5.61 Fall 2017
Problem Set #9 Solutions

Problems 1 and 2 use the concept of "electronegativity" to analyze the strength of a polar AB bond and to contrast the π-bonding ability of C and Si. "Electronegativity" is closely related to the ionization energy of an atomic orbital, and it is expressed in units of eV. You will need to use non-degenerate perturbation theory to answer these questions. Electronegativity is a positive number. It is largest for an atom that has a large Ionization Energy.

1. In this problem we want to approximate the strength of a two electron bond between two atoms (A and B) with different electron negativities. Approximate the molecular orbitals as linear combinations of one valence orbital on A and another valence orbital on B

$$\psi \equiv c_1\phi_A + c_2\phi_B.$$

For simplicity, assume that the atomic orbitals are approximately orthogonal

$$S \equiv \int \phi_A \phi_B d\tau \approx 0.$$

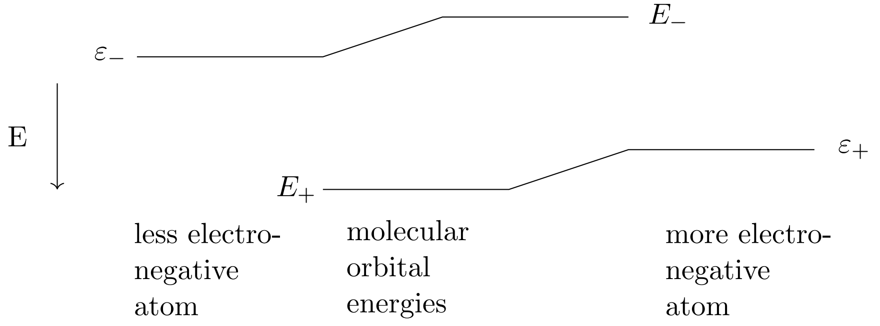
A. We now want to approximate the energy of the AB bond for a fixed atom A bonding to different partners B with varying electronegativity. To this end, fix the electronegativity of atom A (ε_A) and allow the electronegativity of B (ε_B) to vary freely. Finally, assume that the coupling matrix element is independent of the electronegativity and (arbitrarily) equal to 1

$$V \equiv \int \phi_A \widehat{H} \phi_B d\tau \approx 1.$$

Within this model, compute the binding energy of the lowest energy MO as a function of ε_B. The B.E. is $\varepsilon_{\max} - E_+$ where $\varepsilon_{\max}$ is the larger of ε_A and ε_B. That is to say, compute the difference in energy between the lowest energy MO and the lowest energy AO as you vary the electronegativity of atom B. What electronegativity difference produces the strongest AB bond? Does this agree with your chemical intuition? You may wish to look up a few A-B bond strengths to support your argument.

Solution:

Let us replace the electro-negativities of atoms A and B, ε_A and ε_B, by ε_+ and ε_-. The larger electronegativity, ε_+, corresponds to the *more stable* atomic orbital. The relevant energy levels are illustrated by the energy level diagram:



The binding energy of the resultant molecular orbital is

$$\text{B.E.} = E_+ - \varepsilon_+$$

$$|\Psi\rangle = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \quad \widehat{H} = \begin{pmatrix} \varepsilon_+ & V \\ V & \varepsilon_- \end{pmatrix}, \quad \widehat{S} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Assume zero overlap between atomic orbitals for simplicity.

The secular equation is obtained from

$$\widehat{H}\Psi = E\widehat{S}\,|\Psi\rangle = E\,|\Psi\rangle$$

$$\begin{vmatrix} \varepsilon_+ - E & V \\ V & \varepsilon_- - E \end{vmatrix} = 0 = E^2 - (\varepsilon_+ + \varepsilon_-)E + (\varepsilon_+\varepsilon_- - V^2).$$

Use the quadratic formula to obtain the values of E_+ and E_-

$$E_\pm = \frac{(\varepsilon_+ + \varepsilon_-) \pm [(\varepsilon_+ + \varepsilon_-)^2 - 4\varepsilon_+\varepsilon_- + 4V^2]^{1/2}}{2}.$$

We are interested in the energy of the most stable molecular orbital, which we will call E_+ according to the energy level diagram above

$$E_+ = \frac{(\varepsilon_+ + \varepsilon_-) + [(\varepsilon_+ + \varepsilon_-)^2 - 4\varepsilon_+\varepsilon_- + 4V^2]^{1/2}}{2}.$$

Note that $(\varepsilon_+ + \varepsilon_-)^2 - 4\varepsilon_+\varepsilon_- = (\varepsilon_+ - \varepsilon_-)^2$.

