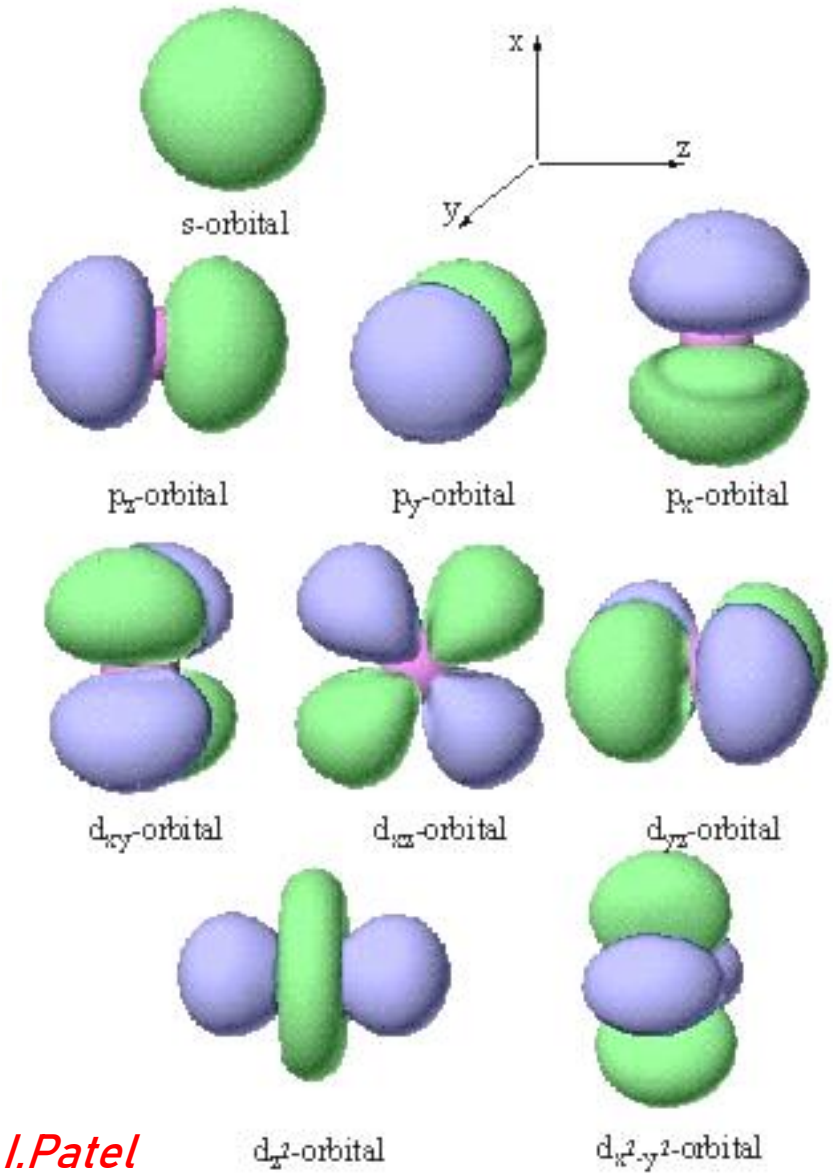
$$\varphi_T = 2\begin{vmatrix} \varphi_{a(1)}\alpha_{(1)} & \varphi_{a(1)}\alpha_{(1)} \\ \varphi_{a(2)}\alpha_{(2)} & \varphi_{a(2)}\alpha_{(2)} \end{vmatrix}$$

$$\varphi_T = 0$$



In an atom or molecule, no two electrons can have the same 4 quantum numbers.
Maximum only 3 Q.N. are same.

Molecular Orbital treatment for Octahedral Complex.



