

**Chemistry 112 Laboratory**  
**Experiment 5: Visualizing Molecular Orbitals:**  
**A MacSpartan Pro Experience**  
(This experiment will be conducted in OR341)

**Introduction**

In class we have discussed Lewis structures, resonance, VSEPR, hybridization and molecular orbitals. These concepts are useful for understanding chemical bonds and molecular shapes. In this experiment you will have the opportunity to use the modern software MacSpartan Pro to draw molecules, calculate their optimum structures, and perform calculations to generate 3-dimensional representations of molecular orbitals.

The molecular orbital approach to chemical bonding is much more powerful than simpler approaches based on valence bond theory. For example, the shapes of molecular orbitals can provide valuable insights into the fundamental question of what holds atoms together in chemical bonds. In addition, molecular orbital calculations can predict the quantized energies of electrons in orbitals, magnetic properties of molecules, locations in molecules where electrons are most concentrated, and a variety of other critical molecular characteristics.

This experiment will provide an opportunity for you to use computers and professional computational chemistry software to calculate and observe shapes of molecular orbitals of a variety of molecules. We hope that you enjoy using the MacSpartan software as you gain a new perspective on molecular orbitals. MacSpartan is a “common thread” through our chemistry curriculum since it is used for related applications in the organic, physical, and advanced inorganic chemistry courses at Macalester College.

**Drawing Structures and Calculations of Molecular Orbitals with MacSpartan**

The best way to learn about MacSpartan is to explore the software with different molecules. Let's explore the molecule  $H_2$  and its molecular orbitals as a first example! **Address each question of this activity in a clear and organized way in your laboratory notebook. The answers to these questions (bulleted) constitute your Experiment 6 laboratory report.**

It is always useful to draw the Lewis structure of a molecule before constructing it in the MacSpartan workspace.

- Copy the analysis of dihydrogen from your ASA into your lab notebook.

In the case of hydrogen, we are familiar with the energy level diagram and its molecular orbitals. Therefore, we know that its energy level diagram features two molecular orbitals ( $\sigma_{1s}$  and  $\sigma^*_{1s}$ ). However, the total number of molecular levels can be calculated for any molecule by simply tallying the number of valence orbitals that each atom possesses. Hydrogen only has one valence orbital (the  $1s$  orbital). When two hydrogen atoms combine to form molecular hydrogen, two molecular orbitals result from the combination of two atomic valence orbitals. The application of this rule (sometimes called the Law of Orbital Conservation) will prove to be invaluable in this activity since it is impossible for MacSpartan to calculate all of the molecular orbitals for a molecule using a single command. **It is very useful to know how many molecular orbitals one is expecting before starting a molecular orbital calculation using MacSpartan Pro.**

OK, now we are ready to draw the molecule!

