

## Lab 02: Molecular Structure

### INTRODUCTION

#### Goals

- Represent the bonding of a covalent molecule or ion by a Lewis structure.
- Describe the geometry of a covalent molecule or ion from a Lewis structure using VSEPR theory.
- Compare theoretical bond angles between two molecular structures.
- Rationalize observed bond angles in a molecular structure by explaining deviations from a theoretical structure.

#### Background

The bonding structure of a molecule determines its behavior. Many properties, including chemical reactivity, phase change characteristics, and appearance of compounds depend on the arrangement of atoms in a molecule and how that geometry lends itself to the distribution of the molecule's electron cloud. This lab procedure will work through the process of understanding the sub-microscopic view of molecular structure and geometry using various tools to symbolically represent molecules of compounds, and then use that model to inform later discussions of the observable behavior of those compounds.

The first tool commonly used for representing the **covalent (electron-sharing) bonding** of a molecule is the **Lewis diagram or structure**. While originally developed empirically to explain observations like compound polarity and phase changes, a few of its principles continue to hold up under the modern lens of the quantum model of the atom and offer insight into how the quantum mechanical treatment of electrons leads to bonding interactions. In particular, two concepts stand out:

- Only the electrons with the highest principle quantum number  $n$  participate in covalent bonding, or the **valence electrons**, as the electrons in lower energy states are in orbitals or waves that do not overlap well with the orbitals/waves of other atoms. This means that the number of bonding electrons available to each atom in a molecule can be determined by simply counting where it is in a row or period of the periodic table, starting from the left side of the table.
- The most energetically favorable state for an atom is usually one where all the orbitals with the highest principle quantum number  $n$  are filled with electrons. As the elements in the second and third rows/periods of the periodic table only have electrons with  $n = 2$  or  $3$  in their ground or lowest energy state, this means the most favorable bonding interactions are those that give each of those atoms the equivalent of 8 valence electrons, corresponding the Lewis diagrams' octet rule.

With both of these concepts, there are notable exceptions, such as transition metals having the  $d$  orbitals with  $n$  one level lower than the highest available contributing to bonding and elements like

boron not making a full octet when bonding, but they cover enough cases to make them still useful for discussing covalent bonding.

It is important to remember though that Lewis diagrams do not adequately convey enough information to explain a compound's behavior from its molecules. As typically drawn, these structures imply that bonds occur at 90° angles, and don't make any prediction how they should be arranged when there are more than one type of bond made to a single atom. The **Valence Shell Electron Pair Repulsion (VSEPR) Theory** attempts to remedy this by invoking **Coulomb repulsion** as a driving factor for determining which arrangement of bonds is the most energetically favorable. Each covalent bond in a molecule represents an area of higher electron density and will repel other areas of higher electron density - the other bonds or lone (or nonbonding) pairs of valence electrons. Therefore, the bonds and lone pairs of valence electrons will spread out around the atom in question to minimize the total repulsions between areas of high density in the electron cloud. Assuming that they spread evenly, the geometry of the bonds around an atom in a molecule can be predicted by the total number of bonds and lone pairs of valence electrons around that atom, or its **steric number (SN)**. Figure 1 shows the predicted geometries for steric numbers of up to 6.


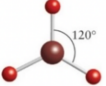
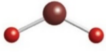

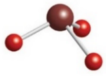
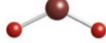

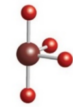
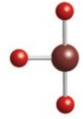



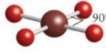
Steric Number = X + E	No lone pairs	1 lone pair (E = 1)	2 lone pairs (E = 2)	3 lone pairs (E = 3)
2	Linear (180°) 			
3	Trigonal planar (120°) 	Bent (<120°) 		
4	Tetrahedral (109.5°) 	Trigonal pyramidal (<109.5°) 	Bent (<109.5°) 	
5	Trigonal bipyramidal (90° and 120°) 	Seesaw (<90° and <120°) 	T-shaped (<90°) 	Linear (180°) 
6	Octahedral (90°) 	Square pyramidal (< 90°) 	Square planar (90°) 	

Figure 1: The molecular geometries predicted by VSEPR theory organized by the steric number of and number of lone pairs around the central atom.

