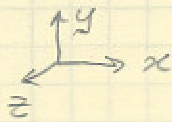
Using Hückel MO theory to calculate π electronic energy for 1,3 butadiene.

$$H_2C = CH - CH = CH_2$$



$$\phi_i = p_{z_i}$$

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$$

secular determinant

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} \end{vmatrix}_{4\times 4} = 0$$

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

$$\begin{vmatrix} \frac{\alpha-E}{\beta} & 1 & 0 & 0 \\ 1 & \frac{\alpha-E}{\beta} & 1 & 0 \\ 0 & 1 & \frac{\alpha-E}{\beta} & 1 \\ 0 & 0 & 1 & \frac{\alpha-E}{\beta} \end{vmatrix} = 0$$

Let

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

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

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

$$x\left[x\left(x^2-1\right)-1\left(x-0\right)\right] - 1\left[1\left(x^2-1\right)-1\left(0-0\right)\right] = 0$$

$$x\left(x^3-2x\right)-\left(x^2-1\right)=0$$

$$x^4-2x^2-x^2+1=0$$

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

Let $x^2 = A \Rightarrow \quad A^2 - 3A + 1 = 0$

$$A = \frac{3 \pm \sqrt{9-4}}{2} = \frac{3 \pm \sqrt{5}}{2}$$

$$\Rightarrow x^2 = \frac{3 \pm \sqrt{5}}{2} = 2.618 \text{ OR } 0.3819$$

$$\therefore x = \pm 1.618, \ \pm 0.618$$

$$x = 1.618, 0.618, -0.618, -1.618$$

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