

# Unit 3 Review 2

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ADVANCED LEWIS STRUCTURES, VSEPR

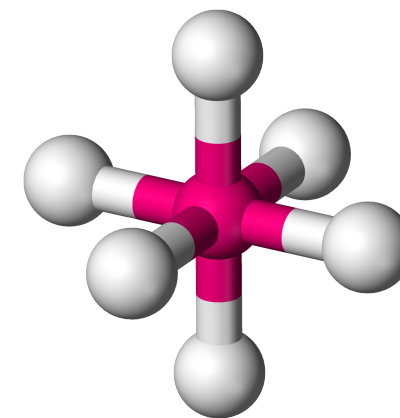
CHECK IT OUT:

<http://mccord.cm.utexas.edu/courses/fall2017/ch301/vsepr/>

# To-Do before Thursday

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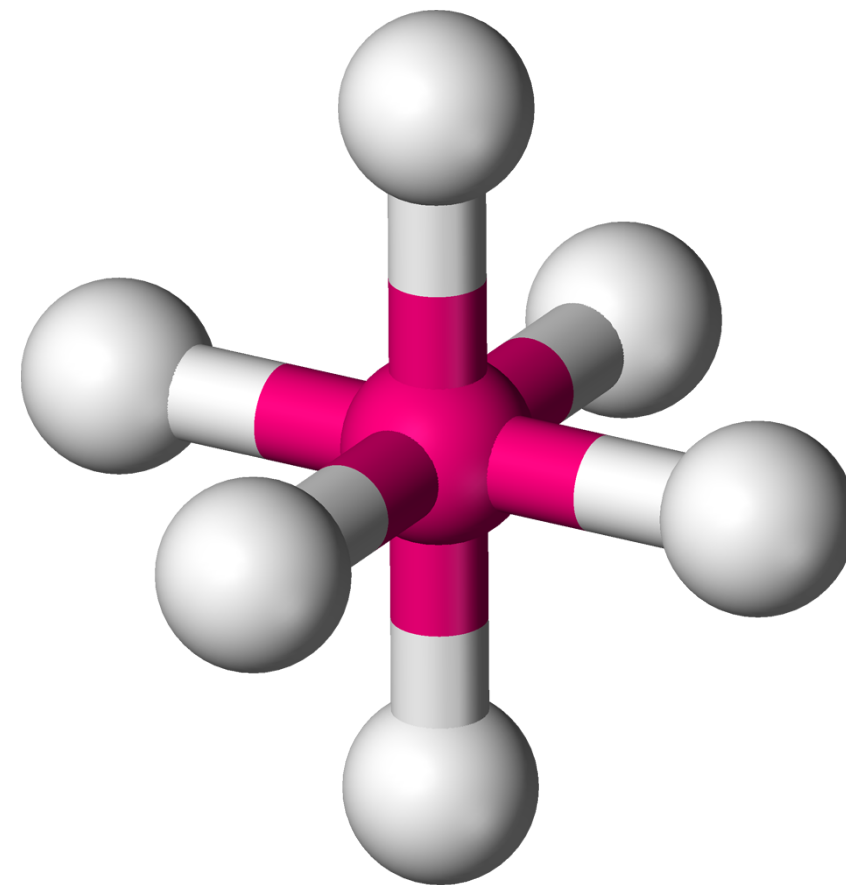
- **Finish homework**
  - The Sapling homework has some really good problems that will prepare you for the exam
  - For the exam, use your professor's definition of polarity, not what you see on Sapling/online.
  - Use Chrome!!!
- **Extra practice:**
  - Canvas extra practice
  - Gchem > Bonding Unit > Additional Content > Helpsheets and Worksheets
  - Another good exercise is drawing out the Lewis Structures of ALL polyatomic ions:
    - Draw the structure (might have resonance!)
    - Determine the formal charges on the atoms for your acceptable structures
    - Determine the VSEPR geometry and bond angles
    - Check your work with wikipedia



# Goals for Today

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- **Complex Lewis Structures**
  - Incomplete, Expanded Octet
  - Resonance
- **VSEPR Theory**
  - Basic and complex shapes
  - Bond Angles
  - Application to large organic molecules
  - Molecular polarity



# Covalent Bond Definitions

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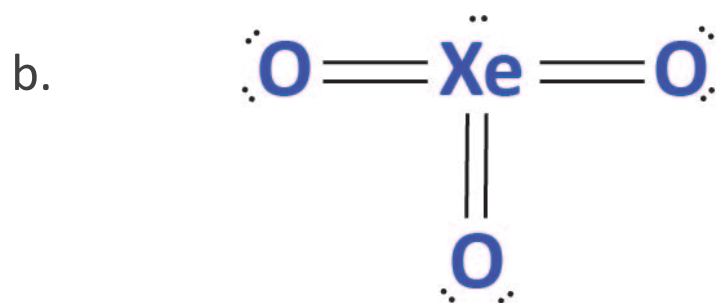
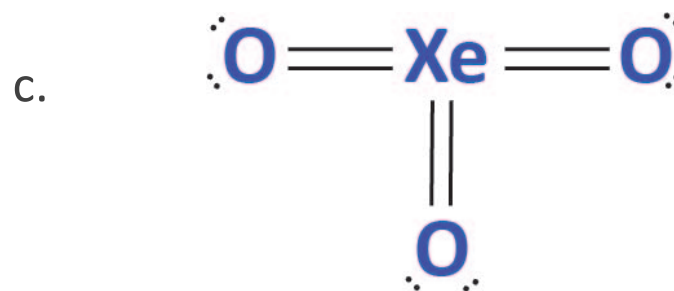
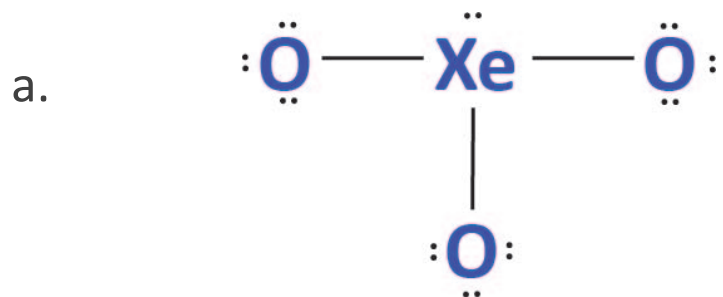
- **Bond strength**: the energy required to break a covalent bond (also known as Bond Dissociation Enthalpy)
- **Bond order**: a measurement of the average number of chemical bonds between two atoms in a species
  - This gets more detailed as time goes on; for now, think of single, double, and triple bonds
- **Bond length**: the distance between atoms in a bond
- **Electronegativity**: a measurement of the electron-withdrawing nature of an element in a bond. Leads to unequal sharing of electrons in a covalent bond, or polarity.
- **Resonance**: multiple acceptable Lewis Structures are available for a given compound, meaning that the compound actually exists as the average of all acceptable structures
- **Delocalized electrons**: in the case of resonance, electrons are not confined to a single bond. Instead they “resonate” over multiple bonds. We call this delocalization.

Note: bond strength and order are both indicators of stability. Higher bond order means a higher bond strength, which also correlates inversely with bond length.

