Patna University

Application of HMO Theory - Butadiene

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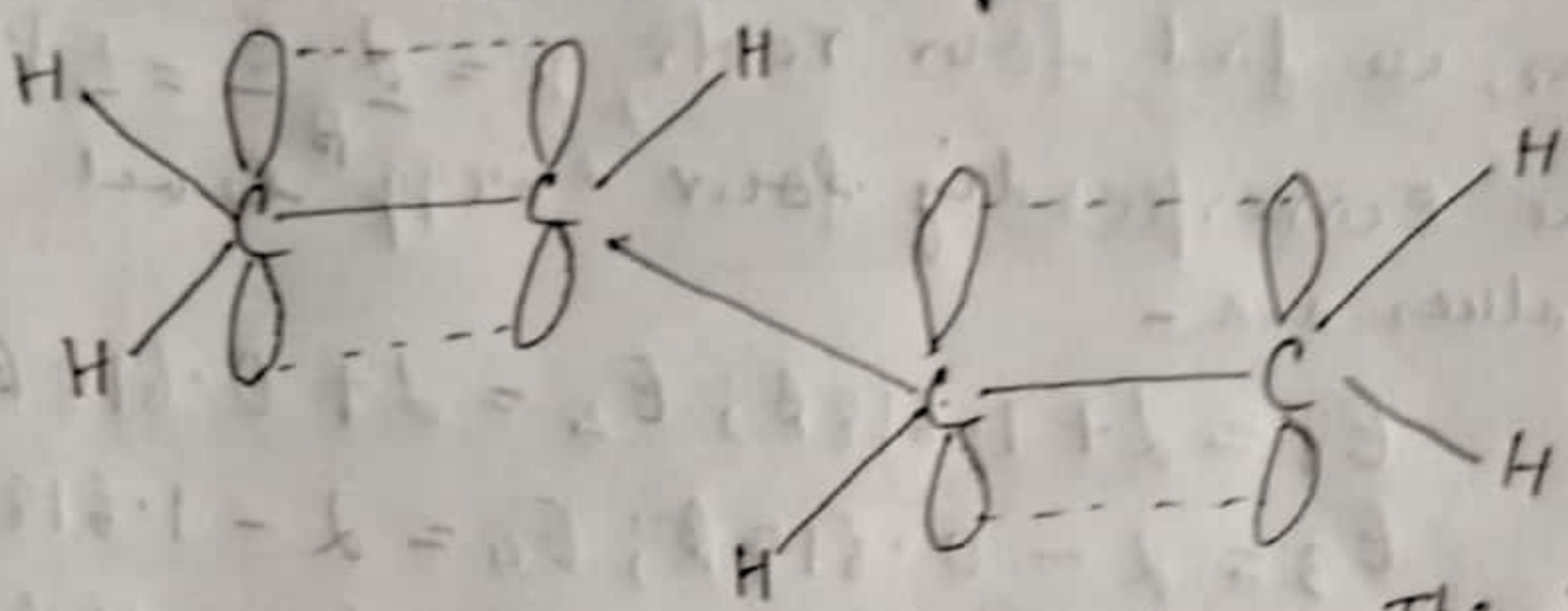
Application of the Huckel molecular orbital theory to butadiene.

Butadiene - N=4

The secular determinant for butadiene molecule (The butadiene molecule is shown in fig) each containg one $2p_\pi$ electron)



containing four carbon atom. The secular determinant (4x4) for the molecule is -

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

Dividing each elements of the determinant by β and setting $\frac{\alpha-\beta}{\beta} = x$ we get

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

On expanding the determinant, the secular equation obtained, is

$x^4 - 3x^2 + 1 = (x^2)^2 - 3(x^2) + 1 = 0$

Solving this equation for x^2, we get

$$x^2 = \frac{3 \pm \sqrt{3^2 - 4}}{2} = \frac{3 \pm \sqrt{5}}{2}$$

$$x = \left(\frac{3+\sqrt{5}}{2}\right)^{1/2} \text{ or } \left(\frac{3-\sqrt{5}}{2}\right)^{1/2}$$

or $= \pm 1.618$, or ± 0.618

Thus, we find four roots, $x = \frac{\alpha - E}{\beta} = \pm 1.618, \pm 0.618$

The corresponding four energy values are -

$E_1 = \alpha + 1.618\beta$; $E_2 = \alpha + 0.618\beta$

$E_3 = \alpha - 0.618\beta$; $E_4 = \alpha - 1.618\beta$

For butadiene we thus have four Molecular orbitals corresponding to the four energy levels. Of these four MO's those with energies E_1 and E_2 are antibonding orbitals. four π-electrons will occupy two bonding MO's as

E_4 ——

E_3 ——

E_2 ——↑↓

E_1 ——↑↓

Total π- electron energy $= 2(\alpha + 1.618\beta) +$
$2(\alpha + 0.614\beta) = 4\alpha + 4.48\beta$

The ground state configuration of the molecule $\psi_1^2 \psi_2^2$.

Delocalisation energy :- If we consider the butadiene to consist of two ethene units, then the total π electron energy of the molecule is $2(2\alpha + 2\beta) = (4\alpha + 4\beta) = 0.48\beta$ is called the delocalisation energy of the butadiene. Since β is negative, the delocalisation energy 0.48β is a negative quantity Hence, this extra amount of energy stabilizes the butadiene molecule.

