

CHEMICAL BONDING

Quantum mechanical calculations are based on solving the Schrodinger equation $\hat{H}\psi = E\psi$, where \hat{H} is the Hamiltonian energy operator and ψ is an amplitude function, which is the eigenfunction with E as eigen value. An interesting issue for the scientists in general for a long time was to find the mode of mechanism that binds together atoms in molecules. With the popularity of Quantum mechanics a no of methods were explored.

It was observed that Schrodinger equation is powerful enough to explain a no of properties of systems but it is too complicated to find a solution of systems having more than one electron.

To simplify the procedure, Born-Oppenheimer approximation is therefore adopted in which it is assumed that the nuclei may be treated as stationary while the electrons move around them. This approximation sounds fairly reasonable as the nuclei are much heavier than an electron.

So, we have two approaches for the calculation of molecular structure—Molecular Orbital Method
—Valence Bond Method.

A no of quantum chemical codes employ MO method.

MOLECULAR ORBITAL METHOD: [LCAO]

Developed by Mulliken, in this method acceptable molecular wave functions called 'Molecular Orbitals' which describe molecular energy state are computed first.

The MO cover all the nuclei in it and hence is polycentric, every electron contributes to the strength of every bond. They have the same significance as of atomic orbitals. Once the molecular orbitals are obtained, the orbitals accept the electrons in accordance with Pauli's exclusion principle.

As molecules consists of atoms, MO may be taken as a function of atomic orbitals centered on the individual atoms. The most commonly used approach for obtaining the MO is the LCAO more popularly known as Linear Combination of Atomic Orbitals.

In this approach, the molecular orbital ψ is written as a linear combination of atomic orbitals as

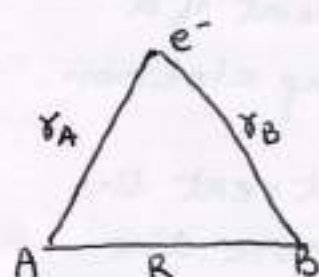
$$\psi = c_1 \psi_1 + c_2 \psi_2$$

where ψ_1, ψ_2, \dots are the individual atomic orbitals. The constants c_1, c_2, \dots are to be selected in such a way that the energy given by ψ is minimum.

To generate an effective MO by LCAO method, the combining atomic orbitals must have

- (i) energies of comparable magnitude
- (ii) considerable overlapping
- (iii) the same symmetry

MO TREATMENT OF H_2^+ ION



A, B \rightarrow nuclei
 $e^- \rightarrow$ electron

The simplest of all the diatomic molecules is H_2^+ ion, i.e., the hydrogen molecule ion, consisting of an electron of charge $-e$ associated with two protons A and B, each with +ve charge separated by a distance R .

Writing the hamiltonian of the system \downarrow

$\hat{H} =$ KE of proton A + KE of proton B + KE of electron
 + PE of interaction between nuclei and electron

$$\text{or } \hat{H} = -\frac{\hbar^2}{2M} \nabla_A^2 - \frac{\hbar^2}{2M} \nabla_B^2 - \frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R}$$

In atomic units: $\hbar \rightarrow 1$, $m_e \rightarrow 1$, $4\pi\epsilon_0 \rightarrow 1$
 Mass of proton in = 1837
 terms of m_e

In the above equation for hamiltonian we see that there are n variables \Rightarrow looks impossible to solve. But if we compare the mass of nuclei with that of an electron we find that nucleus is much heavier as compared to an electron. Hence, we expect a sort of unenergetic movement from nucleus. With this logic it makes some sense (although a crude one) to visualise a sluggish movement of a nucleus with that of a fast moving electron.

\therefore to a good approximation we can treat the two nuclei as stationary. So we ignore the nuclear motion and fix nuclei at a distance R . Here it needs to be mentioned that this approximation causes practically no error in ground state electronic energy level of molecule. This idea was propagated by Born & Oppenheimer and later on it was known as BO approximation.

After using the BO approximation and as the hamiltonian can now be written as

$$\hat{H} = -\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

assuming both the nuclei to be fixed we proceed for electronic structure calculation

Now we look for a suitable wavefunction i.e. approximate ψ .

For this we imagine that the electron is in the vicinity of A so the distance of electron from A is less than the distance of e from B.

