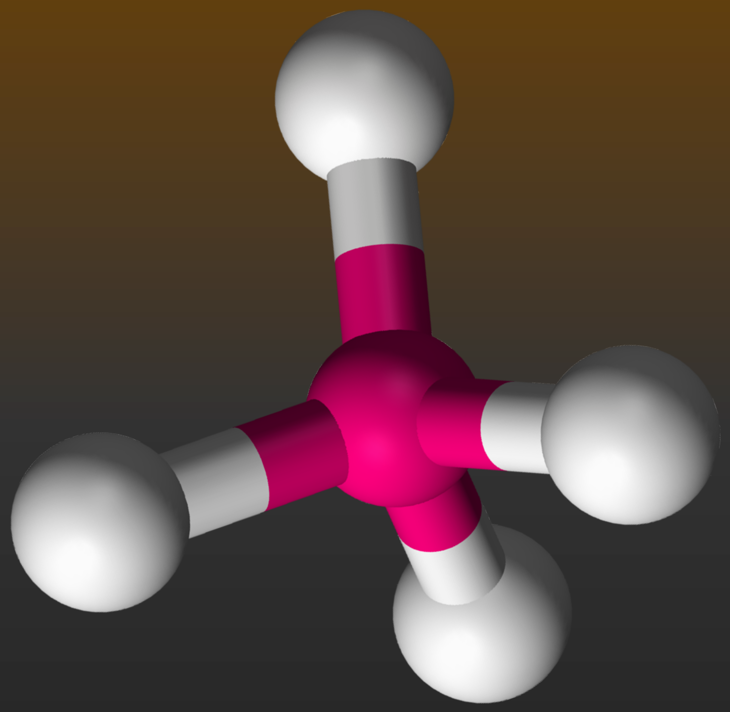


Unit 3 Review

COVALENT BONDS, LEWIS STRUCTURES, RESONANCE, VSEPR

Goals for Today

- Covalent Compounds
  - Basic definitions
  - Lewis Structures
  - Resonance
  - Expanded Octet
- Valence Shell Electron Pair Repulsion (VSEPR)
  - What is the electronic and molecular geometry of a molecule in three dimensional space?
  - What is the relationship between geometry, lone pair electrons, and bond angles?
  - How does the geometry relate to molecular polarity?

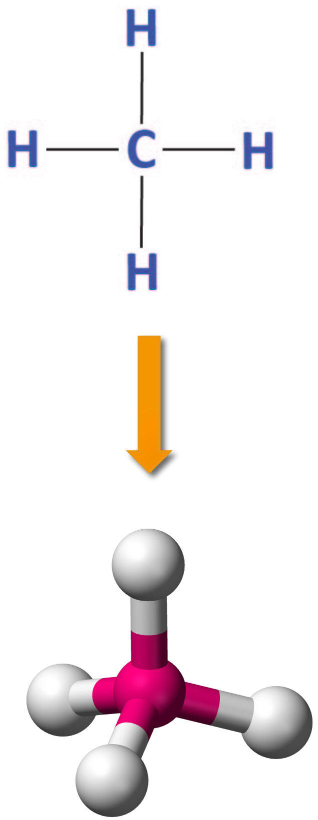
Covalent Compound Definitions

- 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
- 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.

VSEPR Theory Definitions

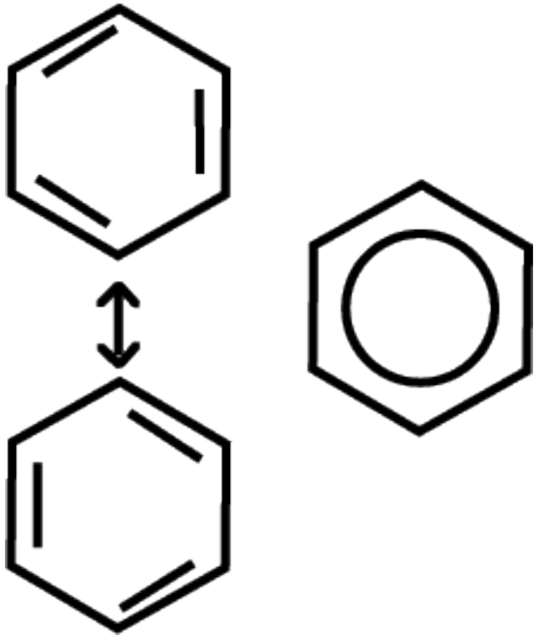
- VSEPR theory is a qualitative method of understanding molecular shapes in three dimensional space.
- The theory gets its name from the fact that electron regions have **the lowest energy** when repulsions are minimized.
  - In other words, **electron-dense regions want to be as far away from each other 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

