1 Introduction to Computational Chemistry

Start PCModel by clicking Start / Programs / PCModel.

Exercise 1 Study of H-X-H Bond Angles (suitable for general chemistry).

Structure of CH_4

Click the periodic table tool (15th down, PT). Be sure that the C atom is selected (1st column, 1st row) and click Exit.

Click the draw tool (3rd down, Draw) and click once in the workspace. (A small gray circle should appear.)

Click the add H atoms tool (6th down, H/AD). (Four H atoms should appear attached to a C atom and all atoms will be numbered if View / Labels / Atom Numbers is selected.)

The structure may be rotated by right clicking and dragging.

This structure contains idealized bond lengths and angles. A more accurate structure can be found by carrying out an energy minimization using molecular mechanics, semi-empirical methods, or *ab initio* calculations. PCModel has several different molecular mechanics methods available and the default MMX method will be used. PCModel also serves as a graphical interface to GAUSSIAN and to GAMESS which permit other levels of calculations.

Click File / Save.

Navigate to c:\pcmodel files (or any suitable folder) and Save as CH4MMX.pcm.

Click Compute / Minimize. (The calculations should be completed within a second or so.) The Stop Calculations window at the bottom right is "active" only during the running of a job and may be used to terminate a calculation–otherwise it may be ignored.

Click File / Save.

Click on the query tool (13th down, Query).

Click one of the H atoms, on the C atom, and in the workspace away from the molecule (the C-H bond length of ~1.113 Å appears). Record the value of the C-H bond length _____ Å (1.091 Å literature).

To clear the information, click the Update tool (5th down, Update).

Click on the query tool; click on a H atom, the C atom, and another H atom; and click in the workspace away from the molecule (the bond angle of ~109.5 ° appears). Record the value of the H-C-H bond angle _____° (109.4712 ° literature) and clear the information.

If GAUSSIAN or GAMESS is installed, the above experiment may be performed at various higher levels of theory (e.g., PM3 for semiempirical or B3LYP/6-31G(d) for density functional theory) for better accuracy.

Save.

Erase the workspace by clicking Edit / Erase or Close the program.

Structure of NH_3

Click the draw tool and click once in the workspace. (A small gray circle should appear.)

Click the periodic table tool and choose the N atom. Click on the gray circle in the workspace to change it to a N atom. Click exit on the periodic table.

Click the add H tool (three H atoms should appear attached to the N atom). Depending on the settings under View / Labels, the position of the unshared pair of electrons may be indicated by a number in the workspace.

Click File / Save.

Navigate to c:\pcmodel files (or any suitable folder).

Save as NH3MMX.pcm.

Perform the MMX geometry optimization as above.

Record the value of the N-H bond length _____ Å (1.012 Å literature).

Record the value of the H-N-H bond angle _____° (106.67 ° literature).

Save and Close.

Structure of H_2O

Build H_2O using the above procedure. Choose the O atom in the periodic table tool.

Save the file as H2OMMX.pcm.

Perform the MMX geometry optimization as above.

Record the value of the O-H bond length _____ Å (0.959 Å literature).

Record the value of the H-O-H bond angle _____° (103.9 ° literature).

Save and Close.

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?

Exercise 2 Study of Rotation Barrier Energy about Carbon-Carbon Bonds (suitable for organic chemistry).

Structure of Ethane, CH_3CH_3

Click the build tool (4th down, Build). (A CH_3-CH_3 molecule should appear in the workspace.)

Save as C2H6MMX.pcm.

Minimize the structure by clicking Compute / Minimize.

Save.

Click the select atom tool (1st down, Sel-Atm) and click a H atom, the connected C atom, the second C atom, and a H atom connected to the second C atom to define a dihedral angle.

Choose Compute / Dihedral Driver to open the dihedral driver window which indicates the four atoms chosen and the current angle of ±60 °, ±180 °, or ±300 °.

Enter -180, 180 and 10 in the boxes and click OK (a dialog box will open for saving the output structure–use C2H6MMXrot.pcm).

After a few seconds the calculation is finished and a plot of energy against the dihedral angle appears.

Record the greatest and least values of the energy and calculate the barrier energy for rotation of the CH_3 groups around a C-C bond _____ kcal mol^{-1} - _____ kcal mol^{-1} = _____ kcal mol^{-1} (2.9 kcal mol^{-1} literature). Record the dihedral angles for the minima _____°, _____°, _____°, and _____° and for the maxima _____°, _____°, and _____°.

Save and Close.

Structure of Ethene, CH_2CH_2

Click the build tool. Click the add H tool to remove the H atoms.

Click the add bond tool (7th down, Add_B) and click the center of the C-C single bond. The center will be indicated by a small × on the bond as the cursor gets close enough. (The bond will change to a double bond.)

Click the add H tool to add the proper number of H atoms.

Save as C2H4MMX.pcm.

Minimize and Save.

Define a H-C=C-H dihedral angle as above.

Run the dihedral driver as above using the range of 0 ° to 180 °. Save the output file as C2H4MMXrot.pcm.

Record the greatest and least values of the energy and calculate the barrier energy for rotation of the CH_2 groups around a C=C bond _____ kcal mol^{-1} - _____ kcal mol^{-1} = _____ kcal mol^{-1} (68 kcal mol^{-1} literature).

Does the maximum energy occur at 90°? _____ What happens above 127°? _____

Save and Close.

Exercise 3 Study of the Molecular Orbitals in Ethene, CH_2CH_2 (suitable for physical chemistry).

This exercise requires the program Orbdraw to display the molecular orbital and electron density output calculated by GAUSSIAN or GAMESS.

Open C2H4MMX.pcm and save As C2H4ORB.pcm.

Minimize and Save.

After creating and running the input file to GAUSSIAN or GAMESS, choose Compute / Orbitals to open an Orbdraw dialog window. Choose the respective output file.

Click View / Orbital and choose the various orbitals to view. These orbitals can be rotated by right clicking and dragging.

Depending on the program and level of theory used, the first two orbitals may be the 1s orbitals on the C atoms. The lowest molecular orbital is the σ bonding between the C atoms and usually the HOMO shows the π bonding between the C atoms and the LUMO shows the π* antibonding orbital.

Click View / Density and the full electron density plot will be generated.

Save and Close.

Exit PCModel.