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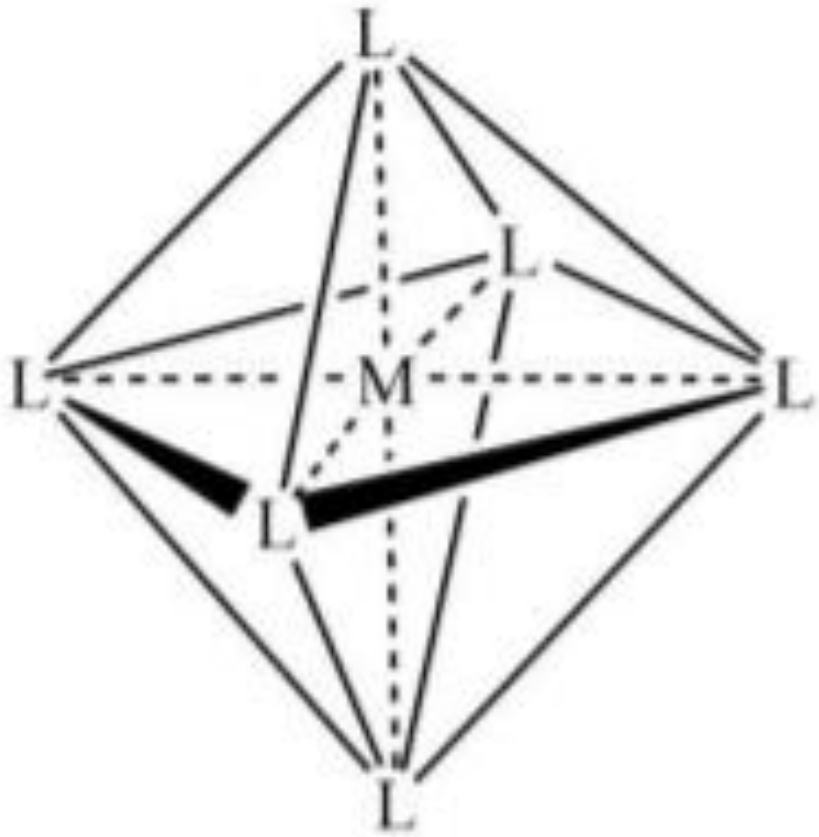
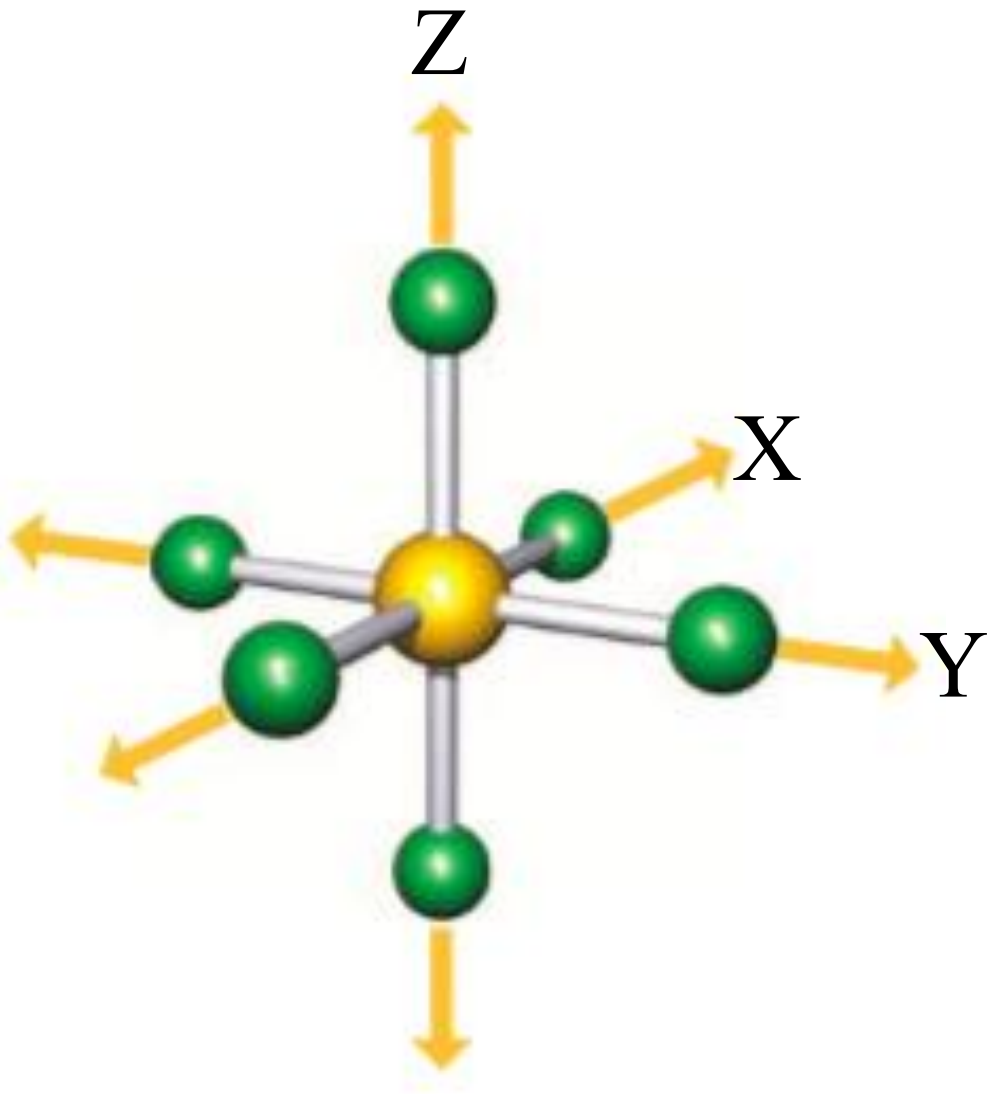
M.O. treatment for Oh complexes.

$[ML_6]$ Octahedral





M.O. treatment for Oh complexes.

