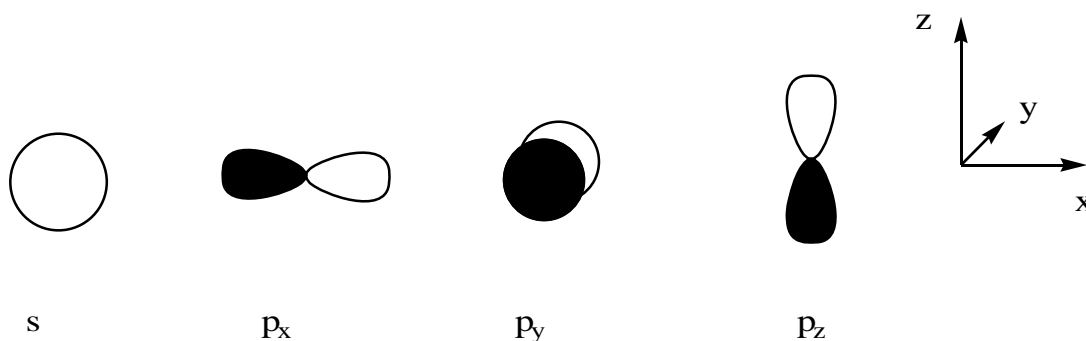


## Quantum Mechanical Calculations of Organic Molecules

One of the main goals of chemistry is to understand the details of chemical reactions. Why do some molecules react one way but not another. Theoretical calculation of electronic distribution within molecules is one of the tools used to explore reactivity patterns. Calculations can provide information not only on overall molecular energies but also bond strengths, and charges on atoms.

The computer program used in these exercises, Gaussian 03, requires that you supply the geometry of the molecule so that the program may calculate the properties of the molecule. You can do this by entering the x, y, z coordinates of each atom (painful, at best) or by entering the bond lengths, bond angles and dihedral angles (much easier) or pictorially build your molecule (actually, sort of fun). More on this later.

You have to become familiar with several quantum mechanical concepts to understand the functioning of the program and interpret the results of the calculations. Recall that for atoms the electrons reside in atomic orbitals. For example, an uncharged carbon atom has six electrons which occupy the 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> orbitals. Each orbital can hold at most two electrons. The atomic orbitals have different shapes and orientation as shown below.



The s orbitals are spherical in shape whereas the p orbitals are shaped like a bow tie. There are three different p orbitals (p<sub>x</sub>, p<sub>y</sub> and p<sub>z</sub>) aligned parallel to the x, y, and z axes. The orbitals are actually mathematical functions which assign a numerical value to each point in space relative to the nucleus.

For example, the 1s atomic orbital of hydrogen atom is proportional to

$$e^{-\alpha r}$$

where e and  $\alpha$  are numerical constants and r is the distance from the nucleus to the point at which the orbital is being evaluated. The important thing here is that the value of the function depends only on the distance from the nucleus; hence spherical in shape.

On the other hand, the 2p<sub>z</sub> atomic orbital is proportional to

$$ze^{-\alpha r}$$

where  $z$  is  $z$  coordinate of the point where the orbital is being evaluated relative to the nucleus. Depending on the point where it is evaluated the  $p$  orbital may be either positive or negative. We represent the algebraic sign by shading (here, black or white) for the  $p$  orbitals shown above.

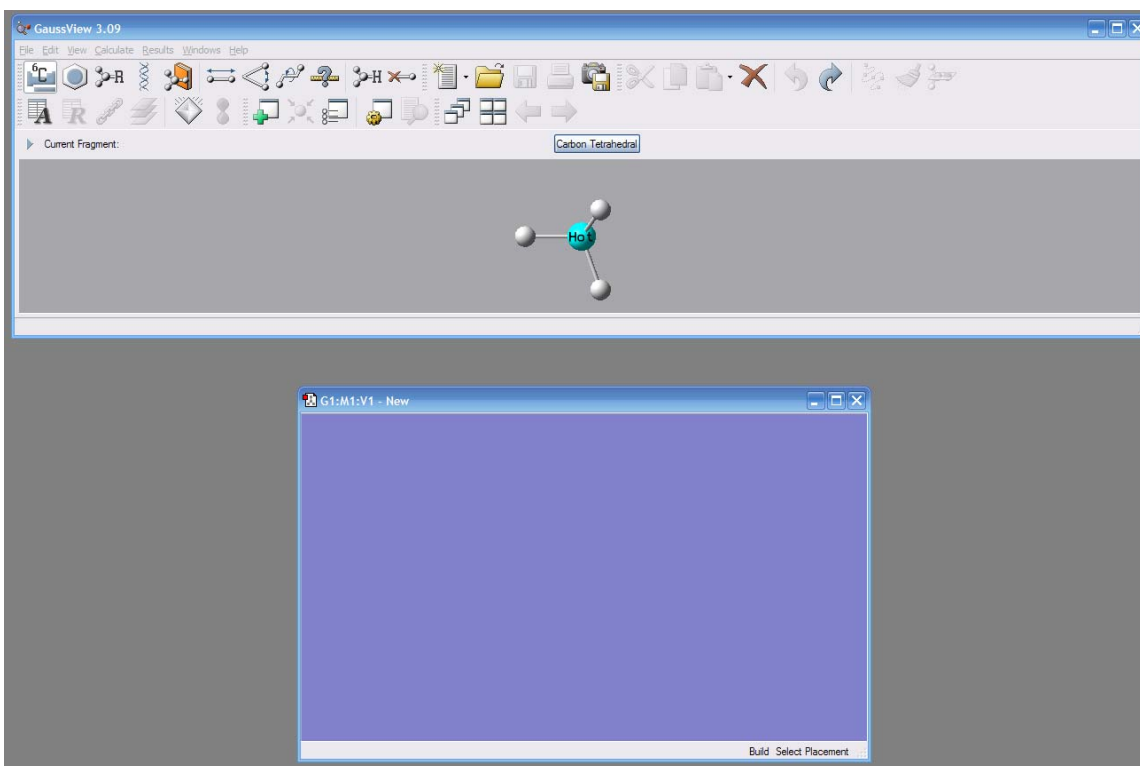
The aim of this experiment is to calculate properties of molecules. We need to specify the geometry for the molecule: where the nuclei are located. Making use of bond lengths, bond angles and rotational angles you could calculate the  $x$ ,  $y$ ,  $z$  coordinates of each nucleus and provide them to the program. For simple molecules such as  $H_2$  this is easily done. For even slightly more complex cases such as methane the calculations would be cumbersome. The GaussView program, part of the Gaussian suite of programs, provides a graphical, visual way for both an initial specification and then tools to modify the molecular structure.

