Patna University

Chemical Bonding II

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APPLICATION OF LCAO-MO THEORY TO H_2^+ ION

Hydrogen Molecule-ION :- This simplest molecule consists of two Protons and one electron. We will consider the simplest possible case of the Hydrogen molecule ion. If one is interested in determining the ground state energy of this species, one can construct trial wave function from a linear combination of the 1S orbitals of the hydrogen atoms. Initially it is imagined that the nuclei are separated by an infinite distance leading to the following arrangement:

$H^\bullet$ $\quad$ H^+
(a) $\quad$ (b)

In this case, there is an electron on atom a, and in the ground state the molecular orbital will be represented by the atomic orbital

$$\psi_a = \psi_{1S(a)}$$

If one assumes that the electron is associated with electron b, then the new situation arises as

H^+ $\quad$ $H^\bullet$
(a) $\quad$ (b)

The ground state molecular-orbital for the above mentioned case will be the atomic orbital

$$\psi_b = \psi_{1S(b)}$$

If the two nuclei are permitted to come together, It would be justified to consider that the resultant one electron molecular

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will be characteristic of the two atomic orbitals This leads to the approximation of linear combination of atomic orbitals (LCAO). Thus, one can say that the one electron molecular orbital for the first electron is

$$\psi_1 = c_1\psi_a + c_2\psi_2 \quad -(1)$$

As there is one electron in the hydrogen molecule ion, the total wave function $\psi_{MO} = \psi_1$, i.e

$$\psi_{MO} = \psi_1 = c_1\psi_a + c_2\psi_b \quad -(2)$$

As the Molecular orbital of one electron in hydrogen molecule ion is here represented as a linear combination of two independent terms, the secular determinant will take the form as given below

$$\begin{vmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - ES_{bb} \end{vmatrix} = 0$$

At the hydrogen atoms, and therefore, the ground state atomic orbitals are identical. It should be

$$H_{aa} = H_{bb}, \quad H_{ba} = H_{ab}, \quad S_{ba} = S_{ab}$$

Further, if one uses normalised wave function, $S_{aa} = S_{bb} = 1$, consequently, the secular determinant will now be reduced to

$$\begin{vmatrix} H_{aa} - E & H_{ba} - ES \\ H_{bb} - ES & H_{aa} - E \end{vmatrix} = 0$$

and this leads to the expression

$$(H_{aa} - E)^2 - (H_{ba} - E_S)^2 = 0$$

If one solves the above expression by means of quadratic equation, two roots are obtained

$$E_S = \frac{H_{aa} + H_{ba}}{1+S} \quad -3$$

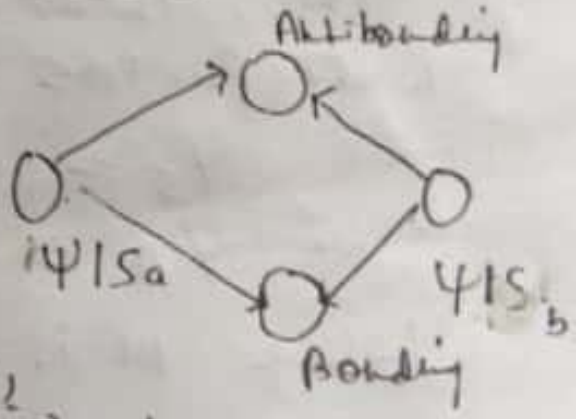
and

$$E_A = \frac{H_{aa} - H_{ba}}{1-S}$$

where E_S and E_A denote symmetric and antisymmetric energy states respectively.

