1.7: Hückel Theory 2 (Eigenvalues)

The energies (eigenvalues) may be determined by using the Hückel approximation.

$$\psi_{A_{1g}} = \frac{1}{\sqrt{6}}\left(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6\right)$$

$$E\left(\psi_{A_{1g}}\right) = \int \psi_{A1g}\, H\, \psi_{A1g} d\tau = \left\langle \psi_{A_{1g}} \mid H \mid \psi_{A_{1g}} \right\rangle$$

$$= \left\langle \frac{1}{\sqrt{6}}\left(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6\right) \middle| H \middle| \frac{1}{\sqrt{6}}\left(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6\right) \right\rangle$$

$$= \frac{1}{6}\Big(\underset{\alpha}{H_{11}} + \underset{\beta}{H_{12}} + H_{13} + H_{14} + H_{15} + \underset{\beta}{H_{16}} + \underset{\beta}{H_{21}} + \underset{\alpha}{H_{22}} + \underset{\beta}{H_{23}} + H_{24} + H_{25} + H_{26}$$

$$+ \underset{\alpha+2\beta}{H_{3i}(i=1-6)} + \underset{\alpha+2\beta}{H_{4i}(i=1-6)} + \underset{\alpha+2\beta}{H_{5i}(i=1-6)} + \underset{\alpha+2\beta}{H_{6i}(i=1-6)}\Big)$$

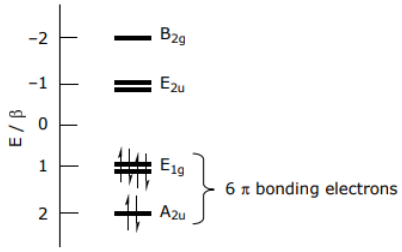
$$E\left(\psi_{B_{2g}}\right) = \frac{1}{6}(6)(\alpha - 2\beta) = \alpha - 2\beta \tag{1.7.1}$$

The energies of the remaining LCAO's are:

$$E\left(\psi^a_{E_{1g}}\right) = \left(\psi^b_{E_{1g}}\right) = \alpha + \beta \tag{1.7.2}$$

$$E\left(\psi^a_{E_{2u}}\right) = \left(\psi^b_{E_{2u}}\right) = \alpha - \beta \tag{1.7.3}$$

Note the energies of the E orbitals are degenerate. Constructing the energy level diagram, we set α = 0 and β as the energy parameter (a negative quantity, so an MO whose energy is positive in units of β has an absolute energy that is negative),



The energy of benzene based on the Hückel approximation is

$$E_{total} = 2(2\beta) + 4(\beta) = 8\beta \tag{1.7.4}$$

What is the delocalization energy (i.e. π **resonance energy**)?

To determine this, we consider cyclohexatriene, which is a six-membered cyclic ring with 3 localized π bonds; in other terms, cyclohexatriene is the product of three condensed ethylene molecules. For ethylene,

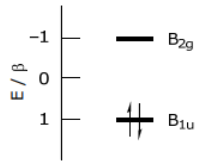
Following the procedures outlined above, we find,

$$\psi_1(A) = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

$$\psi_2(B) = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

$$\mathrm{E}\left(\psi_1\right)=\left\langle \frac{1}{\sqrt{2}}\left(\phi_1+\phi_2\right)|\mathrm{H}|\frac{1}{\sqrt{2}}\left(\phi_1+\phi_2\right)\right\rangle=\frac{1}{2}(2\alpha+2\beta)=\beta$$
$$\mathrm{E}\left(\psi_2\right)=\left\langle \frac{1}{\sqrt{2}}\left(\phi_1-\phi_2\right)|\mathrm{H}|\frac{1}{\sqrt{2}}\left(\phi_1-\phi_2\right)\right\rangle=\frac{1}{2}(2\alpha-2\beta)=-\beta$$

The above was determined in the C_2 point group. Correlating to D_{2h} point group gives A in C2 → B_{1u} in D_{2h} and B in C_2 → B_{2g} in D_{2h}:



The Hückel energy of ethylene is,

$$E_{total}=2(\beta)=2\beta \tag{1.7.5}$$

Therefore, the energy of cyclohexatriene is 3(2β) = 6β. The resonance energy is therefore,

$$E_{res}(C_6H_6) = 8\beta - 6\beta = 2\beta$$
$$\downarrow \quad \downarrow$$
$$E_{total} \quad E_{total}$$
benzene cyclohexatriene

The **bond order** is given by,

$$\text{B.O.} = \sum_{i,j} n_e c_i c_j$$

coefficients of electron i and electron j in a given bond

orbital e⁻ occupancy

Consider the B.O. between the C_1 and C_2 carbons of benzene

$$[\psi_1(A_{2u})]=2(\frac{1}{\sqrt{6}})(\frac{1}{\sqrt{6}})=\frac{1}{3} \tag{1.7.6}$$

$$[\psi_3(E^a_{1g})]=2(\frac{1}{\sqrt{12}})(\frac{1}{\sqrt{12}})=\frac{1}{3} \tag{1.7.7}$$

$$[\psi_4(E^b_{1g})]=\frac{1}{2}(0)(\frac{1}{2})=\frac{0}{\frac{2}{3}} \tag{1.7.8}$$