The **GaussView** program will be used to specify the structure of the molecule, initiate the calculations, and view the calculated results. Only a few features of the program will be used. The basic steps, described in more detail later, are

1. Specify the structure of the molecule using GaussView. The tools provided include
  - a. a *Molecular Structure Window* (MSW) in which you assemble the new structure.
  - b. a *library of molecular fragments* which may be added to the molecule you are building
  - c. the capability to *rotate the entire molecular* structures for easy viewing
  - d. *substitution* of one atom for another
  - e. *modification of geometric parameters*: bond lengths, bond angles and rotational angles about bonds (dihedral angles)
  - f. *automatic adjustment* of a molecular structure after modification, etc.
2. Specification of some technical parameters for the calculation and starting the actual calculation.
3. Retrieval of the results of the calculation which can include
  - a. *Energy* of the molecule
  - b. *Charges* on individual atoms
  - c. An *Electrostatic Potential Surface (EPS) map* which indicates the stabilization (destabilization) of putting a charge at different positions around a molecule.
  - d. Display of the *individual molecular orbitals*.

## 1. Structure Specification

If the GaussView program is not running start the program from the Start menu. GaussView starts and displays a methane molecule. A blank *Molecular Structure Window (MSW)* with a name such as G1:M1:V1 is also presented. The MSW is where you will build your molecule.



Molecular structures and fragments, stored in libraries, are displayed in the GaussView window for your consideration. They may then be added to the molecule you are building in the MSW. The GaussView window is initialized with the methane molecule.

The following is a description of some of the tools used to build a molecule in the MSW.



**Obtain a new Molecular Structure Window (MSW)** by clicking the *New* button in the GaussView toolbar. A new window with a name such as G1:M1:V1 will appear. This is where the molecule to be calculated is designed. A structure is copied from the GaussView window to a blank structure window by clicking on the structure window.

Structures may be **rotated** in any window by dragging the mouse over the window.

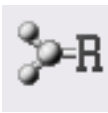
Molecules or atoms are first created in the GaussView window and then brought into the MSW for a calculation to be done. When a structure is presented in the GaussView window one atom will be designated as **Hot**. When an atom in the molecule being built in the MSW is clicked the Hot atom (and the rest of the structure in the GaussView window) replaces the atom you clicked. If you choose to have a different atom be Hot in the GaussView window simply click it.



Clicking on the **Element Fragment** icon presents a Periodic Table. If the Periodic Table has been utilized previously an additional click is needed. First select an element. A choice of the bare atom itself or the atom linked to hydrogens in various hybridizations is presented below the Periodic Table. Make your selection by clicking the icon. Your selection now appears in the GaussView window with one atom designated as a *Hot Atom*. If you click an empty space in the MSW then the entire structure in the GaussView window is copied to the MSW. If there is a molecule already under construction in the MSW and you click on an atom in that molecule the Hot Atom (and accompanying atoms) replaces the clicked atom.



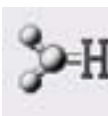
The **Ring Fragment** icon will present a **library of common ring structures** from which you may select a structure. Clicking on a ring will bring it into the GaussView window. If the ring library has been utilized previously an additional click may be needed. Clicking on an empty space in the MSW will copy the ring into the MSW. Alternatively, clicking on an atom in a molecule being built in the MSW will replace that atom using the Hot Atom of the ring.



Clicking the **Group Fragment** icon presents an array of **common molecular structures** which can be brought into the GaussView window. If the molecular structure panel has been utilized previously an additional click is needed. Subsequent clicking on an empty space in the MSW will copy the structure into the MSW. Alternatively, clicking on an atom in a molecule being built in the MSW will replace that atom with the Hot Atom of the structure.



**Deleting an Atom** is accomplished by selecting this icon and then clicking the atom in the MSW.



After selecting the **Add Valence** icon you may add a H to the atom you click in the MSW.

In summary, an atom or more complex structure obtained from a library of structures may be copied from the GaussView Window to a blank Molecular Structure Window (MSW) by clicking in the MSW. If there is already a molecular structure in the MSW clicking on an atom replaces it with the structure in the GaussView window. The atom labeled “Hot” in the GaussView window will take the place of the atom clicked in the MSW.

### **Structure Improvement.**

As described above molecules are built by combining fragments and, if desired, substituting one atom for another. Your structure may be improved by further modification. The program provides two methods to improve the structure.



**Rebonding** may be accomplished by clicking on this icon. The program will assume atoms close to each other are bonded and adjust the display accordingly. This will improve the pictorial representation of your molecule but not affect the calculations.



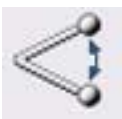
**Cleaning** is done by clicking this icon. This generally improves an estimated structure when, for example, a nitrogen replaces a carbon or a new atom is added to a molecule.

### Structure Modification.

Working with bond lengths, angles and dihedral angles is done only to allow you to easily specify the geometry of the molecule. The bonds you have designated do not affect the calculated properties of the molecule. Bond lengths, bond angles and dihedral angles (for rotations about bonds) may be modified as below.



