5.61 Fall 2017
Problem Set #8 Solutions

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?

Solution: The overlap, interaction, and energy integrals are plotted as a function of internuclear distance, R, in Figure 2. Inspecting the curves, we see that the overlap integral S is repulsive, while the interaction H_{12} and energy ε integrals are attractive, and ε decays most quickly with distance ($\sim e^{-2R}$). This quantity represents the average energy of an electron in a single 1s orbital centered on one H atom. It increases as R→ 0 because it includes the energy of the nuclear electrostatic repulsion ($\sim R^{-1}$).

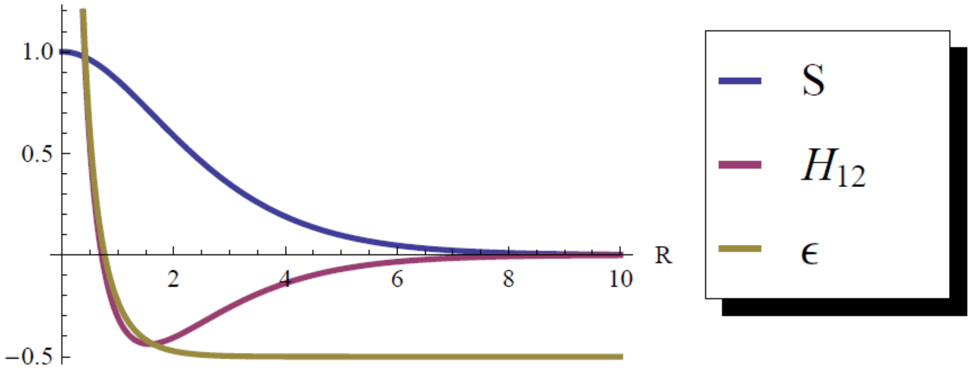


Figure 2. The R–dependence of the overlap S, interaction H_{12}, and energy ε integrals of $\mathbf{H}_2^+$.

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:

The one-electron MO energy eigenvalues obtained by solving the variational problem are

$$E_\sigma = \frac{\varepsilon + H_{12}}{1+S} \qquad E_{\sigma^*} = \frac{\varepsilon - H_{12}}{1-S}. \tag{1.1}$$

These energies (minus the energy of the 1s electron at infinite separation) are plotted as a function of R in Figure 3.

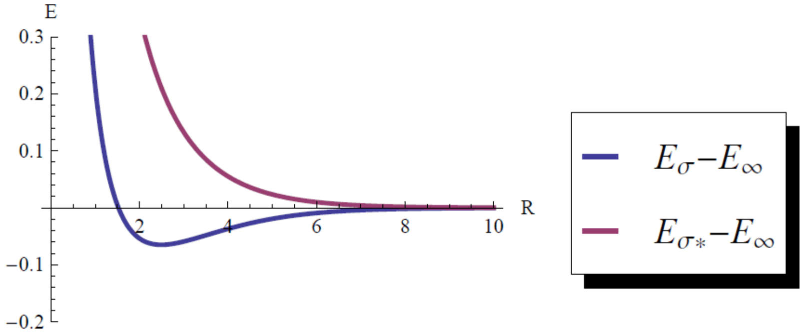


Figure 3: The MO energies of H_2^+ as a function of internuclear distance R.

The equilibrium bond length for H_2^+ in this model is found by finding the minimum of $E_\sigma(R)$. Using the above expressions and finding the root of the equation $dE_\sigma/dR = 0$ (must be done numerically, e.g. with Mathematica's FindRoot), yields $R_e = 249\ a.u. = 1.32$ Å. The binding energy at $R = 2.49$ a.u. is $-(E_\sigma(2.49) - E_\sigma(\infty)) = 0.5648 - 1/2 = 0.0648 = 1.76\ eV$. These are in the ballpark of the experimental values of 1.06 Å, and 2.8 eV.

The sum of $E_\sigma(R)$ and $E_{\sigma^*}(R)$ (which corresponds to one non-interacting electron in each MO) reach limiting values of -1 as $R \to \infty$ and ∞ as $R \to 0$. Both limits make sense. The former corresponds to two independent electrons in hydrogen 1s orbitals (each with energy $-1/2$). In the latter case, we expect internuclear repulsion to dominate.