Resonance

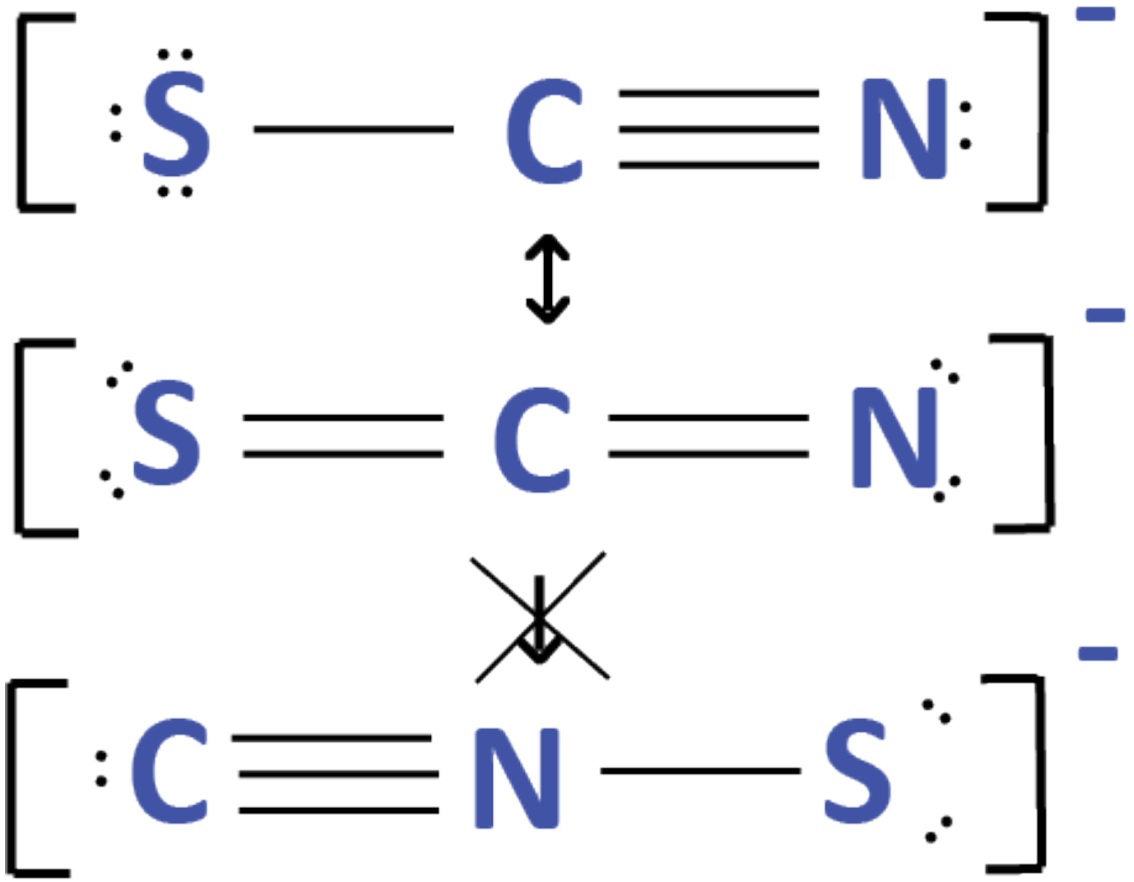
- Resonance occurs whenever a structure has multiple acceptable Lewis Structures.
- The science behind this is that the electrons do not exist in a single place, nor do they "flicker" back and forth between the bonds. Instead, electrons are delocalized and their average charge is spread out over among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



