CHEM 3110

Name:

**Comparing Homonuclear and Heteronuclear Diatomic Molecules with WebMO**

**Instructions:** This activity can be done on any computer or device with internet access, either through a web browser or the WebMO app (iPhone/iPad or Android). WebMO is a graphical user interface that allows you to set up, submit, and view calculations performed on a remote server. As not everyone will be on campus when completing this activity, we will be using the WebMO demo server at Hope College for this activity. Complete the activity as instructed and submit a copy of your answers to Dropbox.

**Part 1: Introduction to using WebMO**

Follow this link to log into WebMO: <https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi>

* User name: guest
* Password: guest

*To use the WebMO app (instead of the web browser) click on “connect using WebMO app”*

**Build and Optimize Molecular Structures**

***Build and Optimize CH4***

1. Go to “New Job” and select “Create New Job.” A window opens where you build molecules.
2. The default atom that is selected is carbon (selected atom is shown at the bottom of the build window). If you wish to choose a different atom, you may simply type the atom symbol *or* click on the Periodic Table icon, , and choose the atom you want.
3. Click once in the center of the workspace. A black carbon atom appears. (If you click too many times and have extra atoms, choose Edit > Undo).
4. Next click the brush icon . This will activate “Comprehensive Cleanup using Idealized Geometry.” *You should now have methane.* There are additional cleanup techniques under the Cleanup menu item at the top.
5. Experiment with the Rotate , Translate,  and Zoom  tools to view the structure you have built.

*This structure contains idealized bond lengths and angles. A more accurate structure can be found by carrying out a geometry optimization using molecular mechanics, semiempirical methods, density functional theory, or ab initio calculations. In computational chemistry, more accurate results generally come from more “expensive” computational methods (calculations take longer to complete) To balance between accuracy and time required for the calculations, a lower level density functional theory method will be used.*

1. Click the blue “continue” arrow in the lower right side of the Build Molecule window. Choose NWChem as the computational engine (this is the software that is doing the actual calculations). Click the blue “continue” arrow.
2. Type in/Choose the following:
	* Job Name: CH4 Opt\_your initials
	* Calculation: Geometry Optimization
	* Theory: DFT
	* DFT Functional: B3LYP
	* Basis Set: Basic: 3-21G
	* Charge: 0
	* Multiplicity: Singlet
3. Click on the blue “continue” arrow. You should now see your job listed in the job manager. To kill or stop a job, you can click on the red “X” under Actions on the right side.
4. When the status of the job is “complete,” click on the job name to open the “View Job” window.
5. Choose the Select arrow and click on one of the H atoms in the structure (it will be highlighted). The bottom of the build window will show the hybridization and charge of the selected atom. Under preferences you can change your atom labels from symbol to number (index).
6. Click on the C atom (both atoms are now highlighted). The bond length is displayed just below the molecule. Record the values of all the C-H bond lengths in the table. (1.091Å is the experimental literature value). You can “clear” the atom selections by clicking on the background, away from the molecule. Check the other C-H bond lengths.
7. Click on one of the H atoms, then the C atom, followed by another H atom. The bond angle is displayed just below the molecule. Record the values of all the H-C-H bond angles in the table (109.4712° is the experimental literature value).
8. Click on Job Manager under actions to return to the job manager window

|  |  |  |  |
| --- | --- | --- | --- |
| **Bond** | **Bond Length** | **Angle** | **Bond Angle** |
| C(1)-H(2) |  | H(2)-C(1)-H(3) |  |
| C(1)-H(3) |  | H(2)-C(1)-H(4) |  |
| C(1)-H(4) |  | H(2)-C(1)-H(5) |  |
| C(1)-H(5) |  | H(3)-C(1)-H(4) |  |
|  |  | H(3)-C(1)-H(5) |  |
|  |  | H(4)-C(1)-H(5) |  |

***Build and Optimize BF3***

1. Go to New Job and choose Create New Job.
2. Build a B atom. Build 3 F atoms around the B and add bonds by dragging the pointer between the atoms
3. Click the cleanup icon to get the idealized geometry for BF3
4. Click the blue continue arrow. Use Job Name BF3 Opt\_your initials and perform the geometry optimization using the same settings as for CH4.
5. Record the values of the B-F bond lengths (1.3070 Å experimental) and angles (120.00° experimental) in the table.