1. Select **New** from the **File** menu. The Model Kit window will appear. This is your palette for drawing essentially any chemical species (atoms, molecules, ions, or even groups of molecules/ions).
2. In Entry mode (the palette default) of the Model Kit window, select the hydrogen atom. A tetrahedral carbon is generally selected initially when the palette is opened.
3. Click once on the screen to place a hydrogen atom in the workspace.
4. Now click on the “half-bond” of the hydrogen atom to attach the second hydrogen atom.
5. Select **Calculations...** from the **Setup** menu. The resulting window can be used to establish appropriate parameters for the calculation. Under the “Calculate” heading select “**Equilibrium Geometry**” with “**Semi-Empirical**” and “**AM1**”. The latter two terms refer to the type of calculation that will be employed. “**Initial geometry**” should be indicated under the “Start from” heading. The only other options that should be checked in the window are “**symmetry**” and “**apply globally**”. Click OK once your selections in this window are complete.
6. The goal of this calculation is to calculate the molecular orbital surfaces of hydrogen. Our next step is to request the orbitals we want to examine. Select **Surfaces** under the **Setup** menu. A “Surfaces” window will appear.
7. In the **Surfaces** window, click on “**Add**”. Now we need to select the orbitals we want to calculate. Under “Surface”, select **HOMO** and then OK. HOMO should appear in the surfaces window. HOMO is shorthand for **Highest Occupied Molecular Orbital**. This is the orbital of highest energy for a molecule that contains electrons. We already know that the hydrogen molecule only has one occupied molecular orbital ( $\sigma_{1s}$ ) so this is also the HOMO. The empty molecular orbital that is closest in energy to the HOMO is called the LUMO (**Lowest Unoccupied Molecular Orbital**). This is also called  $\sigma_{1s}^*$  for our hydrogen molecule. To select LUMO, click on “**Add**”, choose **LUMO** from the “Surface” heading, and then click OK. Both hydrogen molecular orbitals should now be listed in the Surfaces window.
8. Now we are ready to start the calculation! Select **Submit** under the **Setup** menu. Since this is the first time you are using MacSpartan today, you will be asked to save your molecule. Use your name or a similarly generic tag to name your file, as the same name will be used throughout this experiment. Click on Save, then click OK to acknowledge that the calculation has started. Click OK again when the calculation has completed.
9. Before we examine the molecular orbitals, let’s “play” with our optimized hydrogen molecule to learn more about MacSpartan Pro. (You can skip this if you remember it!)
10. Enlarge/Reduce the Molecule: Depress the option and apple keys simultaneously while dragging the mouse in the appropriate direction to achieve the desired effect.
11. Molecule Representation: The way in which a molecule is displayed can be changed by switching between the “wire”, “ball and wire”, “tube”, “ball and spoke”, and “space filing” options under the **Model** menu. Try out these different options for fun.

12. Move the Molecule: Depress the mouse and option key simultaneously while moving the mouse.
  13. Rotate the Molecule in the X/Y Plane: Click on the background and drag the mouse in the desired direction.
  14. Rotate the Molecule in the Z Plane: Depress the mouse and apple key simultaneously while dragging the mouse in the desired direction.
  15. Now let's look at the molecular orbitals! In the Surfaces window (if you've closed it, bring it up by selecting **Surfaces** under the **Display** menu), select the HOMO box: the  $\sigma_{1s}$  molecular orbital should appear. Note that the same mouse/keyboard functions described earlier can be used to move, rotate, or scale these orbitals.
  16. The orbitals can be displayed in different ways as well. Click on the molecular orbital to select it (a yellow circle will appear around it). Select **Properties** under the **Display** menu. Adjust the "style" from "solid", "dots", "transparent" and "mesh" (my personal favorite) to examine your options. Note that the "**Properties**" window can be toggled between "Surface Properties" and "Molecule Properties" by clicking on the orbital or the background. In this experiment, we will only need to use the "Surface Properties" window.
  17. When you are finished examining the  $\sigma_{1s}$  orbital, go back to the "Surfaces" window (**Surfaces** under the **Display** menu). Deselect HOMO and choose LUMO to display the  $\sigma_{1s}^*$  orbital. Note that both the HOMO and LUMO can be displayed simultaneously if desired.
  18. Notice the node between the two hydrogen nuclei in the LUMO. This is a diagnostic feature of a  $\sigma$  antibonding orbital. The software employs different colors to indicate lobes with opposite wavefunction signs (these waves destructively interfere when the atomic orbitals come together and the result is a node - a region of zero electron density). In this case, one lobe is blue while the other is red. In the case of the HOMO, there is no node between the nuclei and the molecular orbital features the same wavefunction sign throughout (all the same color). The HOMO is classified as  $\sigma$  bonding since electron density exists in the area directly between the nuclei. This is the orbital that is responsible for the single bond in hydrogen.
- **Construct an energy level diagram for hydrogen in your laboratory notebook.** (include the appropriate hydrogen atomic orbitals on the left and right with the resulting molecular orbitals in the center). **Label** each molecular orbital using both the scheme provided in Chapter 11 and the scheme used by MacSpartan Pro (HOMO/LUMO). Include the appropriate orbital electron occupation in your diagram. Finally, **sketch** each surface adjacent to the corresponding energy level. Shade your lobes (or leave them unshaded) to indicate different wave function signs.
  - How does your electron classification based on the  $H_2$  Lewis structure compare with the results of the molecular orbital analysis (i.e., do the sigma, pi, and nonbonding electron counts agree between the two methods)? Explain.
22. When you are completely finished with hydrogen and its orbitals, delete your molecule by choosing **Select All** and then **Cut** from the **Edit** menu. (If **Select All** is greyed out, click on the green background screen to activate it.) You might see some funny stuff on the screen, but it

