

153

153

125 possible w/o ~~structure~~

HF and



KEY

Name(s) _____

105

Visualizing Molecular Orbitals: A MacSpartan Pro Experience

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.

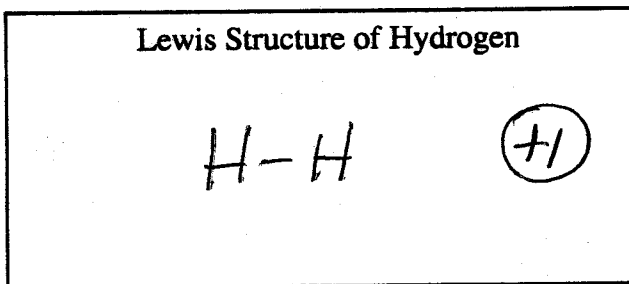
The molecular orbital approach to chemical bonding (pp. 404-414 of Silberberg) is much more powerful than simpler approaches based on Valence Bond Theory (p. 393). For example, the shapes of molecular orbitals can provide valuable insights into the fundamental question of what holds atoms together in 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!

1. It is always useful to draw the Lewis structure of a molecule before constructing it in the MacSpartan workspace. Draw the Lewis structure of H_2 below and then answer the following questions.



How many total valence electrons populate the molecular orbitals of this molecule?

2 (+1)

Based on your Lewis structure, how many of these electrons are classified as sigma (σ) type?

2 (+1)

Based on your Lewis structure, how many of these electrons are classified as π type?

0 (+1)

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)

0 (+1)

How many total molecular orbitals do you anticipate for this molecule?

2 (+1)

In the case of hydrogen, we are familiar with the energy level diagram and its molecular orbitals (p. 405 of our text). Therefore, we know that its energy level diagram features two molecular orbitals (σ_{1s} and σ^*_{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!

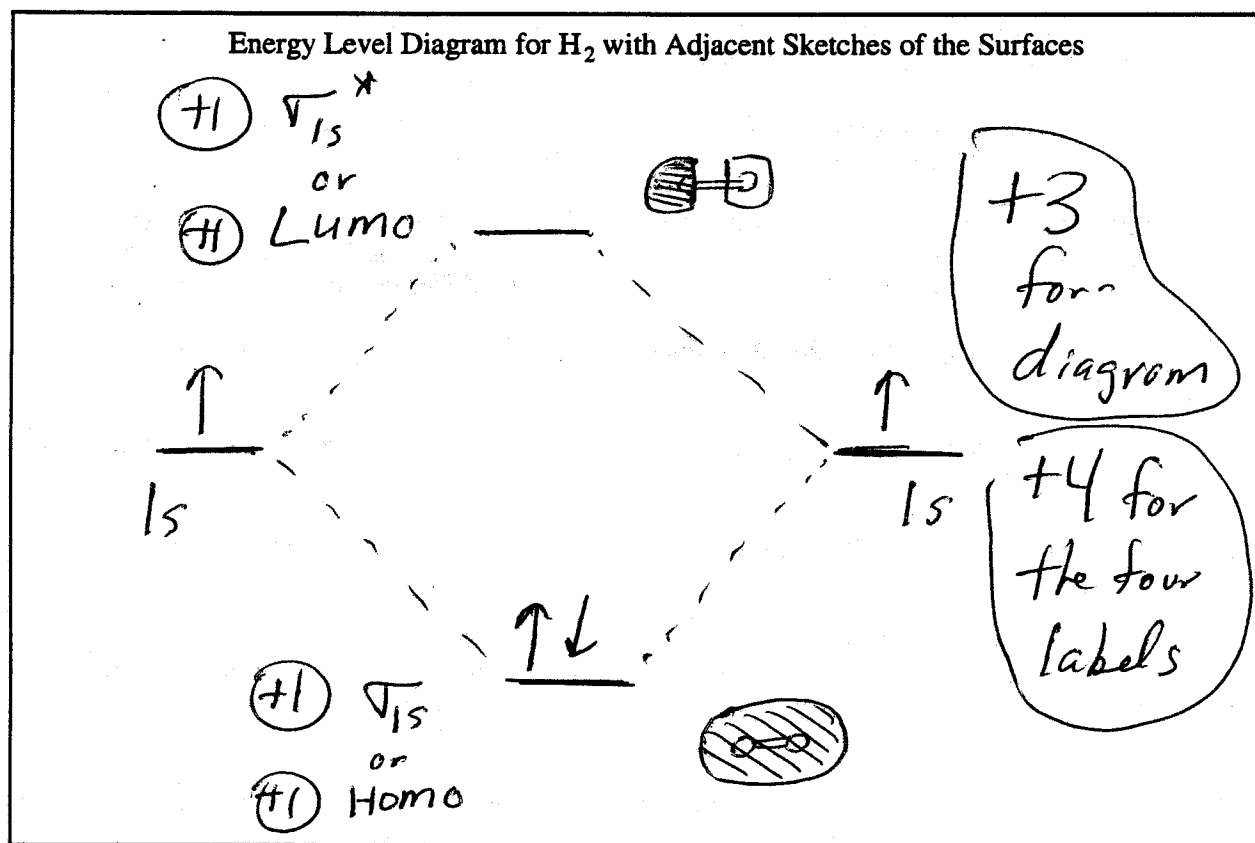
2. Select **New** from the **File** menu. The Model Kit window will appear. This is your palette for drawing essentially any chemical species (atoms, molecules, ions, or even groups of molecules/ions).
3. In Entry mode (the palette default) of the Model Kit window, select the hydrogen atom. A tetrahedral carbon is generally selected initially when the palette is opened.
4. Click once on the screen to place a hydrogen atom in the workspace.
5. Now click on the "half-bond" of the hydrogen atom to attach the second hydrogen atom.
6. Select **Minimize** under the **Build** menu. This triggers an initial optimization of the structure. This isn't really necessary for the simple hydrogen molecule but is a good habit to get into for more sophisticated molecules.
7. Return to view mode by selecting **View** from the **Build** menu.
8. It is necessary to save every structure before beginning calculations. First create a folder for your group within the User Folder of the hard disk. Save your structure to this new folder by selecting **Save As** from the **File** menu. Use an obvious name that will be easy to remember.
9. 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.