**Bond Lengths** are modified by clicking the **Modify Bond** icon, clicking on the two atoms of the bond in the MSW and then, in the dialog that appears, entering a numerical value or using the slider to alter the bond length. Keep the Translate Group option selected for atom 1 and atom 2. You may indicate the bond multiplicity as none (non-bonded), single, double, etc.



**Bond Angles** are modified by clicking the **Modify Angle** icon, clicking on the three atoms of the bond angle in the MSW, and then, in the dialog that appears, entering a numerical value for the bond angle or using the slider. You may specify how the atoms in the bond angle are moved. You may choose that one or two atoms not move as the bond angle is modified by choosing Fixed. Alternatively they may be moved along with their substituents as a unit by choosing “rotate group”.

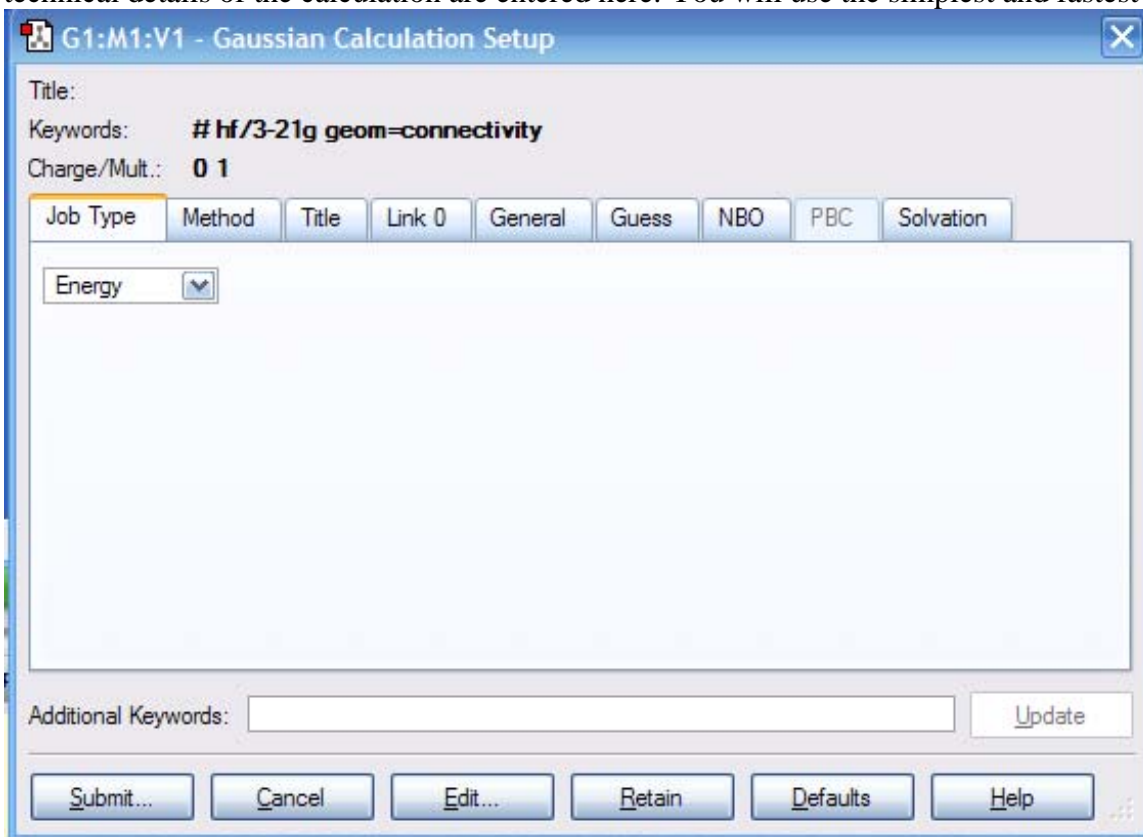


**Dihedral Angles** are modified by clicking the **Modify Dihedral** icon, clicking on four atoms (Atom 1, Atom2, Atom3, and Atom 4) of the molecule in the MSW. Rotation occurs around the Atom 2 – Atom 3 bond. Enter a numerical value, in the dialog that appears, or use the slider. Drop down boxes provide options on how the atoms should be moved in the rotation process. A value of 0 means that A and D eclipse each other while a value of 180 specifies an *anti* geometry.

## 2. Performing the Calculation

After you have satisfactorily specified a molecular structure in the MSW the calculation is done as follows

In GaussView choose the drop down menu Calculate → Gaussian. The set-up menu appears. The technical details of the calculation are entered here. You will use the simplest and fastest methods.



Choose the **Job Type** tab. From the drop down menu you can choose either

1. *Energy* which will calculate the energy of the exact molecular structure as you have created it or
2. *Optimization* which will automatically change the geometry parameters so as to obtain the geometry which provides the best (most negative) energy

Choose the **Method** tab. Use the defaults as shown except

1. *Basis Set* choose STO3G,
2. *Charge* is set appropriate to the system you are calculating (usually 0, 1 for a +1 cation, -1 for a -1 anion, etc.)
3. *Spin* is set to Singlet

Choose the **Title** tab.

1. Enter a title for your calculation. It should consist of your initials and the name of the molecule.

At the bottom of the window click the **Submit** button.

A dialog appears asking you to **Save the Gaussian Input File** before proceeding. Click **Save**. A Save File dialog box will appear and you must enter a name for the Gaussian Input File. It should consist of your initials and the name of the molecule. Click **OK**.

A dialog appears asking if you want to **run the calculation**. Choose **OK**. The calculation initiates.