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

Resonance

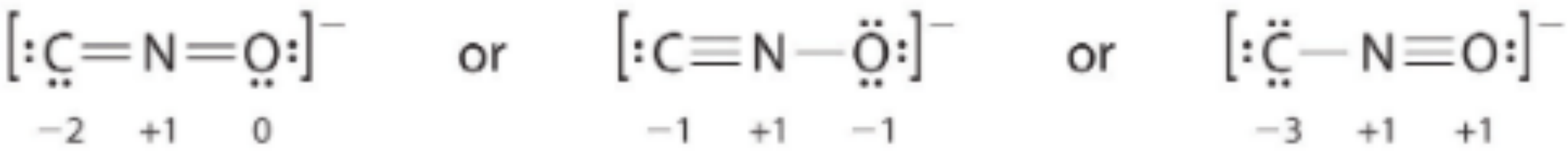
- What constitutes an "acceptable" Lewis Structure?
  - The charge is placed on only the electronegative atoms and minimized on your central atom
  - Any individual charge does not exceed +/- 1 (generally)
  - Put your charges on as few atoms as possible
  - **Your structure accurately reflects the number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



Resonance

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

A B C



Lewis Structures

- Lewis structures are the main form of drawing molecules. There are two important equations to know when drawing Lewis Structures:

$$S = N - A$$

- The number of shared electrons is equal to the total electrons **needed** to fill the valence minus the electrons **available**
- You can then calculate the number of bonds by dividing the shared electrons by two

$$FC = \text{Valence} - (\text{lone electrons} + \text{bonds})$$

- The formal charge of any atom in a molecule is equal to the the valence electrons of the atom (as seen on the periodic table) minus the "things it's touching" in the Lewis structure (the lone electrons and the number of bonds)

General Formal Charge Rules

- Formal charge defines the distribution of charge throughout a molecule. More specifically, it is used to show the charge on each atom in a molecule.
- The formal charge of a molecule is the sum of the individual formal charges of the atoms in the molecule. Formal charges should be minimized in your Lewis Structures.

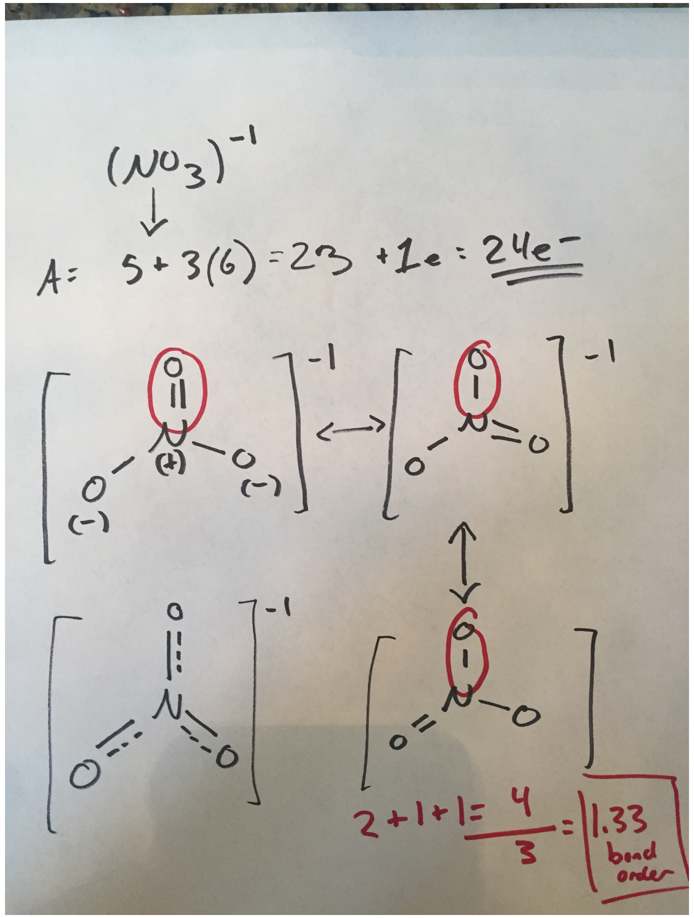
Element	-1 Charge	Neutral	+1 Charge
Carbon	3 bonds*	4 bonds	5 bonds*
Nitrogen	2 bonds	3 bonds	4 bonds
Oxygen	1 bond	2 bonds	3 bonds