2/2

10. 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.
11. 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 (σ_{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 σ_{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. This window can now be closed.
12. Now we are ready to start the calculation! Select **Submit** under the **Setup** menu. Click OK to acknowledge that the calculation has started and then completed.
13. Before we examine the molecular orbitals, let's "play" with our optimized hydrogen molecule to learn more about MacSpartan Pro.
14. Enlarge/Reduce the Molecule: Depress the option and apple keys simultaneously while dragging the mouse in the appropriate direction to achieve the desired effect.
15. 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.
16. Move the Molecule: Depress the mouse and option key simultaneously while moving the mouse.
17. Rotate the Molecule in the X/Y Plane: Click on the background and drag the mouse in the desired direction.
18. Rotate the Molecule in the Z Plane: Depress the mouse and apple key simultaneously while dragging the mouse in the desired direction.
19. Now let's look at the molecular orbitals! Select **Surfaces** under the **Display** menu. Select the HOMO box and the σ_{1s} molecular orbital should appear. Note that the same mouse/keyboard functions described earlier can be used to move, rotate, or scale these orbitals.
20. 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.
21. When you are finished examining the σ_{1s} orbital, go back to the "Surfaces" window (**Surfaces** under the **Display** menu). Deselect HOMO and choose LUMO to display the σ_{1s}^* orbital. Note that both the HOMO and LUMO can be displayed simultaneously if desired.

22. Notice the node between the two hydrogen nuclei in the LUMO. This is a diagnostic feature of a σ 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 σ 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 below (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.

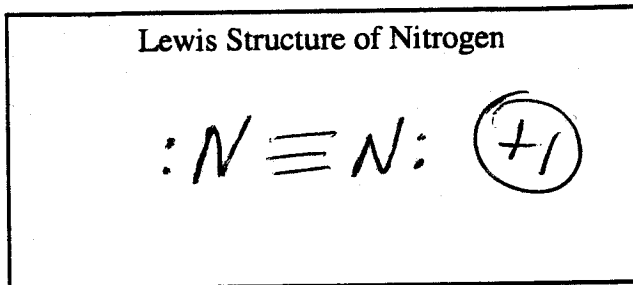
$+4$ Yes, the Lewis structure predicts that hydrogen has neither nonbonding nor pi electrons and this is consistent with the molecular orbital outcome. Both electrons in H_2 are σ type; this is the conclusion of both the Lewis structure and M.O. analysis.

23. When you are completely finished with hydrogen and its orbitals, select **Close** under the **File** menu. The file doesn't need to be saved. It is important to officially "Close" each molecule before starting another experiment.

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

N_2

Draw the Lewis structure of N_2 :



How many total valence electrons populate the molecular orbitals of this molecule?

10 (+1)

Based on your Lewis structure, how many of these electrons are classified as sigma (σ) type?

2 (+1)

Based on your Lewis structure, how many of these electrons are classified as π type?

4 (+1)

Based on your Lewis structure, how many electrons should be classified as nonbonding?

4 (+1)

How many total molecular orbitals do you anticipate for this molecule?

8 (+1)

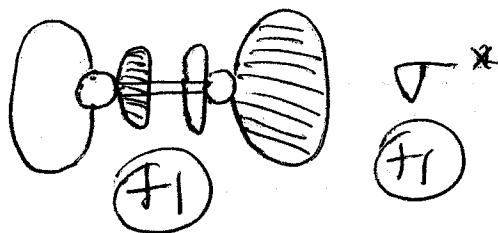
Draw a molecule of nitrogen in the workspace using the same general protocol employed for hydrogen (start with #2 of the previous list). Your Lewis structure should clearly indicate which atoms you need to connect from the Model Kit "Entry" window. All selections should be the same in the "Calculation" window as they were for hydrogen. Add the following orbital labels to the "Surfaces" window before submitting the calculation: LUMO+2, LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2, HOMO-3, HOMO-4. This number of orbitals should match your response to the final question above.

Examine each orbital surface and then answer the following questions.

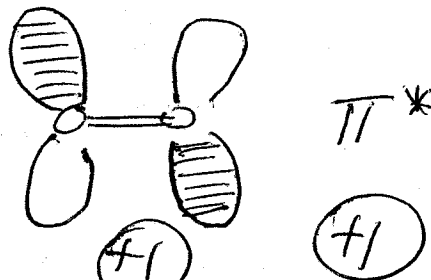
(6/6)

Sketch each orbital (with appropriate shading of the lobes) and classify each as σ , σ^* , π , π^* 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.

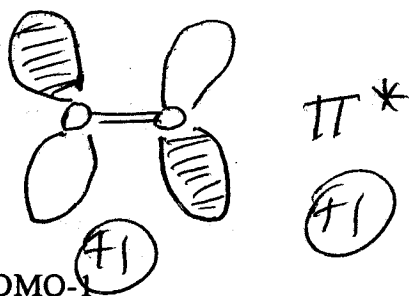
LUMO+2



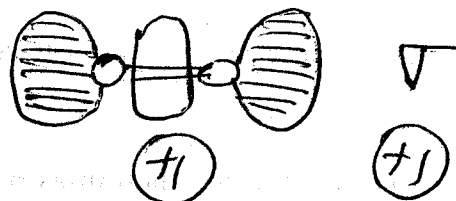
LUMO+1



LUMO

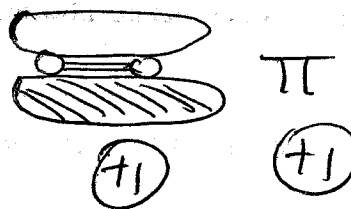
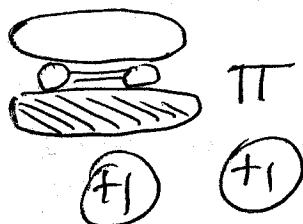