# Exam Question

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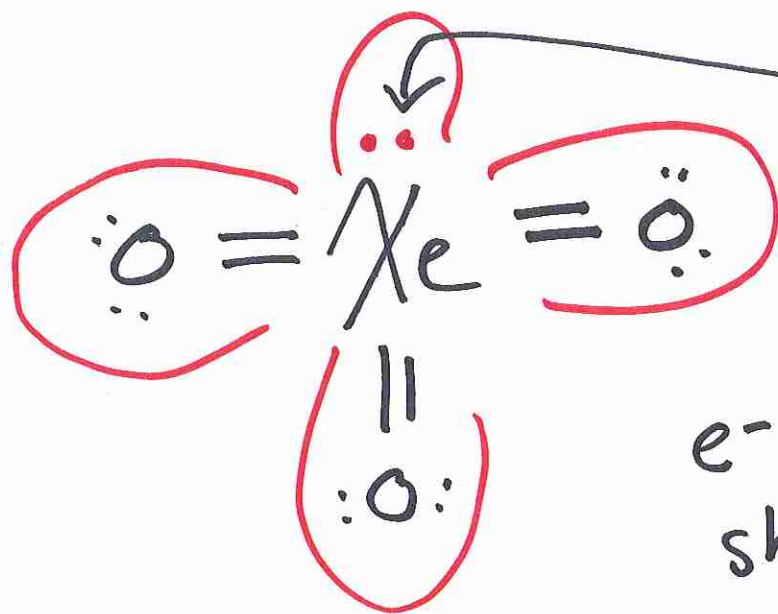
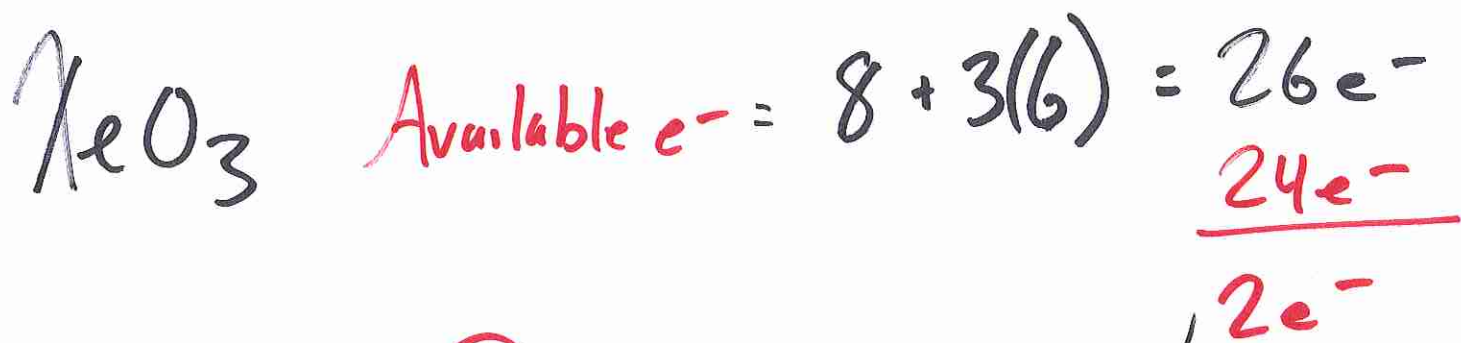
Which of the following Lewis Structures is the correct drawing for Xenon Trioxide ( $\text{XeO}_3$ )?



d. None of the above

Study follow-up: What is the formal charge on Xe?  
What is the electronic geometry?

Molecular geometry? Bond angles? Polar/Non-polar?



$e^-$  geometry: tetrahedral  
shape: trigonal pyramidal  
angles: less than  $109.5^\circ$

Polar: Yes

# Lewis Structure Formal Charge Foundations

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Element	-1 Charge	Neutral	+1 Charge
Hydrogen	x	1 bond	x
Carbon*	3 bonds, 1 LP (rare)	4 bonds	x
Nitrogen	2 bonds, 2 LP (rare)	3 bonds, 1 LP	4 bonds
Oxygen	1 bond, 3 LP	2 bonds, 2 LP	3 bonds, 1 LP
Halogens**	x	1 bond, 3 LP	x

This chart represents a “best guess” to draw out simple Lewis Structures. The formal charges are calculated based on a full octet and no exceptions.

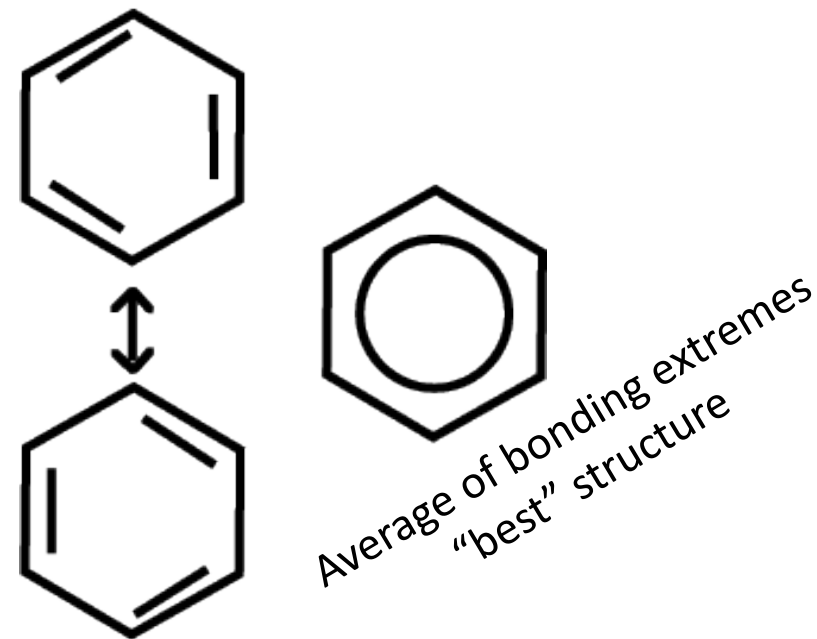
\*Carbon almost always has four bonds. Some notable exceptions are CO, CN<sup>-</sup>, CNO<sup>-</sup>

\*\*Represents halogens as a peripheral atom, not a central atom. In other words, this applies to the fluorine in ClF<sub>3</sub> but not the chlorine.

# Resonance

We call either the top or bottom drawings of Benzene “acceptable” structures. However, only the drawing on the right shows the actual delocalization of electrons (**a perfect average of the acceptable structures**)

- Resonance occurs whenever a structure has multiple acceptable Lewis Structures.
- The science behind this is that the electrons do not exist in a single place, nor do they “flicker” back and forth between the bonds. **Instead, electrons are delocalized and their average charge is spread out over among multiple bonds**

