EDU 106 lab Molecular Modeling II

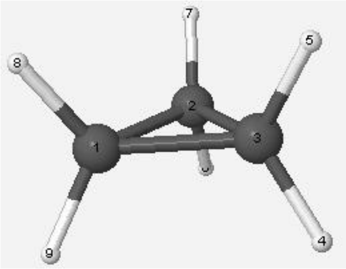
Further Explorations Using WebMO

http://www.webmo.net/

I. Choice of Basis Set *Exercise 1 - Structure of Cyclopropane*

In the WebMO Editor window, build a molecule of cyclopropane (C_3H_6) by making a triangle of C atoms.

Choose Clean-Up > Comprehensive-Mechanics. You should now have the basic structure.



Click the blue "continue" arrow in the lower right side of the Build Molecule window.

Choose Gaussian as the computational engine. Click the blue "continue arrow" (lower right).

Type in/Choose the following:

Job Name: C3H6 STO-3G
Calculation: Geometry Optimization
Theory: Hartree-Fock
Basis Set: Minimal STO-3G
Charge: 0
Multiplicity: Singlet

Click on the blue "continue" arrow. You should now see your job listed.

Click on the hyperlinked name (C3H6 STO-3G) to open the "View Job" window.

Choose the Select arrow (4th icon down on left).

Click on one of the H atoms in the structure (the other atoms and bonds will "fade").

Shift and Click the attached C atom (both atoms are now highlighted).

The bond length is displayed just below the molecule. Record the value of the C-H bond length in the table on the next page. Check the other C-H bond lengths.

Click on one of the C atoms in the structure, then Shift and Click the attached C atom. Record the value of the C-C bond length in the table. Check the other C-C bond lengths.

Click on one of the H atoms, then Shift and click the C atom, followed by the other H atom. The bond angle is displayed just below the molecule. Record the value of the H-C-H bond angle in the table. Check the other H-C-H bond angles.

Also check the C-C-C bond angles and the C-C-H bond angles. Place representative values in the table.

Record the calculation time in the table (located under 'Summary', left of the molecule display).

Item	STO-3G	6-31G(d)	6-311+G(d,p)	Experimental	Calculation time
C-C distance				**1.501Å**	
C-H distance				**1.083Å**	
H-C-H angle				**114.5°**	
C-C-C angle				**60.000°**	
C-C-H angle				**117.937°**	

Repeat the entire process described above, but use 6-31G(d) as a basis set. Record the results in the above table.

Repeat the entire process described above, but use 6-311+G(d,p) as a basis set. Record the results in the above table

Questions:

1. **Compare the calculated values with the experimental values. Does the choice of basis set affect the bond distances a great deal?**

2. **Which basis set gives the best bond angles? ___________________________________**

3. **Look at the three calculation times.**
    a. **Approximately how many times longer did the calculation take to run using 6-31G(D) vs. STO-3G?**

    b. **Approximately how many times longer did the calculation take to run using 6-311+G(d,p) vs. STO-3G?**

Exercise 2 - Bond Length of the H-F Molecule

In this exercise you will build H-F and optimize the geometry using either Hartree-Fock or MP4 with several different basis sets. Electron correlation is known to be an important factor in calculating the bond length for this system. The experimental bond length in the H-F molecule is 0.917Å.

In the WebMO Editor window, place an atom of fluorine (F) in the workspace.
Choose Clean-Up > Comprehensive-Mechanics. You should now have the H-F molecule.

Click the blue "continue" arrow in the lower right side of the Build Molecule window.
Choose Gaussian as the computational engine. Click the blue "continue arrow" (lower right).

Type in/Choose the following:
  Job Name: HF HF STO-3G
  Calculation: Geometry Optimization
  Theory: Hartree-Fock
  Basis Set: 3-21G
  Charge: 0
  Multiplicity: Singlet
Click on the blue "continue" arrow. You should now see your job listed.

Determine the bond length, and place the value in the table below:

Basis Set	Hartree-Fock	Moller Plesset 4
3-21G		
6-31G(d)		
6-311+G(d,p)		

Repeat the above process using Hartree-Fock and the 6-31G(d) and 6-311+G(d,p) basis sets. Record the bond length values in the table.

Repeat the above process using Moller Plesset 4 and the 3-21G, 6-31G(d), and 6-311+G(d,p) basis sets. Record the bond length values in the table.

Question:

1. **Which basis set and method gave the result closest to the experimental value (0.917Å)?**

II. Geometry Optimization

Exercise 1 – Potential Energy Surface of Bond Stretching in Dinitrogen

Build a molecule of N_2 (triple bond!).

Perform a geometry optimization using PM3 (Job Name: N2PM3) using Gaussian or Mopac.

Click on New Job Using This Geometry > Open Editor.

