The Electronic Structure of Molecules

An Experiment Using Molecular Orbital Theory

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Reading: Olmstead and Williams Sections 10.4-10.5
Purpose: Obtain molecular orbital results for total electronic energies, dipole moments, and bond orders for HCl, H_2, NaH, O_2, NO, and O_3. The computationally derived bond orders are correlated with the qualitative molecular orbital diagram and the bond order obtained using the NO bond force constant.

Introduction to Spartan/Q-Chem
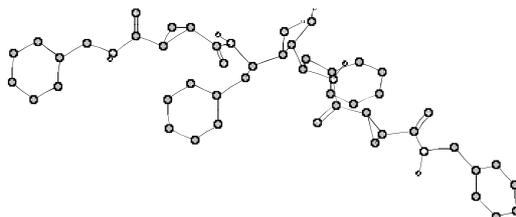
The molecule, above, is an anti-HIV protease inhibitor that was developed at Abbot Laboratories, Inc. Modeling of molecular structures has been instrumental in the design of new drug molecules like these inhibitors. The molecular model kits you used last week are very useful for visualizing chemical structures, but they do not give the quantitative information needed to design and build new molecules. Q-Chem is another "modeling kit" that we use to augment our information about molecules, visualize the molecules, and give us quantitative information about the structure of molecules. Q-Chem calculates the molecular orbitals and energies for molecules. If the calculation is set to "Equilibrium Geometry," Q-Chem will also vary the bond lengths and angles to find the lowest possible energy for your molecule. Q-Chem is a text-only program. A "front-end" program is necessary to set-up the input files for Q-Chem and to visualize the results. We will use the Spartan program as a graphical "front-end" for Q-Chem. In other words Spartan doesn't do the calculations, but rather acts as a go-between you and the computational package.

   In terms of "good-better-best" for the models that we use to understand molecular structure, Lewis structures are "good," molecular mechanics calculations are "better," and molecular orbital calculations are "best." Among the molecular orbital approaches themselves, semi-empirical-PM3 is "good," Hartree Fock 3-21G(*) is "better," and higher levels including 6-31G* are even better. You will learn more about the different levels of molecular orbital calculations if you go on in chemistry.

Electron Surfaces

A useful way to visualize the results of a molecular orbital calculation is to look at the total electron density. Electron density plots at low contour levels (0.002), called density surfaces or size density surfaces, can be used to see the size of molecules. These plots are more realistic than using Van der Waals radii and space-filling models. Higher contour values (0.08), called bond density surfaces, can be used to understand bonding interactions. Bond density surfaces show the increase or decrease of electron density between the atoms in bonds.
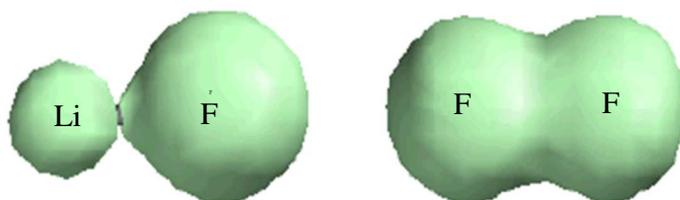

