# 3D Modeling of Molecular Structures[*]

## INTRODUCTION

Computational chemistry is an important branch of chemistry that uses chemical principals and theories along with the aid of computer programs to calculate molecular structures and predict material properties. Computational chemistry plays an important role in scientific research. Results from theoretical calculations are often used to interpret experimental data taken from laboratory measurements. Scientists also apply the tools of computational chemistry to search for new molecules and materials and predict their properties (this is often used in the drug discovery). It is especially useful for those molecules that are not easily synthesized on the bench. Because of its power and importance, computational chemistry has been incorporated into the curriculum of many upper level classes/labs at many universities.

**Learning Goals**

In this new lab activity, you will learn how to make predictions of molecular structures using Lewis structure and VSEPR theory and then verify them with 3D visualization software. The objective is to introduce you to a few basic concepts and give you a flavor for what computational chemistry is. Most importantly this activity is designed to help you to better understand the concepts and theory discussed in chapters 12 and 13 in the textbook.

You will use software, called **Avogadro**, to model molecular structures in 3D. Given a molecule, first you can use VSEPR to predict the geometry. Then Avogadro utilizes a force field method to search for the most stable structure. This is better than the VSEPR theory, and has the advantage of much greater physical and mathematical accuracy. The visualization of molecular structures can help you verify molecular geometries predicted based on Lewis structures and VSEPR theory from the textbook.

**Overview**

In this lab activity, you will first determine the Lewis structure of a molecule following the octet or/and duet rule and apply the VSEPR theory to predict the geometric arrangements of bonding and non-bonding electron pairs around the central atom. Finally, you use Avogadro to optimize the 3D structure. The molecular structures can then be visualized, and bond distances and bond angles can be measured.

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[*]This manual is developed by Xinxin Cheng supervised by Prof. Li Wang

[†] In mathematics, the maximum and minimum of a function are the largest and smallest values within a given neighboring range (local maximum or local minimum) or the entire domain of a function (global maximum or global minimum).[4] Similarly, the energy of a molecule can be

**THEORETICAL BACKGROUND**

*Lewis Structures*

The Lewis structures of molecules represent the bonding between atoms and the lone pairs of electrons in the molecules. In Lewis structures, chemical bonds are drawn as lines between atoms and excess lone electron pairs are drawn as dots next to the atoms. Lewis structures generally follow the *octet rule* (each atom accommodates 8 valence electrons), where atoms tend to achieve noble gas electron configurations by gaining, losing or sharing electrons. There are some exceptions to the octet rule. For example, hydrogen follows the duet rule (each H atom accommodates 2 valence electrons) to obtain a stable electronic configuration while sulfur can have a valence shell with 12 electrons in $SF_6$.

To draw Lewis Structures, please follow these steps[1]:
    i.    <u>Sum the valence electrons from all the atoms.</u> The total number of electrons shown in a Lewis structure should equal the sum of valence electrons. Non-valence electrons are not included in Lewis structure. Valence electrons are the electrons of an atom that can participate in chemical reactions and form chemical bonds with other atoms. For main group elements (and the elements we will use in this lab), the valence electrons are simply the outermost electrons in the atom. The number of valence electrons is equal to the group number. For example, oxygen is in main group VI and therefore it has six valence electrons. Hydrogen is in main group I and therefore it has one valence electron. So $H_2O$ has 1+1+6=8 valence electrons.
    ii.    <u>Use  pairs of electrons to form  bonds between atoms.</u> A line is used to indicate a pair of bonding electrons.

<p style="text-align:center">H———O———H</p>
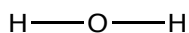
    iii.    <u>Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements. Please refer to Chapter 13, page 627-631 for exceptions to the octet rule.</u>  In the example of $H_2O$, four electrons have been used to form the two single H-O bonds; therefore, four (8-4=4) electrons remain to be arranged. The hydrogen atoms are satisfied with the duet rule, but oxygen still needs four electrons to satisfy the octet rule. Thus the remaining four electrons should be added to oxygen as two lone pairs. Eventually we can draw:

<p style="text-align:center">••<br>H———O———H<br>••</p>
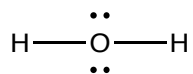
    iv.    To see if your Lewis structure is correct, check:
    a.    The total number of electrons.
    b.    The octet rule or duet rule for each atom. If there are not enough electrons to satisfy the octet rule for all the atoms, multiple bonds (double bond or triple bond for instance) should be used. As previously showed, there are some exceptions. Please refer to Chapter 13, page 627-631 for more examples. In the

future, you will get a deeper understanding of these exceptions after learning the hybridization and orbital theories given in Chapter 14 of the textbook.

