THEORY OF CHEMICAL BONDING

The process of combination of atoms to give molecules is called chemical bonding. It the union atoms takes place by the transference of ēs from one atom to the other, the bonding is called ionic and if it takes place the mutual sharing of ēs between atomes concerned the bonding is said to be co-valent.

G.N-Lewis was the 1st to suggest in 1916, that atoms may combines with one another by sharing of electrons in their valency shell so that the combining atoms get the nearest noble gas configuration. Lewis concept explains the bonding between atoms which have a tendency to gain ēs. It also adequately explains the polarity of molecules. But the concept remains purely quantitative and it cannot answer number of questions like,

1. why covalent bond is formed, at all?
2. How are es arranged in a molecule?
3. what are forces of attraction interactions in a molecule
4. What are the concept of bond energy in a covalent bond?
5. How does sharing of ēs sharin explains the geometry of molecules?

Wave mechanics has provided satisfactory answer to most of these and this has led to the development of two important theories of covalent bonding. They are

a) The valence Bond theory

b) The molecular orbital theory.

Our major problem is to find the answer to the questions how the atoms are held together in a molecule and why total energy of atoms is lowered when they combines. From the point of view of chemical bonding it is not the KE, but the PE of a molecule is important. PE is the sum of its electronic energy (due to inter electronic repulsion and nuclear electronic attraction) and nuclear energy (due to nuclear repulsion) for a diatomic molecule, PE depending only on the internuclear distance as follows:

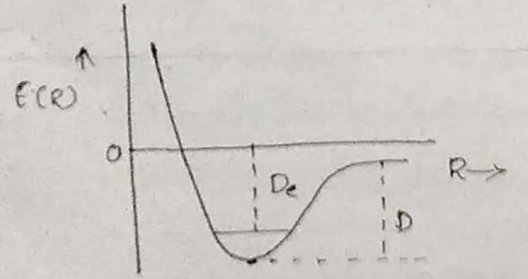


Fig: PE curve for diatomic molecule.

For the normal state of the molecules, the PE curve exhibits a minimum at a particular value of R, which is the equilibrium ~~btw~~ inter nuclear distance or bond distance (Re). The depth of the minimum (D) represents the energy required to dissociate the molecule into atoms. However the observed dissociation energy (De) is   the zero point vibrational energy.

Born-oppen heimer approximation (2 mark)

If one writes the schrodinger equation for a molecule, it will be a partial differential eqn involving number of variables and hence no body can solve it. But we know that en is much lighter than the nuclei and consequently its motion is much faster than that of nuclei. There fore the es is able to adjust instantaneously to the positions of the nuclei. So it get an idea about the electronic motion and electronic energy. We assume the nuclei to be not moving and consider a situation where the nuclei are fixed at a particular distance. This is known as Born Oppenheimer approximation.

This approximation is achieved by writing the total wave function as a product of electronic wave function and nuclear wave function.

The former depends on the coordinates of both the $\bar{e}n$ and nuclei while the latter depends only on the coordinate of the nuclei.

ie, $\psi = \psi_e \psi_N$

$$\hat{H} = \hat{T}_N(R) + \hat{H}_e(r,R) \text{, where}$$

$\hat{H}$ = hamiltonion of a molecule,

$\hat{T}_N$ = Nuclear KE operator, $\hat{H}_e$ - electronic hamiltonian operator.

$\hat{H}_e$ describes motion of $\bar{e}$s for fixed positions of nuclei. Schondinger eq: for a molecule is,

$$\hat{H}\psi = E\psi.$$

$$(\hat{H}_n + \hat{H}_e)\psi = E\psi.$$

$$(\hat{H}_n + \hat{H}_e)\psi_e\psi_N = E\psi_e\psi_N$$

The electronic wavefunction ψ_e is defined by

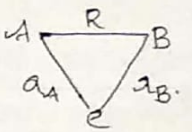
$$\hat{H}_e\psi_e = E_e\psi_e \text{ and } \psi_N \text{ by } (\hat{H}_n + E_e)\psi_N = E\psi_N$$

E_e - electronic energy which depends only on the co-ordinates of the nuclei. It represents the electronic energy for the fixed co-ordinates of the nuclei.

$\hat{H}_n$ - hamiltonion operator for the nuclear motion includes nuclear KE operator and the electronic wave-function,

$$E = \text{Total}E = KE + PE.$$

eg: Consider H_2^+ molecule, (two nuclei and one $\bar{e}n$)



There are two nuclei and one $\bar{e}n$. The Schordinger wave eqn may be written as,

$$\hat{H}\psi = E\psi.$$

$$✓\ \hat{H} = \frac{-\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 - \frac{Ze^2}{r_A} - \frac{Ze^2}{r_B} + \frac{e^2}{R} - \frac{\hbar^2\nabla^2}{2m_e}$$

In a.u

$$\hat{H} = \left[-\frac{1}{2}\frac{\nabla_A^2}{m_A} + \frac{\nabla_B^2}{m_B} + \nabla^2\right] - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

Applying Born oppenheimer approximation.

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

Here,

∇_A and ∇_B are very small so they can be neglected

Secular Determinant

Consider a linear combination of two functions ψ_1 and ψ_2. Let us assume that ψ_1 and ψ_2 stands for the atomic orbitals of two different atoms. Therefore $\psi = a_1\psi_1 + a_2\psi_2$. This method is called LCAO. It gives molecular bond formation.

According to the postulates of quantum

mechanics, expectation value of an observable E is given by, $\bar{E} = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi \psi^* \, d\tau}$

This formula can be applied in the case of MO

$$\therefore \quad E = \frac{\int (a_1\psi_1 + a_2\psi_2)\hat{H}(a_1\psi_1 + a_2\psi_2)\,d\tau}{\int (a_1\psi_1 + a_2\psi_2)(a_1\psi_1 + a_2\psi_2)\,d\tau}$$

(all orbitals are real)

$$= \frac{\int (a_1^2\psi_1\hat{H}\psi_1 + a_1a_2\psi_1\hat{H}\psi_2 + a_1a_2\psi_2\hat{H}\psi_1 + a_2^2\psi_2\hat{H}\psi_2)\,d\tau}{\int (a_1^2\psi_1^2 + 2a_1a_2\psi_1\psi_2 + a_2^2\psi_2^2)\,d\tau}$$

let $\int \psi_1 \hat{H} \psi_1 \, d\tau = H_{11}$ $\quad \int \psi_1^2 \, d\tau = S_{11}$ $\quad H_{12} = H_{21}$

$\int \psi_1 \hat{H} \psi_2 \, d\tau = H_{12}$ $\quad \int \psi_1\psi_2 \, d\tau = S_{12}$ $\quad S_{12} = S_{21}$

$\int \psi_2 \hat{H} \psi_2 \, d\tau = H_{22}$ $\quad \int \psi_2^2 \, d\tau = S_{22}$

$$\therefore \bar{E} = \frac{a_1^2H_{11} + 2a_1a_2H_{12} + a_2^2H_{22}}{a_1^2S_{11} + 2a_1a_2S_{12} + a_2^2S_{22}}$$

we have to choose a_1 and a_2 in such a way that energy is minimum.

$$\text{ie,} \quad \frac{dE}{da_1} = \frac{dE}{da_2} = 0.$$

let $\bar{E} = \frac{N}{D} = \frac{\text{Numerator}}{\text{denominator}}$

$$\frac{dE}{da_1} = \frac{d}{da_1}(N/D) = \left[\frac{1}{D}\cdot\frac{dN}{da_1} - \frac{N}{D^2}\frac{dD}{da_1}\right] = 0.$$

$$= \left[\frac{dN}{da_1} - \frac{N}{D}\frac{dD}{da_1}\right]\frac{1}{D} = 0$$

|||ly $$\frac{dE}{da_2} = \left[\frac{dN}{da_2} - \frac{N}{D}\frac{dD}{da_2}\right]\frac{1}{D} = 0.$$

$$\frac{dN}{da_1} = 2a_1H_{11} + 2a_2H_{12}$$

$$\frac{dD}{da_1} = 2a_1S_{11} + 2a_2S_{12}$$

(Since $\frac{N}{D} = E$)

$$\frac{dN}{da_1} - \frac{N}{D}\frac{dD}{da_1} = 0$$

ie, $2a_1H_{11} + 2a_2H_{12} - \bar{E}(2a_1S_{11} + 2a_2S_{12}) = 0.$

$$a_1(H_{11} - \bar{E}S_{11}) + a_2(H_{12} - \bar{E}S_{12}) = 0 \quad \text{— ①}$$

|||ly $$\frac{dN}{da_2} - \frac{N}{D}\frac{dD}{da_2} = 0.$$

$(2a_1H_{12} + 2a_2H_{22}) - \bar{E}(2a_1S_{12} + 2a_2S_{22}) = 0.$

$$a_1(H_{12} - \bar{E}S_{12}) + a_2(H_{22} - \bar{E}S_{22}) = 0 \quad \text{— ②}$$

These are two (① and ②) homogeneous linear algebraic equations are called Secular equations. These are simultaneous equations which can not be solved easily because their RHS = 0.

Secular equations have non trivial solutio only if the determinant of the coefficient of a_1 and a_2 is zero.

$$\begin{vmatrix} H_{11}-\bar{E}S_{11} & H_{12}-\bar{E}S_{12} \\ H_{21}-\bar{E}S_{21} & H_{22}-\bar{E}S_{22} \end{vmatrix} = 0.$$

Such a determinant is called secular determinant. This is a 2nd order determinant equation. Therefore it will have two roots, E_1 and E_2. The lower value of the two will give minimum energy corresponding to the trial function.

let ψ be a linear combination of ψ_1, ψ_2 and ψ_3.

$$\begin{vmatrix} H_{11}-\bar{E}S_{11} & H_{12}-\bar{E}S_{12} & H_{13}-\bar{E}S_{13} \\ H_{21}-\bar{E}S_{21} & H_{22}-\bar{E}S_{22} & H_{23}-\bar{E}S_{23} \\ H_{31}-\bar{E}S_{31} & H_{32}-\bar{E}S_{32} & H_{33}-\bar{E}S_{33} \end{vmatrix} = 0$$

This on simplification gives a polynomial which can be solved for 3 values of E. one is meant for bonding 2nd antibonding and 3rd non bonding M.O.

Molecular orbital theory

M.O theory was developed by Hund, Mulliken and others. In this treatment the atoms which combines to form a molecule are supposed to loose their individual characters. ie an ēn moves in a field of more than one nucleus. In otherwards molecular orbitals are bicentric or polycentric. The following assumptions of quantum mechanics are applied in MO theory.

① Each ēn in a molecule is described by a certain wavefunction 'ψ'. Since the wave function ψ represents the orbital of the ēn in the molecule, it's called a molecular orbital.

② Each ψ is defined by a certain quantum numbers which are responsible for its energy and shape.

③ Each ψ is associated with a definite energy value and the total energy of the molecule is the sum of the energies of the occupied molecular orbitals corrected for mutual interaction between the ēn.

④ Each ē has a spin ±½.

⑤. The molecular orbitals are formed when the atomic orbitals to be bound come close together. So that the individual atomic orbitals merge into molecular orbitals. After the molecular orbitals are formed, the ēs are spread into the orbitals. The pauli's exclusion principle is obeyed and also aufbau principle and Hund's rule are obeyed.

Since the wave equation for an ēn moving in a field of several nuclei can not be solved exactly, a one ēn molecular orbitals is considered and is extended to multi ēn systems with some approximations

The 1^{st} of these approximations is the linear combination of atomic orbitals (LCAO)

LCAO Method

If ψ_A and ψ_B are the wave functions for any two isolated, non reacting systems (atoms) A and B with energies E_A and E_B respectively. Then the total wave functions for those non-interacting systems will be given by,

$\psi = \psi_A \cdot \psi_B$ and the energy of the system is given by,

$$E = E_A + E_B.$$

If there are several wave functions, say ψ_1, ψ_2, $\psi_3 \cdots \psi_n$ for the same system, then the true wave functions ψ is obtained by combining the several wave functions linearly.

ie, $\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \dots + c_n\psi_n.$

where $c_1, c_2, c_3 \cdots c_n$ are the various coefficients which are subjected to get a state of lowest energy.

LCAO - MO approximation

This is a quantitative approximation in which ēn is supposed to be nearer to one of the nuclei than to the other. Consider a diatomic molecule made up of atoms A and B. The ēn nearer to A may be assumed to be influenced exclusively by A or B. Then wave function ψ_A① describe the behaviour of ēn ①, when it is close to A $|||^{ly}$ the wave function ψ_B① will describe the behaviour of ēn ①, when it is nearer to B. Since the ēn is under the influence of both A and B, the wave function of the single ēn moving in the field of nuclei A and B is obtained by the linear combination of ψ_A① and ψ_B①.

ie, $\psi_1 = c_1\psi_A\textcircled{1} + c_2\psi_B\textcircled{1}.$

The values of the coefficients describe the most satisfactory molecular orbital and these values are determined by variation method.

$|||^{ly}$ for the 2^{nd} ēn,

$$\psi_2 = c_1\psi_A\textcircled{2} + c_2\psi_B\textcircled{2}.$$

According to MO theory if we have a simple co-valent bond composed of two ēs described by one ēn molecular wave functions ψ_1 and ψ_2 respectively, the combined wave functions for the systems is the product of two wave functions.

ie, $\psi_{MO} = \psi_1 \cdot \psi_2$

$$= (c_1\psi_{A}①+c_2\psi_{B}①)(c_1\psi_{A}②+c_2\psi_{B}②)$$

In general if there n ēs, the combined wave function for the system is,

$\psi_{MO} = \psi_1\psi_2 \cdots \psi_n$, when ψ_1, ψ_2 etc are the ēn molecular orbitals.

Hydrogen molecule ion (H_2^+) (MO treatment)

The H_2^+ ions is the only one molecular system for which the Schrodinger eqn can be solved. The Schrodinger equation for hydrogen atom is seperable in spherical co-ordinates with nucleus at the centre while that for H_2^+ ion is seperable in elliptical co-ordinates with the two nuclei at the two foci of the elipse. The wave function for hydrogen atom are called atomic orbitals and those for H_2^+ ion are called molecular orbitals.

Instead of finding an exact solution using elliptical co-ordinates. It is more convenient to follow the approximate procedure of using a trial LCAO-MO function. This treatment involve

1) Calculation of energy of H_2^+ using the trial LCAO-MO function and

2) Determination of ēn density in the different region of the molecule.

