B.Sc. SEMESTER-6
Type of course: Major Discipline Specific course
Name of course: Fundamentals of Chemistry IV (Major1)
Course Code-SC23MJDSCCHE601
UNIT-1 : Valency (Chemical Bonding)

- *Variation Method, Application of Variation method, Secular Equation*
- *Stability of H_2^+ ion, stability of H_2 molecule, Classical interaction energy*
- *Representation of wave function, bond angle and bond strength for SP, SP^2, and SP^3*
- *Quantum mechanical representation of Pauli's Exclusion principle.*
- *MO treatment of Octahedral complex.*

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How define physical properties (Energy) of electron ?

Using eigen equation or Q.M. Postulate 3 and 4 $\hat{A}\varphi = \lambda\varphi$

$$p\varphi = P\varphi \qquad -\frac{h}{2\pi i}\frac{\partial}{\partial r}\varphi = P\varphi$$

$$H\varphi = E\varphi$$

H$= \frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V$

$$E = \frac{H\varphi}{\varphi}$$

$$E = \frac{\int_{-\infty}^{+\infty} \varphi H\varphi \ dr}{\int_{+\infty}^{+\infty} \varphi\varphi \ dr}$$

$$E = H$$

E= Energy of particle
H= Operator (Symbol)

To define Energy or any physical properties, Wave function must be.

How define Wave function for system ?

1. Variation Method
2. Perturbation Method
3. Self consistent field Method
4. Independent electron Method

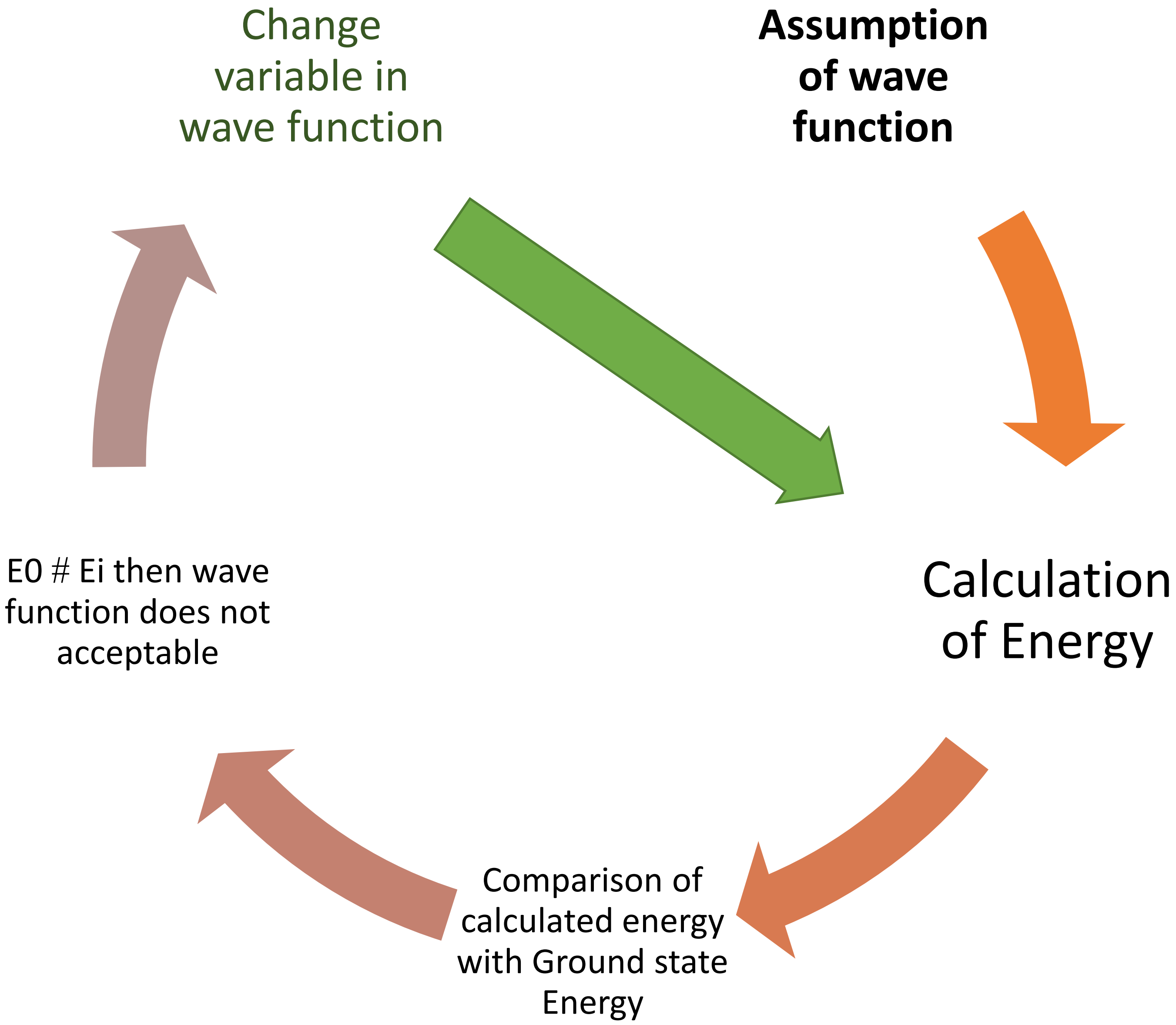
Variation Method ચલાયમાન પધ્ધતિ
(to define the wave function for system)

1. Assumption of wave function
2. Calculation of Energy

$$E = \frac{\int_{-\infty}^{+\infty} \varphi H \varphi \; dr}{\int_{+\infty}^{+\infty} \varphi \varphi \; dr}$$

3. Comparison of calculated energy with Ground state Energy/ZPE/Potential Energy(E_0)
4. Selection of Wave function for system.

$E_i = E_0$; than wave function is acceptable.



Change variable in wave function

Assumption of wave function

Calculation of Energy

Comparison of calculated energy with Ground state Energy

E0 # Ei then wave function does not acceptable

$$E = \frac{\int_{-\infty}^{+\infty} \varphi H \varphi \ dr}{\int_{+\infty}^{+\infty} \varphi \varphi \ dr}$$

ચલાયમાન C ને આધારે શક્તિ E મા થતો ફેરફાર

$$\frac{\partial E}{\partial C} \cong 0$$

Example : m દ્રવ્યમાન ધરાવતો કણ a લંબાઈની એક પરીમાણ પેટીમા x દિશામા ગતિમાન છે. જેની ગ્રાઉંન્ડ સ્ટેટ શક્તિ નીચે મુજબ છે તો તરંગ ફલન નક્કિ કરો. $E_0 = \frac{h^2}{8ma^2}$

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૧. ધારોકે આપેલ પ્રણાલી માટેનું તરંગ ફલન $\varphi_x = ax$

૨. તરંગ ફલન માટે શક્તિ ગણવી

$$E = \frac{\int_{-\infty}^{+\infty} \varphi H \varphi \; dr}{\int_{+\infty}^{+\infty} \varphi\varphi \; dr}$$

અહી H હેમીલ્ટોનિયન કારક $\mathrm{H} = \frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V$

કણ સતત ગતિમાન હોવાથી V=0

$$\mathrm{H} = \frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}$$

$$E_x = \frac{\int_0^a \left[ax\left\{\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}\right\}ax\right]dx}{\int_0^a a^2x^2 \, dx}$$

$$E_x = 0 \neq E_0$$

૩. તરંગ ફલન માટેની શક્તિ ની સરખામણી સાથે કરતા. $E_x = 0 \neq E_0 = \frac{h^2}{8ma^2}$

ધારેલ તરંગ ફલન $\varphi_x = ax$ આપેલ પ્રણાલી માટે યોગ્ય નથી

તરંગ ફલનમાં ચલાયમાન બદલતા $\varphi_x = ax^2$

તરંગ ફલન માટે શક્તિ ગણવી

$$E = \frac{\int_{-\infty}^{+\infty} \varphi H \varphi \; dr}{\int_{+\infty}^{+\infty} \varphi \varphi \; dr}$$

$$\mathrm{H} = \frac{-h^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2}$$

$$E_x = \frac{\int_0^a \left[ax^2 \left\{ \frac{-h^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} \right\} ax^2 \right] dx}{\int_0^a a^2 x^4 \, dx}$$

$$E_x = \frac{\int_0^a \left[ax^2 \left\{ \frac{-h^2}{8\pi^2 m} \; 2a \right\} \right] dx}{\int_0^a a^2 x^4 \, dx}$$

$$E_x = \frac{-2h^2}{8\pi^2 m} \frac{\int_0^a [a^2 x^2] dx}{\int_0^a a^2 x^4 \, dx}$$

$$E_x = \frac{-2h^2}{8\pi^2 m} \frac{\left[a^2 \cdot \frac{x^3}{3}\right]_0^a}{\left[a^2 \cdot \frac{x^5}{5}\right]_0^a}$$

$$E_x = \frac{-2h^2}{8\pi^2 m} \frac{\left[a^5/3\right]}{\left[a^7/5\right]}$$

$$E_x = \frac{-2h^2}{8\pi^2 m} \; \frac{a^5}{3} \times \frac{5}{a^7}$$

$$E_x = \frac{-10h^2}{24\pi^2 m a^2}$$

$$E_x = -0.04 \frac{h^2}{8ma^2}$$

$$E_x \lll E_0 = \frac{h^2}{8ma^2}$$

ધારેલ તરંગ ફલન $\varphi_x = ax^2$ આપેલ પ્રણાલી માટે યોગ્ય નથી

તરંગ ફલન માં ચલાયમાન બદલતા $\varphi_x = ax - x^2$

તરંગ ફલન માટે શક્તિ ગણવી $E = \dfrac{\int_{-\infty}^{+\infty} \varphi H \varphi \; dr}{\int_{+\infty}^{+\infty} \varphi\varphi \; dr}$

$$H = \frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}$$

$$E_x = \frac{\int_0^a \left[(ax - x^2)\left\{\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}\right\}(ax - x^2)\right] dx}{\int_0^a (ax - x^2)^2 \; dx}$$

$$E_x = \frac{\frac{-h^2}{8\pi^2 m}\int_0^a \left[(ax - x^2)\left\{\frac{\partial^2}{\partial x^2}\right\}(ax - x^2)\right] dx}{\int_0^a (a^2x^2 - 2ax^3 + x^4) \quad dx}$$

$$E_x = \frac{-h^2}{8\pi^2 m}\frac{\int_0^a (ax - x^2)(-2)\,dx}{\int_0^a (a^2x^2 - 2ax^3 + x^4)\,dx}$$

$$E_x = \frac{+2h^2}{8\pi^2 m}\frac{\left[\frac{ax^2}{2} - \frac{x^3}{3}\right]_0^a}{\left[a^2\frac{x^3}{3} - 2a\frac{x^4}{4} + \frac{x^5}{5}\right]_0^a}$$

$$E_x = \frac{2h^2}{8\pi^2 m}\frac{\left[a^3/2 - a^3/3\right]}{\left[\frac{a^5}{3} - a^5/2 + \frac{a^5}{5}\right]}$$

$$E_x = \frac{2h^2}{8\pi^2 m}\frac{\left[a^3/6\right]}{\left[a^5/30\right]}$$

$$E_x = \frac{2h^2}{8\pi^2 m}\frac{a^3}{6}\times\frac{30}{a^5}$$

$$E_x = \frac{10h^2}{(3.14)^2 8ma^2}$$

$$E_x \approx \frac{h^2}{8ma^2} \approx E_0$$

ધારેલ તરંગ ફલન $\varphi_x = ax - x^2$ આપેલ પ્રણાલી માટે યોગ્ય છે.

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$$\frac{\partial E}{\partial C} \cong 0$$

APPLICATION OF VARIATION METHOD

Secular Equation & Secular Matrix

To define the Energy for Polyatomic Molecules

Wave function for Polyatomic Molecule by LCAO Method

Linear Combination of Atomic Orbitals

Diatomic Molecule

$$\varphi = C_1\varphi_1 + C_2\varphi_2$$

Triatomic Molecule

$$\varphi = C_1\varphi_1 + C_2\varphi_2 + C_3\varphi_3$$

N-atomic Molecule

$$\varphi = C_1\varphi_1 + C_2\varphi_2 + C_3\varphi_3 + \cdots \ldots \ldots .. + C_n\varphi_n$$

Define Energy for Diatomic Molecule

Diatomic Molecule $\varphi = C_1\varphi_1 + C_2\varphi_2$

$$E = \frac{\int_{-\infty}^{+\infty} \varphi H \varphi \ dr}{\int_{+\infty}^{+\infty} \varphi\varphi \ dr}$$

$$E = \frac{\int [(C_1\varphi_1 + C_2\varphi_2\ )H(C_1\varphi_1 + C_2\varphi_2\ )]}{\int [(C_1\varphi_1 + C_2\varphi_2\ )^2]}$$

$$E = \frac{\int [(C_1\varphi_1 H C_1\varphi_1 + C_1\varphi_1\ \mathrm{H} C_2\varphi_2 + C_2\varphi_1 H C_1\varphi_1 + C_2\varphi_2 H C_2\varphi_2)]dr}{\int C_1^2\varphi_1^2 + 2\,C_1\varphi_1 C_2\varphi_2 + C_2^2\varphi_2^2\ \ dr}$$

$$E = \frac{C_1^2 \int \varphi_1 H \varphi_1\, dr + C_1 C_2 \int \varphi_1 H \varphi_2\, dr + C_1 C_2 \int \varphi_2 H \varphi_1\, dr + C_2^2 \int \varphi_2 H \varphi_2\, dr}{C_1^2 \int \varphi_1^2 dr + 2\, C_1 C_2 \int \varphi_1\varphi_2\ \ dr + C_2^2 \int \varphi_2^2\, dr}$$

$$E = \frac{C_1^2 \int \varphi_1 H \varphi_1 \, dr + C_1 C_2 \int \varphi_1 H \varphi_2 \, dr + C_1 C_2 \int \varphi_2 H \varphi_1 \, dr + C_2^2 \int \varphi_2 H \varphi_2 \, dr}{C_1^2 \int \varphi_1^2 dr + 2\, C_1 C_2 \int \varphi_1 \varphi_2 \, dr + C_2^2 \int \varphi_2^2 \, dr}$$

H-Hermitian Operator, Than $\int \varphi_1 H \varphi_2 \, dr = \int \varphi_2 H \varphi_1 \, dr$

$$E = \frac{C_1^2 \int \varphi_1 H \varphi_1 \, dr + 2 C_1 C_2 \int \varphi_1 H \varphi_2 \, dr + C_2^2 \int \varphi_2 H \varphi_2 \, dr}{C_1^2 \int \varphi_1^2 dr + 2\, C_1 C_2 \int \varphi_1 \varphi_2 \, dr + C_2^2 \int \varphi_2^2 \, dr}$$

Use Symbol for Integration function

$$\int \varphi_1 H \varphi_1 \, dr = H_{11} \qquad \int \varphi_1 \varphi_1 \, dr = S_{11}$$

$$\int \varphi_1 H \varphi_2 \, dr = \int \varphi_2 H \varphi_1 \, dr = H_{12} \quad \int \varphi_1 \varphi_2 \, dr = \int \varphi_2 \varphi_1 \, dr = S_{12}$$

$$E = \frac{C_1^2 H_{11} + 2 C_1 C_2 H_{12} + C_2^2 H_{22}}{C_1^2 S_{11} + 2 C_1 C_2 S_{12} + C_2^2 S_{22}}$$

Applying Variation Method

$$\varphi = C_1\varphi_1 + C_2\varphi_2$$

$$\frac{\partial E}{\partial C_1} = \frac{\partial E}{\partial C_2} = 0$$

$$E = \frac{C_1^2 H_{11} + 2C_1C_2H_{12} + C_2^2 H_{22}}{C_1^2 S_{11} + 2C_1C_2S_{12} + C_2^2 S_{22}}$$

$$E = \frac{u}{v}$$

$$\frac{\partial u}{\partial C_1} = 2C_1H_{11} + 2C_2H_{12} + 0$$

$$\frac{\partial E}{\partial C_1} = \frac{v\frac{\partial u}{\partial C_1} - u\frac{\partial v}{\partial C_1}}{v^2}$$

$$\frac{\partial v}{\partial C_1} = 2C_1S_{11} + 2C_2S_{12} + 0$$

$$\frac{\partial E}{\partial C_1} = \frac{(C_1^2 S_{11} + 2C_1C_2S_{12} + C_2^2 S_{22})(2C_1H_{11} + 2C_2H_{12}) - (C_1^2 H_{11} + 2C_1C_2H_{12} + C_2^2 H_{22})(2C_1S_{11} + 2C_2S_{12})}{v^2}$$

$$0 = (C_1^2 S_{11} + 2C_1C_2S_{12} + C_2^2 S_{22})(2C_1H_{11} + 2C_2H_{12}) - (C_1^2 H_{11} + 2C_1C_2H_{12} + C_2^2 H_{22})(2C_1S_{11} + 2C_2S_{12})$$

$$(C_1^2S_{11} + 2C_1C_2S_{12} + C_2^2S_{22})(2C_1H_{11} + 2C_2H_{12}) = (C_1^2H_{11} + 2C_1C_2H_{12} + C_2^2H_{22})(2C_1S_{11} + 2C_2S_{12})$$

$$(2C_1H_{11} + 2C_2H_{12}) = \frac{(C_1^2H_{11} + 2C_1C_2H_{12} + C_2^2H_{22})}{(C_1^2S_{11} + 2C_1C_2S_{12} + C_2^2S_{22})}(2C_1S_{11} + 2C_2S_{12})$$

$$(2C_1H_{11} + 2C_2H_{12}) = E\ (2C_1S_{11} + 2C_2S_{12})$$

$$(C_1H_{11} + C_2H_{12}) = E\ (C_1S_{11} + C_2S_{12})$$

$$(C_1H_{11} + C_2H_{12}) = (C_1ES_{11} + C_2ES_{12})$$

$$C_1\ (H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) = 0$$

$$\frac{\partial E}{\partial C_2} = \frac{v\frac{\partial u}{\partial C_2} - u\frac{\partial v}{\partial C_2}}{v^2}$$

$$C_1\,(H_{21} - ES_{21}) + C_2(H_{22} - ES_{22}) = 0$$

$$C_1\,(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) = 0$$

$$C_1\,(H_{21} - ES_{21}) + C_2(H_{22} - ES_{22}) = 0$$

$$\begin{bmatrix} C_1 \\ C_2 \end{bmatrix} \begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} = 0$$

Secular Equation & Secular Matrix for Diatomic Molecule

Secular Equation & Secular Matrix for Triatomic Molecule

$$\varphi = C_1\varphi_1 + C_2\varphi_2 + C_3\varphi_3$$

$$C_1\,(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) + C_3(H_{13} - ES_{13}) = 0$$

$$C_1\,(H_{21} - ES_{21}) + C_2(H_{22} - ES_{22}) + C_3\,(H_{23} - ES_{23}) = 0$$

$$C_1\,(H_{31} - ES_{31}) + C_2(H_{32} - ES_{32}) + C_3\,(H_{33} - ES_{33}) = 0$$

$$\begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix} \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} \end{vmatrix} = 0$$

Secular Equation & Secular Matrix for n-atomic Molecule

$$\varphi = C_1\varphi_1 + C_2\varphi_2 + C_3\varphi_3 + \cdots \ldots \ldots .. + C_n\varphi_n$$

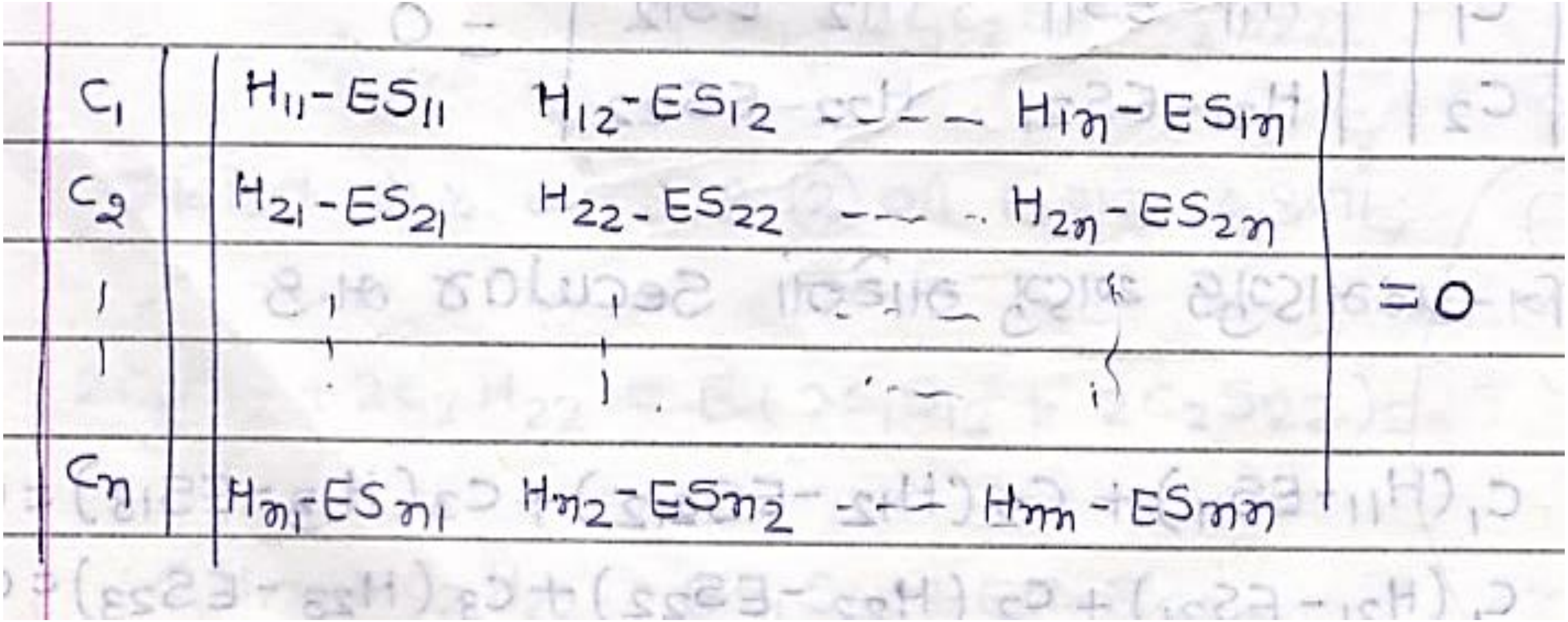
$$C_1\,(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) + \cdots + C_n(H_{1n} - ES_{1n}) = 0$$

$$C_1\,(H_{21} - ES_{21}) + C_2(H_{22} - ES_{22}) + \cdots + C_n\,(H_{2n} - ES_{2n}) = 0$$

$$C_1\,(H_{31} - ES_{31}) + C_2(H_{32} - ES_{32}) + \cdots + C_n\,(H_{3n} - ES_{3n}) = 0$$

$$C_1\,(H_{n1} - ES_{n1}) + C_2(H_{n2} - ES_{n2}) + \cdots + C_n\,(H_{nn} - ES_{nn}) = 0$$