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?

Solution:

To investigate the relationship between the overlap S and the binding energy BE(R)$= -(E_\sigma(R) - 1/2)$, we can make a parametric plot of the two quantities, as shown in Figure 4. We see that, for small overlap ($S < 0.3$), the binding energy is indeed roughly proportional to S. However, this intuitive idea completely breaks down for $S > 0.3$. The reason is that the overlap in H_2^+ is correlated with the internuclear distance, and so repulsive effects are built into the overlap dependence. In general, all else being equal, we still expect binding energy to scale roughly with increasing overlap.

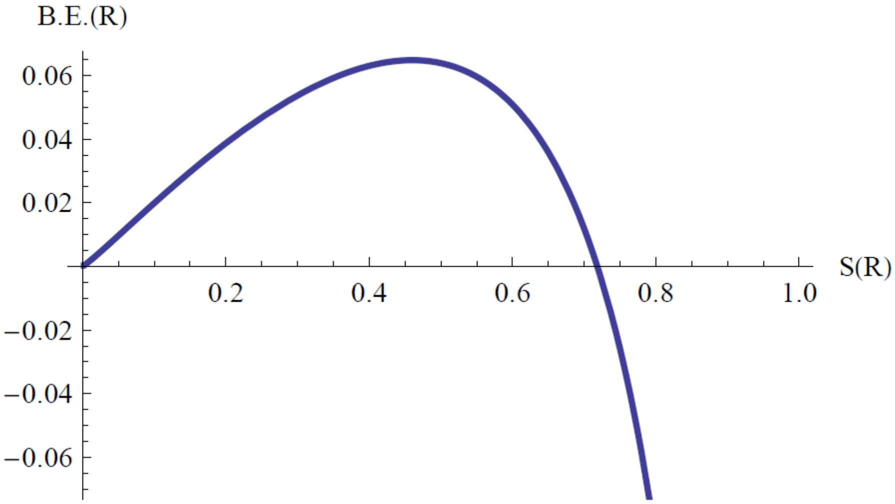


Figure 4. Dependence of binding energy on overlap integral.

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:

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

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

Solution:

Given the orthonormal functions $\{\psi_1, \psi_2, \psi_3\}$, we define the following two wavefunctions:

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

In vector notation, the two wavefunctions are represented by column vectors. Each element of the vector corresponds to the coefficient of the basis function.

$$\psi = \begin{pmatrix} 2 \\ 0 \\ \sqrt{3} \end{pmatrix}, \qquad \phi = \begin{pmatrix} i\sqrt{2} \\ 1 \\ 0 \end{pmatrix} \tag{2.1}$$

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

Solution: The † operator takes the conjugate transpose:

$$\psi^\dagger = \begin{pmatrix} 2 & 0 & -\sqrt{3} \end{pmatrix}, \qquad \phi^\dagger = \begin{pmatrix} -i\sqrt{2} & 1 & 0 \end{pmatrix} \tag{2.2}$$

(Notice that the $\dagger$ operator converts column vectors to row vectors.)

C. Normalize ψ and ϕ.

Solution:

To normalize a vector $\vec{v}$, we take $\vec{v} \to \vec{v}/|\vec{v}|$, where $|\vec{v}| \equiv \sqrt{\vec{v}^\dagger \cdot \vec{v}}$ is the *norm* or magnitude of $\vec{v}$.