Figure 1: Bond density surfaces. Left: 87% ionic LiF. Right: 100% covalent F_2
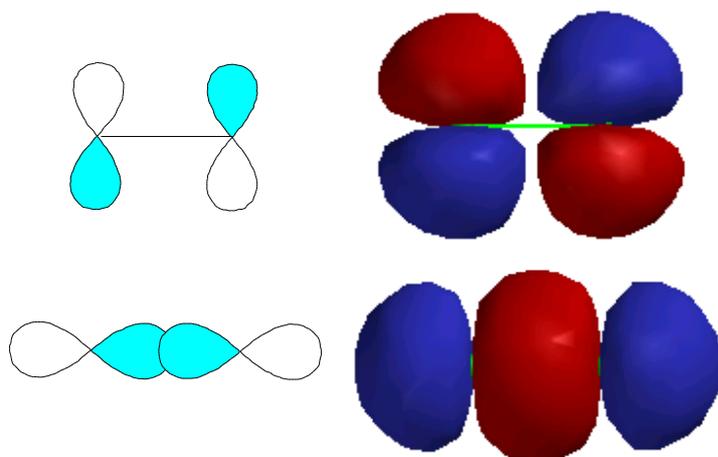
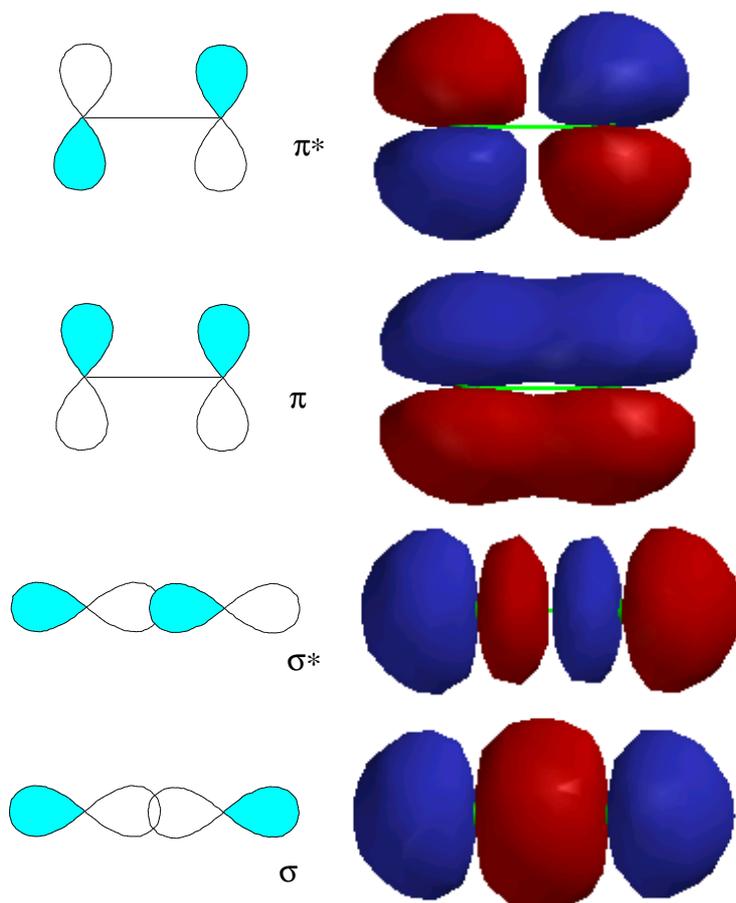Figure 2: Pi-type (top) and Sigma type (bottom) molecular orbitals

Molecular orbital surfaces can be viewed to understand how atomic orbitals overlap to make molecular orbitals. Better overlap makes for stronger bonding. To judge if an orbital is sigma or pi type, we look at the direction of overlap of the p orbitals on the two atoms, Figure 2. Sigma bonds are usually stronger because the atomic p-orbitals point towards each other and have better overlap. For double bonds, the first bond is sigma type and the second bond is pi-type.

When two atomic orbitals overlap, two molecular orbitals are formed. One of the molecular orbitals is bonding and the second is anti-bonding. Bonding molecular orbitals increase the electron density between the two nuclei, while anti-bonding orbitals decrease the electron density between the two nuclei. The trick to strong bonding is to have a configuration with many bonding electrons and few anti-bonding electrons.

Molecular orbital surfaces are very useful for visualizing the difference between bonding and anti-bonding orbitals. Figure 3 shows the normal cartoon of a bonding and anti-bonding orbital, alongside the corresponding MO surfaces. The trick to determining bonding or anti-bonding behavior is to look at the phases, or colors, of the orbitals in the overlap region. A change in sign of the orbital between the two nuclei signifies an anti-bonding orbital.

