1 Introduction to Computational Chemistry

Start GaussView by clicking Start / Programs / GaussView. The main control panel should show the Carbon Tetrahedral fragment as the Current Fragment and an empty active view window in which the molecule will be built.

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

Structure of CH_4

Click in view window. CH_4 appears.

Click the Clean icon (1st row, 24th across).

Rotate by left 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. 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.

Choose Calculate / Gaussian. Choose Optimization and defaults in the Job Type panel; Ground State, Semi-empirical, Default spin, PM3 and defaults in the Method panel; type methane in the Title panel; type location (or click the Check Point File button and browse to the desired location) and type the name for saving the checkpoint file as CH4PM3.chk and use defaults in the Link 0 panel; use defaults in the General, Guess, NBO and Solvation panels.

Click Submit. Save as CH4PM3.gjf in the same directory as the checkpoint file.

Click OK in the Run Gaussian window. (The calculations should be completed within a second or so.)

After the job is completed, click Yes to close the Gaussian Window and Yes to open a result file. Click the CH4PM3.chk file and click open. A new view window opens containing the optimized molecule.

Choose Results / Summary to observe a summary of the calculations.

Click on the Inquire icon (1st row, 9th across).

In the optimized view window, click on the C atom and on a H atom. The C-H bond length will appear near the bottom left of the window.

Record the value of the C-H bond length _____ Å (1.091 Å literature) / close by clicking “ok”.

Click in the blank area of the window away from the molecule to clear the choice.

Click on a H atom, the C atom, and another H atom. The H-C-H bond angle will appear near the bottom left of the window. Record the value of the H-C-H bond angle _____° (109.4712 ° literature) / close by clicking “ok”.

Close all windows except the main control panel.

Structure of NH_3

Click File / New / Create MolGroup to open a new View workspace. Click on the Element Fragment icon on the main control panel to activate the Current Fragment.

Click the Element Fragment icon (1st row, 1st across). Click the N icon in the periodic table in the Select Element window and choose the N tetravalent icon (5th across bottom). The Select Element window closes and the N tetravalent fragment appears in the Current Fragment area.

Click in the workspace. NH_3 appears.

Click the Clean icon.

Choose Calculate / Gaussian. Choose Job: Optimization and defaults; Method: Ground State, Semi-empirical, PM3 and defaults; Title: ammonia; Link 0: NH3PM3.chk and defaults; defaults in the remaining panels.

Click Submit. Save as NH3PM3.gjf and click OK.

After the job is completed, click Yes twice. Open the NH3PM3.chk file.

Choose Results / Summary to observe a summary of the calculations.

Use Inquire icon to determine the N-H bond length and the H-N-H bond angle.

Record the value of the N-H bond length _____ Å (1.012 Å literature) and the value of the H-N-H bond angle _____° (106.67 ° literature).

Close all windows except the main control panel.

Structure of H_2O

Build H_2O using the above procedure. Use the tetravalent O (3rd across) in the periodic table.

Save the file as H2OPM3.chk.

Perform the PM3 geometry optimization as above. Save as H2OPM3.gjf and use the word water as the title.

Using the Inquire icon, record the value of the O-H bond length _____ Å (0.959 Å literature) and the H-O-H bond angle _____° (103.9 ° literature).

Close all windows except the main control panel.

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

Open GaussView or click File / New / Create MolGroup and click on the Element Fragment icon to activate the Current Fragment. Be sure that the C tetravalent atom is the Current Fragment.

Click once in the View workspace. CH_4 appears. Click on one of the H atoms. CH_3CH_3 in the staggered form appears. Click the Clean icon.

Click the Inquire icon and click a H atom, the attached C atom, the other C atom, and the H atom that is attached to the second C atom and forms a dihedral angle of ±180 ° (the last H atom lines in the plane formed by the H-C-C atoms) as seen at the bottom left of the window.

Click the Redundant Coordinate Editor icon (2^{nd} row, 2^{nd} across) to open the editor dialog window.

Click the Create a New Coordinate icon (1^{st} across the top).

