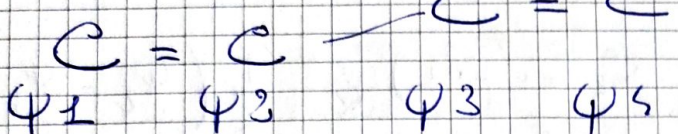
Simmetria molecolare del butadiene



C_{2h}	E	C_2	σ_h	i	
A_g	1	1	1	1	xy, x^2, y^2, z^2
A_u	1	1	−1	−1	z
B_g	1	−1	−1	1	xz, yz
B_u	1	−1	1	−1	x, y

Valuto l'effetto delle operazioni di simmetria, relative a ciascuna rappresentazione irriducibile, per ogni orbitale atomico p_z che costituisce la base dell'orbitale molecolare risultante.

A_g

$$\bar{P}_{A_g}\psi_1 = \frac{1}{4}\left(E + C_2 + i + \sigma_h\right)\psi_1 = \frac{1}{4}\left(\psi_1 + \psi_4 - \psi_4 - \psi_1\right) = 0 = \bar{P}_{A_g}\psi_4$$

$$\bar{P}_{A_g}\psi_2 = \frac{1}{4}\left(E + C_2 + i + \sigma_h\right)\psi_2 = \frac{1}{4}\left(\psi_2 + \psi_3 - \psi_3 - \psi_2\right) = 0 = \bar{P}_{A_g}\psi_3$$

A_u

$$\bar{P}_{A_u}\psi_1 = \frac{1}{4}\left(E + C_2 - \sigma_h - i\right)\psi_1 = \frac{1}{4}\left(\psi_1 + \psi_4 + \psi_1 + \psi_4\right) = \frac{1}{2}\left(\psi_1 + \psi_4\right) = \bar{P}_{A_u}\psi_4$$

$$\bar{P}_{A_u}\psi_2 = \frac{1}{4}\left(E + C_2 - \sigma_h - i\right)\psi_2 = \frac{1}{4}\left(\psi_2 + \psi_3 + \psi_2 + \psi_3\right) = \frac{1}{2}\left(\psi_2 + \psi_3\right) = \bar{P}_{A_u}\psi_3$$

B_g

$$\bar{P}_{B_g}\psi_1 = \frac{1}{4}\left(E - C_2 + i - 2_4\right)\psi_1 = \frac{1}{4}\left(\psi_1 - \psi_2 - \psi_4 + \psi_1\right) =$$

$$= \frac{1}{2}\left(\psi_1 - \psi_4\right) = \bar{P}_{B_g}\left(-\psi_4\right)$$

$$\bar{P}_{B_g}\psi_2 = \frac{1}{4}\left(E - C_2 + i - 2_4\right)\psi_2 = \frac{1}{4}\left(\psi_2 - \psi_3 - \psi_3 + \psi_2\right) =$$

$$= \frac{1}{2}\left(\psi_2 - \psi_3\right) = \bar{P}_{B_g}\left(-\psi_3\right)$$

B_u

$$\bar{P}_{B_u}\psi_1 = \frac{1}{4}\left(E - C_2 - i + 2_4\right)\psi_1 = \frac{1}{4}\left(\psi_1 - \psi_2 + \psi_4 - \psi_1\right)$$

$$= 0 = \bar{P}_{B_u}\psi_4$$

$$\bar{P}_{B_u}\psi_2 = \frac{1}{4}\left(E - C_2 - i + 2_4\right)\psi_2 = \frac{1}{4}\left(\psi_2 - \psi_3 + \psi_3 - \psi_2\right) =$$

$$= 0 = \bar{P}_{B_u}\psi_3$$

Si ottengono 4 funzioni delle basi combinate di

2 funzioni simmetriche B_g:

$$\psi_a = \frac{1}{\sqrt{2}}\left(\psi_1 - \psi_4\right) \qquad \psi_b = \frac{1}{\sqrt{2}}\left(\psi_2 - \psi_3\right)$$

2 funzioni simmetriche A_u

$$\psi_c = \frac{1}{\sqrt{2}}\left(\psi_1 + \psi_4\right) \qquad \psi_d = \frac{1}{\sqrt{2}}\left(\psi_2 + \psi_3\right)$$

L'Hamiltonien discrete si forme matricelle.

$$H = \begin{bmatrix} H_{a,a} & H_{a,b} & 0 & 0 \\ H_{a,b} & H_{b,b} & 0 & 0 \\ 0 & 0 & H_{c,c} & H_{c,d} \\ 0 & 0 & H_{c,d} & H_{d,d} \end{bmatrix} = \begin{bmatrix} H^{Bf} & 0 \\ 0 & H^{Au} \end{bmatrix}$$

$H_{a,c}$ $H_{a,d}$, $H_{b,c}$ $H_{b,d}$ ... nulle, simetrie

$$H_{a,a} = \frac{1}{2}\left(\psi_a \middle| \bar{H} \middle| \psi_a\right) = \frac{1}{2}\left(\psi_1 - \psi_2 \middle| \bar{H} \middle| \psi_1 - \psi_2\right) = \alpha$$

$$H_{a,b} = \frac{1}{2}\left(\psi_a \middle| \bar{H} \middle| \psi_b\right) = \frac{1}{2}\left(\psi_1 - \psi_2 \middle| \bar{H} \middle| \psi_2 - \psi_3\right) = \beta$$

$$H_{b,b} = \frac{1}{2}\left(\psi_b \middle| \bar{H} \middle| \psi_b\right) = \frac{1}{2}\left(\psi_2 - \psi_3 \middle| \bar{H} \middle| \psi_2 - \psi_3\right) = \alpha - \beta$$

$$H^{Bf} = \begin{vmatrix} \alpha & \beta \\ \beta & \alpha - \beta \end{vmatrix}$$

$$\frac{\alpha - E}{\beta} = x \qquad \frac{\beta}{\beta} = 1$$

$$\frac{\alpha - E - \beta}{\beta} = (x - 1)$$

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

$$E_2 = \alpha + 0.61\beta$$

$$E_1 = \alpha - 1.62\beta$$

$$H_{c,c} = \frac{1}{2}\left(\psi_c \mid \bar{H} \mid \psi_c\right) = \frac{1}{2}\left(\psi_1 + \psi_2 \mid \bar{H} \mid \psi_1 + \psi_2\right) = \alpha$$

$$H_{c,d} = \frac{1}{2}\left(\psi_c \mid \bar{H} \mid \psi_d\right) = \frac{1}{2}\left(\psi_1 + \psi_2 \mid \bar{H} \mid \psi_2 + \psi_3\right) = \beta$$

$$H_{d,d} = \frac{1}{2}\left(\psi_d \mid \bar{H} \mid \psi_d\right) = \frac{1}{2}\left(\psi_2 + \psi_3 \mid \bar{H} \mid \psi_2 + \psi_3\right) = \alpha + \beta$$

$$H^{Au} = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha+\beta \end{bmatrix} : \qquad \frac{\alpha - E}{\beta} = x \qquad \frac{\beta}{\beta} = 1$$

$$\frac{\alpha - E + \beta}{\beta} = (x+1)$$

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

$$E_3 = \alpha - 0.61\beta$$

$$E_4 = \alpha + 1.62\beta$$