The trial LCAO-MO function of H_2^+ is,

$\psi = a_1 1S_A + a_2 1S_B$ where $1S_A$ and $1S_B$ are the atomic orbitals and in a.u they are,

$$1S_A = \frac{1}{\sqrt{\pi}} e^{-r_A} \text{ and } 1S_B = \frac{1}{\sqrt{\pi}} e^{-r_B}.$$

The energy is given by,

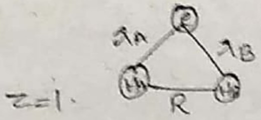
$$E = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi \psi^* \, d\tau}$$

where $\hat{H}$ is the electronic hamiltonian.

The ēn density (ψ^2) can be determined by knowing the expression for ψ. ie, by determining the unknown coefficients a_1 and a_2.

Calculation of energy

The complete hamiltonian for H_2^+ ion is given by,



(Two nucleus one ēn)

$$\hat{H} = \frac{-\hbar^2}{2}\left[\frac{\nabla_A^2}{m_A} + \frac{\nabla_B^2}{m_B} + \frac{\nabla^2}{m_e}\right] - \frac{e^2}{r_A} - \frac{e^2}{r_B} - \frac{e^2}{R} \quad -(1)$$

where A and B refer to two H nuclei. 'M' mass of nucleus, 'm' that of an ēn, 'e' is the charge of ēn. r_A and r_B are distance of ēn from the nuclei A and B respectively and 'R' distance b/w the two nuclei.

By applying a.u and Born-oppenheimer approximation we get,

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

Then energy, $\bar{E} = \dfrac{\int (a_1 1s_A + a_2 1s_B)\hat{H}(a_1 1s_A + a_2 1s_B)\,d\tau}{\int (a_1 1s_A + a_2 1s_B)(a_1 1s_A + a_2 1s_B)\,d\tau}$

$$= \frac{\int a_1^2 1s_A \hat{H} 1s_A + a_1 a_2 1s_A \hat{H} 1s_B + a_1 a_2 1s_B \hat{H} 1s_A + a_2^2 1s_B \hat{H} 1s_B)\,d\tau}{\int (a_1^2 1s_A^2 + 2a_1 a_2 1s_A 1s_B + a_2^2 1s_B^2)\,d\tau}$$

$$= \frac{a_1^2 H_{11} + 2a_1 a_2 H_{12} + a_2^2 H_{22}}{a_1^2 S_{11} + 2a_1 a_2 S_{12} + a_2^2 S_{22}}$$

Where $H_{11} = \int 1s_A \hat{H} 1s_A\,d\tau$

$H_{21} = H_{12} = \int 1s_B \hat{H} 1s_A\,d\tau = \int 1s_A \hat{H} 1s_B\,d\tau$.

$H_{22} = \int 1s_B \hat{H} 1s_B\,d\tau$

$S_{11} = \int 1s_A 1s_A\,d\tau$,

$S_{12} = S_{21}$

$= \int 1s_A 1s_B\,d\tau$

$= \int 1s_B 1s_A\,d\tau$

$S_{22} = \int 1s_B 1s_B\,d\tau$.

The secular equation is,

$$\frac{dE}{da_1} = 0 \text{ and } \frac{dE}{da_2} = 0.$$

$$\frac{dE}{da_1} = 2a_1 H_{11} + 2a_2 H_{12} - \bar{E}(2a_1 S_{11} + 2a_2 S_{12}) = 0.$$

ie, $a_1 H_{11} + a_2 H_{12} - \bar{E}(a_1 S_{11} + a_2 S_{12}) = 0$.

or

$a_1(H_{11} - \bar{E}S_{11}) + a_2(H_{12} - \bar{E}S_{12}) = 0$ — ②.

$$\frac{dE}{da_2} = 2a_1 H_{12} + 2a_2 H_{22} - \bar{E}(2a_1 S_{12} + 2a_2 S_{22}) = 0$$

or

$a_1(H_{12} - \bar{E}S_{12}) + a_2(H_{22} - \bar{E}S_{22}) = 0$.

Secular determinant is,

$$\begin{vmatrix} H_{11} - \bar{E}S_{11} & H_{12} - \bar{E}S_{12} \\ H_{21} - \bar{E}S_{21} & H_{22} - \bar{E}S_{22} \end{vmatrix} = 0$$

Since the two hydrogen atoms in H_2^+ are like ($H_{11} = H_{22}$) the operator $\hat{H}$ being hermitian $H_{12} = H_{21}$ is orbitals are already normalised therefore $S_{12} = S_{21} = S$ and $S_{11} = S_{22} = 1$.

$$\begin{vmatrix} H_{11} - \bar{E} & H_{12} - \bar{E}S \\ H_{12} - \bar{E}S & H_{11} - E \end{vmatrix} = 0$$

ie, $(H_{11} - \bar{E})^2 - (H_{12} - \bar{E}S)^2 = 0$.

$$(H_{11}-\bar{E})^2 = (H_{12}-\bar{E}S)^2$$

$$H_{11}-\bar{E} = \pm (H_{12}-\bar{E}S)$$

The +ve value on RHS gives Emax and -ve value gives Eminimum.

ie, $H_{11}-\bar{E} = H_{12}-\bar{E}S$.

$$H_{11}-H_{12} = \bar{E}-\bar{E}S$$

$$= \bar{E}(1-S).$$

$$\bar{E}_{max} = \frac{H_{11}-H_{12}}{1-S}$$

$$H_{11}-\bar{E} = -H_{12}+\bar{E}S.$$

$$H_{11}+H_{12} = \bar{E}+\bar{E}S$$

$$= \bar{E}(1+S)$$

$$\bar{E}_{min} = \frac{H_{11}+H_{12}}{1+S}.$$

Therefore inorder to find the values of Emax and Emin we should know the values of H_{11} and H_{12}.

$$H_{11} = \int 1S_A \hat{H}\, 1S_A\, d\tau.$$

$$= \int 1S\left(-\tfrac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \tfrac{1}{R}\right) 1S\, d\tau.$$

$$= \int 1S_A\left(-\tfrac{1}{2}\nabla^2 - \frac{1}{r_A}\right) 1S_A\, d\tau - \int 1S \frac{1}{r_B} 1S\, d\tau$$

$$+ \int 1S\, \tfrac{1}{R}\, 1S\, d\tau$$

$$= E_H - P + \tfrac{1}{R}.$$

$H_{11} = E_H - P + \tfrac{1}{R}$ where P is the energy of attraction b/w $\bar{e}$n and nucleus B.

ie H_{11} represents the energy of the hydrogen atom A perturbed by a proton B and is quite close to energy of an unperturbed hydrogen atom (except for small values of R).

where $E_H = \int 1S\left(\frac{-1}{2}\nabla^2 - \frac{1}{r_A}\right) 1S\, d\tau$. = energy of a single H atom.

$P = \int 1S \frac{1}{r_B} 1S\, d\tau$ The $1S_A$ orbital is normalised. ie, $\int 1S\, 1S_A\, d\tau = 1$.

$H_{12} = E_H S + \frac{1}{R} S - Q$ → exchange energy.

H_{12} is called the resonance integral and represent the energy of the overlap density under the influence of the attractive field of both the nuclei. Here 'Q' arises due to the exchange of $\bar{e}$n between the two nuclei and hence is called exchange energy.

$$H_{12} = \int 1S_A \hat{H}\, 1S_B\, d\tau$$

$$= \int 1S_A\left(-\tfrac{1}{2}\nabla^2 - \frac{1}{r_A}\right) 1S_B\, d\tau - \int 1S_A \cdot \frac{1}{r_B} \cdot 1S_B\, d\tau$$

$$+ \frac{1}{R}\int 1S_A\, 1S_B\, d\tau$$

$= E_H S - Q + \frac{S}{R}$ where $S = \int 1S_A\, 1S_B\, d\tau$

$Q = \int 1S_A \frac{1}{r_B} 1S_B\, d\tau$

$$E_{max} = \frac{E_H(1-S) - (P-Q) + \frac{1}{R}(1-S)}{(1-S)}$$

$$= E_H - \left(\frac{P-Q}{1-S}\right) + 1/R.$$

$$E_{min} = \frac{E_H(1+S) - (P+Q) + \frac{1}{R}(1+S)}{1+S}$$

$$= E_H - \frac{(P+Q)}{1+S} + \frac{1}{R}.$$

we have $\psi = a_1 1S_A + a_2 1S_B$

The values of a_1 and a_2 are obtained from secular eqn by the following way.

$$a_1(H_{11} - \bar{E}) + a_2(H_{12} - \bar{E}S) = 0 \quad -③.$$

Take $H_{11} - \bar{E} = H_{12} - \bar{E}S$ (+ve value)

The above ② =>

$$a_1 = -a_2 \quad \text{(for maximum)}$$

If we take $H_{11} - \bar{E} = -(H_{12} - \bar{E}S)$ (-ve value)

eqn ③ => $a_1(H_{11} - \bar{E}) - a_2(H_{11} - \bar{E}) = 0.$

i.e., $a_1 = a_2$ (for minimum)

for lower energy, the wave function;

$$\psi_1 = a_1 1S_A + a_1 1S_B \quad (\text{since } a_1 = a_2).$$

$$= a_1(1S_A + 1S_B).$$

on normalising ψ_1 we get the value of a

$$\int \psi_1^2 d\tau = 1$$

$$\int a_1^2 (1S_A + 1S_B)^2 d\tau = 1.$$

$$a_1^2 \int (1S_A^2 + 2\, 1S_A 1S_B + 1S_B^2)\, d\tau = 1$$

$$a_1^2(1 + 2S + 1) = 1$$

$a_1^2(2+2S) = 1$

$$a_1^2 = \frac{1}{2(1+S)}$$

$$a_1 = \frac{1}{\sqrt{2(1+S)}}$$

$$\psi_1 = \frac{1}{\sqrt{2(1+S)}}(1S_A + 1S_B)$$

for higher energy the wave function,

$$\psi_2 = a_1 1S_A - a_1 1S_B$$

$$= a_1(1S_A - 1S_B)$$

on normalising we get the value of a_1 as,

$$a_1 = \frac{1}{\sqrt{2(1+S)}}$$

$$\psi_2 = \frac{1}{\sqrt{2(1+S)}}(1S_A - 1S_B)$$

The values of P, Q and S are -ve and we can see that $E_1 < E_2$ or $E_{min} < E_{max}$ i.e., in the ground state of H_2^+ the en occupies the molecular orbital ψ_1 and in the excited state it occupies ψ_2.

Molecular orbital treatment of Hydrogen molecule

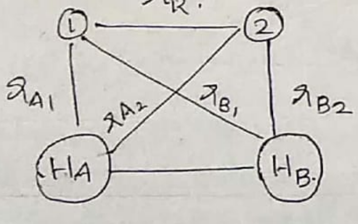
H molecule is the simplest example of a diatomic molecule having more than one ēn. The Schordinger equation is,

$$\hat{H}\psi(1,2) = E\psi(1,2)$$

where ψ(1,2) is the wave function of the two ēn and $\hat{H}$ is the electronic hamiltonian in a.u. i.e,

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} + \frac{1}{R}.$$

1 and 2 stands for two ēs. A x B refer to the two H nucleus.



$$\hat{H} = \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}}\right) + \left(\frac{-1}{2}\nabla_2^2 - \frac{1}{r_{B2}} - \frac{1}{r_{A2}}\right) + \frac{1}{r_{12}} + \frac{1}{R}.$$

$$= \hat{H}_{(1)} + \hat{H}_{(2)} + \frac{1}{r_{12}} + \frac{1}{R}.$$

where $\hat{H}_{①}$ and $\hat{H}_{②}$ are the electronic hamiltonian for two seperate H_2^+ system.

During electronic motion, R does not change. Therefore the value of $1/R$ does not change. We may calculate the electronic energy (E) for a particular value of R by using the operator.

$\hat{H} = \hat{H}_{①} + \hat{H}_{②} + \frac{1}{r_{12}}$ and then add the internuclear repulsion energy $\frac{1}{R}$ to it to get the total energy of the molecule.

The Orbital approximation.

We model the structure of H_2 by adding an ēn to the H_2^+. By using orbital approximation consider that, in the ground state the two ēn wave-functions ψ(1,2) of hydrogen is the product of two one ēn H_2^+ like wave-functions or molecular orbital of σg(1) and σg(2).

i.e, ψ(1,2) = σg(1)·σg(2).

This is just analogous to the case of the He atom for which

ψ(1,2) = 1s①·1s②.

where 1s① and 1s② are H-like wave functions or atomic orbitals. The $\sigma g(1)$ and $\sigma g(2)$ are given as,

$$\sigma g(1) = \frac{1}{\sqrt{2(1+S)}}\, 1S_A(1) + 1S_B(1).$$

$$\sigma g(2) = \frac{1}{2\sqrt{1+S}}\, 1SA(2) + 1S_B(2).$$

In two ēn system we have to consider pauli's exclusion principle, ie, the product function should be antisymmetric. Here it is not antisymmetric but it can be antisymmetrised by multipling with antisymmetric spin combination.

$$\psi_{as}(1,2) = \sigma g(1) \cdot \sigma g(2) \frac{1}{\sqrt{2}} [\alpha_{(1)}\beta_{(2)} - \alpha_{(2)}\beta_{(1)}] - (1)$$

OR.

$$\psi_{as}(1,2) = \frac{1}{\sqrt{2}} (\sigma g(1)\, \bar{\sigma} g(2) - \bar{\sigma} g(1)\, \sigma g(2))$$

$$\sigma g(1) = \sigma g(1)\, \alpha_1$$

$$\bar{\sigma} g(2) = \sigma g(2)\, \beta(1).$$

$$\begin{cases} \sigma(1)\alpha_1 = \sigma 1 \\ \sigma(1)\beta_1 = \sigma^{-1} \\ \sigma(2)\alpha(2) = \sigma 2. \\ \sigma 2\, \beta(2) = \sigma^{-2} \end{cases}$$

where $\frac{1}{\sqrt{2}}$ is the normalisation factor for the spin function and σg and $\bar{\sigma} g$ denote the spin orbitals with spins α and β. $\psi(1,2)$ can be expressed as a determinant.

$$\psi_{as}(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma g(1) & \bar{\sigma} g(1) \\ \sigma g(2) & \bar{\sigma} g(2) \end{vmatrix}$$

we see that the ēs in H_2 have the same molecular orbital, ie, σg but different spin orbital σg and $\bar{\sigma} g$. In other words in H_2 with configuration $\sigma^2 g$, the two ēs have opposite spin α and β ie, the spins are paired (↑↓).