HOMO



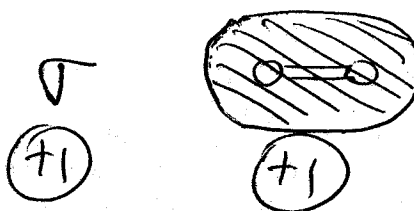
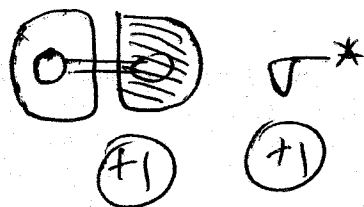
HOMO-1

HOMO-2



HOMO-3

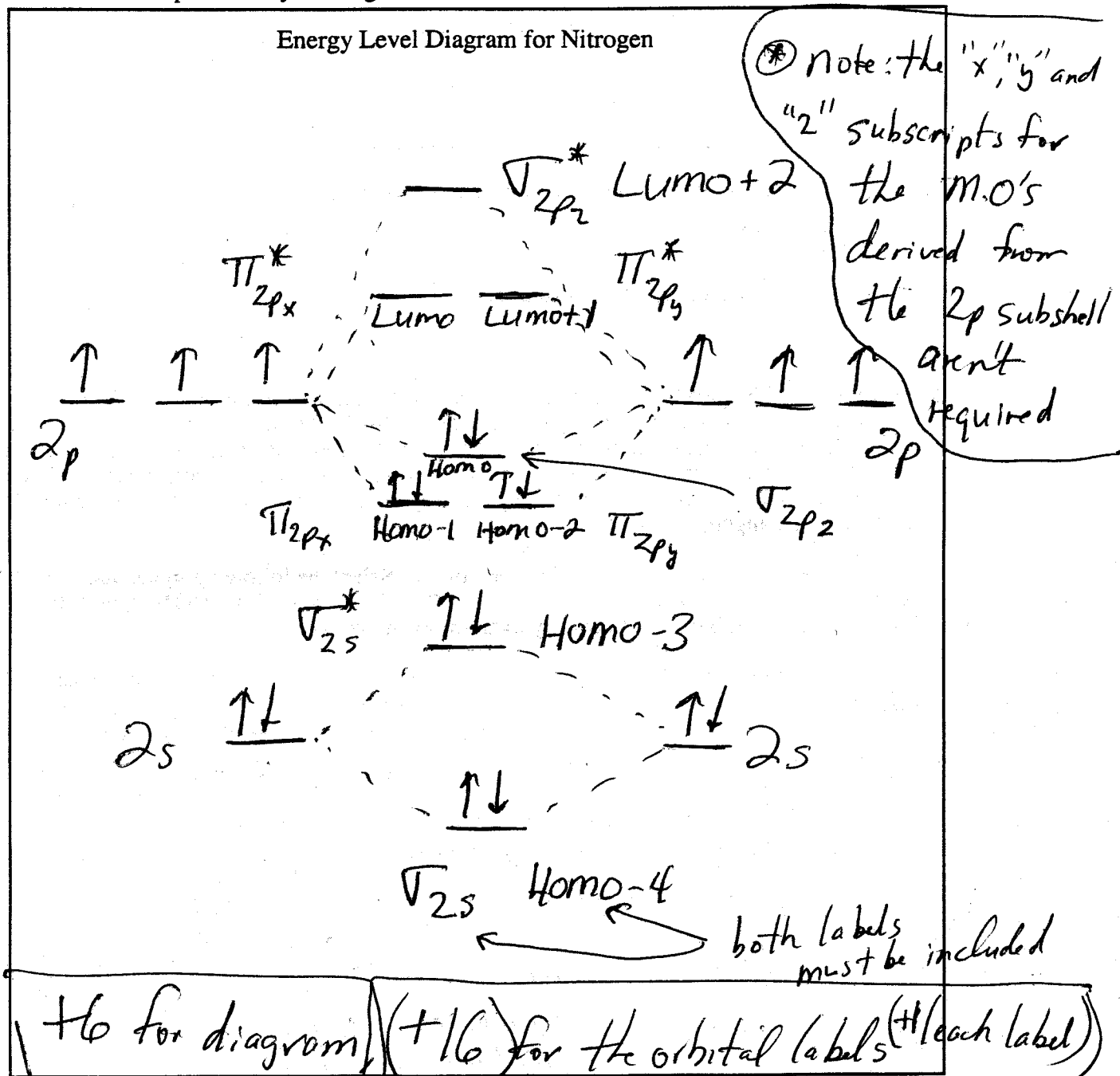
HOMO-4



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?

(+2) These orbital sets have the exact same shapes but are oriented ^{at a 90° angle} (orthogonal) with respect to each other. These orbitals are degenerate (have the same energy) (18/15)

Construct an energy level diagram for nitrogen below (include the appropriate atomic orbitals on the left and right with the molecular orbitals in the center). Label each molecular orbital using those used by MacSpartan (HOMO-4, etc.) and your own labels (σ , π , etc.). Include the appropriate orbital electron occupations in your diagram.



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?

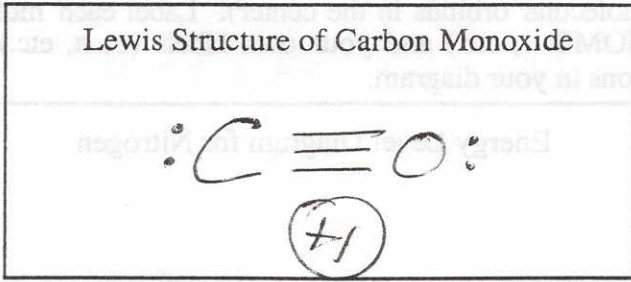
25/25

	<u>Lewis structure conclusion</u>		<u>M.O conclusion</u>	M.O. and Lewis
σ	2	<div style="border: 1px solid black; border-radius: 50%; width: 40px; height: 40px; display: flex; align-items: center; justify-content: center;"> +3 </div>	6	structure approaches are more compatible for hydrogen
π	4		4	
nonbonding	4		0	

Let's try CO next! Start by constructing the Lewis structure below:

the electron density is more likely to reside on the less electronegative carbon

electron density is more likely to reside on the less electronegative carbon. In the π^ MOs*



How many molecular orbitals are expected for this molecule?