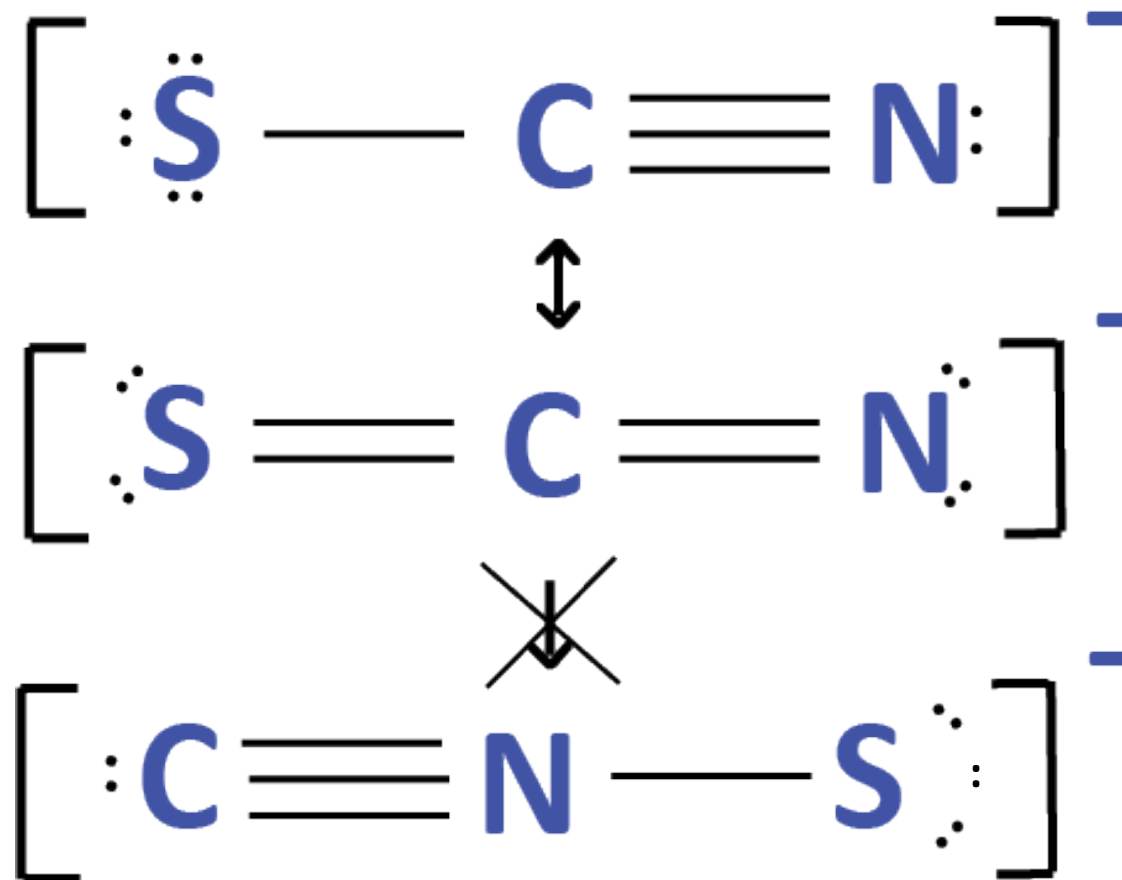


Acceptable structures



# Resonance

- What constitutes an “acceptable” Lewis Structure?
  1. The negative charge is placed on only the electronegative atoms and minimized on your central atom (generally)
  2. Any individual charge does not exceed +/- 1 (generally)
  3. Put your charges on as few atoms as possible
  4. **Your structure accurately reflects the number of available electrons in your atoms**



SCN<sup>⊖</sup>

$$4-4=0$$

$$\left[ \begin{array}{c} \ddots \\ \vdots \\ \mathcal{S} - \mathcal{C} \equiv \mathcal{N} \\ \vdots \\ \ddots \end{array} \right]^{-1}$$

$$6-7=-1$$

$$5-5=0$$

$$4-4=0$$

$$\left[ \begin{array}{c} \vdots \\ \mathcal{S} = \mathcal{C} = \mathcal{N} \\ \vdots \end{array} \right]^{-1}$$

$$6-6=0$$

$$5-6=-1$$

$$5-4=+1$$

$$\left[ \begin{array}{c} \vdots \\ \mathcal{C} \equiv \mathcal{N} - \mathcal{S} \\ \vdots \end{array} \right]^{-1}$$

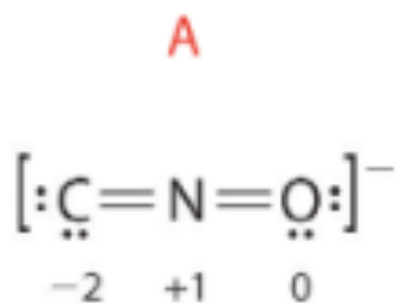
$$4-5=-1$$

$$6-7=-1$$

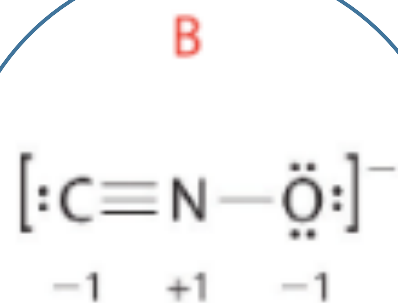
# Resonance

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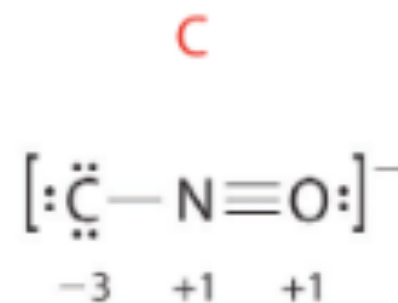
Which of the three Lewis structures is the most important for the fulminate ion ( $\text{CNO}^-$ )? Select all of the correct answers.



or



or



# Resonance Exam Question

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Which of the following compounds would be expected to have the longest N-O bonds?

1. NO
2.  $\text{NO}_3^-$
3.  $\text{NO}_2^-$
4. they will all be the same

- Resonance structure drawings represent the “acceptable” depictions, but the molecule actually exists as a perfect average of all structures
- Bond order is normally just the number of bonds (single bond, double, triple, etc.). However, in resonance:

$$B.O. = \frac{\text{total \# of bonds in resonance}}{\text{total \# of bonding regions in resonance}}$$

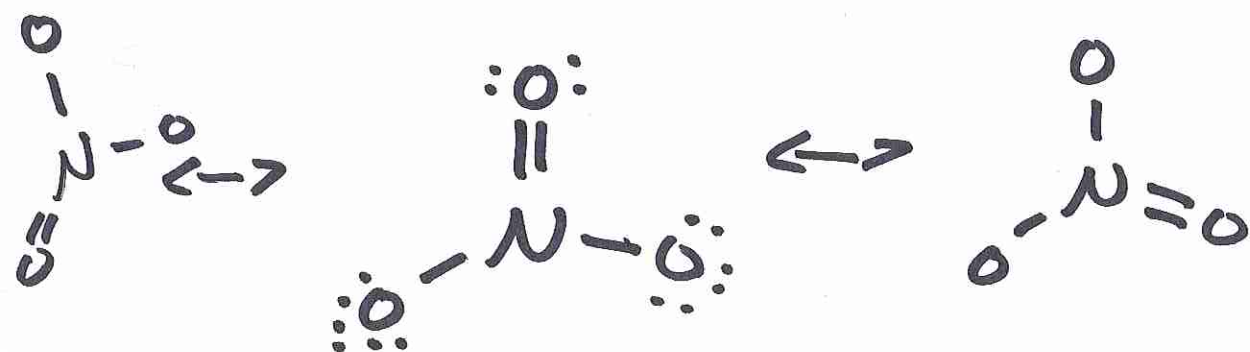
- **This works for bond strength and length, as well!**

Bond order  $\uparrow$  Bond strength  $\uparrow$  Bond length  $\downarrow$

Which compound has the weakest bonds?