\Rightarrow implies that r_A is important and not r_B as influence of A is maximum. So, if we don't have to worry about B or we say that we are interested in the wave function in the region around A then we shall ignore r_B and then we can write

$$\hat{H} = -\frac{\nabla^2}{2} - \frac{1}{r_A} [\text{KE of } e + e \text{ interaction with A}]$$

and if we have a single e interacting with a single nucleus (neglecting the influence of other nucleus) then this is the GS of system which is nothing but 1s orbital. It is like a hydrogen atom problem (after ignoring the effect of B)

Electron is having KE and at the same time interacting with nucleus A and \therefore if Schrodinger equation is solved with the simplified Hamiltonian the answer we get is 1s atomic orbital with nucleus A

$$\text{or } \psi_{1s}(r_A) = \frac{1}{\sqrt{\pi}} e^{-r_A} \quad (\text{near A})$$

and if e is near B then $\psi_{1s}(r_B) = \frac{1}{\sqrt{\pi}} e^{-r_B} \quad (\text{near B})$

So the wave function should behave or look like $\Psi_{1s}(r_A)$

So, we get an idea of how to choose the trial wave function which should be of the form

$$\phi = C_A \Psi_{1sA} + C_B \Psi_{1sB}$$

$C_A, C_B \rightarrow$ constants
 Ψ_{1sA} atomic orbital centered on A
 Ψ_{1sB} atomic orbital centered on B

In this equation we see that the two atomic orbitals are being added
 \rightarrow Linear Combination of atomic orbitals (LCAO)

The energy of the system

$$E = \frac{\int \phi^* \hat{H} \phi dz}{\int \phi^* \phi dz}$$

$$= \frac{\int (C_A \Psi_{1sA} + C_B \Psi_{1sB})^* \hat{H} (C_A \Psi_{1sA} + C_B \Psi_{1sB}) dz}{\int dz (C_A \Psi_{1sA} + C_B \Psi_{1sB})^* (C_A \Psi_{1sA} + C_B \Psi_{1sB})}$$

Since Ψ is atomic orbital - real $\therefore * \rightarrow$ removed

$$= \frac{\int (C_A \Psi_{1sA} + C_B \Psi_{1sB}) \hat{H} (C_A \Psi_{1sA} + C_B \Psi_{1sB}) dz}{\int dz (C_A \Psi_{1sA} + C_B \Psi_{1sB})^2}$$

$$C_A^2 \int \Psi_{1sA} \hat{H} \Psi_{1sA} dz + C_B^2 \int \Psi_{1sB} \hat{H} \Psi_{1sB} dz$$

$$+ C_A C_B \int \Psi_{1sA} \hat{H} \Psi_{1sB} dz + C_B C_A \int \Psi_{1sB} \hat{H} \Psi_{1sA} dz$$

$$= \frac{C_A^2 \int \Psi_{1sA}^2 dz + C_B^2 \int \Psi_{1sB}^2 dz + 2 C_A C_B \int \Psi_{1sA} \Psi_{1sB} dz}{\int \Psi_{1sA}^2 dz + \int \Psi_{1sB}^2 dz + 2 \int \Psi_{1sA} \Psi_{1sB} dz}$$

In denominator $\Psi_{1SA} \rightarrow$ normalised

$$\therefore \int \Psi_{1SA}^2 = \int \Psi_{1SB}^2 = 1$$

and $\int \Psi_{1SA} \Psi_{1SB} \neq 0$ as they are eigen functions of different hamiltonian

Let $\int \Psi_{1SA} \Psi_{1SB} \rightarrow S$ [Overlap integral]

$$E = \frac{C_A^2 H_{AA} + C_B^2 H_{BB} + C_A C_B H_{AB} + C_B C_A H_{BA}}{C_A^2 + C_B^2 + 2C_A C_B S} \quad \text{--- (1)}$$

where

$$H_{AA} = \int \Psi_{1SA} \hat{H} \Psi_{1SA} dz ; H_{BB} = \int \Psi_{1SB} \hat{H} \Psi_{1SB} dz \rightarrow \text{COULOMB INTEGRAL}$$

$$H_{AB} = \int \Psi_{1SA} \hat{H} \Psi_{1SB} dz ; H_{BA} = \int \Psi_{1SB} \hat{H} \Psi_{1SA} dz \rightarrow \text{EXCHANGE INTEGRAL}$$