* In this class carbon is nearly always neutral (4 bonds). The main exception to this is Carbon monoxide.

Resonance

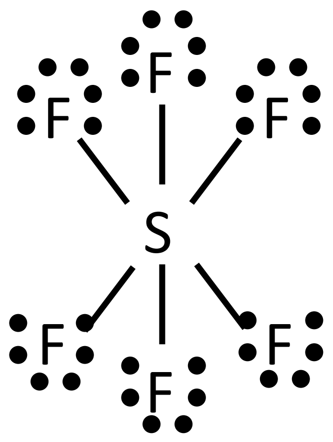
Draw the Lewis Structure for Nitrate $(NO_3)^{2-}$

What is the bond order of a nitrogen-oxygen bond in your structure?



Solving For Lewis Structure Exceptions

1. Find the number of electrons **available** (valence electrons plus the charges – subtract for positive charge, add for negative).
2. Add your bonds create the lowest possible formal charges possible.*
3. Add lone pairs to your peripheral atoms
4. If you have any electrons left based on your **available** electrons from step 1, add them to your central atom.
5. Confirm your molecule's structure by checking the formal charge

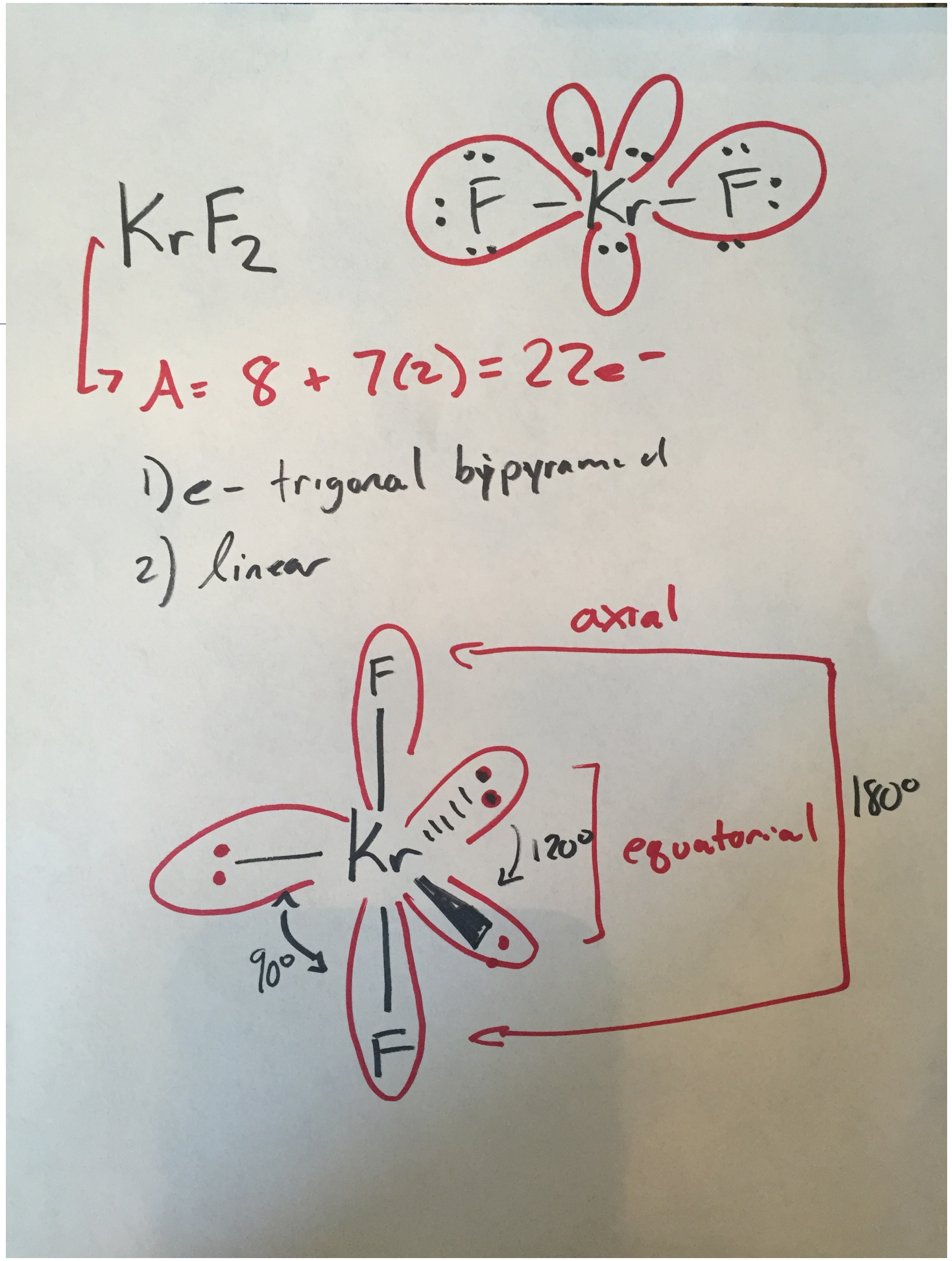


*By this I mean be smart about adding your bonds. The more you practice, the easier this step will be to make a sensible first-attempt at a structure

Expanded Valence

Draw the Lewis Structure for KrF_2

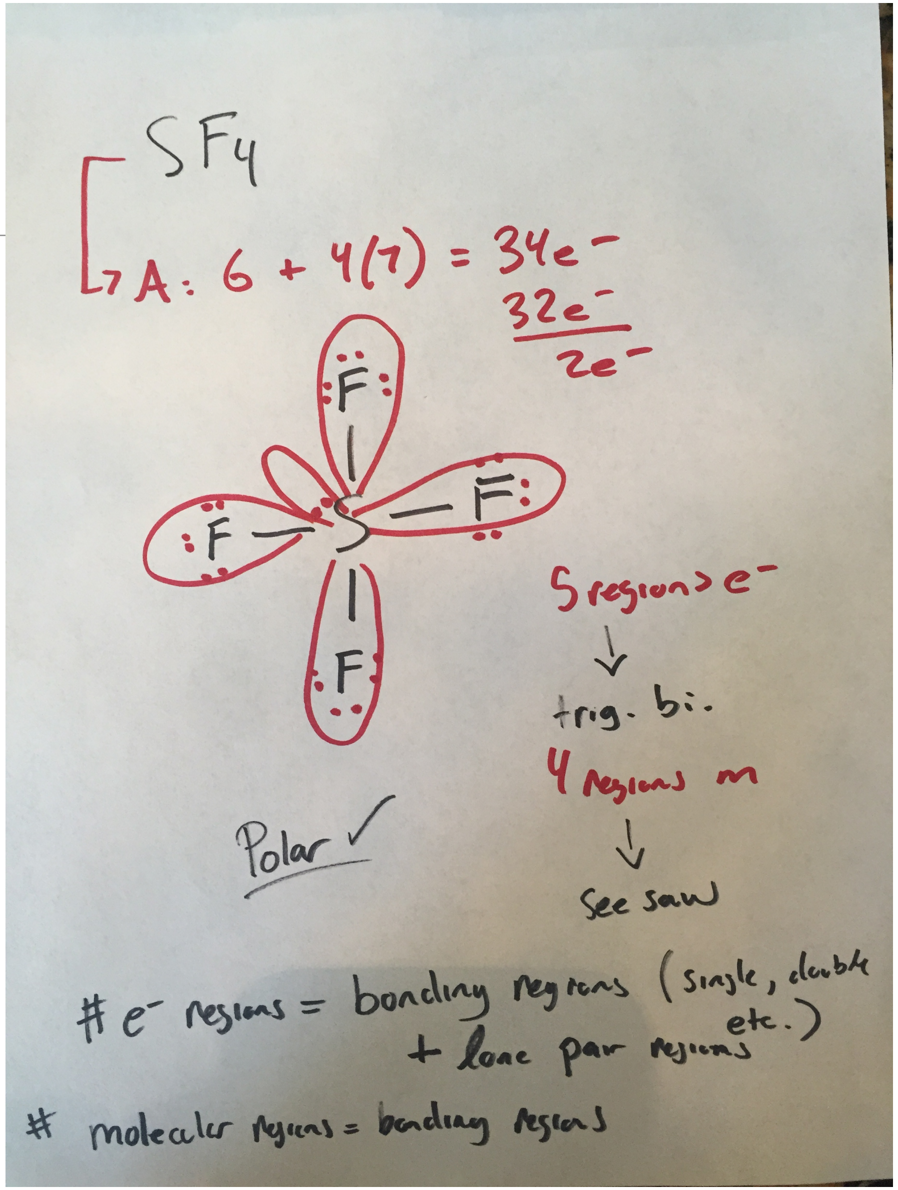
What is the molecular and electronic geometry of your structure? Is the molecule polar or non-polar?