(+1) 8

How many electrons will occupy these orbitals?

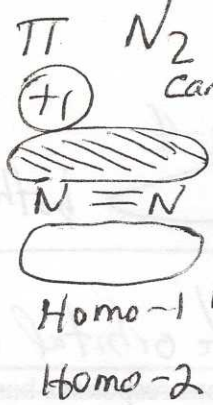
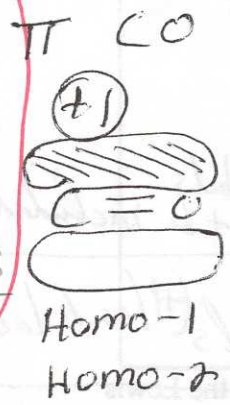
(+1) 10

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. Finally, select the type of bond that carbon makes to oxygen in your Lewis structure from the choices in the third row of square options. Click on the workspace to add this carbon. Next change the element to oxygen by clicking on the element box (the other parameters should remain unchanged).

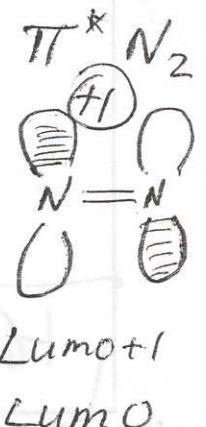
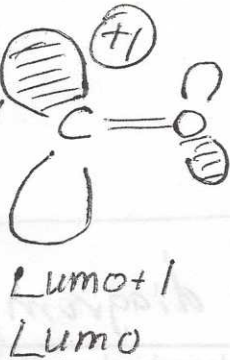
The rest of the procedure can be followed as previously. Select the following molecular orbital surfaces before beginning the calculation: LUMO+2, LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2, HOMO-3, HOMO-4. Carefully examine each orbital.

Sketch the shapes of the π and π^* orbitals of carbon monoxide and provide their MacSpartan Pro labels (HOMO-4, etc.). Compare these orbitals with the π and π^* orbitals of N_2 . Account for the difference in the shapes of these orbital sets for these two molecules (HINT: Consider electronegativity).

+2 for comment
NOTE - not + since 0 is similar you checked to 0



Since oxygen is more electronegative than carbon, the π bonding orbital in CO should have more density towards the oxygen while the nonpolar N_2 should have an equal distribution of electron density in its π orbital.



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?).

- HOMO-4 is occupied $2e^-$ this is a σ bonding orbital (+4)
- HOMO-3 is occupied $2e^-$ this is a σ^* orbital
- HOMO-2 is occupied $2e^-$ this is a π bonding orbital
- HOMO-1 is occupied $2e^-$ this is a π bonding orbital
- HOMO is occupied $2e^-$ this is a σ bonding orbital

Bond Order = $\frac{1}{2}(8-2) = 3$

↑ ↑
bonding antibonding

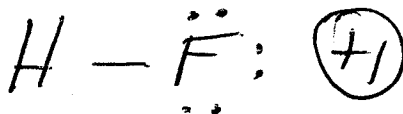
Should this question be exact?

It is difficult to tell any difference with MacSpartan. However, CO

13/13

How about HF? This diatomic molecule is very dangerous since it can etch glass. Don't worry about any damage to your computer screen, however! :o)

Lewis Structure of Hydrogen Fluoride



How many molecular orbitals are expected for hydrogen fluoride?

5 $\textcircled{+1}$

How many electrons will occupy these orbitals?

8 $\textcircled{+1}$

This molecule is can be constructed in "Entry" mode of the Model Kit window. Follow the same procedure as described previously. Select LUMO, HOMO, HOMO-1, HOMO-2, and HOMO-3 as the desired molecular orbitals before submitting the calculation.

It is sometimes helpful to change the "percentage of the surface displayed" for these orbitals to ease their classification. To do this for each 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 each of the hydrogen fluoride orbitals. 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.

Classify each surface as σ , σ^* , π , π^* or n (nonbonding).

LUMO σ^* $\textcircled{+1}$

HOMO $\textcircled{+1}$ n (Simply a F 2p orbital)

HOMO-1 n (Simply a F 2p orbital) $\textcircled{+1}$

HOMO-2 σ $\textcircled{+1}$

HOMO-3: Nonbonding (Note: Although your surface may appear "bonding", a more exact calculation would indicate this orbital as nonbonding.)

Based on the molecular orbitals, account for the single bond of HF.

HOMO-3 $2e^-$ (nonbonding)

HOMO-2 $2e^-$ (σ bonding)

HOMO-1 $2e^-$ (nonbonding)

HOMO $2e^-$ (nonbonding)

Bond Order = $\frac{1}{2}$ (bonding - antibonding)

$$= \frac{1}{2} (2 - 0) = \textcircled{1}$$

Single bond!

$\textcircled{+4}$

Based on Molecular Orbital Theory, where are the nonbonding electrons of HF "localized"? (i.e., what atomic orbitals do they occupy?). Compare and contrast the Lewis structure and the Molecular Orbital Theory conclusions regarding the nonbonding electrons. (HINT: Is the number of nonbonding electrons the same in both models? Think about the Lewis structure lone pair "locations" in terms of VSEPR theory. Is this view of the nonbonding electrons compatible with the Molecular Orbital Theory outcome?) Discuss.