Bonding atomic Orbitals of Metal and Legend

n=4,5,6

$$nS = a_{1g}$$

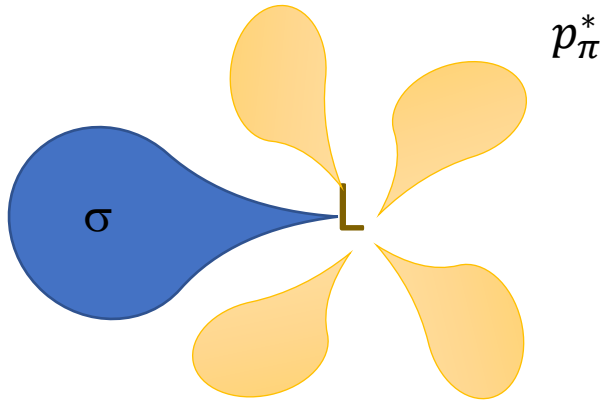
$$nP = (P_x, P_y, P_z) = t_{1u}$$

$$(n-1)d = (d_{xy}, d_{yz}, d_{xz}) = t_{2g}$$

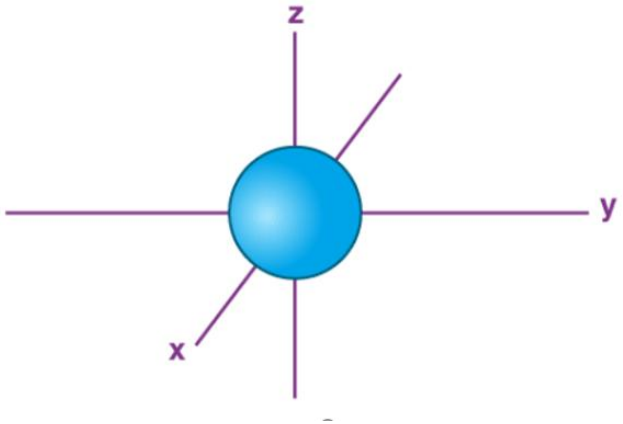
$$= (d_{x^2-y^2}, d_{z^2}) = eg$$

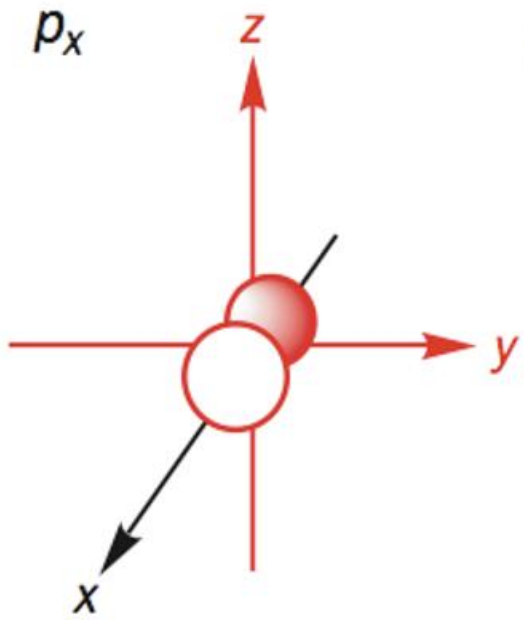
Coordination Covalent Bond