should disappear when you click on the + button, or select **Add Fragment** from the **Build** menu, We strongly recommend AGAINST (further) use of using **Open**, **Close**, or **New** on the **File** menu. We also advise against using **Clear** on the **Edit** menu, since using that will clear out the surfaces menu. The suggested approach keeps the surfaces you have already entered, which saves a lot of time in this lab!

Let's proceed to other molecules! We'll start with the same general protocol.

## N<sub>2</sub>

- Copy your analysis of dinitrogen from your ASA into your lab notebook.

Draw a molecule of nitrogen in the workspace using the same general protocol employed for hydrogen (start with #2 of the previous list). Your Lewis structure should clearly indicate which atoms you need to connect from the Model Kit "Entry" window. All selections should be the same in the "Calculation" window as they were for hydrogen. Add the following orbital labels to the "Surfaces" window before submitting the calculation: LUMO+14, LUMO+13, LUMO+12, LUMO+11, LUMO+10, LUMO+9, LUMO+8, LUMO+7, LUMO+6, LUMO+5, LUMO+4, LUMO+3, LUMO+2, LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2, HOMO-3, HOMO-4, HOMO-5, HOMO-6, HOMO-7, HOMO-8, HOMO-9, HOMO-10, HOMO-11, HOMO-12, HOMO-13, HOMO-14. Sorry, I know the entry system is a pain, but there's no faster way. This list consists of many more molecular orbitals than dinitrogen actually has, but by entering all of these now you avoid having to worry about adding anything further to the Surfaces window as you go through the lab. Non-existent orbitals will not be calculated by MacSpartan, and simply show up as "pending," even after you **Submit** the molecule for calculation.

Examine each occupied orbital surface in dinitrogen and then answer the following questions:

- Sketch all of the molecular orbitals calculated by MacSpartan, (with appropriate shading of the lobes) and classify each as  $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$  or n (nonbonding). A nonbonding molecular orbital is one that is neither bonding nor antibonding in character. For a diatomic molecule, a nonbonding molecular orbital features an unchanged atomic orbital on one of the molecule's atoms. Although every energy level diagram features bonding and antibonding molecular orbitals, nonbonding orbitals are less pervasive.
- How are the LUMO and LUMO+1 orbitals related to each other? HOMO-1 and HOMO-2? (HINT: Examine these orbital surfaces simultaneously.) What term describes sets of orbitals that are related in this fashion?
- Construct an energy level diagram for nitrogen (include the appropriate atomic orbital energy levels and labels on the left and right, and place the appropriate molecular orbital energy levels in the center). Label each molecular orbital using both the designations used by MacSpartan (HOMO-4, etc.) and the standard nomenclature ( $\sigma$ ,  $\pi$ , etc.). Indicate the electron occupation in your diagram as well.
- How do your molecular orbital results compare with your previous responses based on the Lewis structure of nitrogen? Are the Lewis structure and Molecular Orbital approaches more compatible for hydrogen or nitrogen?

Remember, the best way to get rid of N<sub>2</sub> and prepare for working on your next molecule is **Select All** and then **Cut** from the **Edit** menu, followed by **Add Fragment** from the **Build** menu.

Let's try **CO** next!

- Copy your analysis of carbon monoxide from your ASA into your lab notebook.

It is best to use the “**Expert**” mode within the Model Kit window for building carbon monoxide. Begin by selecting carbon as the “element.” Select the “-X” box, since carbon is only linked to one other atom in CO. Click on the workspace to add this carbon. Then, select the type of bond that carbon makes to oxygen in your Lewis structure from the choices in the third row of rectangular options, and double-click on center of the bond to change it to the correct type. Next, change the element to oxygen by clicking on the element box, and then click on the existing bond from carbon to add it to your structure (the other parameters should remain unchanged).