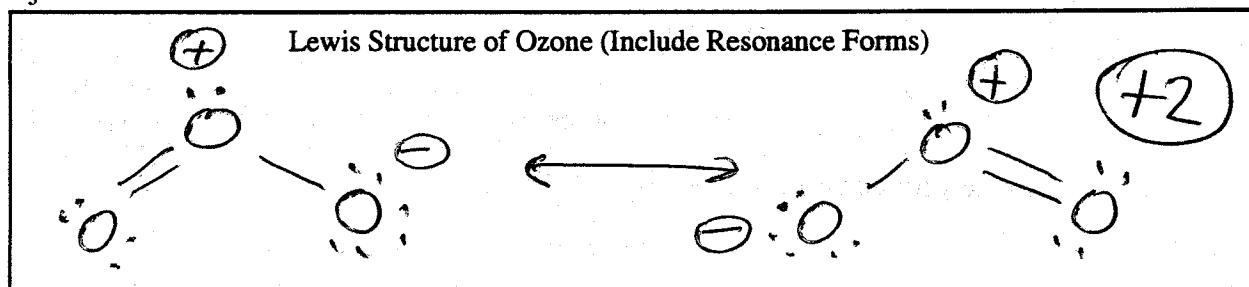
+4 • nonbonding electrons are localized in 2 2p orbitals of F and the HOMO-3. The Lewis structure also predicts 6 nonbonding electrons but it predicts that they will be in equivalent positions (sp^3 hybrid orbitals) on F

i.e. $H-F$ sp^3 hybridized } not all in the same type of orbital in

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

M.O. theory.

O₃



The concept of resonance is more readily understood using molecular orbital theory compared to analyzing 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 π 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.

How many molecular orbitals do you expect for ozone?

\uparrow --- 2p
2s
 $4 \times 3 = 12$

~~15~~ 12 (+1)

18 (+1)

How many valence electrons will occupy these orbitals?

8/8

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. Once you have made your selection, correctly choose the bond type (second from the left of the third row of icons) to indicate that the oxygen-oxygen bonds formally possess a bond order of 1.5. This can be deduced by examining the ozone resonance forms. Click the central oxygen onto the workspace.

The terminal oxygens can be added by changing the "X" icon to "-X" and clicking on the half bonds in the workspace. You may need to rotate the central fragment first to permit easy access to its half-bonds.

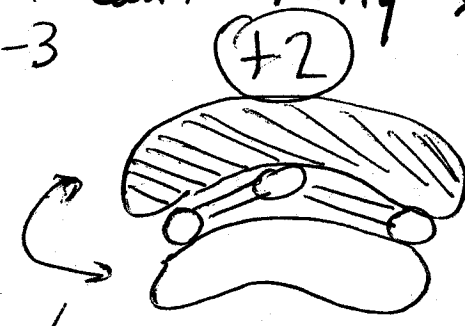
Minimize the structure and then set up the calculation as usual. Choose the following molecular orbital surfaces before submitting the calculation: LUMO+2, LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2, HOMO-3, HOMO-4, HOMO-5, HOMO-6, HOMO-7, HOMO-8.

Examine each molecular orbital (feel free to adjust the Isovalue to 0.070 if desired)

Which molecular orbital best accounts for the delocalization of π 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?

→ can't specify x vs. y vs. z

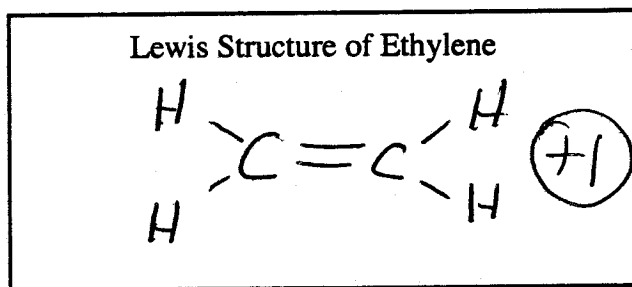
HOMO-3



3 oxygen $2p$ orbitals that are perpendicular to the plane of the atoms can combine to generate this molecular orbital ($2p_z$ orbitals)

Let's try ethylene next!

C_2H_4



How many molecular orbitals do you expect for ethylene?

12 (+1)

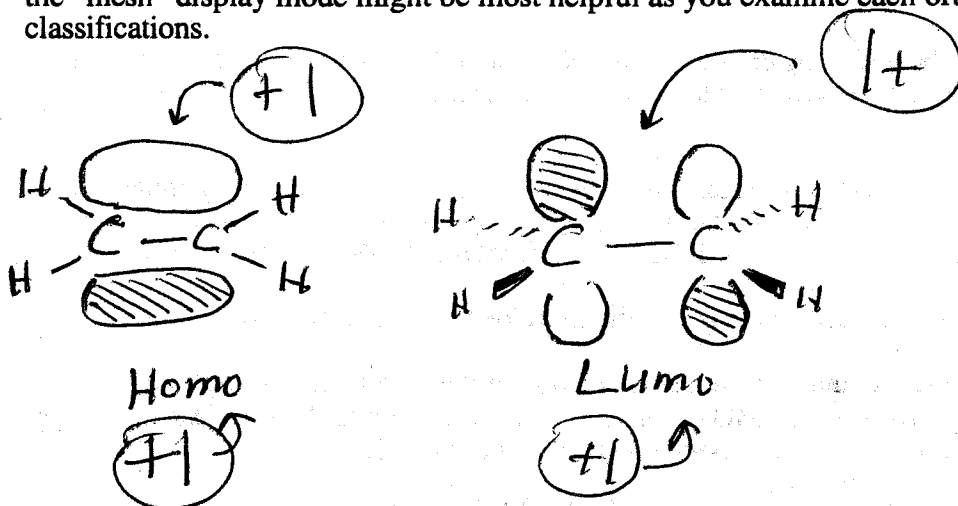
How many valence electrons will occupy these orbitals?

12 (+1)

~~6~~ 6 (+1)

Generate this molecule using the "Entry" mode of the Model Kit window. Calculate and inspect the following surfaces: LUMO+5, LUMO+4, LUMO+3, LUMO+2, LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2, HOMO-3, HOMO-4, HOMO-5.

