1. LCAO-MO for H_2^+

In class, we discussed the MO picture of H_2^+ and found simple solutions for the energies of the σ and σ^* orbitals in terms of a few integrals. After significant effort, these integrals can all be worked out:

$$S = e^{-R}\left(1 + R + \frac{1}{3}R^2\right)$$

$$H_{12} = e^{-R}\left(\frac{1}{\mathbf{R}} - \frac{1}{2} - \frac{7}{6}\mathbf{R} - \frac{1}{6}\mathbf{R}^2\right)$$

$$\varepsilon = -\frac{1}{2} + e^{-2R}\left(1 + \frac{1}{\mathbf{R}}\right)$$

A. Plot (rough sketch is OK) these functions as a function of the distance, R, between the two hydrogen nuclei. Which terms decay most quickly with distance? Note that ε is the average energy of a $1s$ electron on hydrogen atom A. Why is this energy not exactly equal to the energy of a hydrogen 1s electron?

B. Plot the energies of the σ and σ^* orbitals as a function of R. What is the equilibrium bond length for H_2^+ at this level of approximation? What is the binding energy? Compare these to the experimental values of 1.06 Å and 2.8 eV, respectively. How does the sum of the MO energies, $E_0 + E_0$ vary with distance?

Solution:

C. In other chemistry classes, you may have been taught that the strength of a chemical bond is proportional to the overlap of the atomic orbitals involved. Based on your results above, how accurate is this approximation for H_2^+? When does it break down?

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2. Matrix Mechanics

In class we discussed matrix mechanics, which we will use increasingly often in the remainder of the course. The following problems provide practice in the mechanics of the use of matrix notation. Suppose ψ and ϕ are wavefunctions composed of a linear combination of three orthonormal basis functions ψ_1, ψ_2, and ψ_3:

$$\psi = 2\psi_1 - \sqrt{3}\psi_3$$
$$\phi = i\sqrt{2}\psi_1 + \psi_2$$

A. How would we express ψ and ϕ in matrix mechanics? That is, what are the vectors ψ and ϕ?

B. What are $\psi^\dagger$ and $\phi^\dagger$?

C. Normalize ψ and ϕ.

D. Compute the inner products $\psi^\dagger \cdot \phi$ and $\phi^\dagger \psi$. Do you notice any relationship between these two numbers?

E. Are ψ and ϕ orthogonal?

F. From the information given, can you tell which wavefunction has more nodes?

G. For each of the following eleven matrices, decide whether the matrix could or could not represent the Hamiltonian for this system. For matrices that could not be the Hamiltonian, explain why not.

$$\begin{pmatrix} 1 & -1 \\ -1 & 2 \end{pmatrix} \begin{pmatrix} -1 & -1 \\ -1 & -2 \end{pmatrix} \begin{pmatrix} 1 & i \\ i & 2 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & -i \\ 0 & 2 & 0 \\ i & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 & 2 & 2 \\ 0 & -1 & 1 \\ 0 & 0 & 3 \end{pmatrix} \begin{pmatrix} i & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2i \end{pmatrix}$$

$$\begin{pmatrix} 1 & -1 & 0 & 0 \\ -1 & 2 & 0 & 0 \\ 0 & 0 & -3 & 0 \\ 0 & 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} 1 & -i & 1 & 1 \\ -i & 2 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}$$

# 3. This problem deals with the Hückel MO theory of π–conjugated systems

To answer each question, you will need to construct the Hückel MOs for each of the molecules pictured, divide them into sets of occupied and unoccupied orbitals, and determine the relevant properties, such as ground state energy, bond order, etc.

NOTE: For all parts **A–D** we take $\alpha = \alpha_C = -11.2$ eV and $\beta = \beta_{CC} = -0.7$ eV.

A. Determine the ionization potential of benzene [IP $= E(B^+) - E(B)$]. Compare this to the IP of hexatriene. Which molecule, B^+ or B, holds its outermost electron most tightly?


Benzene

Versus

Hexatriene
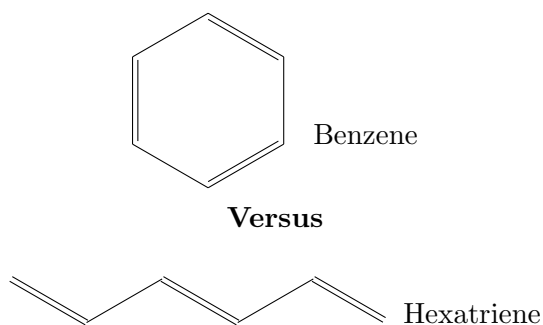
B. Compare the total energies of the two 10-electron conjugated systems below. Which one is more stable? How do you explain this?

