

Basic Molecular Modeling

Exploring Molecules Using WebMO



<http://www.webmo.net/>



WebMO is a web-based interface to computational chemistry software engines that allows simple molecule building (or download), job set-up and submission, and viewing of results.

WebMO Pro is a commercial add-on that also allows visualization of graphics-intensive surfaces (atomic and molecular orbitals, electron density maps, electrostatic potentials, etc.).

WebMO Enterprise enables usage on large computer clusters for many users. It allows WebMO to integrate with existing system-level queuing systems, authentication mechanisms, system accounts/storage, and user groups.

We will access WebMO Pro located at Earlham College in eastern Indiana. Go to the following URL: <http://bobsced.cluster.earlham.edu/cgi-bin/login.cgi>

Your instructor will provide login credentials for the above site.

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

Exercise 1 Study of H-X-H Bond Angles

Importing Molecular Structures

WebMO allows import of structure files in a variety of different formats, such as .mol files that can be produced in the freeware program, ACD/Chemsketch, which is available for download at <http://www.acdlabs.com/download/chemsketch/>. If you have the *methane.mol* file saved, upload with the following instructions. If not, proceed with Drawing the Structure of CH₄, below.

In the WebMO Job Manager window, click “New Job” to open the Build Molecule window.

Click “Import Molecule” at the bottom to open the Import Molecule window.

Choose MOL Format in the Format pull-down menu. Click the Generate Bonds box.

In the Select File area, Browse to the location of the file to be imported, then click Import Molecule. Close the Import Molecule window.

Continue with the ‡ step in the directions below:

Drawing the Structure of CH₄

Click “New Job”. The Build Molecule window will appear.

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

Click once in the center of the workspace. A gray carbon atom appears.

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

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

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 GO (The “GO” stands for **G**eometry **O**ptimization)

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 ~5 seconds) until you see that your job is Complete (under Status).

Click on the hyperlinked name (CH4 PM3) 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 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 continue on to the next exercise, choose New Job > Create New Job.

Structure of NH₃

Build NH₃ using the above procedure (or import your molecule in the proper file format).

Use Job Name H3N PM3 GO, 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.

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

Structure of H₂O

Build H₂O using the above procedure.

Use Job Name H2O PM3 GO, 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).

Return to Job Manager.

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?

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, CH₂CH₂

Click “New Job”.

Click on the Periodic Table icon (5th 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 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.

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

Once the job is complete, click the hyperlinked name (C2H4 PM3) 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 (CH4 PM3 MO) to open the “View Job” window.

Scroll down to the Molecular Orbitals table. Using the ‘occupancy’ values as your judge, identify both the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). View these orbitals by clicking on the magnifying glass icon. The orbitals can be rotated by clicking and dragging in the viewer window. If you hold down the Shift key while clicking and dragging, you can zoom in and out. The

HOMO is the π -orbital between the carbon atoms. The LUMO is the antibonding π^* orbital. View some of the other orbitals. Note that all orbitals viewed appear as a tab in the View Job window. Clicking on the tab brings that orbital back into the window. Close the viewer window and return to Job Manager.

To explore more about bonding and antibonding orbitals, see the Web site:

<http://winter.group.shef.ac.uk/orbitron/>

Scroll down to the 'N₂, Dinitrogen' section to observe formation of π and π^* type molecular orbitals.

Exercise 3 Study of the Rotation Barrier Energy about C-C Bond in Ethane

Build C₂H₆ 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 Build Molecule window. Identify the two H atoms that form a dihedral angle (H-C-C-H) of $\sim 180^\circ$ (or -180°). 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	0					
3	H3	2	1.115	0	1	110.979	0		
4	H4	2	1.115	0	1	111.005	0	3	119.998
5	H5	2	1.115	0	1	110.994	0	3	-119.985
6	H6	1	1.115	0	2	110.996	0	3	-60.066
7	H7	1	1.115	0	2	110.999	0	3	179.919
8	H8	1	1.115	0	2	110.973	0	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 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. In the View Job window, click on the Options tab (fourth one from left), then click on the Axes tab. In the Axes window change the x-axis settings to Start (-180), Stop (180), and Interval (60). Click OK.

Does the graph make sense? Describe in detail the relationship between the dihedral angle and energy you observe.

Exercise 4

Part A. Repeat Exercise #3 using 1,2-dichloroethane and 1,2-difluoroethane and compare the three results. Do the numbers obtained make sense?

Part B.

Build molecules that are of interest to you and your students, and use the above instructions to optimize the geometry, etc. To compare the calculated values of bond lengths and angles, dipole moments, etc. with experimental ones, visit the Computational Chemistry Comparison and Benchmark DataBase (CCCBDB) at: <http://cccbdb.nist.gov/>

In the left-hand window, click Experimental data

In the right-hand window under single molecule, click All Experimental Data for One Molecule, then type in the chemical formula. The database is limited to smaller, simple compounds.