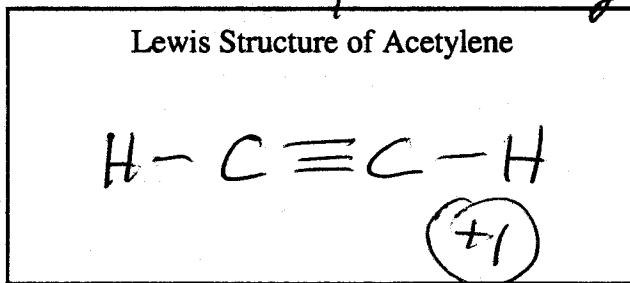
Identify and sketch all the π and π^* orbitals of ethylene. Be careful when making your selections- the "mesh" display mode might be most helpful as you examine each orbital and make your classifications.



Would you expect the CH_2 groups to rotate freely about the $\text{C}=\text{C}$ bond? Why or why not?

(+3) No, the HOMO is responsible for the $\text{C}=\text{C}$ bond. For the CH_2 groups to rotate, the overlap required for this orbital to exist would need to be compromised (bond rotation requires breaking of the π bond!).

C_2H_2 (acetylene)



How many molecular orbitals do you expect for acetylene?

10 (+1)

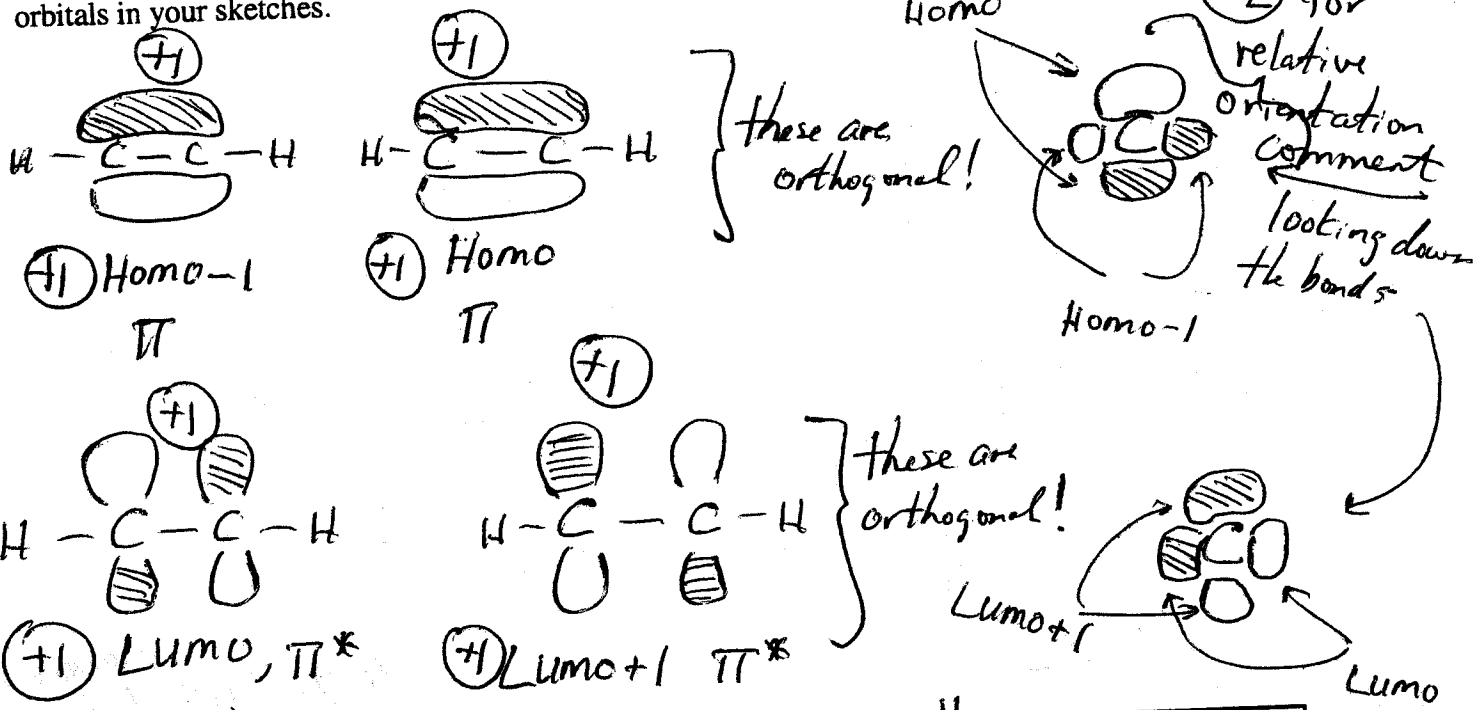
How many valence electrons will occupy these orbitals?

10 (+1)

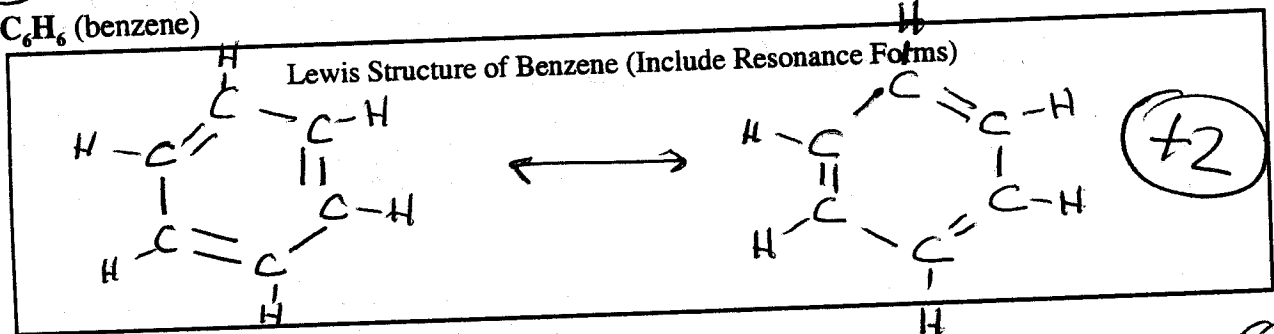
10/10

Generate this molecule using the "Entry" mode of the Model Kit window. Calculate and inspect the following surfaces: LUMO+4, LUMO+3, LUMO+2, LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2, HOMO-3, HOMO-4.