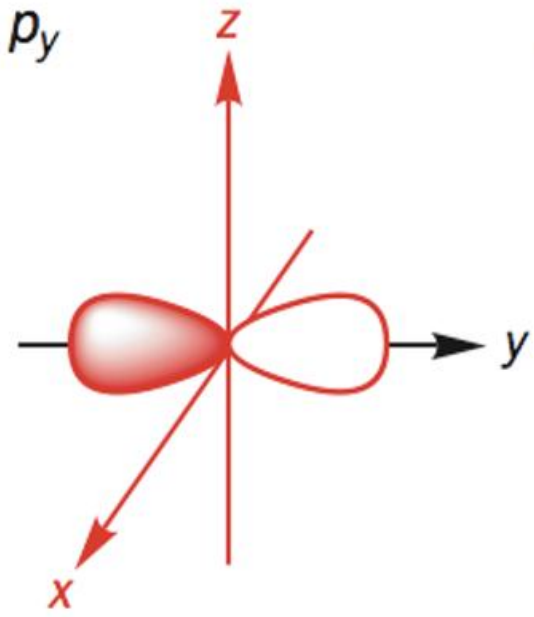
d π-pπ Bond

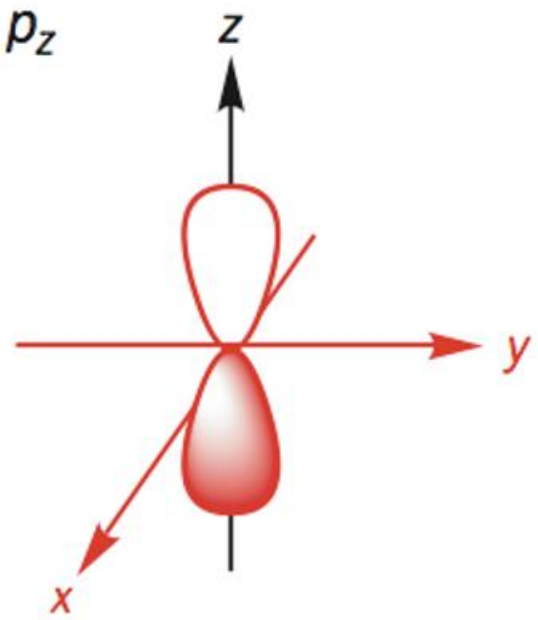


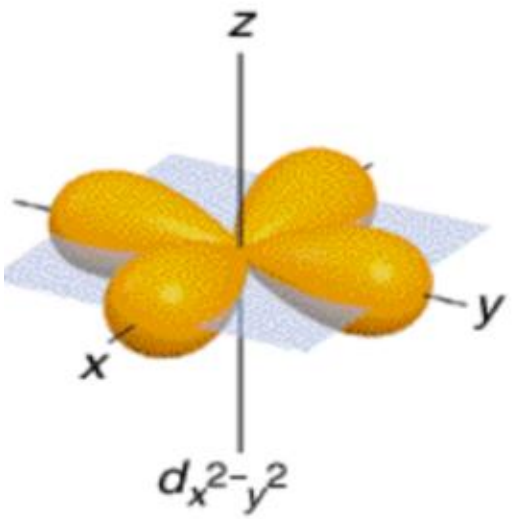
σ-bonded orbitals of CMI

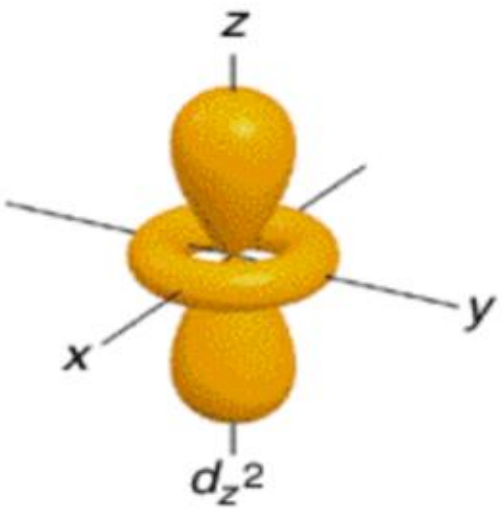




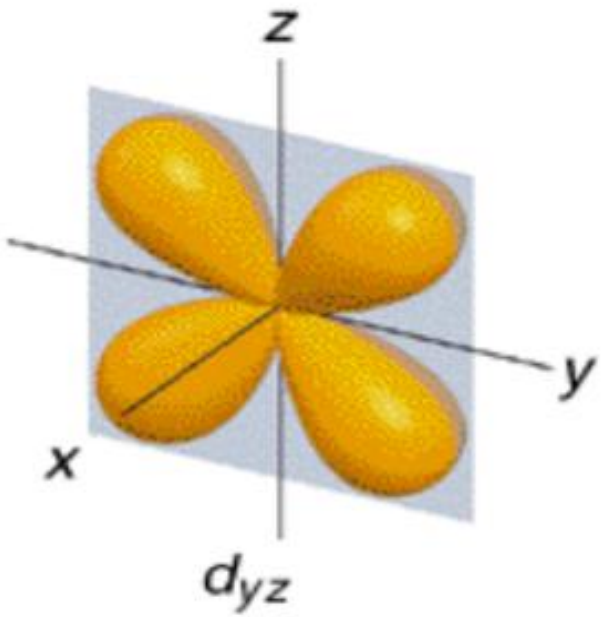


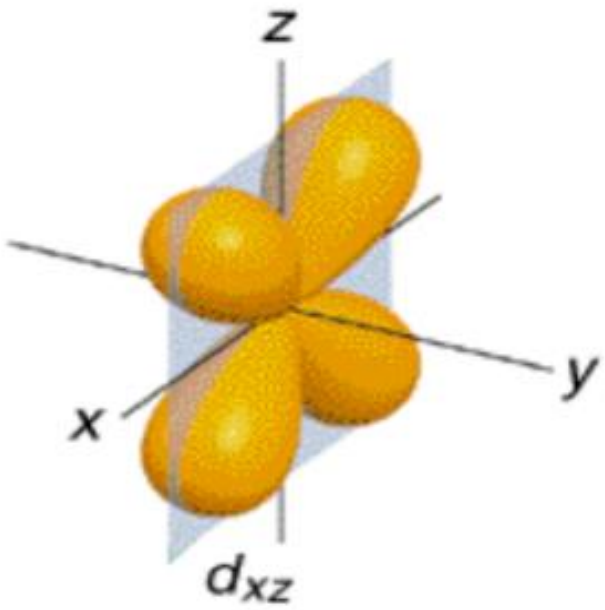


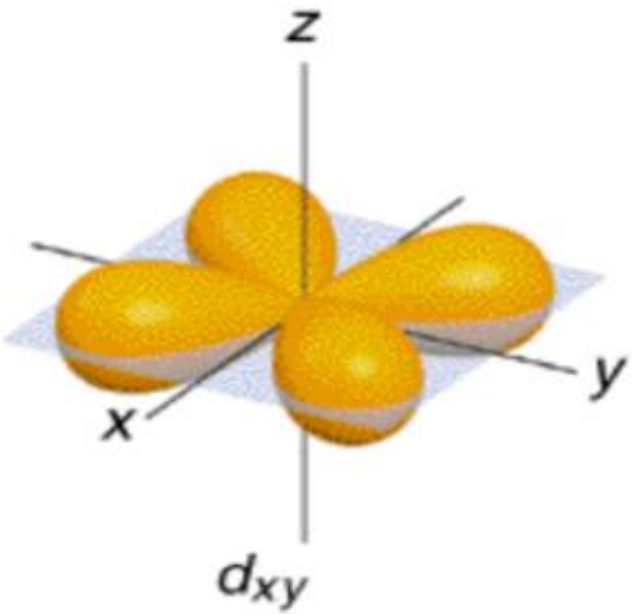




