5.04, Principles of Inorganic Chemistry II
MIT Department of Chemistry
Lecture 8: Hückel Theory 2 (Eigenvalues)

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

$$\psi_{A1g} = \frac{1}{\sqrt{6}}\left(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6\right)$$

$$E\left(\psi_{A1g}\right) = \int \psi_{A1g}\ H\ \psi_{A1g} d\tau = \left\langle \psi_{A1g}\ |\ H\ |\ \psi_{A1g} \right\rangle$$

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

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

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

$$E\left(\psi_{A1g}\right) = \frac{1}{6}(6)(\alpha + 2\beta) = \alpha + 2\beta$$

The energy of the LCAO, ψ_{B2g}…

$$E\left(\psi_{B2g}\right) = \left\langle \psi_{B2g}\ |\ H\ |\ \psi_{B2g} \right\rangle$$

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

$$= \frac{1}{6}\Big(\underset{\underset{\alpha}{\downarrow}}{H_{11}} - \underset{\underset{\beta}{\downarrow}}{H_{12}} + H_{13} - H_{14} + H_{15} - \underset{\underset{\beta}{\downarrow}}{H_{16}} \quad \Rightarrow (\alpha\text{-}2\beta)$$

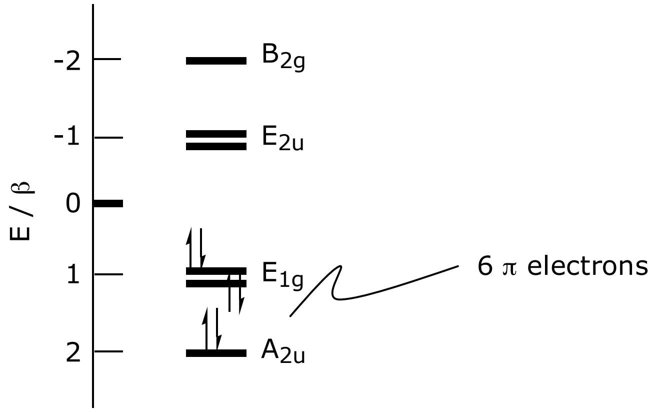
$$+ \underset{\underset{\alpha-2\beta}{\downarrow}}{H_{2i}(i = 1-6)} + \underset{\underset{\alpha-2\beta}{\downarrow}}{H_{3i}} + \underset{\underset{\alpha-2\beta}{\downarrow}}{H_{4i}} + \underset{\underset{\alpha-2\beta}{\downarrow}}{H_{5i}} + \underset{\underset{\alpha-2\beta}{\downarrow}}{H_{6i}}\Big)$$

$$E\left(\psi_{B2g}\right) = \frac{1}{6}(6)(\alpha - 2\beta) = \alpha - 2\beta$$

The energies of the remaining LCAO’s are:

$$E\left(\psi_{E_{1g}^{a}}\right) = E\left(\psi_{E_{1g}^{b}}\right) = \alpha + \beta$$
$$E\left(\psi_{E_{2u}^{a}}\right) = E\left(\psi_{E_{2u}^{b}}\right) = \alpha - \beta$$

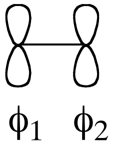
Note the energies of the E orbitals are degenerate. Constructing the energy level diagram, we set $\alpha = 0$ and β as the energy parameter (a negative quantity, so an MO whose energy is positive in units of β has an absolute energy that is negative),



The energy of benzene based on the Hückel approximation is

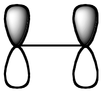
$$E_{total} = 2(2\beta) + 4(\beta) = 8\beta$$

What is the delocalization energy (i.e. π resonance energy)?
To determine this, we consider cyclohexatriene… the cyclic with 3 localized π bonds. In other terms, the product of three condensed π molecules. For ethylene,

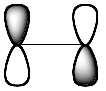


Following the procedures outlined above, we find,

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



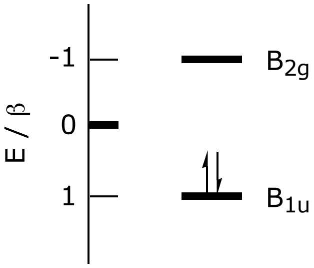
$$\psi_2(B) = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \Rightarrow$$



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

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

The above was determined in the C_2 point group… correlating to D_{2h}…
A in $C_2 \rightarrow B_{1u}$ in D_{2h} and B in $C_2 \rightarrow B_{2g}$ in D_{2h} :



The Hückel energy of ethylene is,

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

Therefore, the energy of cyclohexatriene is $3(2\beta) = 6\beta$)… thus the resonance energy is:

$$E_{res}(C_6H_6) = \underset{\substack{\uparrow \\ E_{total} \\ \text{benzene}}}{8\beta} - \underset{\substack{\uparrow \\ E_{total} \\ \text{cyclohexatriene}}}{6\beta} = 2\beta$$

The bond order is given by,

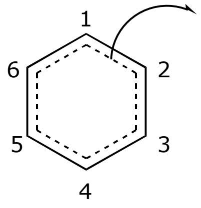
coefficients of a given bond

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

e^- occupancy

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

$$\begin{aligned}
\left[\psi_1(A_{2u})\right] &= 2\left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) = \frac{1}{3}\\
\left[\psi_3(E_{1g}{}^{a})\right] &= 2\left(\frac{2}{\sqrt{12}}\right)\left(\frac{1}{\sqrt{12}}\right) = \frac{1}{3}\\
\left[\psi_4(E_{1g}{}^{b})\right] &= \frac{1}{2}\left(0\right)\left(\frac{1}{2}\right) = \underline{\quad 0 \quad}\\
& \qquad\qquad\qquad\qquad \frac{2}{3}
\end{aligned}$$



B.O = 2/3 (pπ bond order)