Identify and sketch all the π and π^* orbitals of acetylene. Indicate the relative orientations of these orbitals in your sketches.



C_6H_6 (benzene)



How many molecular orbitals do you expect for benzene?

30 (+1)

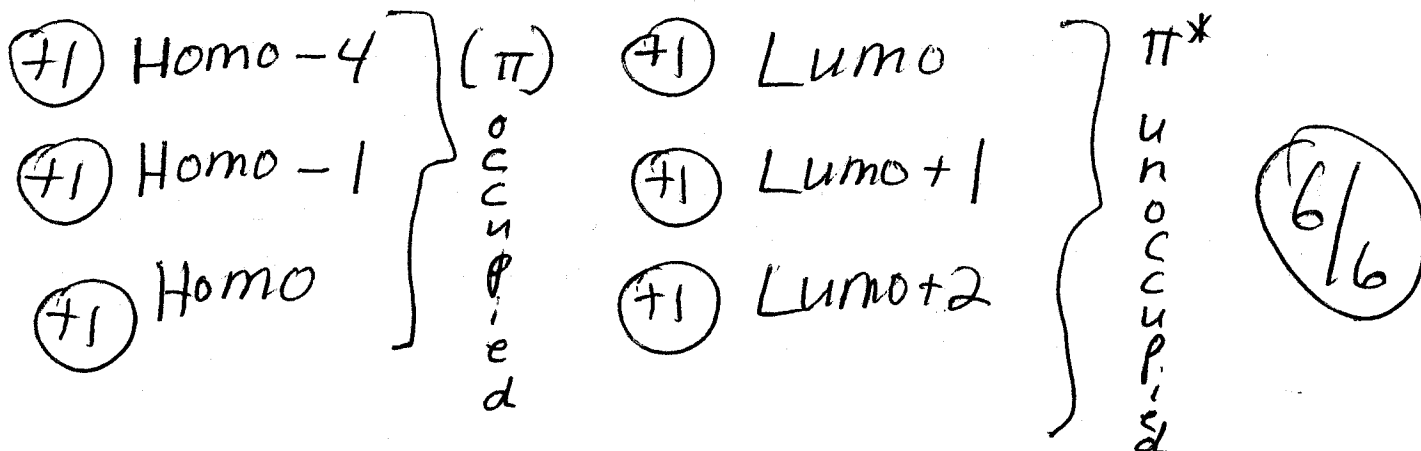
How many valence electrons will occupy these orbitals?

30 (+1)

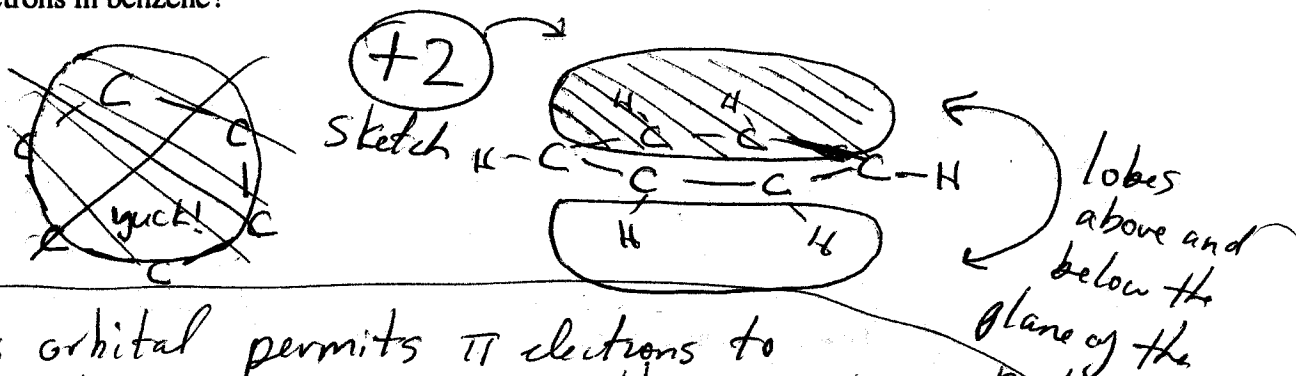
Benzene is trivial to construct if one selects it from the rings list in the "Entry" mode of the Model Kit window. Click on the screen to add benzene to the workspace. Calculate the following surfaces: LUMO+14, LUMO+13, LUMO+12, LUMO+11, LUMO+10, LUMO+9, LUMO+8, LUMO+7, LUMO+6, LUMO+5, LUMO+4, LUMO+3, 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. Whew! Benzene has 30 molecular orbitals!!

14/14

Which orbitals in benzene are involved in π bonding? Provide the label for every molecular orbital of benzene that is either π or π^* (both occupied and unoccupied).

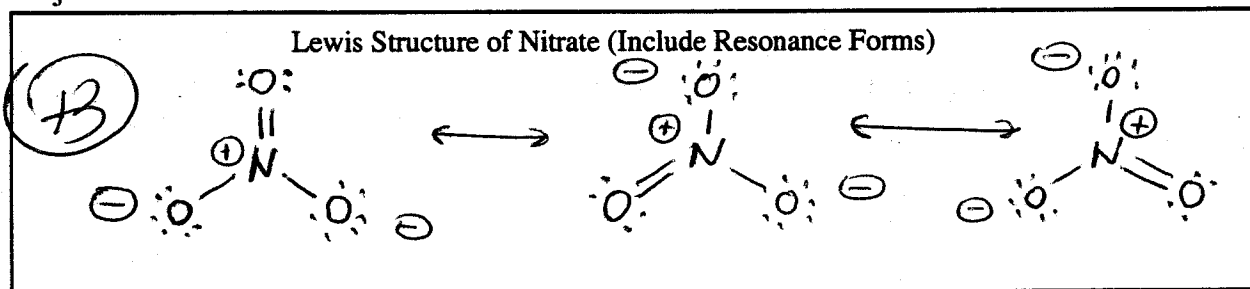


Sketch the lowest energy π molecular orbital. How does this orbital account for the delocalization of π electrons in benzene?