In the Coordinate window, for the top drop down window at the bottom choose Dihedral and click on the same H-C-C-H atoms as before. Atoms numbers will replace the ? Entries in the small windows. Choose Scan Coordinate in the lower drop down window at the bottom and type 37 for the number of steps and 10 for the degree entry.

In the Set Value window, choose Increments by 10 with a minimum of -180 and a maximum of 180. Click OK.

Click Calculate / Gaussian. Job: Scan, Relaxed (Redundant Coord); Method: Semi-empirical, PM3; Title: ethane rotation; Link 0: C2H6PM3.chk; defaults for other tabs.

Click Submit. Save as C2H6PM3.gjf. Click OK. The calculation will take a few minutes to run. Click Yes twice and open the C2H6PM3.chk file.

Choose Results / Summary.

Rotate the molecule to look along the C-C bond. Click the green button at the top of the View window and the various conformers will be animated. Clicking the red × will stop the animation. Each individual conformer may be observed by clicking the up/down arrows at the top. Values of the dihedral angles may be determined by use of the Inquire icon as above.

Record the value of energy for conformer #12 _____ Eh and #6 _____ Eh. Subtract these values and multiply by (627.5095 kcal mol^{-1}/1 Eh) to obtain the barrier energy for rotation of the CH_3 around a C-C bond _____ kcal mol^{-1} (2.9 kcal mol^{-1} literature). All of the energy values are found in a summary at the end of the C2H6PM3.log file which can be opened using a text editor such as WordPad.

Close all windows except the main control panel.

Structure of Ethene, CH_2CH_2

Click File / New / Create MolGroup and click on the Element Fragment icon to activate the Current Fragment. Click the Element Fragment icon, select C and click the C triavalent atom (4^{th} icon) as the Current Fragment.

Click in the View workspace. Click again at the end of the C= bond. CH_2=CH_2 appears. Click the Clean icon.

Click the Redundant Coordinate Editor icon. Click the Create a New Coordinate icon. In the Coordinate window, choose Dihedral and click on a H atom, the attached C atom, the other C atom, and the H atom that is attached to the second C atom and is *cis* to the first H atom. Choose Scan Coordinate in the lower drop down

window at the bottom and type 11 for the number of steps and 10 for the degree entry. In the Set Value window, choose Increments by 10 with a minimum of 0 and a maximum of 110. Click OK.

Click Calculate / Gaussian. Choose the same settings as above. Use ethene rotation as the title and save the file as C2H4PM3.chk. Click Submit and save as C2H4PM3.gjf.

After the calculations are completed, chose Results / Summary.

View the molecule to look along the C=C bond. Record the minimum energy for conformer #1 _____ Eh and the energy at 90 ° (confomrer #9) _____ Eh. Calculate the barrier energy for rotation of the CH_2 groups around a C=C bond _____ kcal mol^{-1} (68 kcal mol^{-1} literature).

Does the maximum energy occur at 90°? _____

Close all windows except the main control panel.

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

Open GaussView or click File / New / Create MolGroup and click on the Element Fragment icon to activate the Current Fragment. Click the Element Fragment icon, select C and click the C triavalent atom as the Current Fragment.

Construct $CH_2=CH_2$. Click the Clean icon.

Click Calculate / Gaussian. Job: Optimization and defaults; Method: Semi-empirical, PM3, and defaults; Title: ethene orbitals; Link 0: C2H4ORB.chk; Guess: click Save Orbitals to checkpoint file; defaults for others. Click Submit and save as C2H4ORB.gjf.

Open the resulting .chk file.

Click the Molecular Orbital editor icon (2^{nd} row, 6^{th} across) to open the MOs dialog window.

Click the Visualize tab. Choose All for Add Type and click the Update button. After a few seconds small gray squares will appear in the Occupancy Diagram window at the right. Clicking these squares will generate the molecular orbital surface.

The σ bonding between the C atoms is orbital 1, the HOMO showing the π bonding between the C atoms is orbital 6, and the LUMO showing the π* antibonding is orbital 7.

Close the MOs window.

Choose Results / Surfaces. Click the Cube Actions button and choose New Cube. Choose Total Density for Kind the click OK.

After the Cube has been created, click the Surface Actions button and choose New Surface. Choose Electron density from Total SCF Density.

Close.