π-bonded orbitals of CMI

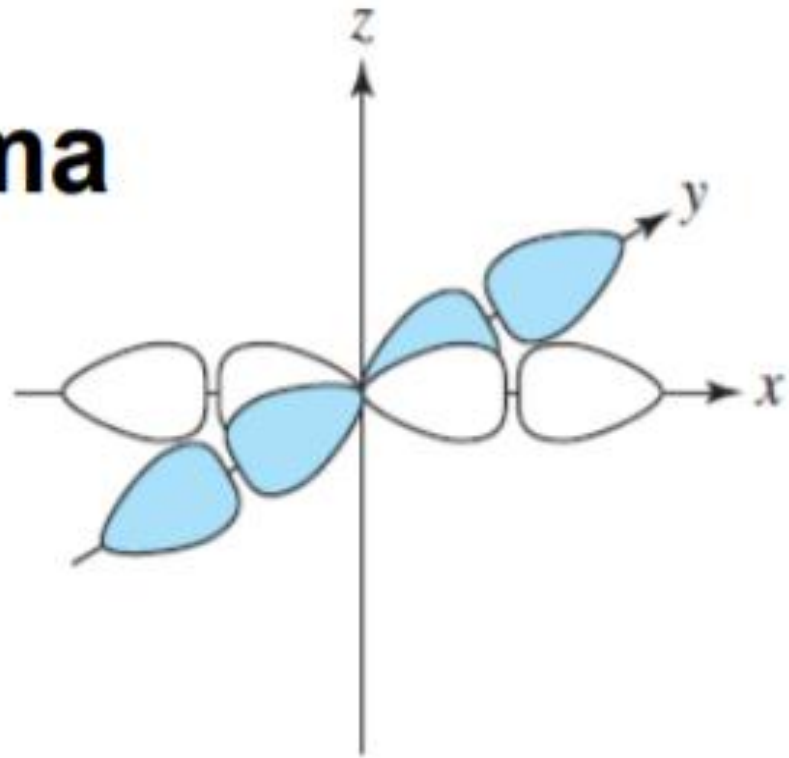






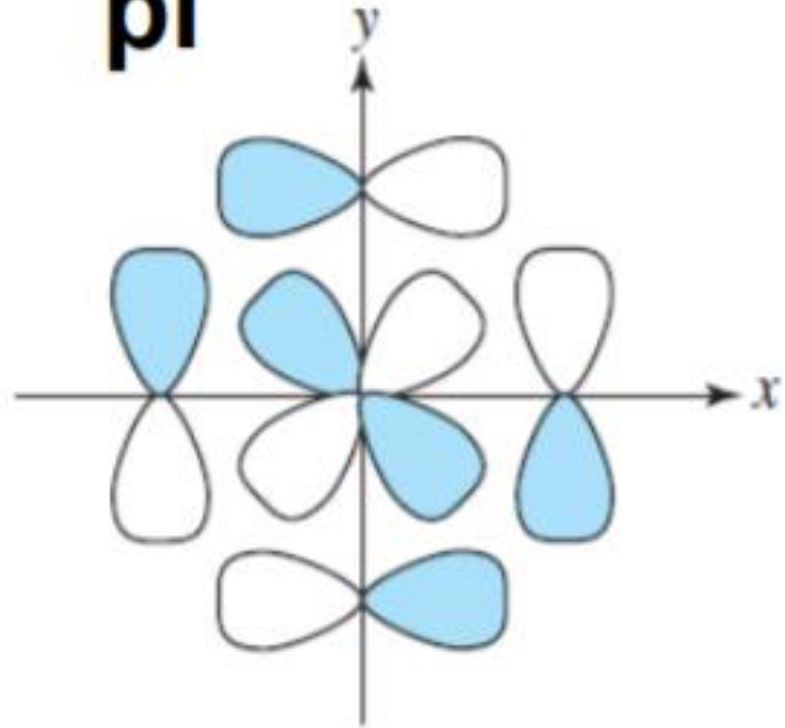
Sigma bonding interaction between two ligand orbitals and metal d_{z^2} orbital

sigma



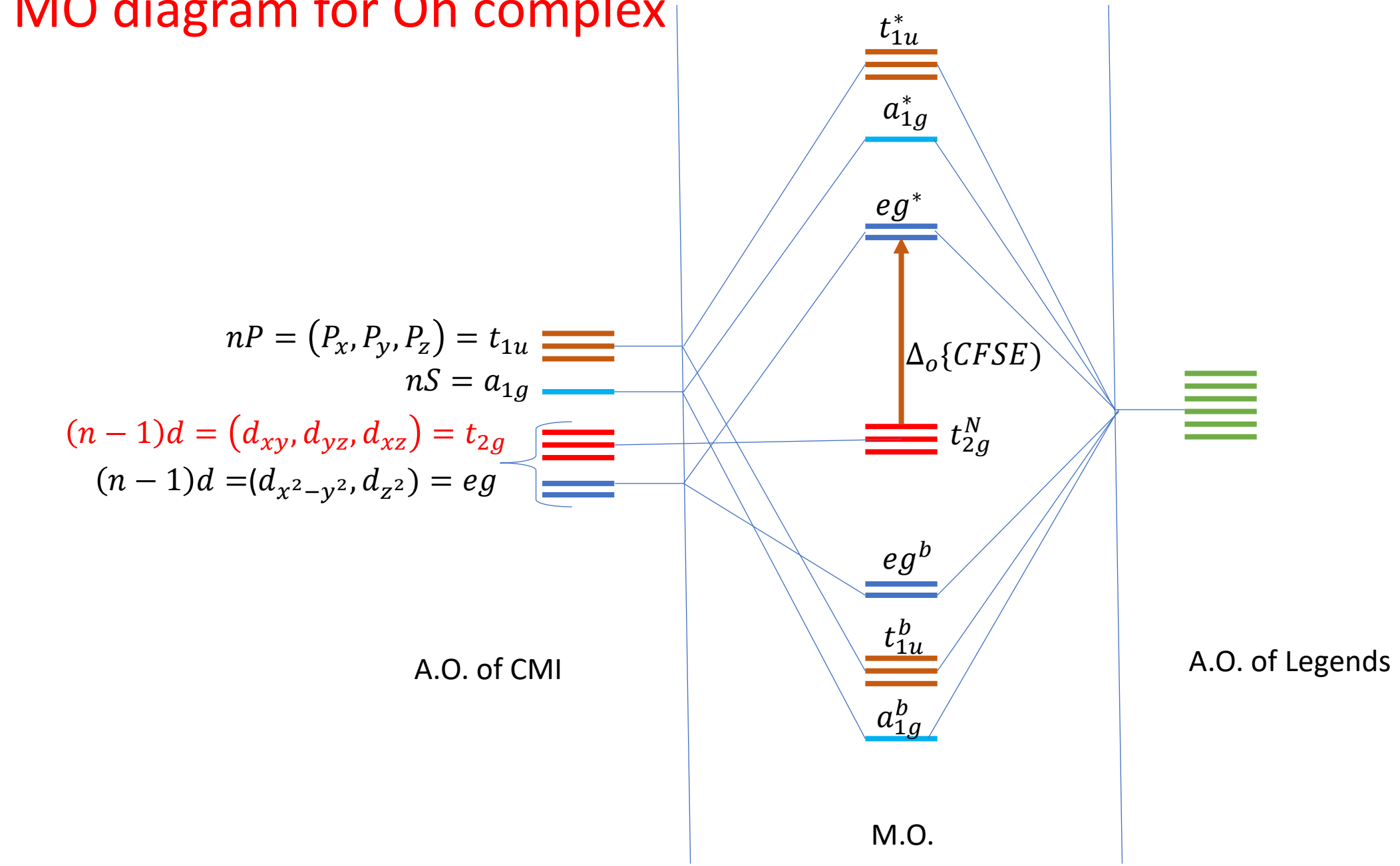
Sigma bonding interaction between four ligand orbitals and metal $d_{x^2-y^2}$ orbital

