Chemical Bonding and Molecular Structure

After completing this lab, you will be able to:

- Draw the Lewis structures of covalent molecules.
- Recognize the electron domains and bonding domains in covalent molecules.
- Predict the three-dimensional geometry of the molecules by applying the principles of Valence Shell Electron Pair Repulsion (VSEPR) theory.
- Correlate the predicted molecular geometry with hybridization of bonding atoms in covalent molecules.
- Predict bond angles and hybridization of various atoms in complex molecules.

Introduction

Let us consider two compounds with seemingly similar molecular formulae: H_2O (water) and N_2O (nitrous oxide also known as laughing gas). We are all familiar with the fact that water is liquid at room temperature, and as the name suggests, laughing gas is a gas. Does water behave in our body the same way as laughing gas does? Common wisdom indicates that the chemical properties (and therefore biochemical behavior) of water and laughing gas are vastly different. *So how is it that the physical and chemical properties of water and laughing gas are different even though their molecular formulae appear very similar?*

One of the critical skills for your success in chemistry is to develop sound understanding of the physical and chemical behavior of various substances. The key to understanding and successfully predicting a wide range of physical and chemical properties of various substances lies in following two fundamental ideas:

1. **Bonding arrangement** of atoms in a given molecule indicated by their *Lewis structures.*

2. **Electronic Geometry,** or the overall shape and spatial arrangement of electronic domains in a given molecule predicted by different bonding theories.

Lewis structures are derived by the number of valence electrons of all atoms in a given molecule. When used in conjunction with Valence Shell Electron Pair Repulsion (VSEPR) Theory, they explain a lot about the structure and properties of covalent compounds. Drawing Lewis Structures takes understanding and practice, although a few simple rules will suffice for most structures. Of course, there are exceptions to some rules! Through practice you will learn how to apply the rules and how to recognize the exceptions. After the Lewis Structure is determined, a molecular shape can be assigned using the fundamental concepts of VSEPR Theory.

Guidelines for drawing Lewis structures

We will illustrate the steps for drawing Lewis structures by considering two molecules – water and nitrous oxide.

Step 1: Determine the **total number of valence electrons** indicated by the molecular formula:

- Count the valence electrons for each element in the compound and add them up to get the total number of valence electrons that are involved in bonding. The number of valence electrons for each atom is indicated by the “group number” of the group in which the element is located in the periodic table.
- Adjust for charge: Add one electron for each negative charge and subtract one electron for each positive charge.

Water: H_2O	**Nitrous oxide: N_2O**
Total Valence electrons: 1(H) + 1(H) + 6(O) = 8	Total valence electrons: 5(N) + 5 (N) + 6(O) = 16

Step 2: Draw the **skeleton of the molecule** by considering one of the atoms as the central atom and others connected to the central atom by a single bond. Use the following rules to determine the central atom:

- Hydrogen atoms can never serve as central atoms. They are always outside because they can participate in no more than a single bond.
- In most cases, with the exception of hydrogen, the less electronegative atom is the central atom. This is most often the first element listed in the chemical formula.
- Attach the atoms together with a "–" to indicate a two-electron bond between the central atom and each atom on the outside.

Water: H_2O	**Nitrous oxide: N_2O**
Central atom: **O** *Skeleton:* H—O—H	*Central atom:* **N** *Skeleton:* N—N—O

Step 3: Determine the number of **remaining valence electrons** not utilized by the single bonds in the skeleton:

- Count the number of **electrons used in single bonds** indicated in the skeleton (2 electrons for each line or single bond drawn).
- Determine the number of **remaining electrons** by subtracting the number of electrons accounted by single bonds from the total number of valence electrons found in Step 1. These electrons may be used to form double or triple bonds or may serve as lone pairs.

Water: H_2O	**Nitrous oxide: N_2O**
H—O—H Electrons used in single bonds = 2 x 2 = 4 ***Remaining electrons*** = 8 – 4 = 4	N—N—O Electrons used in single bonds = 2 x 2 = 4 ***Remaining electrons*** = 16 – 4 = 12

Step 4: Account for **double or triple bonds and lone pairs** (if any): Place the remaining electrons around the atoms in pairs, satisfying the octet rule around outer atoms before placing electrons on the central atom. The octet rule states that atoms have a tendency to have eight electrons in the valence shell.

