EXPERIMENT 12

Molecular Structure

Objective

The purpose of this experiment is to use molecular models to build and study structures of molecules and ionic species. In addition we will use molecular modeling software to analyze the bonding in a variety of compounds.

There are a number of theoretical models concerning the bonding between atoms in chemical compounds. We can explain bonding based upon empirical evidence and trends, as well as by applying fundamental physical principles to the particles in question. We must keep in mind that the efficacy of a model, however, is based upon its ability to predict and explain chemical phenomena. While a specific model may provide a very reasonable interpretation of certain characteristics exhibited by a system, it is never possible to say that this representation is complete or absolute. The failing of a model in one aspect or another preceded some of the most interesting events in science.

We shall use ball and stick models to show correct molecular geometries. They offer no information concerning atomic sizes or bond lengths. Wooden spheres represent atoms of various elements according to a color code. A number of holes drilled into each of these units are positioned so that proper bond angles are portrayed when the spheres are connected. The connections represent chemical bonds (shared electron pairs) and are made by means of wooden or plastic dowels (single bonds) or flexible springs (multiple bonds).

Procedure

Part I

Create models and draw Lewis structures for the molecules and ions in Table 12.2 , Table 12.3 , and Table 12.4 examples of each step are shown in Example 12.1:

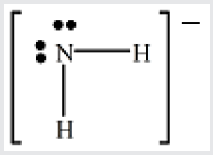
EXAMPLE 12.1 NH_2^-

1. Determine the total number of valence electrons that must be included in the Lewis dot structure. For molecules (neutral species) this equals the sum of the valence electrons for all atoms as determined by the group number for each element. For ionic species, this equals total valence electrons plus (or minus for cations) the ionic charge. This will include all of the valence electrons of each atom as determined by the group number of the element on the periodic table.

Two atoms of hydrogen (Group IA) each contribute one valence electron, 1 atom of nitrogen (Group VA) contributes five valence electrons, the minus one charge indicates one additional electron, yielding a total of eight electrons for the Lewis structure.

2 H	$2e^-$
1 N	$5e^-$
–1 ion charge	$1e^-$
Total	**$8e^-$**

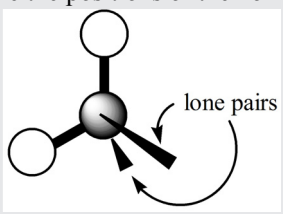
2. Draw a Lewis electron dot structure for the species.



3. Build the model. If using the wooden balls and sticks, follow these conventions.

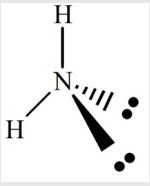
Valence Electrons on Central Atom	Ball Color (Number of Holes)
2	dark blue (2)
3	light green (3)
4	black (4)
5	brown (5)
6	silver (6)

For the atoms surrounding the central atom use the same conventions but include the yellow balls for hydrogen (one hole) which can only form one bond. Represent each non-bonding (unshared) pair of electrons in the Lewis structure with a dowel. This will help you to visualize the positions of the non-bonding pairs:



EXAMPLE 12.1 NH_2^-

4. Study carefully the model that you have constructed. Note the geometry of the connected atoms and of all the electron pairs about the central atom. Now draw in the space provided, a three-dimensional representation using your model as a guide:



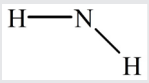
The wedges represent a bond or electron pair coming out of the plane of the page. A dotted line represents a bond behind the plane of the page, and the solid lines are in the plane of the page.

5. Determine the orbital (electron pair) geometry about the central atom using VSEPR theory and indicate the hybridization of the central atom.

The orbital geometry of NH_2^- is tetrahedral and the hybridization is sp^3.

6. Determine the molecular shape of the molecule or ion. This is based on the atomic geometry about the central atom. The molecular shape structure often excludes unshared pairs. Ionic charge is often included using brackets around the species.