Double Bond  
Strongest, shortest



$$\frac{4}{3} = \frac{\text{total \# of bonds in resonance}}{\text{total \# of bonding regions}} = 1.33 \text{ bonds}$$

weakest, longest

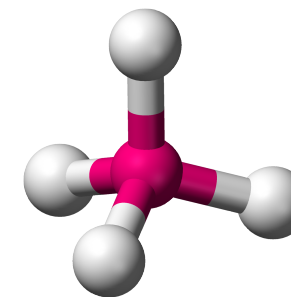
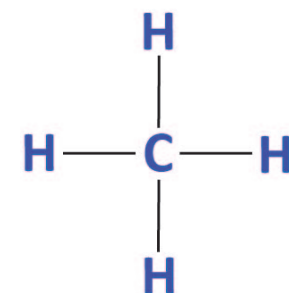


$$\frac{3 \text{ bonds}}{2 \text{ locations}} = 1.5 \text{ bonds}$$

# VSEPR Theory Definitions

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- VSEPR theory is an empirical method of understanding molecular shapes in three dimensional space.
- The theory gets its name from the fact that electron regions have **the lowest energy** when repulsions are minimized.
  - In other words, **electron-dense regions want to be as far away from each other as possible** in 3D space.
- VSEPR gives us two different 3D geometries: **electronic geometry and molecular geometry**.
  - **Electronic geometry**: the shape of all electron-rich regions around a central atom (lone pair regions and bonding regions)
  - **Molecular geometry**: the shape of only the bonding regions around a central atom
- Knowing the geometry around a central atom can clue you in on the approximate **bond** angles that exist around the central atom and whether the molecule is **polar or nonpolar**.



2D to 3D image of methane

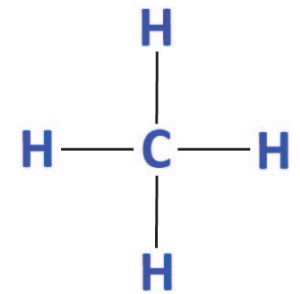
# Exam Question

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What are the approximate bond angles around the central atom of methane ( $\text{CH}_4$ ) in 3D space?

a. 90 degrees

c. 120 degrees



b. 109.5 degrees

d. 180 degrees

Remember: VSEPR gives the lowest energy positions of peripheral atoms in three dimensional space.

# VSEPR Theory: Simple Geometries

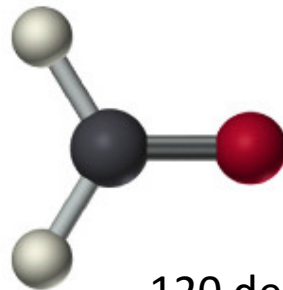
- VSEPR Theory electronic geometries are named after the shape you observe if you enclose your electron-dense regions in a 3D structure.



180 degrees



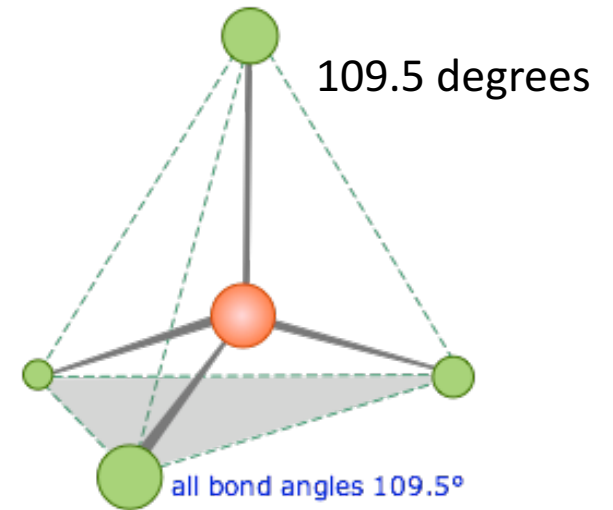
**Linear**



120 degrees



**Trigonal Planar**



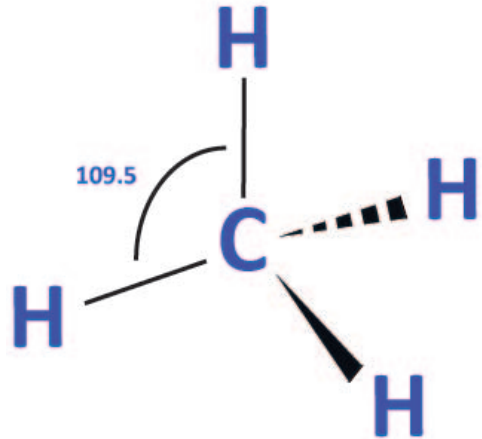
**Tetrahedral**

Note: these examples have the same electronic and molecular geometries because there are no lone pairs (the number of electron-dense regions is equal to the number of bonding regions).

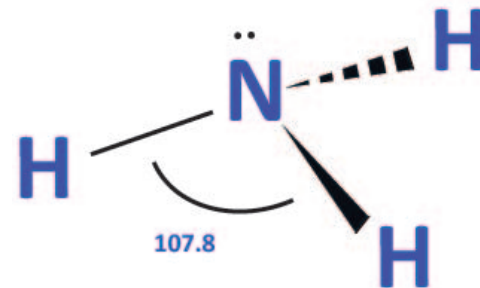


# VSEPR Geometries: 4 e<sup>-</sup> Regions

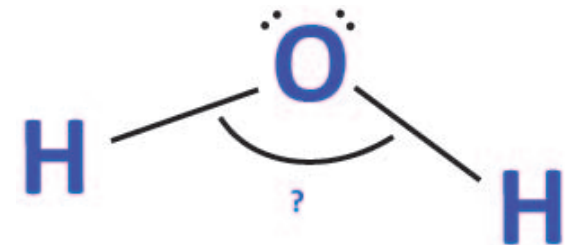
- What happens when we have fewer bonding regions than total electron-dense regions?
- In other words, what happens when we replace a bond with a lone-pair region?
  - Your molecular geometry is determined by looking first at the number of electron-dense regions and then at the number of bonding regions.



Tetrahedral



Trigonal Pyramid

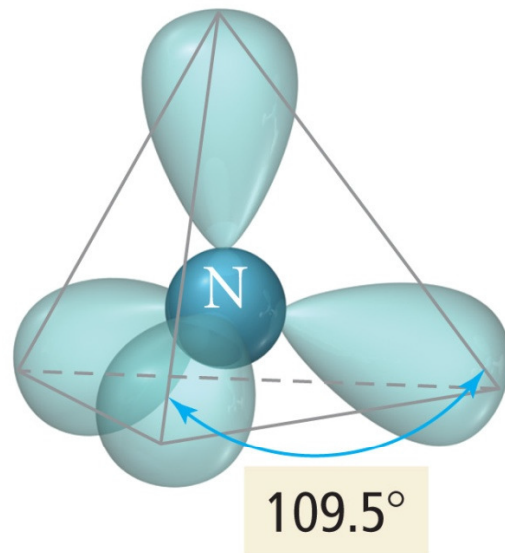


Bent

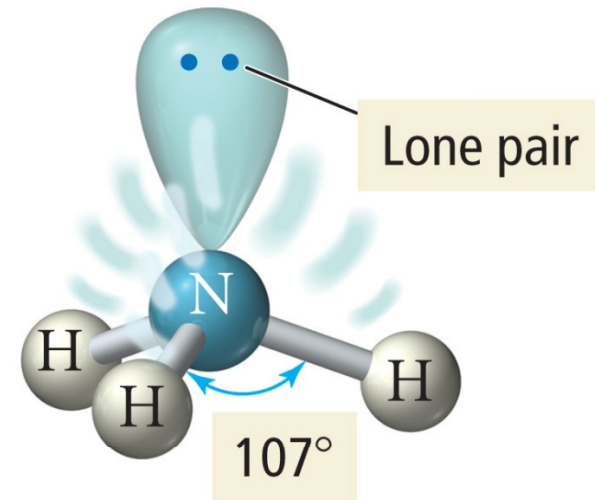
All of the above have tetrahedral electronic geometry

