# Introduction to Molecular Modeling

In the following laboratory activities you will examine three-dimensional models of molecules using the computer-based molecular viewing program called Jmol.[*] You can access a version of Jmol for use with these activities at http://cheminfo.chem.ou.edu/~mra/home.html.

Instructions:

After obtaining access to the Jmol program you should see an image on your computer screen that looks similar to the following figure.
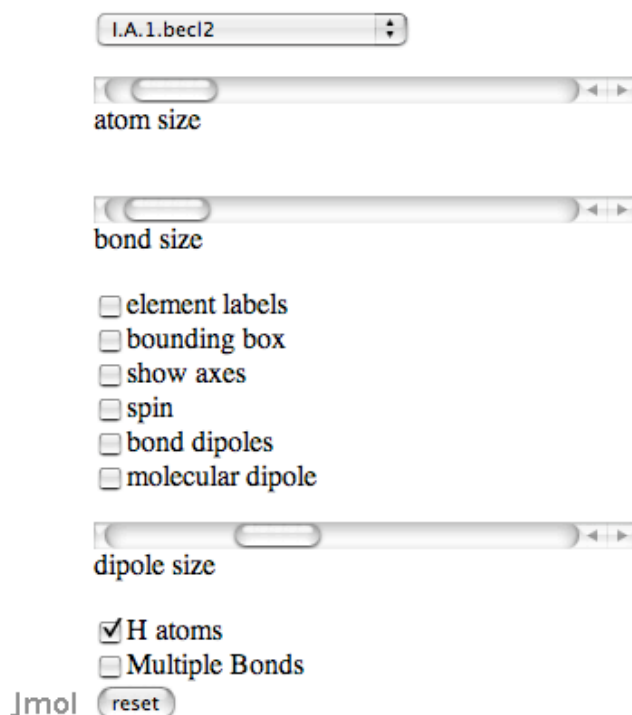
You can view the molecules you will need for the following activities through the drop down menu on the upper right of your screen. The names of the molecules are labeled so that they correspond to the activities. So, for example the molecules for the I. VSPER activities are labeled with a "I." All of the molecules are labeled by number and alphabet in outline form and listed in order to make them easy to find.

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[*] Jmol is a free, open source molecule viewer for students, educators, and researchers in chemistry and biochemistry. It is cross-platform, running on Windows, Mac OS X, and Linux/Unix systems (see: http://jmol.sourceforge.net/). A team of researchers are updating and improving the program on a constant basis. Robert Hanson of St Olaf College has been particularly helpful to the authors of these activities.

As an example, let's open the file for methane, CH_4. It can be found in the Jmol menu list as I.C.1.ch4. Highlight the molecule in the list and then click. The molecule window should now be showing the CH_4 molecule:
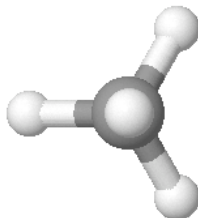
Jmol

You can now interact with the molecule in a number of different ways. To rotate the molecule, click anywhere in the window and drag your mouse around. You can rotate the molecule in the plane of the screen and resize it by using the shift key when you click/drag the mouse side by side or up and down.

There are a number of different ways of viewing the molecule. The Jmol window has a number of operations that can be utilized by a click box or slider bar. These include: slider bars to control atom and bond size, click boxes to label the atoms, superimpose bounding boxes, add axes, spin the molecule, add bond and molecule dipoles. Try each function out to see how it affects the molecule. In addition you can access a number of other functions by control clicking" (mac) or right clicking (pc) in the molecule window.

Jmol

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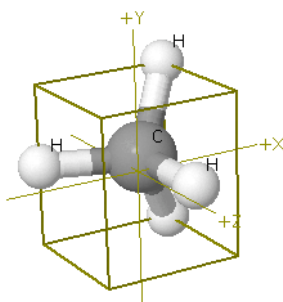
To measure a bond length, hold the cursor over an atom until an atom label appears. Double click on the atoms. A plus sign should replace the cursor arrow. As you move the plus sign to another atom a colored dotted line should appear. When you place the cursor over a second atom double click on it when the atom label appears. The colored line should change color and a value for the length should appear. Jmol seems to be a little sensitive to this operation so you might have to try this several times.