In concert with the geometries predicted by VSEPR theory, additional information about the constituent atoms in a molecule can allow us to begin predicting the observable macroscopic behavior of a molecule. The **electronegativity** of an element describes its ability to draw the electron density of a covalent bond towards itself and away from equal sharing with another atom. More electronegative elements, such as chlorine, fluorine, and oxygen, will draw electron density away from less electronegative atoms, such as boron, carbon, and hydrogen. The unequal distribution of electron density means an unequal distribution of charge density; the more electronegative atom in a bond will have a greater electron density and gain a partial negative charge (represented in a diagram by  $\delta^-$ ) while the less electronegative atom in a bond will have a lesser electron density

and therefore a partial positive charge ( $\delta^+$ ). A covalent bond with unequal distribution of the electron cloud density like this is known as a **polar covalent bond** and has an associated **dipole moment**,  $\vec{\mu}$ , which measures the amount of charge separation  $q$  and the distance (and direction) between those separated charges  $\vec{d}$ :

$$\vec{\mu} = q\vec{d} \quad (1)$$

The amount of the partial charges around the atoms and by extension the magnitude of the dipole moment depends on the difference between the electronegativity of the two elements. The greater the difference in electronegativity, the greater the polarity of the bond and its associated dipole. Bonds where there is no or very little difference in electronegativity are known as **nonpolar covalent bonds** and have no associated dipole moment.

When determining the overall behavior of the molecule, each of the individual bonds' dipoles must be considered. Both the magnitude and direction of the individual dipoles influence how they add together; dipoles that are facing in the same direction will add together, while dipoles facing in opposite directions will subtract one from another, canceling out if they have the same magnitude. For example, the linear molecule carbon dioxide has two polar carbon-oxygen bonds, but they both have dipoles pointing opposite directions towards the central carbon atom - these dipoles cancel, making carbon dioxide a nonpolar molecule.

If they are pointing at angles other than  $0^\circ$  and  $180^\circ$  from each other, then the addition will be somewhere in between the two extremes. The portion of the dipole moments that oppose each other will cancel out, while the portion of the dipole moments pointing in the same direction add together. The water molecule has two polar hydrogen-oxygen bonds at an angle to each other (VSEPR predicts  $109.5^\circ$ , but the extra repulsion from the lone pairs on oxygen puts it closer to  $104.5^\circ$ ). Therefore, the parts of the dipoles that point along the line between the hydrogen atoms cancel out while the rest of the dipoles add together, creating a net dipole moment. Figure 2 demonstrates a few examples of adding individual dipole moments together to determine if a molecule has a net dipole or not.

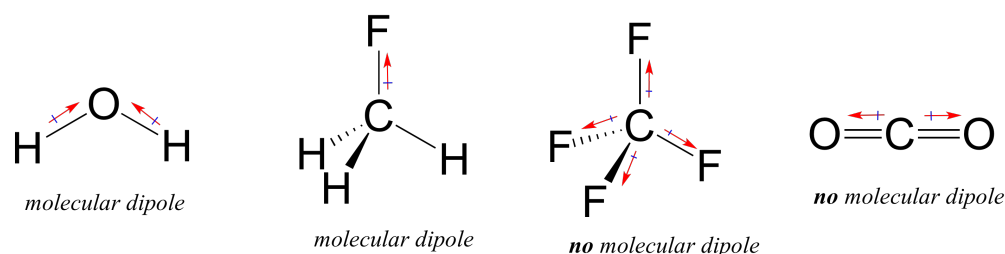


Figure 2: Examples of molecules with polar bonds and determinations of whether they have a net molecular dipole or not. The arrows represent the dipole moments of individual polar covalent bonds.

The polarity of molecules plays a roll in determining the physical characteristics. Although carbon dioxide has a greater molecular mass than water, it is a gas at room temperature while water is a liquid. The dipole moment of the water molecule (along with its ability to participate in intermolecular interactions called hydrogen bonds, but that is outside the scope of this lab) allows it to attract other water molecules, holding them to a condensed phase of matter. The lack of a

dipole moment in carbon dioxide means it has much smaller attractions between its molecules, and therefore it behaves as a gas at room temperature.

**PREPARING FOR LAB 02: MOLECULAR STRUCTURE**

- For this lab activity, you do not need to have a procedure outline in your lab notebook. Instead, instructions will be provided as part of the post-lab worksheet. Still read through the procedure and prepare space in your notebook for measurements, data tables, calculations, and qualitative observations.
- Check that the PHeT Molecular Shapes tool found at <https://phet.colorado.edu/en/simulation/molecule-shapes> works on your computer and internet browser.
- Bring your computer with you to the lab.

**EXPERIMENTAL, LAB 02: MOLECULAR STRUCTURE****SAFETY**

While this lab activity will be performed entirely digitally, please be cognizant of materials for other experiments stored in the lab. Broken glass can be just as dangerous whether or not you're the one who used the glassware, and chemicals spilled on the lab bench can still be harmful even if the bench top looks clean.