pi

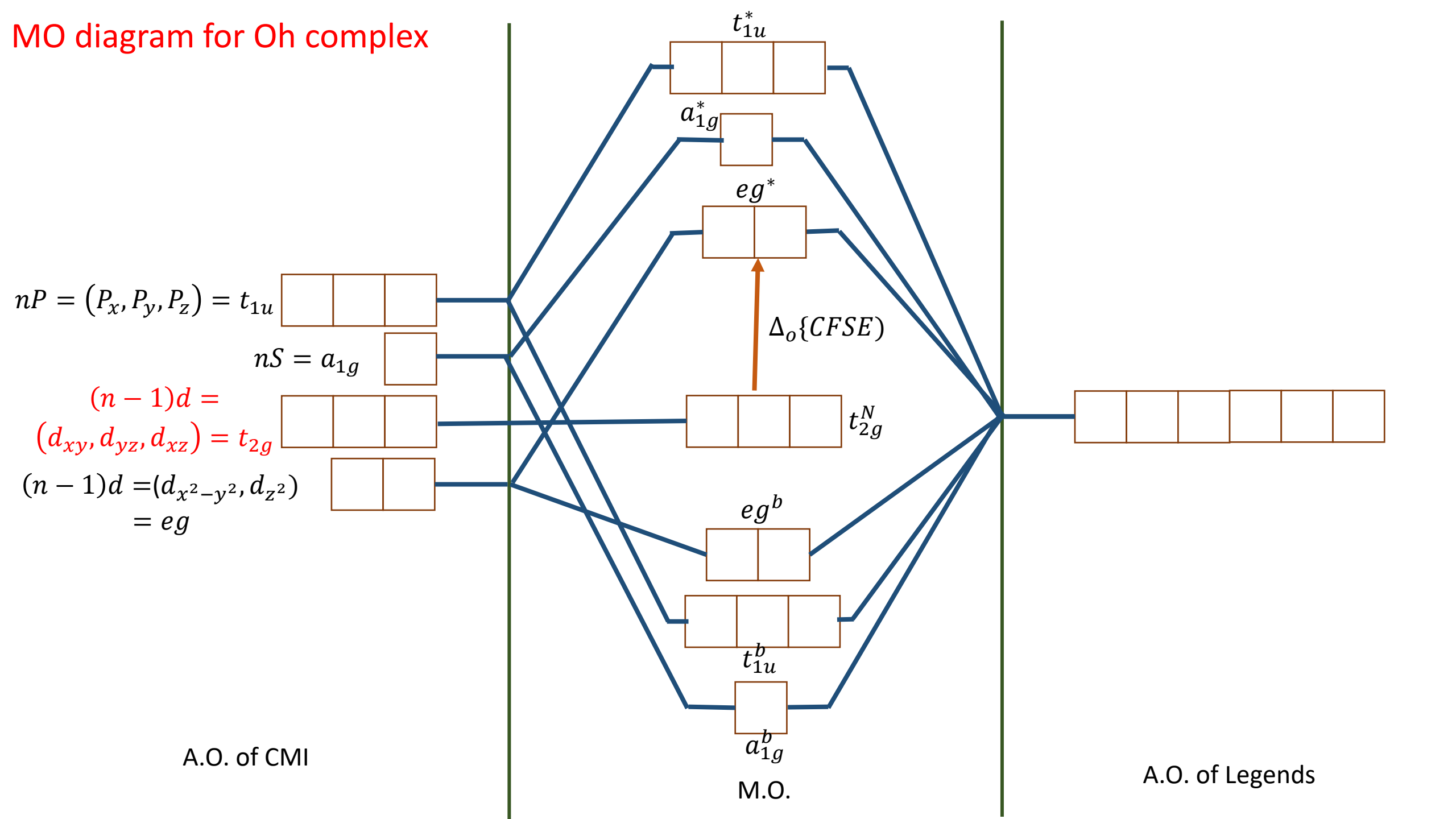


Pi bonding interaction between four ligand orbitals and metal d_{xy} orbital

MO diagram for Oh complex



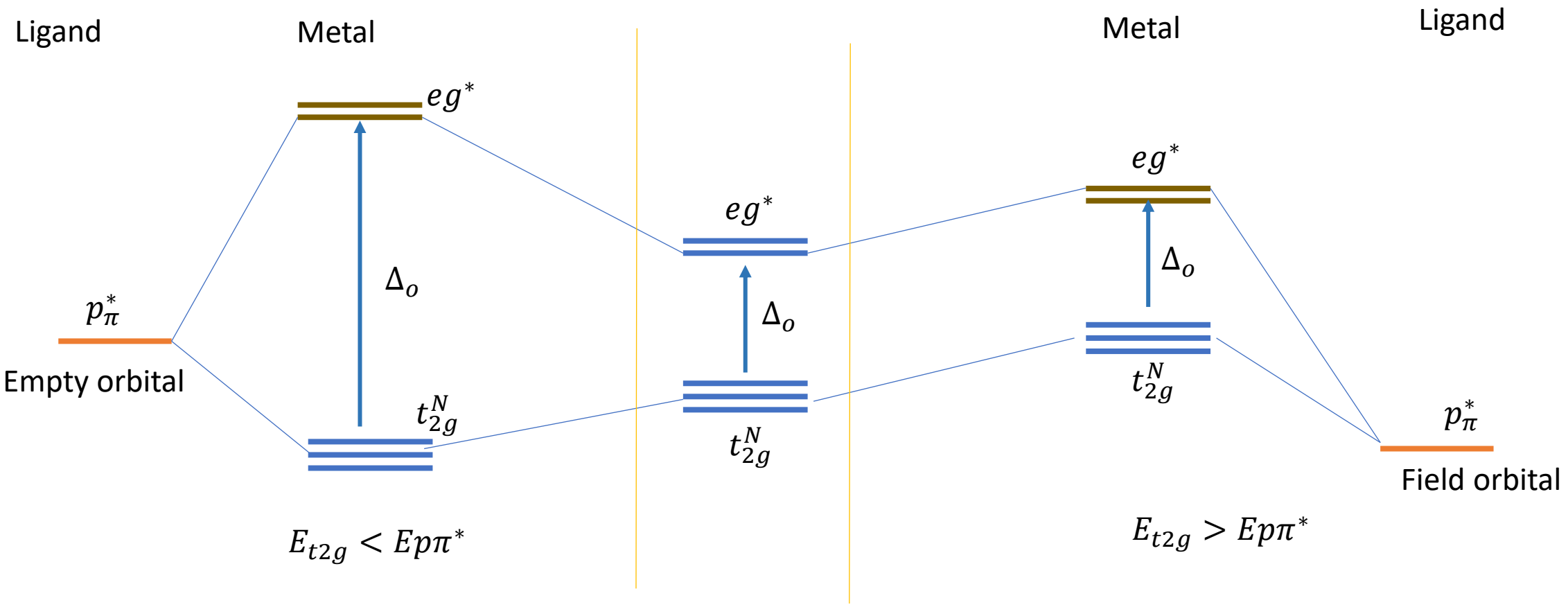
MO diagram for Oh complex



π -bonding in Oh Complex

Back donation/strong pi bonding

Week pi bonding



Strong ligand