To measure a bond angle, double click on one of the end atoms when the atom label appears. Then drag the plus cursor to the middle atom in the angle. Single click on this atom when the atom label appears and then move the cursor to the other end atom and double click when the atom label appears. The angle in degrees should appear as the dotted line changes color.
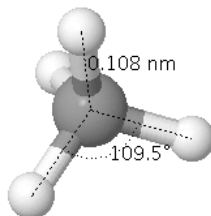
Jmol

If you want to compare two or more molecules, you can open additional browser windows.

I. VSEPR

Name_____   Lab Section_____

For this activity, all of the file labels will begin with a roman numeral I. Each of the questions asks you to examine molecules that are designated with letters. For example, for part A, all of the molecule files will be labeled I.A.

It may be helpful for you to refer to the table of molecular geometries found in most general chemistry textbooks.

A. Using Jmol, examine the two molecules labeled I.A. Write the molecular formula for each molecule. Draw and label the molecules and measure and record their bond angles.

B. Using Jmol, examine the two molecules labeled I.B. Write the molecular formula for each molecule. Draw and label these molecules and measure and record their bond angles. Draw the Lewis structure for each molecule. Why is SO_2 shaped like it is and is not linear? How is it different from the molecules in section A? What is similar about all of the molecules in List B? Describe any difference between the angles you measure and the theoretical ones (see your textbook to see what the theoretically expected angles should be.)

C. Repeat step B for the three molecules labeled I. C. (i.e. open them, measure their bond angles, and draw the Lewis Structures). Write the molecular formula for each molecule. What is similar about all of the molecules in List C? Compare the actual bond angles with the theoretically expected angles. Explain any trend in bond angles that you observe.

D. All of the five molecules Labeled I.D. have five regions of electron density around the central atom. Open the I.D.1.pf5 molecule, and examine the two different FPF angles in the molecule. Draw and label this molecule. Predict where the lone pairs will go in molecules that have one, two, and three lone pairs. Now, open the other files, write the molecular formula for each molecule, measure their bond angles, and draw the molecules. Were your predictions correct? At what locations do the lone pairs go in five-coordinate molecules?

E. Using Jmol, examine the three molecules labeled I.E., all of which have six regions of electron density. Write the molecular formula for each molecule. Draw the molecules and measure their bond angles. Draw the Lewis structure for each molecule. How do nonbonding (lone pair - LP) electrons explain the molecular geometries of XeF_4 and IF_5? Explain any differences you notice between the theoretically expected bond angles and your observed values.

II. Carbon Compounds

Name_____   Lab Section_____

For this activity, all of the file labels will begin with a roman numeral II.

    A. Bond Types

        1. In Jmol, open the II.A.1, II.A.2, and II.A.3 molecules. Measure and record the carbon-to-carbon bond lengths for single (CH3CH3), double (CH2CH2), and triple (CHCH) bonds. Make a generalization comparing the lengths of single, double, and triple bonds. Propose a reason for your generalization.

        2. Draw the Lewis structure for benzene - C_6H_6 - and predict the carbon-to-carbon bond lengths in the molecule. Using Jmol, open II.A.4, the benzene molecule (C6H6), and measure the carbon-to-carbon bond lengths. Is your prediction correct? Compare the bond lengths in benzene to those of the single, double and triple bond in section A.1. Does benzene contain single and/or double C-C bonds? Why? How do you explain you observations?

B. Cyclic Compounds

In Jmol, open the three six carbon cyclic structures in II.B.1, II.B.2, and II.B.3. Compare and contrast these molecules. Focus on the C-C bond types and the geometries of these compounds.

C. Summary

From A and B, what relationship did you find between (carbon-to-carbon) bond types and molecular geometries?

III. Periodic Trends

Name_____ Lab Section_____

For this activity, all of the file labels will begin with a roman numeral III.

A. Draw the Lewis structures for the molecules ONBr, ONCl, ONF, and ONI. Predict the molecular geometries and bond angles for each molecule.

B. In Jmol, examine the four molecules labeled III.A. Draw and label the molecules and measure and record their bond lengths and bond angles.