Secular Equation & Secular Matrix for n-atomic Molecule



$$\begin{array}{c||cccc|} c_1 & H_{11}-ES_{11} & H_{12}-ES_{12} & \cdots & H_{1n}-ES_{1n} \\ c_2 & H_{21}-ES_{21} & H_{22}-ES_{22} & \cdots & H_{2n}-ES_{2n} \\ \vdots & \vdots & \vdots & \cdots & \vdots \\ c_n & H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \cdots & H_{nn}-ES_{nn} \end{array} = 0$$

Physical meaning of Integration function

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$$H_{ii} = \int \varphi_i H \varphi_i dr$$

$$H_{ij} = \int \varphi_i H \varphi_j dr$$

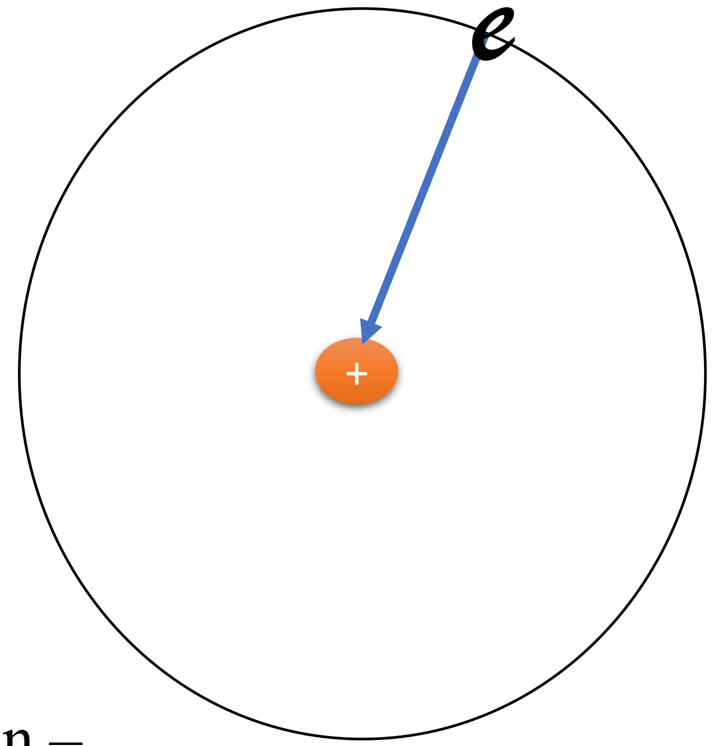
$$S_{ii} = \int \varphi_i \varphi_i dr = 1$$

$$S_{ij} = \int \varphi_i \varphi_j dr$$

Physical Meaning of following Symbol

$$H_{ii} = \int \varphi_i H \varphi_i dr = \alpha = q \qquad i = 1, 2, 3 \ldots..$$

Columbic integration function



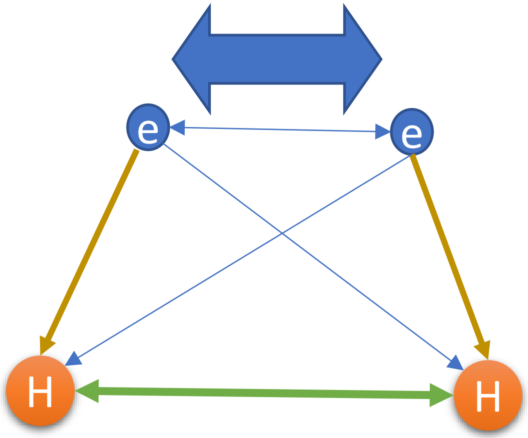
- Single wave function - Represent single atom
- H-Hemiltonian operator represent Energy of single atom
- In single atom, columbic force between Nucleus and electron – represent columbic energy.
- Attraction force between Nucleus and electron – indicate lower energy – Columbic interagral value is always negative (–ve)

Physical Meaning of following Symbol

$$H_{ij} = \int \varphi_i H \varphi_j dr = \beta \qquad i \neq j$$

$$i \,\&\, j = 1,2,3.....$$

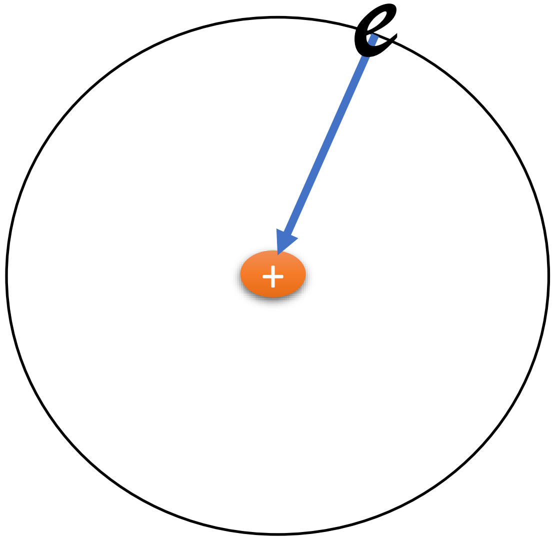
Resonance integration function



- Two wave function - Represent diatomic molecules
- H-Hemiltonian operator represent Energy of diatomic molecules
- Two atom bonding with each other – resonance between two electron
- Represented resonance energy of diatomic molecules
- No bonding between two atoms : H_{ij}=0
- Bonding between two atoms: H_{ij}>0

Physical Meaning of following Symbol

$S_{ii} = \int \varphi_i \varphi_i dr = 1$ $\quad i = 1, 2, 3, \ldots\ldots$



Normalisation integration function

- Single wave function - Represent single atom
- Do not represent Energy: (H is not present)
- Represented electron density in atom.
- Electron density is unique in atom
- Then intergral value is always unique (1)

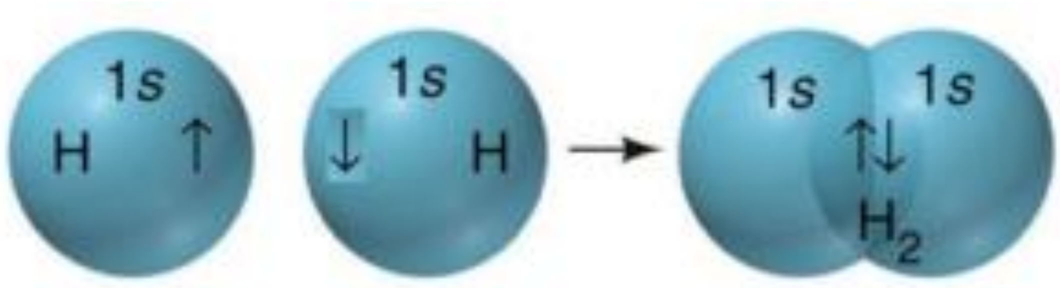
$$S_{ij} = \int \varphi_i \varphi_j dr \qquad i \neq j \qquad i \,\&\, j = 1, 2, 3, \ldots\ldots$$

Overlapping integration function

- Two wave function - Represent diatomic molecule
- Do not represent Energy: (H is not present)
- Represented electron density diatomic molecule.
- Represented Overlapping between two atom.

$S_{ij} = 0$

$S_{ij} > 0$



Energy Level for Diatomic Molecule
&
Electron distribution (Electron Density) in H_2

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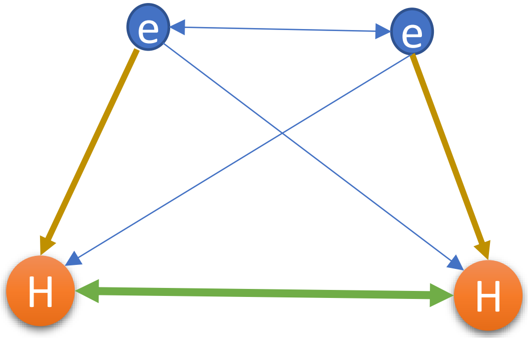
Energy level for Diatomic Molecule (H_2)



Wave function for Diatomic Molecule $\varphi = C_1\varphi_1 + C_2\varphi_2$

Energy for Diatomic Molecule

$$\begin{bmatrix} C_1 \\ C_2 \end{bmatrix} \begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} = 0$$

Where, C1 and C2 are not zero (0),

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} = 0$$

Use some symbol

$$\begin{bmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{11} - E \end{bmatrix} = 0$$

$H_{11} = H_{22} = \alpha, \leftrightarrow \varphi_1 = \varphi_2$

$H_{12} = H_{21} = \beta = H' \because Hermician\ Operator$

$S_{11} = S_{22} = 1$, Normalized condition

$$\begin{bmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{11} - E \end{bmatrix} = 0$$

$$(H_{11} - E)^2 - (H_{12} - ES_{12})^2 = 0$$

$$(H_{11} - E) \quad + (H_{12} - ES_{12}) \quad = 0$$

$$H_{11} - E + H_{12} - ES_{12} = 0$$

$$H_{11} + H_{12} - E(1 + S_{12}) = 0$$

$$H_{11} + H_{12} = E(1 + S_{12})$$

$$E = \frac{H_{11} + H_{12}}{1 + S_{12}}$$

$$E = \frac{\alpha + \beta}{1 + S_{12}}$$

$$(S_{12}) = 0$$

$$(H_{11} - E) \quad - (H_{12} - ES_{12}) \quad = 0$$

$$H_{11} - E - H_{12} + ES_{12} = 0$$

$$H_{11} - H_{12} - E(1 - S_{12}) = 0$$

$$H_{11} - H_{12} = E(1 - S_{12})$$

$$E = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

$$E = \frac{\alpha - \beta}{1 - S_{12}}$$

Columbic intriagral value is always negative (–ve)

$$E_s = \alpha + \beta \qquad E_A = \alpha - \beta$$

$$E_s < E_A$$

Energy level diagram for H2 Molecule

$E_s = \alpha + \beta$ $\qquad$ $E_A = \alpha - \beta$

$E_s < E_A$

$E_A = \alpha - 3\beta$

$E_A = \alpha - 2\beta$

$E_A = \alpha - \beta$

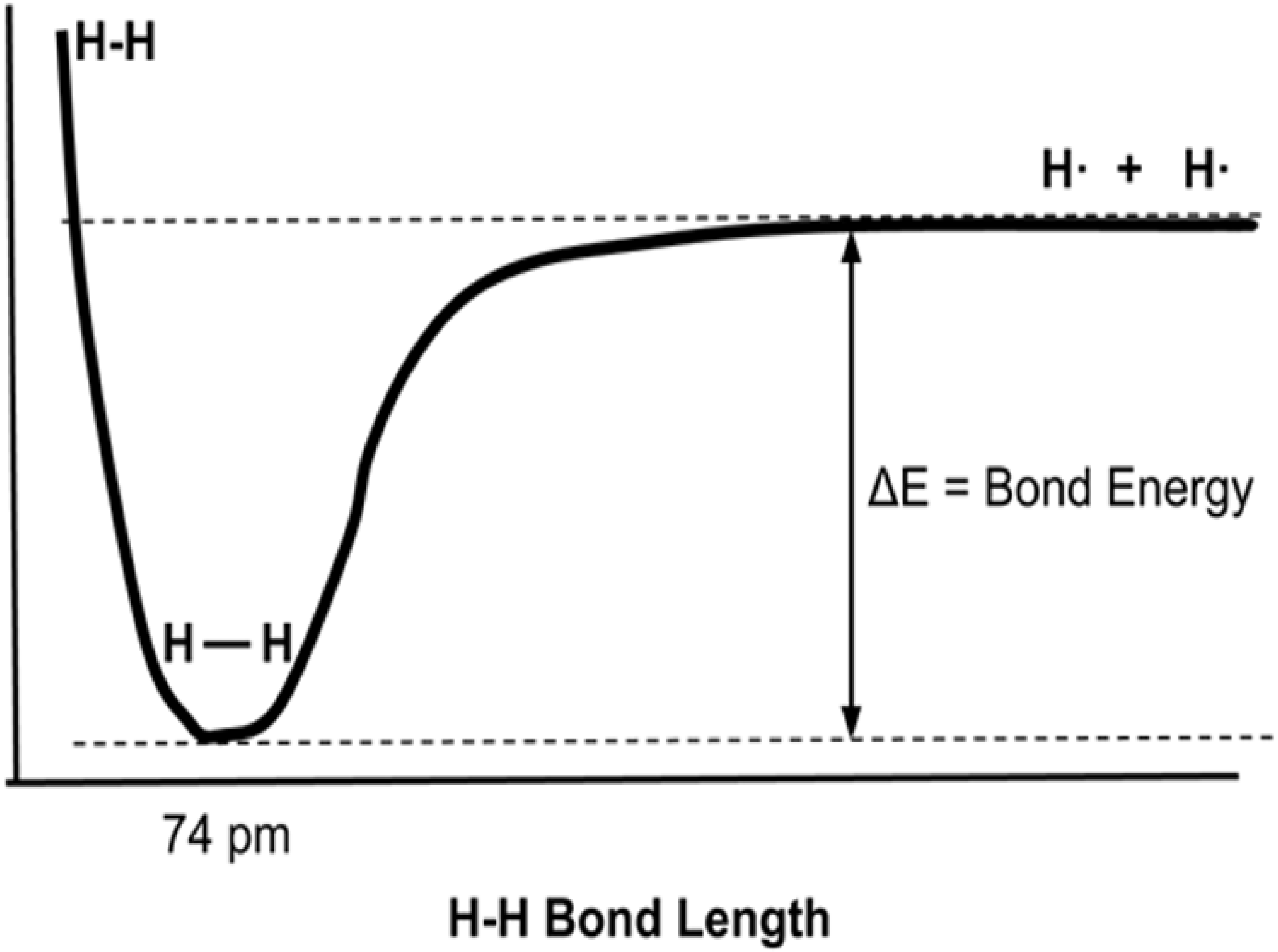
$E_s = E_A = \alpha$

$E_s = \alpha + \beta$

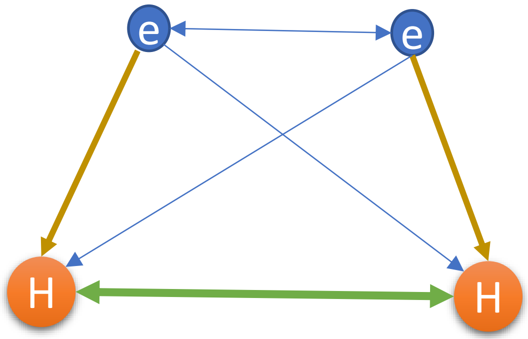
$E_s = \alpha + 2\beta$

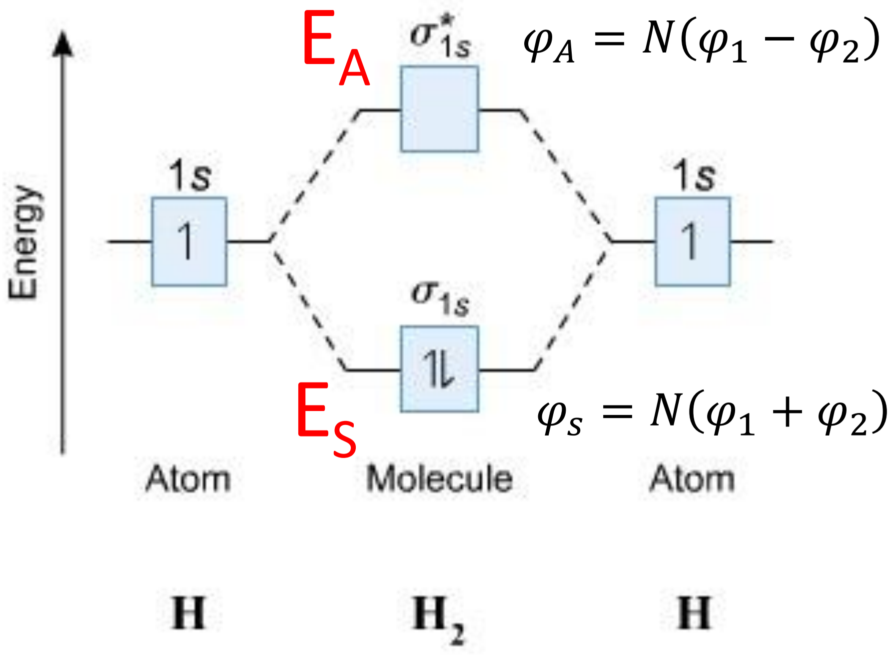
$E_s = \alpha + 3\beta$

$E_s = \alpha + 4\beta$



Electron Density distribution in H_2 Molecule





$$\varphi_A = Wave\ fuction$$

$$\varphi_A^2 = Electron\ density\ in\ ABMO$$

$$\varphi_B = Wave\ fuction$$

$$\varphi_B^2 = Electron\ density\ in\ BMO$$

$$\varphi_s = N(\varphi_1 + \varphi_2)$$

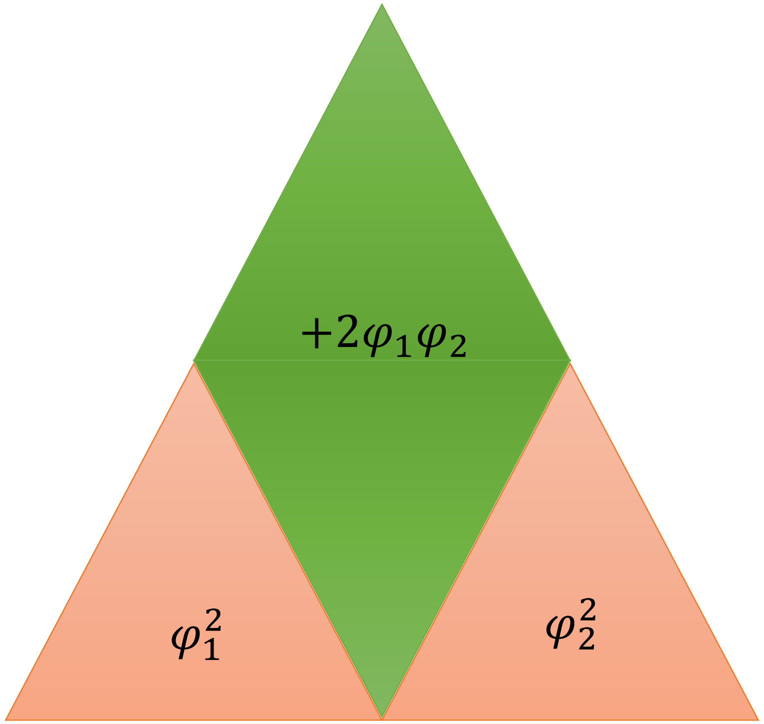
$$(\varphi_s)^2 = N^2(\varphi_1 + \varphi_2)^2$$

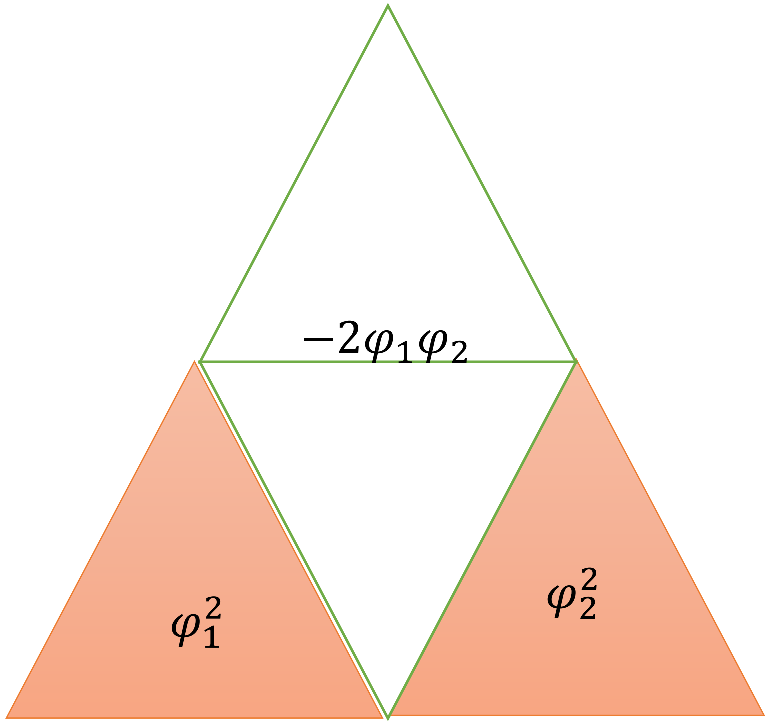
$$\varphi_A = N(\varphi_1 - \varphi_2)$$

$$(\varphi_A)^2 = N^2(\varphi_1 - \varphi_2)^2$$

$$(\varphi_s)^2 = N^2(\varphi_1^2 + \varphi_2^2 + 2\varphi_1\varphi_2)$$

$$(\varphi_A)^2 = N^2(\varphi_1^2 + \varphi_2^2 - 2\varphi_1\varphi_2)$$





B.Sc. SEMESTER-6
PAPER-601
UNIT-1 : Valency (Chemical Bonding)

Stability of Hydrogen Molecule Ion.
OR
Energy Level for H^+_2

Dr. N.I.Patel
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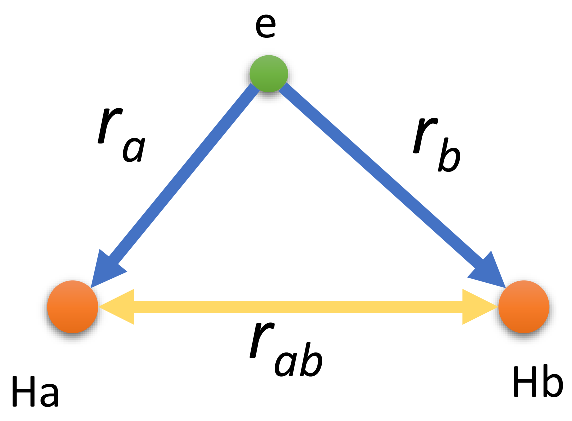
Structure and Wave function of H_2^+ molecule ion.