Often, the highest occupied molecular orbital, or HOMO, and the lowest unoccupied molecular orbital, or LUMO are the dominant factors in determining the chemical reactivity of a substance. We will visualize the HOMO and LUMO for O_2. You will be able to predict the nature of the HOMO and LUMO from molecular orbital theory, that is, are the HOMO and LUMO sigma or pi type, bonding or anti-bonding?

π*

π

σ*

σ

Figure 3: Bonding and anti-bonding (*) molecular orbitals

Part I: Polar Covalent Bonds and Molecular Interactions[1]

Introduction

Two things are needed for a molecule to have a dipole moment: polar bonds and an unsymmetrical shape. For example, homonuclear diatomic molecules like H_2 and O_2 can't have a dipole moment because the two atoms are identical and the bond will be 100% covalent. Other examples are C-H bonds, which are not normally very polar so compounds with only C and H have very small dipole moments if any. C-Cl bonds are very polar but CCl_4 has no dipole moment, because this tetrahedral molecule is too symmetrical and the bond dipoles cancel out, Figure 4. The presence of a molecular dipole moment has a big effect on the properties of molecules and their reactivity. For example, the boiling point of polar liquids is much higher than the boiling point of a non-polar liquid with a comparable molecular weight.
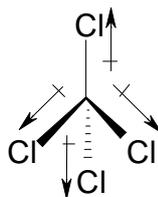

Figure 4. Cancellation of bond dipoles in a tetrahedral molecule.

Polarity effects are sometimes difficult to visualize. Electron density plots and electric potential surfaces can be very helpful in visualizing these effects[2]. Electron density plots tell you where the electrons are in a molecule. Electric potential surfaces tell you if the electron density is skewed from the distribution in isolated atoms. The electric potential is calculated by the energy of interaction between the molecule and an imaginary point charge. The point charge is a single positive charge and corresponds to the potential energy a H^+ ion would see. The point charge is moved around on the electron density surface, so the potential is mapped for a constant value of the electron density. Some examples will be useful and easier to grasp than the description of the calculation itself. We will first look at the electron density surfaces for H_2, HCl, and NaH.

As you generate these surfaces look at the distance from the nucleus of each atom to the surface. The greater this distance, or in other words the bigger the surface, the more electron density surrounds the atom. Also look at the size of the density surface along the internuclear axis between the two nuclei. This internuclear area is where electron density must build for a strong bond to form. Red coloring from the electric potential means that the net charge in that area of the molecule is negative. That is, a red color shows that the atom is surrounded by more electrons than it would have in a neutral atom. Blue coloring shows a positive net charge. A purely covalent bond, such as in H_2, should not show any skewing of electron density and should be uniformly colored.

Building HCl, H_2, and NaH

1) Start Spartan by clicking on the Spartan icon at the bottom of the Macintosh screen or by opening to the Applications folder and the Spartan 14 folder. The Spartan icon is a water molecule.

Click on the New Build icon in the icon bar, , or pull down the File menu and choose New Build. You will see a "model kit" of atomic fragments to the right. In the Spartan Editor window, draw your molecule. As an example of how to use the builder, the instructions are given below for HCl. You can build other molecules in a very similar fashion.

   i). Click on the single-bond Cl (–Cl), then click on the open region.
   ii). Click on single-bond H (-H). Move your pointer to the end of theCl bond (unfilled valences are colored yellow), and click again. You should now have HCl. To move the molecule:

left-drag to rotate
command-drag to move (X and Y translate)
command-drag to scale up/down

   iii). Press the **Minimize** button, , at the lower right at the bottom of the Builder menu to adjust the bond length to a reasonable guess. These guesses are derived from bond length tables. This Minimization is a molecular mechanics minimization based on treating bonds as springs. This minimization is a very rough guess to the molecular structure.

   iv). To return to the View screen click on the "eyeglasses icon",

i) The "Save Changes…" dialog box will appear; click on **Yes**. A file librarian dialog box will appear. Specify a file name for your molecule. Make sure that the file names start with a letter and contain no spaces or punctuation marks (i.e. periods, /, \, colons, semi-colons, etc.). Click **Save As**.