C. Identify any trends you observe in the measurements you recorded. How are these trends related to the periodic table and to electron configurations? Explain why these trends exist.

D. Draw the Lewis structures for the molecules CH_3F, CH_3CH_3, CH_3OH, and CH_3NH_2. Predict the molecular geometries and bond angles for each molecule.

E. In Jmol, examine the four molecules labeled III.B. Draw and label the molecules and measure and record their bond lengths and bond angles.

F. Identify any trends you observe in the measurements you recorded. How are these trends related to the periodic table and to electron configurations? Explain why these trends exist.

IV. Solids

Name_____   Lab Section_____

For this activity, all of the file labels will begin with a roman numeral IV.

A. In Jmol, open the SCS file in IV.A.1. Click the Bounding Box and Axes function keys. Use the atom size and bond size and slider bars to adjust the view so that the bounding box and axes can be easily seen. Move the figure around to a position that shows the 3-D orientation of the spheres and draw the figure below.

B. This figure is the basis for some solid compounds and ions. This particular structure is called a Simple Cubic packing Structure (SCS) and is one way atoms, ions, or molecules are arranged in a three dimensional matrix (called a lattice). Polonium, Iridium, and Ruthenium are examples of the few elemental solids that utilize the SCS arrangement. The Jmol figure is the simplest unit of the SCS structure. A sample of a solid substance would be represented by adding spheres in the x, y, and z planes to make a large matrix. Describe the orientation of the spheres to each other in this matrix

Taking the continuous nature of the lattice into account, how many nearest neighbors does each sphere have? _____ This number is called the coordination number.

The Bounding box defines what is called the Unit Cell for the structure. The lattice can be constructed by repeating unit cells in the x, y, and z directions. Only the spheres or partial spheres that are inside of the bounding box are considered to be in the unit cell (see figure).
How many spheres are contained in the SCS unit cell? _____
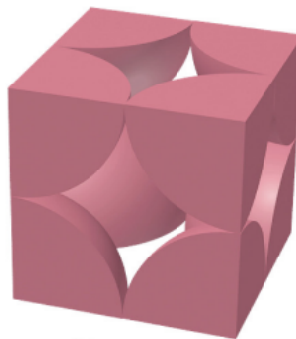
C. Adjust the sizes of the spheres using the atom size slider bar until the spheres just touch each other. The space between the spheres (called a Hole) can be occupied by other atoms, ions or molecules depending on their sizes. As an example, if the spheres showing in the Jmol figure are the anions of an ionic salt, the hole could contain the cation.

If all of the holes in an SCS lattice were filled what would be the ratio of cations to anions?_____

Estimate the relative maximum sizes of the cations and anions in an SCS lattice.

D. Calculate the density (packing efficiency) of the SCS packing arrangement. (Hint: calculate the volume of the spheres (the sum of all the parts) contained in the unit cell and divide that by the total volume of the unit cell. The dimensions can be determined from the bond lengths.)

E. Another solid packing structure is the body centered cubic packing or BCC. In Jmol open the BCC file (IV.A.2). The alkali metals are examples of the elemental solids that utilize the BCC arrangement. Draw this unit cell structure and describe the orientation of the spheres to each other. Why is this structure called body centered cubic?

F. Use the same procedure that you used for the SCS structure to answer the following questions.

What is the coordination number for BCC packing? _____

How many spheres are contained in the BCC unit cell? _____

Calculate the density (packing efficiency) of the BCC packing arrangement. (When you adjust the size of the spheres, make them as large as possible without overlapping the boundaries of any of the spheres.)

G. In Jmol open the CP file (IV.A.3). This kind of packing is called a closest packing structure. It is called a closest packing arrangement because the spheres are packed together as close as they can be. Manipulate the model until you can see two layers of spheres viewed from the side.
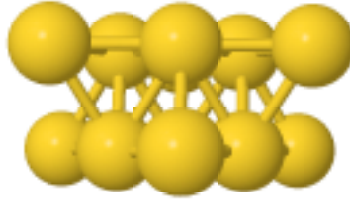
How is this packing arrangement different from the SCS and BCC packing?

