# Lab #3: Choice of Theoretical Method

These directions assume the user is familiar with the WebMO interface and can build molecules, set up calculations, etc.

Exercise 1 - Determine the Proton Affinity for Pyridine

Using AM1

Build a molecule of C_5H_5N. Clean up the structure by selecting Clean-Up > Comprehensive – Mechanics.

Choose Mopac as the computational engine. Type in/Choose the following: pyridine
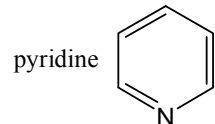
       Job Name: C5H5NAM1

       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 the filename to open the View Job window. Scroll down and record the Heat of Formation value here: _____ kcal mol^{-1}.

Click on New Job Using This Geometry, click Open Editor, and add an H atom to the N atom.

Choose the 'Adjust' tool (Arrow 6th down on left) and click on the H atom you just added. With this H atom highlighted, choose 'Adjust' on the pull-down menu and select 'Charge'. Type in +1, click Apply followed by OK.

Close the Editor, click the blue continue arrow, and Type in/Choose the following:

       Job Name: C5H6N(+1)AM1

       Calculation: Geometry Optimization

       Theory: AM1

       Charge: +1

       Multiplicity: Singlet

Click on the blue continue arrow. You should now see your job listed. When the calculation is finished, click on the filename to open the View Job window. Scroll down and record the Heat of Formation value here: _____ kcal mol^{-1}.

Start a New Job, Open the Editor, Click on the Periodic Table, Select H, and click one in the Editor screen. A white H atom should appear. Click the 'Adjust' tool (Arrow, 6th down on left), click on the H atom to select it. Click on the 'Adjust' pull-down menu, select Charge, and type in +1. Click Apply, followed by OK.

Close the Editor, click the blue continue arrow, and Type in/Choose the following:

       Job Name: H(+1)AM1

       Calculation: Geometry Optimization

       Theory: AM1

       Charge: +1

       Multiplicity: Singlet

Click on the blue "continue" arrow. You should now see your job listed. When the calculation is finished, click on the filename to open the View Job window. Scroll down and record the Heat of Formation value here: _____ kcal mol^{-1}.

Calculate the $\Delta_r H$ = PA for: $C_5H_5N + H^+ \rightarrow C_5H_5NH^+$

Using $\Delta_r H = \Delta_f H(C_5H_5NH^+) - [\Delta_f H(C_5H_5N) + \Delta_f H(H^+)] =$ _____ kcal mol^{-1}.
The literature value is -219.2 ± 1.7 kcal mol^{-1}. Calculate the percent difference = _____.

Using PM3
Build a molecule of C_5H_5N. Clean up the structure as before.
Choose Mopac as the computational engine. Type in/Choose the following:
      Job Name: C5H5NPM3
      Calculation: Geometry Optimization
      Theory: PM3
      Charge: 0
      Multiplicity: Singlet
Click on the blue "continue" arrow. You should now see your job listed. When the calculation
      is finished, click on the filename to open the View Job window. Scroll down and record
      the Heat of Formation value here: _____ kcal mol^{-1}.
Click on New Job Using This Geometry, click Open Editor, and add an H atom to the N atom.
Choose the 'Adjust' tool (Arrow 6th down on left) and click on the H atom you just added. With
      this H atom highlighted, choose 'Adjust' on the pull-down menu and select 'Charge'.
      Type in +1, click Apply followed by OK.
Close the Editor, click the blue continue arrow, and Type in/Choose the following:
      Job Name: C5H6N(+1)PM3
      Calculation: Geometry Optimization
      Theory: PM3
      Charge: +1
      Multiplicity: Singlet
Click on the blue "continue" arrow. You should now see your job listed. When the calculation
      is finished, click on the filename to open the View Job window. Scroll down and record
      the Heat of Formation value here: _____ kcal mol^{-1}.
Start a New Job, Open the Editor, Click on the Periodic Table, Select H, and click one in the
      Editor screen. A white H atom should appear. Click the "Adjust" tool (Arrow, 6th down
      on left), click on the H atom to select it. Click on the "Adjust" pull-down menu, select
      Charge, and type in +1. Click Apply, followed by OK.
Close the Editor, click the blue continue arrow, and Type in/Choose the following:
      Job Name: H(+1)PM3
      Calculation: Geometry Optimization
      Theory: PM3
      Charge: +1
      Multiplicity: Singlet
Click on the blue "continue" arrow. You should now see your job listed. When the calculation
      is finished, click on the filename to open the View Job window. Scroll down and record
      the Heat of Formation value here: _____ kcal mol^{-1}.
Calculate the $\Delta_r H = PA$ for: $C_5H_5N + H^+ \rightarrow C_5H_5NH^+$
Using $\Delta_r H = \Delta_f H(C_5H_5NH^+) - [\Delta_f H(C_5H_5N) + \Delta_f H(H^+)] =$ _____ kcal mol^{-1}.
Calculate the percent difference from the literature value given above = _____.