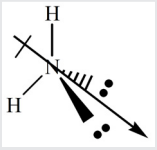
NH_2^- has bent molecular geometry:



7. Now list the electronegativities of the bonded atoms and calculate the differences in their electronegativities. Determine from this which bonds are polar and which are nonpolar:

H	2.2
N	3.0
ΔEN	**0.8**

8. If the molecule has all nonpolar bonds, write 'nonpolar'. If polar bonds are present draw another structure as in part (d) and add the dipole arrow to indicate the net dipole of the species. If the bond dipoles cancel due to the symmetry, show this and label the diagram as "nonpolar'. A compound may have polar bonds and still



be nonpolar, if the bond dipoles cancel due to symmetry (as in boron trifluoride).

EXAMPLE 12.1 NH_2^-

9. Give the oxidation number for each element in the compound.

For NH_2^- the H's have an oxidation number of +1 and the nitrogen must have an oxidation number of -3. Remember that the sum of the oxidation numbers must be equal to the charge on the particular species. Refer to your text for the rules for assigning oxidation numbers.

10. Give the formal charge for each atom in a compound. Remember that the formal charge is nothing more that a means to make a better guess at the correct Lewis structure of a compound or ion. Formal charge does not have any real physical significance.

For NH_2^- there really isn't any reason to calculate formal charges since there is only one possible way to put these atoms together. That is, if we do not force H to bond more than once. Formal charge on an atom is equal to the group number minus the number of electrons surrounding atom (all lone pairs plus ½ shared pairs). NH_2^- is shown:

$$\text{N} \qquad 5 - \left[4 + \frac{1}{4}(4)\right] = -1$$

$$\text{H} \qquad 1 - \frac{1}{2}(2) = 0 \qquad \textbf{(EQ 12.1)}$$

Molecular Polarity. The polarity of a molecule can be determined by looking at the shape of the molecule and the bonds withing the molecule. A polar molecule occurs when there is a net dipole moment on the molecule as determined by electronegativity differences between atoms. A nonpolar molecule will not have a net dipole moment. There are some visual indicators that can help determine if a molecule is polar. For example, a molecule can usually be classified as polar if: there is a lone pair (or lone pairs) on the central atom, or there are different types of atoms (or groups of atoms) on the central atom with different electronegativity values. Be careful using these rules especially with expanded octets and molecules with multiple central atoms.

Part II

Use Spartan to build the molecules. Measure bond lengths and bond angles with MMFF calculations. Then use semi-empirical calculations (AM1) to measure dipole moments, surfaces and investigate molecular orbitals. Complete Table 12.5 and Table 12.6 .

Spartan Molecular Modeling. When you open the Spartan application you see a blank screen with menus on top and along the side. To build a molecule, select an atom from the menu and click on the screen. The atom appears on the screen. Select another atom and click. The new atom is bonded to the first one. Continue adding one atom at a time until the molecule is complete. The computer adjusts the bond angles and bond lengths to give the correct molecular shape.

Now click on the "Energy" button"  That's it! What you see on the screen is a ball-and-stick representation of your molecule. You can change the structure to a space-filling model, a wire frame, or other choices by selecting options under the MODEL menu.

The energy button. The energy button performs a calculation to determine the most stable arrangement of atoms in your molecule. Using Hooke's Law, the bond lengths and bond angles are adjusted until the structure with the lowest potential energy is produced. In the parlance of molecular modeling, we say "the structure is minimized", in terms of its potential energy.

Once the molecule is built, you have several methods to investigate your structure:

- You can rotate the structure to see the 3-D arrangement of atoms; click and drag with the mouse.
- Click on the menu buttons to inspect bond length or bond angle, use menu options to view properties such as dipole moment or heat of formation.
- Use the calculation menu to generate an electron density surface for the molecule.

One of the more useful applications of Spartan is the **electron density surface** (electron cloud). The size and shape of the electron cloud defines the size and shape of an atom or molecule. You can make the surface transparent and view the atoms within. If you make the surface opaque, you get a structure that is very similar to a space-filling model. A space-filling model illustrates the van der Waal volumes for each atom, showing how the atomic orbitals penetrate into each other.