Note: Please refer to chapter 13, page 622-626 for more information about Lewis Structures.


## *VSEPR*

VSEPR is short for *Valence Shell Electron Pair Repulsion*. This acronym can be pronounced as "vesper." It is very useful in predicting the geometry or shape of molecules formed from nonmetals. The main postulate of VSEPR is that the valence electron pairs and the lone pairs surrounding an atom all mutually repel each other and therefore the structure around a specific atom is determined by minimizing the repulsions. The strength of repulsive forces is arranged as:

Lone pair-lone pair (L-L) > lone pair-bond pair (L-B) > bond pair-bond pair (B-B)

To determine the geometry of molecules with VSEPR, please follow these steps[1]:

    i.    <u>Draw the Lewis structure.</u> For example, $NH_3$ can be drawn as:
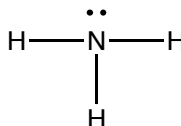


    ii.    <u>Count the electron pairs (including bonding and lone pair) around the central atom. Arrange them in the way to minimize repulsions, i.e. put the pairs as far apart as possible.</u> In the example of $NH_3$, there are 3 bonding pairs and one lone pair. There are 4 electron pairs in total so we know that the best arrangement is a tetrahedral geometry.
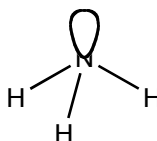


    iii.    <u>Determine the position of the atoms from the geometry of the electron pairs. Use the</u> "AXE" method described below to help. The steric number is equal to the number of electron pairs (including bonding and lone pair). In the example of $NH_3$, the steric number is 4.
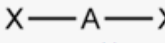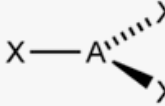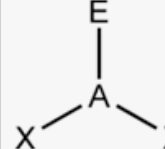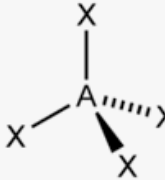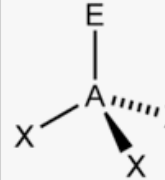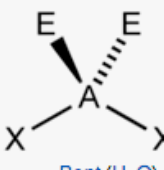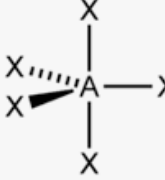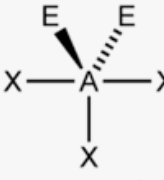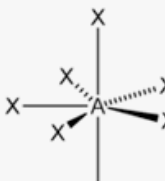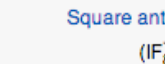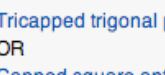
    iv.    <u>Name the molecular structure.</u> The name of the molecular structure is based only on the positions of the atoms, not the arrangement of the electron pairs. For example, $NH_3$ has a **tetrahedral** arrangement of electron pairs but its molecular structure is **trigonal pyramidal** (as shown below)
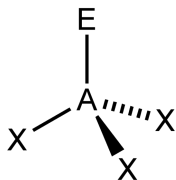
(For NH$_3$:  A - N atom, X - H atom, E – lone pair)

When applying the VSEPR theory, the "AXE" method of electron counting and geometry determining is generally used. A is the central atom; X means the ligand atom (in the case of **double and triple bonds**, it is still one X) and E represents a lone pair. The total number of X's and E's is called "steric number" and will be used to determine the arrangement of the electron pairs. Both bonding and lone pairs of electrons determine the electron pair arrangements. The geometric name of a molecule is determined by the positions 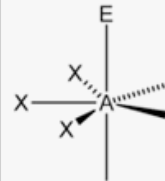of the atoms (bonding pairs). Based on the steric number and the number of X's and E's, VSEPR theory predicts the geometries or shapes of molecules. These are given in the following table[2]:

Table 1: Molecular Geometries

| Steric No. | Basic geometry 0 lone pair | 1 lone pair | 2 lone pairs | 3 lone pairs |
|---|---|---|---|---|
| 2 | Linear ($CO_2$) | | | |
| 3 | Trigonal planar ($BCl_3$) | Bent ($SO_2$) | | |
| 4 | Tetrahedral ($CH_4$) | Trigonal pyramidal ($NH_3$) | Bent ($H_2O$) | |
| 5 | Trigonal bipyramidal ($PCl_5$) | Seesaw ($SF_4$) | T-shaped ($ClF_3$) | Linear ($I_3^-$) |
| 6 | Octahedral ($SF_6$) | Square pyramidal ($BrF_5$) | Square planar ($XeF_4$) | |
| 7 | Pentagonal bipyramidal ($IF_7$) | Pentagonal pyramidal ($XeOF_5^-$) | Pentagonal planar ($XeF_5^-$) | |
| 8 | Square antiprismatic ($IF_8^-$) | | | |
| 9 | Tricapped trigonal prismatic ($ReH_9^{2-}$) OR Capped square antiprismatic | | | |

Note: Please refer to chapter 13, page 637-645 for more information about the VSEPR Model

### 3D Modeling of Molecular Structures

The 3D modeling of molecular structures will be carried out using a free online computational chemistry software called "Avogadro."[3] This modeling program allows you to verify the molecular geometries predicted from the VEEPR theory, visualize molecular structures in 3D, and obtain the bond distances and bond angles from the calculations.  Since Chem 0330 is an introductory course, you are not expected to understand the theory behind the molecular modeling.  However, if you are interested, the following paragraph gives more information about molecular modeling.

Molecular modeling includes all theoretical methods and computational techniques in order to predict the properties or mimic the behavior of molecules. Depending on the fundamental theory used in the program, there are many types of molecular modeling methods including *ab initio*, density functional, semi-empirical and empirical, molecular mechanics, molecular dynamics, etc. These methods have different ranges of applicability. The "Avogadro" program used in this lab activity utilizes the molecular mechanics method and employs certain force fields to optimize molecular geometries.  More information can be found in Ref. 3.

Here is a screen shot showing the user interface (UI) of Avogadro (based on a Mac operation system):
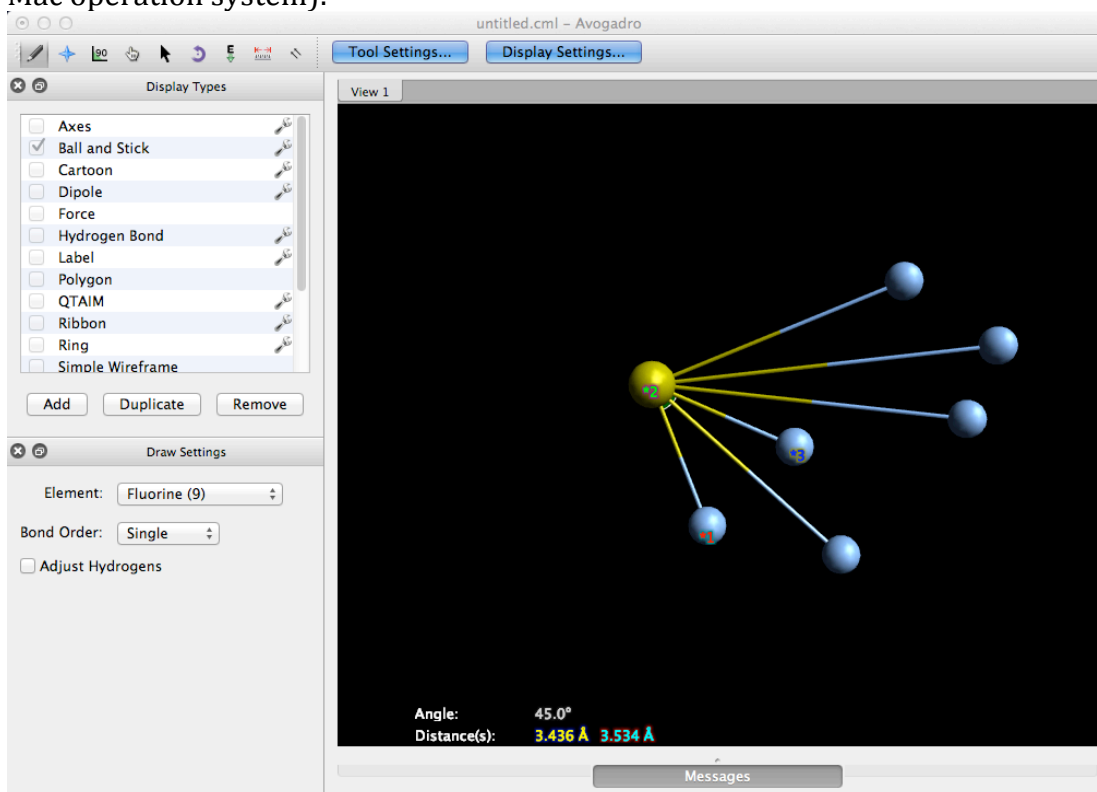