Molecule's possible structure

$$H_a^+ . H_b \leftrightarrow \varphi_1$$

$$H_a H_b^+ \leftrightarrow \varphi_2$$

Diatomic Molecule

$$\varphi = C_1\varphi_1 + C_2\varphi_2$$

Energy level for H_2^+ molecule ion. (Diatomic Molecule)

$$\begin{bmatrix} C_1 \\ C_2 \end{bmatrix} \begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} = 0$$

Where, C1 and C2 are not zero (0),

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} = 0$$

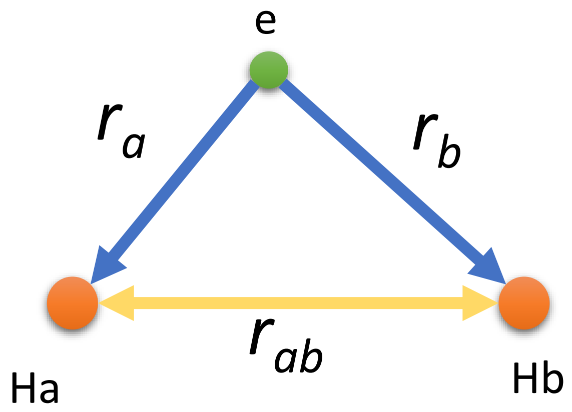
$$E_s = \frac{H_{11} + H_{12}}{1 + S_{12}} \qquad E_A = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

H_{11} (Columbic Intragyral) for H_2^+ molecule ion. (Diatomic Molecule)

$$H_{11} = \int \varphi_1 H \varphi_1 dr = \alpha = q$$

$$\text{H} = \frac{-h^2}{8\pi^2 m}\nabla^2 - V$$

$$V = \sum \pm \frac{q_1 q_2}{r}$$



$$\text{H} = \frac{-h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{r_{ab}}$$

$$H_{11} = \int \varphi_1 \left[\frac{-h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{r_{ab}}\right] \varphi_1 dr$$

$$E_0 = H_0 = \frac{-h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_a}$$

$$H_{11} = \int \varphi_1 \left[E_0 - \frac{e^2}{r_b} + \frac{e^2}{r_{ab}}\right] \varphi_1 dr$$

$$H_{11} = E_0 \int \varphi_1 \varphi_1 dr - e^2 \int \frac{1}{r_b} \varphi_1 \varphi_1 dr + \frac{e^2}{r_{ab}} \int \varphi_1 \varphi_1 dr$$

$$H_{11} = E_0 \int \varphi_1 \varphi_1 dr - e^2 \int \frac{1}{r_b} \varphi_1 \varphi_1 dr + \frac{e^2}{r_{ab}} \int \varphi_1 \varphi_1 dr$$

$$H_{11} = E_0 + \frac{e^2}{r_{ab}} - e^2 \int \frac{1}{r_b} \varphi_1 \varphi_1 dr$$

J$= e^2 \int \frac{1}{r_b} \varphi_1 \varphi_1 dr$

$$\boxed{H_{11} = E_0 + \frac{e^2}{r_{ab}} - J}$$

H_{12} (Resonance integral function)for H_2^+ molecule ion. (Diatomic Molecule)

$$H_{12} = \int \varphi_1 H \varphi_2 dr$$

$$\mathrm{H} = \frac{-h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{r_{ab}}$$

$$H_{12} = \int \varphi_1 \left[\frac{-h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{r_{ab}}\right] \varphi_2 dr$$

$$E_0 = H_0 = \frac{-h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_a}$$

$$H_{12} = \int \varphi_1 \left[E_0 - \frac{e^2}{r_b} + \frac{e^2}{r_{ab}}\right] \varphi_2 dr$$

$$H_{12} = E_0 \int \varphi_1 \varphi_2 dr - e^2 \int \frac{1}{r_b} \varphi_1 \varphi_2 dr + \frac{e^2}{r_{ab}} \int \varphi_1 \varphi_2 dr$$

$$H_{12} = E_0 S_{12} + \frac{e^2}{r_{ab}} S_{12} - e^2 \int \frac{1}{r_b} \varphi_1 \varphi_2 dr$$

$$\mathrm{K} = e^2 \int \frac{1}{r_b} \varphi_1 \varphi_2 dr$$

$$H_{12} = E_0 S_{12} + \frac{e^2}{r_{ab}} S_{12} - K$$

E_S & E_A for H_2^+ molecule ion. (Diatomic Molecule)

$$H_{11} = E_0 + \frac{e^2}{r_{ab}} - J \qquad H_{12} = E_0 S_{12} + \frac{e^2}{r_{ab}} S_{12} - K$$

$$E_s = \frac{H_{11} + H_{12}}{1 + S_{12}}$$

$$E_S = \frac{E_0 + \frac{e^2}{r_{ab}} - J + E_0 S_{12} + \frac{e^2}{r_{ab}} S_{12} - K}{1 + S_{12}}$$

$$E_S = \frac{E_0(1 + S_{12})}{1 + S_{12}} + \frac{\frac{e^2}{r_{ab}}(1 + S_{12})}{1 + S_{12}} - \frac{(J + K)}{1 + S_{12}}$$

$$\boxed{E_S = E_0 + \frac{e^2}{r_{ab}} - \frac{(J + K)}{1 + S_{12}}}$$

$$E_A = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

$$E_A = \frac{E_0 + \frac{e^2}{r_{ab}} - J - E_0 S_{12} - \frac{e^2}{r_{ab}} S_{12} + K}{1 - S_{12}}$$

$$E_A = \frac{E_0(1 - S_{12})}{1 - S_{12}} + \frac{\frac{e^2}{r_{ab}}(1 - S_{12})}{1 - S_{12}} - \frac{(J - K)}{1 - S_{12}}$$

$$\boxed{E_A = E_0 + \frac{e^2}{r_{ab}} - \frac{(J - K)}{1 - S_{12}}}$$

$$E_S = E_0 + \frac{e^2}{r_{ab}} - \frac{(J+K)}{1+S_{12}}$$

$$E_A = E_0 + \frac{e^2}{r_{ab}} - \frac{(J-K)}{1-S_{12}}$$

$$S_{12} = 0$$

$$E_S = E_0 + \frac{e^2}{r_{ab}} - J - K$$

$$E_A = E_0 + \frac{e^2}{r_{ab}} - J + K$$

$$H_{11} = E_0 + \frac{e^2}{r_{ab}} - J$$

$$E_S = H_{11} - K = \alpha - K$$

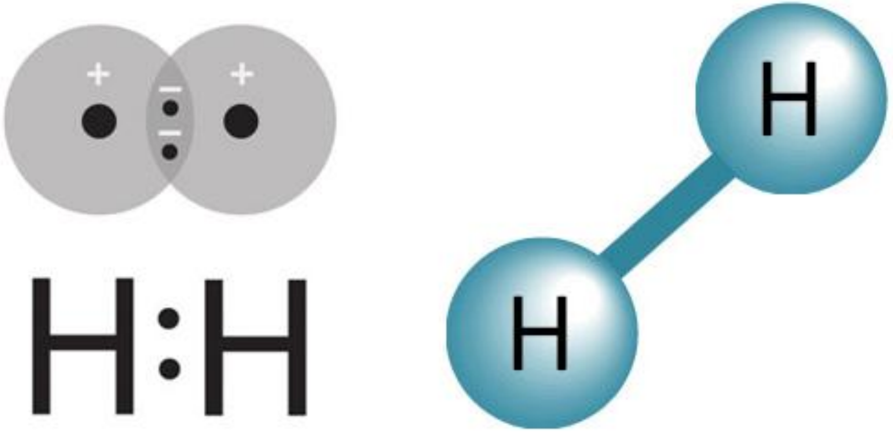
$$E_A = H_{11} + K = \alpha + K$$

$$E_S > E_A$$

$$K = e^2 \int \frac{1}{r_b} \varphi_1 \varphi_2 dr$$

B.Sc. SEMESTER-6
PAPER-601
UNIT-1 : Valency (Chemical Bonding)

Stability of H_2 Molecule.
&
Energy Level for H_2



Hydrogen (H_2)

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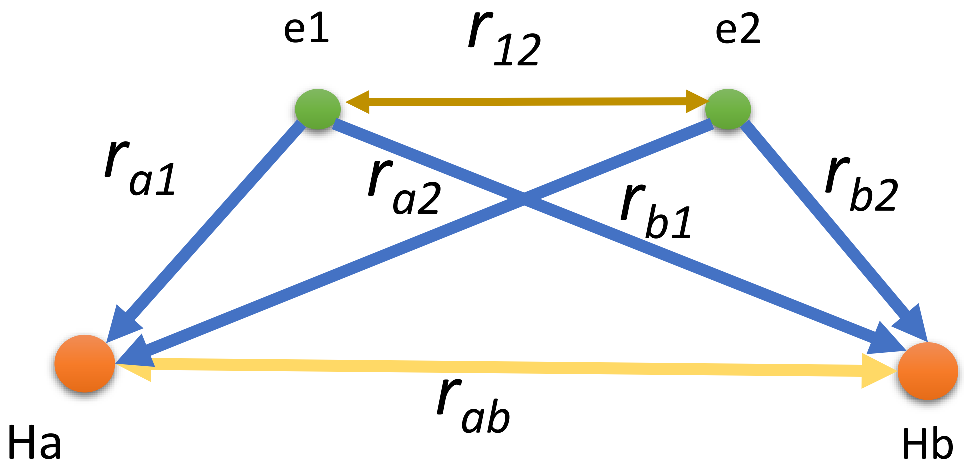
Chemistry Department,
The HNSB. Ltd. Science College, Himatnagar

Structure and Wave function of H_2 molecule.



Molecule's possible structure & wave function

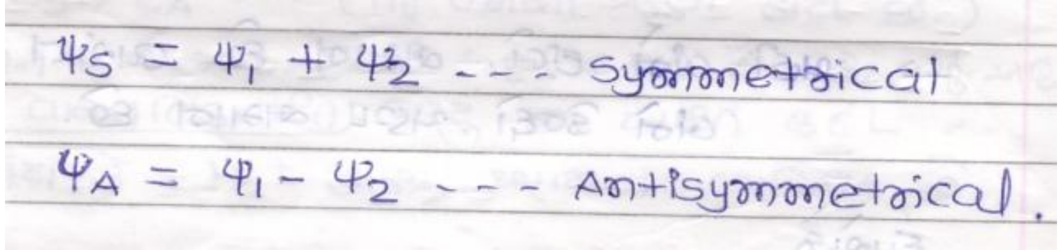
$$H_{A(1)}H_{B(2)} = \varphi_{a(1)}\varphi_{b(2)} = \varphi_1$$

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

Diatomic Molecule $\varphi = C_1\varphi_1 + C_2\varphi_2$

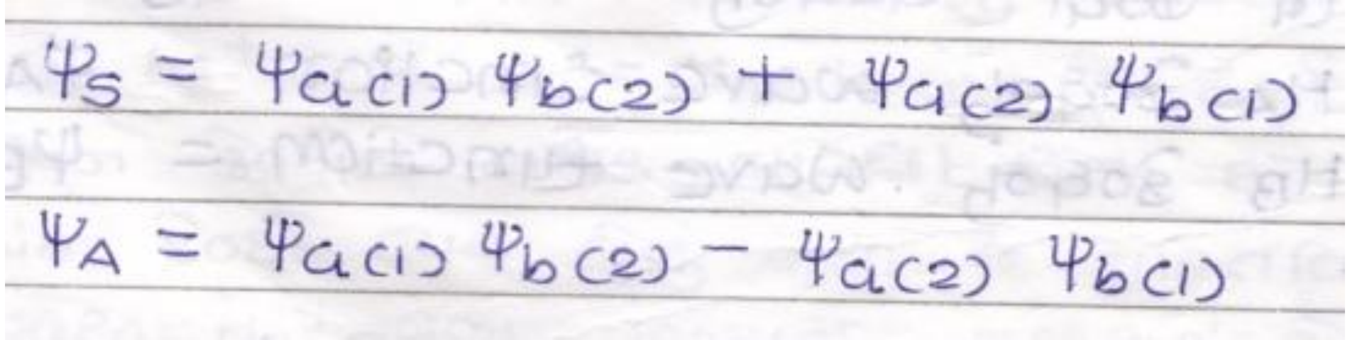
Other Wave function

Covalent Wave Function



$\psi_S = \psi_1 + \psi_2$ --- symmetrical

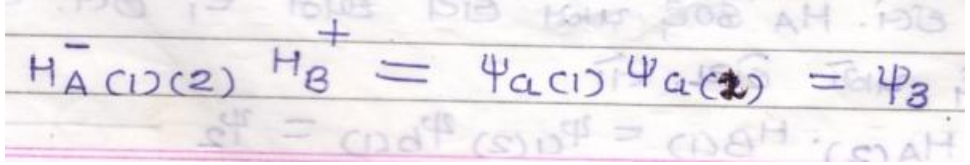
$\psi_A = \psi_1 - \psi_2$ --- Antisymmetrical.



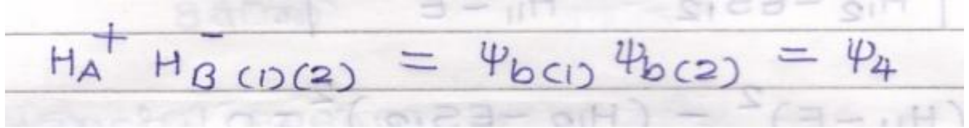
$\psi_S = \psi_{a(1)} \psi_{b(2)} + \psi_{a(2)} \psi_{b(1)}$

$\psi_A = \psi_{a(1)} \psi_{b(2)} - \psi_{a(2)} \psi_{b(1)}$

Ionic Wave Function



$H_{A(1)(2)}^{-} H_B^{+} = \psi_{a(1)} \psi_{a(2)} = \psi_3$



$H_A^{+} H_{B(1)(2)}^{-} = \psi_{b(1)} \psi_{b(2)} = \psi_4$

These wave function are:

Angular Wave function

n, l and m dependent w.f.

Energy level for H_2 molecule. (Diatomic Molecule)

$$\begin{bmatrix} C_1 \\ C_2 \end{bmatrix} \begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} = 0$$

Where, C1 and C2 are not zero (0),

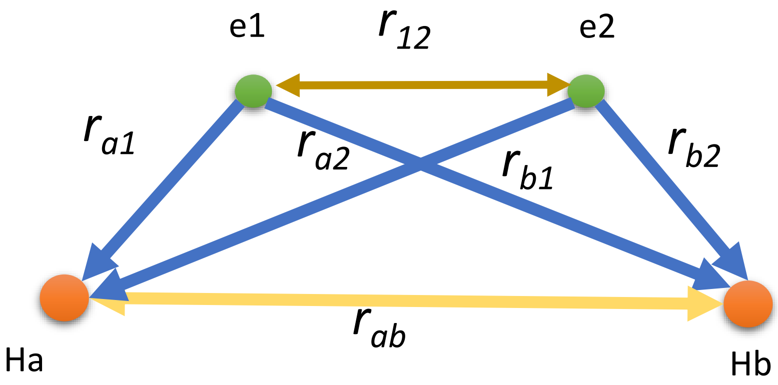
$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} = 0$$

$$E_S = \frac{H_{11} + H_{12}}{1 + S_{12}}$$

$$E_A = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

H_{11} (Columbic Intragyral) for H_2 molecule. (Diatomic Molecule)

$$H_{11} = \int \varphi_1 H \varphi_1 dr = \alpha = q$$



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

$$H = -\frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{ab}}$$

$$H_{11} = \int \varphi_1 \left[-\frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{ab}} \right] \varphi_1 \, . dr$$

$$2E_0 = -\frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{b2}}$$

$$H_{11} = \int \varphi_1 \left[2E_0 - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{ab}} \right] \varphi_1 \, . dr$$

$$H_{11} = 2E_0 \int \varphi_1^2 dr - e^2 \int \frac{1}{r_{a(2)}} \varphi_1^2 dr - e^2 \int \frac{1}{r_{b(1)}} \varphi_1^2 dr + e^2 \int \frac{1}{r_{12}} \varphi_1^2 dr + \frac{e^2}{r_{ab}} \int \varphi_1^2 dr$$

$$H_{11} = 2E_0 + \frac{e^2}{r_{ab}} \; - e^2 \int \frac{1}{r_{a(2)}} \varphi_1^2 dr - e^2 \int \frac{1}{r_{b(1)}} \varphi_1^2 dr + e^2 \int \frac{1}{r_{12}} \varphi_1^2 dr$$

$$\boxed{H_{11} = 2E_0 + \frac{e^2}{r_{ab}} + J_1 - 2J_2}$$

$$J_2 = e^2 \int \frac{1}{r_{a(2)}} \varphi_1^2 dr = e^2 \int \frac{1}{r_{b(1)}} \varphi_1^2 dr$$

$$J_1 = e_2 \int \frac{1}{r_{12}} \varphi_1^2 dr$$

H_{12} (Resonance intragyral function) for H_2 molecule. (Diatomic Molecule)

$$H_{12} = \int \varphi_1 H \varphi_2 dr$$

$$\varphi_1 = \varphi_{a(1)}\varphi_{b(2)}$$

$$\varphi_2 = \varphi_{a(2)}\varphi_{b(1)}$$

$$H = -\frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{ab}}$$

$$H_{12} = \int \varphi_1 \left[-\frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{ab}}\right] \varphi_2 \, . dr$$

$$H_{12} = \int \varphi_1 \left[2E_0 - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{ab}}\right] \varphi_2 \, . dr$$

$$2E_0 = -\frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{b2}}$$

$$H_{12} = 2E_0 \int \varphi_1\varphi_2 dr - e^2 \int \frac{1}{r_{a(2)}} \varphi_1\varphi_2 dr - e^2 \int \frac{1}{r_{b(1)}} \varphi_1\varphi_2 dr + e^2 \int \frac{1}{r_{12}} \varphi_1\varphi_2 dr + \frac{e^2}{r_{ab}} \int \varphi_1\varphi_2 dr$$

$$H_{12} = 2E_0S_{12} + \frac{e^2}{r_{ab}}S_{12} - e^2\int \frac{1}{r_{a(2)}}\varphi_1\varphi_2 dr - e^2\int \frac{1}{r_{b(1)}}\varphi_1\varphi_2 dr + e^2\int \frac{1}{r_{12}}\varphi_1\varphi_2 dr$$

$$K_2 = e^2\int \frac{1}{r_{a(2)}}\varphi_1\varphi_2 dr = e^2\int \frac{1}{r_{b(1)}}\varphi_1\varphi_2 dr$$

$$K_1 = e^2\int \frac{1}{r_{12}}\varphi_1\varphi_2 dr$$

$$\boxed{H_{12} = 2E_0S_{12} + \frac{e^2}{r_{ab}}S_{12} + K_1 - 2K_2}$$

$$E_s = \frac{H_{11} + H_{12}}{1 + S_{12}} \qquad H_{11} = 2E_0 + \frac{e^2}{r_{ab}} + J_1 - 2J_2 \qquad H_{12} = 2E_0 S_{12} + \frac{e^2}{r_{ab}} S_{12} + K_1 - 2K_2 \qquad E_A = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

$$E_s = \frac{2E_0 + \frac{e^2}{r_{ab}} + J_1 - 2J_2 + 2E_0 S_{12} + \frac{e^2}{r_{ab}} S_{12} + K_1 - 2K_2}{1 + S_{12}}$$

$$E_s = 2E_0 + \frac{e^2}{r_{ab}} + \frac{J_1 - 2J_2 + K_1 - 2K_2}{1 + S_{12}}$$

$$E_s = 2E_0 + \frac{e^2}{r_{ab}} + J_1 - 2J_2 + K_1 - 2K_2$$

$$E_s = H_{11} + (K_1 - 2K_2)$$

$$S_{12} = 0$$

$$E_A = \frac{2E_0 + \frac{e^2}{r_{ab}} + J_1 - 2J_2 - 2E_0 S_{12} - \frac{e^2}{r_{ab}} S_{12} - K_1 + 2K_2}{1 - S_{12}}$$

$$E_A = 2E_0 + \frac{e^2}{r_{ab}} + \frac{J_1 - 2J_2 - K_1 + 2K_2}{1S_{12}}$$

$$E_A = 2E_0 + \frac{e^2}{r_{ab}} + J_1 - 2J_2 - K_1 + 2K_2$$

$$E_A = H_{11} - (K_1 - 2K_2)$$

$$E_s < E_A$$

$$K_2 = e^2 \int \frac{1}{r_{a(2)}} \varphi_1 \varphi_2 dr = e^2 \int \frac{1}{r_{b(1)}} \varphi_1 \varphi_2 dr$$

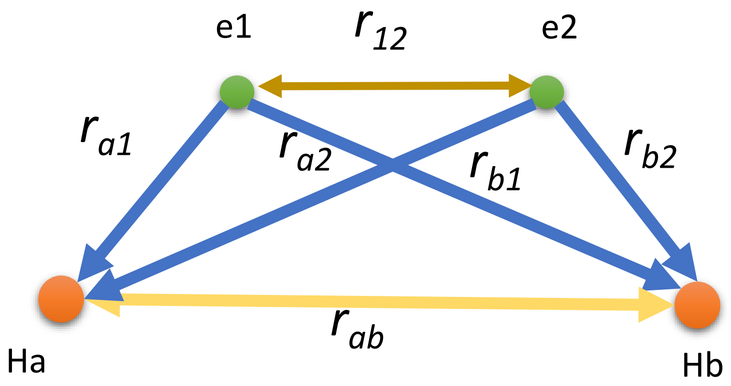
$$K_1 = e^2 \int \frac{1}{r_{12}} \varphi_1 \varphi_2 dr$$

B.Sc. SEMESTER-6
PAPER-601
UNIT-1 : Valency (Chemical Bonding)

Classical Interaction Energy for H_2 Molecule

Dr. N.I.Patel
Chemistry Department,
The HNSB. Ltd. Science College, Himatnagar

Classical Interaction Energy of H_2 molecule.