Running a Molecular Orbital Calculation

2) Pull down the **Setup** menu and choose **Calculate** or click on the **Calculate** icon, .

    i). Use the pull-down menu for the **Calculate:** dialog box and select **Equilibrium Geometry**, if not already shown.

    ii). In a similar fashion, select "**with**" **Hartree-Fock** and **6-31G* in Vacuum**. (See the figure below).

    iii). Set the **Total charge**. For HCl the charge is 0, or neutral.

    iv). Check that the number of Unpaired Electrons is 0.

    v). Press the **Submit** button. A file librarian dialog box will appear. Navigate to the Documents folder. Specify a file name for your molecule. Make sure that the file names start with a letter and contain no spaces or punctuation marks (i.e. periods, /, \, colons, semi-colons, etc.).

3). Close the dialog box that tells you the job was submitted. A dialog box will open when the job is done; close it too.

4). Click the blue Properties-information balloon icon, , or pull down the **Display** menu and choose **Properties**. Record the energy and dipole moment and note the units. Hartrees and atomic units, or au, are synonymous, with 1H = 2625.5 kJ/mol. Drag the Properties dialog box to one side so that you can see the molecule. Click the **Display Dipole Vector** button on the bottom left of the Properties dialog box to view the dipole moment. The "+" end is the positive end of the dipole vector. Sketch a dipole cartoon in your lab notebook. Is the dipole in the direction that you predicted? Next click on an atom. The Properties dialog will change to list the atom properties for that atom. Record the atom charges for each of your atoms. Use the electrostatic charge for this purpose, which gives results that are usually closest to our chemical intuition. To close the Properties dialog window, click on the "go-away" button, the red button with the "X" in the top left of the Properties window border.

5). Measure the bond length by pulling down the **Geometry** menu and choosing **Measure Distance**. Now click on the bond whose length you desire. The length will be listed in the bottom right of the View window. Alternately you can determine the distance between any two atoms, bonded or not, by clicking on those atoms.

6). If you have a triatomic or larger molecule, measure the bond angles by pulling down the **Geometry** menu and choosing **Measure Angle**. Now click on the three atoms whose bond angle you desire. Record this data if applicable.

7). Pull down the **Model** menu and choose how you want to see your model (try the different options). You can rotate your model by holding the left mouse button down while moving the mouse. The space-filling model uses tabular values of the Van der Waals radii for the atomic radii. Therefore the "size" of the atom in this type of display is only suggestive of the electron density surface, and will not vary with the true electron density around the atom. To get a much better representation of the electron density based on the molecular orbitals, use a density surface as described in the Electron Density Surfaces section below. Leave the molecule in the **Ball and Spoke** form.

8). Build and minimize H_2. Remember, to build a new molecule click on the New Build icon in the icon bar, [icon], or pull down the File menu and choose **New Build**. You build and Submit each molecule separately. To set-up the calculations, pull down **Setup Calculations** or use the corresponding icon**. As before, in the **Calculate:** box choose **Equilibrium Geometry** with **Hartree-Fock**. and 6-31G* in vacuum, and **Submit**. New molecules are displayed in a new tab in the View window. Select the tabs arranged along the bottom border of the View window to switch between molecules. Repeat steps 4 and 5 to record the total electronic energy, dipole moment, and bond length.

9). The Organic model builder that we used for HCl and H_2 works well for most organic compounds, but for many inorganic compounds with unusual bonding or expanded octets the **Inorganic** builder is necessary. We will now build NaH to illustrate the use of the Inorganic builder. You can switch back and forth between the Organic and Inorganic builder at any time as often as you like to build different parts of your molecule. To start pull down the **File** menu and choose **New Build** or click the corresponding icon. Click on the **Inorganic** button at the top of the toolbox. In the **Inorganic** builder, click on the button for a monovalent element. This icon looks like "– •". Next click on the long button above the fragment buttons (which will probably be labeled "C(6) Carbon"). Click on Na in the periodic table and click in the builder screen. Click on the Minimize icon (green jagged arrow at the bottom right) and a hydrogen will be substituted for the unfilled valence.