# The Effect of Lone Pairs

- Lone pairs occupy more space on the central atom than a bonding pair of electrons, **meaning they end up being more repulsive than bonding regions**
- The electron density of lone pairs is **ALL on the one central atom** – not shared out over two – as in a conventional bond
- This affects the bond angles at the central atom, making them smaller than expected for a perfect geometry



Ideal tetrahedral  
geometry



Actual molecular  
geometry

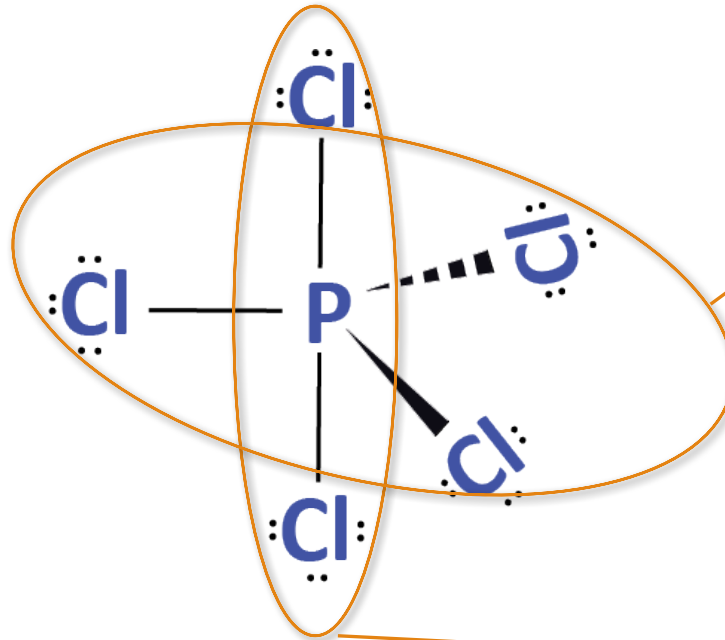
# VSEPR Geometries: 5 e- Regions

- We now know that we can have more than 4 electron regions around a central atom. Five electron regions gives a trigonal bipyramidal electronic geometry

**Electronic:** Trigonal Bipyramid

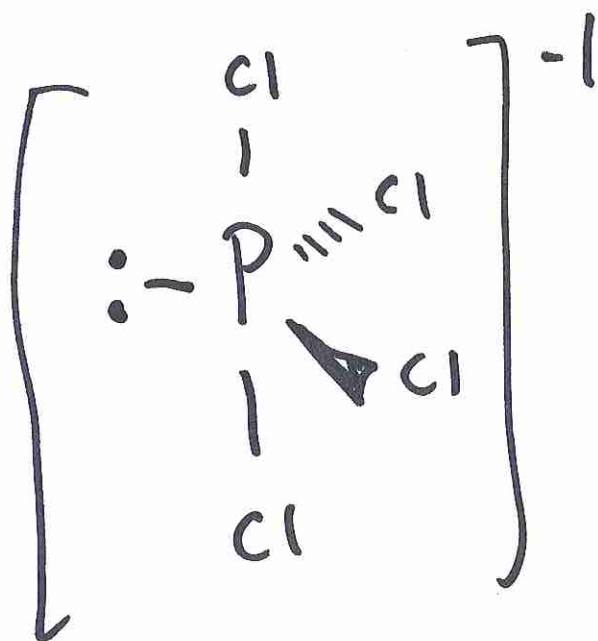
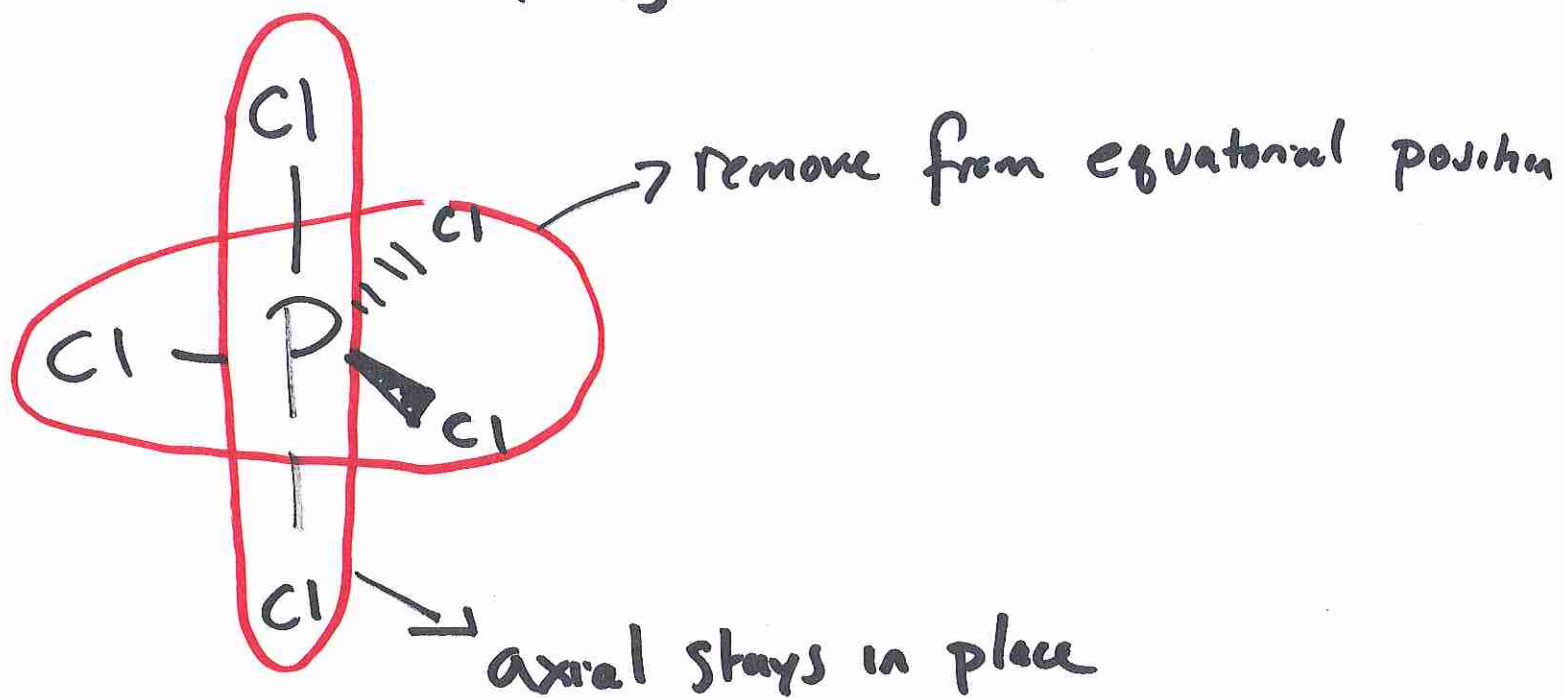
**Molecular:** Trigonal Bipyramid

