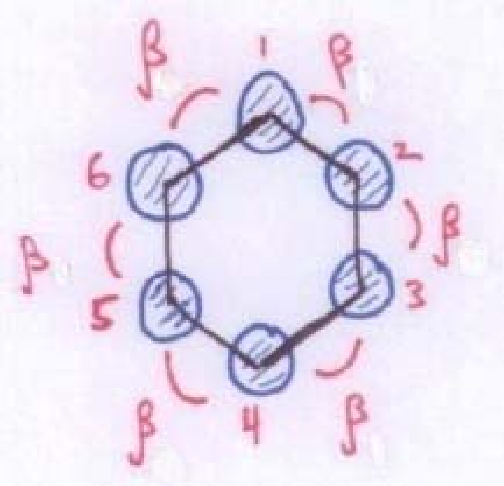
Hückel Theory of Pi-Bonding in Conjugated Hydrocarbon Molecules (Pt. 2)

I) Revisit the Huckel model of pi-bonding in a fully symmetric hydrocarbon:



Benzene, N=6

Consider the matrix Schrodinger Eq. (details on next slide!): $\boldsymbol{H}\vec{c}^{\,(j)} = E_j{}'\vec{c}^{\,(j)}$

Proposed j'th (unnormalized) eigenvector (j=1-6) for benzene (N=6):

$\vec{c}^{\,(j)}$

$$\boldsymbol{H}\left[\begin{bmatrix} 0 & \beta & 0 & 0 & 0 & \beta \\ \beta & 0 & \beta & 0 & 0 & 0 \\ 0 & \beta & 0 & \beta & 0 & 0 \\ 0 & 0 & \beta & 0 & \beta & 0 \\ 0 & 0 & 0 & \beta & 0 & \beta \\ \beta & 0 & 0 & 0 & \beta & 0 \end{bmatrix}\right.\begin{pmatrix} e^{2\pi ij\cdot 1/N} \\ e^{2\pi ij\cdot 2/N} \\ e^{2\pi ij\cdot 3/N} \\ e^{2\pi ij\cdot 4/N} \\ e^{2\pi ij\cdot 5/N} \\ e^{2\pi ij\cdot 6/N} \end{pmatrix} = E_j{}'\begin{pmatrix} e^{2\pi ij\cdot 1/N} \\ e^{2\pi ij\cdot 2/N} \\ e^{2\pi ij\cdot 3/N} \\ e^{2\pi ij\cdot 4/N} \\ e^{2\pi ij\cdot 5/N} \\ e^{2\pi ij\cdot 6/N} \end{pmatrix} \quad ; \; E_j{}' = E_j - \alpha$$

N.B.: i=sqrt(-1) here!

Consider row 3: $$\beta\left(e^{2\pi ij\cdot 2/N} + e^{2\pi ij\cdot 4/N}\right) = E_j{}' e^{2\pi ij\cdot 3/N}$$

Or: $$2\beta\cos(2\pi j / N) = E_j{}'$$

Importantly, the same condition applies for all N=6 rows!

Thus, the following are eigenvector/eigenvalue pairs of **H**:

$$\vec{c}^{\,(j)} \quad \leftrightarrow \quad E_j' = E_j - \alpha = 2\beta\cos(2\pi j/N) \qquad \text{for} \qquad j = 1, 2, \ldots, N$$

Notes: 1) Same eigenvalue spectrum quoted in previous notes (good!)

2) To normalize the (unnormalized) version of c^(j) above,
multiply x 1/sqrt(N).