To return to the View screen click on the "eyeglasses icon", [icon] Choose "Ball and Spoke" as the **Model**.

10). Pull down the **Setup** menu and choose **Calculate** or click on the **Calculate** icon, [icon] . As before, in the **Calculate:** box choose **Equilibrium Geometry**, with **Hartree-Fock**. and 6-31G* in Vacuum, and **Submit**. Repeat steps 4 and 5 to record the total electronic energy, dipole moment, and bond length. Is the dipole in the direction that you predicted? All three molecules should be available as separate tabs.

Electron Density and Electrostatic Potential Surfaces
Do the following for each of your molecules. To change the active molecule, click on the tab along the bottom edge of the View window:

11) Click on the Surfaces icon, [icon], or pull down the **Setup** menu and choose **Surfaces**. Pull down the **Add** menu box and choose **density**. The default isoelectronic density, or isovalue, is 0.002, which is approximately a "90%" contour surface; 90% of the electron density is inside this surface. This surface is an accurate representation of the total electron density. For the electrostatic surface, pull down the **Add** menu box and choose **electrostatic**.

12) From the list of calculated surfaces, select the check box for the line: "density 0.002." Pull down the **Style** menu in the lower right and choose **Transparent**. Move the **Display Surfaces** dialog window to one side so that you can see the molecule. Now you'll see the ball and spoke bonds within the total electron density type electron cloud. Sketch your results in your lab notebook. However, the electron density that is responsible for the strength of the chemical bonds is closer yet to the nuclei. To get a better view of the electron density that is really acting as the "glue" to hold the nuclei together, we need to generate a "bond" density surface. For this type of surface choose the isovalue is set to 0.080: to view the bond density surface, click right on the surface and choose Properties. Change the isodensity value, Isoval, to 0.080. Choose **Transparent** or **Solid** or **Mesh** for the **Style** (try them all to see the difference). Leave the **Style** set at **Transparent**. Sketch the density surface. **Record any observations that you have for each surface. For example, where are the electrons localized? What is the size of the bond density surface around each atom? What is the size of the electron density along the internuclear axis <u>between</u> the two nuclei. Do the density surfaces show a big difference in covalent or ionic character for the molecules?** Clear your surface by clicking on the check box for the current surface.

13) To see the electric potential surface, choose the electrostatic potential map in the Surface list. Set the **Style** as **Solid**, Spartan normally adjusts the coloring to give the full red to blue color range for each surface. Observe the surface. But in this exercise we need to compare the surface for the three molecules, so we need to choose a consistent scaling for each molecule. Click right on the surface and choose **Properties**. In the **Property Range** dialog box enter -240 and 580. Unclick the Bands check box to see a smoother rendering of the colors. The electrostatic surface corresponds to the electrostatic energy in kJ/mol of a positive test charge that is moved over the 0.002 isovalue total electron density surface. By repeating this step for each molecule you can see each of the electric potential surfaces you calculated. For one of the molecules, click on the **Legend** check box. **Record any observations that you have for each surface. For example,**

where are the electrons localized? Is the charge distribution the same as you predicted? Clear your surface by clicking on the corresponding check box. Close the Display Surface dialog box.

14). Check the LABORATORY REPORT section, Part I, at the end of the write-up to make sure you have the data necessary to answer each question. Pull down the **File** menu and choose **Close** for each molecule.

PART II*:* **In this exercise we will investigate the molecular orbitals for diatomic oxygen and nitric oxide. For the energy units 1 au = 1 H = 2625.5 kJ/mol, which is twice the energy of the hydrogen atom.**

Building O_2

1). *Build O_2*: Following step 1, above, build and minimize O_2. To build O_2: in the Organic builder click on double bonded O (=O, sp^2 hybrid), then click in the open building region. Move your pointer to the end of the bond (unfilled valences are colored yellow), and click again. You should now have two oxygens that are double bonded. Continue as you did for HCl to molecular mechanics minimize and return to the View window.