Some simplifying notation:

$$\begin{aligned}
\bar{\varepsilon} &\equiv \frac{\varepsilon_+ + \varepsilon_-}{2} > 0 \\
\Delta &= \frac{\varepsilon_+ - \varepsilon_-}{2} > 0 \\
E_+ &= \bar{\varepsilon} + [\Delta^2 + V^2]^{1/2} \\
\text{B.E.} &= E_+ - \varepsilon_+ = \bar{\varepsilon} - \varepsilon_+ + [\Delta^2 + V^2]^{1/2} \\
\bar{\varepsilon} - \varepsilon_+ &= \frac{\varepsilon_+ + \varepsilon_-}{2} - \frac{2\varepsilon_+}{2} = \frac{\varepsilon_+ - \varepsilon_-}{2} = -\Delta \\
\text{B.E.} &= -\Delta + [\Delta^2 + V^2]^{1/2}.
\end{aligned}$$

There are two limits:

$$\begin{aligned}
\Delta &= 0 & E_+ - \varepsilon_+ &= V \\
\Delta &= \pm\infty & E_+ - \varepsilon_+ &= 0
\end{aligned}$$

The B.E. increases to its maximum value, V, when $\Delta = 0$. Also

$$\frac{\partial \text{B.E.}}{\partial \Delta} = -1 - [\Delta^2 + V^2]^{-1/2}$$

which implies that B.E. is monotonically decreasing as $|\Delta|$ increases.

B. The model above does not include electron-electron interactions. *Qualitatively* speaking, how would you expect the results of part **A** to change if you included electron-electron interactions at the level of the Independent Electron Approximation (IEA)? Be as specific as you can in your answer. For example, will the bond get stronger or weaker? Will the optimal electronegativity change?

Solution:

Since all e^-'s will be in the ground state, expect only Coulomic repulsion of the form Joule.

Expect this to be repulsive, $\therefore$ will make bond weaker.

More polar bonds will have the two e^-'s much more likely to be close to each other (localized near the more electronegative atom) so $\Delta = 0$ is still optimal.

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2. Unsaturation (i.e. the existence of stable multiple bonds) is an extremely important phenomenon for the chemistry of carbon. However, multiple bonding is comparatively rare for silicon even though C and Si have the same valence shell. In this problem, we develop an explanation for this based on MO theory. Consider the ethylene molecule ($H_2C{=}CH_2$) with all atoms located in the x-y plane. At equilibrium, the Hückel MO Hamiltonian for the carbon p_z orbitals is

$$\mathbf{H}_{\text{C-C}} = \begin{pmatrix} -10.9 & -0.8 \\ -0.8 & -10.9 \end{pmatrix}$$

Answer the following questions. In preparing your answer it may prove useful to know the following data:

	Silicon	Carbon
Electronegativity	1.90eV	2.55eV
Atomic Radius	1.46 Å	0.91 Å

A. Consider the two molecules $H_2Si{=}SiH_2$ and $H_2Si{=}CH_2$ at their respective equilibrium geometries. Of the eight matrices below, one represents the Hamiltonian for the p_z orbitals in $H_2Si{=}SiH_2$, while another represents $H_2Si{=}CH_2$. Which is which? Justify your answer.

$$\begin{pmatrix} -8.9 & -0.4 \\ -0.4 & -8.9 \end{pmatrix} \quad \begin{pmatrix} -8.9 & -1.0 \\ -1.0 & -8.9 \end{pmatrix} \quad \begin{pmatrix} -12.3 & -0.4 \\ -0.4 & -12.3 \end{pmatrix} \quad \begin{pmatrix} -12.3 & -1.0 \\ -1.0 & -12.3 \end{pmatrix}$$

$$\begin{pmatrix} -8.9 & -0.6 \\ -0.6 & -10.9 \end{pmatrix} \quad \begin{pmatrix} -12.3 & -0.6 \\ -0.6 & -10.9 \end{pmatrix} \quad \begin{pmatrix} -8.9 & -0.9 \\ -0.9 & -10.9 \end{pmatrix} \quad \begin{pmatrix} -12.3 & -0.9 \\ -0.9 & -10.9 \end{pmatrix}$$

Solution:

$|\alpha_{\text{Si}}| < |\alpha_c|$ since Silicon is less electronegative than Carbon

$|\beta_{\text{CC}}| < |\beta_{\text{SiC}}|$ using electronegativity arguments from Question 1. Bond strength is maximum when $\Delta = 0$.

So the Hamiltonian for $H_2Si = SiH_2$ is $\begin{pmatrix} -8.9 & -0.4 \\ -0.4 & -8.9 \end{pmatrix}$ and that for $H_2Si = CH_2$ is $\begin{pmatrix} -8.9 & -0.6 \\ -0.6 & -10.9 \end{pmatrix}$.

B. Based on your answer to part **A**, how do you expect the strength of the π bonds in $H_2Si{=}SiH_2$ and $H_2Si{=}CH_2$ to compare to the strength of the π bond in ethylene? Justify your answer.

Solution:

$\widehat{H} = \begin{bmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{bmatrix}$ has eigenenergy $\begin{vmatrix} \alpha_1 - E & \beta \\ \beta & \alpha_2 - E \end{vmatrix}$. Same form (as expected) as Question 1.

$$\begin{aligned} &E = \overline{\alpha} \pm \sqrt{\Delta^2 + \beta^{2'}} \quad \overline{\alpha} = \frac{1}{2}(\alpha_1 + \alpha_2);\ \Delta = \frac{1}{2}(\alpha_1 - \alpha_2) \\ &E_-(H_2Si = SiH_2) = -9.3 \\ &E_-(H_2Si = CH_2) = -11.07 \\ &E_-(H_2C = CH_2) = -11.7 \end{aligned}$$

Special Note: Problems **3-6** deal with the computer calculations based on Professor Van Voorhis' two Lectures (28 and 29). Several of these problems require Gaussian calculations, which produce a ".log" file detailing the results of the calculation. In order to receive full credit for this problem set, you must submit the ".log" files for your calculations electronically via the 5.61 website. While we encourage you to work together on these problems, each student is expected to run their own calculations.

