1 Introduction to Computational Chemistry

Start HyperChem by clicking Start / Programs / HyperChem Release 7 / HyperChem Professional

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

Structure of CH_4
Double click the Drawing Tool (1st across). An Element Table appears.
Click on C and close.
Click in the workspace and a small blue circle appears representing a C atom appears.
Double click the Select Tool (2nd across) and CH_4 appears.
Click the Rotate Out of Plane Tool (3rd across). Click and drag to rotate the molecule. Likewise, click the Rotate in Plane Tool and rotate the molecule.
Click Select Tool.
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.
Click File / Save.
Navigate to c:\hyperchem lab (or any suitable folder).
Save using CH4PM3.HIN.
Click Setup / Semiempirical / PM3 and click OK.
Click Compute / Geometry Optimization and click OK.
The calculations should be completed within a second or so.
Click File / Save.
Click midway over a C-H bond.
Record the value of the C-H bond length _____Å (1.091 Å literature) shown in the Status Line at the bottom of the workspace. Right click to unselect the bond.
Click on one of the H atoms, click the C atom, and click on one of the other H atoms (a H-C-H combination should be highlighted).
Record the value of the H-C-H bond angle _____° (109.4712 ° literature) shown in the Status Line.
Save the workspace.

Structure of NH_3
Click File / New.
Build NH_3 using the above procedure.
Save the file as NH3PM3.HIN.
Perform the PM3 geometry optimization as above.
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 _____° (~108.2 °, 106.67 ° literature).
Save.

Structure of H_2O
Click File / New.
Build H_2O using the above procedure.
Save the file as H2OPM3.HIN.
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).
Save.

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 File / New.
Double click the Drawing Tool and choose C as the atom.
Click and drag in center of workspace (a blue line representing a C-C bond appears).
Double click the Select Tool (CH_3CH_3 appears).
Save as C2H6PM3.HIN.
Perform a PM3 optimization.
Save.
Click Select Tool.
Click Display / Labels / Number and click OK.
Click H atom 6. Click the attached C atom 2, the other C atom 1, and the H atom 5 to define a "dihedral" (or "torsion") angle. The value of the dihedral angle appears in the Status Line.
Click Compute / Potential. Enter -180, 180, 10 and click OK. After a few seconds an energy plot will appear.
Click Properties / Data / Data Values.
Scroll through the values and 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).
Close the worksheet.

Structure of Ethene, CH_2CH_2
Click File / New.
Double click the Drawing Tool and choose C as the atom.

Click and drag in center of workspace (a blue line representing a C-C bond appears).
Click on the blue line (two blue lines appear representing a C=C bond appears).
Double click the Select Tool (CH_2CH_2 appears).
Save as C2H4PM3.HIN.
Perform a PM3 optimization.
Save.
Click Select Tool.
Define a HCCH dihedral angle using H atoms *cis* to each other and open.
Click Compute / Potential. Enter 0, 180, 10 and click OK. After a few seconds an energy plot will appear. Does the maximum energy occur at 90°? ____
Click Properties / Data / Data Values.
Scroll through the values and 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} (2.9 kcal mol^{-1} literature).
Close.

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

Click File / Open.
Choose C2H4PM3.HIN.
Click Save As C2H4surfacesPM3.HIN.
Click Compute / Geometry Optimization.
Save the file.
Click Compute / Orbitals.
Choose Number = 1 / Plot to observe the σ bonding between the C atoms (Close Orbital box and rotate structure if desired.) Various presentations (wire mesh, dots, translucent) can be chosen by selecting Options.
Repeat for the various orbitals. The π bonding between the C atoms is Number = 6 and the LUMO showing the π* antibonding is LUMO Number = 7.
Close the Orbital window and right click in the worksheet to remove the orbital.
Click Compute / Plot Molecular Graphs / Molecular Properties: Electrostatic Potential and Mapped Function Options: -1, 1. Click OK.
Close and save all windows.

Exit HyperChem.