### 3. Displaying the Results of the Calculations

- When the Gaussian program is performing calculations the **progress** of the calculation is displayed in a newly created window. To display this window you may have to click the rightmost icon (black letter G) from the Taskbar at the bottom of the screen.
- When the calculation is finished you will be asked if you want to **close the Gaussian Window**, click **OK**.
- A dialog appears asking if you want to open a **Result File**, select **Yes**. An Open File dialog is presented. Change the “File of Type” to “Gaussian Output Files (\*.out, \*.log)”. Select the .log file for the molecule which you calculated. Click **Open**.
- A new MSW is opened displaying the structure of the molecule you have just calculated.
- The **energy** and **dipole moment** are obtained from the GaussView drop down menu Results → Summary. The energy, E(RHF), is in Atomic Units, 1AU/molecule = 627.5 kcal/mol = 2625.5 kJ/Mol and the dipole moment is given in Debyes.
- **Atomic charges** are obtained from the GaussView drop down menu Results → Charges. Select Show Charge Numbers and deselect other options.
- Geometric parameters may be “measured” from a molecule in a MSW by means of the **Inquire** tool. Click on the Inquire button and then click on atoms in the structure displayed in the MSW. The measured value is presented at the bottom of the MSW.
  - Clicking on two atoms measures the distance between the atoms.
  - Clicking on three atoms measures the angle formed by the atoms
  - Clicking on four atoms measures the dihedral angle formed by the atoms.




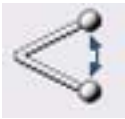




## Exercises

**A.1. Manual Optimization of the O – H bond length of Water.** There are two geometric parameters that must be specified to define the structure of the water molecule: the O–H bond lengths and the H–O–H bond angle. In order to become familiar with how the program works you will perform a series of calculations to see how the energy depends on the O–H bond length. The H–O–H bond angle will be held fixed for the structures you calculate. You will use a value assigned by your instructor between 85 degrees and 115 degrees.

You will seek the bond length which gives the lowest energy (most negative) by calculating the energies of molecular structures with various bond lengths. You will first perform six calculations with the bond lengths having values of 0.85, 0.90, 0.95, 1.00, 1.05 and 1.10.

*A detailed description of how to use the program in this practice exercise follows.*

1		If the GaussView program is not running start it via the Start → All Programs → GaussView folder → GaussView program.
2		If you receive a warning that the Serial Number cannot be located click OK
3		Once the program opens click on the <b>Element Fragment</b> icon. A periodic table will be displayed.
4		Click on the icon for Oxygen. Several bonding patterns will be displayed at the bottom of the window. Click on the one with two single bonds. The periodic table window will close and an oxygen with two hydrogens attached (water) will be displayed.
5		Click any place in the molecular structure window to copy the molecule for calculation. You will not use the default geometry but will have to specify both the bond length and the bond angle.
6		First specify the bond angle. Click the <b>Modify Angle</b> icon on the toolbar and then click on an H, then the O, and then the other H. the selected atoms become highlighted and a bond angle dialog will appear. Type in the bond angle assigned by your instructor. Be sure to use a decimal point. click OK. The highlighting disappears.

7		<p>You will now adjust the bond lengths. Click the Modify Bond tool. Click the O and the H of one bond, the atoms highlight and the dialog box opens. Type in your chosen bond length (0.85, 0.90, etc.) Click OK. The highlighting disappears. <b>Repeat for the other O-H bond.</b></p>
8		<p>Click the Calculate drop-down menu in GaussView → Gaussian. The Gaussian Calculation Setup dialog appears.</p> <p>Choose the <i>Job Type</i> Tab. In the dropdown list select Energy.</p> <p>Choose the <i>Method Tab</i>. Under Basis Set choose STO-3G.</p> <p>Verify that the other parameters are</p> <ul style="list-style-type: none"> <li>Method: Ground State, Hartree Fock,</li> <li>Default Spin,</li> <li>Basis Set: STO-3G and a blank box,</li> <li>Charge: 0</li> <li>Spin: Singlet</li> </ul>
9		<p>Click Submit at the bottom of the dialog. You will be asked to save the input file. Assign it an appropriate name starting with your initials, the name of the molecule (water), and the O – H bond length you used <u>without a decimal point</u> (for example, JMHwater0914). Click OK.</p>
10		<p>The calculation will be done. A dialog box opens (if it does not after a few seconds click on the rightmost button on the taskbar at the bottom of the desktop) asking if the Gaussian window should be closed. Click OK.</p>
11		<p>A new dialog opens asking if you want to open a result file. Click OK. An Open File dialog is presented. Change the File of Type to Gaussian Output Files. Select the one for the molecule which you calculated. Click Open. A new MSW window appears showing the structure used in the calculation. Click the Results drop down menu in GaussView, click Summary and obtain the energy of the molecule. Record it to four digits after the decimal point</p>
12		<p>Change the bond lengths (step 7) as described above and repeat the process for the next O-H bond length.</p>

Use an Excel spread sheet to record and plot your data. Plotting should be done **after** the laboratory exercises are completed.

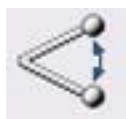
**A.2. Prediction of molecular geometry.** Using GaussView perform calculations on one or more of the following molecules following the directions of your lab instructor.