(+1) This orbital permits π electrons to occupy the entire region above and below the plane of the molecule. We haven't done any charged species yet. Let's try the polyatomic nitrate anion as our last example!

NO_3^-



How many molecular orbitals do you expect for nitrate?

16 (+1)

How many valence electrons will occupy these orbitals? Be careful since this is an ion.

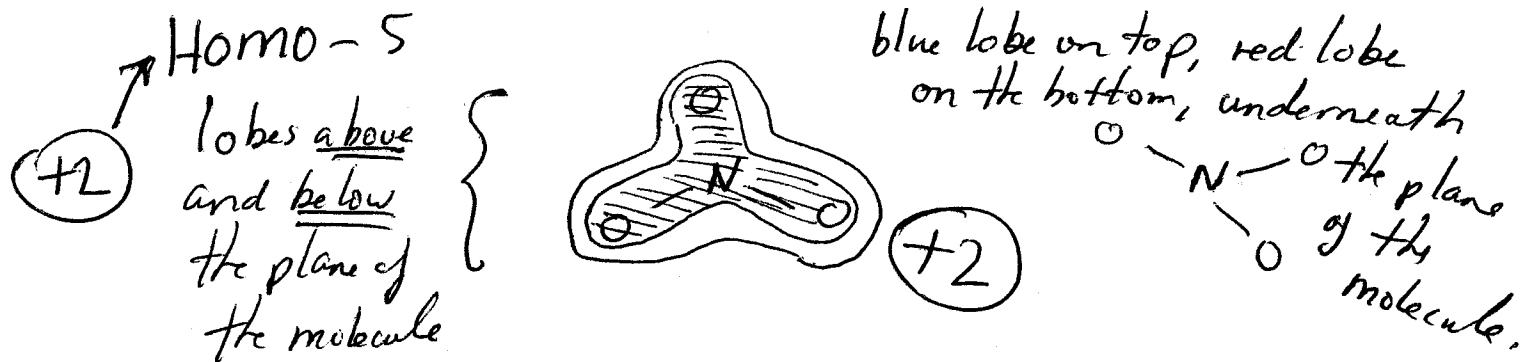
24 (+1)

14/14

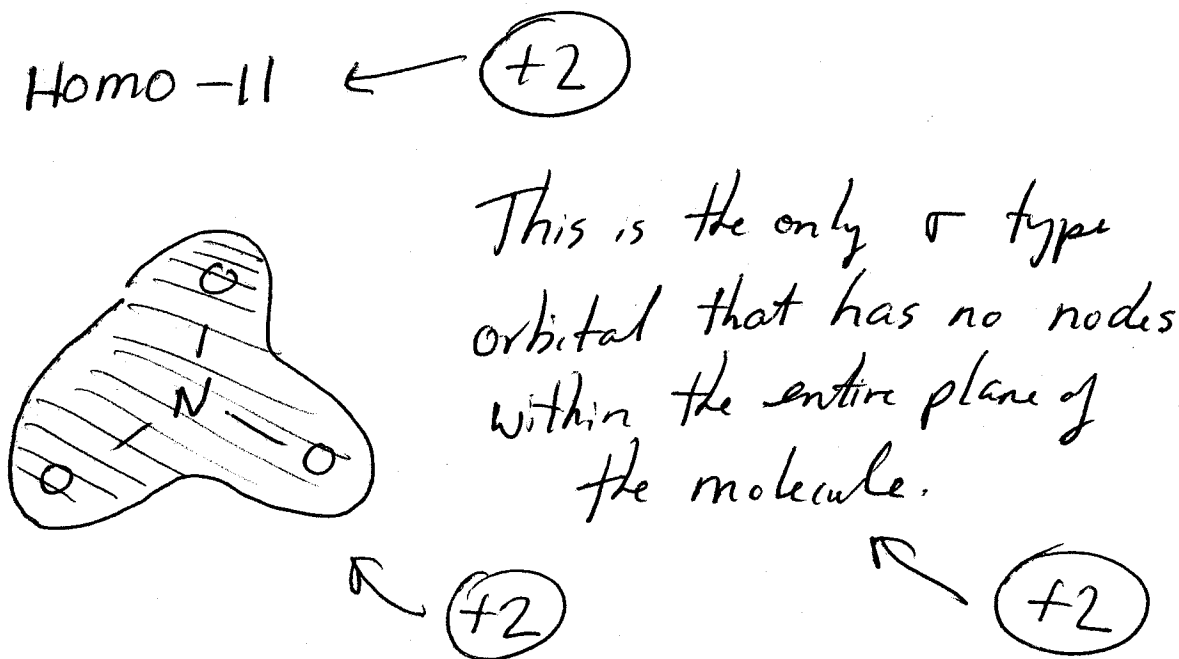
Construct this molecule using the appropriate icons in the "Expert" mode of the "Model Kit" window. Use the same bond type that was used for ozone since these species feature delocalization of π electron density (both ozone and benzene possess bonds of formal 1.5 bond order). The only difference in the 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 following molecular orbitals: 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, and HOMO-11.

Which of these molecular orbitals permits the most effective delocalization of its π electrons? Sketch this molecular orbital below and provide its label.



Which σ molecular orbital is lowest in energy? Sketch this molecular orbital and provide its label. What distinguishes this surface from the other σ molecular orbitals?



Your laboratory report for this experiment is this completed packet. Feel free to try other molecules if you wish after you have completed these examples and questions. Please quit MacSpartan Pro when you are completely finished.