Evaluation of Energy

The electronic energy of H_2 is given by,

$$E_e = \int \psi_{as} \hat{H} \psi_{as}\, d\tau.$$

where ψ_{as} is normalised substituting the value of ψ_{as} from eqnation (1) we get

$$E_e = \frac{1}{2} \int \sigma g(1)\, \sigma g(2) (\alpha_{(1)}\beta_{(2)} - \alpha_{(2)}\beta_{(1)})\, d\tau.$$

The volume element $(d\tau)$ includes both space and spin co-ordinates ($d\tau = dv \cdot ds$) since the hamiltonian does not operate on spin functions, they may be seperated.

$$E_e = \frac{1}{2} \int \sigma g(1)\sigma g(2)\, \hat{H}\, \sigma g(1)\, \sigma g(2)\, dv \int (\alpha_{(1)}\beta_{(2)} - \alpha_{(2)}\beta_{(1)})\, ds$$

$$\int (\alpha_{(1)}\beta_{(2)} - \alpha_{(2)}\beta_{(1)})^2 ds = \int \alpha_{(1)}^2 \beta_{(2)}^2 + \alpha_{(2)}^2 \beta_{(1)}^2 - 2\, \alpha_{(1)}\beta_{(2)}\alpha_{(2)}\beta_{(1)})\, d\tau$$

$= 1+1-0$

$= \underline{\underline{2}}$

Since α and β are orthogonal.

$$E_e = \frac{2}{2}\int \sigma g(1)\,\sigma g(2)\,\hat{H}\,\sigma g(1)\,\sigma g(2)\,dv.$$

$$= \int \sigma g(1)\,\sigma g(2)\left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}\right)\sigma g(1)\,\sigma g(2)\,dv$$

$$= \int \sigma g(1)\,\sigma g(2)\,\hat{H}_1\,\sigma g(1)\,\sigma g(2)\,dv + \int \sigma g(1)\,\sigma g(2)\,\hat{H}_2\,\sigma g(1)\,\sigma g(2)\,dv + \int \sigma g(1)\,\sigma g(2)\,\frac{1}{r_{12}}\,\sigma g(1)\,\sigma g(2)\,dv$$

Since $\hat{H}_1$ operator only on en ① and $\hat{H}_2$ only on en ②

$$E_e = \int \sigma g① \hat{H}_1 \sigma g① dv_1 \int \sigma g② \sigma g② dv_2 + \int \sigma g② \hat{H}_2 \sigma g② dv_2 \int \sigma g① \sigma g① dv_1 + \iint \sigma g①^2 \frac{1}{r_{12}} \sigma g②^2 \, dv_1 dv_2.$$

$$= \int \sigma g① \hat{H}_1 \sigma g① dv_1 + \int \sigma g② \hat{H}_2 \sigma g② dv_2 + \iint \sigma g①^2 \frac{1}{r_{12}} \sigma g② \, dv_2 \, dv_2.$$

Since σg① and σg② are normalised.

$$= E_{H_2^+} + E_{H_2^+} + J.$$

$= 2E_{H_2^+} + J$ where J represents the coloumbic repulsion energy b/w two electronic charges by MO.

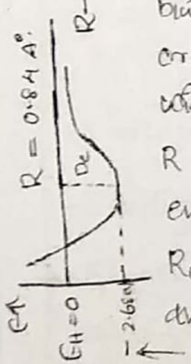
Then the total ground state energy of H_2 including internuclear repulsion energy $1/R$ is given by,

$E = E_e + 1/R$

$= 2E_{H_2^+} + J + 1/2$

$$E = 2E_H - 2\frac{(P+Q)}{1+S} + \frac{1}{R} + J$$

The plot of the calculated value of E against R shows a minimum which lies below $2E_H = 0$ line indicating stability of the molecule and the bond formation. The bond formation is because of the increased en density due to the presence of two ens in the region b/w the two nuclei and overlap of atomic orbitals. The σg molecular orbital has now 2 en with opposite spins. The minimum however lies at R = 0.84 A°. This corresponds to a bond dissociation energy of 2.68 ev. The experimental values are Rexp = 0.74 A° and De = 4.75 ev (56% error) obivously there is some significant short coming in the model.



The short coming in MO treatment and the improvement introduced.

In MO treatment, the expectation energy is calculated using the wave function

$$\psi(1,2) = \sigma g① \sigma g②.$$

$$= \frac{1}{2(1+S)}\left(1S_A① + 1S_B①\right)\left(1S_A② + 1S_B②\right)$$

(Here we are ignoring the spin part since it has no role in the calculation of energy).

$$= \frac{1}{2(1+S)} \left(1S_{A①} \cdot 1S_{A②} + 1S_{B①} 1S_{B②} + 1S_{A①} 1S_{B②} + 1S_{B①} 1S_{A②} \right).$$

The 1st and 2nd terms represent the situations where both the e's are near the nucleus A and near the nucleus B respectively. These corresponds to two ionic structures $H_A^- H_B^+$ and $H_A^+ H_B^-$. The 3rd and 4th represents the situations where the two ēns are shared equally b/w the nuclei. This corresponds to the covalent structures $H_A - H_B$.

In otherwords ψ may be expressed as

$\psi = \frac{1}{2(1+S)} (\psi_{ionic} + \psi_{covalent})$ ie, equal contribution of ions and covalent structure for a molecule like H_2, this is highly unlikely and this is the main reason for such a low calculated value of dissociation energy.

But there is a scope for improvement ie, by allowing for more flexible basic functions, used self constant field method etc. One obivious improvement is to introduce a variable parameter in the exponent of the 1S atomic orbitals (basic functions).

ie, $1S = \frac{\alpha^{3/2}}{\sqrt{\pi}} e^{-\alpha/r}$

The ground state of H_2 is built up from the double occupation of the MO ψ_1 (bonding) which is symmetric with respect to the inversion at the center of the bond. We can construct an excited state with same symmetry as the ground state by promoting both ēns to the MO ψ_2 (antibonding)

$$\psi_1 = \frac{1}{\sqrt{2}} \left| \psi_{1①} \; \psi_{1②} \right|$$

$$= \frac{1}{\sqrt{2}} \left| \psi_{2①} \; \psi_{2②} \right|$$

MO ψ_2 (antibonding) posses a node at the midpoint of the bond and its purpose is to keep the ēn at opposite ends of the molecule. The effect of the configuration ψ_2 is to remove the charge density from internuclear region and to concentrate it in the vicinity of the nuclei. This This is known as left right (or horizontal) co-relation of the electronic motions. This can be affected by mixing ψ_0 (ground state wave function) and ψ_2 (excited state).

An appropriate linear combination of ψ_0 and ψ_2 can give a proper balance b/w the ionic and covalent contribution in the MO picture of H_2.

$$\omega(a) = c(R)\psi_0 + d(R)\psi_2.$$

R - intermediate distance $\omega(a)$ is the improved wave function for the ground state. 'c' and 'd' are vibrational parameters which are functions of R. one can improve the wave function still further by adding additional configuration as long as they have correct symmetries.

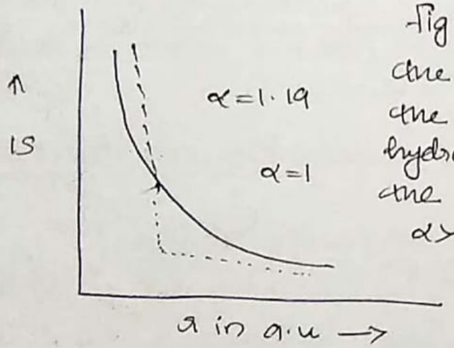


fig: The variation of the wave function of the 1s orbitals of a hydrogen atom from the nucleus for α=1 and α>1.

using the improved function, bond energy is determined which is equal to 3.49 eV and bond length (Req) =0.72Å. when α>1 the function decays more rapidly away from the nucleus indicating that the densities are more compact. (ie, bond formation from atom is accompanied by orbital contraction.

James and coolidge using a 13 term function in the summation.

$$e^{-\alpha(r_1+r_2)}\sum_{mnijk} r_1^m r_2^n he_1^i he_2^j he_{12}^k$$

where m,n,l,j,k are integer and α is a variable parameter obtained a result which is in complete agreement with experimental results. later kolos and woolnie wigs using a 1000 term function for H_2 obtained the exact results.

Electron density (ēn distribution) and bonding in H_2^+.

By definition (ψ^2) represents probability density of finding the ēn or the ēn density which varies from position to position in the molecule. for two energy states E±

$$\psi^2 \text{ or } \psi_1^2 = \frac{1}{2(1+S)}(1s_A^2 + 1s_B^2 + 2\,1s_A 1s_B)$$

At a point midway b/w the two positions. $r_A = r_{B}$ we have $1s_A = 1s_B$.

$$\therefore \psi_1 = \frac{2\,1s_A}{\sqrt{2(1+S)}} \text{ and } \psi_1^2 = \frac{4\,1s_A^2}{2(1+S)}.$$

$$\psi_2 = 0 \text{ and } \psi_2^2 = 0.$$

ie, more electron density is found b/w the nuclei in the state ψ_1 This means that MO ψ_1 has the effect of concentrating the ēn density is responsible for the stability (or bonding) in H_2^+

∴ ψ_1 is called bonding molecular orbital.

In the state ψ_2, density at the center of the bond is zero and is therefore less than the sum of ēn densities of seperate atoms ψ_2 is called antibonding molecular orbital. The densities along the internuclear axis is shown below.

Here dotted line → mo
solid line → ēn density

In order to get better results, the LCAO treatment must be improved. If H^+ and H atoms are infinitely a part, the energy and wave function of such a system becomes same as those of a 'H' atom. If these two species are brought together thus the system reduces to He^+, the 1s orbital of which has the orbital exponent twice as large as that of the 1s orbital of hydrogen. So a linear combination of 1s orbitals with variable exponent must be used.

ie, $$1S_A = \frac{\alpha^{3/2}}{\alpha^{1/2}} e^{-\alpha/r_A}$$ where α must be in bwo 1 and 2.

$$1S_B = \frac{\alpha^{3/2}}{\alpha^{1/2}} e^{-\alpha/r_B}.$$

Another improvement is suggested by Dickenson. An atom in a molecule is different from an isolated atom which has always a spherically symmetrical ēn distribution. This spherical symmetry is destroyed on molecular formation and the atomic orbital is therefore polarised or distorted. Therefore it is not correct to use the trial function

$$\psi = a_1 1S_A + a_2 1S_2.$$

Dickenson employed the following linear combination.

$$\left[1S_{A}\textcircled{2} + C_2 2P_{A}\textcircled{2}\right] + \left[1S_{B}\textcircled{2} + (2\phi_{B}(\alpha))\right]$$

2p orbitals were oriented along the line joining the two nuclei. Effect of adding 2p type orbital to polarise 1s orbital. (Here c is an additional variable parameters).

Valence Bond theory

Valence bond theory is near to classical lewis concept of ēn pair bond and it is older than the MO theory. In VB theory no new orbital is formed, the ēs are supposed to be present in the atomic orbitals. It is not certain which orbital is occupied by which ēn since the ēs are indistinguishable so the wave function has to be such that it allows the presence of an ēn in either of the overlapping orbitals. Here the molecule is considered to be a collection of atoms and their interactions are considered.

LCAO - VB approximation

Let $\psi_{A(1)}$ and $\psi_{B(2)}$ are the wave functions representing the ēn ① and ēn ② associated with the nuclei A and B. Combined wavefunction ψ_1 for the system,

$$\psi_1 = \psi_{A(1)} \cdot \psi_{B(2)}.$$

Since the ēs are indistinguishable, there is an equal probability that ēn ① in B and ēn ② in A.

$$\therefore \psi_2 = \psi_{A②} \cdot \psi_{B①}$$

As the atoms are brought together the standing wave will interact and a new wave motion will result; which (Heither and London suggested) would be described as a linear combination of ψ_1 and ψ_2.

$$\therefore \psi_{VB} = c_1\psi_1 + c_2\psi_2$$

$$= c_1 \psi_{A①} \cdot \psi_{B②} + c_2 \psi_{A②} \psi_{B①}.$$

This is the principle of VB theory.

Hydrogen molecule : VB treatment of H_2

For a pair of H atom, H_A and H_B seperated infinitly, the total electronic hamiltonian is, $\hat{H} = \hat{H}_{A①} + \hat{H}_{B②}$, where $\hat{H}_{A①}$ and $\hat{H}_{B②}$ are the hamiltonians of the two H atoms seperately; 1 and 2 refer to the ēs in the two atoms. The combined wave function for the two ēs would be

$\phi_1 = 1s_{A①} \cdot 1s_{B②}$, where 1s is the atomic orbital of each H atom.

When the atoms are bonded to give H_2, the hamiltonian in au is,

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} + \frac{1}{R}$$

$$= \hat{H}_{A①} + \hat{H}_{B②} + \hat{H}^1$$

where $\hat{H}_{A①} = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}}$ is the hamiltonian for a hydrogen A.

$\hat{H}_{B②} = -\frac{1}{2}\nabla_2^2 - \frac{1}{r_{B2}}$ is the hamiltonian for a hydrogen B.

$$\hat{H}' = -\frac{1}{r_{A2}} - \frac{1}{r_{B1}} + \frac{1}{r_{12}} + 1/R$$

using the trial wave function we can calculate the eigen value or energy of the above hamiltonian is equal to energy of H_2.

ie, $E = \iint 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}} \left(\hat{H}_{A\textcircled{1}} + \hat{H}_{B\textcircled{2}} + H'\right) 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}}\, d\tau_1 d\tau_2$

$$= \int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, \hat{H}_{A\textcircled{1}}\, 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, d\tau_1 + \int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, \hat{H}_{B\textcircled{2}}\, 1s_{A\textcircled{1}}\, 1s_{B_2}\, d\tau_2 + \iint 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}}\, \hat{H}'\, 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}} \cdot d\tau_1 d\tau_2$$

$$= \underline{\underline{E_{H_A} + E_{H_B} + Q}}.$$

Since, $\int 1s_{A\textcircled{1}} \cdot 1s_{A\textcircled{1}} = 1$ and $\int 1s_{B\textcircled{2}} \cdot 1s_{B\textcircled{2}} = 1$.

where $Q = \int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}} \cdot \left(\frac{-1}{r_{A\textcircled{2}}}\right) 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, d\tau +$

$\int 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}} \cdot \left(\frac{-1}{r_{B\textcircled{1}}}\right) 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}}\, d\tau +$ -ve q'

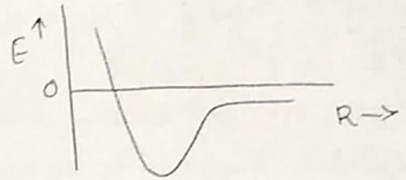
$\int 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}} \left(\frac{1}{r_{12}}\right) 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}} \cdot d\tau +$ +ve q'

$\int 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}}\, \frac{1}{R} \cdot 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}} \cdot d1$.

$$= -J - J + J' + 1/R$$

'J' coulombic attraction energies of the $\bar{e}$n ① and ② with nuclei B and A respectively. 'J'' coulombic repulsion energy b/w the two $\bar{e}$n

$\frac{1}{R}$ nuclear repulsion energy on plotting E vs R we get,



Here De(dissociate)) = 25 kg, but experimental value is 423 kJ. It is clear that the choice of the trial f^n is not correct.