Applying normalization to our two wavefunctions yields

$$\psi^\dagger\psi = \begin{pmatrix}2 & 0 & -\sqrt{3}\end{pmatrix}\begin{pmatrix}2\\0\\-\sqrt{3}\end{pmatrix} = 4+0+3 = 7 \tag{2.3}$$

$$\rightarrow \psi_{\text{normalized}} = \psi/\sqrt{7} \tag{2.4}$$

$$\phi^\dagger\phi = \begin{pmatrix}+i\sqrt{2} & 1 & 0\end{pmatrix}\begin{pmatrix}-i\sqrt{2}\\1\\0\end{pmatrix} = 2+1+0 = 3 \tag{2.5}$$

$$\rightarrow \phi_{\text{normalized}} = \phi/\sqrt{3} \tag{2.6}$$

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

Solution:

The inner products of the two wavefunctions are

$$\psi^\dagger\phi = \begin{pmatrix}2 & 0 & -\sqrt{3}\end{pmatrix}\begin{pmatrix}-i\sqrt{2}\\1\\0\end{pmatrix} = -i2\sqrt{2}+0+0 = -i2\sqrt{2} \tag{2.7}$$

$$\phi^\dagger\psi = \begin{pmatrix}+i\sqrt{2} & 1 & 0\end{pmatrix}\begin{pmatrix}2\\0\\-\sqrt{3}\end{pmatrix} = +i2\sqrt{2}+0+0 = +i2\sqrt{2} \tag{2.8}$$

We note that in general, $\psi^\dagger\phi = (\phi^\dagger\psi)^*$.

E. Are ψ and ϕ orthogonal?

Solution:

Two wavefunctions are orthogonal if their inner (dot) product is zero. In part **D** we computed non-zero inner products, so these states are *not* orthogonal.

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

Solution:

NO. This can be made rigorous by scaling the wavefunctions and switching labels around. Convince yourself that we have insufficient information to make any claims comparing the nodes of either wavefunction.

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.

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

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

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

Solution:

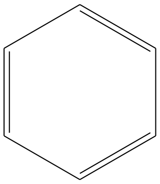
The only condition for a valid Hamiltonian is that it is a *Hermitian* matrix such that $H = H^\dagger = (H^*)^T$. The matrices that satisfy this requirement are 1, 2, 5, 6, 9, and 11. Matrices 3, 4, 7, 8, and 10 are non–Hermitian.

3. This problem deals with the Hückel MO theory of $\boldsymbol{\pi}$–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.

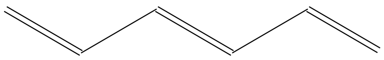
NOTE: For all parts **A**–**D** we take $\alpha = \alpha_\mathrm{C} = -11.2$ eV and $\beta = \beta_\mathrm{CC} = -0.7$ eV.

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

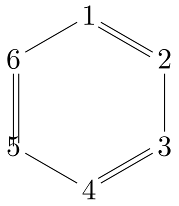
Versus



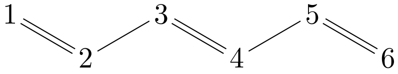
Hexatriene

Solution:

The arbitrary numbering scheme I will use for this problem is



Versus



Let's build the Hückel MO Hamiltonian from the 6 carbon atoms. The differences between benzene and hexatriene are only connectivity:

$$H_{\text{benzene}} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix} \qquad H_{\text{hexatriene}} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & 0 \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ 0 & 0 & 0 & 0 & \beta & \alpha \end{pmatrix} \tag{3.1}$$

We now substitute α and β with the values above and find the eigenvalues of each Hamiltonian numerically. The eigenvalues of $\mathrm{H}_{\text{benzene}}$ (in eV) are

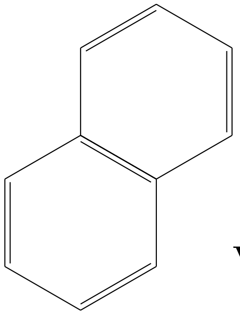
$$E^{\mu} = \{-12.6, -11.9, -11.9, -10.5, -10.5, -9.8\} \tag{3.2}$$

and the eigenvalues of $\mathrm{H}_{\text{hexatriene}}$ are

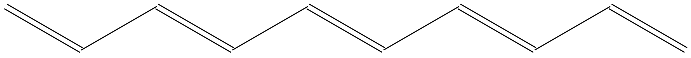
$$E^{\mu} = \{-12.5, -12.1, -11.5, -10.9, -10.3, -9.9\} \tag{3.3}$$

The ionization potential in this model is simply the energy of the HOMO of the ground state of each molecule (this is the orbital from which the electron is ejected). Since there are 6 π–electrons, we can fill the three lowest MOs and the HOMO will be the third lowest. Therefore, the **IP of benzene is 11.9 eV**, and the **IP of hexatriene is 11.5 eV.** and we conclude that benzene holds its HOMO electrons tighter. Experimental values are 9.24384 ± 0.00006 eV and 8.30 ± 0.02 eV, respectively, which agree with the trend predicted by the Hückel theory. What are some reasons the experimental values are systematically lower in magnitude?