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

$$E = \frac{\int_{-\infty}^{+\infty} \varphi H \varphi \ dr}{\int_{+\infty}^{+\infty} \varphi \varphi \, dr}$$

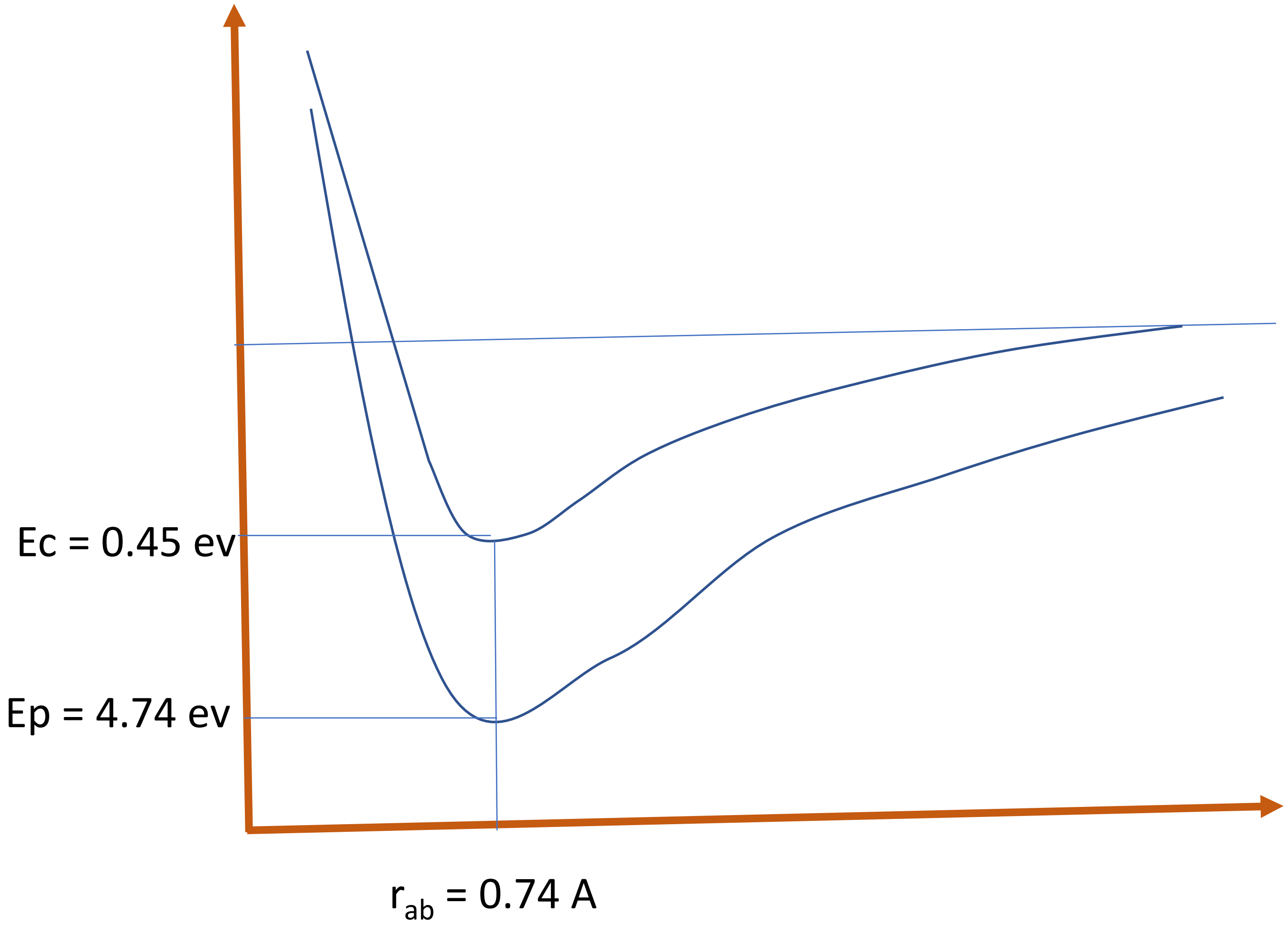
$$E_0 = \frac{H_{11}}{S_{11}}$$

$$J_1 = e_2 \int \frac{1}{r_{12}} \varphi_1^2 dr$$

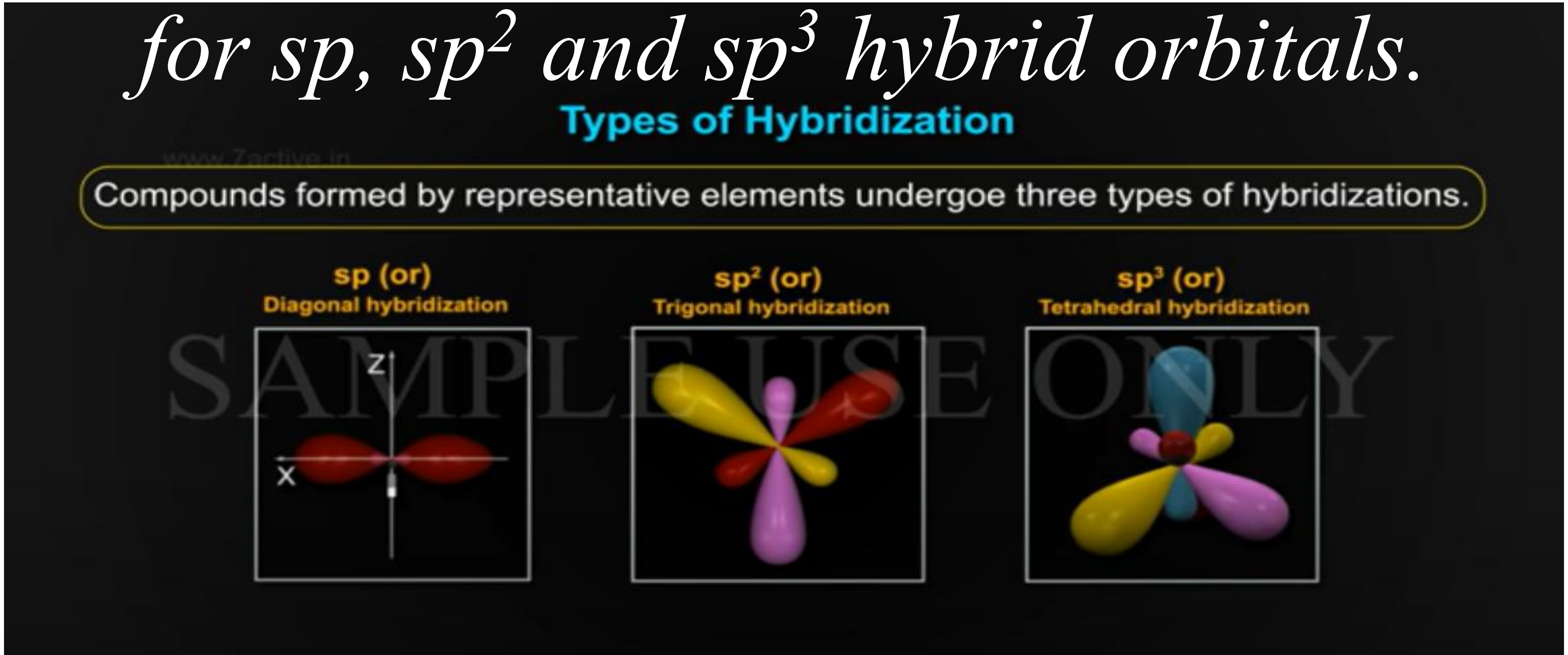
$$E_C = H_{11} = 2E_0 + \frac{e^2}{r_{ab}} + J_1 - 2J_2$$

$$J_2 = e^2 \int \frac{1}{r_{a(2)}} \varphi_1^2 dr = e^2 \int \frac{1}{r_{b(1)}} \varphi_1^2 dr$$

$$E_C = H_{11} = 2E_0 + \frac{e^2}{r_{ab}} + J_1 - 2J_2$$



Representation of Wave function, Bond strength and Bond angle for sp, sp^2 and sp^3 hybrid orbitals.



Types of Hybridization

Compounds formed by representative elements undergoe three types of hybridizations.

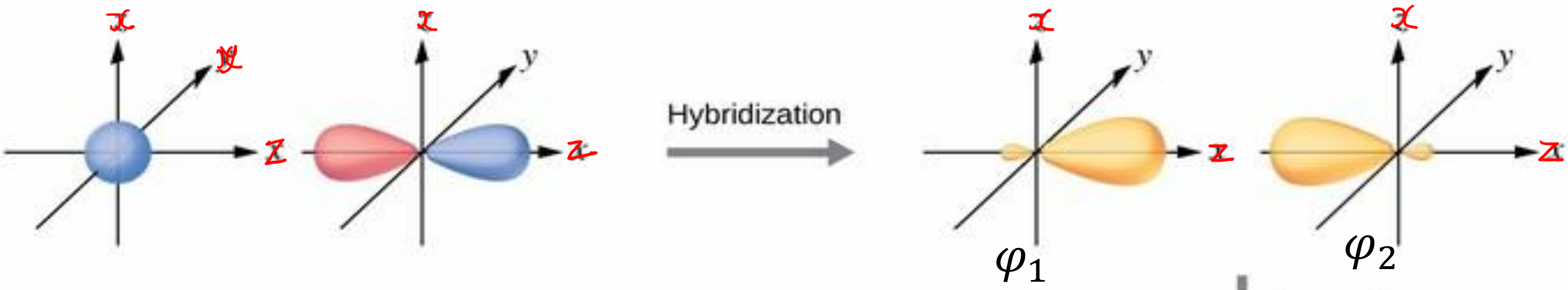
sp (or)
Diagonal hybridization

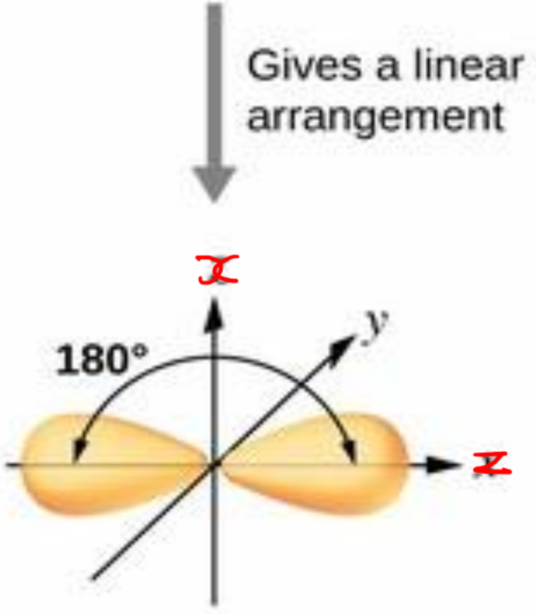
sp^2 (or)
Trigonal hybridization

sp^3 (or)
Tetrahedral hybridization

Wave function of *sp* hybrid orbitals

$BeCl_2$; CO_2, $HgCl_2$





Wave function by LCAO

$$\varphi_1 = a_1\varphi_s + b_1\varphi_{pz}$$

$$\varphi_2 = a_2\varphi_s + b_2\varphi_{pz}$$

Define values of constant

1. Equivalent Law (સમતુલ્યતાની શરત)
2. Normalization Law (સમાનીકરણ શરત)
3. Orthogonal Law (લંબત્વ શરત)

1. Equivalent Law S-orbital is spherical & contribution of S-orbital is equal to all wave function of hybrid orbitals.

S કક્ષકના તરંગ ફલનના સહગુણાકનો વર્ગ = S કક્ષકનો ફાળો

$$\varphi_1 = a_1\varphi_s + b_1\varphi_{pz}$$
$$\varphi_2 = a_2\varphi_s + b_2\varphi_{pz}$$

$$a_1^2 = a_2^2 = \frac{1}{2}$$

$$\boxed{a_1 = a_2 = \frac{1}{\sqrt{2}}}$$

2. Normalization Law

$\int \varphi_1^2\, dr = 1 \leftrightarrow a_1^2 + b_1^2 = 1$

$\varphi_1 = a_1\varphi_s + b_1\varphi_{pz}$

$b_1 = \frac{1}{\sqrt{2}}$

3. Orthogonal Law

$\int \varphi_1\varphi_2\, dr = 0 \leftrightarrow a_1a_2 + b_1b_2 = 0$

$$\varphi_1 = a_1\varphi_s + b_1\varphi_{pz}$$
$$\varphi_2 = a_2\varphi_s + b_2\varphi_{pz}$$

$b_2 = -\frac{1}{\sqrt{2}}$

$$\varphi_1 = \frac{1}{\sqrt{2}}\varphi_s + \frac{1}{\sqrt{2}}\varphi_{pz} \qquad \varphi_2 = \frac{1}{\sqrt{2}}\varphi_s - \frac{1}{\sqrt{2}}\varphi_{pz}$$

Cartesian wave function of orbitals

$$\boxed{\varphi_s = \frac{1}{\sqrt{4\pi}}}$$

$$\boxed{\varphi_{px} = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\emptyset}$$

$$\boxed{\varphi_{py} = \sqrt{\frac{3}{4\pi}}\sin\theta\, sin\,\emptyset}$$

$$\boxed{\varphi_{pz} = \sqrt{\frac{3}{4\pi}}\cos\theta}$$

$$\varphi_1 = \frac{1}{\sqrt{2}}\varphi_s + \frac{1}{\sqrt{2}}\varphi_{pz}$$

$$\varphi_2 = \frac{1}{\sqrt{2}}\varphi_s - \frac{1}{\sqrt{2}}\varphi_{pz}$$

$$\varphi_1 = \frac{1}{\sqrt{4\pi}}\frac{1}{\sqrt{2}}\left(1 + \sqrt{3}\cos\theta\right)$$

$$\varphi_2 = \frac{1}{\sqrt{4\pi}}\frac{1}{\sqrt{2}}\left(1 - \sqrt{3}\cos\theta\right)$$

Bond Strength

$$B.S. = \frac{\varphi_1(max)}{\varphi_s} = \frac{\varphi_2(max)}{\varphi_s}$$

$$\varphi_1 = \frac{1}{\sqrt{4\pi}}\frac{1}{\sqrt{2}}\left(1+\sqrt{3}\cos\theta\right)$$

$$\cos(0) = 1$$

$$\cos(180) = -1$$

$$B.S. = \frac{\frac{1}{\sqrt{4\pi}}\frac{1}{\sqrt{2}}\left(1+\sqrt{3}\right)}{\frac{1}{\sqrt{4\pi}}}$$

$$\varphi_1 max = \frac{1}{\sqrt{4\pi}}\frac{1}{\sqrt{2}}\left(1+\sqrt{3}\right)$$

$$B.S. = \frac{1}{\sqrt{2}}\left(1+\sqrt{3}\right)$$

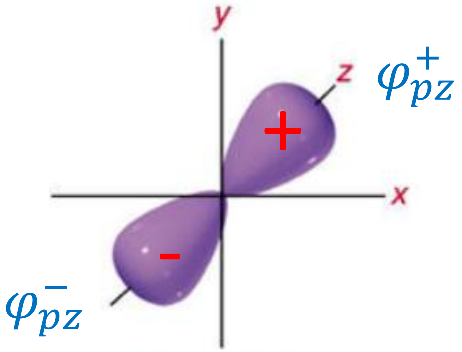
$$B.S. = \frac{1}{1.4142}(1+1.7320)$$

$$B.S.(sp\ hybrid\ orbital) = 1.932$$

Bond Angle

$$\varphi_1 = \frac{1}{\sqrt{2}}\varphi_s + \frac{1}{\sqrt{2}}\varphi_{pz}$$

$$\int \varphi_1'\varphi_1'' \quad dr = 0$$



2p$_z$ orbital

$$\boxed{\varphi_1' = \frac{1}{\sqrt{2}}\varphi_s + \frac{1}{\sqrt{2}}\varphi_{pz}^{+}}$$

$$\boxed{\varphi_1'' = \frac{1}{\sqrt{2}}\varphi_s + \frac{1}{\sqrt{2}}\varphi_{pz}^{-}}$$

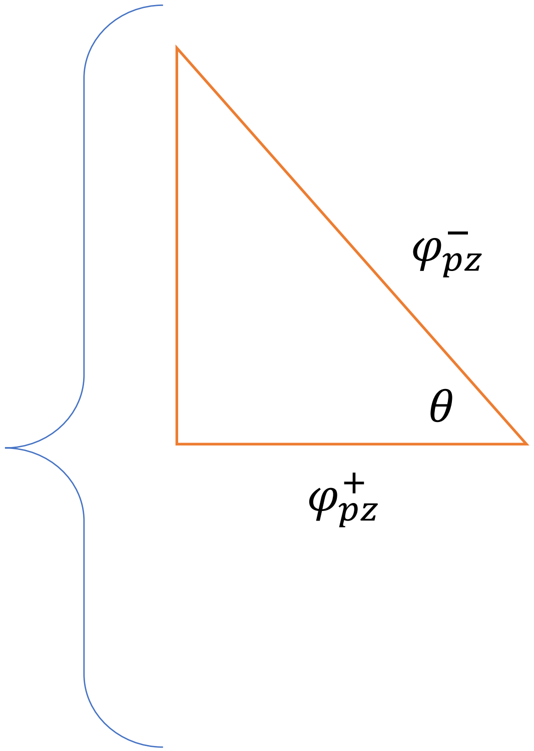
$$\int \left(\frac{1}{\sqrt{2}}\varphi_s + \frac{1}{\sqrt{2}}\varphi_{pz}^{+}\right)\left(\frac{1}{\sqrt{2}}\varphi_s + \frac{1}{\sqrt{2}}\varphi_{pz}^{-}\right) dr = 0$$

$$\frac{1}{2}\int \varphi_s^2\, dr + \frac{1}{2}\int \varphi_s\varphi_{pz}^{-}\, dr + \frac{1}{2}\int \varphi_s\varphi_{pz}^{+} dr + \frac{1}{2}\int \varphi_z^{+}\varphi_z^{-} dr = 0$$

$$\frac{1}{2} + \frac{1}{2}\int \varphi_z^{+}\varphi_z^{-} dr = 0$$

$$\frac{1}{2} + \frac{1}{2}\cos\theta \int \varphi_z^{-}\varphi_z^{-} dr = 0$$

$$\frac{1}{2} + \frac{1}{2}\cos\theta = 0$$



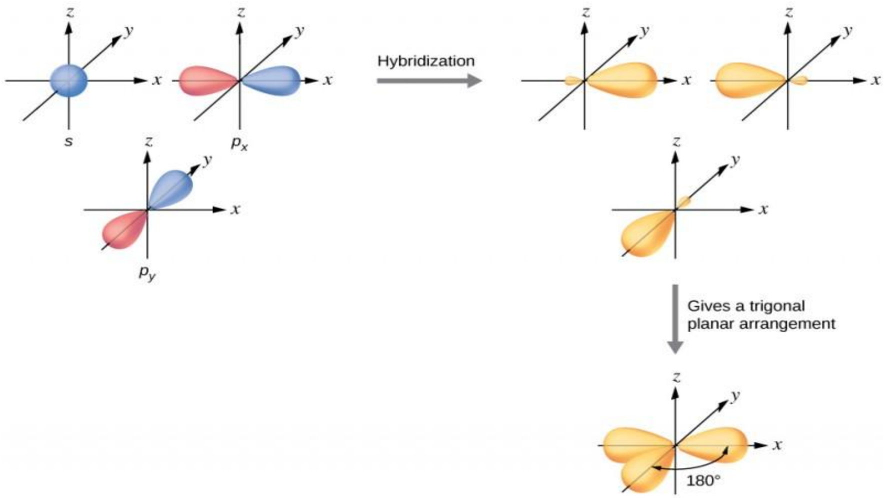
$$\cos\theta = \frac{\varphi_{pz}^{+}}{\varphi_{pz}^{-}}$$