Heitler and London argued that the $\bar{e}$s can not be labelled (not distinguishable) an equally good wave function for H_2 could be

$$\phi_2 = 1s_{A\textcircled{2}}\, 1s_{B\textcircled{1}}.$$

They further argued that, when the two hydrogen atoms approach each other their degeneracy is removed and the system is represented by a wave f^n which is a linear combination of ϕ_1 and ϕ_2.

ie, $\psi_{(1,2)} = a_1\phi_1 + a_2\phi_2$.

$$= a_1 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}} + a_2 1s_{A\textcircled{2}}\, 1s_{B\textcircled{1}}.$$

where a_1 and a_2 being the mixing parameters whose values are determined by the minimization of energy. The energy E is given by

$$E = \frac{\int \psi \hat{H} \psi^* d\tau}{\int \psi \psi^* d\tau}$$

Apply variation theorem (as follows)

$$E = \frac{\int (a_1\phi_1 + a_2\phi_2) \hat{H} (a_1\phi_1 + a_2\phi_2) d\tau}{\int (a_1\phi_1 + a_2\phi_2)^2 d\tau}$$

$$= \frac{a_1^2 H_{11} + 2a_1a_2 H_{12} + a_2^2 H_{22}}{a_1^2 + 2a_1a_2 S^2 + a_2^2}$$

where $H_{11} = \int \phi_1 \hat{H} \phi_1 d\tau$, $H_{12} = H_{21} = \int \phi_1 \hat{H} \phi_2 d\tau$

$H_{22} = \int \phi_2 \hat{H} \phi_2 d\tau$.

$$\int \phi_1 \phi_1 d\tau = \int \phi_2 \phi_2 d\tau = 1$$

one of the 1s orbital is centred on A and the other on B. The integral $\int 1s_A(1)\, 1s_B(1)\, d\tau = S$ is non zero when $1s_A$ + $1s_B$ are simultaneously nonzero. This occur only for the regions in which the two orbitals overlap with each other. Since the magnitude of the integral depends on the extend of overlapping of $1s_A$ and $1s_B$. It is called overlap integral.

$$\int \phi_1 \phi_2 d\tau = \int 1s_A(1)\, 1s_B(2)\, 1s_A(2)\, 1s_B(1) = S^2$$

Since $S = \int 1s_A(1)\, 1s_B(2)\, d\tau = \int 1s_A(2)\, 1s_B(2)\, d\tau$

The secular eqn is,

$$\frac{dE}{da_1} = \frac{dE}{da_2} = 0.$$

$$\frac{dE}{da_1} = 2a_1H_{11} + 2a_2H_{12} - E(2a_1 + 2a_2S^2) = 0.$$

$$a_1H_{11} + a_2H_{12} - E(a_1 + a_2S^2) = 0$$

$$a_1(H_{11} - E) + a_2(H_{12} - ES^2) = 0 \quad ①.$$

$$\frac{dE}{da_2} = 2a_1H_{12} + 2a_2H_{22} - E(2a_1S^2 + 2a_2) = 0.$$

$$a_1(H_{12} - ES^2) + a_2(H_{22} - E) = 0$$

In the case of H_2 the two hydrogen atoms are identical. ie, $H_{11} = H_{22}$.

ie, $a_1(H_{12} - ES^2) + a_2(H_{11} - E) = 0$ ②

From ① and ②, the secular determinant is,

$$\begin{vmatrix} H_{11} - E & H_{12} - S^2E \\ H_{12} - S^2E & H_{11} - E \end{vmatrix} = 0$$

ie, $(H_{11} - E)^2 - (H_{12} - S^2E) = 0$.

$$H_{11} - E = \pm(H_{12} - ES^2)$$

To calculate Emax and Emin

$$H_{11} - E = H_{12} - ES^2$$

$$H_{11} - H_{12} = E - ES^2 = E(1 - S^2)$$

$$\therefore E = \frac{H_{11} - H_{12}}{(1 - S^2)}$$

III^{rly} $E_{min} = \dfrac{H_{11}+H_{12}}{(1+S^2)}$

Determination of a_1 and a_2 corresponding to E_{max} and E_{min}

1- For E_{min}

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

The secular eqn ① is $a_1(H_{12}-ES^2)+a_2(H_{11}-E)=0$

OR.

$$a_1(H_{11}-E) + a_2(H_{11}-E) = 0.$$

$$a_1(H_{11}-E) = -a_2(H_{11}-E).$$

$$\therefore a_1 = -a_2$$

Corresponding wave function is, suppose $a_1=a_2=1$

$$\psi_{\substack{\text{bonding}\\(\text{min})}} = a\left[1S_{A\textcircled{1}}\cdot 1S_{B\textcircled{2}} + 1S_{A\textcircled{2}}\,1S_{B\textcircled{1}}\right]$$

for max

$$H_{11}-E = H_{12}-ES^2.$$

$\therefore$ secular eqn $\Rightarrow$ $a_1(H_{11}-E)+a_2(H_{11}-E)=0.$

$$a_1+a_2=0$$

$$a_1=-a_2.$$

$$\therefore \psi_{\substack{\text{anti bonding}\\(\text{max})}} = a\left[1S_{A\textcircled{1}}\cdot 1S_{B\textcircled{2}} - 1S_{A\textcircled{2}}\,1S_{B\textcircled{1}}\right]$$

To find the value of a in ψ_b.

On normalizing the wave function ψ_b we get,

$$\int \psi_b^2\, d\tau = 1$$

OR.

$$\int a^2\left(1S_{A\textcircled{1}}\cdot 1S_{B\textcircled{2}} + 1S_{A\textcircled{2}}\,1S_{B\textcircled{1}}\right)^2 d\tau = 1.$$

$$a^2\int\left[1S_{A\textcircled{1}}^2\cdot 1S_{B\textcircled{2}}^2 + 2\,1S_{A\textcircled{1}}1S_{B\textcircled{2}}1S_{A\textcircled{2}}1S_{B\textcircled{1}} + 1S_{A\textcircled{2}}^2\cdot 1S_{B\textcircled{1}}^2\right]d\tau=1$$

$$a^2\,(1+2S^2+1) = 1$$

$$a^2\,2(1+S^2) = 1$$

$$a^2 = \frac{1}{2(1+S^2)}$$

$$a = \frac{1}{\sqrt{2(1+S^2)}}$$

$$\therefore \psi_b = \frac{1}{\sqrt{2(1+S^2)}}\left[1S_{A\textcircled{1}}\cdot 1S_{B\textcircled{2}} + 1S_{A\textcircled{2}}\,1S_{B\textcircled{1}}\right]$$

value of a in ψ_a

On normalising ψ_a, $\int \psi a^2 d\tau = 1$

$$a^2\int \left[1S_{A\textcircled{1}}\cdot 1S_{B\textcircled{2}} + 1S_{A\textcircled{2}}\,1S_{B\textcircled{1}}\right]^2 d\tau = 1$$

$$a^2(1-2S^2+1) = 1$$

$$a = \frac{1}{\sqrt{2(1-S^2)}}$$

$$\therefore \psi_a = \frac{1}{\sqrt{2(1+S^2)}}\left(1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}} - 1s_{A\textcircled{2}}\, 1s_{B\textcircled{1}}.\right)$$

Evaluation of energy

$$E_{min} = \frac{H_{11}+H_{12}}{1+S^2}.$$

$$H_{11} = \int \phi_1 \hat{H} \phi_1 d\tau = \int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, \hat{H} \cdot 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, d\tau$$

$$= \int 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}}\, \hat{H}_{A\textcircled{1}}\, 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}}\, d\tau.$$

$$+ \int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, \hat{H}_{B\textcircled{1}}\, 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, d\tau.$$

$$+ \int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, \hat{H}_{B\textcircled{2}}\, 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, d\tau$$

$$+ \int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{1}}\, \hat{H}'\, 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, d\tau$$

$$H_{11} = E_H + E_H + \phi$$

$$\text{where } \phi = \int 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}} \left(\frac{-1}{r_A}\right) 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}} +$$

$$\int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}} \left(-\frac{1}{r_{B\textcircled{1}}}\right) 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}} +$$

$$\int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, \frac{1}{r_{12}}\, 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}} +$$

$$\int 1s_{A\textcircled{1}} \cdot 1s_{B\textcircled{2}}\, \frac{1}{R}\, 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}$$

$$= -J - J + J' + 1/R.$$

$$= J + \frac{1}{R} \quad \text{where } J = J' - 2J$$

J – Coulombic attraction

J' – Coulombic repulsion

$\frac{1}{R}$ – nuclear repulsion.

$$H_{12} = \int \phi_1 \hat{H} \phi_2 d\tau.$$

$$= \int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}} \left(H_{A\textcircled{1}} + H_{B\textcircled{2}} + H'\right) 1s_{A\textcircled{2}}\, 1s_{B\textcircled{1}}\, d\tau$$

$$= E_H S^2 + E_H S^2 + \phi'$$

$$\text{where } \phi' = \int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}} \left(\frac{-1}{r_{A2}}\right) 1s_{A\textcircled{2}}\, 1s_{B\textcircled{1}}\, d\tau +$$

$$\int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}} \left(-\frac{1}{r_1}\right) 1s_{A\textcircled{2}}\, 1s_{B\textcircled{1}}\, d\tau +$$

$$\int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, \frac{1}{r_{12}}\, 1s_{A\textcircled{2}}\, 1s_{B\textcircled{1}}\, d\tau +$$

$$\int 1s_{A\textcircled{1}}\, 1s_{B\textcircled{2}}\, \frac{1}{R}\, 1s_{A\textcircled{2}}\, 1s_{B\textcircled{1}}\, d\tau.$$

$$= K + \frac{S^2}{R}$$

$$H_{12} = 2E_H S^2 + K + \frac{S^2}{R} \quad \text{OR} \quad H_{12} = 2E_H S^2 + \phi'$$

K arises only because we are using a wave function of the form which explicity recognize the destinguishabile by of the ēn. Therefore 'k' is strictly a quantum mechanical quantity and it arises when these are exchanged b/w the two nuclei and it is called exchange integral.

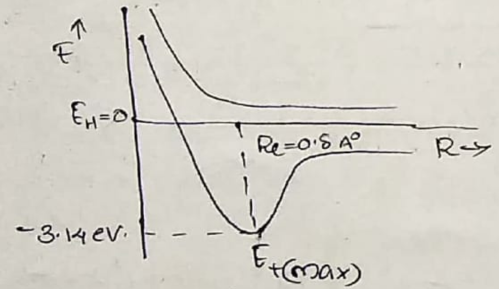
$$E_{mini} = \frac{2E_H + J + \frac{1}{R} + 2E_H S^2 + K + S^2/R}{1+S^2}$$

$$= \frac{2E_H(1+S^2) + J + K + \frac{1}{R}(1+S^2)}{1+S^2}$$

$$= 2E_H + \frac{J+k}{1+S^2} + \frac{1}{R}$$

$$E_{max} = 2E_H + \frac{1}{R} + \frac{J-k}{1-S^2} \text{ or } E_{max} = 2E_H + \frac{Q-Q'}{1-S^2}$$

Heitler and London evaluated the value of J and K Both are bound to be -ve. This makes $E_{max} < E_{mini}$. E_H is known to have the value of -½ a.u. On plotting E against R we get.



bonding
De = 303 kJ/mol.

Even though the calculated value of De is smaller than the experimental value (423 kJ/mol). It can be seen that the value is much better than that obtained by MO. i.e., simple VB theory is superior to MO theory. The wave function ψ_b is same as $\psi_{covalent}$. Bonding valence bond picture arises due to the presence of H_{12} integral and ψ_b tells us about the ēn sharing. Strong binding energy in H_2 is due to the exchange of ēn between the two nuclei and the integral H_{12} is called exchange integral or resonance integral.

ground state wave function ψ_+ is symmetric with respect to the exchange of positional co-ordinates of two ēn. Therefore in order to satisfy pauli's rule the function must be combined with the antisymmetric spin function to get a singlet state.

$$\therefore \psi_+ = \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2(1+S^2)}} \left(1S_{A①} 1S_{B②} + 1S_{A②} 1S_{B①}\right)(\alpha_1\beta_2 - \alpha_2\beta_1)$$

ψ_- is antisymmetric with respect to the interchange of positional co-ordinates. pauli's principle requires that ψ be associated with symmetric spin function to get a.

Electron density distribution

The ēn density in the symmetric state and antisymmetric state is given by,

$$\psi_\pm^2 = \frac{1}{2 \pm 2S^2}\left(1S_{A①}^2 1S_{B②}^2 + 1S_{A②}^2 1S_{B①}^2 \pm 2\, 1S_{A①} 1S_{B②} 1S_{A②} 1S_{B①}\right)$$

The ēn density of one ēn is obtained by integrating this eqn over the co-ordinates of the other ēn so that,

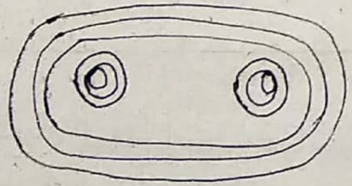
$$\rho_1 = \int \psi_{\pm}^2(1,2)\,d\tau = \frac{1}{2 \pm 2S^2}\left(1s_{A(1)}^2 + 1s_{B(1)}^2 \pm 2S\,1s_{A(1)}1s_{B(1)}\right)$$

$$\rho_2 = \int \psi_{\pm}^2(1,2)\,d\tau = \frac{1}{2 \pm 2S^2}\left(1s_{A(2)}^2 + 1s_{B2}^2 \pm 2S\,1s_{A(2)}1s_{B(2)}\right)$$

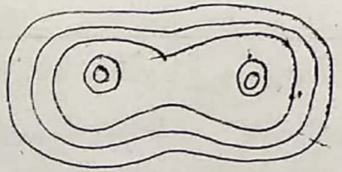
The total ēn density, $\rho = \rho_{(1)} + \rho_{(2)}$

Electron density contour

In the symmetric state, there is a concentration of ēn. cloud between the nuclei which corresponds to attraction or formation of the bond. In the antisymmetric state ēn cloud is away from the space between the nuclei corresponding to repulsion and existance of a nodel plane in the middle. The ēn density contours for symmetric and antisymmetric state are shown below.