FIGURE 12.1

Menu options allow you to calculate the electrostatic potential for all points on the electron density surface. The electrostatic potential is defined as the energy of interaction between a point-positive charge and the nuclei and/or electrons in a molecule.

If the point charge is placed in a region of high electron density, the interaction is attractive, the potential is negative, and Spartan colors these regions red. If the point charge is placed near low electron density regions, the interaction is repulsive, the potential is positive and Spartan colors these regions blue. Yellow and green regions represent intermediate values for the potential.

You must use higher-level calculations (semi-empirical or ab initio methods) to view dipole moment, heat of formation and density surfaces. All these choices are available under the setup menu. Below are some basic directions for using Spartan:

Spartan and Electron Density Viewing:

1. Go to **START** and select **PC SPARTAN PLUS**.
2. Build molecule.
3. Drop down **SET UP** menu and click on **CALCULATIONS**.
4. Click **OK**.
5. Drop down **SET UP** menu and **SURFACES**.
6. Click **ADD:** Surface **DENSITY** and Property **DENSITY**.
7. Click **OK** and leave screen on the desktop.
8. Click **SET UP** again and select **SUBMIT**.
9. Be patient, the calculations can take a few minutes.
10. Save your file when prompted.

11. After Spartan says it has completed the save, click **DISPLAY**.
12. Select **PROPERTIES**.
13. On the Surfaces List screen put a check mark in the yellow density box.
14. Click on a part of the molecule. The property screen will toggle between molecule properties and surface properties.
15. Have fun looking at the molecules in a new way!

Spartan and Molecular Orbitals:

1. Using the same programs, create a model for the formate ion, HCO_2^-. Be sure to designate when you set up the calculations that the molecule has a minus one charge.
2. This time, have the program show the molecular orbitals for the molecule by checking the appropriate model.
3. Select **SET UP** then **SURFACES** check **ADD** under **SURFACE** select **HOMO** and click **OK.** Select **SET UP** then **SUBMIT.**
4. Repeat with **LUMO**, etc.
5. Draw the three molecular orbitals, labeling them as pi, n (nonbonding), and pi^* orbitals. Note which is the highest occupied molecular orbital (HOMO) and which is the lowest unoccupied molecular orbital (LUMO).

Prelaboratory Sheet

1. Complete the following table:

Valence shell electron pairs	Bonding electron "clouds"	Lone pairs	Formula	Orbital geometry	Approximate bond angles	Molecular geometry	Hybridization
			AX				
			AX_2				
			AX_3				
			$\ddot{A}X_2$				
			AX_4				
			$\ddot{A}X_3$				
			$:\ddot{A}X_2$				
			AX_5				
			$\ddot{A}X_4$				
			$:\ddot{A}X_3$				
			$:\ddot{A}X_2$				
			AX_6				
			$\ddot{A}X_5$				
			$:\ddot{A}X_4$				

Report Sheet

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge		VSEPR Theory and Valence Bond Theory Classifications
HCN Indicate the hybridization of both the C and N Total Valence Electrons	H-C-N bond angle	Polarity	Molecular Geometry Hybridization Carbon _____ Nitrogen_____ Orbital Geometry
H_2O Total Valence Electrons	H-O-H bond angle	Polarity	Molecular Geometry Hybridization Orbital Geometry
SO_2 Show all resonance structures and formal charges. Total Valence Electrons	O-S-O bond angle	Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
$CHCl_3$ Total Valence Electrons	H-C-Cl bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
PF_3 Total Valence Electrons	F-P-F bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
NH_4^+ Total Valence Electrons	H-N-H bond angle	Molecular Geometry Hybridization of central atom Orbital Geometry

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
CS_2 Total Valence Electrons	S-C-S bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
O_3 Show all the resonance structures and formal charges. This is a non-cyclic molecule. Total Valence Electrons	O-O-O bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
$AsCl_5$ Are the Cl atoms equato-rial, axial, or both? Total Valence Electrons	Cl-As-Cl bond angles _____and _____ Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
XeF_4 Are the F atoms equatorial, axial, or both? Total Valence Electrons	F-Xe-F bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
ICl_3 Are the Cl atoms equatorial, axial, or both? Total Valence Electrons	Cl-I-Cl bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
SO_3^{2-} Show all resonance structures and formal charges. Total Valence Electrons	O-S-O bond angle	Molecular Geometry Hybridization of central atom Orbital Geometry