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

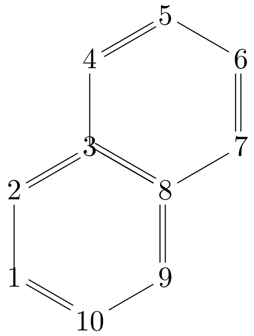


Versus

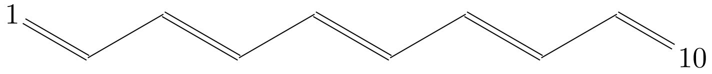


Solution:

This problem is another straightforward application of Hückel theory. My numbering scheme will be



Versus



The two Hückel Hamiltonians for the cyclic and linear systems are (with zeroes omitted)

$$H_{\text{cyclic}} = \begin{pmatrix} \alpha & \beta & & & & & & & & \beta \\ \beta & \alpha & \beta & & & & & & & \\ & \beta & \alpha & \beta & & & & \beta & & \\ & & \beta & \alpha & \beta & & & & & \\ & & & \beta & \alpha & \beta & & & & \\ & & & & \beta & \alpha & \beta & & & \\ & & & & & \beta & \alpha & \beta & & \\ & & \beta & & & & \beta & \alpha & \beta & \\ & & & & & & & \beta & \alpha & \beta \\ \beta & & & & & & & & \beta & \alpha \end{pmatrix} \tag{3.4}$$

$$H_{\text{linear}} = \begin{pmatrix} \alpha & \beta & & & & & & & & \\ \beta & \alpha & \beta & & & & & & & \\ & \beta & \alpha & \beta & & & & & & \\ & & \beta & \alpha & \beta & & & & & \\ & & & \beta & \alpha & \beta & & & & \\ & & & & \beta & \alpha & \beta & & & \\ & & & & & \beta & \alpha & \beta & & \\ & & & & & & \beta & \alpha & \beta & \\ & & & & & & & \beta & \alpha & \beta \\ & & & & & & & & \beta & \alpha \end{pmatrix} \tag{3.5}$$

Finding the eigenvalues of these Hamiltonians numerically yields (in eV):

$$E^{\mu}_{\text{cyclic}} = \{-12.8, -12, 4, -12.1, -11.8, -11.5, -10.9, -10.7, -10.0, -9.9, -9.7\} \tag{3.6}$$

$$E^{\mu}_{\text{linear}} = \{-12.5, -12, 4, -12.1, -11.8, -11.4, -11.0, -10.6, -10.3, -10.0, -9.9\} \tag{3.7}$$

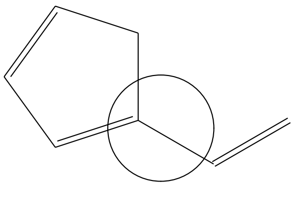
The ground state of each molecule has 10 electrons in the first 5 MOs. Summing these MO energies yields

$$E^{\text{GS}}_{\text{cyclic}} = 2(-12.8) + 2(-12.4) + 2(-12.1) + 2(-11.8) + 2(-11.5) = -\mathbf{121.2}eV \tag{3.8}$$

$$E^{\text{GS}}_{\text{linear}} = 2(-12.5) + 2(-12.4) + 2(-12.1) + 2(-11.8) + 2(-11.4) = -\mathbf{120.4}eV \tag{3.9}$$

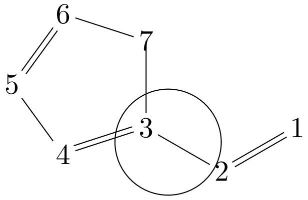
We predict the cyclic structure to be more stable by roughly 0.8 eV, presumably due to "aromaticity".