Symmetric state in H_2



antisymmetric state in H_2.

Ionic Contribution in the VB function

Heitler and London wave function has a serious defect, i.e, it does not consider the probability of a situation when both the ēn may be near one nucleus (it excludes ionic structures). we shall get better result if we include ionic structures $H_A^+H_B^-$ and $H_A^-H_B^+$, though the probability of such a situation is not high. The better wave fn should be,

$$\psi = N\left[\{1s_{A(1)}1s_{B(2)} + 1s_{A(2)}1s_{B(1)}\} + \lambda\{1s_{A(1)}1s_{A(2)} + 1s_{B(1)}1s_{B(2)}\}\right]$$

OR

$$\psi = N\left[\psi_{cov} + \lambda\psi_{ionic}\right]$$ where N = normalization factor

variation treatment leads to $\lambda = 1/6$. This raises the calculated value of dissociation energy (D_e) to 396 kJ/mole, i.e, Bond in H_2 is mainly covalent but some ionic character too.

Resonance

In terms of VB theory, H_2 molecule is stable because the pair of ēs in it exchange their orbitals. The exchange energy (H_{12}) according to Suguira's calculation, contributes about 85 to 90% towards the total binding energy. Even better results are obtained by including ionic structures. It may therefore be concluded that the stability of the H_2 molecule is due to the different possible electronic arrangements in the system. A linear combination of all the corresponding eigen functions then represents the actual state of the system. In VB terminology this is called resonance of the molecule among the possible electronic structures. The wavefunction ψ is given by,

$$\psi = a_1\psi_1 + a_2\psi_2 + a_3\psi_3 + \ldots$$

The energy E corresponding to ψ will be lower than any of the energy values $E_1, E_2, E_3 \ldots$ If E_1 is the lowest of individual contributions, then $E_1 - E$ will be called the resonance energy of the molecule.

~~Molecular~~ orbitals ~~for~~ H_2^+ excited states

The two lowest approximate wave

Comparison of VB and MO theories.

① Both the theories are approximations.

It is an approximation to assume that the pairing of two ēs in a molecule is unique, rendering all other possible pairings relevant. This gives an error of 1 to 2 ev/molecule. Further there is a limitation to the amount of calculations, which gives us an additional error of about 2 to 3 ev/molecule. Such a large error shows that calculation is approximate.

② Both theories assert that the bonded ēs belongs to both the nuclei.

③ Both the theories emphasis the overlap of all orbitals and the cause of bonding is shown to be due to the displacement of an ēn density into the internuclear region. According to both the theories, stabilization is due to the exchange integral H_{12} (lowering of energy by the exchange of one ēn between the two atomic orbitals).

In MO theory, $H_{12} = \int \phi_A \hat{H} \phi_B \, d\tau$ which refers to the exchange of one ēn between two atomic orbitals. ϕ_A and ϕ_B. This implies the interaction or coupling b/w two atomic orbitals.

In VB theory, $H_{12} = \int \phi_{A①} \phi_{B②} \hat{H} \phi_{A②} \phi_{B①} d\tau$

This refers to the exchange of a pair of ēn b/w the two atomic orbitals. In this way VB theory, retains the concept of en pair bond b/w two atoms. But in MO theory, there is a continuous ēn density distribution over the whole molecule with no localization of ēn pair, so the bond is not identifiable.

④ In VB theory, electronic structure of the molecule is described interms of atomic orbitals, while in MO theory, it is done interms of linear combination of atomic orbitals while in MO theory, atomic orbitals loose their identity.

⑤ groundstate of H_2 is either theory corresponds to a symmetrical spatial wave function,

$$\psi_{MO} = (a_1 1S_{A①} 1S_{B①} + a_2 1S_{A②} 1S_{B②})$$

$$\psi_{V.B} = (a_1 1S_{A①} 1S_{B②} + a_2 1S_{A②} 1S_{B①})$$

According to pauli's exclusion principle, the ēn wave function should be antisymmetric with respect to exchange of ēn. This is acheived by multipling with spin combination $(\alpha_1\beta_2 - \alpha_2\beta_1)$.

⑥ The typical V.B function for a bond in homonuclear molecule is Heitler and London (H-L) -function

$$\psi^{VB} = \phi_{A①} \phi_{B②} + \phi_{B①} \phi_{A②}$$

$$\psi^{MO} = (\phi_{A①} + \phi_{B①})(\phi_{A②} + \phi_{B②})$$

$$= \phi_{A①} \phi_{A②} + \phi_{A①} \phi_{B②} + \phi_{B①} \phi_{A②} + \phi_{B①} \phi_{B②}.$$

The 1st and 3rd term in ψ^{MO} corresponds to the H-L wave function and the other two represents ionic bonds $H_A^- - H_B^+$ and $H_A^+ H_B^-$ ie ψ^{MO} is an equal mixture of covalent and ionic functions.

ψ^{VB} completely ignores ionic functions. In short, according to VB theory, if one ēn of H_2 is in the orbital of $1S_A$ the other must be in $1S_B$ and there is no chance for both the en being in the same $1S_A$ or $1S_B$. This is known as complete charge correlation, the tendency of an en to resist the presence of another ēn in the same orbital. But MO theory under estimates the change correlation ie, if one ēn is in orbital $1S_A$ the other may be in either A or B.

⑦ ψ^{MO} and ψ^{VB} have different implications. VB theory predicts the dissociation of H_2 like, $H_2 \rightarrow H + H$. But MO theory predicts two re^{ns} $H_2 \rightarrow H^+ + H^-$ OR $H_2 \rightarrow H + H$. These two re^{ns} are of equal probability. This prediction of ψ^{MO} is not in good agreement with the actual experience (ie $H_2 \rightarrow H^+ + H^-$ in the ground state is less possible).

⑧ VB calculations using H-L function gives a dissociation energy = 3.14 eV for H_2. MO theory gives $D_e = 2.68$ eV. Both the values are far below the experimental value 4.75 eV. But simple VB theory is superior to MO theory.

⑨ ψ^{MO} and ψ^{VB} represents two extremes of the situations. For small values of R (internuclear distance) there is a greater chance for finding 2e^n in one orbital. Therefore MO theory applied better. For larger values of R, VB treatment seems more adequate.

⑩ VB and MO treatments are improved.

VB treatment is improved by the use of "ion-covalent resonance" which means adding ionic function to the H-L function for H_2 molecule, it is expressed as,

$$\psi^{VB}_{H^2} = \psi(H-H) + \lambda(\psi_{H^+H^-} + \psi_{H^-H^+})$$

λ is calculated by variation method ($\lambda = 1/6$). This means 3% ionic contribution to the bond.

MO treatment was improved by including configuration interaction which means taking a linear combination of the functions corresponding to different electronic configurations having the same symmetry.

For eg: in H_2, the ground state configuration is $\sigma g(1)\, \bar{\sigma} g(2)$ and the doubly excited state ie, $\sigma n(1)\, \bar{\sigma}(n)(2)$. Both have the same symmetry. Therefore it is better to take a linear combination of two functions.

$$\therefore \psi^{MO} = |\sigma g(1)\, \bar{\sigma} g(2)| + \mu |\sigma n(1)\, \bar{\sigma} n(2)|$$

where μ is a mixing parameter.

Both can be further improved by using effective nuclear charge in the exponent of 1s orbital.

⑪ MO theory provides a more convenient explanation for electronic transitions in molecules as compared to VB theory.

⑫ mo theory gaind popularity due to its mathematical simplicity for larger molecules VB treatment involves large number of determinents. But mo treatment is less tedious and it is easy to programme on computers.

⑬ In mo approach molecule is regarded as a collection of nuclei and e̅n. Thus we build up molecular orbitals for a collection of nuclei and then assign e̅n to them.

In VB approach molecule is considered as collection of atoms and the interactions b/w these are considered.

⑭ mo treatment of a molecule assumes a single structure and is built on the concept of delocalization of the molecular orbitals and e̅s. VB treatment on the other hand requires structure for the same molecule and the equivalent delocalisation of molecular orbitals is to be seen in the resonance of the wave functions corresponding to different VB structures

⑮ Both the concept of hydbridisation of mo's and the perfect pairing scheme of VB structure suffer complete breakdown in the case of conjugated π systems. In the case of conjugated systems we are applying HMO theory, where we have ~~feed~~ find the coulombic energy (α) and exchange energy (β)

⑯ mo theory can explain the paramagnetic property of oxygen, where as VB theory can not.

Molecular orbitals of H_2^+ excited state.

The two lowest approximate wave f^ns for H_2^+ electronic state are,

$$\Psi_b = \frac{1s_A + 1s_B}{2(1+S)}$$

$$\Psi_a = \frac{1s_A - 1s_B}{2(1-S)}$$

Now we can constant approximation functions for further excited states inorder to build up a supply of H_2^+ like mo. These orbitals may be used for a qualitative discussion of many e̅n systems.

To get approximations to higher mo's we can use the method of linear variation function. For eg, to get approximations ~~to higher~~ molecular orbitals for the 1st 6 (lowest 6) H_2^+ states, we can take a linear combination of 3 lowest m=0 hydrogen like functions on each atom (ie, to get higher states we add on more atomic orbitals to the linear combination)

$$\psi = (a_1 1S_A + a_2 2S_A + a_3 (2P_0)_A) + (a_4 1S_B + a_5 2S_B + a_6 (2P_0)_B).$$

The atomic orbitals enter into effective combinations depending on the following facts.

1) AO's of only matching symmetry w.r.to bond axis can combine.

2) AO's of only matching energy can combine.

3) AO's that can overlap can combine.

The linear combination of two AO's from two atoms can be expressed as,

$$\psi = a_1\phi_1 + a_2\phi_2$$

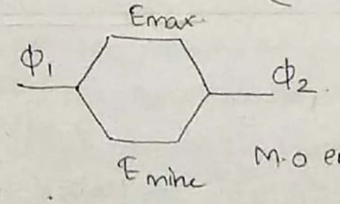
Then the Secular determinant will be,

$$\begin{vmatrix} H_{11}-E & H_{12}-ES \\ H_{12}-ES & H_{22}-E \end{vmatrix} = 0 \quad — ①$$

H_{12} - exchange integral

S - overlapping "

H_{11} and H_{12} represent the energy of an $\bar{e}$ in ϕ_1 and ϕ_2 (not in isolated atoms). The determinant gives two roots for E. (ie, E_{BMO} and E_{AMO}).



M.O energy level diagram.

If ϕ_1 and ϕ_2 do not have the same symmetry, exchange integral and overlaping integral vanishes.

$$\begin{vmatrix} H_{11}-E & 0 \\ 0 & H_{22}-E \end{vmatrix} = 0 \quad — ②$$

ie, $H_{11}-E=0$ and $H_{22}-E=0$. The two energies are energies of AO's. No lowering of energy and hence no combination.

From the secular determinant ① we get

$$(H_{11}-E)(H_{12}-E) = (H_{12}-ES)^2.$$

Energy of an AO depends on its size. If H_{11} and H_{22} are not of comparable magnitude and if $H_{11} <<< H_{22}$, the orbital ϕ_1 will be much smaller than ϕ_2 and the overlap integral and exchange integral will be very small. $E \simeq H_{11}$ OR $E \simeq H_{22}$.

$$\therefore \frac{a_2}{a_1} = \frac{E-H_{11}}{H_{12}-ES} \text{ if } E \simeq H_{11} \quad a_1 >>> a_2.$$

Contribution of ψ_2 in the MO wave function is very small.

ie, $\psi = \phi_1$

||^{ly} if $E \simeq H_{22}$, $a_2 >>> a_1$

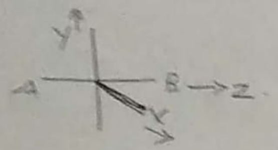
$\psi = \phi_2$.

If AB is a molecule in which all the AO's of A cannot combine with all the atomic orbitals of B.

1S of A cannot combine with 2S of B.

$2P_z$ of A cannot combine with $2P_x$ or $2P_y$ of B.

(P_z is symmetric with respect to rotation about AB but P_x and P_y are antisymmetric.



MO's of Homonuclear Diatomic molecule.

A quantitative but satisfactory molecular treatment of homonuclear diatomic molecule is mainly due to Lennard Jones when we bring two atoms together each atom level, ϕ_a or ϕ_b, split into two, whose LCAO forms are $\phi_a + \phi_b$ and $\phi_a - \phi_b$ (i.e., bonding and antibonding MO).

when two 1s orbitals overlap,

$\phi_b = 1S_A + 1S_B$ $\phi_a = 1S_A - 1S_B$

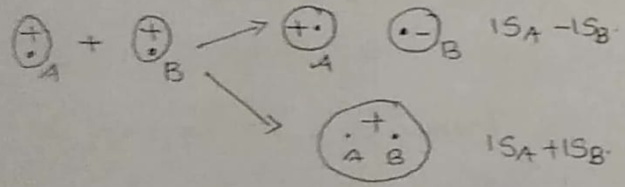
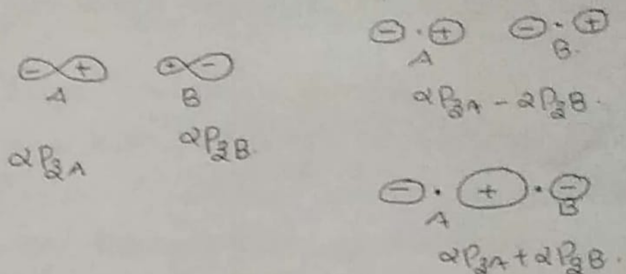


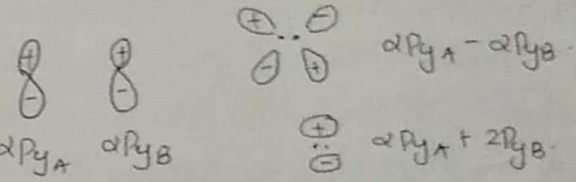
Fig. The boundary contours of bonding and anti-bonding MO's in s-type orbitals.

111ly in the case with 2s orbitals. However since the 2s AO has a nodal sphere while the 1s AO does not, each of these MO's has one more nodal surface than the corresponding $\sigma g1s$ OR $\sigma^* 1s$ MO.

