## MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Chemistry

5.61 Quantum Mechanics
Fall 2012
Problem Set #9
Reading Assignment: McQuarrie 11.1-11.8)
(● = Easier ■= More Challenging ◆=Most Challenging; =Computer)

1. ■/ This problem considers 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.

   a. Determine the electron affinity of benzene [IP=E(B-)-E(B)]. Compare this to the EA of hexatriene. Which is more electrophillic?
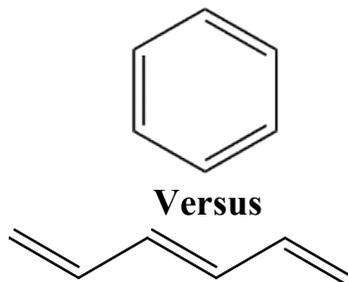

Versus

   b. Compare the total energies of the 10-electron conjugated systems below. Which is most stable? How do you explain this?
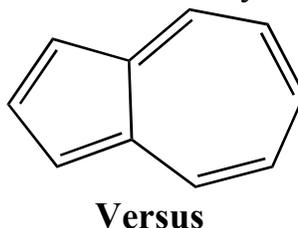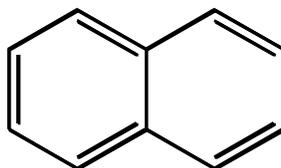

Versus

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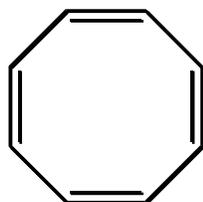
c. What is the bond order of the selected bond in the molecule below? How can you rationalize this result in terms of resonance structures?
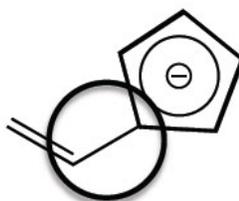
d. Plot the HOMO and LUMO for each molecule below. Is there anything about these orbitals that might tell you about the relative degree of conjugation between the substituents in the ortho (top) meta (middle) and para (bottom) positions?
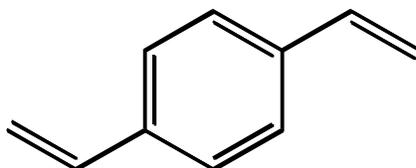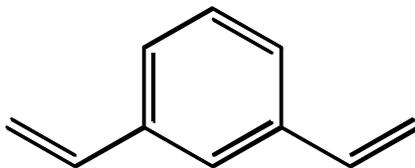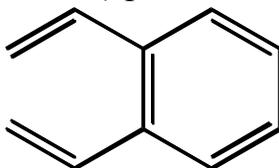
2. ■/ It is straightforward to extend Huckel Theory to deal with π systems containing elements besides carbon and hydrogen.
   a. First, let us consider including heteroatoms such as nitrogen inside of conjugated rings. To use the Huckel prescription, we simply need α values for C and N and β values 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	$\beta(CN)$=-0.65
$\alpha(N)$=-11.2 eV	$\beta(CN)$=-0.70
$\alpha(N)$=-12.2 eV	$\beta(CN)$=-0.75

b. Use the parameters you chose in part a. to compute the π MOs of the molecules below. Compare your results for the different molecules. Do you notice any trends? What is the partial charge on nitrogen in each case? How does the pattern of MO energies change? What are the C-N bond orders? Do these results make sense?
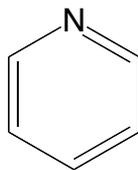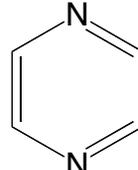
Benzene   Pyridine   Pyrazine
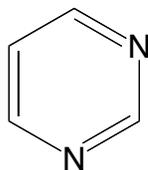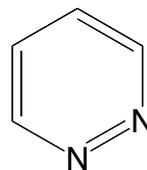
Pyrimidine   Pyridazine

c. We can also use Huckel 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 $\alpha(C)$=-11.4 eV. Use this parameterization to compute the MOs of 1-flourobenzene. 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. But which sites will the flourines prefer? To answer this question, compute the energies of all six of the diflourinated isomers below. Which has the lowest energy? How can you rationalize your result?
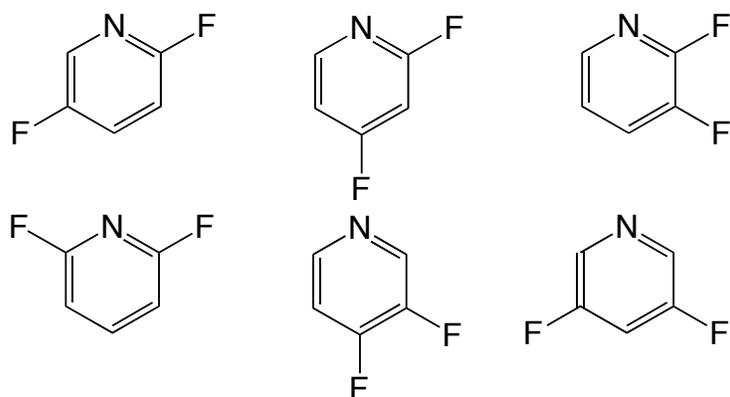
3. ●/🍎 In this problem we're going to familiarize ourselves with using Gaussian by finding the equilibrium structure of a single formaldehyde molecule.

   a. Make a reasonable guess at the structure of H_2CO using GaussView. Then, determine the equilibrium structure of the molecule in the Hartree-Fock (HF) approximation using the 6-31G(d,p) basis. What are the predicted equilibrium bond lengths, bond angle and dipole moment of the molecule? Compare your results with the experimental values of R_{CH}=1.111 Å, R_{CO}=1.205 Å, θ_{HCH}=116.1° and μ=2.33 Debye, respectively.

   b. Use GaussView to visualize the molecular orbitals. What are the HOMO and LUMO? Are they bonding? Antibonding? σ or π? Lone pair orbitals? What does this tell you about where the electron would come from if you ionized formaldehyde to make H_2CO^+?