Rotate the structure to view it from the top.
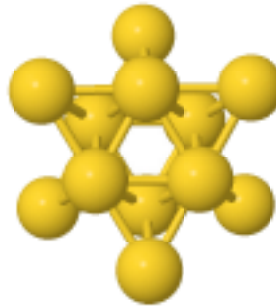
If you were to place a third layer on top of this structure you have two choices. Describe how these two structures would be different from each other. (Hint: one would have what is called an abab orientation and the other would have an abcabc orientation. What do you think this means?)

H. One of these two possible closest packing arrangements is called face centered cubic packing (FCC). In Jmol, open the FCC file (IV.A.4). Al, Ni, Cu, and Ag are examples of elemental solids that utilize the FCC arrangement. This arrangement is also called Cubic Closest Packing or CCP. It is called a closest packing arrangement because the spheres are packed together as close as they can be. Draw this unit cell structure and describe the orientation of the spheres to each other. Manipulate the model so as to convince yourself that this cube comes out of a closest packing structure. Draw this structure. Which of the two orientations, abab or abcabc, is this?

I. Use the same procedure that you used for the SCS and BCC structures to answer the following questions.

What is the coordination number for FCC packing? _____

How many spheres are contained in the FCC unit cell? _____

Calculate the density (packing efficiency) of the FCC packing arrangement.

J. The second of the two possible closest packing arrangements is called hexagonal closest packing (HCP). In Jmol, and open the HCP file (IV.A.5). Unlike FCC, SCS, and BCC this arrangement does not form a cube. Co, Zn, and Cd are examples of elemental solids that utilize the HCP arrangement. Draw this unit cell structure and describe the orientation of the spheres to each other. Manipulate the model so as to convince yourself that this cube comes out of a closest packing structure. Which of the two orientations, abab or abcabc, is this?

K. Use the same procedure that you used for the SCS and BCC structures to answer the following questions.

What is the coordination number for HCP packing? _____

In Jmol, open the HCPuc file (IV.A.6). Use the HCPuc file to help define the unit cell. How many spheres are contained in the HCP unit cell? _____

Optional: Calculate the density (packing efficiency) of the HCP packing arrangement.

L. Although it's not obvious why different elemental metals are found in different packing arrangements, there are some that can be rationalized. How does the different packing arrangement for the alkali metals, which are soft enough to be cut with a knife, and metals such as copper and silver, which are harder?

M. In Jmol, open the NaCl.LM file (IV.B.1). In a separate window, open the NaCl file (IV.B.2). This lattice represents NaCl. What packing arrangement is used by the Na^+ ions? Describe the orientation of the holes that contain the Cl^- ions.

N. In Jmol, open the CsCl.LM file (IV.B.3.CsCl). In a separate window, open the CsCl file (IV.B.4.CsCl). This lattice represents CsCl. What packing arrangement is used by the Cs^+ ions? What packing arrangement is used by the Cl^- ions?

Since both Na and Cs are both alkali metals, what can account for the differences in their packing structures?

O. In Jmol, open the Diamond file (IV.B.5). In a separate window, open the Graphite file (IV.B.6). Compare the atomic make up of these two compounds. How are they similar? Compare the structures of the two compounds? Graphite is used as a dry lubricant. Diamond is used on saw blades. How do the solid crystal structures account for the different physical properties of graphite and diamond?

V. Isomerism

Name_____ Lab Section_____

For this activity, all of the file labels will begin with a roman numeral V.

A. In Jmol, open the $C_2H_4Cl_2$#1 file (V.A.1). Open a new window and then open the $C_2H_4Cl_2$#2 file (V.A.2). Use the slider bar and clicker box function keys, make any adjustments to the molecules you want to aid viewing. Manipulate the molecules so that you can compare them. Draw a Lewis structure for each molecule. Discuss the structural differences between the molecules.