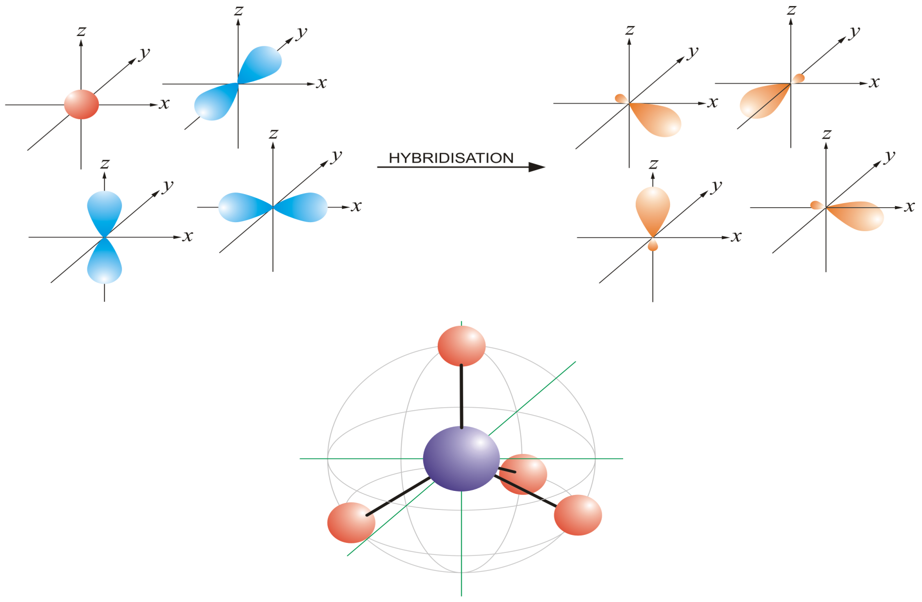
$$\theta = cos^{-1}(-1)$$

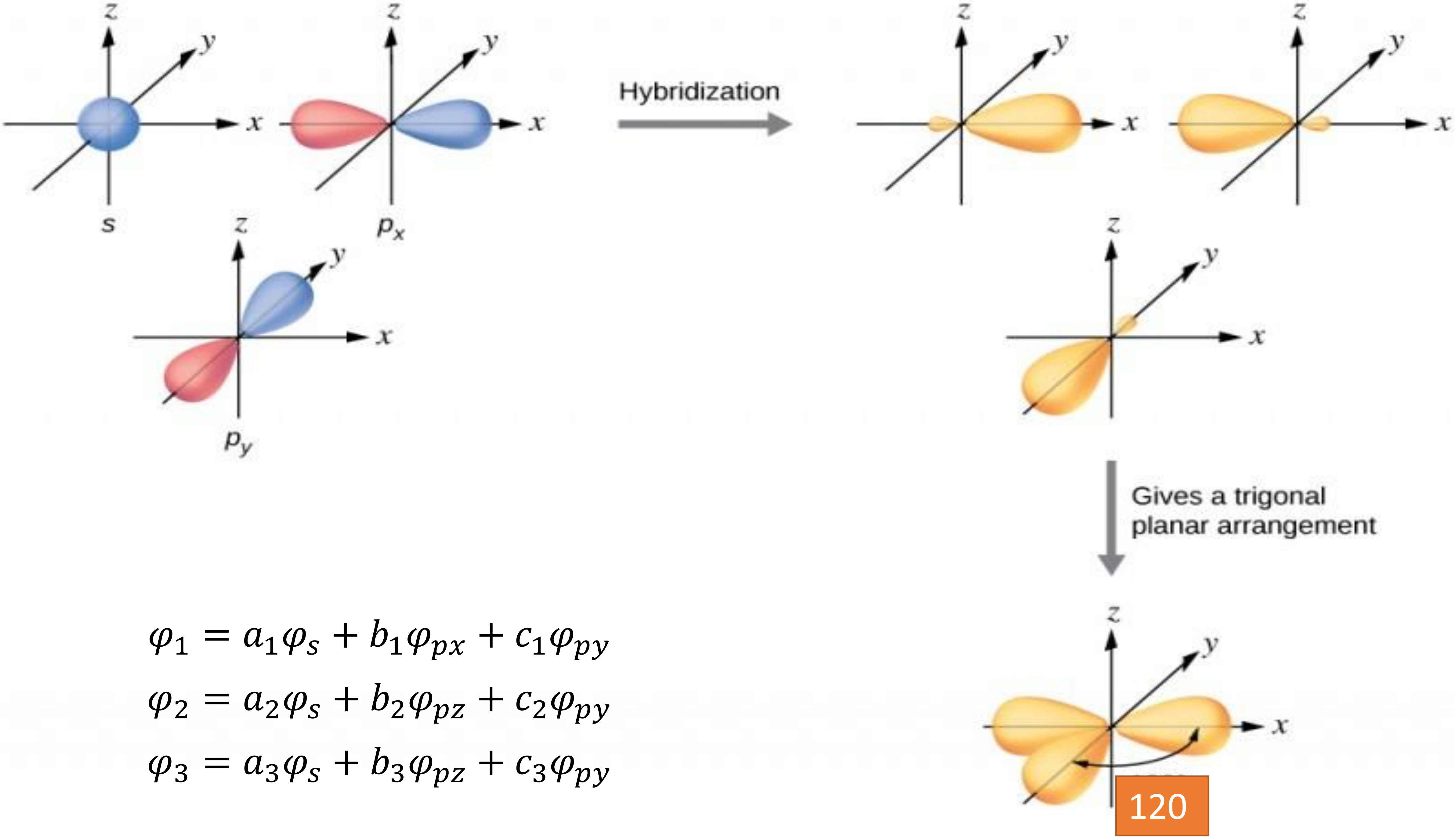
$$\theta = 180$$

Sp^2 & Sp^3 Hybridization

Wave function
Bond strength
Bond angle







$$\varphi_1 = a_1\varphi_s + b_1\varphi_{px} + c_1\varphi_{py}$$

$$\varphi_2 = a_2\varphi_s + b_2\varphi_{pz} + c_2\varphi_{py}$$

$$\varphi_3 = a_3\varphi_s + b_3\varphi_{pz} + c_3\varphi_{py}$$

Define values of constant

Equivalent Law $a_1^2 = a_2^2 = a_3^2 = \frac{1}{3}$

$$\boxed{a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}}$$

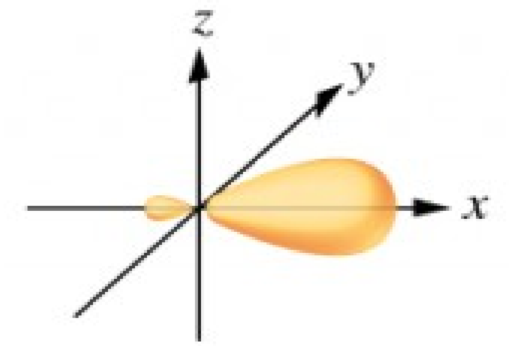
$$\varphi_1 = a_1\varphi_s + b_1\varphi_{px} + c_1\varphi_{py}$$

$$\varphi_2 = a_2\varphi_s + b_2\varphi_{pz} + c_2\varphi_{py}$$

$$\varphi_3 = a_3\varphi_s + b_3\varphi_{pz} + c_3\varphi_{py}$$

$\varphi_1\ H.O.\ is\ on\ the\ x\ axis$

$Contribution\ of\ Px \ggg Py\ in\ \varphi_1\ H.O.$



$$\boxed{c_1 = 0}$$

Normalisation and Orthogonality rules

$$\int \varphi_1^2\, dr = 1 \leftrightarrow a_1^2 + b_1^2 + c_1^2 = 1$$

$$b_1 = \sqrt{\frac{2}{3}}$$

$$\int \varphi_1 \varphi_2\, dr = 0 \leftrightarrow a_1 a_2 + b_1 b_2 + c_1 c_2 = 0$$

$$b_2 = -\sqrt{\frac{1}{6}}$$

$$\int \varphi_2^2\, dr = 1 \leftrightarrow a_2^2 + b_2^2 + c_2^2 = 1$$

$$c_2 = \sqrt{\frac{1}{2}}$$

$$\int \varphi_1 \varphi_3\, dr = 0 \leftrightarrow a_1 a_3 + b_1 b_3 + c_1 c_3 = 0$$

$$b_3 = -\sqrt{\frac{1}{6}}$$

$$\int \varphi_2 \varphi_3\, dr = 0 \leftrightarrow a_2 a_3 + b_2 b_3 + c_2 c_3 = 0$$

$$c_3 = -\sqrt{\frac{1}{2}}$$

$$\varphi_1 = \frac{1}{\sqrt{3}} \varphi_s + \sqrt{\frac{2}{3}} \varphi_{px}$$

$$\varphi_2 = \frac{1}{\sqrt{3}} \varphi_s - \frac{1}{\sqrt{6}} \varphi_{pz} + \sqrt{\frac{1}{2}} \varphi_{py}$$

$$\varphi_3 = \frac{1}{\sqrt{3}} \varphi_s - \sqrt{\frac{1}{6}} \varphi_{pz} - \sqrt{\frac{1}{2}} \varphi_{py}$$

$$\varphi_s = \frac{1}{\sqrt{4\pi}}$$

$$\varphi_{px} = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\emptyset$$

$$\varphi_{py} = \sqrt{\frac{3}{4\pi}}\sin\theta\; sin\,\emptyset$$

$$\varphi_{pz} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$\varphi_1 = \frac{1}{\sqrt{3}}\varphi_s + \sqrt{\frac{2}{3}}\varphi_{px}$$

$$\varphi_1 = \frac{1}{\sqrt{3}}\frac{1}{\sqrt{4\pi}} + \sqrt{\frac{2}{3}}\sqrt{\frac{3}{4\pi}}\sin\theta\cos\emptyset$$

$$\sin\theta = \sin 90 = 1$$

$$\varphi_1 = \frac{1}{\sqrt{3}}\frac{1}{\sqrt{4\pi}}\left(1 + \sqrt{6}\cos\emptyset\right)$$

Bond Strength

$$B.S. = \frac{\varphi_1(max)}{\varphi_s} = \frac{\varphi_2(max)}{\varphi_s}$$

$$\boxed{\varphi_1 = \frac{1}{\sqrt{3}}\frac{1}{\sqrt{4\pi}}(1+\sqrt{6}\cos\emptyset)}$$

$$\cos(0) = 1$$

$$\cos(180) = -1$$

$$\boxed{\varphi_{1max} = \frac{1}{\sqrt{3}}\frac{1}{\sqrt{4\pi}}(1+\sqrt{6})}$$

$$B.S. = \frac{\frac{1}{\sqrt{3}}\frac{1}{\sqrt{4\pi}}(1+\sqrt{6})}{\frac{1}{\sqrt{4\pi}}}$$

$$B.S. = \frac{1}{\sqrt{3}}(1+\sqrt{6})$$

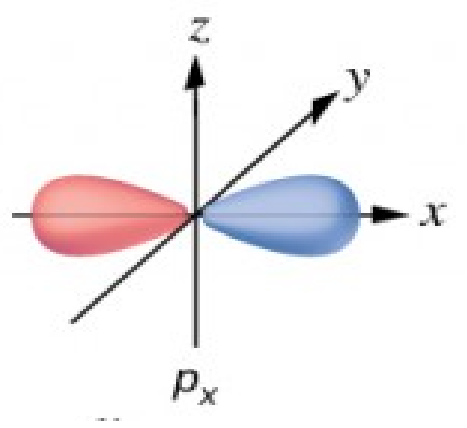
$$B.S. = \frac{1}{1.7320}(1+2.4494)$$

$$B.S. of\ sp2\ hybrid\ orbitals = 1.992$$

Bond Angle

$$\boxed{\varphi_1 = \frac{1}{\sqrt{3}}\varphi_s + \sqrt{\frac{2}{3}}\varphi_{px}}$$

$$\varphi_1' = \frac{1}{\sqrt{3}}\varphi_s + \sqrt{\frac{2}{3}}\varphi_{px}^{+} \qquad \varphi_1'' = \frac{1}{\sqrt{3}}\varphi_s + \sqrt{\frac{2}{3}}\varphi_{px}^{-}$$



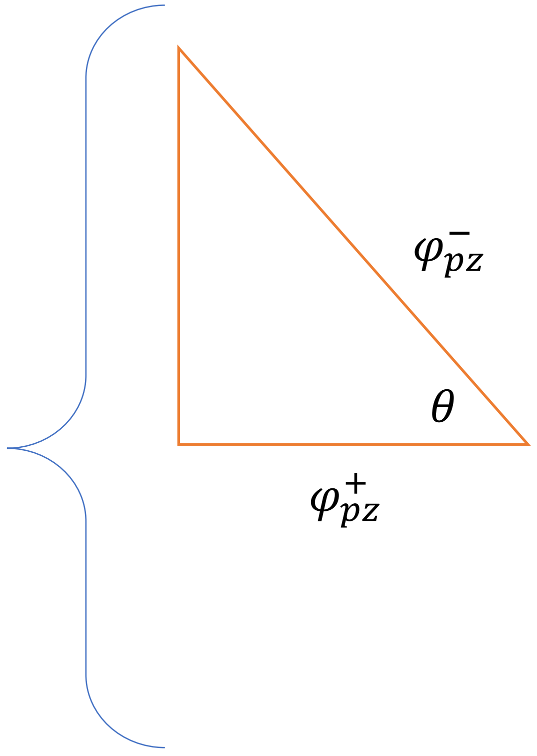
$$\int \varphi_1' \varphi_1'' dr = 0$$

$$\int\left(\frac{1}{\sqrt{3}}\varphi_s + \sqrt{\frac{2}{3}}\,\varphi_{px}^{+}\right)\left(\frac{1}{\sqrt{3}}\varphi_s + \sqrt{\frac{2}{3}}\,\varphi_{px}^{-}\right)dr = 0$$

$$\frac{1}{3}\int \varphi_s^2\,dr + \frac{\sqrt{2}}{3}\int \varphi_s\varphi_{pz}^{-}\,dr + \frac{\sqrt{2}}{3}\int \varphi_s\varphi_{pz}^{+}dr + \frac{2}{3}\int \varphi_z^{+}\varphi_z^{-}dr = 0$$

$$\frac{1}{3} + \frac{2}{3}\int \varphi_z^{+}\varphi_z^{-}dr = 0$$

$$\frac{1}{3} + \frac{2}{3}\cos\theta\int \varphi_z^{-}\varphi_z^{-}dr = 0$$



$$\cos\theta = \frac{\varphi_{pz}^{+}}{\varphi_{pz}^{-}}$$

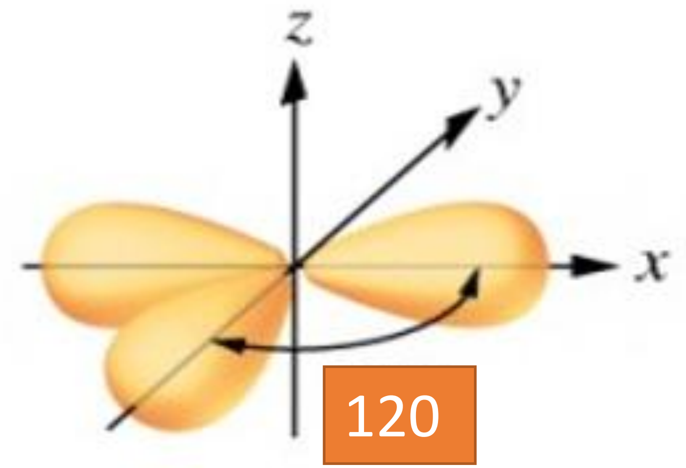
$$\frac{1}{3}+\frac{2}{3}\cos\theta\int \varphi_z^- \varphi_z^- dr = 0$$

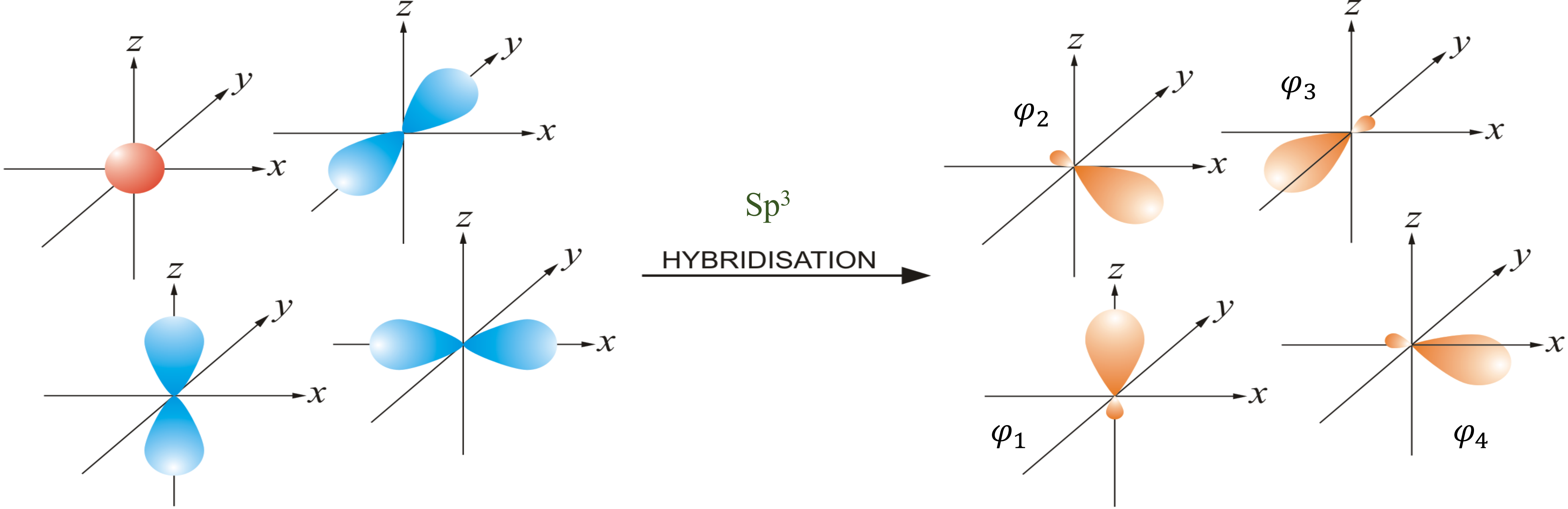
$$\frac{1}{3}+\frac{2}{3}\cos\theta=0$$

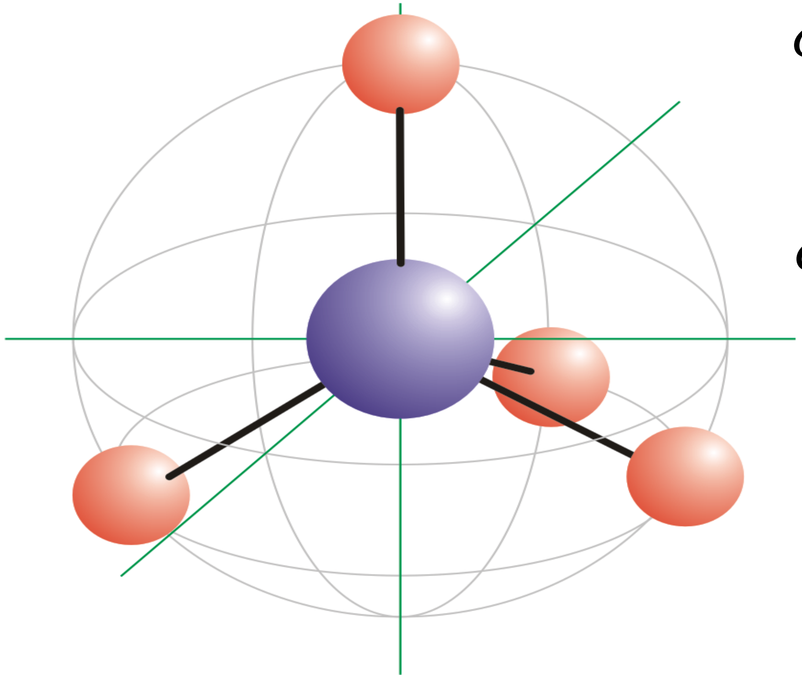
$$\cos\theta=-\frac{1}{3}\times\frac{3}{2}$$

$$\theta= cos^{-1}(-\frac{1}{2})$$

$$\theta\ =120$$







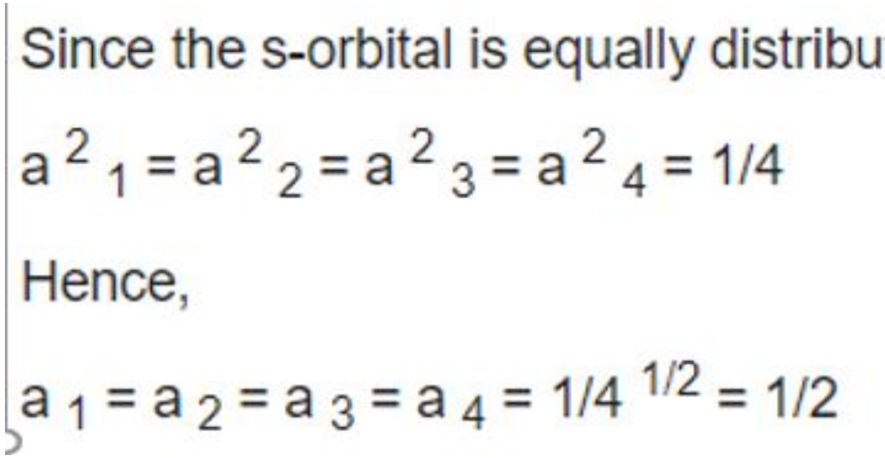
$$\varphi_1 = a_1\varphi_s + b_1\varphi_{px} + c_1\varphi_{py} + d_1\varphi_{pz}$$

$$\varphi_2 = a_2\varphi_s + b_2\varphi_{px} + c_2\varphi_{py} + d_2\varphi_{pz}$$

$$\varphi_3 = a_3\varphi_s + b_3\varphi_{px} + c_3\varphi_{py} + d_3\varphi_{pz}$$

$$\varphi_4 = a_4\varphi_s + b_4\varphi_{px} + c_4\varphi_{py} + d_4\varphi_{pz}$$

Equivalent contribution Law



Since the s-orbital is equally distributed among the four hybrid orbital, we will get the following:

$a^2_1 = a^2_2 = a^2_3 = a^2_4 = 1/4$

Hence,

$a_1 = a_2 = a_3 = a_4 = 1/4^{1/2} = 1/2$

$$\varphi_1 = a_1\varphi_s + b_1\varphi_{px} + c_1\varphi_{py} + d_1\varphi_{pz}$$

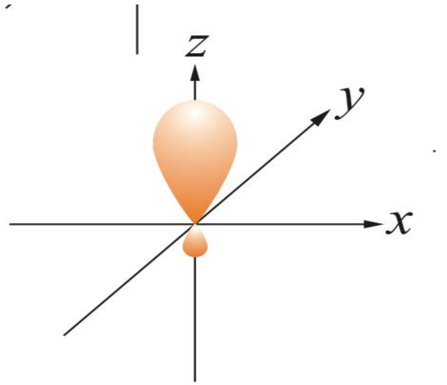
$$\varphi_2 = a_2\varphi_s + b_2\varphi_{px} + c_2\varphi_{py} + d_2\varphi_{pz}$$

$$\varphi_3 = a_3\varphi_s + b_3\varphi_{px} + c_3\varphi_{py} + d_3\varphi_{pz}$$

$$\varphi_4 = a_4\varphi_s + b_4\varphi_{px} + c_4\varphi_{py} + d_4\varphi_{pz}$$

Equivalent contribution Law

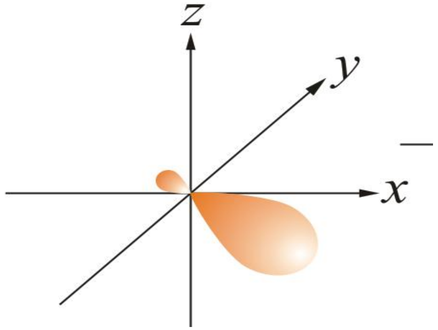
φ_1 H.O. is along the z-axis, that is this hybrid orbitals will get contribution from s and Pz orbitals.
So there is no contribution of Px and Py orbital in H.O. φ_1
Than we can write b1=c1=0



$$\varphi_1 = a_1\varphi_s + b_1\varphi_{px} + c_1\varphi_{py} + d_1\varphi_{pz}$$

Suppose that Ψ_2 lies in the XZ plane, the hybrid orbital will have contributions form s , p_x and p_z orbitals only. The contribution of p_y to ϕ_2 would be equal to zero. Hence,