- Hydrogen can only participate in a single bond and NEVER has lone pairs. Therefore, it forms what is called a duet. This is a result of the fact that hydrogen only has a 1s orbital that can only accommodate two electrons.
- If electrons remain after the octet rule if fulfilled around all outer atoms, add the remaining electrons around the central atom. Elements in Period 3 or lower on the periodic table are large enough to accommodate more then eight electrons.
- If you run out of electrons before satisfying the octet rule around the central atom(s), then lone pairs, usually from outer atoms, are used to form multiple bonds (double or triple) to complete the octet around the central atom(s).

- Account for non-zero formal charges (if any) on each atom. The net charge must match the charge provided along with the molecular formula. The formula charge for each atom may be calculated using the following equation:

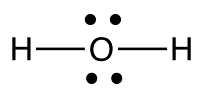
Formal Charge = # valence electrons - # bonds drawn to the atom - # lone electrons

This step needs careful attention to details!! Let us see how this is applied to our example molecules:

Water: H_2O

Skeleton from Step 2: H—O—H

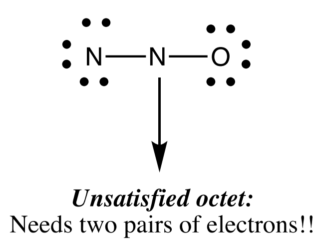
Remaining electrons from Step 3: 4 electrons
These electrons need to be accommodated on oxygen to satisfy its octet. The duet of hydrogen is already satisfied by the single bonds. The resulting Lewis structure for water is indicated below. There is no net charge indicated with the molecular formula of water and you can confirm that all atoms in the following Lewis structure possess zero formal charge.



Nitrous oxide: N_2O

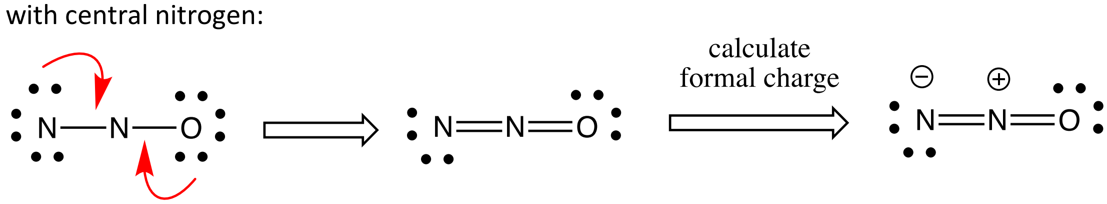
Skeleton from Step 2: N—N—O

Remaining electrons from Step 3: 12 electrons
The following arrangement is obtained when we accommodate these 12 electrons around oxygen and outer nitrogen:

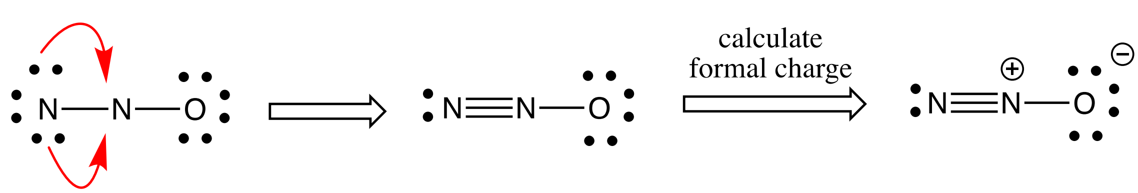


The problem of unsatisfied octet on the central nitrogen can be solved in two ways:

Solution 1: One lone pair from outer nitrogen and from oxygen can be used to form two double bonds with central nitrogen:



Solution 2: Two lone pairs from the outer nitrogen can be shared with the central nitrogen to form a triple bond between the two nitrogens.



Note that using two lone pairs from oxygen to form a triple bond between central nitrogen and oxygen is not a viable option because that arrangement results in non-zero formal charges on all three atoms, which is not a stable bonding arrangement because of excessive charge separation.

So which solution gives the correct Lewis structure of nitrous oxide? Both solutions provide a reasonable (and correct) Lewis structure for nitrous oxide and in reality; the actual structure is a hybrid between the two structures provided by Solutions 1 & 2. This is known as a resonance hybrid.

Activity 1

Build each molecule below using the molecular modeling sets. Then, complete the following tables. Use lines and wedges to represent 3-D structures as appropriate. Complete the following table:

Formula	Name	Skeleton	# of valence e^-	e^- used in single bonds	Remaining electrons	Complete Lewis structure
CH_4	methane					
NH_3	nitrogen trihydride (ammonia)					
H_2S	dihydrogen sulfide					
HOCN	cyanic acid					
BF_3	boron trifluoride					

Formula	Name	Skeleton	# of valence e^-	e^- used in single bonds	Remaining e^-	Complete Lewis structure
O_3	ozone					
CH_2O	formaldehyde					
SO_3	sulfur trioxide					
Cl_2O	dichlorine monoxide					
NOCl (central N)	nitrosyl chloride					
CO_2	carbon dioxide					
SeO_2	selenium dioxide					
NO	nitric oxide					
HCN	hydrogen cyanide					

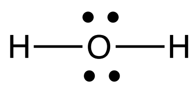
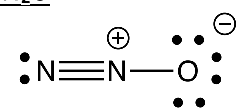
Activity 2

Several species containing central atoms from third period or below in the periodic table possess expanded octets in order to lower the formal charges on individual atoms. Complete the following table; take into account the expanded octet for each species.