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
SF_6 Are the F atoms equatorial, axial, or both? Total Valence Electrons	F-S-F bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
P_4 All of the phosphorus atoms are equivalent with no multiple bonds or expanded octets. Draw the entire molecule. Total Valence Electrons	P-P-P bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
I_3^- Don't forget the formal charges! Are the I atoms equatorial, axial, or both? Total Valence Electrons	I-I-I bond angle	Molecular Geometry Hybridization of central atom Orbital Geometry

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
$AsCl_3F_2$ Are the F atoms equatorial, axial, or both? Are the Cl atoms equatorial, axial, or both? Total Valence Electrons	Cl-As-Cl bond angle F-As-F bond angle Polarity F-As-Cl bond angle	Molecular Geometry Hybridization of central atom Orbital Geometry
SO_4^{2-} Look for some resonance structures that expand the valence of sulfur. Remember to show the formal charges. Total Valence Electrons	O-S-O bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
SF_4 Are the F atoms equatorial, axial, or both? Total Valence Electrons	F-S-F bond angles _____and _____ Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry

TABLE 12.2 Inorganic Compounds - Be sure to show the proper geometries!

Species	Lewis Dot Structure and Resonance structures including formal charge	VSEPR Theory and Valence Bond Theory Classifications
BF_3 Show all possible resonance structures. Indicate which structures are likely to form and why. Be sure to include formal charges. Total Valence Electrons	F-B-F bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
NO_2 Show all four resonance structures and charges. Identify the advantages of each. Total Valence Electrons	O-N-O bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry
$BeCl_2$ Show all possible resonance structures. Be sure to include formal charges. Total Valence Electrons	Cl-Be-Cl bond angle Polarity	Molecular Geometry Hybridization of central atom Orbital Geometry

TABLE 12.3 Organic Compounds - Fill in the missing bonds, atoms, and/or lone pairs.

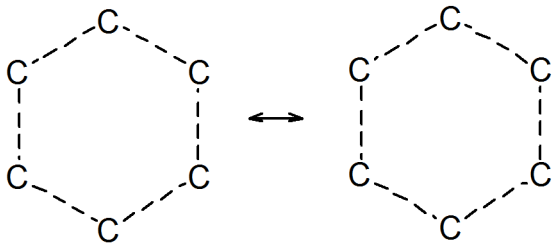
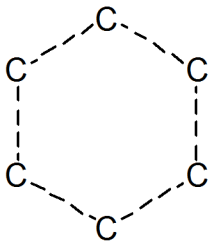
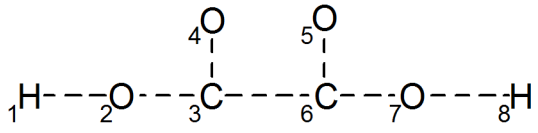
Species	Lewis Dot Structure	VSEPR Theory and Valence Bond Theory Classification
C_6H_6 is benzene. Show the two resonance structures for this cyclic molecule Total Valence Electrons		Hybridization of carbon atoms C-C-H bond angle Polarity
C_6H_{12} is cyclohexane. There will be one large ring formed out of the carbon atoms. Total Valance Electrons		Hybridization of carbon atoms C-C-H bond angle Polarity
$H_2C_2O_4$ Oxalic acid aka Ethanedioic acid Total Valence Electrons	Complete Lewis Structure on the skeleton below:  Redraw with the proper geometry:	Orbital Geometry C_3 O_2 Hybridization of specified atom C_3 O_2

TABLE 12.3 Organic Compounds - Fill in the missing bonds, atoms, and/or lone pairs.