Before you start the activity, take a moment to look around your lab space, putting away left out glassware and setting aside materials set up for other labs. Wipe down and dry your bench space. It's best to get in the habit of starting with a clean work area now when the danger is relatively low!

**Materials**

- Molecular model kits
- Internet browser capable of running the PHeT Molecular Shapes Tool

**Procedure**

In the first part of the lab, we will use molecular visualization tools to look at molecules in three dimensions. To start, log on to the PheT Molecular Shapes simulation located at: <https://phet.colorado.edu/en/simulation/molecule-shapes>.

Click on the play arrow and then select the “Model” option to enter the simulation area. You will see a screen like the one shown in Figure 3. Take a moment to see the options:

- You can add (or remove) bonds to the structure using the Bonding palette in the top right. You can add (or remove) lone pairs as well. “Remove All” gets rid of everything but the central atom.
- Notice that there is also an option to see the bond angle, molecule geometry (shape), and electron geometry. It's recommended to turn at least the molecular geometry on.

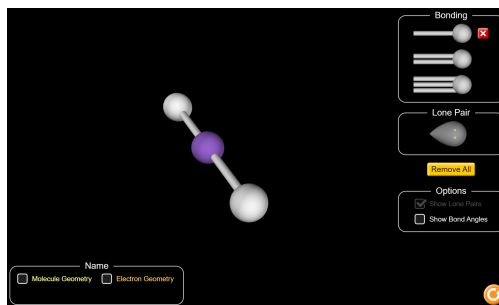


Figure 3: Starting screen for the PHeT Molecular Shapes tool in Model mode.

Use the worksheet in concert with the PHeT Molecular Shapes tool and the molecular model kits

to work through determining the Lewis structures and VSEPR geometries for the given molecules. For the first few molecules, show your Lewis structures and recreated model using the kit to your instructor before continuing to the next one.

When using the model kits:

- Pick a sphere for your central atom that has a number of bonding points corresponding to the steric number (SN, sum total of atoms and lone pairs around the central atom) from your Lewis structure.
- You can use either the SN 5 (pink sphere for phosphorous) or SN 6 (orange sphere for sulfur) atoms for linear molecules - just ignore the extra holes! The SN 5 atom can be used for trigonal planar molecules by ignoring the two poles.
- The gray connectors are for representing double and triple bonds.

For example, if you wanted to make a carbon-oxygen double bond, start with a black sphere for carbon, attach two gray connectors to it, then the red oxygen.

- Use either a different color sphere or no sphere at all to represent lone pairs of electrons. Some of the atoms already remove bonding points for lone pairs, such as the red ones for oxygen.

### Resonance Structures and Theory:

After completing the first section on Lewis Structures and VSEPR Geometries, watch the two videos posted to Blackboard and answer the questions on resonance below. To access the videos:

- Go to Blackboard: <https://learn.bu.edu>
- Click on “Lab content”, then “Molecular Structure” (Lab 02)
- There will be two video links in that folder; start with the video called “Introduction to resonance”
- Then work through “Drawing resonance structures”

Name:

BUID:

TF Name:

Section:

## POST-LAB ASSIGNMENT 02: MOLECULAR STRUCTURE

Complete this assignment while still in the lab. You may discuss it with your group, but you will each hand in your own, individual work when you are done. Ask your instructor to initial the Lab Etiquette section **before** uploading to Gradescope and make sure it's submitted correctly **before leaving the lab**. Remember to show your work for any calculations to receive full credit!

1. Let's investigate the molecule  $\text{BF}_3$ . Use the spaces provided below to answer the following:
  - (a) **Draw the Lewis structure** for the molecule in your lab notebook and write the steric number (SN) for the central atom.
  - (b) **Create a model of the molecule using the kit**. What is the class of molecule ( $AX_\#E_\#$  - where  $X_\#$  is the number of bonded atoms and  $E_\#$  is the number of lone pairs)? The PHeT tool and Figure 1 in the lab document on Blackboard will help with this!
  - (c) Use the **PheT simulation to model** the molecule. Add another single-bonded atom to make a total of three grey atoms bonded to the purple central atom. Based on the simulation, what is the molecular geometry (shape) of the molecule?
  - (d) Redraw your Lewis structure, this time as a **3D representation**, similarly to how you redrew the water molecule in the pre-lab assignment. You can rotate the simulated molecule or use your physical model to get a better view.
  - (e) Use the simulation to **measure the bond angles**. Write down the bond angle(s) between the terminal atoms (grey in the simulation) and the central atom.
  - (f) **Draw partial charges** ( $\delta^+$  and  $\delta^-$ ) on your 3D sketch for any polar bonds.
  - (g) Based on your sketch, is the molecule polar? How do you know?