- 1) Staggered Ethane (vary the C-C distance)
- 2) Staggered Ethane (vary all the H-C-C angles simultaneously)
- 3) Dimethyl ether (vary both the C-O distances simultaneously)
- 4) Dimethyl ether (vary the C-O-C angle)
- 5) Formaldehyde,  $\text{H}_2\text{CO}$  (vary the C-O distance)
- 6) Formaldehyde,  $\text{H}_2\text{CO}$  (vary H-C-H angle)
- 7) Ethene,  $\text{H}_2\text{C}=\text{CH}_2$  (vary the C-C distance)
- 8) Ethene,  $\text{H}_2\text{C}=\text{CH}_2$  (vary both of the H-C-H angles simultaneously)
- 9) Ammonia (vary all the N-H distances simultaneously)
- 10) Cyclopropane (vary all the C-C distances)
- 11) Nitrous Oxide, N-N-O (vary the N-N distance)
- 12) Nitrous Oxide, N-N-O (vary the N-O distance)
- 13) Nitrogen tetroxide,  $\text{O}_2\text{N}-\text{NO}_2$  (vary the N-N distance)
- 14) Nitrogen tetroxide,  $\text{O}_2\text{N}-\text{NO}_2$  (vary all the N-O distances simultaneously)
- 15) Nitrogen tetroxide,  $\text{O}_2\text{N}-\text{NO}_2$  (vary both the O-N-O angles simultaneously)
- 16) Allene,  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$  (vary both of the C-C distances simultaneously)
- 17) Allene,  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$  (vary both of the H-C-H angles simultaneously)

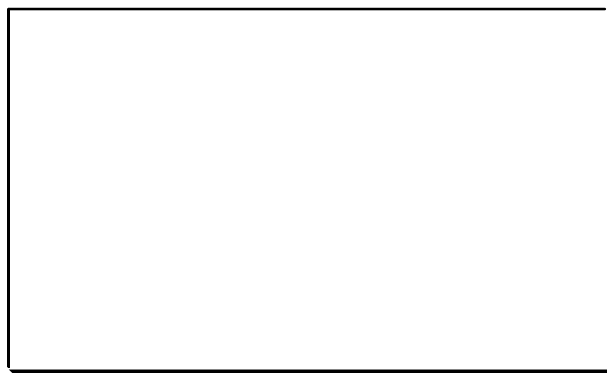
By doing a calculation as described above obtain the energy of your molecule. Record the energy to four positions after the decimal point. Systematically vary the geometric parameters specified for



your molecule (equivalent bond lengths and/or bond angles should all be varied at the same time). Vary the geometric parameters both above and below those supplied by the program as an initial guess. The “best” geometry will be the one which produces the lowest (most negative) energy. You should vary the bond angles in steps of three degrees and the bond lengths in steps of 0.05 angstrom being sure that you have found a minimum in the energy for the bond length or bond angle you are changing.



Sketch your molecule and show **all** geometric data.  
You will have to use the **Inquire** tool to "measure" the molecule.



Estimate the best energy (most negative) for your molecule. You will need to plot how your calculated energies depend on the geometric parameter you optimized.

**Energy** \_\_\_\_\_

**A.3 Automated prediction of Molecular Geometry.** Again set up the GaussView program to calculate the molecule(s) you investigated in the previous section. All the parameters you enter should be the same as earlier except that you should choose "Optimize" in the Job Type panel of the Gaussian Calculation Setup window. The program will now predict the best geometry for you without your having to individually vary the bond lengths or bond angles. Compare the automated results to those which you obtained.

Sketch your optimized molecule and show **all** geometric data.  
You will have to use the **Inquire** tool to "measure" the molecule.



Report the Energy for the optimized structure.

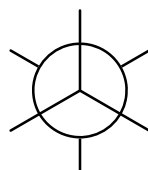
**Energy** \_\_\_\_\_

## B. Rotational Barriers.

- In this section you will calculate the rotational energy curve for one or more molecules. As an example the calculations are now described for butane. The other molecules are done similarly.
- Butane is constructed in the MSW. First methane is brought into the GaussView window and then copied by a click into the MSW. Check that the C of the methane as displayed in the GaussView window is the Hot atom. Click on a hydrogen in the MSW to construct ethane, click on a methyl hydrogen to build propane and then again to build butane. The butane in the MSW will be staggered. Verify this by rotating the molecule in the MSW and examining it carefully. Be sure that the methyl groups are anti to each other. This is the 180 degree conformation. If they are not anti you may make them anti by clicking on the *Modify Dihedral* button, clicking carbon atoms C1, C2, C3, and C4 in that order, and entering 180 in the panel that appears. Be sure that "Rotate Group" is selected for Atoms 1 and 4.
- Run the calculation being sure that "Energy" is selected in the Job Type panel of the Gaussian Calculation Setup window. You will obtain the energy for the conformation displayed in the MSW. Click on the *Modify Dihedral* button to modify the dihedral angle. Now click on the atoms C1, C2, C3, and C4 in that order. A panel appears and allows you to rotate around the C2-C3 bond. Be sure that "Rotate Group" is selected for Atoms 1 and 4. Change the angle by 30 degrees and calculate and record the energy for each conformation that you have produced. Repeat the process until the full rotation of 0 to 180 and 0 to -180 degrees is accomplished. For each conformation record the energy to four decimal positions. After leaving the computational laboratory use Excel to make a plot of energy vs. angle of rotation. Be sure that the conformations are clearly indicated on your plot. On your plot indicate the geometry of the zero degree conformation and the direction of rotation



Following the directions of your laboratory instructor select one or more of the following molecules, define the starting conformation and record it on the Newman projection template below. Indicate the direction of rotation.



Obtain, as described above, the energy curve for rotation about the indicated bond.

- 1) butane (C2-C3)
- 2) 2-fluoro-3-methyl butane (C2-C3)
- 3) 2,3-difluoro butane (C2-C3)
- 4) Hydrogen peroxide (O-O)
- 5) 1,4-difluoro butane (C2-C3)
- 6) 1,1,1-trifluoro butane (C2-C3)
- 7) 2,2,3-trimethyl pentane (C3-C4)
- 8) Hydrazine,  $\text{H}_2\text{N-NH}_2$  (N-N)
- 9) 1-fluoro-1-chloro-propane (C1-C2)
- 10) 1,2-difluoro-1-chloro-propane (C1-C2)
- 11) 2,3-dimethyl butane (C2-C3)
- 12) 2-methyl butane (C2-C3)

13) 2,2-dimethyl butane (C2-C3)

14) 2,3-dimethyl butane (C2-C3)

-150	-120	-90	-60	-30	0

30	60	90	120	150	180

### C. Charge Distribution.

The Gaussian program is capable of estimating the charge on each atom in a molecule. In this section you will look at how charges are distributed in molecules and ions. In particular, you will investigate how introducing a new group such as a halogen, nitro group, or OH group will **change** the charge distribution. The approach will be to calculate a reference molecule, make a change in the molecular structure, perform another calculation and observe the change.