3. In this problem we're going to familiarize ourselves with using Gaussian by finding the equilibrium structure of a single methanol molecule.

A. Make a reasonable guess at the structure of CH_3OH 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 $R_{OH} = 0.956$ Å, $R_{CO} = 1.427$ Å, $R_{CH} = 1.096$ Å, $R_{CH} = 1.096$ Å, $\theta_{HCH} = 109.0°$, $\theta_{HOC} = 108.9°$ and $\mu = 1.70$ Debye, respectively.

Solution:

No solution given

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^+?

Solution:

No solution given

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4. Methanol combustion in the gas phase follows the reaction:

$$CH_3OH\,(g) + \frac{3}{2}\,O_2(g) \;\rightarrow CO_2(g) + 2\,H_2O\,(g) \qquad \Delta E = \text{ (to be computed)}$$

This reaction is extremely exothermic and makes methanol, which is a very efficient fuel. In this problem, we will use various methods to approximate the energy released by this reaction.

$$\Delta \text{E}{=}\text{E}(CH_3OH) + \frac{3}{2}\,\text{E}(O_2) - \text{E}(CO_2) - 2\,\text{E}(H_2O)$$

A. First, let's try using the HF/6-31G(d,p) approximation that works well for the structure of methanol above. Obtain HF/6-31G(d,p) optimized structures for the reactants and for both products. Compare your bond lengths to the experimental values. For O_2 $R_{OO} = 1.208$ Å; for CO_2 $R_{CO} = 1.162$ Å; and for water $R_{OH} = .958$ Å, $\theta = 104.5°$.

Solution:

No solution given

B. Use the final energies of CH_3OH, O_2, CO_2, and H_2O to compute the energy released in burning one molecule of methanol. Compare your prediction to the experimental result $\Delta E = -7.1$ eV. Note that your answer will not be very close to the experimental value. Does this surprise you? Why?

Solution:

No solution given

C. The discrepancy above must be due to one of two sources: either the basis set is not large enough, or the Hartree-Fock energy expression is not sufficiently accurate. First, let us see whether the basis set is the problem. Choose a larger basis set than 6-31G(d,p) for this system and justify why you chose this basis. Now, compute the reaction energy in this basis. Does a larger basis significantly change your answer? [Note: If you chose an extremely large basis, this calculation could take a very long time.]

Solution:

No solution given

D. Next, let's see whether a better energy function can improve matters. Use density functional theory (DFT) to compute the reaction energy. Does DFT bring your answer into 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.]

Solution:

No solution given

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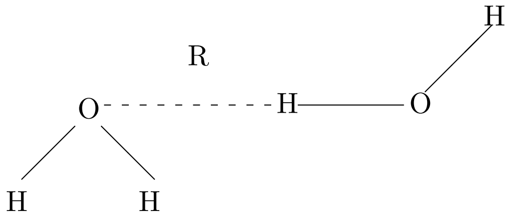
5. One of the most important intermolecular interactions in chemistry is the hydrogen bond. In particular, hydrogen bonding in water is an extremely important topic. In this problem, we will study the hydrogen bond between two water molecules.

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?

Solution:

No solution given

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

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?

Solution:

No solution given

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

Solution:

No solution given

D. Next, 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. $\rightarrow \cdots \rightarrow$) in which case the interaction energy is given by

$$\Delta E = -2\frac{\mu_A \mu_B}{R^3_{\text{AB}}}$$

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.

Solution:

No solution given

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

Solution:

No solution given

F. Do your results in parts **D** and **E** support the existence of a "hydrogen bond" between two water molecules?

Solution:

No solution given

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6. Answer one of the following five 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 $(\text{Ala})_2$?

$$\text{Ala}{-}\text{OH} + \text{H}{-}\text{Ala} \rightarrow \text{Ala}_2 + \text{H}_2\text{O}$$

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

$$\text{Ala}{-}\text{OH} + \text{H}{-}\text{Val} \rightarrow \text{Ala}{-}\text{Val} + \text{H}_2\text{O}$$

Solution:

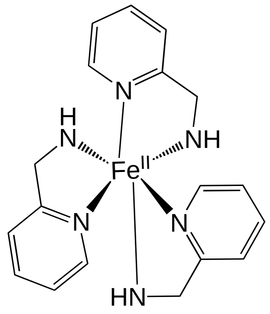
No solution given

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}?

Solution:

No solution given

C. What is the energy difference between the high and low spin states of Fe(2-picolylamine)$_3$, shown below?



Solution:

No solution given

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?

Solution:

No solution given

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

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