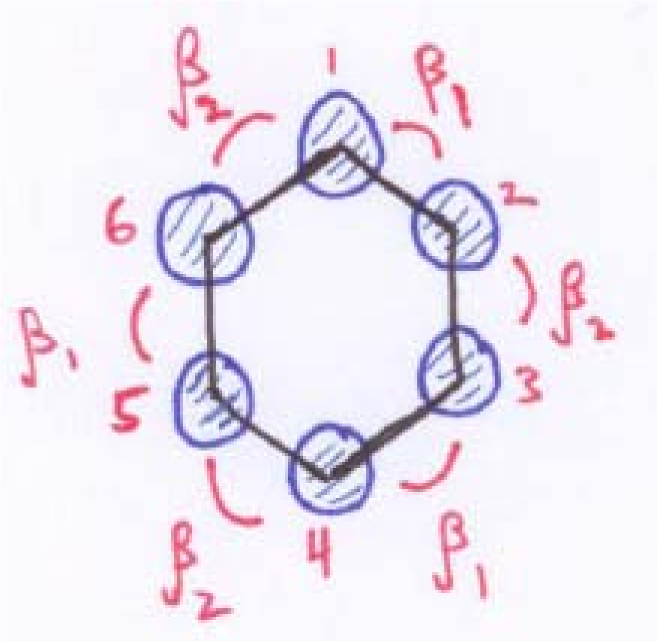
3) There is degeneracy in the energy spectrum (see figure below).

4) Range of j: any continuous patch of j's will do.

Degeneracy patterns for pi-bonding
MO energies in even/odd cyclic hydrocarbons:

N=5 N=6

II) Hückel model of pi-bonding in an "alternating hydrocarbon" chain, i.e., one with two alternating values of the Hückel coupling parameter β.



Example, N=6

Proposed j’th eigenvector:

$$\begin{bmatrix} 0 & \beta_1 & 0 & 0 & 0 & \beta_2 \\ \beta_1 & 0 & \beta_2 & 0 & 0 & 0 \\ 0 & \beta_2 & 0 & \beta_1 & 0 & 0 \\ 0 & 0 & \beta_1 & 0 & \beta_2 & 0 \\ 0 & 0 & 0 & \beta_2 & 0 & \beta_1 \\ \beta_2 & 0 & 0 & 0 & \beta_1 & 0 \end{bmatrix} \begin{pmatrix} ae^{2\pi ij\cdot 1/N} \\ be^{2\pi ij\cdot 2/N} \\ ae^{2\pi ij\cdot 3/N} \\ be^{2\pi ij\cdot 4/N} \\ ae^{2\pi ij\cdot 5/N} \\ be^{2\pi ij\cdot 6/N} \end{pmatrix} = E' \begin{pmatrix} ae^{2\pi ij\cdot 1/N} \\ be^{2\pi ij\cdot 2/N} \\ ae^{2\pi ij\cdot 3/N} \\ be^{2\pi ij\cdot 4/N} \\ ae^{2\pi ij\cdot 5/N} \\ be^{2\pi ij\cdot 6/N} \end{pmatrix} \quad ; \; E' = E - \alpha$$

Picking any two sequential “(a,b)” rows in the above Schrodinger matrix equation, leads to a 2-dim. eigenvalue/eigenvector problem that determines a,b and E’.
For example, focusing on rows 3,4:

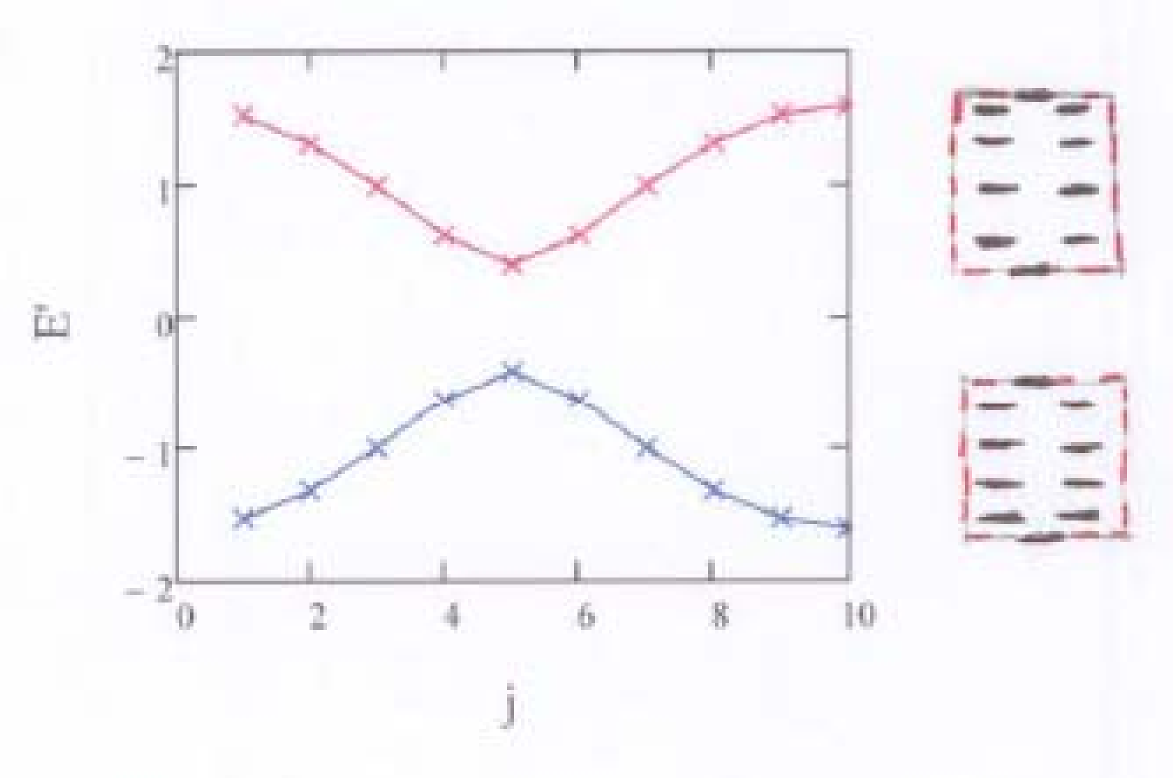
$$\begin{bmatrix} 0 & \beta_2 e^{-2\pi ij/N} + \beta_1 e^{2\pi ij/N} \\ \beta_2 e^{2\pi ij/N} + \beta_1 e^{-2\pi ij/N} & 0 \end{bmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E' \begin{pmatrix} a \\ b \end{pmatrix}$$

Solving this 2-dim. eigenvalue/eigenvector yields:

$$E_j' = \pm\left[\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos(4\pi j / N)\right]^{1/2}$$

Note: Importantly, for this 2-dim eigenvalue/vector problem to result in the cases of rows (1,2) and (N-1,N), must have *j = integer*.

Both +/- branches of E' are plotted here for N=20 and $\beta_1 = -0.6$, $\beta_2 = -1.0$



Conduction Band

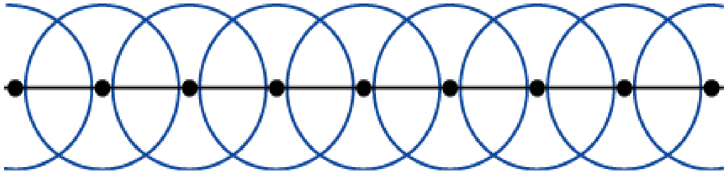
Valence Band

Further points:

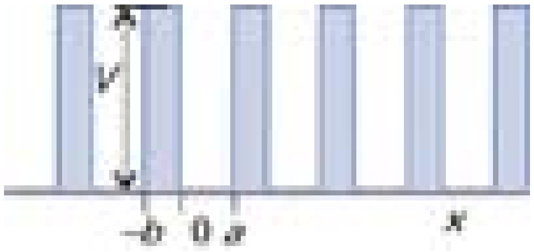
1) Since there are a total of N unique eigenvectors for an NxN matrix, the range of j should be restricted to j=1,2,…,N/2 .

2) If there are N electrons contributed to the pi system (one from each 2pz orbital), then, using the Aufbau principle (2 electrons per MO), the ground electronic state configuration of the alternating hydrocarbon system defined above is: the entire valence band is filled while the entire conduction band is empty.

3) Similar band gaps occur for an electron moving in any periodic potential. Such potentials naturally occur in solids:



Periodic array of atoms (and "attached" orbitals) in a 1D solid.



Periodic potential V(x) that the free electrons in this solid move in.