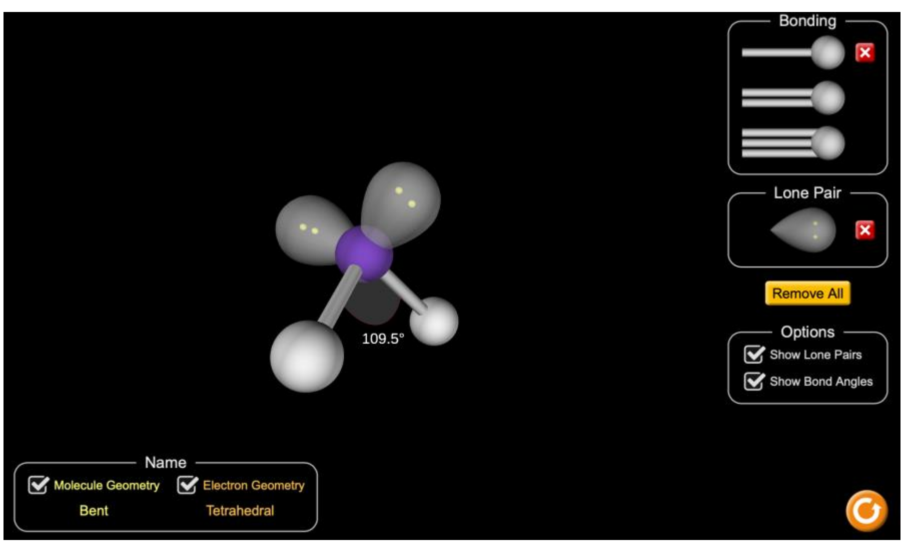
Formula	Name	Skeleton	# of valence e^-	e^- used in single bonds	Remaining e^-	Complete Lewis structure
$[PO_4]^{3-}$	phosphate anion					
$[SO_4]^{2-}$	sulfate anion					
PCl_5	phosphorous pentachloride					
SF_4	Sulfur tetrafluoride					
SF_6	Sulfur hexafluoride					
BrF_3	Bromine trifluoride					
IF_5	Iodine pentafluoride					

Predicting Molecular Geometry

The Lewis structures you explored in the last section provided us with the bonding arrangement as well as positions of the lone pair(s) on various species. In order to predict the physical and chemical properties of any compound, in addition to the bonding arrangement, we need to know the molecular geometry – the positions of nuclei in relation to each other. The molecular geometry is dependent on the number of electron domains around the central atom and this information is explicitly indicated by the Lewis structures. Lewis structures combined with the **V**alence **S**hell **E**lectron **P**air **R**epulsion **(VSEPR)** Theory allows us to predict the spatial arrangement of electron domains as well as the molecular geometry of the given species. The VSEPR Theory is based on a simple concept that electron domains around a central atom repel each other and arrange themselves as far apart as possible to minimize those repulsions. The total number of electron domains around a central atom can be determined simply by counting all single bonds, double bonds (both bonds between two atoms taken together), triple bonds (all three bonds between two atoms taken together) and lone pair of electrons. Let us count the electron domains on the central atoms on our example molecules.

Water: H_2O	**Nitrous oxide: N_2O**
 Total number of electron domains around the central oxygen = 2 single bonds + 2 lone pairs = 4 electron domains.	 Total number of electron domains around the central nitrogen = 1 single bond with oxygen + 1 triple bond with outer nitrogen + no lone pairs = 2 electron domains. In the same manner, we can determine the electron domains around oxygen (even though it is not the central atom) = 1 single bond with nitrogen + 3 lone pairs = 4 electron domains.

The molecular geometry and bond angles between various electron domains can be visualized by using molecular models or the Phet computer simulation "Molecular Shapes" (link provided in activity 3). The screenshot for water (4 electron domains) is reproduced below.



Activity 3

The goal of this activity is to visualize the electron domain geometry and the molecular geometry for various arrangements of electron domains for up to 6 domains.

