5.04 Principles of Inorganic Chemistry II
Fall 2008

5.04, Principles of Inorganic Chemistry II
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Lecture 7: Hückel Theory 2 (Eigenvalues)

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

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

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

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

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

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

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

The energy of the LCAO, $\psi_{B_{2g}}$

$$E\left(\psi_{B_{2g}}\right) = \left\langle \psi_{B_{2g}} \,|\, \mathrm{H} \,|\, \psi_{B_{2g}} \right\rangle$$

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

$$= \frac{1}{6}\Big(\underset{\substack{\downarrow\\ \alpha}}{H_{11}} - \underset{\substack{\downarrow\\ \beta}}{H_{12}} + H_{13} - H_{14} + H_{15} - \underset{\substack{\downarrow\\ \beta}}{H_{16}} + \underset{\substack{\downarrow\\ \alpha-\beta}}{H_{2i}}(i = 1-6) + \underset{\substack{\downarrow\\ \alpha-2\beta}}{H_{3i}} + \underset{\substack{\downarrow\\ \alpha-2\beta}}{H_{4i}} + \underset{\substack{\downarrow\\ \alpha-2\beta}}{H_{5i}} + \underset{\substack{\downarrow\\ \alpha-2\beta}}{H_{6i}}\Big)$$

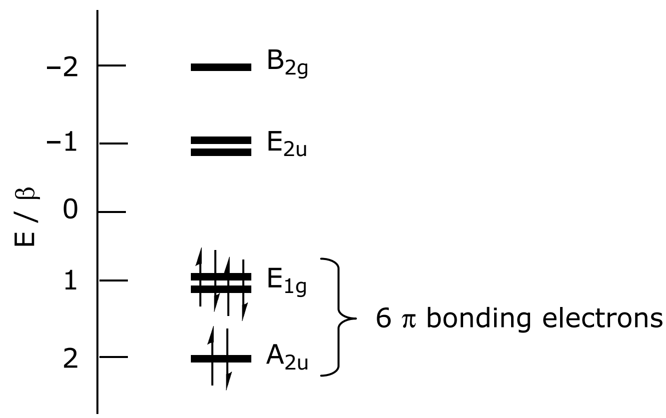
$$E\left(\psi_{B_{2g}}\right) = \frac{1}{6}(6)(\alpha - 2\beta) = \alpha - 2\beta$$

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),

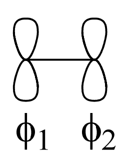


The energy of benzene based on the Hückel approximation is

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

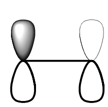
What is the delocalization energy (i.e. π **resonance energy**)?

To determine this, we consider cyclohexatriene, 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,

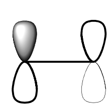


Following the procedures outlined above, we find,

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



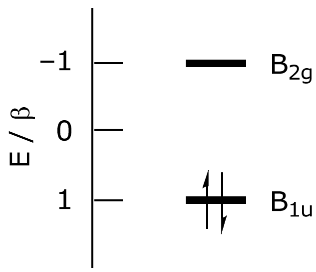
$$\psi_2(B) = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$



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

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

The above was determined in the C_2 point group. Correlating to D_{2h} point group gives A in $C_2 \rightarrow B_{1u}$ 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 $3(2\beta) = 6\beta$. The resonance energy is therefore,

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

The **bond order** is given by,

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

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

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

$$\left[\psi_3(E_{1g}{}^{a})\right] = 2\left(\frac{2}{\sqrt{12}}\right)\left(\frac{1}{\sqrt{12}}\right) = \frac{1}{3}$$

$$\left[\psi_4(E_{1g}{}^{b})\right] = \frac{1}{2}(0)\left(\frac{1}{2}\right) = \underline{0}$$

$$\frac{2}{3}$$