Choose the Adjust tool (Arrow, 6th down) and click on one N atom. Hold down the shift key and click on the other N atom. Record the bond length: _________ Å (literature, 1.098Å).

Choose Tools > Z-matrix.

To the right of the bond length, select "S" from the pull down menu, then type in the values for Start, Stop, and # Steps shown below. We will calculate the energy of the molecule every 0.05 Å between the limits we have set.

Click OK, then Close Editor. Click the blue continue arrow. Choose the same engine used above.

Choose/Type in the following:

Job Name: N2Scan
Calculation: Coordinate Scan
Theory: PM3
Basis Set: Basic: 3-21G (or accept default)
Charge: 0
Multiplicity: Singlet

Click the blue continue arrow. When the job is complete, open the file and scroll down to the Coordinate Scan data. Click on the magnifying glass in the title bar.

On the graph that appears, use your mouse and place the cursor on the lowest energy point. Look at the coordinate values above the graph

Exercise 2 – Potential Energy Surface of Bond Angle Bending in Water

Build a molecule of H_2O.

Perform a geometry optimization using PM3 (Job Name: H2OPM3) using Gaussian or Mopac.

Click on New Job Using This Geometry > Open Editor.

Choose the Adjust tool (Arrow, 6th down) and click on one H atom. Hold down the shift key and click on the O atom, and then the remaining H atom. Record the bond angle: ________ Å (literature, 103.9 °).

Choose Tools > Z-matrix.

To the right of the bond angle, select "S" from the pull down menu, then type in the values for Start, Stop, and # Steps shown below. We will calculate the energy of the molecule every 0.5 ° between the limits we have set.

Click OK, then Close Editor. Click the blue continue arrow. Choose the same engine used above.

Choose/Type in the following:

Job Name: H2OScan

Calculation: Coordinate Scan

Theory: PM3

Basis Set: Basic: 3-21G (or accept default)

Charge: 0

Multiplicity: Singlet

Click the blue continue arrow. When the job is complete, open the file and scroll down to the Coordinate Scan data. Click on the magnifying glass in the title bar.

On the graph that appears, use your mouse and place the cursor on the lowest energy point. Look at the coordinate values above the graph.

III. Electron Density, Electrostatic Potentials, and Reactivity Prediction

Exercise 1 - Visualizing Different Bond Types

Build H_2 and perform a geometry optimization (Mopac) using the choices shown below:

Job Name: H2 PM3 Geom Opt
Calculation: Geometry Optimization
Theory: PM3
Charge: 0
Multiplicity: Singlet

Once the job is complete, view the molecule and click New Job Using This Geometry, click the blue "continue" arrow, choose Mopac, the type in/Choose the following:

Job Name: H2 PM3 MO
Calculation: Molecular orbitals
Theory: PM3
Charge: 0
Multiplicity: Singlet

Click on the blue "continue" arrow. You should now see your job listed.

Once the job is complete, open the file, scroll down to the Molecular Orbitals table, and click on the magnifying glass next to Electron Density. (depending on your computer's security, you may have to do this twice).

The WebMO default value for the electron density surface is 0.0030 $e^- Å^{-3}$. Adjust this value to 0.01 $e^- Å^{-3}$ by clicking on the Preferences box in the MOViewer window (7th across top, to the right of the binoculars.) In the "Iso. value (ED)" box, replace 0.0030 with 0.01, then click OK.

You should now see a gray blob. You can zoom in/out using a Shift/Click/Drag with your mouse. To see the atomic positions inside the surface, reopen the Preferences box and use the slider bar to adjust the Opacity to ~66%. Click OK. Rotate the displayed electron density (click and drag), and describe the distribution of electron density relative to the atomic positions. <u>Does the electron density distribution make sense? Why or why not?</u>

Click on the magnifying glass next to Electrostatic Potential. You will need to change the "Iso. Value (ED)" to 0.01 and adjust the opacity, as above. The blue color represents relative (+) charge, while red represents (-). <u>Does the charge distribution make sense</u>?

Build HF and perform a geometry optimization as shown above for H_2.

Follow the above steps to calculate the molecular orbitals.

As before, scroll down to the Molecular Orbitals table and view the Electron Density. Change the "Iso. Value (ED) to 0.01 and adjust the opacity. Describe the distribution of electron density relative to the atomic positions. <u>Does the electron density distribution make sense? Why or why not?</u>

Now look at the Electrostatic Potential and make the necessary changes in the Preferences box, as before. <u>Does the charge distribution make sense</u>?

Build LiH and repeat the above procedures.

As above, change the settings in the Preferences box, view and rotate the displayed electron density (click and drag), and describe the distribution of electron density relative to the atomic positions. Does the electron density distribution make sense? Why or why not?

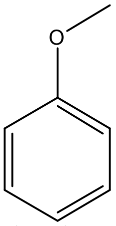
Look at the Electrostatic Potential, making the necessary changes in the Preferences box. Does the charge distribution make sense?