The icons/buttons you will most frequently used include "Draw Tool", "Navigation Tool", "Auto Optimization Tool" and " Measure Tool". The function of each icon is indicated by the symbols.  More details and explanations can be found by keeping the mouse steady over an icon for several seconds.

**PROCEDURE (work in groups of 2 to 3 students)**

*Materials*

Laptop (Mac and Windows OS are both compatible. This manual is written based on a Mac operation system. Though most parts should be the same, Windows users may experience some difference in the UI such as functional button arrangements.)

Lecture Textbook (recommended)

*Notice:* because Avogadro is a free, open source program and is still under construction, it may get stuck from time to time or stop responding. In this case, just simply close the whole program and reopen it. It should behave normally after restarting.

The molecules you are going to work on include $OCl_2$, $CS_2$, $BF_3$, $NF_3$ and $SF_6$.

I. **Use "AXE" method to predict the geometry**

1. Figure out the central atom and setric number.
2. Refer to the "AXE" table to obtain the geometry of the molecule predicted by VSEPR thoery.
3. Fill in the first four blank columns in the table of question 2 in the lab report.

II. **Use "Avogadro" to visulize and verify the molecular structure**

1. Install the cross-platform modeling software: Avogadro [3]
   a. Go to the Avogadro software website (http://avogadro.openmolecules.net/wiki/Main_Page) and download the installer by clicking 'Get Avogadro'. Mac/Windows/Linux versions are available on the website. Download the version that best matches your operating system.
   b. Follow the instructions to install the software. For Mac system, simply drag the app to the Application folder. For Windows system, double click the installer to install.
2. Build a specific molecule ($OCl_2$ is used as an example)
   a. Open the Avogadro program.
   b. Use the 'Draw Tool' (click the pencil icon ) to build the molecules. Click on the icon to choose the tool. Left mouse: click and drag to create atoms and bonds. Right mouse: delete atoms. Change the atom type by clicking the 'Element' pull-down menu.
   c. First draw the center atom (if there is one) and then draw the outside atoms (ligands). Check the 'Adjust Hydrogens' box when Hydrogen atoms are the main ligands of a particular center atom. Uncheck this box when other (non-hydrogen) ligands are needed. As an example,

let's take the first molecule in the lab report, $OCl_2$. With the 'Draw Tool,' choose 'Oxygen' in the pull-down 'Element' menu, uncheck the 'Adjust Hydrogen' box, and click in the blank working area. Now the working area should show an oxygen atom (in red). It is the central atom in $OCl_2$.

d. Then we draw the ligands of $OCl_2$. Continue by choosing 'Chlorine' in the 'Element' menu and 'Single' in the 'Bond Order' menu. Click on the oxygen atom, hold and drag to any blank working area to create an oxygen-chlorine single bond. Now you should be able to see a green chlorine atom connected to the red oxygen atom with a half-red-half-green single bond. Draw another Chlorine using the same method.

e. Now you can see your $OCl_2$ molecule is completely built up into certain structure, which may not be in a good shape. For now don't worry about the structure or the bond distance or the bond angle. The geometry will be optimized later.