The rest of the procedure can be followed as before. Be sure to **Submit** your molecule for calculation, and then carefully examine each orbital.

- Sketch the shapes of the  $\pi$  and  $\pi^*$  orbitals of carbon monoxide and provide their MacSpartan Pro labels (HOMO-4, etc.). Compare these orbitals with the  $\pi$  and  $\pi^*$  orbitals of N<sub>2</sub>. Account for the difference in the shapes of these orbital sets for these two molecules. (HINT: Consider electronegativity!)
- On the basis of the molecular orbitals, account for the triple bond in this molecule (*i.e.*, Which orbitals are occupied and what bond order does this suggest?).

Our world would be pretty boring if it only contained diatomic molecules! Let's try some molecules that are more sophisticated!

### O<sub>3</sub>

- Copy your analysis of ozone from your ASA into your lab notebook.

The concept of resonance is more readily understood using molecular orbital theory than it is with Lewis structures. The resonance structures for ozone indicate that two electrons are delocalized simultaneously over both oxygen-oxygen linkages. We first need to envision electrons as waves and not particles if we hope to conceptualize this idea. Particles are inherently “localized” while a wave can be spread out between two points (or in this case, between three atoms).

For electrons to be delocalized over more than two atoms, a molecular orbital must be available that extends over the atoms involved. We typically think about delocalization involving  $\pi$  orbitals. Let's treat ozone with molecular orbital theory and discover the molecular orbital that permits its two electrons to “spread out” over all three oxygen atoms.

Ozone is best built in the “Expert” mode of the Model Kit window. Select oxygen as the element. Now select the icon from the first two rows that best represents the geometry around the central oxygen atom. Insert the central oxygen atom, and then adjust the bonds to indicate that the oxygen-oxygen bonds formally possess a bond order of 1.5 by selecting the line + dashed line icon and double-clicking on the

centers of the two half bonds on your oxygen. (This bond order can be deduced by examining the ozone resonance forms.)

The terminal oxygens can be added by changing the “X” icon to “-X” and clicking on the half bonds in the workspace. (You don’t have to worry about setting the bond type, as these are automatically matched to the half-bond you click,) You may need to rotate the central fragment first to permit easy access to its half-bonds. Once you have built ozone, **Submit** it.

Examine each molecular orbital. It is sometimes helpful to change the “percentage of the surface displayed” for these orbitals to ease their classification. To do this for an orbital, select “**Properties**” under the **Display** menu when a molecular orbital surface is in the workspace. We are interested in the surface properties window. Adjust the “Isovalue” to 0.070 for an ozone orbital. Hit return to cause the isovalue change. This lowers the percentage of the displayed surface. Feel free to adjust the isovalue to facilitate your classification of any surface.

- Which molecular orbital best accounts for the delocalization of  $\pi$  electrons in this molecule? Provide the corresponding label (i.e., LUMO+1, etc.) and sketch the orbital below. Which oxygen atomic orbitals constructively interfere to generate this molecular orbital?

Let’s try ethylene next!

### **C<sub>2</sub>H<sub>4</sub>**

- Copy your analysis of ethylene from your ASA into your lab notebook.

Generate this molecule using the “Entry” mode of the Model Kit window. Calculate and inspect its molecular orbitals.

- Identify and sketch all the  $\pi$  and  $\pi^*$  orbitals of ethylene. Be careful when making your selections- the “mesh” display mode might be most helpful as you examine each orbital and make your classifications.
- Would you expect the CH<sub>2</sub> groups to rotate freely about the C=C bond? Why or why not?

### **C<sub>2</sub>H<sub>2</sub>**

- Copy your analysis of acetylene from your ASA into your lab notebook.

Generate this molecule using the “Entry” mode of the Model Kit window. Calculate and inspect its molecular orbitals.

- Identify and sketch all the  $\pi$  and  $\pi^*$  orbitals of acetylene. Indicate the relative orientations of these orbitals in your sketches.

### **C<sub>6</sub>H<sub>6</sub>**

- Copy your analysis of benzene from your ASA into your lab notebook.