$H_{AB} = H_{BA}$ since H is hermitian

\therefore eq (1) can be written as

$$E = \frac{C_A^2 H_{AA} + C_B^2 H_{BB} + 2C_A C_B H_{AB}}{C_A^2 + C_B^2 + 2C_A C_B S}$$

From variational theorem we know that

$$E \geq E_0 \text{ (GS)}$$

We find value of C_A / C_B for which $E \rightarrow \min$

$$\text{or } E(C_A^2 + C_B^2 + 2C_A C_B S) = C_A^2 H_{AA} + C_B^2 H_{BB} + 2C_A C_B H_{AB}$$

Differentiating this equation partially wrt C_A / C_B

$$\frac{\partial E}{\partial C_A} (C_A^2 + C_B^2 + 2C_A C_B S) + E (2C_A + 2C_B S) = 2C_A H_{AA} + 2C_B H_{AB}$$

For energy to be min $\partial E / \partial C_A \rightarrow 0$

$$\text{or } E (2C_A + 2C_B S) = 2C_A H_{AA} + 2C_B H_{AB}$$

$$\text{or } (H_{AA} - E) C_A + C_B (H_{AB} - ES) = 0$$

Similarly, differentiating E wrt C_B partially gives A(i,ii)

$$(H_{AB} - ES) C_A + (H_{BB} - E) C_B = 0$$

Now we have two equations and we have to find the best values of C_A, C_B and then substitute in eq 1

Writing A (i,ii) in matrix form

$$\begin{bmatrix} H_{AA} - E & H_{AB} - ES \\ H_{AB} - ES & H_{BB} - E \end{bmatrix} \begin{bmatrix} C_A \\ C_B \end{bmatrix} = 0$$

Square matrix A Column matrix C

$$A \cdot C = 0$$

suppose A is such that it has an inverse (A^{-1})

$$\therefore A^{-1} \cdot A \cdot C = A^{-1} \cdot 0$$

$$\text{or } C = 0$$

[$A^{-1}A \rightarrow$ Identity]

$$\hookrightarrow C_A, C_B = 0$$

$\hookrightarrow \neq 0 \Rightarrow$ But this means that e is absent which is impossible

$$\therefore C_A, C_B \neq 0$$

⇒ So it means that matrix should not have an inverse. when is that a matrix doesn't have an inverse

↳ when the determinant of matrix = 0

∴ Writing the determinant form

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{AB} - ES & H_{BB} - E \end{vmatrix} = 0$$

On expansion we get

$$(H_{AA} - E)(H_{BB} - E) - (H_{AB} - ES)(H_{AB} - ES) = 0 \quad (2)$$

Since A, B both are protons

Estimate of energy of e sitting on ψ_{1sA} orbital

$$\begin{matrix} \downarrow \\ \downarrow \end{matrix} \quad \begin{matrix} \leftarrow H_{AA} = \int d\tau \psi_{1sA} \hat{H} \psi_{1sA} \\ \dots \dots \dots \text{on } \psi_{1sB} \text{ orbital} \\ \leftarrow H_{BB} = \int d\tau \psi_{1sB} \hat{H} \psi_{1sB} \end{matrix}$$

On assuming the two nuclei to be identical we can say

$$H_{AA} = H_{BB}$$

∴ Re writing eq (2)

$$(H_{AA} - E)^2 - (H_{AB} - ES)^2 = 0$$

Two solutions

$$H_{AA} - E = + (H_{AB} - ES)$$

$$H_{AA} - E = - (H_{AB} - ES)$$

We get two solutions as below

$$E_g = \frac{H_{AA} + H_{AB}}{1 + S} \quad \text{--- (3)}$$

$$E_u = \frac{H_{AA} - H_{AB}}{1 - S} \quad \text{--- (4)}$$

Now to find C_A & C_B corresponding to E

Taking A(i) and (3)

we get $C_A = C_B$

Similarly with the second value of energy we have from A(ii)

$$C_A = -C_B$$

For some reason $E_g \rightarrow$ lower, $E_u \rightarrow$ higher
[g \rightarrow gerade, u \rightarrow ungerade]