MO's formed from 's' orbitals and P_z orbitals are σ because they have m=0 (symmetric about the z-axis i.e. internuclear axis.



In the case of $P_x - P_x$ overlap and $P_y - P_y$ overlap |m| = 1. Therefor bond formed will be π bond



The combination of two $2P_x$ orbitals leads precisely to the similar molecular orbitals as before except that they are turned through 90° around the molecular axis since the x and y axis are equivalent in space. the corresponding MO's ($2Py_A + 2Py_B$) and ($2Py_A - 2Py_B$) must be by symmetry degenerate with there x counter parts.

Molecular orbitals of diatomic molecules.

Mo's of diatomic molecule can be designated in terms of symmetry and angular momentum in a manner similar to atomic orbitals. Atomic orbitals are designated by l and m (orbital angular momentum of the e^- and its 'z' component). In the case of atoms there are 2l+1 orientations for the z-component. For a diatomic molecule the z-axis is fixed. (ie, internuclear axis). Therefore MO's are distiguished from each other by the z-component of the angular momentum. It is given by, $\lambda h/2\pi$ where $\lambda = 0, \pm1, \pm2 \ldots$ λ corresponds to m of atomic orbitals and it may be regarded as the eigen function of L_z.

The MO's can be labelled as $\sigma, \pi, \delta \ldots$ for $\lambda = 0, \pm1, \pm2 \ldots$ respectively, just as AO's are labelled as s, p, d ... corresponding to $l = 0, 1, 2 \ldots$ Except for $\lambda = 0$, the MO's are doubly degenerate. The MO's formed from s and p_z AO's $(m=0)$ are σ MO's. The two real π functions are considered to be formed by the linear combinations of $2p_{xA}$ and $2p_{xB}$ and the other by the linear combinations of $2p_{yA}$ and $2p_{yB}$. They are designated as π_x and π_y. The -ve combination lead to π^*_x and π^*_y.

In homonuclear molecules, (A_2 or B_2) the inversion centre lies in the middle point of the internuclear axis. The bonding σ MO's are σ_g (symmetric) and the anti bonding are σ_u (antisymmetric). The bonding π molecular orbitals are π_u (+ve combination) and antibonding π MO's are π_g (-ve combinatio).

For heteronuclear diatomic molecules, there is no "g-u" symmetry and these orbitals will be simply denoted as σ1s, σ2s, σ2p etc.

Order of MO Energy levels.

The energy of a MO depends on the factors,

① The type of AO from which it built up.
② The extent of overlap b/w the AO's.

$$E = \frac{H_{11} \pm H_{12}}{1 \pm S}$$

Calculations show that the exchange integral H_{12}, which stabilises a molecule, is directly proportional to the overlap integral 's'. Thus the σMO, $1s_A + 1s_B$, will have much lower energy the another σ MO, $2S_A+2S_B$ (not simply because 1S AO has much lower energy than 2S) IIIrly σ MO of $2S_A+2S_B$ type will have lower energy than the σ MO of $2P_{zA}+2P_{zB}$ type, except for H, 2S AO has lower energy than 2P. generally, π MO's have greater, energy than the σ MO's due to weaker overlap b/w two $2P_x$ or two $2P_y$ AO's. As P_x and P_y AO's are degenerate, the π_{xu} and π_{yu} MO's are degenerate too and so are π_{xg} and π_{yg}. The antibonding MO's have higher energy than the corresponding bonding MO's. The MO's can now be labelled and arranged in order of their increasing energies. The order of energy level is,

$$\sigma 1S,\ \sigma^* 1S,\ \sigma 2S,\ \sigma^* 2S,\ \sigma 2P_z,\ \pi 2P_x = \pi 2P_y$$

$$\pi^* 2P_x = \pi^* 2P_y,\ \sigma^* 2P_z.$$

There are some anomalies. Experimentally it is found that among the homonuclear diatomic molecules of the IInd row elements, the π_x and π_y orbitals is lower in energy than $\sigma 2P_z$ for Li_2 to N_2. for O_2 and F_2 the ordinary level described above reverse is true.

Reason for anomalies are as follows,

When the 2S AO is much lower in energy than 2P (as in O and F) no interaction is possible b/w the two and the σ MO's are given by,

$$\Psi_{2S} = a_1 2S_A + a_2 2S_B.$$

$$\Psi_{2P_z} = a_1 2P_{zA} + a_2 2P_{zB}.$$

But when 2S is not much lower than 2P (as in the case of Li_2 to N_2) the 's' and P_z AO's mix and the σ MO's are given by,

$$\Psi = a_1 2S_A + a_2 2S_B + a_3 2P_{zA} + a_4 2P_{zB}.$$

Such an interaction b/w the 's' and P_z AO's depresses the 1st two σ MO's ($2\sigma_g$ and $2\sigma_u$) and raises the next two σ MO's ($\sigma 2P_z$) $3\sigma_g$ and ($\sigma^* 2P_z$) $3\sigma_u$ to such an extent as to make $2P_x$ and $\pi 2P_y$ (π_u's) lower in energy than the $\sigma 2P_z$ ($3\sigma_g$). Here the order is, (using symmetries).

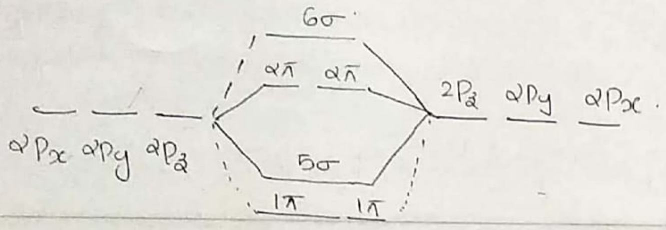
E →.

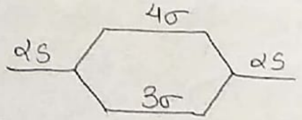
$1\sigma_g,\ 1\sigma_u,\ 2\sigma_g,\ 2\sigma_u,\ 1\pi_u = \pi_u,\ 3\sigma_g,$

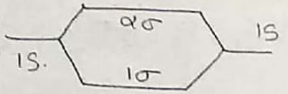
$2\pi^*_g = 2\pi_g,\ 3\sigma_u.$ (fig in next page)

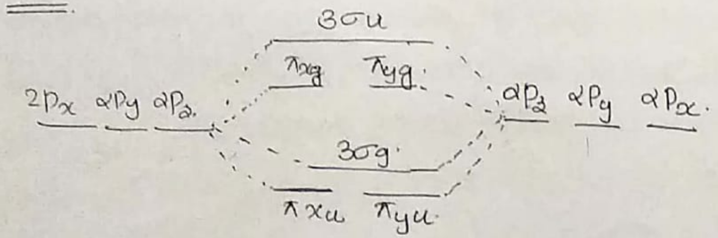
In heteronuclear diatomic molecules (AB), there is no inversion centre, So the MO's cannot be labelled as g or u and they are just numbered.

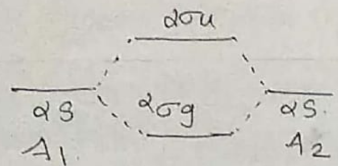
directly making distinations of σ and π (See fig











Electronic structure and bonds

we have to place pairs of ēs with opposite spins in the mols starting with the lowest energy MO and going up, adhering to the principles of paulis and Hund, until all the ēs are acco accounted for. The electronic configuration of some homonuclear and heteronuclear diatomic molecules are given below.

Homonuclear

H_2 (ēs) : $(\sigma g 1S)$

H_2^+ (1ēn) : $(\sigma g (1S)^1$

Li_2 (6ēs) : $(\sigma g 1S)^2 (\sigma u 1S)^2 (\sigma g 2S)^2$

B_2 (10ēs) : $[Li_2] (\sigma u 2S)^2 (\pi u 2Px^1 = \pi u 2Py^1)$

Be_2 (8ēs) $([Li_2] (\sigma u 2S)^2$

C_2 (12ēs) $[Be_2]$ $(\pi u 2Px)^2 = (\pi u 2Py)^2$

N_2 (14ēs) : $[Be_2]$ $\pi u 2 2Px^2 = \pi u 2Py^2 (\sigma y 2P)^2$

O_2 (16ēs) : $[Be]_2$. $(\sigma g 2Pz)^2$ $\pi u 2Px^2 = \pi u 2Py^2$.

$\pi g 2Px^1 = \pi g 2Py^1$.

Heteronuclear.

CO (14ēs)

$(\sigma g 1S)^2 (\sigma u 2S)^2 (\sigma g 2S)^2$

$(\sigma u 2S)^2$ $\pi u 2Px^2 = \pi u 2Py^2$

$(\sigma y 2Pz)^2$

Bond order = [½ (no. of bonding ēs − no of antibonding ēs]

This arrangement explain magnetic properties of molecules for B_2 and O_2 there are unpaired ēs in π_u and π_g MO's respectively. This predicts paramagnetic property for these molecules, and we know that these are highly paramagnetic. This fact can not be explained in terms of the VB theory.

Electronic states and term symbols.

The ēs in diatomic molecules having $\lambda = 0, 1, 2, 3 \ldots$ units are said to be in $\Sigma, \Pi, \Delta, \Phi \ldots$ states respectively. The overall symmetry of the state is governed by the symmetries of the MO's occupied by the ēs, the rule being $g \times g = g$, $u \times u = g$ and $u \times g = u$. Finally the spin multiplicity $(2S+1)$ is determined by Hund's rule.

eg: Ground state of H_2,

Here both the ēs are in $\sigma g1s$ MO. Therefor the overall symmetry is $g \times g = g$. The σ ēs like 's' ēs in AO'S, do not contribute anything towards the orbital angular momentum. ie, $\lambda = 0$. This corresponds to Σ state. Since the ēs are paired, the total spin $S = 0$

$\therefore 2S+1 = 1$ (singlet). Therefor term symbol

$^1\Sigma_g$ (singlet sigma g) t

In the excited state of H_2 having the configuration $\sigma g1s$, $\sigma u1s$ (symmetric $g \times u = u$). The spins may be parallel $(S=1)$ or antiparallel $(S=0)$. Accordingly the excited state may either be $^1\Sigma_u$ OR $^3\Sigma_u$

eg: Find term symbols of N_2 molecules.

N_2

Total number of ēs = 14 ēs.

$EC = [Be_2]\ 2\pi x_u^2 = 2\pi y_u^2\ 3s^2$.

Here all ēs are paired. Hence net symmetry = g.

contribution of σ ēs to λ will be zero.

The two π MO's. ($2\pi x_u$ and $2\pi y_u$) have angular momenta in opposite directions about the nuclear axis their net contribution = 0 ie, $\lambda = 0$.

These corresponds to term Σ.

Since all ēs are paired $S = 0$ $\therefore 2S+1 = 1$.

Term symbol = $^1\Sigma_g$

Molecule	term symbol.
H_2^+	${}^2\Sigma_g$
H_2	${}^1\Sigma_g$
He_2	${}^1\Sigma_g$
He_2^+	${}^2\Sigma_u$
Li_2	${}^1\Sigma_g$
Be_2	${}^1\Sigma_g$
B_2	${}^3\Sigma_g$
C_2	${}^1\Sigma_g$
N_2	${}^1\Sigma_g$
N_2^+	${}^2\Sigma_g$
O_2	${}^3\Sigma_g$
O_2^+	${}^2\pi_g$
F_2	${}^1\Sigma_g$
F_2^+	${}^2\pi_g$.

find term symbol of the following molecule?

1. B_2

Total ēs = 5+5 = 10.

$EC = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2\ \pi_u x^1 = \pi_u y^1$ (2nd row elements.
∴ 2s and 2p_z are

$S = 1$ (Hunds rule ↑↑)

$2S+1 = 3$.

$\Lambda = 0$., the total contribution towards angular momentum is zero.

symmetry $= u \times u = g$.

∴ Term symbol ${}^3\Sigma_g$.

find term symbols for O_2 molecules?

Total no. of ēs = 16 ēs.

$EC = [Be]_2\ 3s^2\ 2\pi x_u^2 = 2\pi y_u^2\ ,\ 2\pi x_g^1 = 2\pi y_g^1$

The term symbols of O_2 depends on, how the two ēs occupy in $\pi_g(\pi^*)$ MO's.

ⓐ if both enter the same $\pi_g(\pi^*)$ MO. Then $\Lambda = 2$. (i.e, net angularmomentum $= \pm 2 \cdot h/2\pi$). Then term $= \Delta$.

Here spins are paired, $S=0$ ∴ $2S+1 = 1$

∴ Termsymbol $= {}^1\Delta_g$

ⓑ if one ē is in πx_g^1 and other in πy_g^1 then the value of $\Lambda = 0$ (see N_2) ∴ Term $= \Sigma$.
The two ēs may have the same spin ($S=1$) or paired ($S=0$). The symmetry will be $g \times g = g$.
This leads to term symbols ${}^3\Sigma_g$, ${}^1\Sigma_g$

Since the ēs in different orbitals suffer less interaction than in the same orbital. The Σ term will be more stable than Δ. According to Hunds rule, we can expect a triplet state has low energy than singlet, the ground state term symbol is $^3\Sigma_g$.

Approximation Methods.

Although schrodinger equation can be solved exactly in many cases, for most problems of chemical interest it is not possible. For example in the case of systems having more than one electron, it is not possible to obtain the exact solution of schrodinger wave equation. This is because in such cases the presence of more than one electron introduces the en repulsion puts $\frac{e^2}{r_{ij}}$ in the hamiltonian, where r_{ij} is the distance b/w the ēs i and j. More over the schrodiger equation cannot be solved exactly for one electron system ~~whose~~ where PE₂ is not spherically symmetrical. eg: Hydrogen atom in an electric or magnetic field. Hence to find exact solution, approximation methods are used.

The commonly used techniques of obtaining approximate solution to wave equation are,

① Method of independent electrons.

② Variation method and ③ perturbation method.