B. Although both molecules have the same formula, $C_2H_4Cl_2$, they have different physical and chemical properties. For example, the molecule labeled #1 has a boiling point of 57.3°C, and the molecule labeled #2 has a boiling point of 83.5°C. Molecules that have the same chemical formulas but different structures are called isomers. The rule for identifying differences is to superimpose the molecules on each other. If all of the atoms match, the molecules are identical. If not, the molecules are isomers. Sometimes, however, superimposing can be tricky. Molecules can be manipulated by rotating the atoms around their bonds. Unless fixed into position, atoms connected by single bonds can be rotated. Atoms connected by multiple bonds, however, cannot be rotated. Open the $C_2H_4Cl_2$#3 file (V.A.3) draw its Lewis structure. Compare the molecule with the $C_2H_4Cl_2$#1 and $C_2H_4Cl_2$#2 file. What is its relationship to each of these two molecules?

C. In Jmol, open the three $C_2H_2Cl_2$ molecules (V.B.1, V.B.2, and V.B.3) in new windows. In the Preferences menu make any adjustments to the molecules you want to aide viewing. Manipulate the molecules so that you can compare them. Draw a Lewis structure for each molecule. Discuss the structural differences between the molecules. How are each of the molecules related to each other?

D. There are several types of isomers. Structural isomers have the same number and kinds of atoms in the molecules, but the atoms are bonded to different atoms. Geometric isomers have the atoms bonded to the same atoms, but they are arranged differently. If similar chemical units are found on the same side of the molecule when a plane divides the molecule in half, these chemical units are said to be "cis" to each other. If they are on opposite sides they are said to be "trans" to each other. In Jmol, open the six isomers of C_4H_8 (V.C.1 - V.C.6). View each molecule and draw the Lewis structures of these isomers. For a less cluttered view of the molecules, use the click function to remove the H atoms. Discuss the isomeric relationship of each of these molecules to each of the others.

E. Optical isomers are another isomer type. An optical isomer is characterized as a molecule that is a mirror image of another molecule. Of course, in order to be an isomer it also cannot be superimposed on that molecule. Optical isomers can be important biochemical molecules. For example, an optical isomer of a molecule might be an effective drug while its other optical isomer is not. The most common type of optical isomer has a carbon atom with four different chemical units attached to it. This carbon is called a chiral center. In Jmol, open the three CHFClBr molecules (V.D.1, V.D.2, and V.D.3). Use he atom size and bond size slider bars to make any adjustments to the molecules you want to aid viewing. Manipulate the molecules so that you can compare them. Draw a structural formula for each molecule. Discuss the isomer relationships between the molecules.

F. Explain why CH_2ClBr and CH_2Cl_2 do not have optical, geometric, or structural, isomers.

G. In Jmol, open the Co(en)$_2$Cl(NH$_3$) molecules (V.E.1, V.E.2, and V.E.3). Use he atom size and bond size slider bars to make any adjustments to the molecules you want to aid viewing. For a less cluttered view of the molecules, remove the H atoms. Manipulate the molecules so that you can compare them. Draw a structural formula for each molecule. Discuss the isomer relationships between the molecules.

H. In Jmol, open the two the Co(en)$_3$ molecules (V.F.1 and V.F.2). Use he atom size and bond size slider bars to make any adjustments to the molecules you want to aid viewing. For a less cluttered view of the molecules, remove the H atoms. Manipulate the molecules so that you can compare them. Draw a structural formula for each molecule. Discuss the isomer relationships between the molecules.

I.   In Jmol, open the two dimethylcyclobutane molecules (V.G.1 and V.G.2). Use he atom size and bond size slider bars to make any adjustments to the molecules you want to aid viewing. For a less cluttered view of the molecules, remove the H atoms. Manipulate the molecules so that you can compare them. Draw a structural formula for each molecule. Discuss the isomer relationships between the molecules.

J.   In Jmol open the three MX_2Y_3 molecules (V.H.1, V.H.2, and V.H.3). Use he atom size and bond size slider bars to make any adjustments to the molecules you want to aid viewing. Draw a structural formula for each molecule. Manipulate the molecules so that you can compare them. Discuss the isomer relationships between the molecules.

K. In Jmol, open the two MX_2Y_4 molecules (V.I.1, and V.I.2). Use the atom size and bond size slider bars to make any adjustments to the molecules you want to aid viewing. Manipulate the molecules so that you can compare them. Draw a structural formula for each molecule. Discuss the isomer relationships between the molecules.