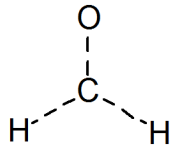
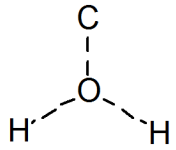
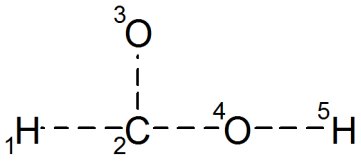
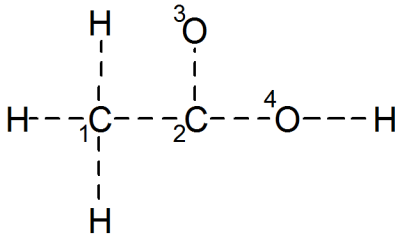
Species	Lewis Dot Structure	VSEPR Theory and Valence Bond Theory Classification
CH_2O HCHO is formaldehyde. Determine the best structure by completing the structures to the right. Total Valence Electrons	Structure 1  Structure 2 	Which structure makes the most sense and why?
HCO_2H Complete the structure for formic acid aka methanoic acid. Total Valence Electrons		Give the bond angles for H_1-C_2-O_3 C_2-O_4-H_5 Polarity
CH_3CO_2H Complete the structure for acetic acid aka ethanoic acid. Total Valence Electrons		Give the hybridization of the numbered atoms 1 2 3 4

TABLE 12.4 Isomers of Organic Compounds

Species	Lewis Dot Structures
C_3H_6 C_3H_6 has two distinct isomers. Draw each one. Total Valence Electrons	
C_4H_8 C_4H_8 has many possible variations. Draw 5 distinct possibilities. Total Valance Electrons	
C_4H_9OH Draw 4 distinct variations; each will have an OH group attached. Do not try to create any isomers without a hydroxyl, OH, group! Total Valence Electrons	

TABLE 12.5 Spartan Molecular Modeling

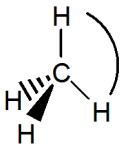
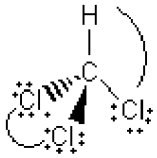
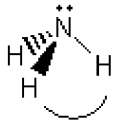
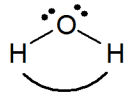
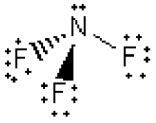
Draw Arrow Representing the Dipole Moment where appropriate on Structure	Bond Angle	Magnitude of Dipole Moment	Electrostatic Potential Surface (Use colored pencils) Several orientations for each molecule are possible.
	H—C—H	Polarity	
	H—C—Cl Cl—C—Cl	Polarity	
	H—N—H	Polarity	

TABLE 12.5 Spartan Molecular Modeling

Draw Arrow Representing the Dipole Moment where appropriate on Structure	Bond Angle	Magnitude of Dipole Moment	Electrostatic Potential Surface (Use colored pencils) Several orientations for each molecule are possible.
	H—O—H	Polarity	
	F—N—F	Polarity	
	F—P—F	Polarity	

Draw the three molecular orbitals, labeling them as pi, n (nonbonding), and pi^* orbitals. Note which is the highest occupied molecular orbital (HOMO) and which is the lowest unoccupied molecular orbital (LUMO).

TABLE 12.6 Spartan Molecular Orbitals

Species	Molecular Orbital Drawings
nitrite ion NO_2^-	

What is the significance to the stability of the nitrite ion of the fully occupied pi orbital?

Post Lab Questions

1. Explain why the bond angles increase or decrease in the following series H-C-H bond in methane, CH_4, H-N-H bond in ammonia, NH_3, H-O-H bond in water, H_2O.

2. Explain the differences between the H-C-H bond angle in methane, CH_4, and the bond angles in trichloromethane, $CHCl_3$ (Be sure to consider both the Cl-C-Cl and H-C-Cl bonding in trichloromethane, $CHCl_3$.).

3. Compare the dipole moments and bond angles for ammonia, NH_3, nitrogen trifluoride, NF_3, and phosphorus trifluoride, PF_3. Does each dipole point in the same direction? Explain.

TABLE 12.7

	NH_3	**NF_3**	**PF_3**
Dipole Moment			
Bond Angles			