$c_2 = 0$



$$\varphi_2 = a_2\varphi_s + b_2\varphi_{px} + c_2\varphi_{py} + d_2\varphi_{pz}$$

$$\int \varphi_1^2\,dr = 1 \leftrightarrow a_1^2 + b_1^2 + c_1^2 + d_1^2 = 1$$

$$d_1 = \frac{\sqrt{3}}{2}$$

$$\int \varphi_1\varphi_2\,dr = 0 \leftrightarrow a_1a_2 + b_1b_2 + c_1c_2 + d_1d_2 = 0$$

$$d_2 = -\frac{1}{2\sqrt{3}}$$

$$\int \varphi_2^2\,dr = 1 \leftrightarrow a_2^2 + b_2^2 + c_2^2 + d_2^2 = 1$$

$$b_2 = \sqrt{\frac{2}{3}}$$

$$\int \varphi_1\varphi_3\,dr = 0 \leftrightarrow a_1a_3 + b_1b_3 + c_1c_3 + d_1d_3 = 0$$

$$d_3 = -\frac{1}{2\sqrt{3}}$$

$$\int \varphi_1\varphi_4\,dr = 0 \leftrightarrow a_1a_4 + b_1b_4 + c_1c_4 + d_1d_4 = 0$$

$$d_4 = -\frac{1}{2\sqrt{3}}$$

$$\int \varphi_2\varphi_3\,dr = 0 \leftrightarrow a_2a_3 + b_2b_3 + c_2c_3 + d_2d_3 = 0$$

$$b_3 = \frac{1}{\sqrt{6}}$$

$$\int \varphi_2\varphi_4\,dr = 0 \leftrightarrow a_2a_4 + b_2b_4 + c_2c_4 + d_2d_4 = 0$$

$$b_4 = -\frac{1}{\sqrt{6}}$$

$$\int \varphi_3^2\,dr = 1 \leftrightarrow a_3^2 + b_3^2 + c_3^2 + d_3^2 = 1$$

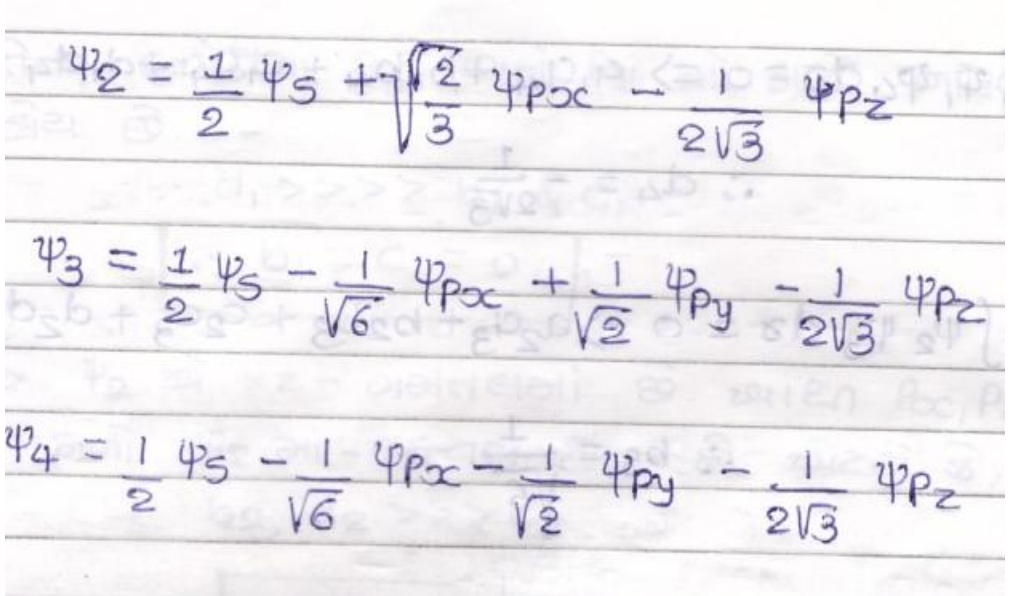
$$c_3 = \frac{1}{\sqrt{2}}$$

$$\int \varphi_3\varphi_4\,dr = 0 \leftrightarrow a_3a_4 + b_3b_4 + c_3c_4 + d_3d_4 = 0$$

$$c_4 = -\frac{1}{\sqrt{2}}$$

$$\left.\begin{aligned}
\varphi_1 &= a_1\varphi_s + b_1\varphi_{px} + c_1\varphi_{py} + d_1\varphi_{pz} \\
\varphi_2 &= a_2\varphi_s + b_2\varphi_{pz} + c_2\varphi_{py} + d_2\varphi_{pz} \\
\varphi_3 &= a_3\varphi_s + b_3\varphi_{pz} + c_3\varphi_{py} + d_3\varphi_{pz} \\
\varphi_4 &= a_4\varphi_s + b_4\varphi_{pz} + c_4\varphi_{py} + d_4\varphi_{pz}
\end{aligned}\right\}$$

$$\varphi_1 = \frac{1}{2}\varphi_s + \frac{\sqrt{3}}{2}\varphi_{pz}$$



$$\psi_2 = \frac{1}{2}\psi_s + \sqrt{\frac{2}{3}}\,\psi_{px} - \frac{1}{2\sqrt{3}}\psi_{pz}$$

$$\psi_3 = \frac{1}{2}\psi_s - \frac{1}{\sqrt{6}}\psi_{px} + \frac{1}{\sqrt{2}}\psi_{py} - \frac{1}{2\sqrt{3}}\psi_{pz}$$

$$\psi_4 = \frac{1}{2}\psi_s - \frac{1}{\sqrt{6}}\psi_{px} - \frac{1}{\sqrt{2}}\psi_{py} - \frac{1}{2\sqrt{3}}\psi_{pz}$$

$$\boxed{\varphi_s = \frac{1}{\sqrt{4\pi}}}$$

$$\boxed{\varphi_{px} = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\emptyset}$$

$$\boxed{\varphi_{py} = \sqrt{\frac{3}{4\pi}}\sin\theta\, sin\,\emptyset}$$

$$\boxed{\varphi_{pz} = \sqrt{\frac{3}{4\pi}}\cos\theta}$$

$$\varphi_1 = \frac{1}{2}\frac{1}{\sqrt{4\pi}} + \frac{\sqrt{3}}{2}\sqrt{\frac{3}{4\pi}}\cos\theta$$

$$\varphi_1 = \frac{1}{2}\frac{1}{\sqrt{4\pi}}(1 + 3\cos\theta)$$

Bond Strength

$$\varphi_1 = \frac{1}{2}\frac{1}{\sqrt{4\pi}}(1 + 3\cos\theta)$$

$$B.S. = \frac{\varphi_1(max)}{\varphi_s}$$

$$\varphi_{1max} = \frac{1}{2}\frac{1}{\sqrt{4\pi}}(1 + 3)$$

$$B.S. = \frac{\frac{1}{2}\frac{1}{\sqrt{4\pi}}(1 + 3)}{\frac{1}{\sqrt{4\pi}}}$$

$$B.S. = \frac{1}{2}\,(1 + 3)$$

$$B.S. of\ sp3\ H.O. = 2$$

$$B.S. of\ sp2\ hybrid\ orbitals = 1.992$$

$$B.S.(sp\ hybrid\ orbital) = 1.932$$

Bond Angle

$$\varphi_1 = \frac{1}{2}\varphi_s + \frac{\sqrt{3}}{2}\varphi_{pz} \qquad \varphi_1' = \frac{1}{2}\varphi_s + \frac{\sqrt{3}}{2}\varphi_{pz}^{+} \qquad \varphi_1'' = \frac{1}{2}\varphi_s + \frac{\sqrt{3}}{2}\varphi_{pz}^{-}$$

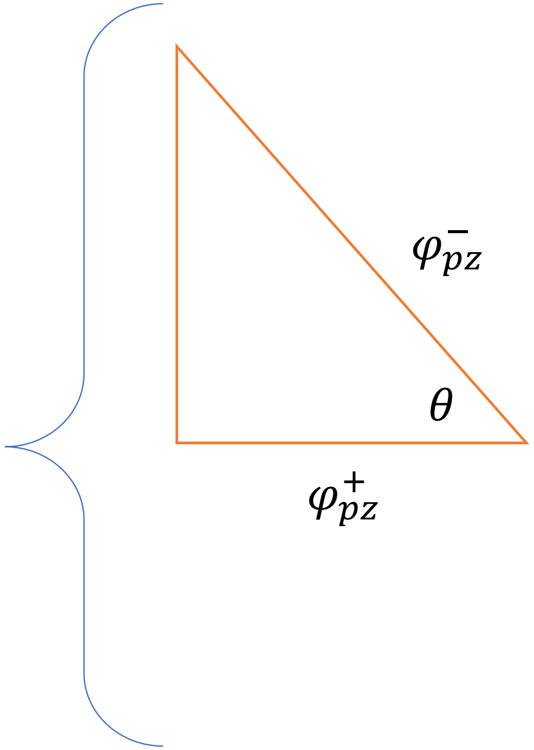
$$\int \varphi_1' \, \varphi_1'' dr = 0$$

$$\int \left(\frac{1}{2}\varphi_s + \frac{\sqrt{3}}{2}\varphi_{pz}^{+}\right)\left(\frac{1}{2}\varphi_s + \frac{\sqrt{3}}{2}\varphi_{pz}^{-}\right) dr = 0$$

$$\frac{1}{4}\int \varphi_s^2 \, dr + \frac{\sqrt{3}}{4}\int \varphi_s \varphi_{pz}^{-} \, dr + \frac{\sqrt{3}}{4}\int \varphi_s \varphi_{pz}^{+} dr + \frac{3}{4}\int \varphi_z^{+} \varphi_z^{-} dr = 0$$

$$\frac{1}{4} + \frac{3}{4}\int \varphi_{pz}^{+}\varphi_{pz}^{-} dr = 0$$

$$\frac{1}{4} + \frac{3}{4}\cos\theta \int \varphi_{pz}^{-}\varphi_{pz}^{-} dr = 0$$



$$\cos\theta = \frac{\varphi_{pz}^{+}}{\varphi_{pz}^{-}}$$

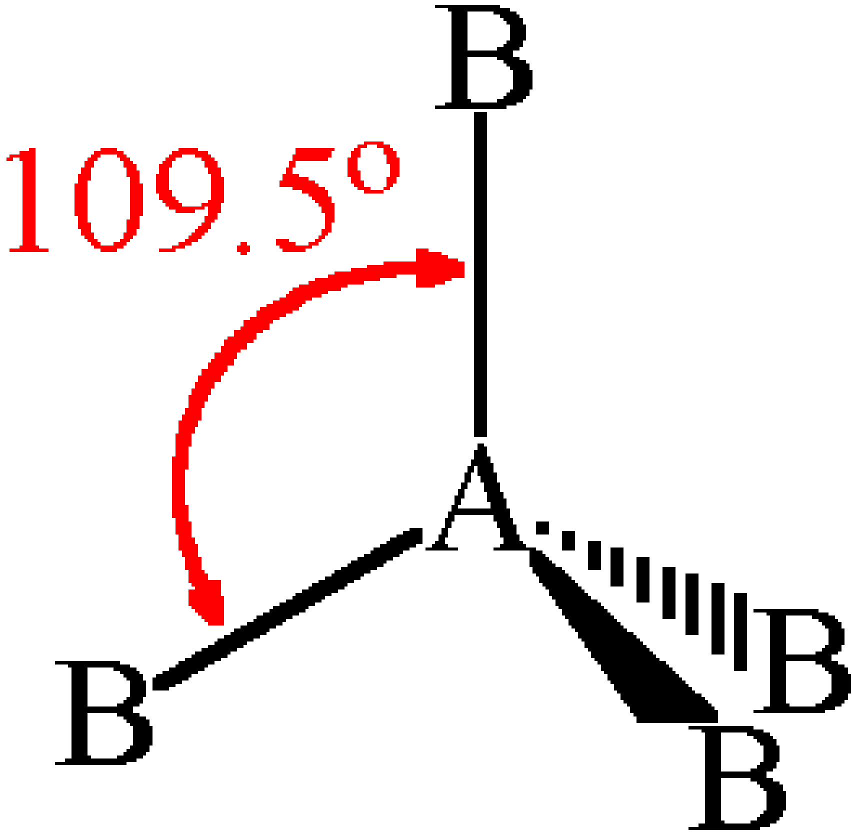
$$\frac{1}{4}+\frac{3}{4}\cos\theta\int \varphi_z^- \varphi_z^- dr = 0$$

$$\frac{1}{4}+\frac{3}{4}\cos\theta=0$$

$$\cos\theta= -\frac{1}{4}\times\frac{4}{3}$$

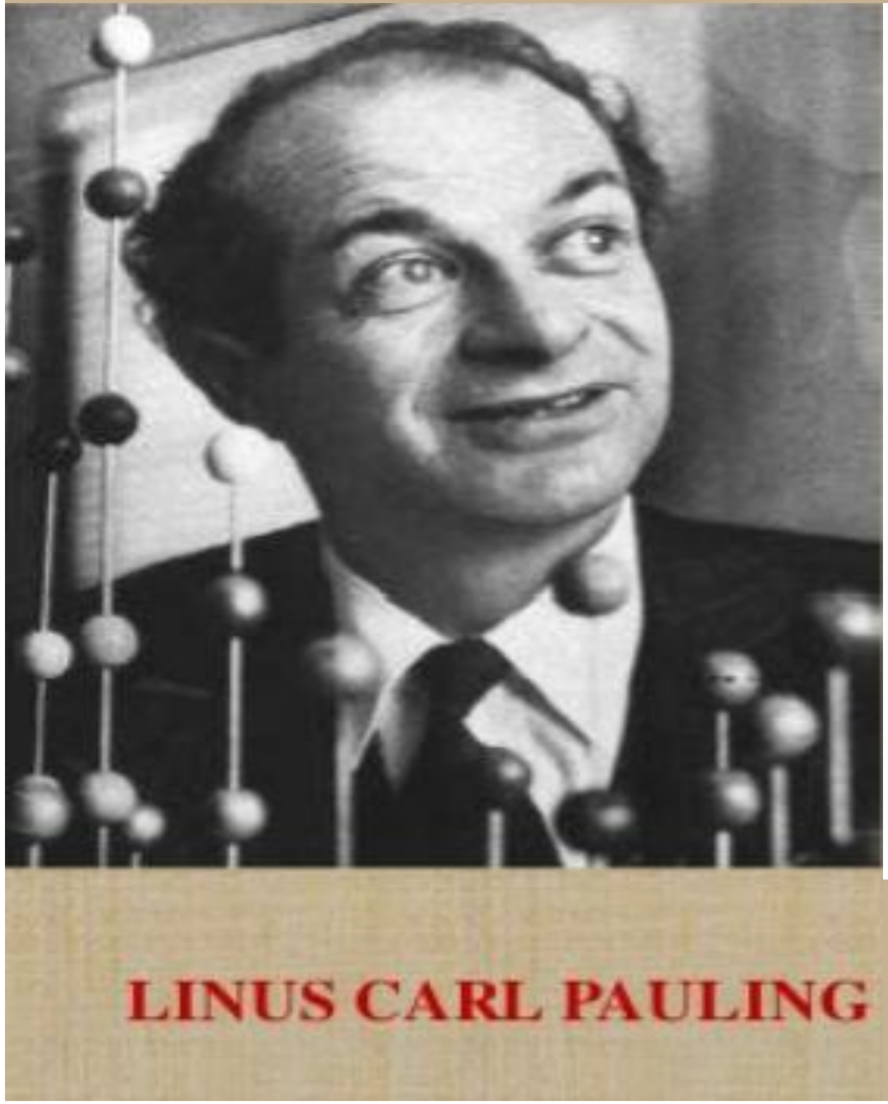
$$\theta= cos^{-1}(-\frac{1}{3})$$

$$\theta\ =109.5$$



Pauli’s Exclusion Principal

by Quantum Mechanical Approach



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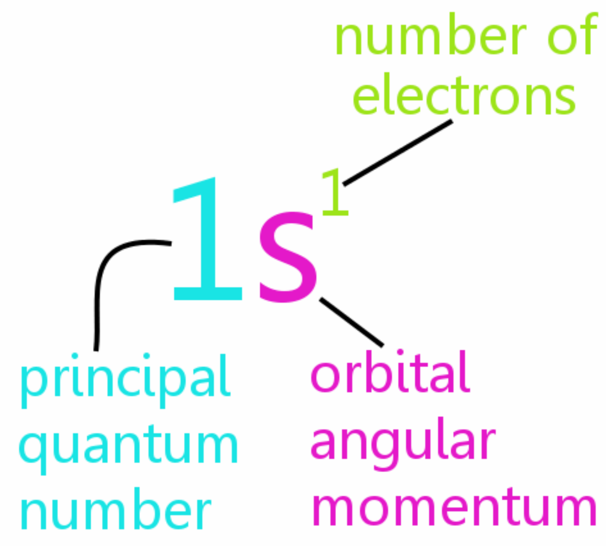
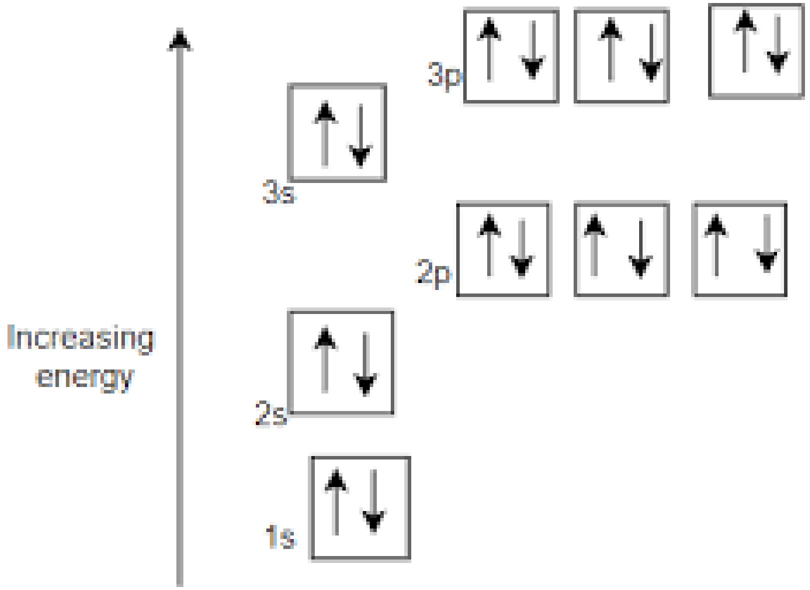
Pauli's Exclusion Principal

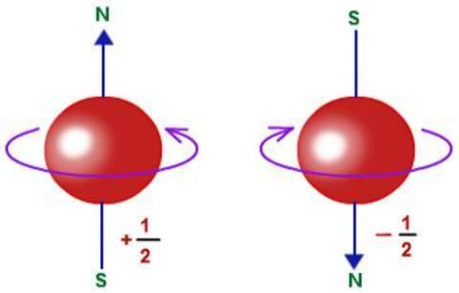
In an atom or molecule, no two electrons can have the same 4 quantum numbers.

Maximum only 3 Q.N. are same.

n; l; m; s



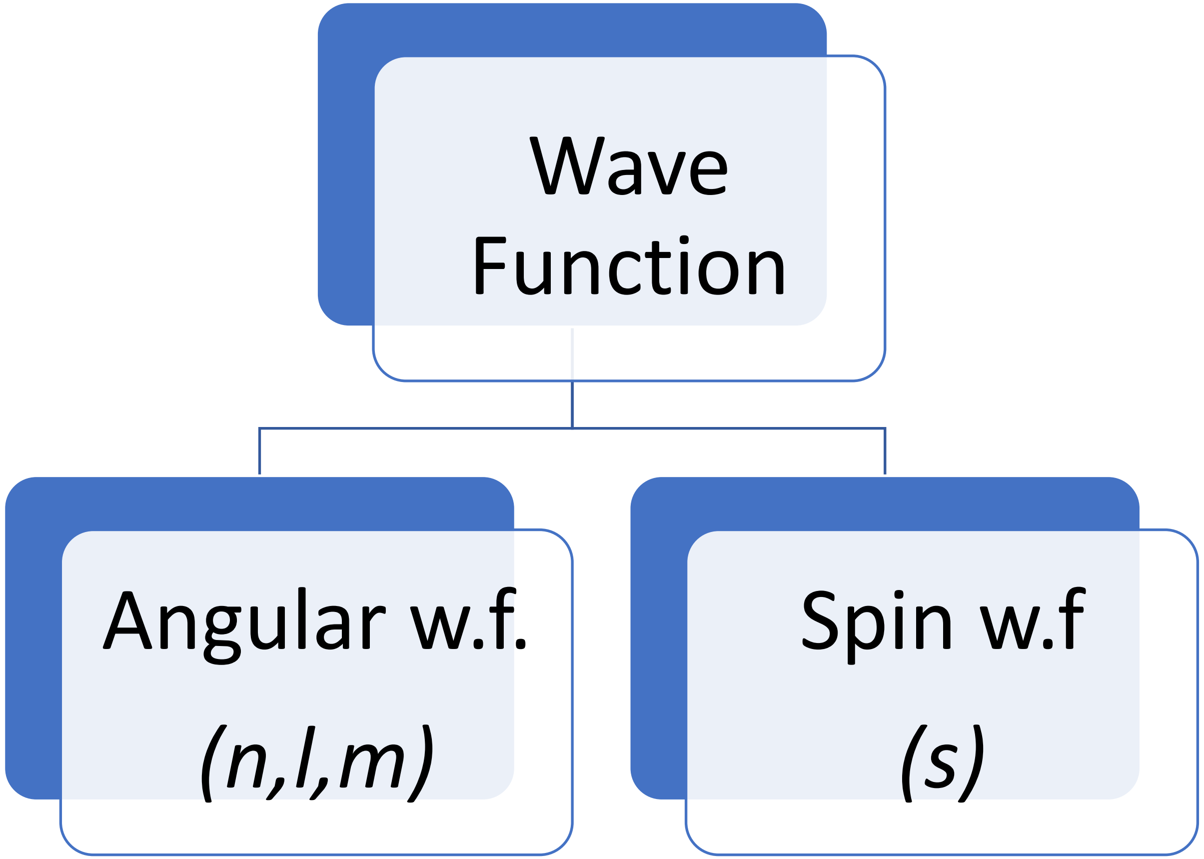




Pauli’s Exclusion Principal-

by Quantum Mechanical Approach

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



Wave Function

Angular w.f.