3. Rotate and view the 3D model

a. Use the 'Navigation Tool' (click the star icon ) to freely rotate the molecule in three-dimensional space. Left mouse: click and drag to rotate the view. Middle wheel: roll up and down to zoom out and in. Right mouse: click and drag to move the view. If you don't have a mouse, use the track pad accordingly.

b. It may be easier to build the molecule when it is rotated the proper direction. Use this tool when building a spatially complicated molecule.

c. This tool can also be used later to get a better idea about the 3D molecular model after you finish building and optimizing the molecule.

4. Optimize the molecular structure

a. Use the 'Auto Optimization Tool' (click the E icon ) to optimize the molecular structure. Use the default force field (UFF) and algorithm (steepest descent) for now (if you are interested in knowing how the program works, the Avogadro website has information on force fields: http://avogadro.openmolecules.net/wiki/Tutorials:Force_fields). Click 'Start' to start the optimization.

b. Use the 'Navigation Tool' to view the optimized 3D structure.

c. (Optional) drag any atom in the molecule with left mouse and observe how the molecule is gradually optimized to the equilibrium structure again.

d. Click 'Stop' when the optimization is done.

e. The $OCl_2$ molecule we just built is used as an example. To optimize it use the 'Manipulation Tool' (the hand icon ) to drag the atoms a very long distance or a very large angle (or whatever unreasonable

geometry you can come up with), and try to optimize it. See if the molecule comes back to the same structure in the end.

    f.   Notes and tips: Based on your fundamental chemistry knowledge[†], if you find the optimized energy is unreasonable, an extremely large value, or very different from the geometry you get from VSPER theory, **you could give the molecular structure a little disturbance by dragging one of the atoms out of position, changing the bond distance, or changing the bond angle.** For example, you may obtain a planar $SF_6$ or $NCl_3$ and you know it's not correct from VSEPR or hybridization theory. Try to rotate the molecule to give you a better view, drag one of the ligands out of the plane and optimize the geometry again. The energy should drop dramatically as the structure changes.

5.   View the 3D model by automatic rotation

    a.   For fun, use the 'Auto Rotation Tool' (click the curved arrow icon

       ) to automatically rotate the 3D model in different directions. Change the direction by sliding the x, y or z rotation bars.

6.   Measure the bond distances and bond angles

    a.   Use the 'Measure Tool' (click the ruler icon    ) to measure specific molecular properties. Click two atoms for the bond distance and three atoms for the bond angle. For example, in $OCl_2$, first click on either Cl to choose the atom, then click on O, you can get one O-Cl bond distance. Continue to click on the other Cl, you can get another O-Cl bond distance and the Cl-O-Cl bond angle. Click on any selected atom again to cancel the selection if necessary.

    b.   Use the 'Navigation Tool' to rotate the molecule to a proper view and measure all the properties you need.

    c.   Fill in the last two blank columns in the table of question 2 in the lab report.

7.   Repeat step 1-6 for $CS_2$, $BF_3$, $NF_3$ and $SF_6$.

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[†] In mathematics, the maximum and minimum of a function are the largest and smallest values within a given neighboring range (local maximum or local minimum) or the entire domain of a function (global maximum or global minimum).[4] Similarly, the energy of a molecule can be represented as an energy function of a set of molecular coordinates such as bond lengths and angles. The energy function is usually a multi-dimensional surface, which has a lot of energy minima and maxima. When you optimize the geometry of a molecule, you are actually searching for the most stable structure. This is the global minimum on the energy surface. However, when you optimize the geometry the molecule may drop into a local minimum of the energy landscape. But that's not our goal. Our goal is to obtain the most stable structure that corresponds to the global minimum.

   Generally there are several local minima, but only one global minimum. The final optimized structure partially depends on the initial starting geometry. That's why sometimes you may have a weird geometry and need to change the initial structure a little bit.

**REFERENCE**

1. Steven S. Zumdahl and Donald J. DeCoste, *Chemical Principles (7th edition)*
2. http://en.wikipedia.org/wiki/VSEPR_theory
3. Marcus D Hanwell, Donald E Curtis, David C Lonie, Tim Vandermeersch, Eva Zurek and Geoffrey R Hutchison; "Avogadro: An advanced semantic chemical editor, visualization, and analysis platform" *Journal of Cheminformatics***2012, 4:17**.
4. http://en.wikipedia.org/wiki/Maxima_and_minima