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?



Solution:

This molecule is



Note that carbon 7 *does not* participate in the π network, being completely saturated. There is no aromatic cyclic structure: the π system runs along carbons 1-2-3-4-5-6. Thus, in terms of Hückel theory, this problem is identical to hexatriene, which we solved above in part **A**. I've numbered this molecule so that we can use the same Hamiltonian, $H_{\text{hexatriene}}$, without needing to permute any rows or columns. However, in this problem, we are interested in the bond order of the 2-3 bond, thus we will need the normalized eigenvector for each MO energy eigenvalue. Calculating these with a computer algebra program yields:

$$\vec{c}^{\,1} = \begin{pmatrix} 0.23 \\ 0.42 \\ 0.52 \\ 0.52 \\ 0.42 \\ 0.23 \end{pmatrix}, \vec{c}^{\,2} = \begin{pmatrix} -0.42 \\ -0.52 \\ -0.23 \\ 0.23 \\ 0.52 \\ 0.42 \end{pmatrix}, \vec{c}^{\,3} = \begin{pmatrix} 0.52 \\ 0.23 \\ -0.42 \\ -0.42 \\ 0.23 \\ 0.52 \end{pmatrix}, \vec{c}^{\,4} = \begin{pmatrix} 0.52 \\ -0.23 \\ -0.42 \\ 0.42 \\ 0.23 \\ -0.52 \end{pmatrix}, \vec{c}^{\,5} = \begin{pmatrix} -0.42 \\ 0.52 \\ -0.23 \\ -0.23 \\ 0.52 \\ -0.42 \end{pmatrix}, \vec{c}^{\,6} = \begin{pmatrix} -0.23 \\ 0.42 \\ -0.52 \\ 0.52 \\ -0.42 \\ 0.23 \end{pmatrix}$$

Our expression for the bond order between atoms i and j involves a sum over each MO (indexed by μ),

$$O_{ij} = \sum_{\mu} n_{\mu} \left(c_i^{\mu}\right)^* c_j^{\mu}, \tag{3.10}$$

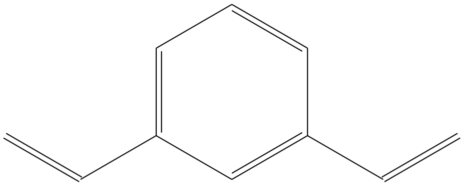
where n_μ is the number of electrons in the μ^{th} orbital. For our molecule, there are 6 π–electrons, so the first three MOs have 2 electrons each (i.e. $n_1 = n_2 = n_3 = 2$). Evaluating the sum for atoms 2 and 3 gives us

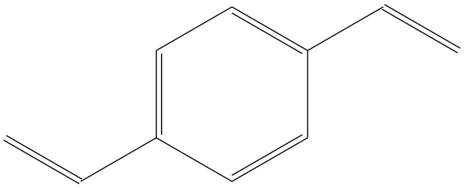
$$O_{23} = \sum_{\mu} n_{\mu} (c_2^{\mu})^* c_3^{\mu} = 2(0.42)(0.52) + 2(-0.52)(-0.23) + 2(0.23)(-0.42) = 0.44 + 0.24 - 0.19 = 0.49. \tag{3.11}$$

Remember that this is the bond order contribution only from the π–network. The σ–framework adds an additional bond order, yielding a total bond order ≈ 1.5. It's useful to note that the first two MOs are bonding in nature (add positively to the bond order sum), while the third MO is anti-bonding with respect to carbons 2 and 3 (adds negatively to the bond order sum). If we were to plot the MOs, we would see a node between atoms 2 and 3 in the third MO.

In terms of resonance structures, the partial bond order makes sense. We can arrow-push to form a di-radical species (on 1 and 6) that has a double bond between carbons 2 and 3. The "average" bond order over all resonance structures is then about 1.5, in agreement with Hückel theory.