Compare/contrast the various surfaces for H_2, HF, and LiH. Are they what you expected?

Exercise 2 - Electrophilic Aromatic Substitution

The electronic nature of substituents on aromatic rings will govern the site of attack of incoming, electrophilic reagents. In this exercise we will build some simple molecules and also investigate the differences between semiempirical and DFT results.

A. Methoxybenzene

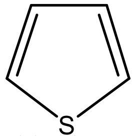

methoxybenzene

Build a molecule of methoxybenzene and clean up the structure. Perform a geometry optimization using Mopac > PM3, then calculate the molecular orbitals using Mopac > PM3.

View the Electrophilic (HOMO) Frontier Density. Choose View > Opacity > Transparent so you can see the atoms. Electrophilic attack will occur at those positions in the rings that are more yellow/green/blue. Attack will NOT occur at the ring carbon where the methoxy group is attached.

What position(s) on the ring will electrophilic attack occur?

B. Thiophene


thiophene

Build a molecule of thiophene and clean up the structure. Perform a geometry optimization using Mopac > PM3, then calculate the molecular orbitals using Mopac > PM3.

View the Electrophilic (HOMO) Frontier Density. Choose View > Opacity > Transparent so you can see the atoms. Attack will NOT occur at the sulfur.

What position(s) on the ring will electrophilic attack occur?

Repeat the experiment with thiophene, but use Gaussian > DFT > B3LYP/6-31G(d) for both the geometry optimization and molecular orbital calculation. View the Electrophilic (HOMO) Frontier Density. Where will attack occur? Is this different than the PM3 result above? Which result do you think is correct?

IV. Modeling in Solution

Exercise 1 - Determine the Enthalpy of Vaporization of Water

Build a molecule of H_2O.

Perform a geometry optimization using PM3 (Job Name: H2OGas) and record $\Delta_f H$ = _______________ kcal mol^{-1} (-57.796 kcal mol^{-1} literature).

Click on "New Job Using This Geometry". Click the blue "continue" arrow, choose Mopac, and Type in/Choose the following:

Job name: H2OLiq
Calculation: Geometry Optimization
Theory: PM3
Charge: 0
Multiplicity: Singlet

Click the Advanced tab. In the Solvent pull-down menu, choose Water. Click the blue "continue" arrow. You should see your job listed.

Record $\Delta_f H$ = _______________ kcal mol$_{-1}$ (-68.315 kcal mol^{-1} literature).

The difference between the two enthalpies of formation is the enthalpy of vaporization $\Delta_{vap}H$ = _______________ kcal mol$_{-1}$ (10.519 kcal mol^{-1} literature).

Exercise 2 - Determine the Frequency Shift for C=O for Formaldehyde Dissolved in Acetonitrile

Build a molecule of CH_2O and choose Clean-Up > Comprehensive – Mechanics.

Perform a geometry optimization using PM3 (Job Name: CH2Ogas).

Click on "New Job Using This Geometry". Click the blue "continue" arrow, choose Mopac, and Type in/Choose the following:

Job name: CH2OGasPM3
Calculation: Vibrational Frequencies
Theory: PM3
Charge: 0
Multiplicity: Singlet

Once the calculation is complete, scroll to Vibrational Modes and click on the filmstrip next to each frequency to animate that frequency. Identify the frequency for the C=O stretch and record it here: _______________ cm$_{-1}$ (literature 1746.07 cm^{-1}).

Click on "New Job Using This Geometry". Click the blue "continue" arrow, choose Mopac, and Type in/Choose the following:

Job name: CH2OLiqPM3
Calculation: Vibrational Frequencies
Theory: PM3
Charge: 0
Multiplicity: Single

Click the Advanced tab. In the Solvent pull-down menu, choose Acetonitrile. Click the blue "continue" arrow. You should see your job listed.

Follow the instructions above, find the frequency for the C=O stretch, and record it here: _______________ cm^{-1} (literature 1723 cm^{-1}).

The difference between these frequencies is the effect on the vibrational frequency as a result of the solvation process. $\Delta\nu$ = _______________ cm_{-1} (literature 23 cm^{-1}).

V. Spectroscopy and Thermodynamics

Exercise 1 - Method Dependence and Scaling for the Infrared Spectrum of Formaldehyde

Build a molecule of formaldehyde. Use Clean-Up > Comprehensive – Mechanics.

Choose Mopac as the computational engine. Type in/Choose the following:

Job Name: CH2O AM1 Geom Opt
Calculation: Geometry Optimization
Theory: AM1
Charge: 0
Multiplicity: Singlet

Click on the blue "continue" arrow. You should now see your job listed. When the calculation is finished, click on New Job Using This Geometry, and Type in/Choose the following:

Job Name: CH2O AM1 IR
Calculation: Vibrational Frequencies
Theory: AM1
Charge: 0
Multiplicity: Singlet

Click on the blue "continue" arrow. You should now see your job listed. When the calculation is finished, open the file and scroll down to the Vibrational Modes window.