4. ■/🍎 Hydrogen combustion is an extremely important reaction in the long range goal of creating cars, trucks and planes that generate fewer harmful emissions. In the gas phase, the reaction is

$$2H_2 + O_2 \rightarrow 2H_2O \qquad \Delta E=???$$

In this problem, we will use various methods to approximate the energy released by this reaction.

$$\Delta E=2E(H_2O) - 2E(H_2) - E(O_2)$$

   a. First, let's try using the HF approximation that worked so well for the structure of water. Choose a series of basis sets (small, medium, large…). In each basis, obtain HF optimized structures for the reactants and product. Each of these calculations should be strictly analogous to the calculation you did in problem #1. Compare your bond lengths to the experimental values: R_{HH}=0.741 Å, R_{OO}=1.208 Å, R_{OH}=0.958 Å, θ_{HOH}=104.5°. How quickly does

the structure converge to the complete basis set limit? How close
are the HF structures to experiment?

b. Next, compare the reaction energies obtained in HF. How quickly
does the energy converge to the basis set limit? How close is HF to
the experimental heat of combustion (-5.0 eV)? Does your result
surprise you? Why or why not?

c. Next, let's see if a better energy function can improve matters. Use
density functional theory (DFT) to compute the reaction energy.
Does DFT bring your answer in closer agreement with
experiment? What do you take home from this exercise? [Note: in
this part, you may use an energy functional and basis set of your
choice, but you must justify your choice.]

d. Finally, let's take a shotgun approach, as is sometimes done in
DFT. For a "good" basis set, compute the reaction energy with
several different density functionals. Which one gets the closest to
the experimental value? What do you take home from this
exercise?

5. ■/ One of the most important intermolecular interactions in chemistry is
the hydrogen bond. In particular, hydrogen bonding in water is an extremely
important topic. In this problem, we will study the hydrogen bond between
two water molecules.

a. Compute the length, R, of a hydrogen bond between two water
molecules using B3LYP in a 6-31G(d,p) basis. To do this, you
will need to optimize the geometry of a pair of water molecules
placed close to one another:

How does the length of the H--O hydrogen bond compare to the O-
H bond in water?

b. Now, compute the binding energy of the hydrogen bond using
B3LYP/6-31G(d,p):

$$\Delta E = E(2\ H_2O) - 2\ E(H_2O)$$

How does the strength of the hydrogen bond compare to the
strength of an OH-bond in water?

c. Redo your calculations from part b. using MP2. Do the density
functional results agree with the correlated calculations as far as
the strength of the hydrogen bond goes? [Note: you will need to
justify your choice of basis set for this part of the problem.]

d. Now, consider a model where the interaction between two water molecules (A and B) is entirely due to their dipole moments (μ_A and μ_B) The most favorable configuration would then place the two dipole moments head-to-tail (i.e. →…→) in which case the interaction energy is given by

$$\Delta E = -2\frac{\mu_A\mu_B}{R_{AB}{}^3}$$

Compute the maximum binding energy of the water dimer within this dipole-dipole model [Hint:You will need to compute the dipole moment of a single water molecule first.]. Does the dipole model agree qualitatively with the computed orientations of the two molecules in the water dimer? Does it accurately predict the binding energy? Explain any discrepancies you find.

e. Now, compute the binding energy of H_2S dimer. How much weaker is the bond between two H_2S molecules, as compared to two water molecules? How close is the energy of $(H_2S)_2$ to the energy predicted by the dipole-dipole model?

f. Do your results in parts d and e support the existence of a "hydrogen bond" between two water molecules?

6. ⬢ Answer one of the following questions using Gaussian calculations. Describe what calculations you performed to obtain your answer and why. Do your answers agree with your chemical intuition? You may use any method/basis combination you wish, but please explain your choice. For extra credit, you may perform multiple portions of this problem.

a. What is the energy gain on forming the peptide bond in $(Ala)_2$?

$$\text{Ala-OH} + \text{H-Ala} \rightarrow Ala_2 + H_2O$$

Compare this to the energy gained from the peptide bond between Alanine and Valine:

$$\text{Ala-OH} + \text{H-Val} \rightarrow \text{Ala-Val} + H_2O$$

b. What is the length of the carbon-carbon bond in C_{60}? Compare this to the bond length in benzene. What does this say about the C-C bond **order** in C_{60}?

c. What is the energy difference between the high and low spin states of cyclopentadienylcobalt dicarbonyl, shown below?
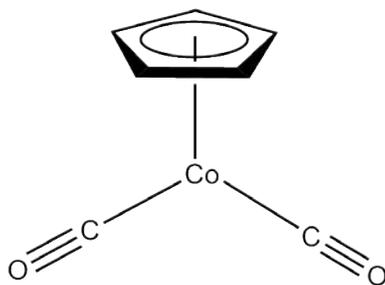
d. What is the ionization potential of Ferrocene, $Fe(C_5H_5)_2$? Where does the ionized electron come from (metal or ligand)? How does the IP compare to the IP for, say, water?

e. Pick a chemical question of interest to you and answer it with a calculation.

5.61 Physical Chemistry
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