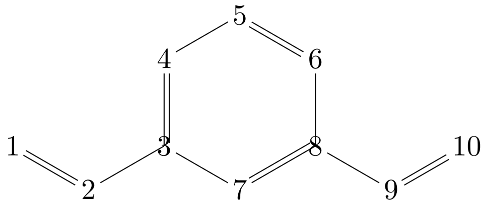
D. Plot the HOMO and LUMO for each molecule below. Is there anything about these orbitals that might tell you about the relative degree of conjugation between the pair of substituents in the meta (left) and para (right) positions?

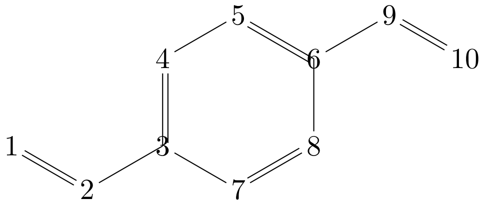




Solution:

This problem asks us to compare the MOs of two different structural isomers of benzene with π–conjugated substituents. My numbering scheme is as follows:





The Hückel Hamiltonians for these isomers are

$$H_{\text{meta}} = \begin{pmatrix} \alpha & \beta & & & & & & & & \\ \beta & \alpha & \beta & & & & & & & \\ & \beta & \alpha & \beta & & & \beta & & & \\ & & \beta & \alpha & \beta & & & & & \\ & & & \beta & \alpha & \beta & & & & \\ & & & & \beta & \alpha & & \beta & & \\ & & \beta & & & & \alpha & \beta & & \\ & & & & & \beta & \beta & \alpha & \beta & \\ & & & & & & & \beta & \alpha & \beta \\ & & & & & & & & \beta & \alpha \end{pmatrix} \tag{3.12}$$

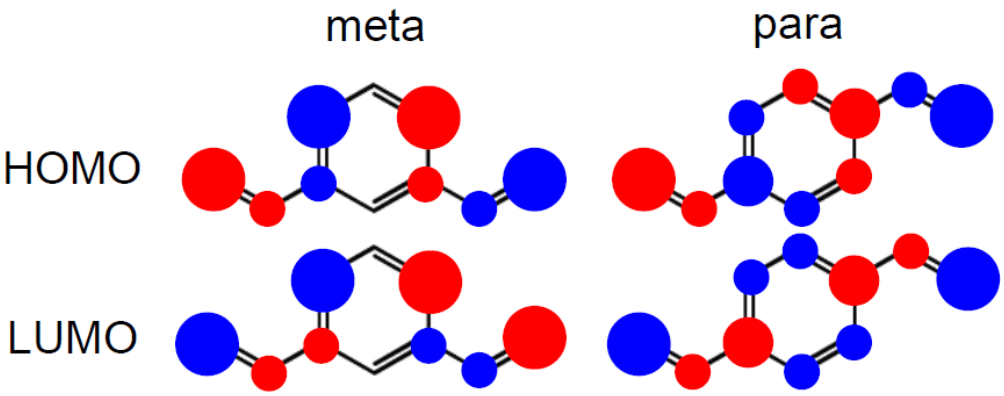
$$H_{\text{linear}} = \begin{pmatrix} \alpha & \beta & & & & & & & & \\ \beta & \alpha & \beta & & & & & & & \\ & \beta & \alpha & \beta & & & \beta & & & \\ & & \beta & \alpha & \beta & & & & & \\ & & & \beta & \alpha & \beta & & & & \\ & & & & \beta & \alpha & & \beta & \beta & \\ & & \beta & & & & \alpha & \beta & & \\ & & & & & \beta & \beta & \alpha & & \\ & & & & & \beta & & & \alpha & \beta \\ & & & & & & & & \beta & \alpha \end{pmatrix} \tag{3.13}$$