Begin by building a model for each line in the table below using the molecular model set, where the sphere represents atoms, sticks represent bonds, and the lobes represent lone pair electrons. To begin find an atom that contains holes that is equal in number to the total number of electron groups. Then attach bonds and lone pairs to the central atom. Observe the shape and predict the bond angles present in this molecule.

Now, use the Phet "Molecular Shapes" simulation to electronically build each molecule in the table below. Begin by selecting "Model" on the first screen that loads. Then check "Show Bond Angles," "Show Lone Pairs," "Molecular Geometry," and "Electron Geometry."

Link: https://phet.colorado.edu/sims/html/molecule-shapes/1.0.0/molecule-shapes_en.html

Total Number of Electron Groups	Number of Bonding Groups	Number of Lone Pairs	Electronic Geometry	Molecular Geometry	Ideal bond angle(s)
2	2	0			
4	1	3			
3	2	1			
5	3	2			
4	3	1			
6	6	0			
5	5	0			
3	3	0			
4	2	2			
5	2	3			
4	4	0			
6	5	1			
6	3	3			

Answer the following questions in the recitation worksheet based on your observations from Phet simulations:

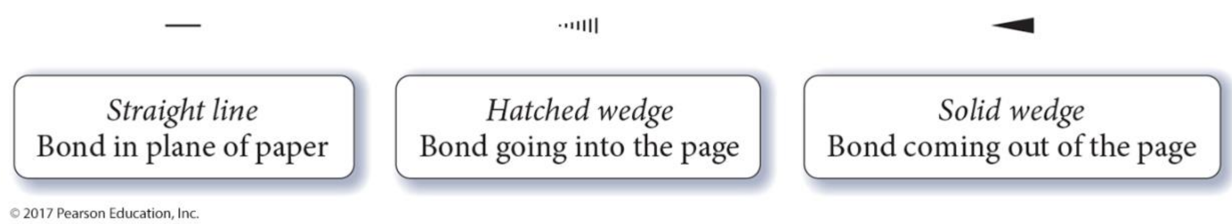
Q 1: Briefly explain in your own words why the bond angle decreases with increase in the number of electron domains.

Q 2: How does electron domain geometry differ from molecular geometry? Briefly explain in your own words.

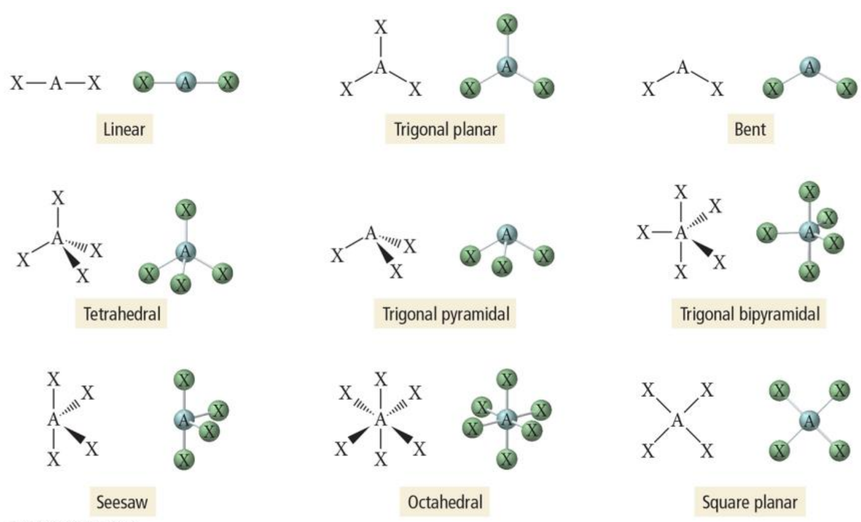
Q 3: Write a list of steps you will utilize to predict the electron-domain geometry for a given species in the absence of Phet simulations. The only information you are provided with is the molecular formula and the net charge.

Representing Molecular Geometry on Paper

In Activity 3, you came across various 3-dimensional patterns of molecular geometry. One of the challenges typically encountered by chemistry students is to represent 3-dimensional shapes on paper (which is in two-dimensions). Typically, chemists use the notation shown below to indicate the spatial arrangements of various bonding groups around a central atom.



These represents are further utilized to depict three-dimensional shapes indicated below. Note that in each example below, **"A"** represents the central atom and **"X"** represents the group bonded to central "A".



(Figures from Organic Chemistry by Loudon & Parise 6th Ed & Chemistry: A Molecular Approach by Tro, 4th Ed)

To apply your understanding, complete the Molecular structure and shape quiz available through Labflow.