**Pure bond angles:** 180 on axial plane, 120 on equatorial plane, 90 degrees from axial to equatorial atoms



The Equatorial Position bonds look like a trigonal planar structure

The Axial position bonds are linear

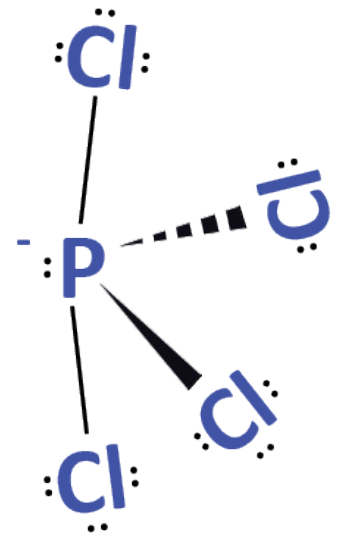


# VSEPR Geometries: 5 e- Regions

- The equatorial and axial positions have differing stability.
- If you want to replace a bond with a lone pair in the trigonal bipyramidal electronic geometry, you must remove an equatorial bond.
- **It is more stable to add lone pairs to the equatorial position**
- Notice the effect of the lone pair on "tweaking" the pure bond angles

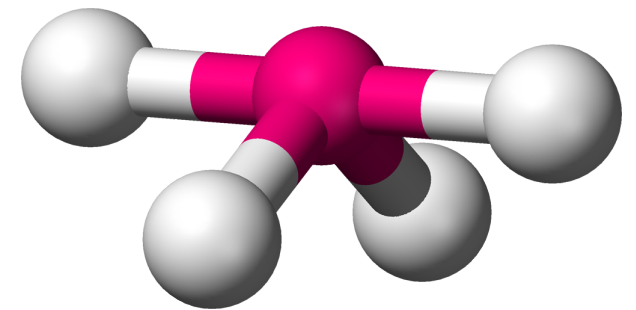
**Electronic:** Trigonal Bipyramid

**Molecular:** Seesaw



Equatorial Position

Axial Position



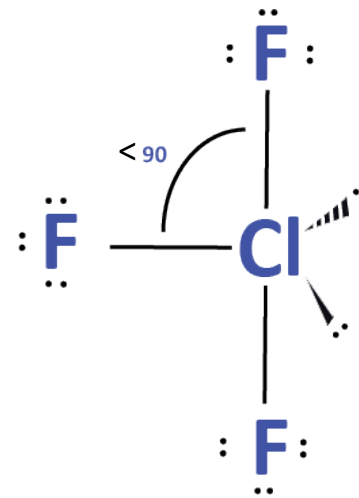
# VSEPR Geometries: 5 e- Regions

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**Electronic:** Trigonal Bipyramid

**Molecular:** T-shaped

- If we continue to replace bonds with lone pairs, we should continue to remove the equatorial positioned bonds



Equatorial Position

Axial Position

# VSEPR Geometries: 5 e- Regions

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**Electronic:** Trigonal Bipyramid

**Molecular:** Linear

- When we remove the last equatorial bond, we end up in a linear geometry with only the most stable axial bonds remaining.



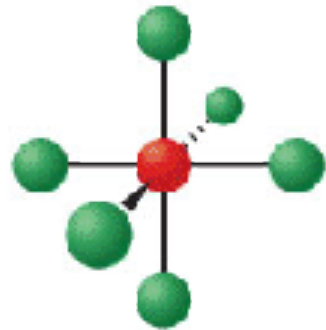
Equatorial Position

Axial Position

Remember: when we remove a bond and replace with a lone pair in the trigonal bipyramid geometry, we ALWAYS remove from the equatorial position

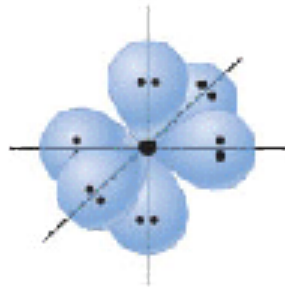
# VSEPR Geometries: 6 e- Regions

- The octahedral molecular geometry is completely symmetrical, so there is no axial/equatorial preference. However, I like to think of it as linear atoms in the axial position, and a square plane made up by equatorial atoms.
- The one rule when replacing bonds with lone pairs is that you must always remove electrons from the opposite position as the last.

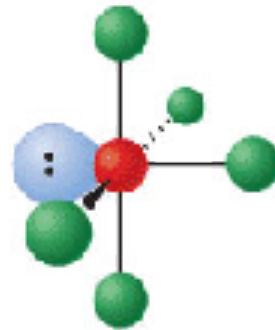


**Molecular:**

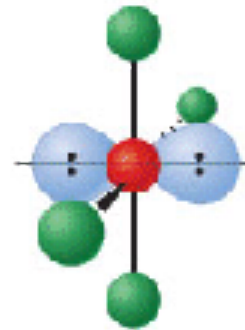
**Octahedral**



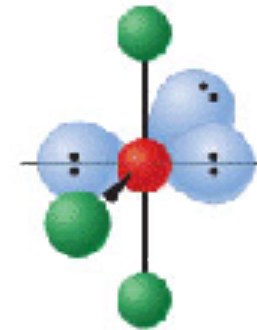
**( $d^2sp^3$ )**



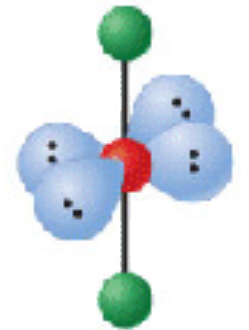
**Square  
pyramidal**



**Square  
planar**



**T-shaped**



**Linear**

**Pure bond angles: 90 and 180**

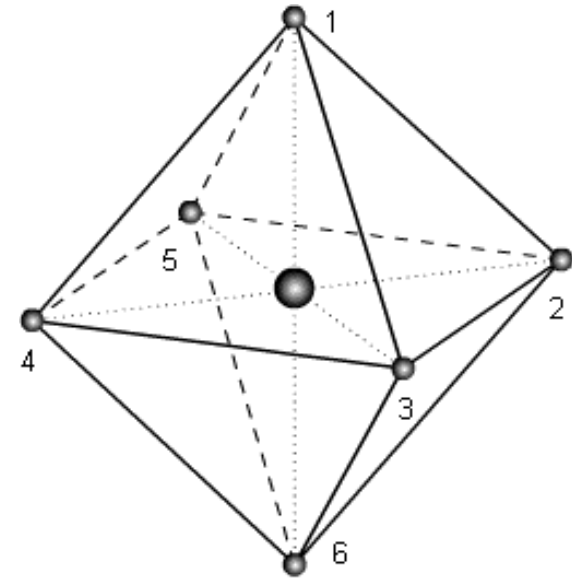
**Electronic: Octahedral**



# VSEPR Geometries: 6 e- Regions

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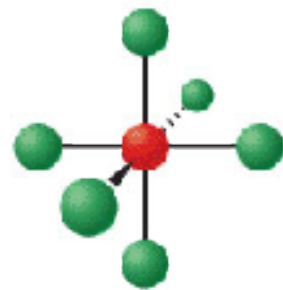
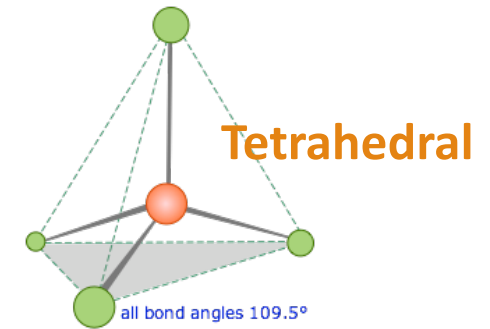
- Why is the geometry called “Octahedral” if it has six peripheral atoms?
- Remember: VSEPR geometries are named after the geometry of the **enclosure**
  - **An octahedral prism has 6 vertices**



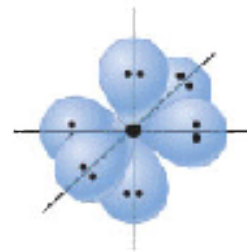
# Exam Question

What is the molecular geometry of  $\text{XeF}_4$ ?