There are 10 π–electrons, so the lowest 5 MOs will be filled in the electronic ground state. The 5th lowest MO is the HOMO and the 6th lowest MO is the LUMO. The eigenvectors corresponding to the 5^{5h} and 6^{th} lowest MOs for the two isomers are:

$$\vec{c}^{\,5}_{\text{meta}} = \begin{pmatrix} -0.43 \\ -0.26 \\ 0.26 \\ 0.43 \\ 0 \\ -0.43 \\ 0 \\ -0.26 \\ 0.26 \\ 0.43 \end{pmatrix}, \quad \vec{c}^{\,6}_{\text{meta}} = \begin{pmatrix} 0.43 \\ -0.26 \\ -0.26 \\ 0.43 \\ 0 \\ -0.43 \\ 0 \\ 0.26 \\ 0.26 \\ -0.43 \end{pmatrix} \tag{3.14}$$

$$\vec{c}^{\,5}_{\text{para}} = \begin{pmatrix} -0.47 \\ -0.26 \\ 0.34 \\ 0.22 \\ -0.22 \\ -0.34 \\ 0.22 \\ -0.22 \\ 0.26 \\ 0.47 \end{pmatrix}, \quad \vec{c}^{\,6}_{\text{para}} = \begin{pmatrix} 0.48 \\ -0.26 \\ -0.34 \\ 0.22 \\ 0.22 \\ -0.34 \\ 0.22 \\ 0.22 \\ -0.26 \\ 0.47 \end{pmatrix} \tag{3.15}$$

Plotting the approximate wavefunctions for these orbitals gives us:



In each case, the HOMO orbital has a bonding interaction within the substituents and an anti-bonding interaction between the substituents and the ring. The LUMO has an anti-bonding interaction within the substituents and bonding interaction between the substituents and the ring. Examining the magnitude of the eigenvector elements closely, we see that the bonding character in the meta substituents is slightly weaker than than in the para substituents
$(0.43 \times 0.26 = 0.11 < 0.47 \times 0.26 = 0.12)$.

4. It is straightforward to extend Hückel Theory to deal with $\boldsymbol{\pi}$ systems containing elements other than carbon and hydrogen.

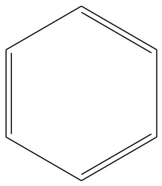
A. First, let us consider including heteroatoms such as nitrogen instead of carbon inside of conjugated rings. To use the Hückel prescription, we simply need α values for C and N and β values for CC and CN bonds. We already know that $\alpha(\mathrm{C}) = 11.2\ eV$ and $\beta(\mathrm{CC}) = –0.7\ eV$.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

$$\begin{array}{ll} \alpha(\mathrm{N}) = -10.2\ eV & \beta(\mathrm{CN}) = -0.65 \\ \alpha(\mathrm{N}) = -11.2\ eV & \beta(\mathrm{CN}) = -0.70 \\ \alpha(\mathrm{N}) = -12.2\ eV & \beta(\mathrm{CN}) = -0.75 \end{array}$$

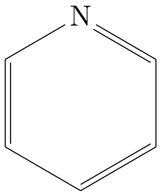
Solution:

Since N is a more electronegative atom than C, α_{N} should be more negative, indicating that it binds its valence electrons more strongly. We will choose $\alpha_{\mathrm{N}} - -12.2$ eV. Different values of β_{CN} could be argued for and against. The CN bond distance in pyridine shortens by only a few percent compared to benzene; however, the N atomic radius is only a few percent smaller than C. I'll consider these effects to roughly cancel out, so that the nearest-neighbor interactions are about the same, i.e. $\beta_{\mathrm{CN}} = -0.7$ eV. Valid arguments can be made to justify other choices of β_{CN}.

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



Solution:

We build the Hückel matrices in the same way as problem 3. Diagonal terms representing orbital energies on N will use α_N, and CN off-diagonal terms will use β_{CN} nearest neighbor interactions.