#### Alkyl Halides.



**C.1 1-fluorobutane** Calculate the **butane** molecule in the default geometry. Display and record the charges on the carbon atoms. Using the Periodic Table tool select a fluorine atom and replace a hydrogen atom with the fluorine, making **1-fluoro butane**. Improve the structure using the **Cleaning** tool. Run the calculations and record the charges.

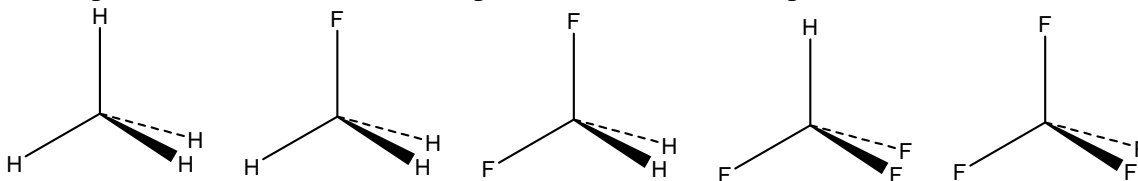
	C1	C2	C3	C4
butane				
1-fluoro butane				
Change caused by introduction of F				

**C.2 2-fluoro butane** Repeat the process above for 2-fluorobutane

	C1	C2	C3	C4
butane				
2-fluoro butane				
Change caused				

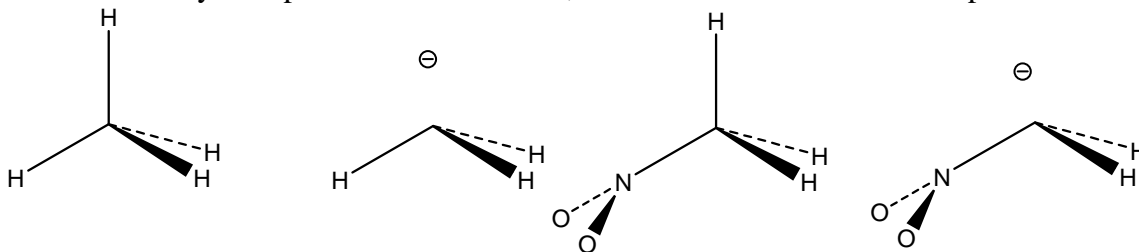
by introduction of F				
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**C.3 Multiple halogenation.** Perform calculations on methane, fluoro methane, difluoro methane, trifluoromethane, and tetrafluoromethane. After introducing each fluorine use the **Cleaning** tool. Obtain the dipole moments and record them below. Indicate the charge next to each atom (two decimal positions). Compare the dipoles of  $\text{CH}_3\text{F}$  and  $\text{CHF}_3$ . Are these as expected on the basis of bond dipole considerations? Explain



\_\_\_\_\_

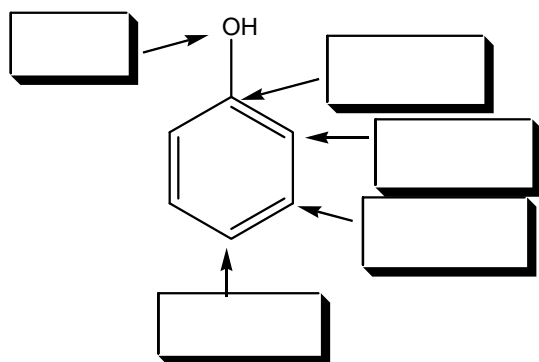
**C.4 Nitro methane.** Specify Optimization as the Job Type and perform calculations on  $\text{CH}_4$ ,  $\text{CH}_3^-$ ,  $\text{CH}_3\text{NO}_2$ , and  $\text{CH}_2\text{NO}_2^-$ . Be sure to specify the molecular charge as -1 for anions in the Method tab of the Gaussian Calculation Setup dialog. Record the charges and calculated energies below. When using the nitro group be sure to initialize your geometry similar to those below. Which do you expect to be more acidic, methane or nitromethane? Explain.



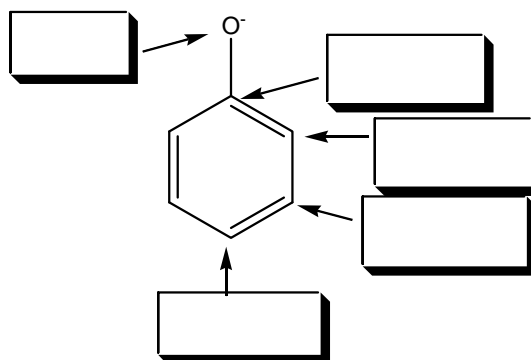
Energy \_\_\_\_\_

Energy differences \_\_\_\_\_

**C.5 Delocalization of Charge (Phenol).** Choose Optimization as the Job Type and obtain the charge distributions in the following molecules and ions. Record your results on the diagrams in the spaces provided. Does the presence of the NO<sub>2</sub> group increase or decrease the ease of ionization of the phenol. Explain.