2). *Molecular Orbital Calculation*: In the **Setup Calculation** dialog choose the **Charge** as **neutral** and **Unpaired Electrons** as **2**.Repeat step 2-5 above, recording the total electronic energy, dipole moment, and electrostatic atom charges. To determine the bond order, with the Properties dialog window still showing, click on the bond between the two oxygen-atoms. The Properties window will switch to display the bond properties. Note that there are several bond order calculations listed. Make sure to use the Löwdin listing, which works the best for comparison with your qualitative molecular orbital diagram. Notice that the bond length is also displayed in the Properties window and at the lower right of the View window. Just clicking on the bond is a short-cut to using the **Measure Distance** facility that we introduced earlier.

3). Click on the Surfaces icon, , or pull down the **Setup** menu and choose **Surfaces**. We now wish to display the density and electrostatic surfaces and several of the molecular orbitals. Pull down the **Add** menu box and choose **density**. Pull down the **Add** menu box and choose **electrostatic**. For molecules with unpaired electrons, the molecular orbitals are calculated for the "up" or alpha spins and the "down" or beta spins, separately. The molecular orbitals are correspondingly listed as a-type for the "up" spins and b-type for the down spins. Pull down the **Add** menu and choose **aHOMO** and again choose **aLUMO**, which gives the lowest unoccupied molecular orbital. The HOMO is a singly occupied orbital in O_2.

4). Using the instructions in steps 11-12, above, display your surfaces**. Record any observations that you have for each surface. For example, where are the electrons localized? For the HOMO and LUMO, are they sigma or pi type, bonding or anti-bonding?**

5). Check the Worksheet section, questions 3-8, to make sure you have the data necessary to answer each question.

The Bonding in NO

We will now build NO using the Inorganic builder. You can switch back and forth between the Organic and Inorganic builder at any time as often as you like to build different parts of your molecules.

1) Click on the New Build icon in the icon bar, , or pull down the File menu and choose New Build. Click on the **Inorganic** button at the top of the toolbox.

2) For nitrogen select the monovalent button $\boxed{- \bullet}$. Then click on the N in the periodic table. Click in the middle of the Builder window. A nitrogen atom with one unfilled valence should be drawn on the screen. Remember, unfilled valences are yellow. Now click on the O in the periodic table and then click on the unfilled valence on the N atom. Do not click on the Minimize button in the Builder window. It is best not to bias your structures if you are working on compounds with unusual bonding or expanded octets by using such a low level minimization procedure. For unusual molecules, it is best to proceed directly to molecular orbital geometry optimization (Equilibrium Geometry). (See Note, below).

3) To return to the View screen click on the "eyeglasses icon", 👓 Choose "Ball and Spoke" as the **Model**. Proceed as before, under "Building HCl, H₂, and NaH," beginning at step 2. However, in the **Setup** dialog choose the **Charge** as **neutral** and **Unpaired Electrons** as **1**.

4) Click the blue Properties-information balloon icon, 🛈, or pull down the **Display** menu and choose **Properties**. <u>Record</u> the total electronic energy. Click on the **Display Dipole Vector** button. <u>Record</u> the dipole moment and sketch a dipole cartoon in your lab notebook. Record the electrostatic atom charges. Record the bond length, and Löwdin Bond Order as instructed above.

5). Set up Surfaces for the aLUMO, aHOMO, aHOMO-1, aHOMO-2, and aHOMO-3 for NO. For the lower energy orbitals, click on the **More Surfaces** button. Choose Surface: HOMO{−} and number 1. Click on the Fixed checkbox, as shown below, and then Apply.
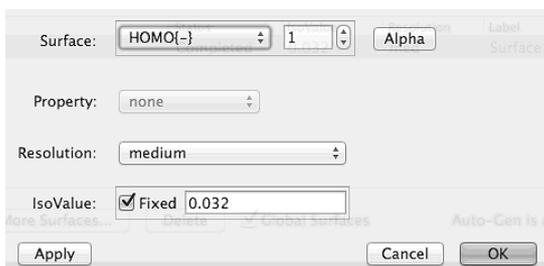
Repeat the same process to add the aHOMO-2, and aHOMO-3. The Surfaces dialog should appear as below. Observe the molecular orbital surfaces and correlate these surfaces with the qualitative molecular orbital diagram that you developed.