(n,l,m)

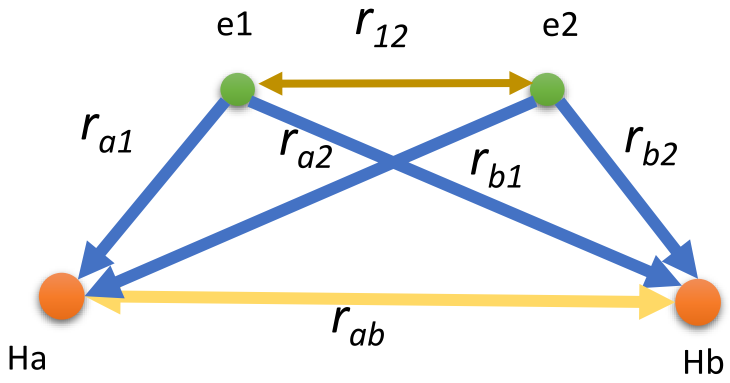
Spin w.f

(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)

$$\left.\begin{array}{ll} \uparrow\downarrow & \varphi_1^s = \alpha_{(1)}\beta_{(2)} \\ \downarrow\uparrow & \varphi_2^s = \alpha_{(2)}\beta_{(1)} \end{array}\right\} \quad \begin{array}{l} \varphi_S^s = \alpha_{(1)}\beta_{(2)} + \alpha_{(2)}\beta_{(1)} \\ \varphi_A^s = \alpha_{(1)}\beta_{(2)} - \alpha_{(2)}\beta_{(1)} \end{array}$$

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

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

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

$$\varphi_T = Angular\,WF \times Spin\,WF$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

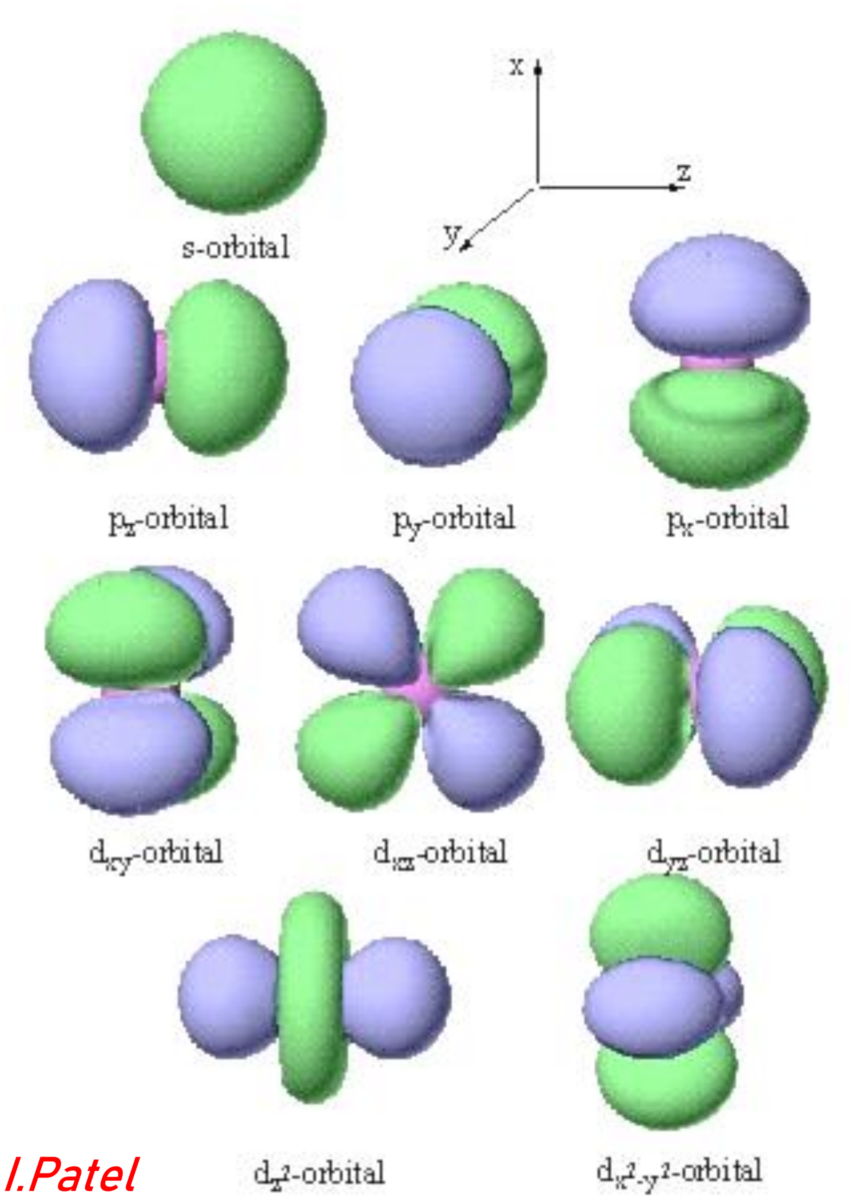
$$\varphi_T = 2\begin{vmatrix} \varphi_{a(1)}\alpha_{(1)} & \varphi_{a(1)}\alpha_{(1)} \\ \varphi_{a(2)}\alpha_{(2)} & \varphi_{a(2)}\alpha_{(2)} \end{vmatrix}$$

$$\varphi_T = 0$$

$\boxed{\uparrow\downarrow}$

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

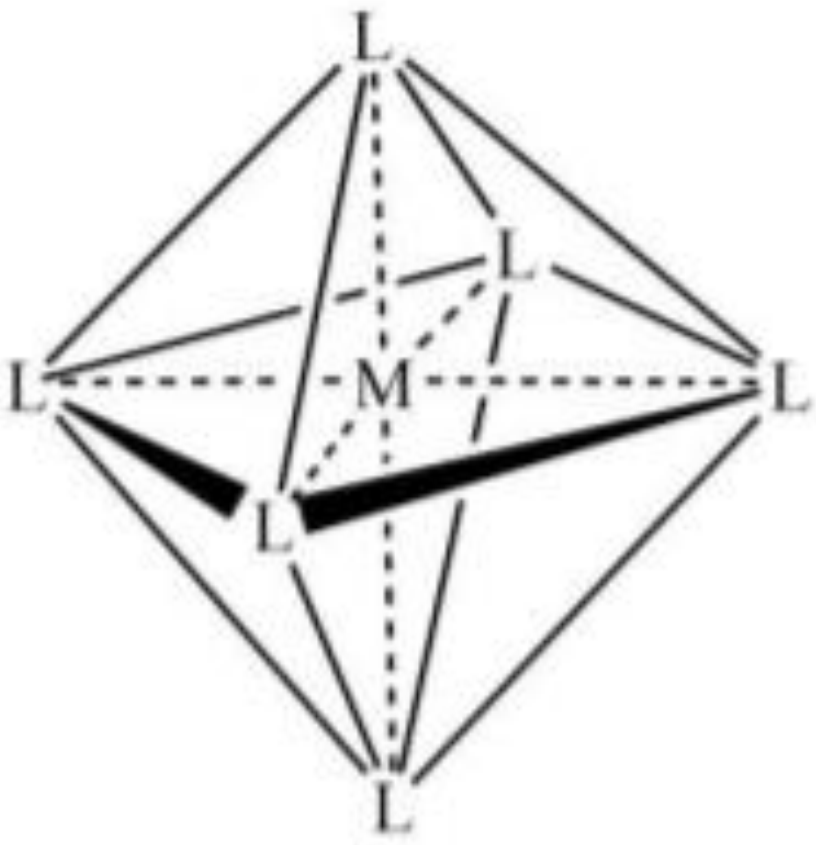
Molecular Orbital treatment for Octahedral Complex.

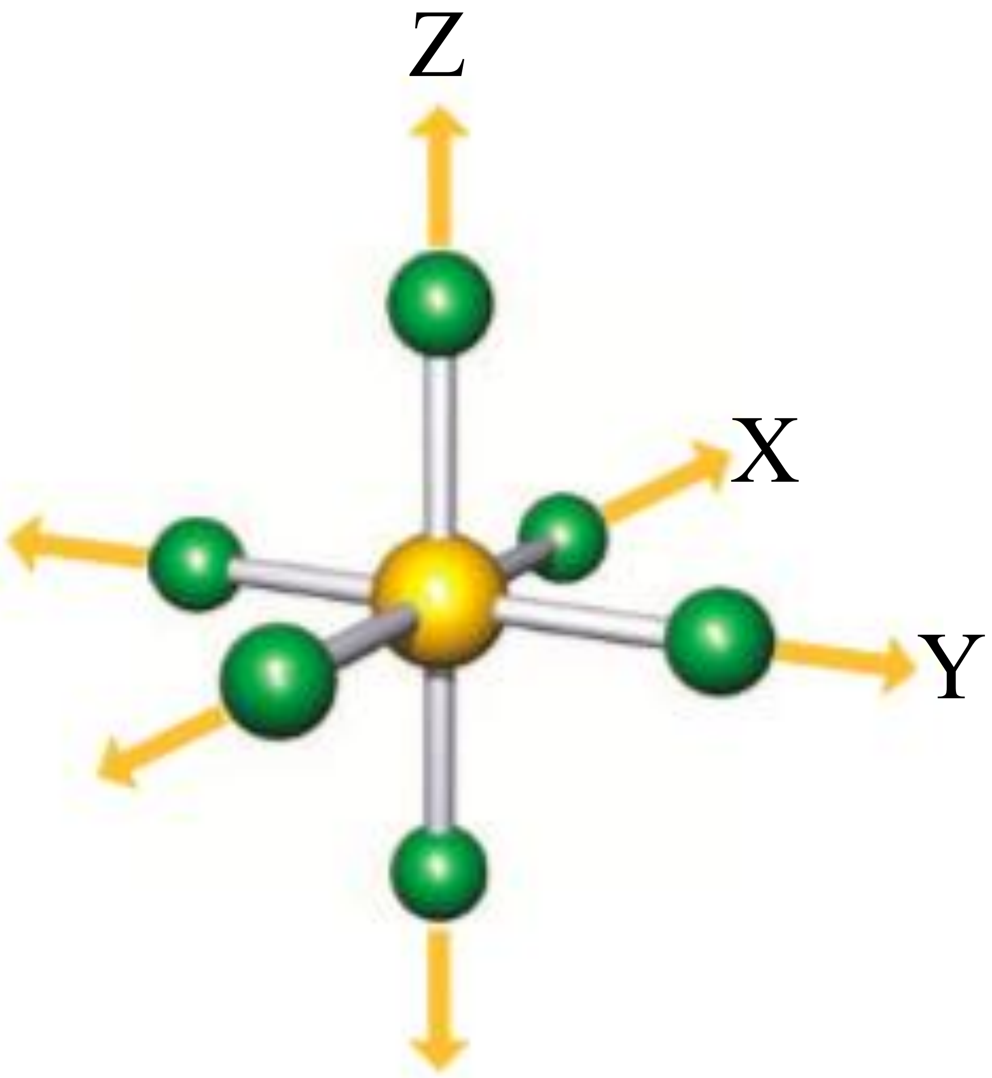


Dr. N.I.Patel
Chemistry Department,
The HNSB. Ltd. Science College, Himatnagar

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

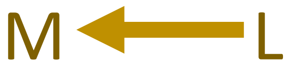
$$nS = a_{1g}$$

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

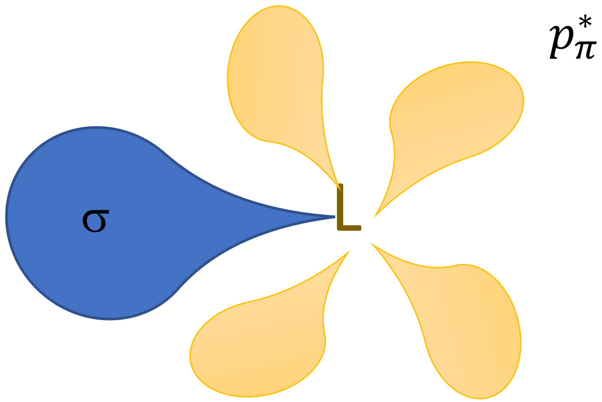
$$(n-1)d = \left(d_{xy}, d_{yz}, d_{xz}\right) = t_{2g}$$