Consequently, the wavefunctions corresponding to the two energies E_g, E_u respectively are

$$\phi_g = C_A (\psi_{1SA} + \psi_{1SB}) \text{ as } C_A = C_B$$

$$\phi_u = C_A (\psi_{1SA} - \psi_{1SB}) \text{ as } C_A = -C_B$$

Now to find C_A, C_B . For this we know that any wave function should be normalised

so for any C_A $\int dz \phi_g^2 = 1$ [as real]

$$C_A^2 \int (\psi_{1SA} + \psi_{1SB})^2 dz = 1$$

$$C_A^2 \left\{ \int \psi_{1SA}^2 dz + \int \psi_{1SB}^2 dz + 2 \int \psi_{1SA} \psi_{1SB} dz \right\} = 1$$

or $C_A^2 \{ 1 + 1 + 2S \} = 1 \Rightarrow C_A = \frac{1}{\sqrt{2(1+S)}}$

$$\text{or } \phi_g = \frac{1}{\sqrt{2(1+S)}} (\psi_{1sA} + \psi_{1sB})$$

Similarly, $C_B = \frac{1}{\sqrt{2(1-S)}}$

and corresponding wave fun $\phi_u = \frac{1}{\sqrt{2(1-S)}} (\psi_{1sA} - \psi_{1sB})$

The coulomb integral can be expressed as

$$H_{AA} = \langle \psi_{1sA} | \frac{\hbar^2}{2m} \nabla^2 - \frac{ke^2}{r_A} | \psi_{1sA} \rangle - \langle \psi_{1sA} | \frac{ke^2}{r_B} | \psi_{1sA} \rangle + \langle \psi_{1sA} | \frac{ke^2}{R} | \psi_{1sA} \rangle$$

The first term on RHS is simply the ground state of hydrogen atom E_H since the operator in it is the hydrogen atom hamiltonian and $\psi_{1sA} \rightarrow 1e$ wave fun

The nuclear repulsion term ke^2/R is independent of electronic coordinates

Writing $V_{AA} = \langle \psi_{1sA} | \frac{ke^2}{r_B} | \psi_{1sA} \rangle$
 $V_{AB} = \langle \psi_{1sA} | \frac{ke^2}{r_A} | \psi_{1sB} \rangle$

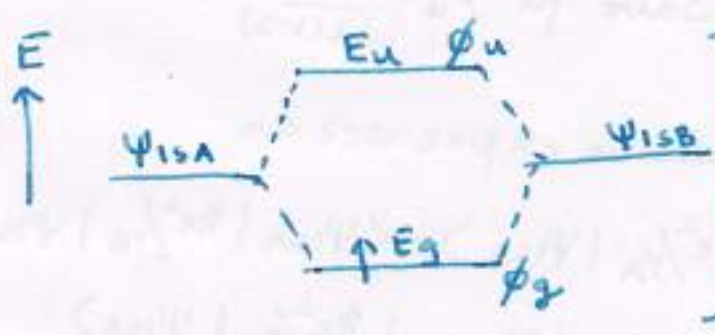
$$H_{AA} = E_H - V_{AA} + \frac{ke^2}{R} - S$$
$$H_{AB} = E_H - V_{AB} + \frac{ke^2}{R} S \quad \text{--- (6)}$$

$V_{AA}, V_{AB}, S, ke^2/R \rightarrow$ dependent on R and are +ve. The overlap $S=0$ if two nuclei are infinitely separated and $S=1$, if they are together.

