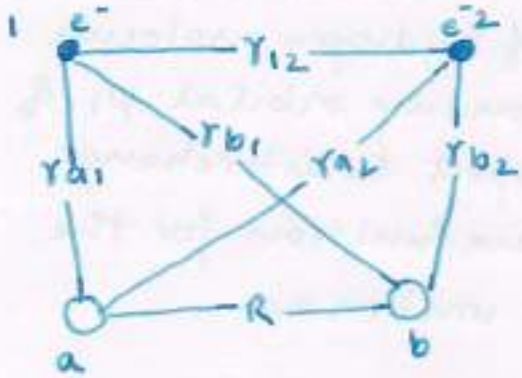
MO Treatment of H_2 Molecule



The MO treatment of H_2 molecule is essentially the same as that in case of H_2^+ molecule.

1, 2 → electrons
a, b → protons

The hamiltonian operator for H_2 molecule can be written as

$$\hat{H} = \left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{ke^2}{r_{a_1}} - \frac{ke^2}{r_{b_1}}\right) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{ke^2}{r_{b_2}} - \frac{ke^2}{r_{a_2}}\right) + \frac{ke^2}{r_{12}} + \frac{ke^2}{R} \quad (1)$$

To make the above eq look a bit compact we write...

$$H(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{ke^2}{r_{a_1}} - \frac{ke^2}{r_{b_1}} \quad (2)$$

$$H(2) = -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{ke^2}{r_{a_2}} - \frac{ke^2}{r_{b_2}} \quad (3)$$

$$H = \left[H(1) + \frac{ke^2}{R}\right] + \left[H(2) + \frac{ke^2}{R}\right] + \frac{ke^2}{r_{12}} - \frac{ke^2}{R} \quad (4)$$

As done before now we have to think about the trial wave function and then calculate the expectation value

As the term $-\frac{ke^2}{}$ is independent of electronic coordinates it makes no difference to electronic wave function whether it is retained in $\hat{H}$ or incorporated later in energy expression as an additional term $-ke^2/R$

The $\hat{H}$ inside the brackets in eq 4 is the same as the one solved for H_2^+ molecule $\therefore$ one can reasonably take that, in the ground state of hydrogen molecule both the electrons occupy the bonding orbital ψ_1 of H_2^+ which is symmetric with respect to interchange of nuclei a and b. The trial wave function for the hydrogen molecule can then be written as

$$\psi_{MO} = \psi_1(1)\psi_1(2) = \frac{\psi_a(1)+\psi_b(1)}{\sqrt{2+2S}} \cdot \frac{\psi_a(2)+\psi_b(2)}{\sqrt{2+2S}}$$

$$= \frac{1}{2(1+S)}\left[\psi_a(1)+\psi_b(1)\right]\left[\psi_a(2)+\psi_b(2)\right] \quad \text{— (5)}$$

We now include 'e' spin and Pauli's principle ~~an~~ into the procedure

$$\text{Symmetric: } \begin{cases} \alpha(1)\,\alpha(2) \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\,\beta(2)+\beta(1)\,\alpha(2)\right] \\ \beta(1)\,\beta(2) \end{cases} \quad \text{— (6)}$$

$$\text{Antisymmetric: } \frac{1}{\sqrt{2}}\left[\alpha(1)\,\beta(2)-\beta(1)\,\alpha(2)\right] \quad \text{— (7)}$$

$\alpha(1) \rightarrow$ first electron is in a spin up state $\uparrow$
$\beta(1) \rightarrow$ " " " " " " down " $\downarrow$

according to Pauli, the total wave function must be antisymmetric w.r.t interchange of electrons. Therefore, the symmetric ψ_{MO} has to combine with the antisymmetric spin part leading to the wave function

$$\frac{1}{2(1+S)}\left[\psi_a(1)+\psi_b(1)\right]\left[\psi_a(2)+\psi_b(2)\right]\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]$$

This is a singlet state as $S=0$. The energy is unaffected by the inclusion of spin part as the Hamiltonian does not contain spin terms. The space part (eq 5), can then be taken as MO for the evaluation of energy. With eq 5 as trial wave function

$$\langle \psi_{MO} | H | \psi_{MO} \rangle = \langle \psi_{MO} | H(1) + \frac{ke^2}{R} | \psi_{MO} \rangle + \langle \psi_{MO} | H(2) + \frac{ke^2}{R} | \psi_{MO} \rangle + \langle \psi_{MO} | \frac{ke^2}{r_{12}} | \psi_{MO} \rangle - \langle \psi_{MO} | \frac{ke^2}{R} | \psi_{MO} \rangle$$

$$E = 2 E_g(R) + \langle \psi_{MO} | \frac{ke^2}{r_{12}} | \psi_{MO} \rangle - \frac{ke^2}{R} \quad \text{— (8)}$$

where $E_g \rightarrow$ energy of H_2^+ molecule. Putting value of E_g from H_2^+

$$E = 2 E_H - 2 \frac{(V_{aa} + V_{ab})}{1+S} + \frac{ke^2}{R} + \langle \psi_{MO} | \frac{ke^2}{r_{12}} | \psi_{MO} \rangle \quad \text{— (9)}$$

Total energy is minimised wrt the internuclear separation R. Coulson from a refined variational calculation obtained $R_e = 0.732$ Å and $D_E = 3.49$ eV. The experimental values are 0.74 Å and 4.75 eV.

The MO given in eq 5 may be written in form

$$\psi_{MO} = \frac{1}{2(1+S)} \left[\psi_a(1)\psi_a(2) + \psi_b(1)\psi_b(2) + \psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2) \right] \quad \text{— (10)}$$

The first two terms correspond to the situation in which both the electrons are associated with same proton.

These represent the ionic structures $H_a^- H_b^+$ and $H_a^+ H_b^-$, respectively. However, the third and fourth terms represent the situation in which the electrons are shared equally by both the protons and hence they correspond to covalent structures of the hydrogen molecule.

The MO selected gives equal importance to ionic and covalent structures which is probably causing the disagreement with the experimental results.