Versus
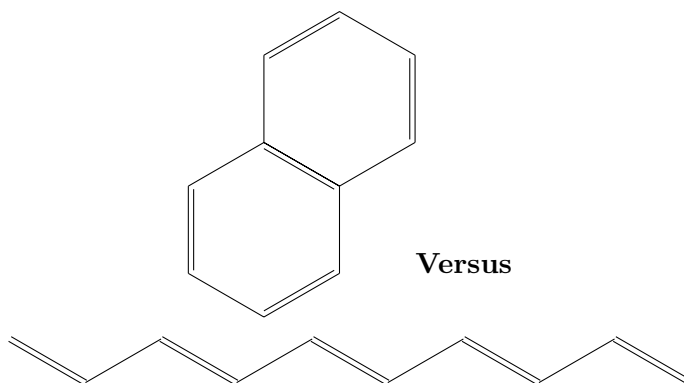
C. What is the bond order of the selected bond in the molecule below? How do you rationalize this result in terms of resonance structures?
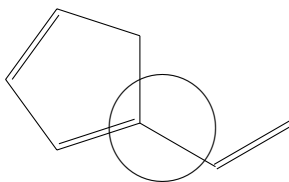
D. Plot the HOMO and LUMO for each molecule below. Is there anything about these orbitals that might tell you about the relative degree of conjugation between the pair of substituents in the meta (left) and para (right) positions?
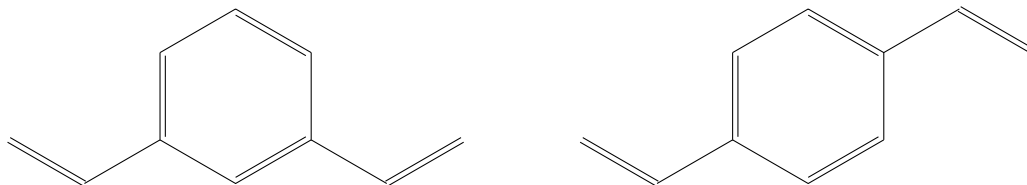

4. It is straightforward to extend Hückel Theory to deal with π systems containing elements other than carbon and hydrogen.

A. First, let us consider including heteroatoms such as nitrogen instead of carbon inside of conjugated rings. To use the Hückel prescription, we simply need α values for C and N and β values for CC and CN bonds. We already know that $\alpha(C) = 11.2\ eV$ and $\beta(CC) = -0.7\ eV$. Which of the following possible values for $\alpha(N)$ and $\beta(CN)$ are most reasonable and why?

$$\alpha(N) = -10.2\ eV \qquad \beta(CN) = -0.65$$
$$\alpha(N) = -11.2\ eV \qquad \beta(CN) = -0.70$$
$$\alpha(N) = -12.2\ eV \qquad \beta(CN) = -0.75$$

B. Use the parameters you chose in part **A** to compute the π MOs of pyridine. Compare your results to what you find for benzene. Do you notice any differences? What is the partial charge on nitrogen in this approximation? Does this make sense?

Versus
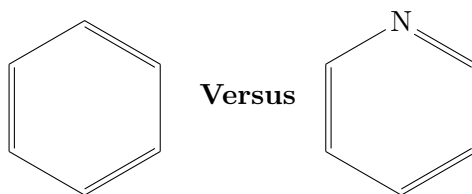
C. We can also use Hückel theory to understand how substituents, like a fluorine atom, will affect the π orbitals. Toward this end, we can assume that a fluorine atom will lower the average energy of the carbon it is attached to by 0.2 eV. Thus a CH carbon will have $\alpha(C) = -11.2\ eV$ while a CF carbon will have $\beta(C) - 11.4\ eV$. Use this parameterization to compute the MOs of 1-fluorobenzene. What is the charge on the substituted carbon?

D. You are attempting a *partial* fluorination of pyridine. You want to selectively fluorinate two of the carbons, while leaving the others untouched. Which sites will the fluorines prefer? To answer this question, compute the energies of all six of the difluorinated isomers below. Which has the lowest energy? How do you rationalize your result?
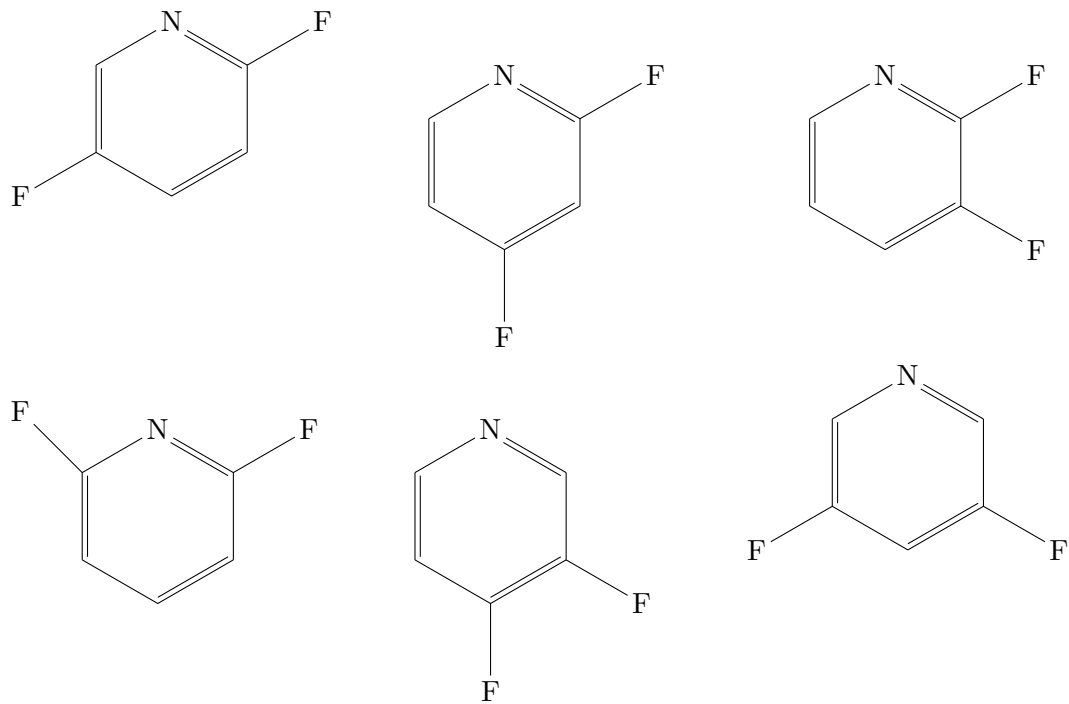
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