|  |  |  |  |
| --- | --- | --- | --- |
| **Bond** | **Bond Length** | **Angle** | **Bond Angle** |
| B(1)-F(2) |  | F(2)-B(1)-F(3) |  |
| B(1)-F(3) |  | F(2)-B(1)-F(4) |  |
| B(1)-F(4) |  | F(3)-B(1)-F(4) |  |

**Part 2: Calculating Molecular Orbitals with WebMO**

***Molecular Orbitals of N2***

1. Sketch the MO diagram of N2 including sp mixing. (You can sketch on paper and include a picture here)
2. Return to Job Manager and choose Create New Job.
3. Draw a nitrogen atom. Click on this atom and drag to one side and release. You should now have N-N. Click and drag from the center of one N atom to the center of the other N atom twice to form the triple bond.
4. Click on the cleanup icon to clean up the structure.
5. Click the blue continue arrow and use Job Name N2 Opt\_your initials perform a geometry optimization as before. Before calculating the molecular orbitals (or any other molecular properties) it’s important to have an optimized geometry. Once the job is complete, click on the hyperlinked name to open the “View Job” window.
6. Click the *New Job Using This Geometry* button (at the bottom), click the blue “continue” arrow, choose NWCHem, and type in/choose the following:
	* Job Name: N2 MO\_your initials
	* Calculation: Molecular orbitals
	* Theory: DFT
	* DFT Functional: B3LYP
	* Basis Set: Basic: 3-21G
	* Charge: 0
	* Multiplicity: Singlet
7. Click on the blue “continue” arrow. You should now see your job listed. Once the job is complete, click on the hyperlinked name to open the “View Job” window.
8. Scroll down to the Molecular Orbitals table. Click on the magnifying glass next to one of orbitals to open the orbital viewer window. The orbitals can be manipulated in the molecular viewer window using the rotate, translate and zoom tools.
9. Insert a picture (File > Save image) and describe each of the following orbitals and compare their energies to the relevant atomic orbitals (The atomic unit (au) of energy is the Hartree. 1 Hartree = 27.211 eV). Keep in mind the calculated MOs will include MOs from all atomic orbitals, not just the valence orbitals. A table of atomic orbital energies is posted on D2L.
* 2s σ MO picture/description:

MO Energy: \_\_\_\_\_\_\_ Energy of N 2s: \_\_\_\_\_\_\_

Based on these energies and orbital picture, is the MO bonding or antibonding? How did you come to that conclusion?

What is the relative contribution of each N atom to this MO?

* 2s σ\* MO picture/description:

How is this orbital different from the 2s σ MO? What indicates that this is an antibonding orbital?

* 2p π MO picture/description:

MO Energy: \_\_\_\_\_\_\_

How many degenerate (same energy) MOs of this type are there? How are they related to each other?

* 2p σ MO picture/description:

MO Energy: \_\_\_\_\_\_\_

Does your calculation predict s-p mixing occurs in N2? Explain how you came to this conclusion.

***Molecular Orbitals of BF***

1. BF is an unstable gas that is isoelectronic with N2 Sketch the MO diagram of BF including sp mixing. (If it’s easier, you can sketch on paper and include a picture here)
2. Return to Job Manager and choose Create New Job.
3. Draw a boron atom. Change the atom type to fluorine and click on the boron atom and drag to one side and release. You should now have B-F. Click and drag between the two atoms twice to form a triple bond.
4. Click on the cleanup icon to clean up the structure. Right click on each atom and select charge to make sure the charge is 0 on each atom.
5. Click the blue continue arrow and use Job Name BF Opt\_your initials perform a geometry optimization as before.
6. Click the *New Job Using This Geometry* button and click the blue “continue” arrow. Use the job name BF MO\_your initials and calculate the molecular orbitals of BF using the same settings as for N2.
7. Click on the blue “continue” arrow. Once the job is complete, click on the hyperlinked name to open the “View Job” window.
8. Scroll down to the Molecular Orbitals table. Click on the magnifying glass next to one of orbitals to open the orbital viewer window.
9. Insert a picture or describe each of the following orbital and compare their energies to the relevant atomic orbitals (The atomic unit (au) of energy is the Hartree. 1 Hartree = 27.211 eV).
* 2s σ MO picture/description:

Based on the MO picture does the B or F 2s contribute more to this MO?

* 2p π MO picture/description:

Compare and contrast this MO with the 2p π MO in N2.

* 2p σ MO picture/description:

If you were to remove an electron from BF to form BF+, should the positive charge go on the B or F atom? Explain the reasoning behind your choice.