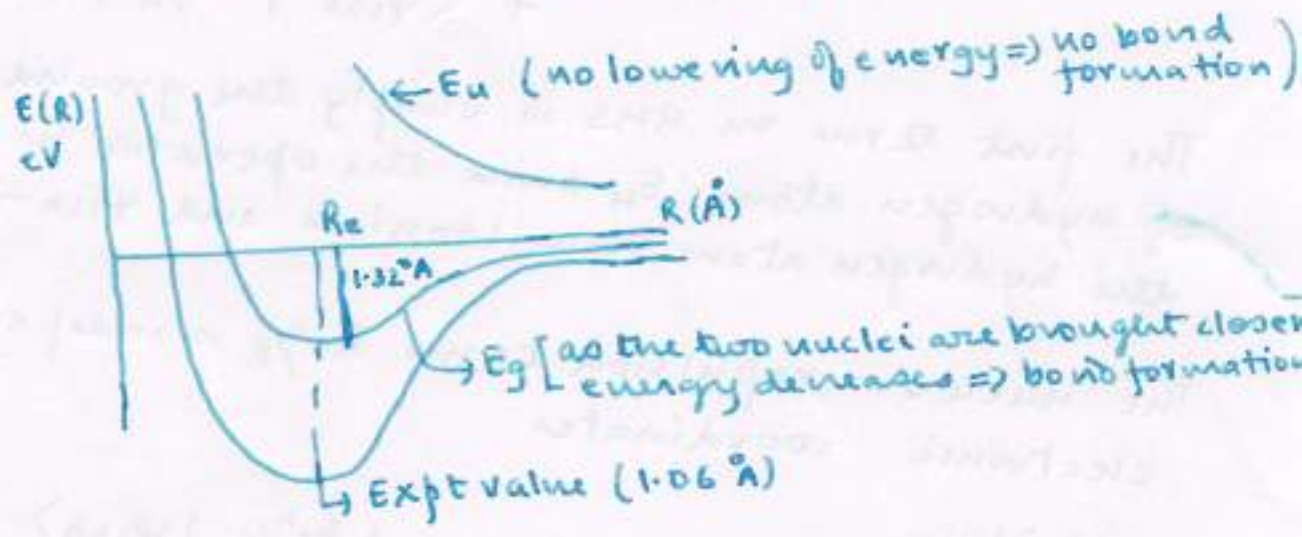
substitution of eq 5, 6 in 3, 4 gives

$$E_g = E_H - \left(\frac{V_{AA} + V_{AB}}{1+S} \right) + \frac{ke^2}{R} \quad -7$$

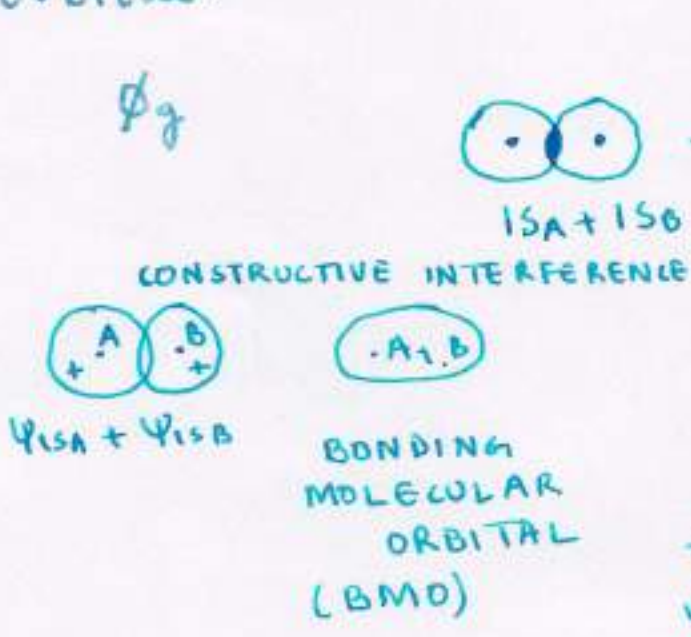
$$E_u = E_H - \left(\frac{V_{AA} - V_{AB}}{1-S} \right) + \frac{ke^2}{R} \quad -8$$



The MO ϕ_g has an energy E_g lower than that of atomic orbital from which it is formed. However, in case of ϕ_u , the energy E_u is higher than that of atomic orbital.



So now we can say that when two atomic orbitals are brought closer they form a molecular orbital.



σ Mol orbital

e density is large in the inter nuclear region as the two orbitals are added up and there is a fairly large value of wave function i.e, large electron density. The electron density is max in the center, both nuclei are bound to electron and molecule is formed. Therefore energy is lowered.



No accumulation of electron density in middle. Wave function has a node. ~~Anti~~ bonding formation. Energy is raised. There is a depletion of charge between the two nuclei and a large nuclear repulsion resulting in ABMO.

Both these bonds are symmetrical about inter nuclear axis. $[\sigma]$