Independent electron approximation

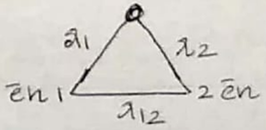
In independent electron method the electrons are assumed to move around the nucleus independent of each other. Hamiltonian for a two electron system is,

$$\hat{H}_{12} \text{ OR } \hat{H} = \frac{-\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$$

Here the subscripts ① and ② refers to two ēns in atomic units $m = e = \hbar = 1$

For a two electron system (He atom) $Z = 2$.

$$\therefore \hat{H}_{12} = -\tfrac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$



Hamiltonian is independent of time. so it has stationary states which are obtained by solving time independent schrodinger equation.

$$\hat{H}_{12}\Psi(1,2) = E(1,2)\Psi(1,2)$$

ie $H\Psi = E\Psi$

$\psi_{(12)}$ and $E_{(1,2)}$ are eigen functions and eigen values of the two electrons taken together in the atom ψ has co-ordinates $\psi_{(1,2)} = \psi_{(x_1 y_1 z_1\ x_2 y_2 z_2)}$

$$\psi^2 d\tau = \left[\psi_{(x_1 y_1 z_1, x_2 y_2 z_2)}\right] dx_1 dy_1 dz_1 dx_2 dy_2 dz_2$$

ψ^2 gives probability density that electron 1 is at a point $(x_1 y_1 z_1)$ and electron 2 at the point $(x_2 y_2 z_2)$ at a given instant.

$\psi^2 d\tau$ = probability that at any instant the electron ① is in the volume element $dx_1 dy_1 dz_1$ and the electron ② in $dx_2 dy_2 dz_2$

On normalising

$$\left[\psi_{x_1 y_1 z_1\, x_2 y_2 z_2}\right]^2 d\tau_1 d\tau_2 = 1.$$

$$d\tau_1 = dx_1 dy_1 dz_1 = r_1^2 dr_1 \sin\theta_1 d\theta_1 d\phi$$

on normalising the term in hamiltonian.

$$\hat{H} = \left(-\tfrac{1}{2}\nabla_1^2 - 2/r_1\right) + \left(-\tfrac{1}{2}\nabla_2^2 - 2/r_2\right) + \frac{1}{r_{12}}$$

$\left(-\tfrac{1}{2}\nabla_1^2 - 2/r_1\right) = \hat{H}_1$ Hamiltonian for He^+ (en①)

$\left(-\tfrac{1}{2}\nabla_2^2 + 2/r_2\right) = \hat{H}_2$ Hamiltonian for electron ②

ie, $\hat{H}_1$ and $\hat{H}_2$ are hamiltonian for two seperate He^+ $(z=2)$. $\hat{H}_{(12)}$ may be considered as the two electron hamiltonians $\hat{H}_1$ and $\hat{H}_2$

unperturbed Hamiltonian $\hat{H}_0$ of the atom $\hat{H}_0 = \hat{H}_1 + \hat{H}_2$.

$\hat{H}_1$ and $\hat{H}_2$ have hydrogen like eigen functions, ϕ_1 and ϕ_2 respectively.

ie, $\hat{H}_1 \phi_1 = E_1 \phi_1$

$\hat{H}_2 \phi_2 = E_2 \phi_2$

$\psi^0 = \phi_1 \phi_2$

$$\begin{aligned}
\hat{H}_0 \psi_0 &= [\hat{H}_1 + \hat{H}_2]\phi_1\phi_2 \\
&= \hat{H}_1[\phi_1\phi_2] + \hat{H}_2(\phi_1\phi_2) \\
&= (\hat{H}_1\phi_1)\phi_2 + (\hat{H}_2\phi_2)\phi_1 \\
&= E_1\phi_1\phi_2 + E_2\phi_2\phi_1 \\
&= \underline{(E_1+E_2)\phi_1\phi_2}
\end{aligned}$$

$\hat{H}_1$ operates on ϕ_1 only and $\hat{H}_2$ operates on ϕ_2 only and $\phi_1\phi_2 = \phi_2\phi_1$

Independent electron approximation assumes that $\phi_1\phi_2 = \psi_0$ which are the true eigen fns of $\hat{H}_0$, is the approximate eigen functions of $\hat{H}_{(1,2)}$ ie, two electron problem is now reduced to two one electron hydrogen like problems.

Consider the ground state of He atom. The two electrons are in the ground state ie in the 1s orbital.

$1S_{(1)} = \sqrt{z^3/\pi}\, e^{-zr_1}$ OR $(z/2)^{3/2} \cdot e^{-2r}$ in atomic unit.

$1S_{(2)} = \sqrt{\frac{z^3}{\pi}}\, e^{-zr_2}$

$= \frac{z^3}{\pi} e^{-z(r_1+r_2)}$

$\psi_{12} = 1S_{(1)} \cdot 1S_{(2)}$

$E_{1S^2}^{(He)} = E_{1S(1)}^{He^+} + E_{1S(2)}^{He^+}$

$= -\frac{1}{2}z^2 + -\frac{1}{2}z^2 = -z^2$

$= -4au$

$= -1.74 \times 10^{-17} J$.

$= \underline{\underline{-108.3 eV}}$.

1au = 27.2eV.

$E_{1S}^{He^+}$ = energy of 1s $\bar{e}$ns of hydrogen like atoms.

$= \underline{-2\pi^2 m z^2}$

in au $= \frac{-z^2}{2n^2}$

If n = 1

$= \frac{z^2}{2}$.

For He atom there are two methods to compare the calculated results with the experimental values.

1) Compare the values of total energy.

2) Compare the values of ionisation potential.

Experimental values of total energy is equal to −78.4 eV ie, calculated value is much above the experimental value.

Ionisation potential of He = $E_{He^+} - E_{He}$

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

$= -\frac{1}{2}z^2 + z^2 = z^2/2 = 4/2 = 2$ Hartree

$= \underline{\underline{54.4 eV}}$

Experimental values of ionisation potential of He = 24.6 eV

This shows that the term $1/r_{12}$ cannot be ignored. It should be included in the hamiltonian.

In order to get better results we may use the exact hamiltonian, $\hat{H}_{12} = \hat{H}_1 + \hat{H}_2 + 1/r_{12}$ and repeat the procedure as in the above case

$E_{1S^2}^{He} = E_{1S(1)}^{He^+} + E_{1S(2)}^{He^+} = \int 1S_{(1)} 1S_{(2)} \frac{1}{r_{12}} 1S_{(1)} 1S_{(2)}\, d\tau_1 d\tau_2$

$= \frac{-z^2}{2} - \frac{z^2}{2} + \frac{5}{8}z$

$= \underline{\underline{-z^2 + \frac{5}{8}z}}$

Here z = 2.

Total energy $E_{1S^2}^{He} = -4 + \frac{5 \times 2}{8} = -4 + 10/8 = -2 - (-11/4)$

$= (-2 + 11/4)$ Hartree

$= \underline{\underline{-20.4 eV}}$

The results are more satisfactory but it has 5% error in total BE (Bond energy) and 17% in ionisation potential.

VARIATION METHOD

Variation method is used for the calculation of approximate energy and approximate solutions of multi electron systems.

Variation theorem

If we make a guess of an approximate wave function of the system based on physical & chemical consideration, then the energy of the system is approximately given by,

$$\langle E \rangle = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi \psi^* d\tau} = \frac{\langle \psi^* \hat{H} \psi \rangle}{\langle \psi \psi^* \rangle}$$

If the trial function (ψ) is normalised,

$$\langle E \rangle = \langle \psi^* \hat{H} \psi \rangle$$

Here $\hat{H}$ is the Complete Hamiltonian of the system. According to variation theorm expectation value $\langle E \rangle$ is always greater than the true energy E_0 (where E_0 is the lowest eigen value of $\hat{H}$) of the System in the ground state. ie $\langle E \rangle > E_0$

On the other hand if we makes several guesses of the functions ie, $\psi_1, \psi_2, \psi_3 \cdots$ which leads to $E_1, E_2, E_3 \cdots$ respectively. Thus according to variation principle if $E_1 < E_2$, E_1 is the better approximation to E_0 and therefore the corresponding wave-function ψ_1 is a better wave f^n for the system than ψ_2.

Variation theorem may be stated as follows. If ψ_t is the trial wave-function of the system whose hamiltonian $\hat{H}$ has a discrete eigen spectrum, then $\langle \psi_t^* \hat{H} \psi_t \rangle \geq E_0$.

Here E_0 is the lowest (exact) eigen value of $\hat{H}$ and assuming that the trial function ψ_t is normalised

proof for hamiltonian variation theorem

Let $\phi_0, \phi_1, \phi_2 \cdots$ be a set of normalised and mutually orthogonal eigen functions of $\hat{H}$ with eigen values $E_0, E_1, E_2 \cdots$ respectively. Then $\hat{H}\phi_0 = E_0\phi_0$, $\hat{H}\phi_1 = E_1\phi_1$, $\hat{H}\phi_2 = E_2\phi_2$ and so on. Suppose the trial function ψ is a linear combination of this set of eigen functions ($\phi_1, \phi_2, \phi_3 \cdots$)

$$\text{ie, } \psi = \sum_{i=0}^{\infty} c_i \phi_i$$

Since ψ is normalised, $\Sigma c_i^2 = 1$ $\qquad \int \phi_i \hat{H} \phi_i d\tau = 1$

more over $\langle \phi_i \hat{H} \phi_i \rangle = E_i$ and

$$\langle \phi_i \hat{H} \phi_j \rangle = E_j \phi_j \phi_i = 0 \text{ (orthogonal)}$$

$$\int \phi_i \hat{H} \phi_j d\tau = 0$$

$E = \int \psi^* \hat{H} \psi d\tau$

$= \int (\Sigma c_i \phi_i)^* \hat{H} (\Sigma c_i \phi_i) d\tau$

$= \Sigma c_i^2 E_i$

Consider the integral $\int \psi^* \hat{H} \psi d\tau = \langle \psi^* \hat{H} \psi \rangle = E$

$$\text{ie, } E = \langle \psi^* \hat{H} \psi \rangle$$
$$= \langle (\Sigma \overset{c}{\Phi}_i \phi_i)^* \hat{H} (\Sigma c_i \phi_i) \rangle$$

$= \langle \sum c_i \phi_i^* \hat{H} \sum c_i \phi_i \rangle$

$= \sum c_i^2 E_i$ because $\langle \phi_i \hat{H}^* \phi_i \rangle = E$.

not $\left\{ \begin{array}{l} \langle \psi_i \hat{H} \phi_j \rangle = 0 \text{ for } i \neq j. \\ \int \phi_i \hat{H} \phi_j \, d\tau = 0 \end{array} \right\}$

If E_0 is the lowest value of $\hat{H}$ then,

$$E - E_0 = \sum c_i^2 (E_i - E_0).$$

$$= \sum c_i^2 E_i - \sum c_i^2 E_0. \quad \text{since } \sum c_i^2 = 1$$

ie, $E - E_0 = \sum c_i^2 (E_i - E_0)$.

Since E_0 is the lowest value of energy. $E_i - E_0$ must be +ve or zero. The quantity $\sum c_i^2 = 1$. Therefore the RHS of the above equation must always be +ve or zero.

ie, $E - E_0 = 0$ OR +ve value.

ie $E - E_0 \geq 0$.

OR $E \geq E_0$. $\int \psi^* \hat{H} \psi \, d\tau = E_0$.

OR $\langle \psi^* \hat{H} \psi \rangle \geq E_0$. This is variation theorem.

If the trial function happens to be the true function of the system, on the lowest energy state we get true energy E_0. Otherwise the variation method always gives upper hand to the true energy, without giving any indication how far the true energy is different from the

Application of variation method involves

1) choose the trial function with some variable parameters.

2) Calculate the integral $\int \psi^* \hat{H} \psi \, d\tau$ OR $\langle \psi^* \hat{H} \psi \rangle$.

3) Since the integral always gives an upper bound to true energy (unless the trial function is the true function) minimise the integral with respect to variable parameters.

4) The function ψ with the optimum value of the parameter is the best approximation of its class to the true function and the lowest value of $\langle \psi^* \hat{H} \psi \rangle$ is the nearest approximation to the true energy.

Application to variation method to the ground state of Helium atom

In the application of variation method first of all we have to choose a trial function. In the case of Helium presence of one electron effectively reduces the nuclear charge for the second electron. ∴ each electron is subjected to an effective nuclear charge somewhat less than the full nuclear charge Z. If one e^- is fully shielded from the other, we would have an effective nuclear charge of (z-1). Since both the electrons are in the same orbital, there will be only partial shielding ∴ we except the effective nuclear charge to lie b/w z-1 and z.

Hamiltonian for He atom is,

$$\hat{H} = \frac{-\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{z'e^2}{r_1} - \frac{z'e^2}{r_2} + \frac{e^2}{r_{12}}$$

where z is less than 2.

$$\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{z'e^2}{r_1} = \hat{H}_1$$, Hamiltonian for $He^{+}_{(1)}$

✓ $$\therefore \hat{H} = \hat{H}_1 + \hat{H}_2 + \frac{e^2}{r_{12}}$$

let ψ be our trial function. In He there are two electrons and those 2 es are in the 1s orbital

$$\psi = \phi_1\phi_2 \quad \text{where } \phi_1 = 1s_{(1)} \quad \phi_2 = 1s_{(2)}$$

$$\phi_1 = 1s_{(1)} = \frac{1}{\sqrt{\pi}}\left(\frac{z'}{a}\right)^{3/2} e^{\frac{z'r_1}{a}}$$

$$\phi_2 = 1s_{(2)} = \frac{1}{\sqrt{\pi}}\left(\frac{z'}{a}\right)^{3/2} e^{-\frac{z'r_2}{a}}$$

$$\therefore \psi = \phi_1\phi_2 = \frac{1}{\pi}\left(\frac{z'}{a}\right)^3 e^{-\frac{z'r_1}{a}} . e^{-z'r_2/a}$$

Variation integral,

$$E_{1s^2} = \frac{\int \psi^* \hat{H}\psi \, d\tau}{\int \psi\psi^* d\tau} = \frac{\iint (\phi_1\phi_2)^* \hat{H}\phi_1\phi_2 \, d\tau_1 d\tau_2}{\iint (\phi_1\phi_2)^*(\phi_1\phi_2)\, d\tau_1 d\tau_2}$$

$$= \frac{\iint 1s_{(1)}1s_{(2)}\hat{H}\, 1s_{(1)}1s_{(2)}\, d\tau_1 d\tau_2}{\iint 1s_{(1)}^2\, 1s_{(2)}^2\, d\tau_1 d\tau_2}$$

But $\int 1s_{(1)}^2 d\tau_1 = 1$ and $\int 1s_{(2)}^2 d\tau_2 = 1$

ie, 1s orbitals are already normalised.

$$\therefore E_{1s^2} = \iint 1s_{(1)}1s_{(2)}\hat{H}\, 1s_{(1)}1s_{(2)}\, d\tau_1 d\tau_2$$

$$= \iint 1s_{(1)}1s_{(2)}\left(\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}\right)1s_{(1)}1s_{(2)}\, d\tau_1 d\tau_2$$

$$= \iint 1s_1 1s_2 \hat{H}_1 1s_1 1s_2 \, d\tau_1 d\tau_2 + \iint 1s_1 1s_2 \hat{H}_2 1s_1 1s_2 \, d\tau_1 d\tau_2$$
$$+ \iint 1s_1 1s_2 \frac{1}{r_{12}} 1s_1 1s_2 \, d\tau_1 d\tau_2$$

This step not necessary $\left\{ \begin{aligned} &= \iint E_{1s}^{He^+} 1s_1^2 1s_2^2 \, d\tau_1 d\tau_2 + \iint E_{1s}^{He^+} 1s_1^2 1s_2^2 \, d\tau_1 d\tau_2 \\ &\quad + \iint 1s_1 1s_2 \frac{1}{r_{12}} 1s_1 1s_2 \, d\tau_1 d\tau_2 \end{aligned} \right.$

$$= 2E_{1s}^{He^+} + J \quad \text{where } J = \frac{5z'}{8}$$

$\langle E_{1s}^{He^+} \rangle = \int 1s\left(-\frac{1}{2}\nabla^2 - \frac{2}{r}\right)1s\, d\tau$ in au, where there is no shielding.