$\sim NCS^- < EDTA^{-4} < NH_3 \sim Py < en < bpy \sim phen$

$NO_2^- < PR_3 < CH_3 < CN^- \sim CO$

Week ligand

$I^- < Br^- < SCN^- < Cl^- < S^{-2} < N_3^- < F^- < ONO^- < OH^- < SO_4^{-2} < NO_4^-$

Spectrochemical series

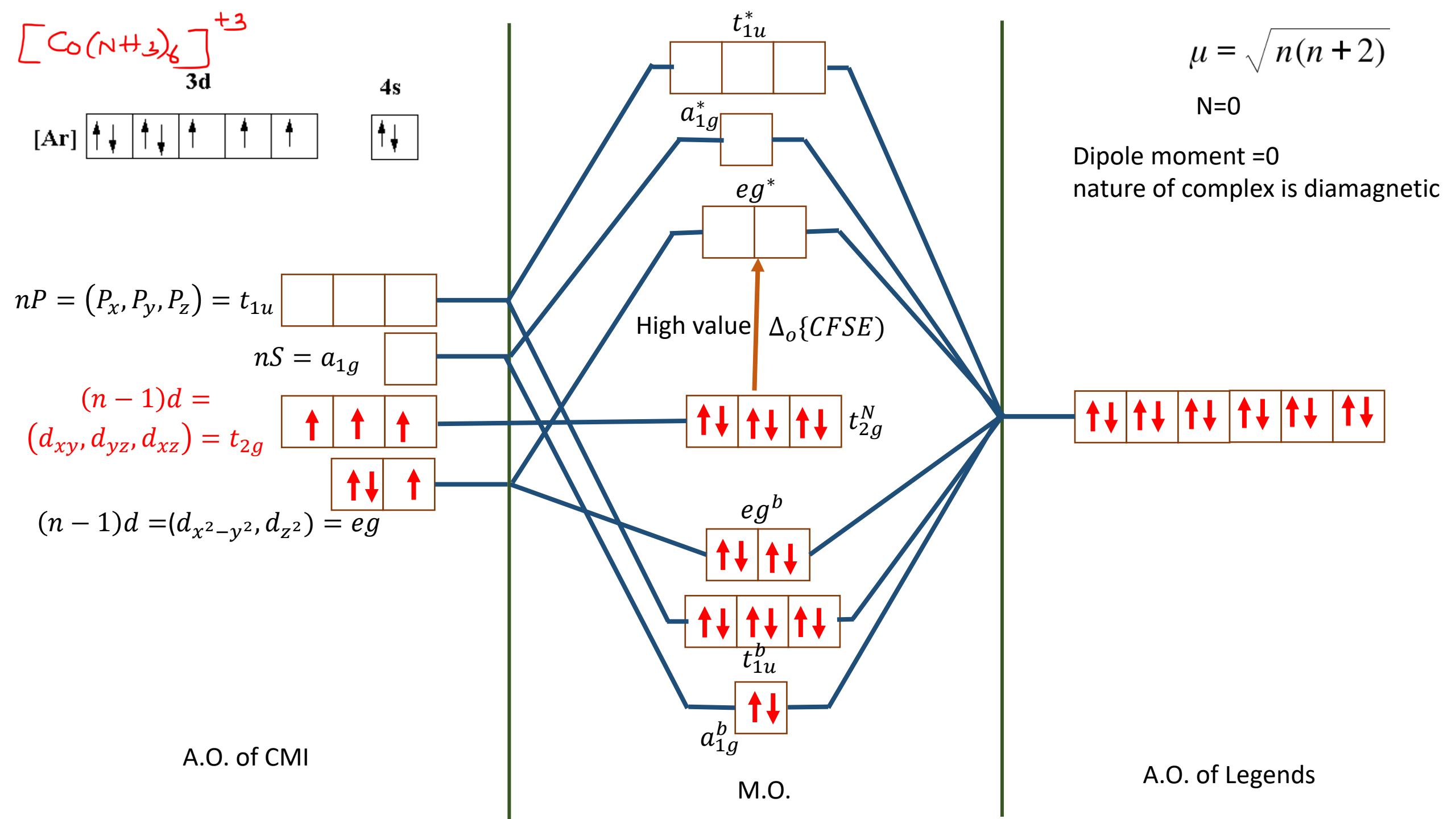
$$I^- < Br^- < SCN^- < Cl^- < S^{-2} < N_3^- < F^- < ONO^- < OH^- < SO_4^{-2} < NO_4^-$$