Bonding and Antibonding orbitals :-

Original 1s energy states of the two hydrogen atom are degenerate, but on combination, they split into two new energy state, one of lower energy (Bonding) and other of higher energy (Antibonding) than the



Original is States. In terms of molecular orbital theory

Electron Distribution in the Hydrogen Molecule Ion — From equation (2), the wave function for the hydrogen molecule ion is

$$\psi_{MO} = a_1\psi_a + a_2\psi_b$$

The two energy states are obtained, one for the symmetric state and the other for antisymmetric state. These can be determined from the general expression relating a_1 to a_2

$$(H_{11} - ES_{11})a_1 + (H_{21} - ES_{21})a_2 = 0$$

or this can be put as

$$(H_{aa} - E_{Saa})a_1 + (H_{ba} - E_{Sba})a_2 = 0$$

In order to achieve the symmetric solution, it becomes necessary to substitute E_S for E in this equation, and for this antisymmetric solution it is necessary to substitute E_A for E. If this is done, and the resultant expression is solved, it is found that $a_1 = a_2$ and $a_1 = -a_2$

This, then, leads to molecular orbital wave functions

$$\psi_S = N_S(\psi_a + \psi_b)$$

$$\psi_A = N_A(\psi_a - \psi_b)$$

Where N is a normalizing constant.

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For the normalized wave function,

$$\int \psi_s^* \psi \, d\tau = 1$$

or $$\int N_s^2 (\psi_a + \psi_b)^* (\psi_a + \psi_b) \, d\tau = 1$$

On expansion this expression becomes as

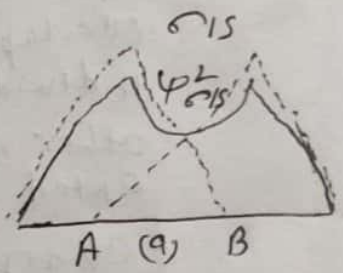
$$N_s^2 \left[\int \psi_a^2 \, d\tau + 2 \int \psi_a \psi_b \, d\tau + \int \psi_b^2 \, d\tau \right] = 1 \quad (4)$$

The complex conjugate forms have been neglected here because both ψ_a and ψ_b are real. Now if one has originally chosen ψ_a and ψ_b to be normalized wave functions, it follow that

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

and by definition

$$\int \psi_a \psi_b \, d\tau = S_{ab}$$



Thus eqn (4) becomes

$$N_s^2 (1 + 2S_{ab} + 1) = 1$$

or $$N_s = \frac{1}{\sqrt{2 + 2S_{ab}}}$$

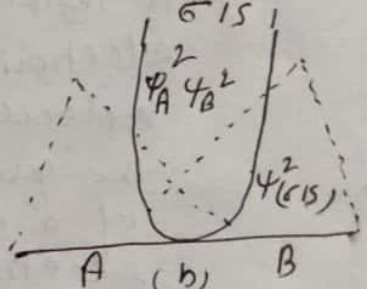


fig (a) and (b)

In the same manner, it can be proved that

$$N_A = \frac{1}{\sqrt{2 - 2S_{ab}}}$$

This now gives us the normalised wave functions

$$\psi_s = \frac{1}{\sqrt{2 + 2S_{ab}}} (\psi_a + \psi_b)$$

$$\psi_A = \frac{1}{\sqrt{2 - 2S_{ab}}} (\psi_a - \psi_b)$$

From the wavefunctions one can be determined

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The distribution of electron charge in the molecule, and from the expression for the energy states, one can calculate the molecular energy levels. Consider the charge distribution first, one can see that if S_{ab} is sufficiently near to zero then

$$\psi_S^2 = \frac{1}{2}\left[\psi_a^2 + \psi_b^2 + 2\psi_a\psi_b\right]$$

and $$\psi_A^2 = \frac{1}{2}\left[\psi_a^2 + \psi_b^2 - 2\psi_a\psi_b\right]$$

From the above expression it follows that the symmetric function results in an increase in electron charge density in the region of overlap between two atoms over that of the individual atoms as described in fig (a). On the other hand, the antisymmetric function is represented in fig (b). The dotted lines represent the charge densities of the individual atom separated to infinity, and the heavy lines represent the electron charge distribution in the hydrogen molecule ion along the line passing through the nuclei. As one considers the formation of a covalent bond to be associated with an electron charge build up in the region of the bond it means that only the symmetric function would result in the formation of a stable molecule.

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