Using B3LYP/6-31G(d)
NOTE: The calculations in this exercise can each take up to 30 minutes to complete.
Build a molecule of C_5H_5N. Clean up the structure as before.
Choose Gaussian (or GAMESS) as the computational engine. Type in/Choose the following:
      Job Name: C5H5NDFT
      Calculation: Geometry Optimization
      Theory: DFT
      DFT Functional: B3LYP
      Basis Set: Routine 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 the filename to open the View Job window. Scroll down and record
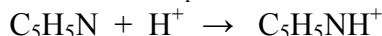   the R-B3LYP Energy value here: _____ h. (Note: Units are hartrees)
Click on New Job Using This Geometry, click Open Editor, and add an H atom to the N atom.
Choose the 'Adjust' tool (Arrow 6th down on left) and click on the H atom you just added. With
      this H atom highlighted, choose 'Adjust' on the pull-down menu and select 'Charge'.
      Type in +1, click 'Apply' followed by 'OK'.
Close the Editor, click the blue continue arrow, and Type in/Choose the following:
      Job Name: C5H6N(+1)DFT
      Calculation: Geometry Optimization
      Theory: DFT
      DFT Functional: B3LYP
      Basis Set: 6-31G(d)
      Charge: +1
      Multiplicity: Singlet
Click on the blue "continue" arrow. You should now see your job listed. When the calculation
      is finished, click on the filename to open the View Job window. Scroll down and record
      the R-B3LYP Energy value here: _____ h.
Given $H(H^+) = 1.481$ kcal mol^{-1}, calculate the $\Delta_rH = $ PA for:
$$C_5H_5N + H^+ \rightarrow C_5H_5NH^+$$
Using $\Delta_rH = [H(C_5H_5NH^+) - H(C_5H_5N)](627.51$ kcal mol^{-1}/h$) + H(H^+)] = $ _____ kcal mol^{-1}.
Calculate the percent difference from the literature value given above = _____.
Compare the results for the AM1, PM3 and B3LYP/6-31G(d) calculations. Look at the 'Time'
      taken for the DFT calculations in the Job Manager window. Was the additional accuracy
      worth the added expense?

Exercise 2 - 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.
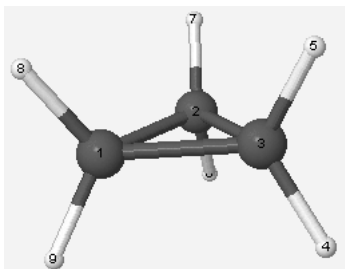
Click the blue "continue" arrow in the lower right side of the Build Molecule window.

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	B3LYP/6-31G(d)	B3LYP 6-311+G(d,p)	Experimental
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°
Calc. time				

Repeat the entire process, but use the following:

        Job Name: C3H6 DFT
        Calculation: Geometry Optimization
        Theory: B3LYP
        Basis Set: Routine 6-31G(d)
        Charge: 0
        Multiplicity: Singlet

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

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

Which basis set gives the best bond angles? _____

Look at the three calculation times. Approximately how many times longer did the calculation take to run using B3LYP/6-31G(D) vs. HF/STO-3G? _____ Approximately how many times longer did the calculation take to run using B3LYP/6-311+G(d,p) vs. HF/STO-3G? _____ Is it worth the extra time? _____

Exercise 3 - Bond Length of the H-F Molecule

In this exercise you will build H-F and optimize the geometry using Hartree-Fock, Density Functional Theory (B3LYP) or Møller Plesset 4 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	HF	B3LYP	MP 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 B3LYP and the 3-21G, 6-31G(d), and 6-311+G(d,p) basis sets. Record the bond length values in the table.

Repeat the above process using Møller 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.

Which basis set and method gave the result closest to the experimental value? _____

**Exercise 4 - Geometry Optimization of Malonaldehyde**

In this exercise you will try several methods to see which is required to give reasonable structural results for the malonaldehyde molecule, pictured below. Experimental bond lengths and angles are listed in the Table below. **NOTE – Your atom numbers may be different!!**

NOTE: The calculations in this exercise can each take up to 30 minutes to complete.

Try using each of the following methods to do your calculations. Record the results in the Table.
1. MOPAC > PM3
2. Gaussian > HF/6-31G(d)
3. Gaussian > HF/6-311+G(d,p)
4. Gaussian > MP2/6-311+G(d,p)
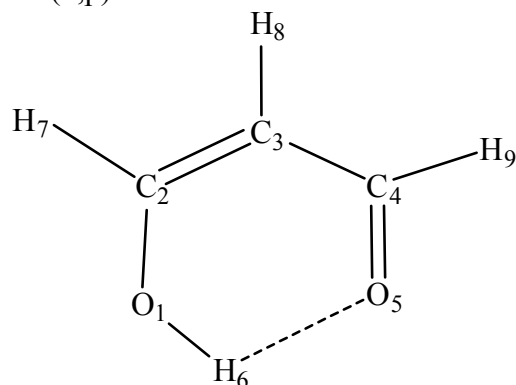
Parameter	PM3	B3LYP/6-311+G(d,p)	MP2/6-311+G(d,p)	Experimental
r(O1-H6)				0.969
r(O1-C2)				1.32

r(C4-O5)				**1.234**
r(O5-H6)				**1.68**
r(C3-H8)				**1.091**
∠(H6-O1-C2)				**106.3**
∠(C2-C3-C4)				**119.4**
∠(O1-C2-C3)				**124.5**
∠(C3-C4-O5)				**123.0**
Calc. time				

About how many times longer did the MP2 calculation take than the PM3? _____ Do the
   results justify the added time? _____
Which method was better overall the MP2 or B3LYP? _____