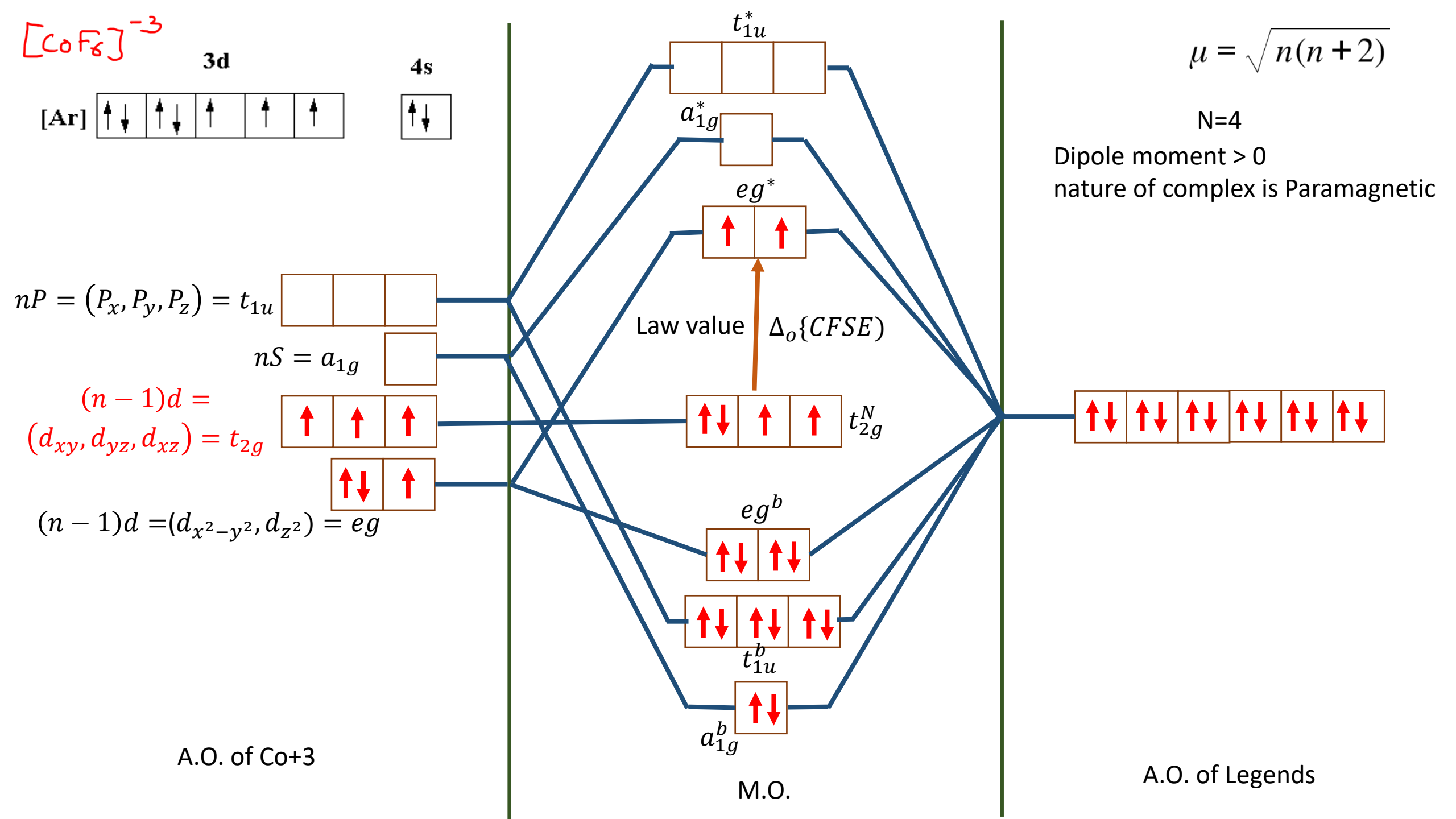
$$< C_2O_4^{-2} < O^{-2} < H_2O \sim NCS^- < EDTA^{-4} < NH_3 \sim Py < en < bpy \sim phen$$

$$< NO_2^- < PR_3 < CH_3 < CN^- \sim CO$$

$From\ I^-\ To\ H_2O\ \ are\ weak\ field\ ligands$

$From\ NCS^-\ To\ CO\ are\ strong\ field\ ligands$


[Co(NH3)6]+3
3d
4s
[Ar]
t_{1u}^{*}
a_{1g}^{*}
eg^{*}
High value $\Delta_o\{CFSE\}$
t_{2g}^{N}
eg^{b}
t_{1u}^{b}
a_{1g}^{b}
$nP = (P_x, P_y, P_z) = t_{1u}$
$nS = a_{1g}$
$(n-1)d = (d_{xy}, d_{yz}, d_{xz}) = t_{2g}$
$(n-1)d = (d_{x^2-y^2}, d_{z^2}) = eg$
$\mu = \sqrt{n(n+2)}$
N=0
Dipole moment =0
nature of complex is diamagnetic
A.O. of CMI
M.O.
A.O. of Legends


$[CoF_6]^{-3}$
3d
4s
[Ar]
t_{1u}^*
a_{1g}^*
eg^*
Law value
$\Delta_o\{CFSE\}$
t_{2g}^N
eg^b
t_{1u}^b
a_{1g}^b
$nP = (P_x, P_y, P_z) = t_{1u}$
$nS = a_{1g}$
$(n-1)d = (d_{xy}, d_{yz}, d_{xz}) = t_{2g}$
$(n-1)d = (d_{x^2-y^2}, d_{z^2}) = eg$
$\mu = \sqrt{n(n+2)}$
N=4
Dipole moment > 0
nature of complex is Paramagnetic
A.O. of Co+3
M.O.
A.O. of Legends