**Choice of Theoretical Method**

Students will be able to:

1. Compare computational results (energies and structures) for different combinations of theoretical method and basis set.
2. Describe the tradeoff between computational “expense” and accuracy of computational results.

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 C5H5N. Clean up the structure with the paintbrush.



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

 Job Name: C5H5N AM1

 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 and add an H atom to the N atom. Right click on the H atom and change the charge to +1. Click Apply followed by OK.

Click the blue continue arrow (you may get a window that says *“Molecule is nearly (but not exactly) symmetric. Continue without symmetrization?* Click OK), 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. Draw an H atom. Set its charge to +1. 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 proton affinity (ΔH) for: C5H5N + H+ → C5H5NH+

Δ*H* = [ΔHf(C5H5NH+] − [ΔHf(C5H5N) + ΔHf(H+)] = \_\_\_\_\_\_\_\_\_\_ kcal mol-1. The literature value is -219.2 ± 1.7 kcal mol-1. Calculate the percent difference = \_\_\_\_\_\_\_\_\_\_.

*Using PM3*

Repeat the previous three calculations using PM3 instead of AM1. You may start with the molecules you built for the AM1 calculations. Open the job by clicking on the job name from Job Manager. Click on New Job Using This Geometry, then click on the blue continue arrow.

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

Job Name: C5H5N PM3

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.

Record the Heat of Formation value for pyridine here: \_\_\_\_\_\_\_\_\_\_ kcal mol-1.

Record the Heat of Formation value for pyridinium ion here: \_\_\_\_\_\_\_\_\_\_ kcal mol-1.

Record the Heat of Formation value for hydrogen ion here: \_\_\_\_\_\_\_\_\_\_ kcal mol-1.

Calculate the proton affinity (ΔH) for: C5H5N + H+ → C5H5NH+

Δ*H* = [ΔHf(C5H5NH+] − [ΔHf(C5H5N) + ΔHf(H+)] = \_\_\_\_\_\_\_\_\_\_ kcal mol-1.  The literature value is -219.2 ± 1.7 kcal mol-1. Calculate the percent difference = \_\_\_\_\_\_\_\_\_\_.

*Using B3LYP/6-31G(d)*

Repeat the three calculations using B3LYP/6-31G(d). Choose Gaussian (or GAMESS) as the computational engine. Type in/Choose the following:

Job Name: C5H5N DFT

Calculation: Geometry Optimization

Theory: DFT

DFT Functional: B3LYP

Basis Set: Routine 6-31G(d)

Charge: 0

Multiplicity: Singlet

Record the RB3LYP Energy value for pyridine here: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ h. (Note: Units are hartrees.)

Record the RB3LYP Energy value for pyridinium ion here: \_\_\_\_\_\_\_\_\_\_ h.

Record the RB3LYP Energy value for hydrogen ion here: \_\_\_\_\_\_\_\_\_\_ h.

Calculate the proton affinity (ΔH) for: C5H5N + H+ → C5H5NH+

Δ*H* = [ΔHf(C5H5NH+] − [ΔHf(C5H5N) + ΔHf(H+)] = \_\_\_\_\_\_\_\_\_\_ kcal mol-1.  The literature value is -219.2 ± 1.7 kcal mol-1. Calculate the percent difference = \_\_\_\_\_\_\_\_\_\_.

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 (C3H6) by making a triangle of C atoms and clicking the paintbrush to clean up.



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. 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 name (C3H6 STO-3G) to open the View Job window. Record the bond lengths and angles in the table below. Record the calculation time in the table.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **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 calculation but use the following:

Job Name: C3H6 DFT Routine

Calculation: Geometry Optimization

Theory: B3LYP

Basis Set: Routine 6-31G(d)

Charge: 0

Multiplicity: Singlet

Record the bond lengths and angles in the table.

Repeat the calculation again, but use 6-311+G(d,p) (Accurate) 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? Explain.

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.  Clean up with the paintbrush. 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. 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 Malondialdehyde**

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

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Try using each of the following methods to do your calculations. Record the results in the Table.

1. MOPAC > PM3
2. Gaussian > HF/6-311+G(d,p)
3. Gaussian > B3LYP/6-311+G(d,p)

4. Gaussian > MP2/6-311+G(d,p)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Parameter** | **PM3** | **HF****6-311+G(d,p)** | **B3LYP****6-311+G(d,p)** | **MP2****6-311+G(d,p)** | **Experimental** |
| *r*(O1-H6)  | 0.968 |  |  |  | **0.969** |
| *r*(O1-C2)  | 1.336 |  |  |  | **1.32** |
| *r*(C4-O5)  | 1.225 |  |  |  | **1.234** |
| *r*(O5-H6)  | 1.826 |  |  |  | **1.68** |
| *r*(C3-H8)  | 1.093 |  |  |  | **1.091** |
| (H6-O1-C2)  | 109.278 |  |  |  | **106.3** |
| (C2-C3-C4)  | 121.788 |  |  |  | **119.4** |
| (O1-C2-C3)  | 124.798 |  |  |  | **124.5** |
| (C3-C4-O5)  | 121.559 |  |  |  | **123.0** |
| Calc. time  | 0.1 sec |  |  |  |   |

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?