O/I	Surface	Status	IsoValue	Resolution	Label
☐	aLUMO	Completed	0.032	med	Surface1
☐	aHOMO	Completed	0.032	med	Surface2
☐	ahomo{−1}	Completed	0.032(Fixed)	med	Surface3
☐	ahomo{−2}	Completed	0.032(Fixed)	med	Surface4
☐	ahomo{−3}	Completed	0.032(Fixed)	med	Surface5

Add ▼   More Surfaces...   Delete   ☑ Global Surfaces   Auto−Gen is active.

6) Check the **Worksheet** section, questions 9-14, to make sure you have the data necessary to answer each question. Pull down the **File** menu and choose **Close** for O₂ and NO.

Building O₃

One of the resonance structures for zone that follows the Lewis rules is a cyclic structure. In this section we determine if the cyclic structure contributes to the overall structure of ozone. In other words, does the cyclic structure contribute or is it just wrong?
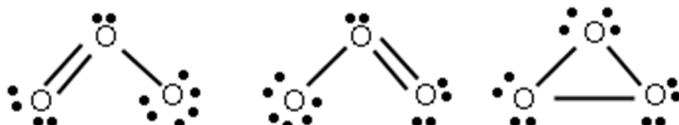
1). *Building O₃*: In the Organic builder, choose the bent oxygen core. Add two oxygens. Take off one of the two open valences using **Delete,** which is the Eraser icon in the lower Builder menu, and clicking on the end of one of the yellow lines. Again click on the Delete-eraser icon and click on the remaining yellow unfilled valence. Proceed as before; the

number of unpaired electrons is **0**. The bonds as constructed are shown as single-bonds, however, graphical builder bond orders are not passed on to the molecular orbital program. Record the energy, Löwdin bond orders, bond lengths, and angle. Display the bond density surface. Is there significant density between the outer oxygens, which results if the cyclic isomer of ozone is a strong contributor to the overall structure.

2). The LUMO, HOMO, and HOMO-4 are the delocalized three-center π-orbitals. Click on the Surfaces icon, , **Add** and display these three orbitals. Determine which of the three is the three-center non-bonding orbital that Olmstead and Williams discusses, Figure 10-29.

3). Determine the bond order between the outer oxygen-atoms to determine if the cyclic isomer of ozone is a strong contributor to the overall structure using the following instructions. To get the Viewer interface to easily list the bond order, we need to build ozone with a bond between the outer atoms. This bond won't change the calculated structure, we add it simply as a shortcut to listing the bond order which exists in the structure in the last question. Build ozone again, but this time <u>do not remove the yellow unfilled valences</u>. Instead, click on the Make Bond icon, the button, and then click on the two yellow unfilled valences. A bond should be drawn between the two outer atoms. <u>Do not use the Minimize button</u> , , so that the bond angle remains close to 109-120°. Proceed as before. The bonds as constructed are shown as single-bonds, however, graphical builder bond orders are not passed on to the molecular orbital program. Record the bond angle to verify that the minimized structure is the same as in the previous step (±0.03°, which is the tolerance of the geometry optimization). Record the Löwdin bond order between the outer atoms.

4). Pull down the **File** menu and choose **Close** for both ozone models.

Literature Cited:

1. This exercise is based on: G. P. Shusterman, A. J. Shusterman, Teaching Chemistry with Electron Density Models, *J. Chem. Educ.* **1997**, *74*, 771.
2. P. Politzer, D. G. Truhlar, Eds., Chemical Applications of Atomic and Molecular Electrostatic Potentials, Plenum: New York, 1981.