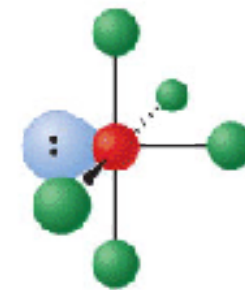
- a. Tetrahedral
- b. Square Planar
- c. T-Shaped
- d. Square Pyramid



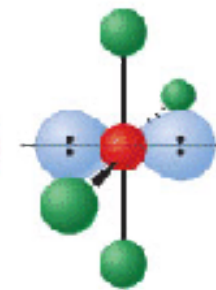
Octahedral



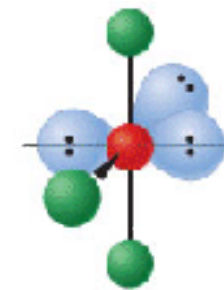
$(d^2sp^3)$



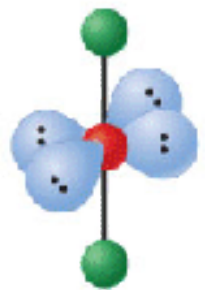
Square pyramidal



Square planar



T-shaped

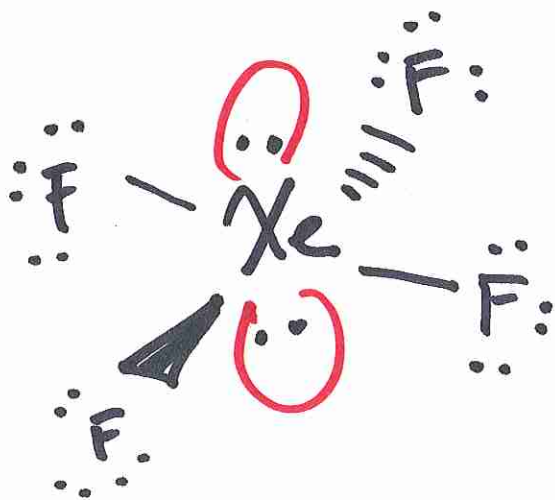
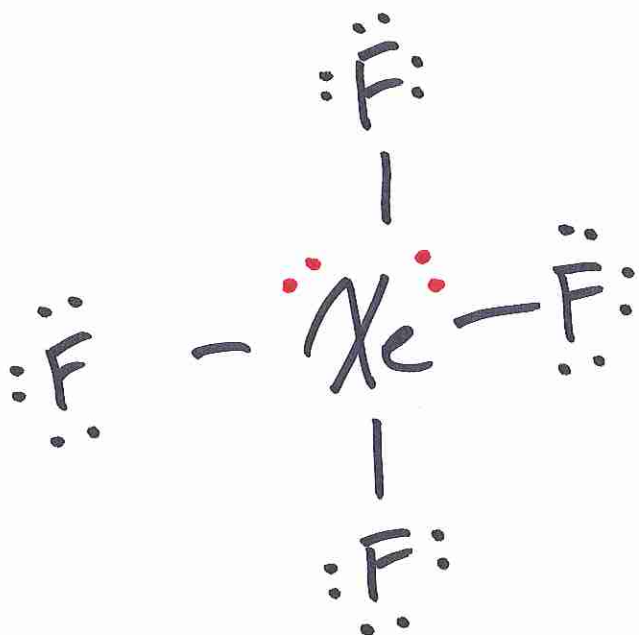


Linear



Available  $e^-$ :  $8 + 7(4) = 36e^-$

$$\frac{32e^-}{4e^-}$$



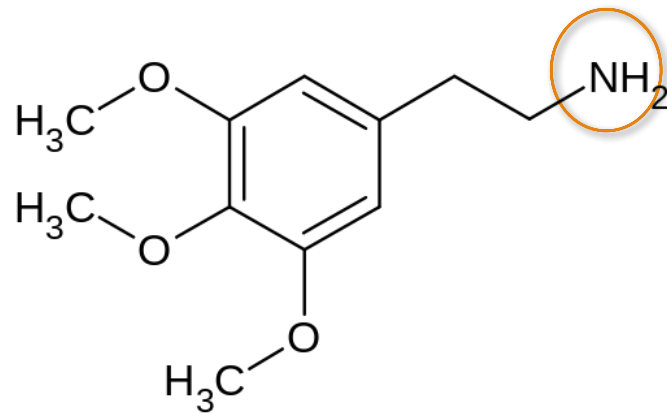
6  $e^-$  regions:  
Octahedral

4 bonding regions:  
Square planar

# Big Molecule Question

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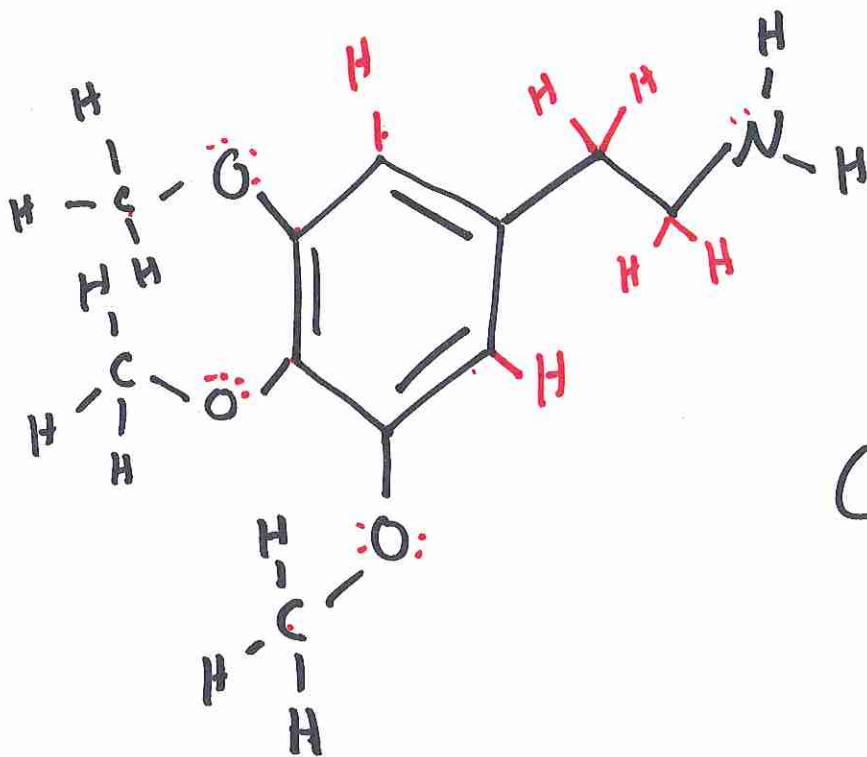
What is the empirical formula of this compound? What are the electronic and molecular geometries around the circled nitrogen? What are the bond angles around nitrogen?