(a) Lewis Structure:

(b) VSEPR Class of Molecule:

(c) VSEPR Molecular Geometry:

(d), (f) "3D" Lewis Structure, Bond Dipoles:

(e) F-B-F Bond Angle(s):

(g) Circle one then explain: Polar Nonpolar



Name:

BUID:

2. Repeat the above in your lab notebook but for  $\text{NH}_3$ .

(a) Why is it important to know the molecular shape before making determinations about molecular polarity?

(b) *For group discussion:* Do you agree with the bond angle that the PHeT simulation reports for the “ideal” structure of ammonia? Let’s investigate! At the bottom of the simulation screen it should say “Real Molecules”. Select  $\text{NH}_3$  from the drop-down list of molecules.

What is the bond angle in the actual ammonia molecule? Why is it different from the model bond angle?

3. Methane,  $\text{CH}_4$ , and water,  $\text{H}_2\text{O}$  both have steric number 4, but they have different bond angles.

(a) Explore both the molecules’ shapes by creating them with the PHeT tool. Which causes the bond angles to be different - a different central atom or the different number of bonded hydrogens/lone pairs?

(b) What are the actual bond angles for methane and water? You can check against the angles reported in the “Real molecules” part of the PheT simulation.

4. Repeat the process from question 1 to practice the following molecules or polyatomic ions in your lab notebook:  $\text{XeF}_2$ ,  $\text{TeCl}_4$ ,  $\text{I}_3^-$ ,  $\text{H}_2\text{CO}$ ,  $\text{BFCl}_2$ ,  $\text{AsF}_5$ ,  $\text{SCl}_4$ .

After practicing the above compounds, ask your TF to review one with you. They’ll select one from the list and you will create a physical model for it and show how both your drawn Lewis structure in your lab notebook and the model represent its geometry. Once you have an accurate representation of the compound, your TF will initial here.

**TF Initials:**

Name:

BUID:

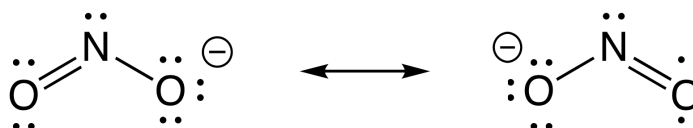
5. Using the PHeT tool and a physical model, create a hypothetical molecule with steric number 5, all single bonds.

(a) Report all the bond angles you observe.

- (b) Remove one of the atoms and replace it with a lone pair ( $AX_4E_1$  configuration), then replace one more ( $AX_3E_2$  configuration). Modify your physical model to match.

According to Figure 1 in the lab document on Blackboard, what is the name of this shape? And do the lone pairs prefer to have larger or smaller angles between them and the atoms with single bonds?

6. (After watching the videos from the **Resonance Structures and Theory** section of the procedure) Consider the two resonance forms shown the nitrite ion,  $\text{NO}_2^-$ .



- (a) Nitrite behaves like the form on the left 50% of the time and the form on the right 50% of the time. If the statement is false, explain why. T F

(b) What are the O–N bond orders in the nitrite molecule? Explain briefly.

- (c) Based on the formal charges on the oxygen atoms in the nitrite ion, is the negative charge of the ion localized on one of the oxygen atoms? Why or why not?

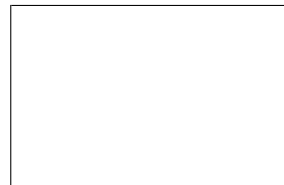
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7. Sketch resonance forms that describe the distribution of electrons in each of these molecules or ions in your lab notebook for practice: selenium dioxide  $\text{OSeO}$ , nitrate ion  $\text{NO}_3^-$ , benzene  $\text{C}_6\text{H}_6$ , and carbonate ion  $\text{CO}_3^{2-}$ . Make sure to include non-zero formal charges where relevant.

**TF Initials:**

After practicing the above compounds, ask your TF to review one with you. They'll select one from the list and ask you to describe how your resonance forms describe the bonding within that molecule or ion. Once you have an accurate representation of the compound, your TF will initial here.



Sketch the resonance forms for formamide in the box below. Formamide is similar to the structure of amino acids, the molecules that are polymerized into proteins. To start your first Lewis structure, use the carbon and nitrogen as central atoms, bonded to each other.

Formamide,  $\text{HCONH}_2$ :