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

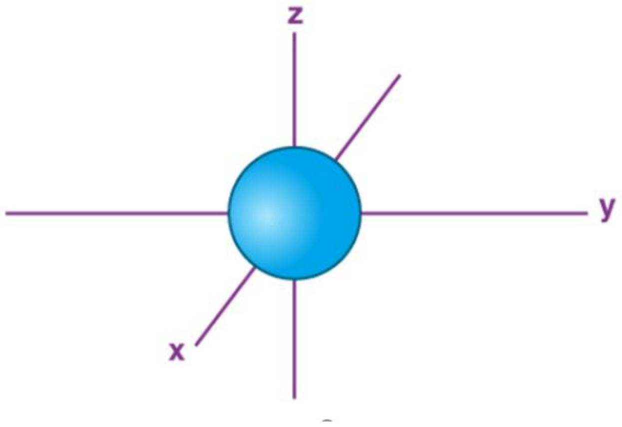
Coordination Covalent Bond

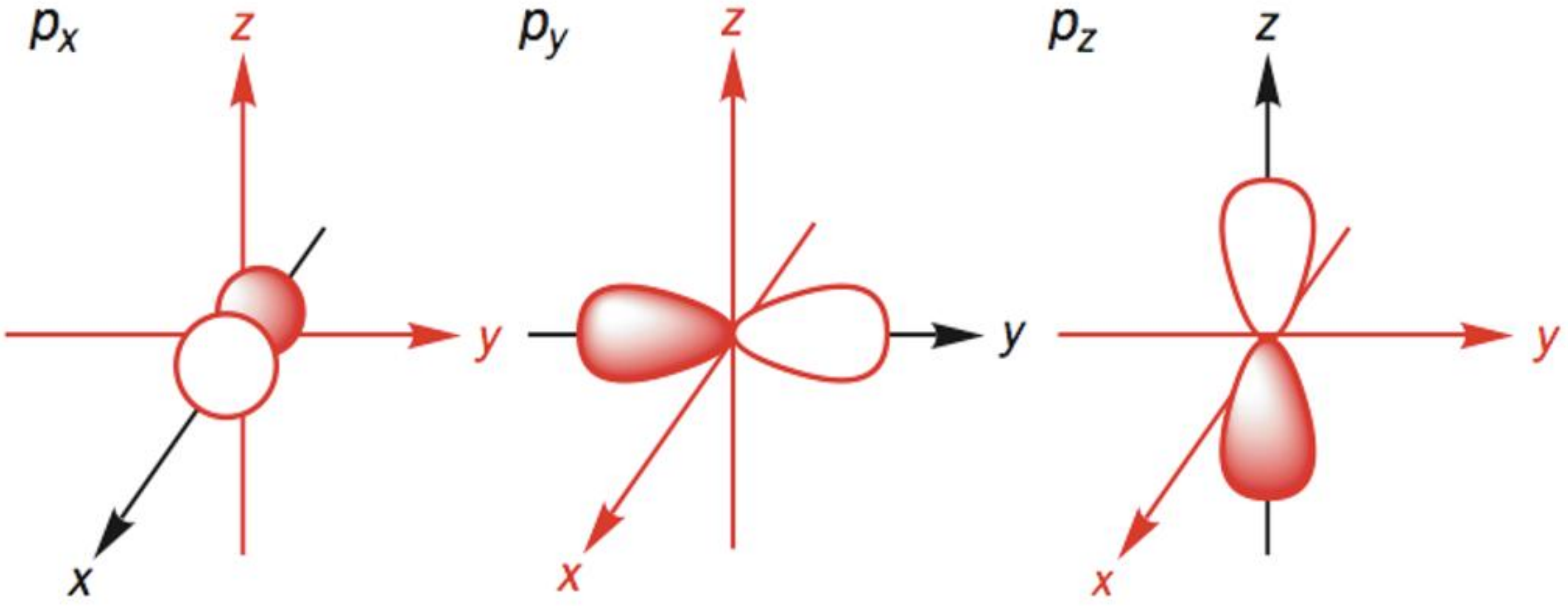


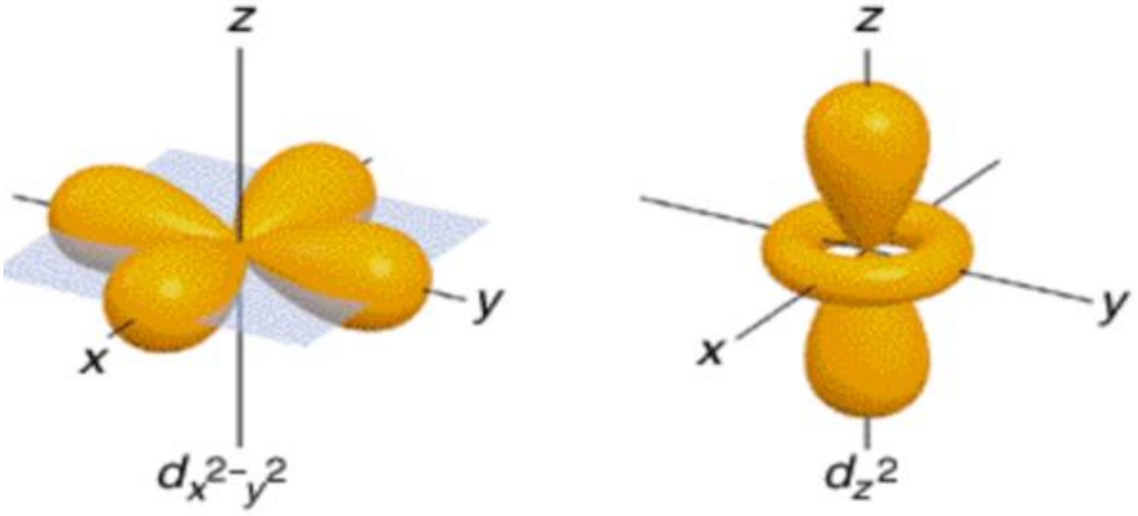
d π-pπ Bond



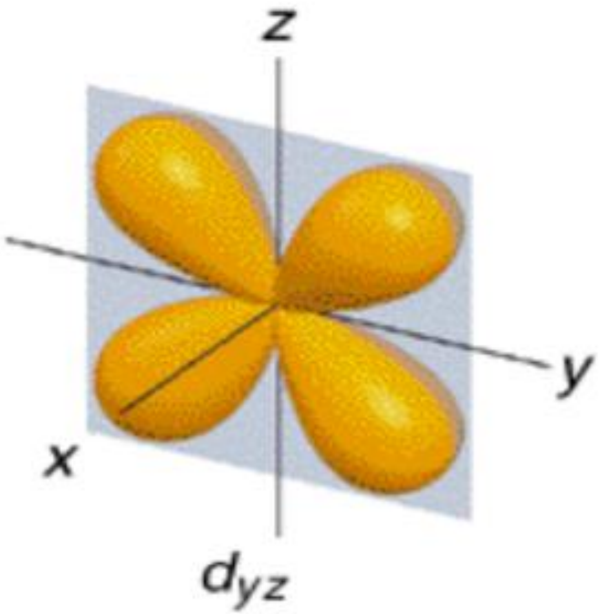
σ-bonded orbitals of CMI

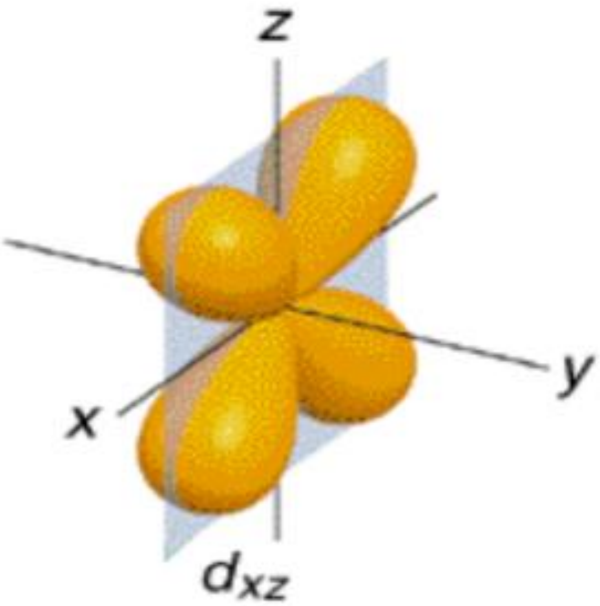


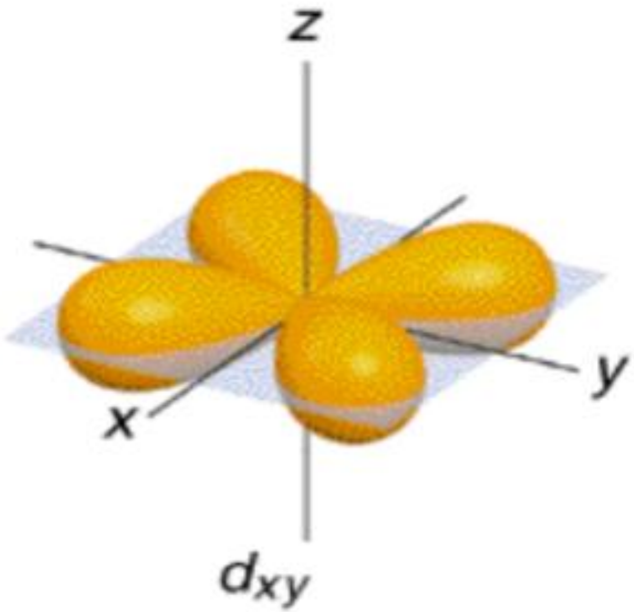




π-bonded orbitals of CMI

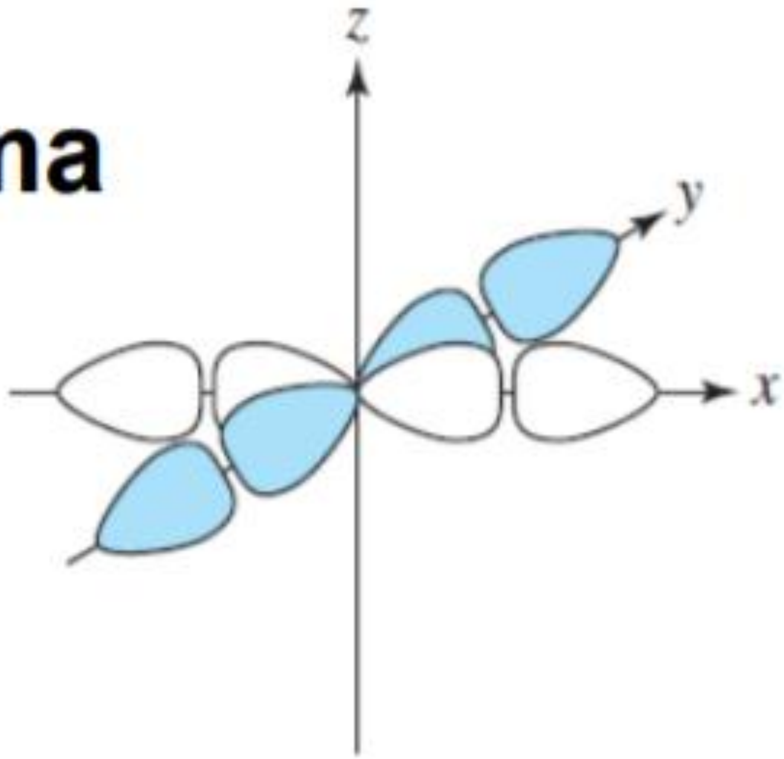






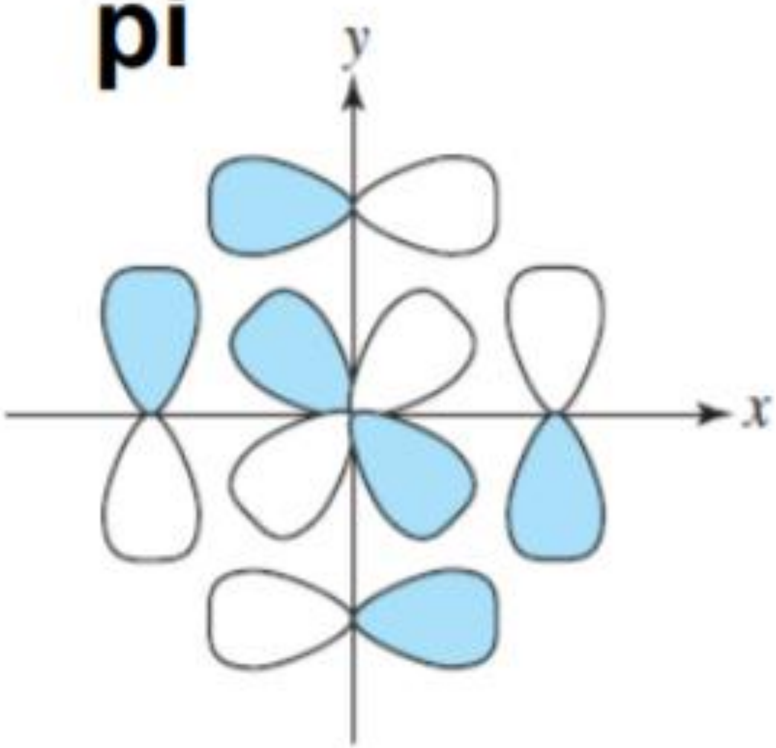
sigma

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



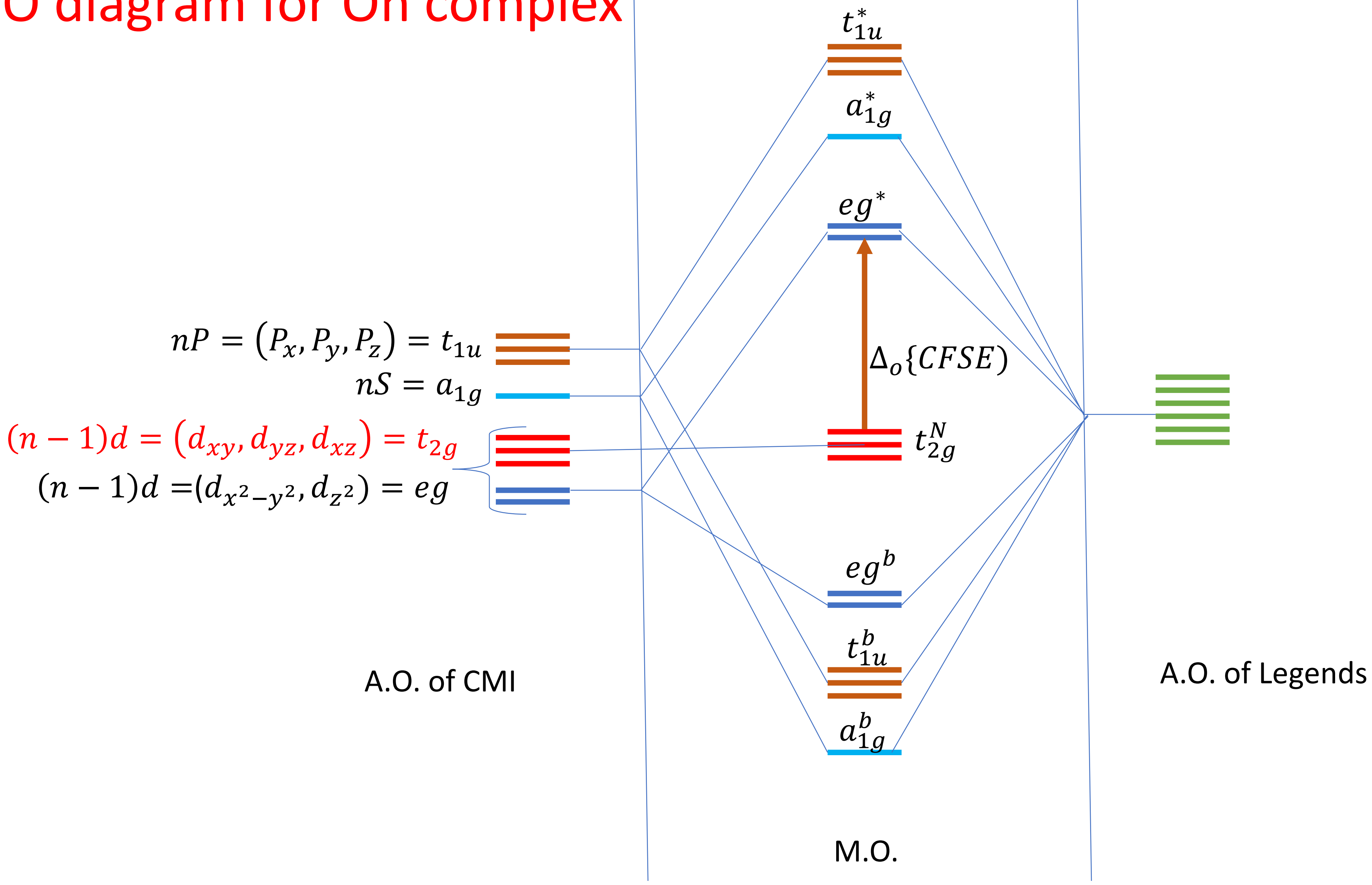
Sigma bonding interaction between four ligand orbitals and metal $d_{x^2-y^2}$ orbital

pi



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

MO diagram for Oh complex



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

$nS = a_{1g}$

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

$(n-1)d = (d_{x^2-y^2}, d_{z^2}) = eg$

A.O. of CMI

t_{1u}^*

a_{1g}^*

eg^*

$\Delta_o\{CFSE\}$

t_{2g}^N

eg^b

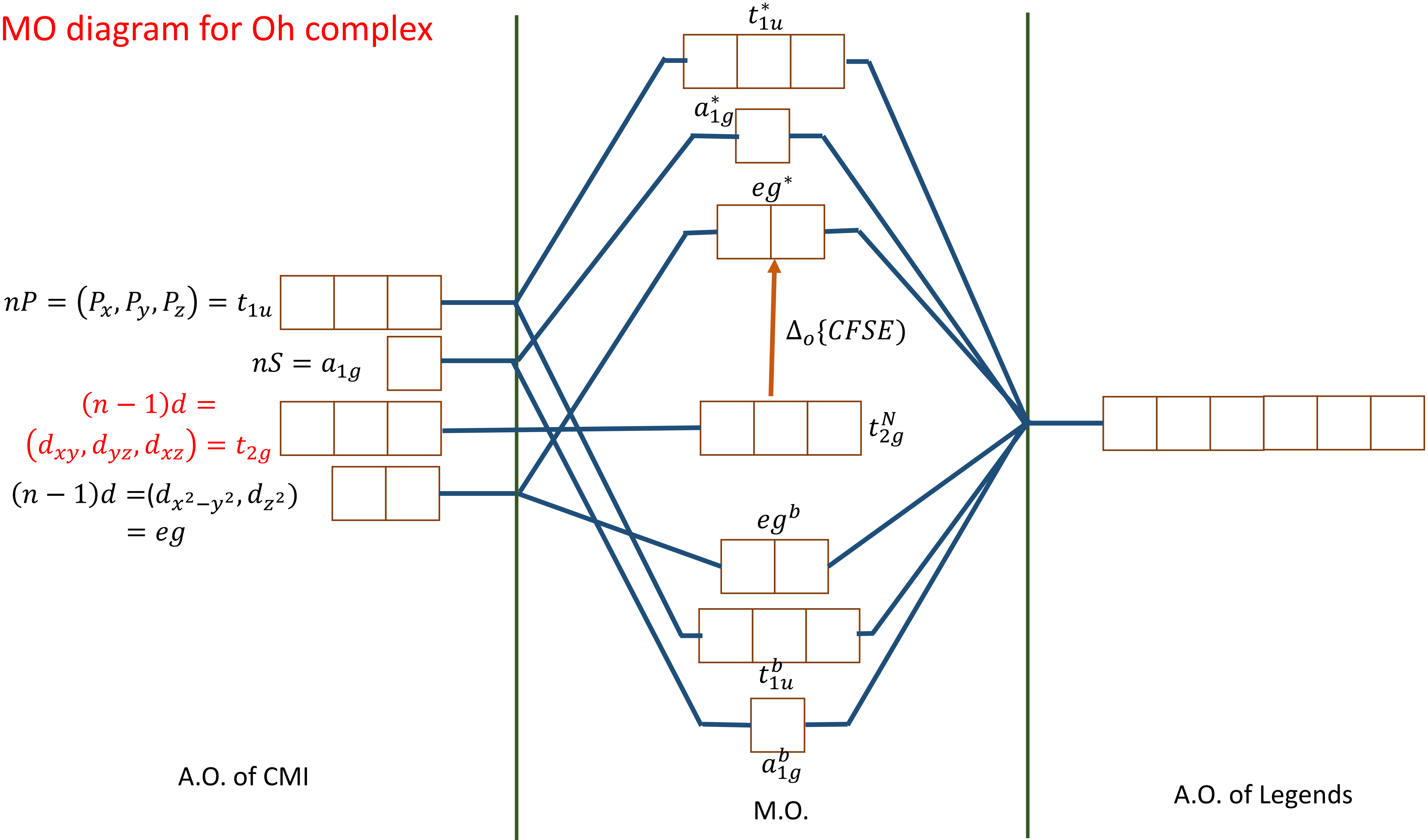
t_{1u}^b

a_{1g}^b

M.O.

A.O. of Legends

MO diagram for Oh complex



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

$nS = a_{1g}$

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

$(n-1)d = (d_{x^2-y^2}, d_{z^2})$
$= eg$

t_{1u}^{*}

a_{1g}^{*}

eg^{*}

$\Delta_o\{CFSE\}$

t_{2g}^{N}

eg^{b}

t_{1u}^{b}

a_{1g}^{b}

A.O. of CMI

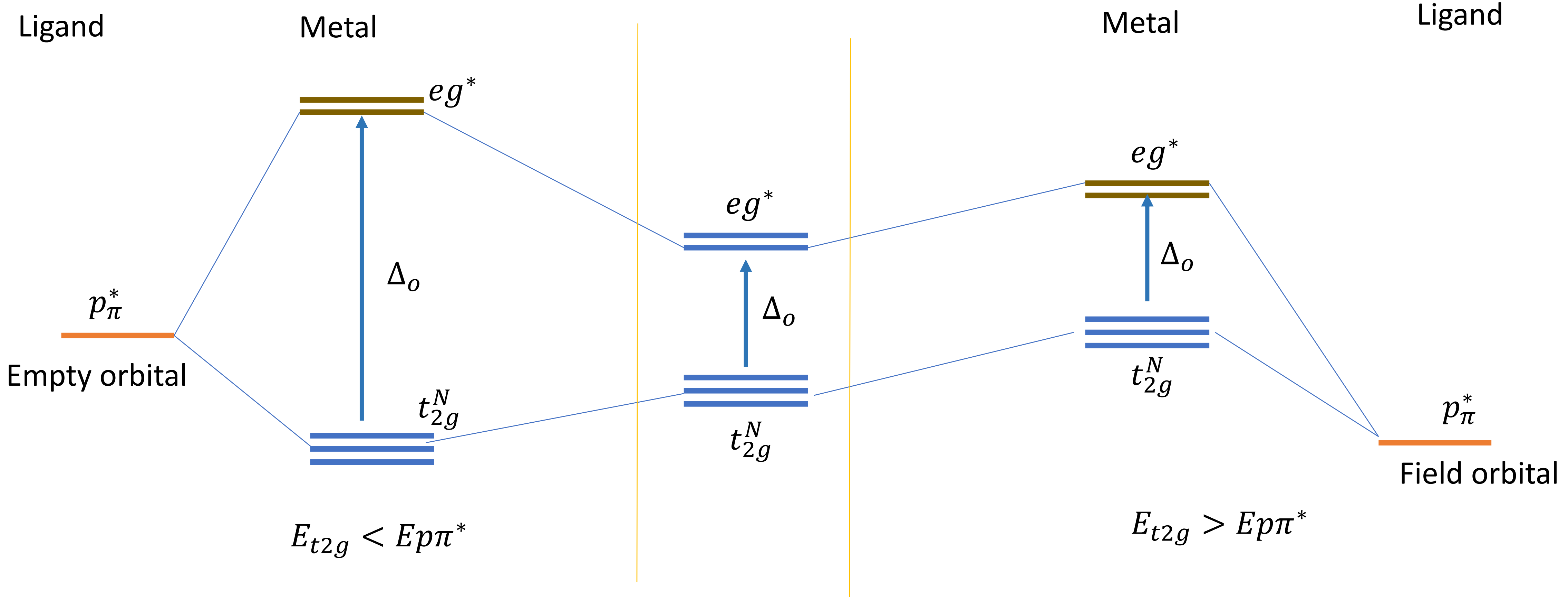
M.O.

A.O. of Legends

π -bonding in Oh Complex

Back donation/strong pi bonding

Week pi bonding



$E_{t2g} < E p\pi^*$

$E_{t2g} > E p\pi^*$

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

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

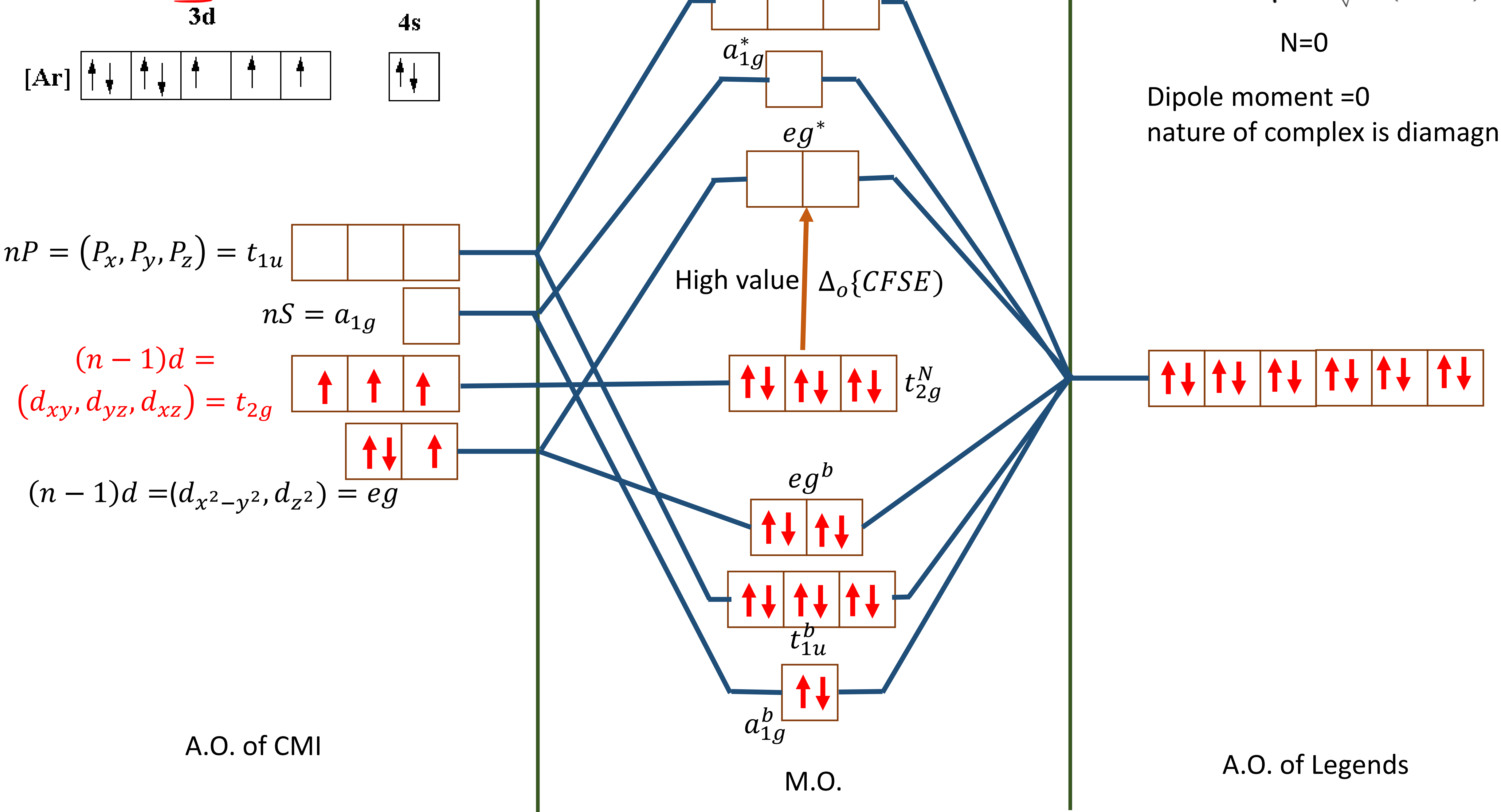
$$< C_2O_4^{-2} < O^{-2} < H_2O \sim NCS^- < EDTA^{-4} < NH_3 \sim Py < en < bpy \sim phen$$

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

From I^- To H_2O are weak field ligands

From NCS^- To CO are strong field ligands

$[Co(NH_3)_6]^{+3}$



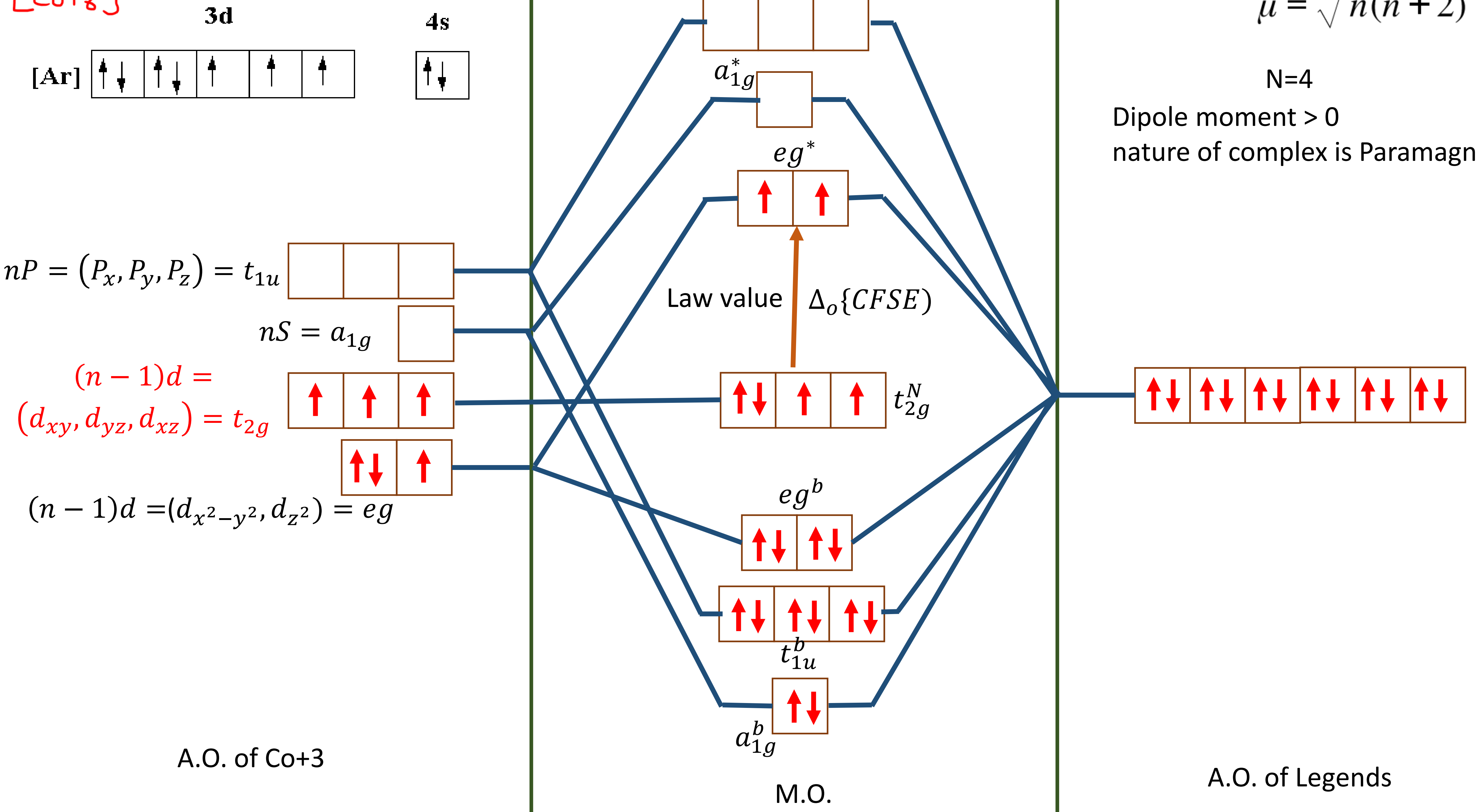
$$\mu = \sqrt{n(n+2)}$$

N=0

Dipole moment =0

nature of complex is diamagnetic

$[CoF_6]^{-3}$



3d

4s

[Ar]

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

$nS = a_{1g}$

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

$(n-1)d = (d_{x^2-y^2}, d_{z^2}) = eg$

t_{1u}^{*}

a_{1g}^{*}

eg^{*}

Law value

$\Delta_o\{CFSE)$

t_{2g}^{N}

eg^{b}

t_{1u}^{b}

a_{1g}^{b}

$$\mu = \sqrt{n(n+2)}$$

N=4

Dipole moment > 0

nature of complex is Paramagnetic

A.O. of Co+3

M.O.

A.O. of Legends