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 (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).
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.
Choose "first available" in the select server pull-down menu. Click the blue "continue" arrow.
Type in/Choose the following:
      Job Name: CH4PM3
      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 (CH4PM3) 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 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 NH₃
Build NH_3 using the above procedure.
Use Job Name H3NPM3, 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 H_2O using the above procedure.
Use Job Name H2OPM3, 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", then "Open Editor".
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 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.
Choose "First available" in the select server pull-down menu. Click on the blue "continue" arrow.
Use Job Name C2H4PM3, and perform the geometry optimization as before (PM3).
Once the job is complete, click on the hyperlinked name (C2H4PM3) to open the "View Job" window.
Click the New Job Using This Geometry button, click the blue "continue" arrow, choose Mopac. and First available, and type in/Choose the following:

        Job Name: C2H4PM3Orb
        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 (CH4PM3Orb) to open the "View Job" window.
Scroll down to the Molecular Orbitals table. Using the energy values as your judge, identify

the HOMO and LUMO. View these orbitals by click on the magnifying glass icon. 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 ~180° (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):

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: C2H6PM3Angle
    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 you observe.
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.

Exercise 4 - Study of C-C Bond Lengths at the Semi-empirical Level of Theory
In this experiment we will investigate the trend of the C-C bond length in simple organic compounds
containing single, double, and triple bonds at the PM3 Semi-empirical Level of Theory.

Literature values:

Compound	Name	r_e/(Å)
$H_3C - CH_3$	Ethane	1.5351
$H_2C = CH_2$	Ethene (Ethylene)	1.339
$HC \equiv CH$	Ethyne (Acetylene)	1.203
C_6H_6	Benzene	1.397

Better results can be obtained by using higher levels of theory with larger basis.

Ethane H_3C-CH_3
Construction of H_3C-CH_3
Click **New Job**.
After the tool bar appears at the left of the "Build Molecule" window, click
  Open Editor. The "WEBMO Editor" window opens.
Click the **Build** icon (4th down).
Click in the workspace to place a C atom.
Click and drag from the C to form C-C with a single bond.
Click on **Clean-Up** / **Comprehensive-Mechanics**.
Click the **Rotate** icon (1st down) to be sure that the staggered structure is formed. If necessary,
  click **Clean-Up** / **Comprehensive-Mechanics** again.
Click the **Close Editor** button in the "Build Molecule" window.
Optimize H_3C-CH_3
Click the right blue arrow (**Continue**).
Choose Mopac as the desired "Computational Engine" and default "Server Name".
Click the right blue arrow (**Continue**).
Click **Job Options** and choose:
  C2H6xxx where x = your initials (for identification) for "Job Name".
  Geometry Optimization for "Calculation".
  PM3 for "Theory".
  Basic: 3-21G or default if asked for a "Basis Set".
  Leave "Charge" as **0** and "Multiplicity" as **Singlet**.
You may click the other tabs for advanced properties and to preview the input file.
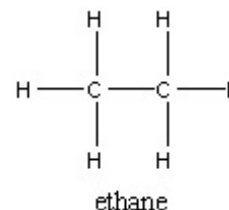Click the right blue arrow (**Continue**).
Your file will appear on the "WEBMO Job Manager" screen as either qued, running, or finished.
After a short period of time, click **Refresh** until the job is complete.
Measure Properties of H_3C-CH_3
Click the **View Job** icon for your job (magnifying glass). The "View Job" output screen will list
  various "Calculate Quantities" and the optimized model.
Click the **Select** icon (4th down).

Click on one of the C atoms and Shift/Click on the other C atom. Record the C-C bond length
_____ Å and compare to the literature value.

Click **Job Manager**.

Ethene H₂C=CH₂
Construction of H₂C=CH₂
Click **New Job** and **Open Editor**.
Click the **Build** icon (4ᵗʰ down).
Click in the workspace to place a C atom.
Click and drag from the C to form C-C with a single bond. Repeat the click/drag operation to
form C=C with a double bond.
Click on **Clean-Up** / **Comprehensive-Mechanics**.
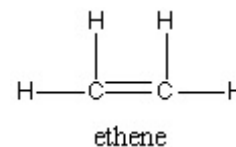Click the **Close Editor** button in the "Build Molecule" window.
Optimize H₂C=CH₂
Optimize by clicking the right blue arrow (**Continue**), choosing Mopac as the desired
"Computational Engine", clicking the right blue arrow (**Continue**) and choosing
C2H4xxx where x = your initials (for identification) for "Job Name", **Geometry**
Optimization for "Calculation", **PM3** for "Theory", **Basic: 3-21G** or default if asked for
a "Basis Set", and leaving "Charge" as **0** and "Multiplicity" as **Singlet**.
Click the right blue arrow (**Continue**).
Measure Properties of H₂C=CH₂
Click the **View Job** icon for your job.
Click the **Select** icon (4ᵗʰ down) and measure and record the C=C bond length _____ Å and
compare to the literature value.

Click **Job Manager**.

Ethyne HC≡CH
Construction of HC≡CH
Click **New Job** and **Open Editor**.
Click the **Build** icon (4ᵗʰ down).
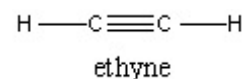Click in the workspace to place a C atom.
Click and drag from the C to form C-C with a single bond. Repeat the click/drag operation two
more times to form C≡C with a triple bond.
Click on **Clean-Up** / **Comprehensive-Mechanics**.
Click the **Close Editor** button in the "Build Molecule" window.
Optimize HC≡CH
Optimize by clicking the right blue arrow (**Continue**), choosing Mopac as the desired
"Computational Engine", clicking the right blue arrow (**Continue**) and choosing
C2H2xxx where x = your initials (for identification) for "Job Name", **Geometry**

Optimization for "Calculation", **PM3** for "Theory", **Basic: 3-21G** or default if asked for a "Basis Set", and leaving "Charge" as **0** and "Multiplicity" as **Singlet**.

Click the right blue arrow (**Continue**). Note that linear molecules are difficult for some lower level theories to handle and this calculation may fail.

Measure Properties of HC≡CH

Click the **View Job** icon for your job.

Click the **Select** icon (4ᵗʰ down) and measure and record the C≡C bond length _____ Å and compare to the literature value.

Click **Job Manager**.

Benzene C₆H₆

Construction of C₆H₆

Click **New Job** and **Open Editor**.

Click the **Build** icon (4ᵗʰ down).

Click in the workspace to place a C atom.

Click and drag from the C to form C-C with a single bond. Repeat the click/drag operation until you have generated a hexagon of single-bonded C atoms. The last operation is made by dragging onto the first C atom.

Construct three double bonds by click/drag between alternate sets of C atoms.

Click on **Clean-Up** / **Comprehensive-Mechanics**.

Click the **Close Editor** button in the "Build Molecule" window.

Optimize C₆H₆

Optimize by clicking the right blue arrow (**Continue**), choosing Mopac as the desired "Computational Engine", clicking the right blue arrow (**Continue**) and choosing **C6H6xxx** where x = your initials (for identification) for "Job Name", **Geometry Optimization** for "Calculation", **PM3** for "Theory", **Basic: 3-21G** or default if asked for a "Basis Set", and leaving "Charge" as **0** and "Multiplicity" as **Singlet**.

Click the right blue arrow (**Continue**).

Measure Properties of C₆H₆

Click the **View Job** icon for your job.

Click the **Select** icon (4ᵗʰ down) and measure and record the C-C and C=C bond lengths _____ and _____ Å and compare to the literature value.

Why does this representation for benzene better represent the bonding between the C atoms than the representation that uses alternating single and double bonds?