Benzene is trivial to construct if one selects it from the rings list in the “Entry” mode of the Model Kit window. Click on the screen to add benzene to the workspace.

- Which orbitals in benzene are involved in  $\pi$  bonding? Provide the label for every molecular orbital of benzene that is either  $\pi$  or  $\pi^*$  (both occupied and unoccupied).
- Sketch the lowest energy  $\pi$  molecular orbital. How does this orbital account for the delocalization of  $\pi$  electrons in benzene?

We haven't done any charged species yet. Let's try the polyatomic nitrate anion as our last example!



- Copy your analysis of nitrate ion from your ASA into your lab notebook.

Construct this molecular ion using the appropriate icons in the “Expert” mode of the “Model Kit” window. Use the same bond type that was used for ozone since these species feature delocalization of  $\pi$  electron density (both ozone and benzene also possess bonds of formal 1.5 bond order). The only difference in the setup process from the other molecules in this activity is that you will need to indicate that this is an **Anion** in the “Total Charge” prompt of the “Calculations” window.

Calculate and inspect the molecular orbitals of nitrate ion:

- Which of these molecular orbitals permits the most effective delocalization of its  $\pi$  electrons? Sketch this molecular orbital and provide its label.
- Which  $\sigma$  molecular orbital is lowest in energy? Sketch this molecular orbital and provide its label. What distinguishes this surface from the other  $\sigma$  molecular orbitals?

Please **Log Out** of your computer when you are finished. To do so, click on the smiley face icon furthest to the right in the “Dock” at the bottom of the screen, then pick **Log Out Macalester...** from the **Apple** menu. Logging out will remove all the files and folders you generated while using the computer, so don't worry about “cleaning up” before you do so. Thanks!

## Experiment 5: Visualizing Molecular Orbitals: A MacSpartan Pro Experience Advance Study Assignment

Please provide the answers to the following questions on this sheet of paper. You should complete this ASA before you arrive for your lab.

For each of the following molecules, do or answer the following:

- Draw the Lewis structure, including relevant resonance forms
- Indicate the bond order(s) in your molecule
- Indicate the number of valence electrons that populate the molecular orbitals of the molecule
- Based on your Lewis structure, how many of these electrons are classified as sigma ( $\sigma$ ) type? (HINT: The first bond between any two atoms is sigma; additional bonds are pi!)
- Based on your Lewis structure, how many of these electrons are classified as pi ( $\pi$ ) type?
- Based on your Lewis structure, how many electrons should be classified as nonbonding? (HINT: Nonbonding electrons are represented as lone pairs in a Lewis structure)
- How many total molecular orbitals do you anticipate for this molecule? (HINT: The total number of molecular orbitals can be calculated for any molecule by simply tallying the number of valence orbitals that the atoms in the molecule possess.)

The dihydrogen molecule ( $H_2$ ) is done for you here as an example:

- |   |  |
|---|--|
| a. H—H                                    | d. 2 $\sigma e^-$ (in the one single bond)                                       |
| b. B.O. = 1 (2 bonding electrons / 2 = 1) | e. 0 $\pi e^-$ (there are no double or triple bonds)                             |
| c. 2 valence $e^-$                        | f. 0 nonbonding electrons (no lone pairs)  |
|   | g. We anticipate 2 MO's (each H atom brings one 1s valence orbital to the table) |

Now it's your turn! Start with an analysis of dinitrogen,  $N_2$ :

Now, that wasn't *too* bad, right? Of course, it gets harder. Try carbon monoxide, CO:

Hey, you're getting good at this! Give ozone ( $O_3$ ) a whirl: it is NOT a ring, it's a bent molecule!

Next, give ethylene a whirl ( $C_2H_4$ ):

On a somewhat similar note, try acetylene next. It's  $C_2H_2$ :

Now things get a bit harder. Give benzene your best shot. It is  $C_6H_6$ , and consists of a ring of six carbon atoms. It has a large number of molecular orbitals, but certainly not too many to count!

Lastly, perform the same analysis on the familiar nitrate ion ( $NO_3^-$ ). You learned in the previous lab that the central atom has a steric number of three, and that the nitrate ion exhibits resonance.