<u>How many transitions are shown (count the number of frequencies)?</u> _____ <u>Is this the number expected?</u> _____

Click on the filmstrip next to one of the frequencies and observe the corresponding vibrational motion. Try to identify the type of motion for each transition. (The molecule can be rotated if needed). <u>In the table on the next page, record the frequencies and type of motion for each</u>.

Repeat the process described above, but use "PM3" in place of "AM1". <u>Observe the vibrational motions, and record the frequency data in the appropriate column on the next page</u>.

Start a New Job, and build a molecule of formaldehyde. Clean up the structure by selecting Clean-Up > Comprehensive – Mechanics.

Choose Gaussian or GAMESS as the computational engine. Type in/Choose the following:

Job Name: CH2O DFT Geom Opt
Calculation: Geometry Optimization
Theory: DFT
DFT Functional: B3LYP
Basis Set: 6-31G(d)
Charge: 0
Multiplicity: Singlet

Click on the blue “continue” arrow. You should now see your job listed. When the calculation is finished, click on New Job Using This Geometry, and Type in/Choose the following:

Job Name: CH2O DFT IR
Calculation: Vibrational Frequencies
Theory: DFT
DFT Functional: B3LYP
Basis Set: 6-31G(d)
Charge: 0
Multiplicity: Singlet

Click on the blue “continue” arrow. You should now see your job listed. When the calculation is finished, open the file and scroll down to the Vibrational Modes window.

As before, click on the filmstrip next to one of the frequencies and observe the corresponding vibrational motion. In the table on the below, record the frequencies.

Which method seems to give the best results? ____________

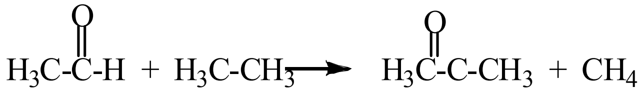
In the “View Job” window, click on Raw Output and investigate the contents of the file.

Due to the approximations implicit in these calculations, calculated vibrational frequencies are often higher than the experimental values. For better comparison with experimental results, the calculated frequencies are often multiplied by a scaling factor (fudge factor!). The scaling factors are listed below. <u>Perform the corrections and list the new results in the appropriate columns. Do the scaled values give a better comparison with the experimental values</u>?

Use the scaling factors (AM1 = 0.9532; PM3 = 0.9761; B3LYP/6-31G(d) = 0.9614)

Motion	**AM1**	**Scaled AM1**	**PM3**	**Scaled PM3**	**B3LYP/ 6-31G(d)**	**Experimental values (cm^{-1})**
						2843
						2782
						1746
						1500
						1249
						1167

Exercise 2 - $\Delta_r H$ for an Isodesmic Reaction:



$H_3C\text{-}\overset{\overset{O}{\|}}{C}\text{-}H + H_3C\text{-}CH_3 \longrightarrow H_3C\text{-}\overset{\overset{O}{\|}}{C}\text{-}C H_3 + CH_4$

Acetaldehyde Ethane Acetone Methane

An isodesmic reaction is one in which the total number of each type of chemical bond is the same in both reactants and products. Because of this equality in bond type, results of calculations using such a reaction should benefit from cancellation of errors.

Build each of the molecules shown above, and perform a geometry optimization using: (1) Mopac/AM1, (2) Mopac/PM3, (3) Gaussian with HF/6-31G(d) and (4) Gaussian with DFT B3LYP/6-31G(d).

For AM1 and PM3 methods, you will see the Heat of Formation ($\Delta_f H$) value listed in the Calculated Quantities window. To find the $\Delta_r H$ value, take the sum of the product $\Delta_f H$ values, and subtract the sum of the reactant $\Delta_f H$ values:

$$\Delta_r H = \sum \Delta_f H(prod) - \sum \Delta_f H(react)$$

The HF and DFT results are given in units of hartrees and must be converted. For the HF/6-31G(d) you will see the RHF Energy listed in the Calculated Quantities window. For the B3LYP/6-31G(d) values, you will see the R-B3LYP energy listed in the Calculated Quantities window. To find $\Delta_r H$ and convert the energy units from hartrees to kcal mol^{-1}, use:

$$\Delta_r H = \left[\sum H(prod) - \sum H(react)\right](627.51\, kcal\, mol^{-1} / h)$$

Place your results in the table below and compare with the experimental value.

AM1	**PM3**	**HF/6-31G(d)**	**B3LYP/6-31G(d)**	**Experimental (kcal mol^{-1})**
				-9.9 ± 0.3