Hückel Molecular Orbital Theory

Pi-bonds built onto the Sigma bond framework

Ethene

Take the case of $H_2C = CH_2$. The molecular axis is along the x-axis

π bonds are composed of the p_z orbitals of the two carbon atoms A and B

Trial wavefunction

$$\phi = \sum_{n=1}^{N} c_i f_i = c_A p_{zA} + c_B p_{zB}$$

Secular equation, secular determinant:

$$\begin{vmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - ES_{BB} \end{vmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0$$

The determinant must go to zero.

$$H_{AA} = \int p_{zA} \hat{H} p_{zA} d\tau = \alpha$$

$$H_{AB} = \int p_{zA} \hat{H} p_{zB} d\tau = \beta$$

$$S_{ij} = \delta_{ij}$$

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

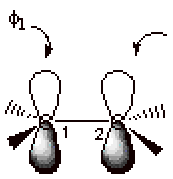
$$(\alpha - E)^2 - \beta^2 = 0$$

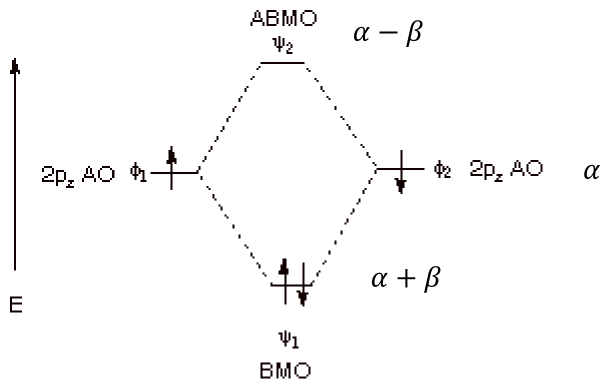
$$E = \alpha \pm \beta$$

$$\beta \sim -75 \text{ kJ mol}^{-1} \text{ (from experimental data)}$$

For two electrons, $E_\pi = 2\alpha + 2\beta$

Stabilization due to π bond $= -150 \text{ kJ mol}^{-1}$





Ethene M.O.s

$$c_A(\alpha - E\ ) + c_B\beta = 0$$

$$c_A\beta + c_B(\alpha - E) = 0$$

Gives, $c_A = c_B \implies \phi = c_A(p_{zA} + p_{zB})$

Normalize: $c_A^2(1 + 2S + 1) = c_A^2(1 + 0 + 1) = 1$

$$\phi_b = \frac{1}{\sqrt{2}}(p_{zA} + p_{zB})$$

Determine for LUMO

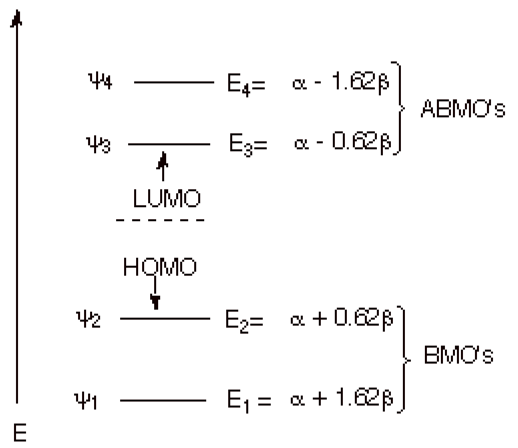
1,3-Butadiene

A linear molecule.

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

Put $x = \frac{\alpha - E}{\beta}$

$$\beta^4 \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$



$$x^4 - 3x^2 + 1 = 0 \implies x^2 = \frac{3 \pm \sqrt{5}}{2} \implies x = \pm 1.618\,, \pm 0.618$$

$$E_\pi = 4\alpha + 4.472\beta$$

$$E_{deloc.} = E_\pi(butadiene) - 2E_\pi(ethene) = 0.472\beta \sim -35\ \text{kJ mol}^{-1}$$

Q. Determine the M.O.'s?