Construction of MO's :- The coefficients of the molecular orbitals corresponding to the energies are obtained by substituting the above each energy value to the four Secular equations.

$$c_1(\alpha + E) + c_2\beta = 0$$
$$c_1\beta + c_2(\alpha - E) + c_3\beta = 0$$
$$c_2\beta + c_3(\alpha - E) + c_4\beta = 0$$
$$c_3\beta + c_4(\alpha - E) = 0$$

if we substitute $E = \alpha + 1.618\beta$ into these equations we have.

$$0.618c_1\beta + c_2\beta = 0$$

$$c_1\beta + 0.618c_2\beta + c_3\beta = 0$$

$$c_2\beta + 0.618c_3\beta + c_4\beta = 0$$

$$c_3\beta + 0.618c_4\beta = 0$$

Dividing by β we get-

$$c_1 + 0.618c_1 + c_2 = 0$$

$$c_1 + 0.618c_2 + c_3 = 0$$

$$c_2 + 0.618c_3 + c_4 = 0$$

$$c_3 + 0.618c_4 = 0$$

These secular equation are solved the additional normalization conditions,

$$c_1^2 + c_2^2 + c_3^2 + c_4^2 = 1$$

The coefficients corresponding to first molecular orbital ψ_1, are found to be

$$c_1 = c_4 = 0.372$$

and $$c_2 = c_3 = 0.602$$

Thus molecular orbital ψ_1, corresponding to energy (1) E_1 is

$$\psi_1 = 0.372\psi_{2p_z(1)} + 0.602\psi_{2p_z(2)} + 0.602\psi_{2p_z(3)} + 0.372\psi_{2p_z(4)}$$

The molecular orbitals corresponding to energies E_2, E_3 and E_4 are obtained in the same way. The resulting wavefunctions are.

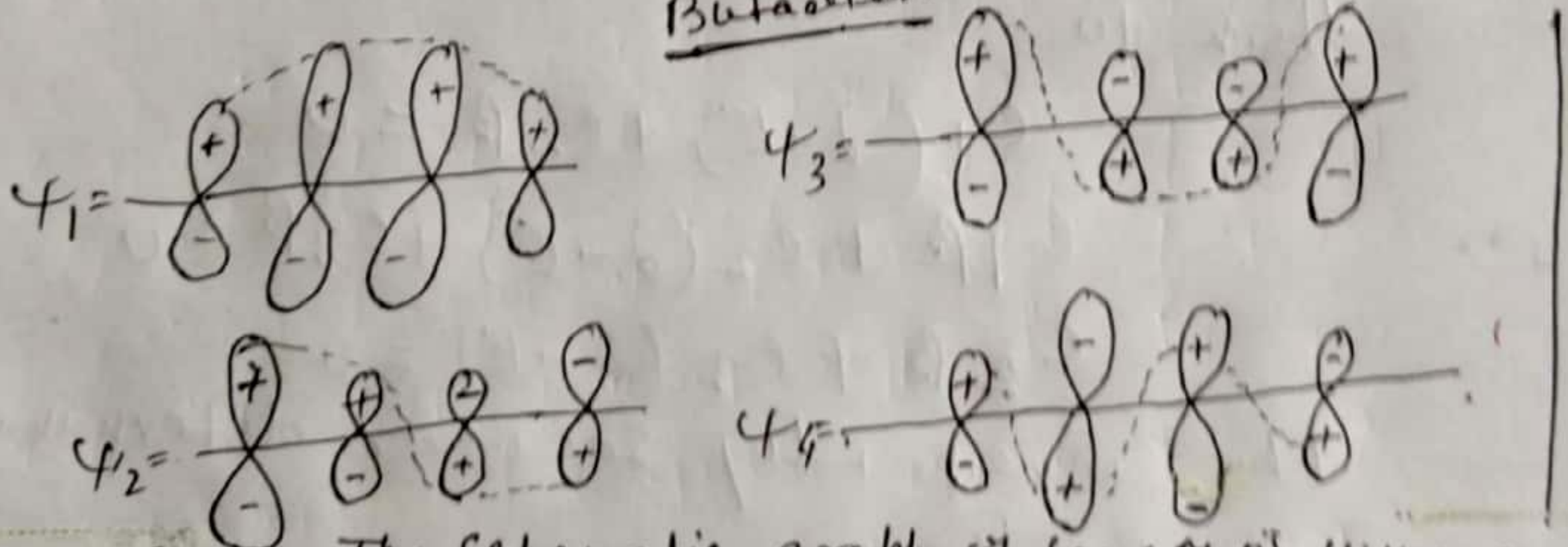
(2) $\psi_2 = 0.602\psi_2 p_2(1) + 0.372\psi_2 p_2(2) - 0.372\psi_2 p_2(3) - 0.602\psi_2 p_2(4)$

(3) $\psi_3 = 0.602\psi_2 p_2(1) - 0.372\psi_2 p_2(2) - 0.372\psi_2 p_2(3) + 0.602\psi_2 p_2(4)$

(4) $\psi_4 = 0.372\psi_2 p_2(1) - 0.602\psi_2 p_2(2) + 0.602\psi_2 p_2(3) - 0.372\psi_2 p_2(4)$

These molecular orbital are shown symbolically in fig along with their energies and nodes the energy of the molecular orbitals increases with the increase in number of nodes.

Butadiene



The schematic graph of four MO's, $\psi_1\psi_2\psi_3$ and ψ_4