overall charge zero

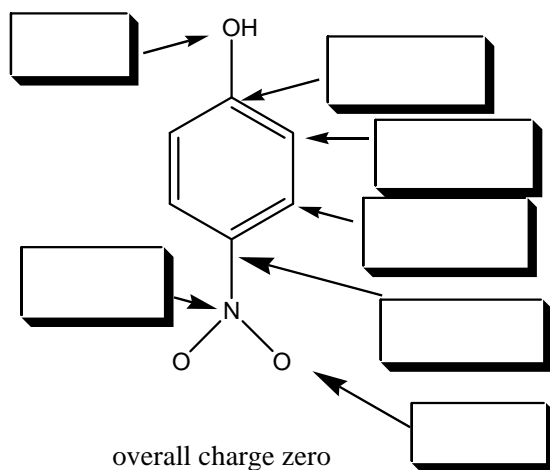


overall charge -1

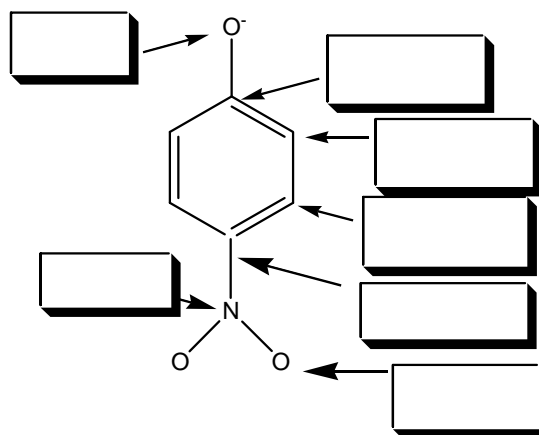
Energies \_\_\_\_\_

\_\_\_\_\_

Energy Difference \_\_\_\_\_



overall charge zero



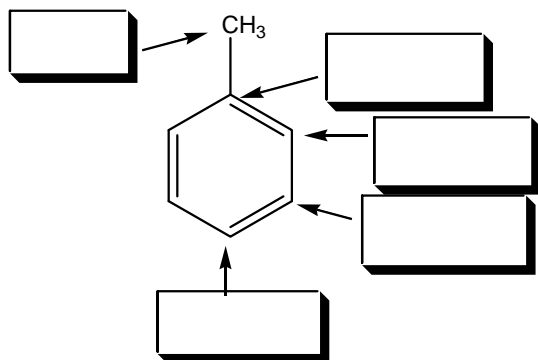
overall charge -1

Energies \_\_\_\_\_

\_\_\_\_\_

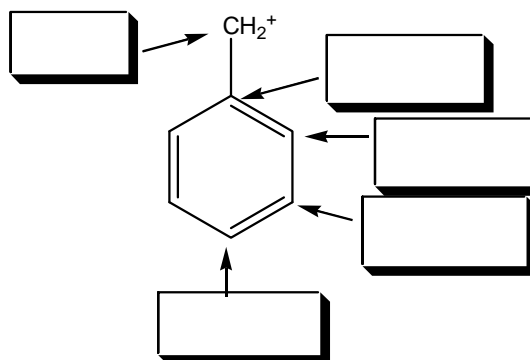
Energy Difference \_\_\_\_\_

**C.6 Delocalization of Charge (Toluene).** Choose Optimization as the Job Type and obtain the charge distributions in the following molecules and ions. Record your results on the diagrams in the spaces provided. Does the presence of the NH<sub>2</sub> group increase or decrease the ease of ionization of the toluene molecule?