- a. 120 degrees
- b. 109.5 degrees

- c. Just less than 109.5 degrees
- d. Just more than 109.5 degrees

- 1) Carbons are @ every terminal and corner
- 2) Hydrogens fill the octet of carbon
- 3) L.P. electrons fill the octet of everything else



$e^-$ : tetrahedral  
 $m$ : trigonal  
 pyramid

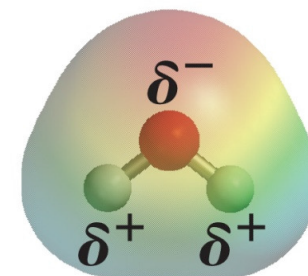
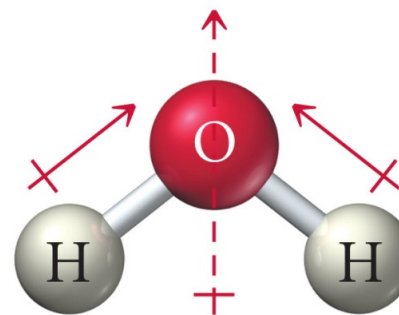
$\sim 107^\circ$




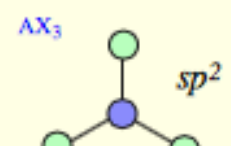
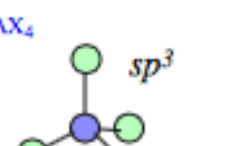
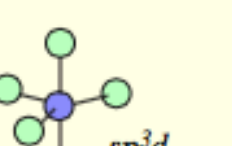

# VSEPR Theory: Molecular Polarity

- VSEPR is important because the shape of the molecule plays an important role in the chemical and physical properties of the molecule.
- An important conclusion that can be made based on VSEPR shapes is **molecular polarity**.
- Polarity in **a bond** occurs when one species disproportionately pulls the electrons closer, causing a dipole moment.
- Polarity in **a molecule** occurs when there are polar bonds and there is a net dipole moment on the molecule.
  - A perfectly symmetrical molecule will always be nonpolar.
  - A central atom bound to different peripheral atoms will be polar, as long as there is a single polar bond. (EXCEPTION: if the axial positions are the same and the equatorial positions are the same, the dipoles will cancel. Still a perfectly symmetrical molecule)
  - Lone pairs are generally an indication that the molecule is polar, except in the square planar and linear molecular geometries

Net dipole moment



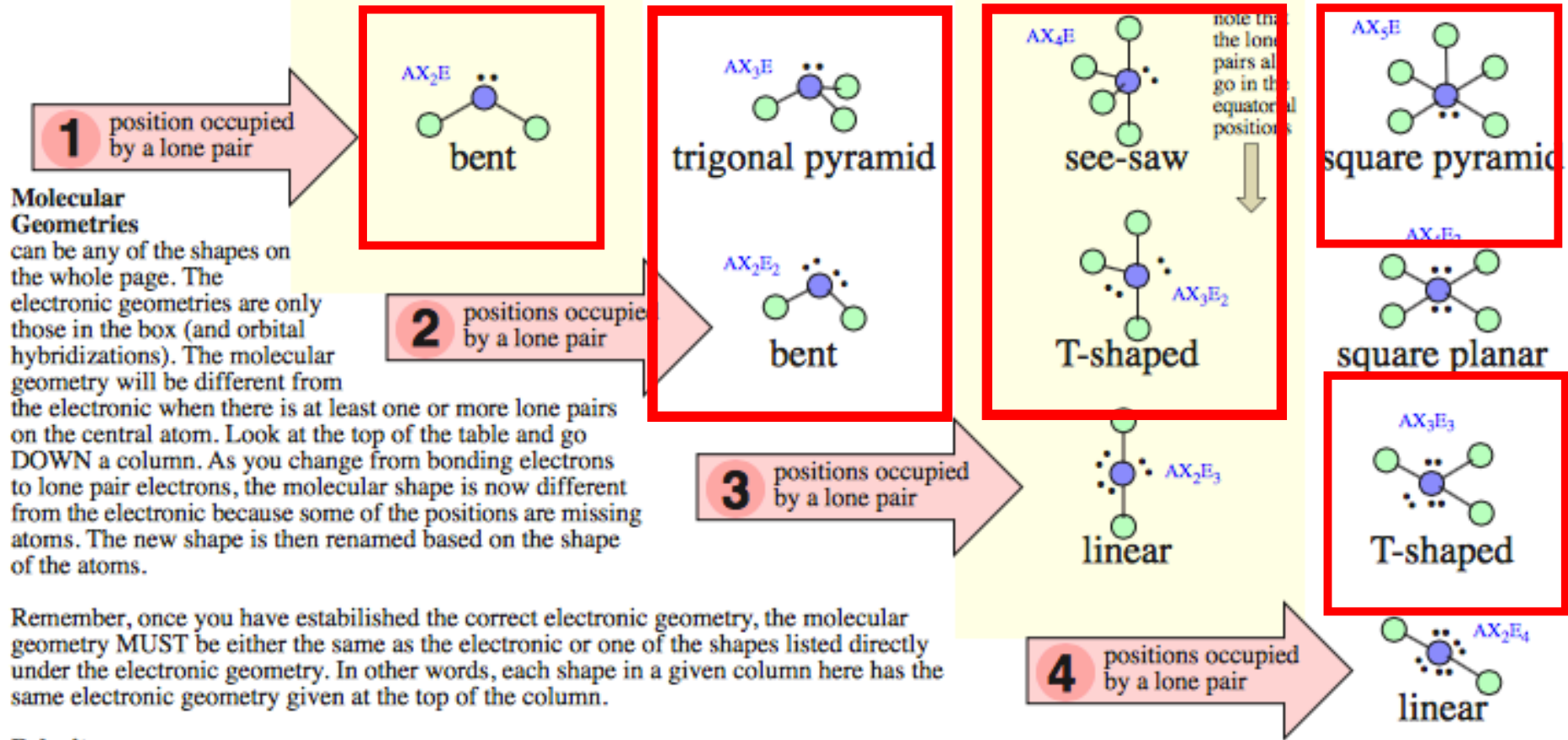
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2 electron regions	3 electron regions	4 electron regions	5 electron regions	6 electron regions
$AX_2$  <i>sp</i>	$AX_3$  <i>sp<sup>2</sup></i>	$AX_4$  <i>sp<sup>3</sup></i>	$AX_5$  <i>sp<sup>3</sup>d</i>	$AX_6$  <i>sp<sup>3</sup>d<sup>2</sup></i>
linear	trigonal planar	tetrahedral	trigonal bipyramid	octahedral

All red shapes are polar

Basic rules for molecular polarity:

1. Look for asymmetry in connectivity.  
CH3Cl
2. Look for lone pair asymmetry.  
EVERYTHING with lone pairs is polar, except for the linear and square planar geometries



Remember, once you have established the correct electronic geometry, the molecular geometry MUST be either the same as the electronic or one of the shapes listed directly under the electronic geometry. In other words, each shape in a given column here has the same electronic geometry given at the top of the column.

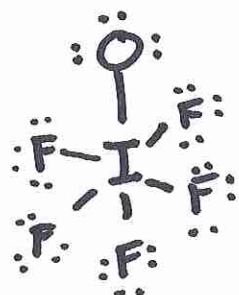
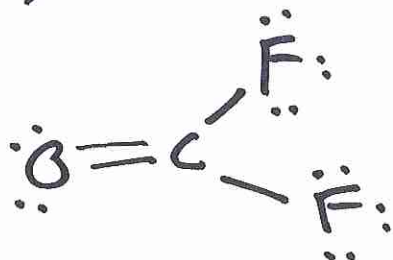
**Polarity**  
If all the positions on the electronic geometry are the same (have the same atoms surrounding the central atom), the molecule is NOT polar because of the symmetry. Any of the other molecular geometries (except square planar and linear) under the box will be polar.



Molecule

Non-Polar

Polar



FYI: A better version of this structure would have a double bond between the I and O to make the formal charge of each atom 0.