L. In Jmol, open the two MX_3Y_3 folders (V.J.1 and V.J.2). Use he atom size and bond size slider bars to make any adjustments to the molecules you want to aid viewing. Manipulate the molecules so that you can compare them. Draw a structural formula for each molecule. Discuss the isomer relationships between the molecules.

VI. Polarity

Name_____   Lab Section_____

For this activity, all of the file labels will begin with a roman numeral VI.

A. Some atoms have a greater attraction for electrons than others. A rough measure of this attraction can be assigned to atoms. The electronegativity is such a measure that can be found in most textbooks. It is defined as the relative ability of an atom that is bonded to another atom to attract electrons to itself. You might want to have an electronegativity table to use for this activity. The consequence of two atoms in a bond having a different attraction for electrons is that more negative charge will accrue to one side of the bond resulting in an electrical polarity. The bond is said to be a dipole with a negative and a positive side. In Jmole, open the HF molecule (VI.A.1). Activate the bond dipole checkbox. The dipole may be easier to view if you reduce the atom and bond sizes and adjust the dipole size. Draw the Lewis structure of the molecule, label the molecule and sketch in the bond dipole. Indicate the negative and positive end of the dipole.

B. Draw the Lewis structure for O_2. Do you expect the O_2 bond to be polar, or nonpolar? Why? In Jmole open the O_2 molecule (VI.A.2) to check your prediction.

C. Draw the Lewis structure for CO. Do you expect the CO bond to be polar, or nonpolar? Why? In Jmole open the CO molecule (VI.A.3). Label the Lewis structure of the molecule and sketch in the bond dipole. Indicate the negative and positive end of the dipole.

D. Molecules that have more than two atoms will have more than one bond. Each of these bonds can be assigned a dipole. Draw the Lewis structure for CO_2. Do you expect the each CO bond to be polar, or nonpolar? Why? In Jmole open the CO_2 molecule (VI.A.4). Label the Lewis structure of the molecule and sketch in the bond dipoles. Indicate the negative and positive end of the dipoles. Compare the relative strength of the two dipoles. Predict how these bond dipoles combine and how would they affect the overall polarity of the molecule. This resultant polarity is called the dipole moment of the molecule. What is this value for CO_2.

E. In Jmole open the CO_2 and COS molecules (VI.A.4 and VI.A.5). Label the Lewis structures of the molecules and sketch in the bond dipoles. Indicate the negative and positive end of the dipoles. Activate the atom dipole checkbox in Jmol for each molecule. Compare the relative strength of the two dipoles in COS. Predict how these bond dipoles combine and how they affect the overall polarity of the molecules. Activate the molecule dipole checkbox in Jmol for each molecule. Discuss the reasons for any differences between these two molecules.

F. Draw Lewis Structures for H_2O, NH_3, CH_4 and CH_3Cl. Draw the 3-D geometries of the molecules and indicate the bond dipoles in your drawings. In Jmol open these molecules (VI.B.1 - VI.B.4) and confirm your drawings. Activate the atom dipole checkbox in Jmol for each molecule. Compare the relative strength of the dipoles. Predict how these bond dipoles combine and how they affect the overall polarity of the molecule. Activate the molecule dipole checkbox in Jmol. Discuss the reasons for any differences between these molecules.

G. Propose a set of rules that will determine if a molecule will be polar or nonpolar.

H. Draw Lewis Structures for BF_3, NH_3 and ClF_3. Draw the 3-D geometries of the molecules and indicate the bond dipoles in your drawings. In Jmol open these molecules (VI.C.1 - VI.C.3) and confirm your drawings. Activate the atom dipole checkbox in Jmol for each molecule. Compare the relative strength of the dipoles. Predict how these bond dipoles combine and how they affect the overall polarity of the molecule. Activate the molecule dipole checkbox in Jmol. Discuss the reasons for any differences between these molecules.

I. Compare BF_3 (VI.C.1) with BF_2Cl (VI.C.4). Draw the 3-D geometries of the molecules and indicate the bond and molecular dipoles in your drawings. Discuss the reasons for any differences between these molecules.