Quantum Chemistry and Normal Modes of Vibration

Purpose:

The purpose of this experiment is to learn about *ab initio* quantum chemistry packages and normal modes of small polyatomic molecules.

Equipment and Chemicals:

A PC running *Spartan* and a printer.

Directions:

See the instructor for directions on how to load and run *Spartan*.

Calculations:

You will perform an *ab initio* 3-21G calculation on a small polyatomic molecule.

Your molecule is: _____

The calculation you will perform may be used to illustrate the connection between charge polarity and the shapes of the frontier molecular orbitals. You will also have the opportunity to calculate a vibrational spectrum and animate the motions for a few characteristic modes.

1. Build your molecule. Select **New** from the **File** menu and select the pieces from the *model kit* to build your molecule. *Click* on **Minimize** under the **Build** menu. In the lower right hand corner you will see information about the energy of the minimum geometry of the molecule. Just below this, you will see the symmetry of your molecule.

My molecule has _____ symmetry.

Select **View** from the **Build** menu to remove the *model kit* from the screen.

2. Enter the **Calculations** dialog (**Setup** menu). Under *Calculate* specify **Equilibrium Geometry** with **Hartree-Fock** with **3-21G(*)** for the level. Make certain that *Total Charge* and *Multiplicity* are properly set (to **Neutral** and **Singlet**, respectively), and select **Elect Charges** and **Atomic Charges**. Then, *click* on **OK** to exit the dialog.

3. Submit the job (**Submit** under the **Setup** menu). You will be asked to save the file and to supply a name (e.g., “formaldehyde_321g”). When complete examine the calculated charges on all of the atoms in the molecule. To do this, first select an atom in the molecule by clicking on it and then click **Properties** from the **Display** menu. In the

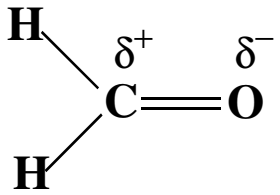
table below, record the **Charges** from the **Atom Properties** sub-menu which appears. Click on another atom in your molecule and record the charges for that atom. Continue until you have recorded the Electrostatic, Mulliken and Natural charges for all atoms in your molecule.

Note that the Electrostatic, Mulliken and Natural atomic charges supplied are different. This reflects the fact that charge cannot be uniquely defined.

The charges on the atoms in my molecule are:

Atom	Electrostatic	Mulliken	Natural

Focus on the sets of charges on two bonding atoms. Do they confirm your expectations about the polarity of the bonds in the molecule? For example, in formaldehyde, the carbon-oxygen double bond, i.e.,



is polar with a partial positive charge (δ^+) on C, and a partial negative charge (δ^-) on O.

When you finish examining atomic charges, close the **Atom Properties** window and click on the last selected atom to remove the high-lighting.

To display the dipole moment vector, select **Properties** from the **Display** menu and then **Dipole** from the sub-menu which appears. Draw a picture of the molecule with the dipole vector:

Are the atomic charges consistent with the direction of the dipole moment in your molecule? Yes or No?

Click on **Dipole** to remove the dipole and close the **Molecule Properties** window when you are finished.

4. Enter the **Surfaces** dialog (**Setup** menu). *Click* **Add …** to reach the sub-menu. Select **HOMO** from the **Surface** pull-down menu then *Click* **OK**. Next, click **Add …** and select **LUMO** from the **Surface** menu and again click on **OK**. Close the window and submit the job (**Submit** from the **Setup** menu).

5. When the calculations have completed, select **Surfaces** from the **Display** menu. *Click* on the line "HOMO". *Click* on the molecule and select **Solid** or one of the other choices from among the available display styles on the bottom right of the screen (the **Style:** pull-down menu). This will display the Highest Occupied Molecular Orbital (HOMO) on the screen. **Print it out and attach to this lab report**.

6. *Click* on the line “HOMO” to **de-select** the HOMO surface. This turns off the display of the HOMO. Now, *Click* on the line "LUMO". Once again, select **Solid** (or Mesh,etc.) from among the available display styles. This will display the Lowest Unoccupied Molecular Orbital (LUMO) of your molecule. **Print it out and attach to this lab report**. It is generally the case that high-energy filled molecular orbitals corresponding to polar bonds are polarized toward the more electronegative atom, while low-energy unfilled molecular orbitals are polarized toward the more electropositive atom.

When you are finished, turn off the display of the LUMO by c*licking* on the line "LUMO" and close the **SURFACES** window.

8. Reenter the **Calculations** dialog (**Set-up** menu) and specify **Freq.** and **Vibrational Modes**. Exit the dialog (**OK**) and then submit the job (**Submit** under the **Setup** menu).

9. When the calculation has completed select **Vibrations** under the **Display** menu.

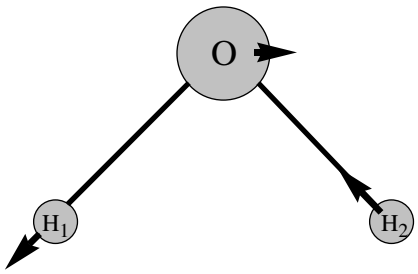
A dialog provides a listing of the vibrational frequencies of your molecule (from smallest to largest) along with their symmetry labels (e.g., A1 or B2). Record these in the following table.

Symmetry Label	Calculated Frequency	Experimental Frequency

Note, that the calculated frequencies are consistently larger than the measured values, typically by about 10%. It is common practice to uniformly scale calculated frequencies by 0.9) to bring them into better accord with experiment.

To animate the individual vibrational motions, *click* on the frequency in **Vibrations** dialog. You should be able to see whether or not the motions you observe are consistent with the experimental assignments.

Attempt to sketch one of the normal modes of the molecule. The following is an example of this type of drawing for one of the normal modes of water:



10. Close the “Vibrations” menu and remove your molecule from the screen by selecting **Close** from the **File** menu. And **Exit** from the **File** menu to close the program.