

## Lab #1: Introductory WebMO Exercises

These directions assume no prior knowledge of the WebMO interface and provide detailed, click by click instructions on building molecules and setting up calculations.

→ Use your provided login credentials to login to WebMO

### Exercise 1 - Study of H-X-H Bond Angles

#### Structure of $CH_4$

Click “New Job”, then “Open Editor”. A small window opens where you build molecules.

Click on the Periodic Table icon (5<sup>th</sup> down the left side). Choose “C” by clicking on it.

Click once in the center of the workspace. A gray carbon atom appears. (If you click too many times and have extra atoms, choose Edit > Undo).

Choose Clean-Up > Comprehensive – Mechanics. You should now have methane.

Experiment with the Rotate, Translate, and Zoom tools (Top 3 icons on left side).

Click Close Editor in the main WebMO window. Methane now appears in the Build Molecule window. This structure contains idealized bond lengths and angles. A more accurate structure can be found by carrying out an energy minimization using molecular mechanics, semiempirical methods, or *ab initio* calculations. To reduce the time required for the calculations and to obtain reasonable results, the semi-empirical method PM3 will be used. This method is available in most molecular modeling programs.

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

Choose Mopac as the computational engine.

Click the blue “continue” arrow.

Type in/Choose the following:

Job Name: CH4 PM3 Geom Opt

Calculation: Geometry Optimization

Theory: PM3

Charge: 0

Multiplicity: Singlet

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

To kill or stop a job, you would click on the red “X” under Actions on the right side.

Click Refresh (every ~10 seconds) until you see that your job is Complete (under Status).

Click on the hyperlinked name (CH4 PM3 Geom Opt) to open the “View Job” window.

Choose the Select arrow (4<sup>th</sup> 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 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 \_\_\_\_\_ Å (1.091 Å literature). Check the other C-H bond lengths.

Click on one of the H atoms, then Shift and click the C atom, followed by another H atom. The bond angle is displayed just below the molecule. Record the value of the H-C-H bond angle \_\_\_\_\_ ° (109.4712 literature). Check the other H-C-H bond angles.

Scroll down and review the information under Calculated Quantities.

When finished, click the Job Manager link under Actions (to the left of the molecule display).

To delete files, click the box to the left of the desired file and choose Delete on the menu.

To continue on to the next exercise, choose New Job > Create New Job.

### *Structure of NH<sub>3</sub>*

Build NH<sub>3</sub> using the above procedure.

Use Job Name H3N PM3 Geom Opt, and perform the geometry optimization as before (PM3).

Record the value of the N-H bond length \_\_\_\_\_ Å (~0.999 Å, 1.012 Å literature).

Record the value of the H-N-H bond angle \_\_\_\_\_ ° (~107.8 °, 106.67 ° literature).

Scroll down and review the information under Calculated Quantities. Click on the magnifying glass next to the reported Dipole Moment, then rotate the molecule to see the vector.

Return to Job manager, and choose New Job > Create New Job.

### *Structure of H<sub>2</sub>O*

Build H<sub>2</sub>O using the above procedure.

Use Job Name H2O PM3 Geom Opt, and perform the geometry optimization as before (PM3).

Perform the PM3 geometry optimization as above.

Record the value of the O-H bond length \_\_\_\_\_ Å (~0.951 Å, 0.959 Å literature).

Record the value of the H-O-H bond angle \_\_\_\_\_ ° (~107.7 °, 103.9 ° literature).

Check out the Dipole Moment, as with NH<sub>3</sub> above.

Return to Job Manager.

1. What conclusion(s) can you make concerning the H-X-H bond angle and the number of unshared (lone) pairs of electrons around the central atom X?
2. What conclusions can you make concerning the size of the central atom X and the X-H bond length?

### **Exercise 2 - Study of the Molecular Orbitals in Ethene, CH<sub>2</sub>CH<sub>2</sub>**

Click “New Job”, then “Open Editor”.

Click on the Periodic Table icon (5<sup>th</sup> down the left side). Choose “C” by clicking on it.

Click once in the workspace. A gray carbon atom appears. Click on this atom and drag to one side and release. You should now have C-C. Click and Drag from the center of one C atom to the center of the other C atom to form the double bond.

Choose Clean-Up > Comprehensive – Mechanics. You should now have ethene.

Click Close Editor in the main WebMO window.

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

Choose Mopac as the computational engine.

Click on the blue “continue” arrow.

Use Job Name C2H4 PM3 Geom Opt, and perform the geometry optimization as before (PM3).

Once the job is complete, click on the hyperlinked name to open the “View Job” window.

Click the New Job Using This Geometry button, click the blue “continue” arrow, choose Mopac, and type in/Choose the following:

Job Name: C2H4 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, click on the hyperlinked name (CH<sub>4</sub> PM3 MO) to open the “View Job” window. If a ‘Warning-Security’ window pops up, click ‘Run’.

Scroll down to the Molecular Orbitals table. Using the energy values and occupancy as your judge, identify the HOMO and LUMO. View these orbitals by click on the magnifying glass icon. (Depending on your computer's security, you may have to repeat this process to view the orbital). The orbitals can be rotated by clicking and dragging in the viewer window. Were your choices correct? View some of the other orbitals. Note that all orbitals viewed appear as a tab in the MOViewer. Clicking on the tab brings that orbital back into the window. Close the viewer window and return to Job Manager.

### Exercise 3 - Study of Rotation Barrier Energy about Carbon-Carbon Bonds

Build  $C_2H_6$  using the above procedure. Be sure to do the Clean-Up as before.

Choose Tools > Z-matrix to open the Z-matrix Editor window. In this window, each atom is numbered. The corresponding number appears on the molecule sketch in the WebMO Editor window. Identify the two H atoms that form a dihedral angle (H-C-C-H) of  $\sim 180^\circ$  (or  $-180^\circ$ ). It may help to rotate the molecule. In the pull-down menu to the right of this listed dihedral angle, choose "S" (See below for H7 and H3):

Order	Atom	Na	Length	Opt	Nb	Angle	Opt	Nc	Dihedral Opt
1	C1								
2	C2	1	1.532	O					
3	H3	2	1.115	O	1	110.979	O		
4	H4	2	1.115	O	1	111.005	O	3	119.998
5	H5	2	1.115	O	1	110.994	O	3	-119.985
6	H6	1	1.115	O	2	110.996	O	3	-60.066
7	H7	1	1.115	O	2	110.999	O	3	179.919
8	H8	1	1.115	O	2	110.973	O	3	59.923

Scan: Start: -180, Stop: 180, # Steps: 72

As shown above, enter the Start (-180) and Stop (180) scan values, along with 72 steps, then click OK to close the Z-Matrix Editor window.

Click Close Editor, then click the blue "continue" arrow. Choose Mopac.

Use the following Job Options:

Job Name: C2H6 PM3 Angle

Calculation: Coordinate Scan

Theory: PM3

Charge: 0

Multiplicity: Singlet

Click the blue "continue" arrow. You should see the job in the queue.

When the job is complete, click on the linked name. Scroll down to the Coordinate Scan table and click on the magnifying glass on the table title bar.

A Coordinate Scan window opens showing the plot of Energy vs. dihedral angle.

Choose Options > Axes and in the Options window change the x-axis settings to Start (-180), Stop (180), and Interval (60). Click OK.

Does the graph make sense? Describe the relationship between the dihedral angle and energy.

View a movie of the dihedral angle rotation by scrolling to the Geometry Sequence box. Choose Loop in the pull down menu, then click the "film" in the upper right corner of the box.

You can use the controls to the left of the molecule to control things.