overall charge zero

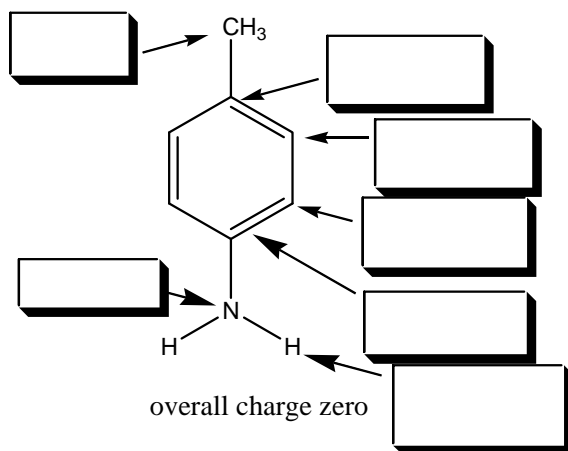
Energies \_\_\_\_\_



overall charge +1

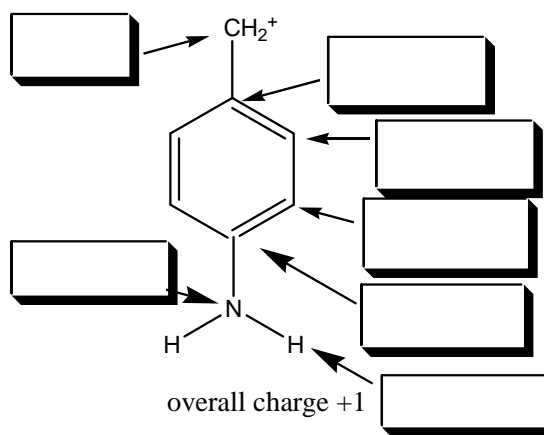
\_\_\_\_\_

Energy Difference \_\_\_\_\_



overall charge zero

Energies \_\_\_\_\_

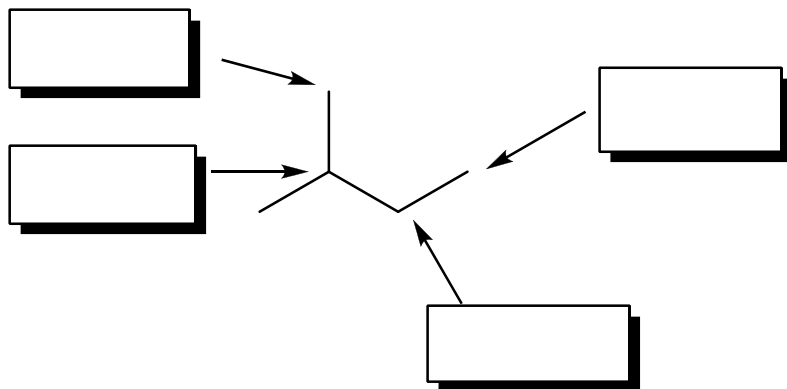


overall charge +1

\_\_\_\_\_

Energy Difference \_\_\_\_\_





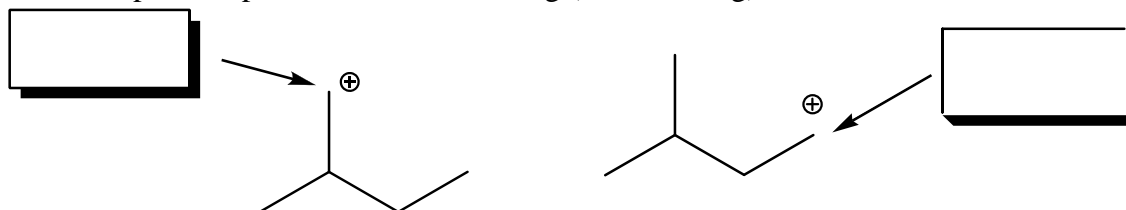
Energy \_\_\_\_\_



Next we generate various carbocations by removing a hydrogen and setting the charge to +1.



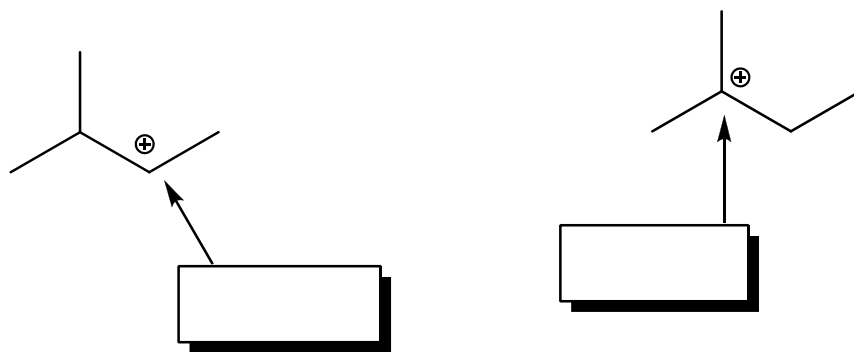
1. Remove a hydrogen atom from a carbon atom in the molecule with the **Delete Atom** tool. This is where the positive charge will be located
2. Perform a “Optimization” calculation (set the charge to 1 and spin state to singlet).
3. Record the energy and charges from the calculation below.
4. Restore the hydrogen to the carbon in the molecule from which you removed it earlier using the **Add Valence** tool.
5. Repeat the process above, removing (and restoring) an H atom from a different carbon atom.



Energies \_\_\_\_\_

a primary carbocation

a primary carbocation



Energies \_\_\_\_\_

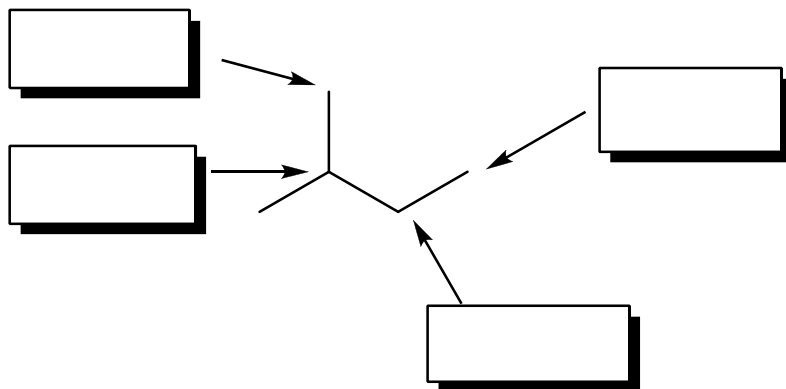
\_\_\_\_\_

a secondary carbocation

a tertiary carbocation

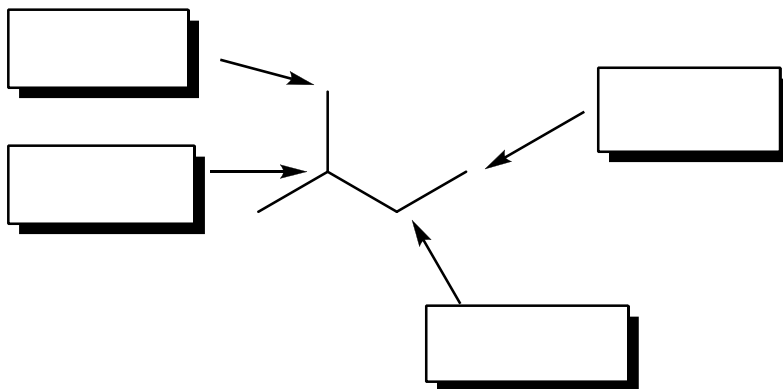
The Gaussian calculations are now complete. The rest of this section should be completed away from the laboratory.

Find the most negative (most stable) of the carbocation energies above; subtract it from each of the entries above for carbocation energies to obtain the relative energies of the four different carbocations and record the relative energies of carbocations located at each site below.



Relative energies of the four possible carbocations.

Similarly, obtain the changes in atomic charge at each carbon atom when a carbocation is generated at that carbon atom by comparing the charges on each carbocation center with the corresponding atom in the neutral 2-methylbutane.



Changes in charge caused by generation of a carbocation at each site.

Correlate relative energy of a carbocation at a carbon atom with the change in charge produced at the carbon atom. Further, classify with respect to primary, secondary and tertiary sites.

Finally, by considering the energies of the possible intermediate carbocations predict the products for addition of HBr to each of the alkenes below.