In the present case 1s is an eigen function of $-\frac{1}{2}\nabla^2 - \frac{z'}{r}$, where $z' < 2$ and the eigen values $= \frac{-z'^2}{2}$

But we donot know the value of z'.

Therefor $E_{1s}^{He^+}$ may be written as,

$$\langle E_{1s}^{He^+} \rangle = \int 1s \left[-\tfrac{1}{2}\nabla^2 - \left(\tfrac{z'}{r} + 2 - z'\right)\right] 1s\, d\tau$$

$$= \int 1s \left[-\tfrac{1}{2}\nabla^2 - \tfrac{z'}{r} - \tfrac{(2-z')}{r}\right] 1s\, d\tau$$

$$= \int 1s \left(-\tfrac{1}{2}\nabla^2 - \tfrac{z'}{r}\right) 1s\, d\tau - \int 1s \tfrac{(2-z')}{r}\, 1s\, d\tau$$

$$= \int 1s \left(-\tfrac{1}{2}\nabla^2 - z'/r\right) 1s\, d\tau - (2-z') \int 1s\, 1/r\, 1s\, d\tau$$

$$= -\frac{z'^2}{2} - (2-z') \int 1s\, 1/r\, 1s\, d\tau$$

where the 1st integral is same as that of energy of hydrogen atom, but z = z'.

$$= \frac{-z'^2}{2} - (2-z')\, z',$$

since $\int 1s\, 1/r\, 1s\, d\tau = z'$

$$= \frac{-z'^2}{2} - 2z' + z'^2$$

$$= \frac{z'^2}{2} - 2z'$$

$$\therefore E_{1s^2}^{He} = 2\, E_{1s}^{He^+} + J.$$

$$= 2\left(\frac{z'^2}{2} - 2z'\right) + \frac{5z'}{8}$$

$$= z'^2 - 4z' + 5/8\, z'$$

$$= z'^2 - \frac{27z'}{8}$$

Because of shielding nuclear charge will be less than 2. z' is the variable parameter, whose value is determined by minimising the energy. [According to variation principle of theorem to find the best value of energy that can be obtained from a function containing one or 2 parameters, these parameters are choosen so as to make the energy minimum)

$$\text{ie, } \frac{d E_{1s^2}^{He}}{dz'} = 0 \;;\quad \frac{d\left(z'^2 - \frac{27}{8}z'\right)}{dz'} = 0$$

$$\text{ie, } 2z' - \frac{27}{8} = 0$$

$$z' = \frac{27}{16}.$$

$$\therefore E_{1s^2}^{He} = \left(\frac{27}{16}\right)^2 - \frac{27}{8}\left(\frac{27}{16}\right)$$

$$= -2.84 \text{ au}$$

$$= -77.48 \text{ eV}$$

$$= -1.24 \times 10^{-17} \text{ J}$$

But the actual value of total energy = −79 eV

The error in the total energy is equal to less than 2%. The calculated IP = 23.06 eV with an error of 6%.

The value of z' is the "effective nuclear charge" ie, charge of the nucleus that the ēns feels due to the partial screening by the other ēn.

$z - z' = 2 - \frac{27}{16} = 5/6$ reperesent the screening effect.

Perterbation method

perterbation method is another technique used for arriving at the energy and wave function for a system for which schordinger eqnation can not be solved. This method can however be used only if the hamiltonian (H_0) the energy (E_0) and the wave f^n (ψ_0) for the unperterbed state are known and if the perterbation is small. For example a simple harmonic oscillator is a perterbed one. The hamiltonian for the unperterbed system is

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2.$$

Let the hamiltonian for perterbed system is,

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 + ax^3 + bx^4,$$ provided 'a' & 'b' are small. The term (ax^3+bx^4), ~~provided a and b are small. The term ax^3+bx^4~~ constitutes a small perterbation $\hat{H}$.

Another excample is hydrogen atom placed in an electric or magnetic field. The interactions of $\bar{e}$s with the field causes perterbat^n. The field direction is taken as the z axis of the co-ordinate system and the field strength 'F'. Then hamiltonion for perterbed system is,

$$\hat{H} = \hat{H}_0 + F_z,$$ where F_z is the perterbation term.

$\hat{H}_0$, E_0 and ψ_0 of the unperterbed hydrogen atom are known.

Perterbation parameters.

perterbation theory involves determinatin of eigen function (ψ_n) and eigen values (E_n) of the perterbed $\hat{H}$ in terms of ψ_n^0 and E_n^0 of unperterbed $\hat{H}_0$.

It is imagined that the perterbation is applied continuously in small steps.

ie, $\hat{H} = \hat{H}^0 + \lambda \hat{H}'$

where λ is a parameter which can vary from 0 to 1. when $\lambda = 0$, the system is unpertourbed and when $\lambda = 1$ the perterbation is complete. Usualy λ is set to one, when a system is sujected to perterbation.

Perterbation Correction.

If perterbation is small, the usual method is to calculate the correction term for eigen functions and eigen values and add them up to those for unperterbed system.

for the unperterbed system, $\hat{H}^0 \psi_n^0 = E_n^0 \psi_n^0$.

for the peterbed system $\hat{H}\psi_n = E_n\psi_n$ —①.

where n denotes the state of a system.

$$\hat{H} = \hat{H}^0 + \lambda H'$$

Here for ① ⇒

$$(\hat{H}^0 + \lambda H')\psi_n = E_n\psi_n \quad - ②$$

As $\hat{H}$ depends on λ, both ψ_n and E_n depends on λ. we can explained the function as Taylor series assuming that $\lambda \hat{H}' << \hat{H}$ (ie perterbation is small)

$$\psi_n = \psi_n^0 + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \lambda^3\psi_n^{(3)} + \ldots\ldots \quad - ③.$$

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots\ldots \quad ④$$

Suppose $\psi_n^{(k)}$ and $E_n^{(k)}$ are the k th order correction term to ψ_n^0 and E_n^0 respectively.

$$\psi_n^{(k)} = \frac{1}{k!}\frac{\partial^k\psi_n}{\partial\lambda^k}$$

$$E_n^{(k)} = \frac{1}{k!}\frac{\partial^k E_n}{\partial\lambda^k}$$

in most of the chemistry problems we need not go beyond the terms $\psi_n^{(2)}$ and $E_n^{(2)}$

Substitute equ: ③ and ④ in eq: ② we get,

$$(H^0 + \lambda \hat{H}_1)(\psi_n^0 + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \ldots)$$
$$= (E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots)(\psi_n^0 + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} \ldots) \quad ⑤$$

On expansion and arranging we get,

$$(\hat{H}^0\psi_n^0 - E_n^0\psi_n^0) + \lambda(H^0\psi_n^1 + H'\psi_n^0 - E_n^0\psi_n^1 - E_n^1\psi_n^0) + \ldots$$
$$\ldots = 0 \quad - ⑥.$$

equ: ① holds good for all values of λ. If we compare the terms on both sides of eqn: ⑤, ~~we~~ ~~can equati the coefficients of each power of λ~~ ~~or~~ coefficient of each power of λ in eqn: ⑥ can be equated to zero.

$$H^0\psi_n^0 - E_n^0\psi_n^0 = 0 \quad \text{OR}.$$

$$H^0\psi_n^0 = E_n^0\psi_n^0 \quad - ⑦$$ unperturbed

$$H^0\psi_n^1 + H'\psi_n^0 - E_n^0\psi_n^1 - E_n^1\psi_n^0 = 0.$$

$$H'\psi_n^0 = E_n^1\psi_n^0 + E_n^0\psi_n^1 - H^0\psi_n^1 \quad - ⑧$$

1st order correc fn term

= and so on for λ^2, λ^3 etc.

✓

equ: ⑦ is schordinger equation for unperterbed system where ψ_n^0 and E_n^0 are supposed to be known.

equ: ⑧ provides 1st order correction terms to unperterbed wavefunction ψ_n^0 and E_n^0.

Correction term for energy

Xing eq: ⑧ by ψ_n^{0*} from the left and integrate.

$$\int \psi_n^{0*} H'\psi_n^0 d\tau = \int \psi_n^{0*} E_n^1\psi_n^0 d\tau + \int \psi_n^{0*} E_n^0\psi_n^1 d\tau$$
$$- \int \psi_n^{0*} H^0\psi_n^{(1)} d\tau \quad - ⑨.$$

since H^0 is hermiation

$$\int \psi_n^{0*} H^0 \psi_n^{(1)} d\tau = \int (H^0 \psi_n^0)^* \psi_n^1 d\tau$$

$$= \int E_n^0 \psi_n^{0*} \cdot \psi_n^1 d\tau$$

$$\int \psi_n^{0*} H^1 \psi_n^0 d\tau = E_n^1 \int \psi_n^{0*} \psi_n^0 d\tau + \int \psi_n^{0*} E_n \psi_n^1 d\tau - \int \psi_n^{0*} E_n^0 \psi_n^1 d\tau .$$

ie, $\int \psi_n^0 H^1 \psi_n^0 d\tau = E_n^1$ — ⑩.

Since $\psi_0^{0*} \psi_n^0 d\tau = 1$.

equ: ⑩ may be expressed as,

$$E_n^{(1)} = H'_{nn} .$$

ie, 1st order correction E_n' to the energy is determined as the expectation values of perterbation operator $\hat{H}'$, using the wave function ψ_n^0 of unperterbed system.

To obtain 2nd order correction term for energy multiply eqnation corresponding to the co-efficient of λ^2 by ψ_n^{0*} and integrate, using the hermiation property of $\hat{H}^0$ and remembering that $\psi_n^{(1)}$ is choosen orthogonal to ψ_0, which is assumed to be normalised.

$$E_n^{(2)} = \int \psi_n^{0*} H^1 \psi_n^1 d\tau = \langle \psi_n^0 H^1 \psi_n^1 \rangle .$$

IIIly $E_n^3 = \int \psi_n^{0*} H^1 \psi_n^2 d\tau = \langle \psi_n^0 H^1 \psi_n^{(2)} \rangle$ and so on.

These eqnations shows that evaluation of nth order energy requires the knowledge of (n-1)th order of eigen function.

Determination of 1st order correction term to wavefunction ψ_n^0.

Any well behaved function can be expressed as a linear combination of a set of eigen functions.

ie, $\psi_n^1 = a_{1n}\psi_1^0 + a_{2n}\psi_2^0 + a_{3n}\psi_3^0 + \dots$

$\psi_n^1 = \Sigma a_{mn} \psi_m^0$ — ⑪.

substitute this value in eq: ⑧ we get,

$(\hat{H}^1 - E_n^1)\psi_n^0 + (\hat{H}^0 - E_n^0)\psi_n^1 = 0$ — ⑧

ie, $(\hat{H}^1 - E_n^1) \cdot \psi_n^0 + (\hat{H}^0 - E_n^0) \Sigma a_{mn} \psi_m^0 = 0$.

Xing by ψ_l^0 and integrating.

$$\int \psi_l^0 \hat{H}_1 \psi_n^0 d\tau - \int \psi_l^0 E_n^1 \psi_n^0 d\tau + \int \psi_l^0 \hat{H}^0 \Sigma a_{mn} \psi_m^0 d\tau - \int \psi_l^0 E_n^0 \Sigma a_{mn} \psi_m^0 d\tau = 0 .$$

we know that,

$$\hat{H}^0 \psi_m^0 = E_m^0 \psi_m^0 ,$$

$$\therefore \psi_l^0 \hat{H}' \psi_n^0 d\tau - \int \psi_l^0 E_n^1 \psi_n^0 d\tau + \int E_m^0 \psi_l^0 \Sigma a_{mn} \psi_m^0 d\tau$$

$$- \int E_n^0 \psi_l^0 \Sigma a_{mn} \psi_m^0 d\tau = 0.$$

ψ_n^0, ψ_m^0 and ψ_l^0 are orthogonal to each other when $l \neq n$ all terms except $l = m$ becomes zero.

Here $l = m$, therefore $\Sigma a_{mn} = a_{mn}$

$$\therefore \int \psi_l^0 \hat{H}' \psi_n^0 d\tau + E_m^0 a_{mn} - E_n a_{mn} = 0.$$

$$\int \psi_l^0 \hat{H}' \psi_n^0 d\tau + a_{mn} [E_m^0 - E_n^0] = 0.$$

$$\therefore a_{mn} = \frac{-\int \psi_l^0 \hat{H}' \psi_n^0 d\tau}{E_m^0 - E_n^0}$$

$$= \frac{\int \psi_l^0 \hat{H}' \psi_n^0 d\tau}{E_n^0 - E_m^0}$$

Therefor equ: ⑪ becomes,

$$\therefore \psi_n^{(1)} = \Sigma \left(\frac{\int \psi_l^0 \hat{H}' \psi_n^0 d\tau}{E_n^0 - E_m^0} \right) \psi_m^0$$

$$\psi_1^{(1)} = \left(\frac{\int \psi_2^0 H' \psi_1^0 d\tau}{E_1^0 - E_2^0} \right) \psi_2^0 + \left(\frac{\int \psi_3^0 H' \psi_2^0 d\tau}{E_2^0 - E_3^0} \right) \psi_3^0 + \cdots$$

here $n = 1$, $l = m = 2, 3, 4, 5 \ldots$

But 2nd and 3rd terms are very small because the denominator is large.

inshort the 1st order correction ψ_n' to the wavefunction can be determined from the eigen-function and eigen value of the unperterbed system. IIIly second order correction term for wave function can be determined.