The Hamiltonian for pyridine is

$$H_{\text{benzene}} = \begin{pmatrix} \alpha_N & \beta_{\text{CN}} & 0 & 0 & 0 & \beta_{\text{CN}} \\ \beta_{\text{CN}} & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta_{\text{CN}} & 0 & 0 & 0 & \beta & \alpha \end{pmatrix} \tag{4.1}$$

The MO eigen-energies for pyridine are:

$$E = \{-12.94, -12.19, -11.9, -10.77, -10.5, -9.89\}$$

Comparing these (and their eigenvectors, not shown) to benzene, we make the following observations:

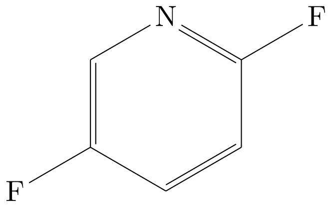
1. The lowest energy MO is lower in energy, due to the stronger electronegativity of N.
2. Only one of each pair of degenerate MOs is brought down in energy. This is because one of each pair has a node through the N atom; in the limits of Hückel theory, this MO will not be affected at all by changes at these sites.
3. The low energy MOs have the largest density on the N atom (we have broken the rotational symmetry of the molecule). This is consistent with N's greater electronegativity pulling in the electron density towards it. The partial charge on N ($q_i = +1 - \sum_\mu n_\mu |c_i^\mu|^2$) is calculated to be ~ -0.49.

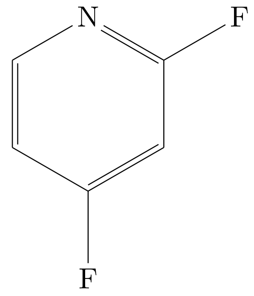
C. We can also use Hückel theory to understand how substituents, like a fluorine atom, will affect the π orbitals. Toward this end, we can assume that a fluorine atom will lower the average energy of the carbon it is attached to by 0.2 eV. Thus a CH carbon will have $\alpha(\text{C}) = -11.2\ eV$ while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

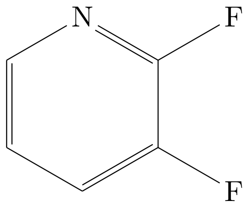
Solution:

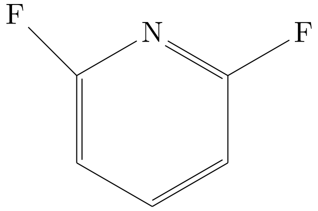
We will perform a similar calculation with 1-fluorobenzene. As fluorine deshields the carbon nucleus, we take $\alpha_C = -11.4$ eV for carbons that have CF bonds. We will assume β remains the same as for benzene. After building the Hamiltonian matrix and calculating its eigenvectors, we find the partial charge on the fluorinated carbon to be -0.11, i.e. the fluorine effectively pulls more electron density onto its C atom.

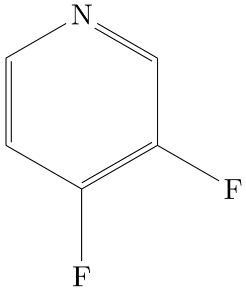
D. You are attempting a *partial* fluorination of pyridine. You want to selectively fluorinate two of the carbons, while leaving the others untouched. Which sites will the fluorines prefer? To answer this question, compute the energies of all six of the difluorinated isomers below. Which has the lowest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

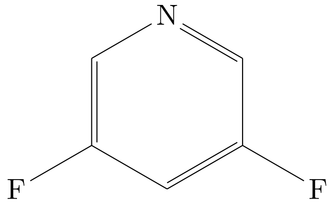












Solution:

We now compare the energies of the six possible di-substituted fluorobenzenes. For each, we build the Hamiltonian matrix, calculate the eigenenergies, occupy these MOs with the 6 π electrons and then sum the one-electron energies of the occupied orbitals to find the energy of the ground electronic state. The energies (in eV) of the six isomers are:

$$\begin{aligned}
E_{2,5} &= -74.446\\
E_{2,4} &= -74.423\\
E_{2,3} &= -74.441\\
E_{2,6} &= -74.409\\
E_{3,4} &= -74.455\\
E_{3,5} &= -74.492
\end{aligned}$$

Hückel theory predicts that the 3,5- and 3,4-difluorobenzene compounds will be the most stable isomers. We could justify this result by noting that these two are the only two isomers *not* to have a fluorine atom ortho to the N atom, indicating that the increased π-electron density associated with fluorinated carbons would interact unfavorably with the increased π–electron density on the electronegative N.

5.61 Physical Chemistry
Fall 2017