Expanded Valence

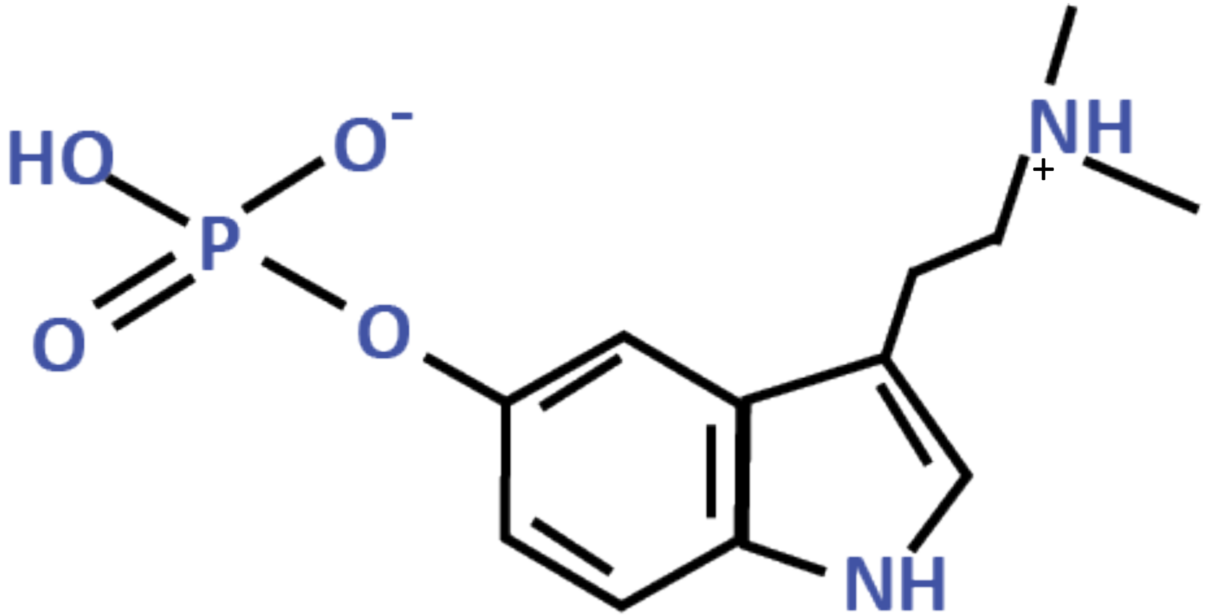
Draw the Lewis Structure for SF_4

What is the molecular and electronic geometry of your structure? Is the molecule polar or non-polar?



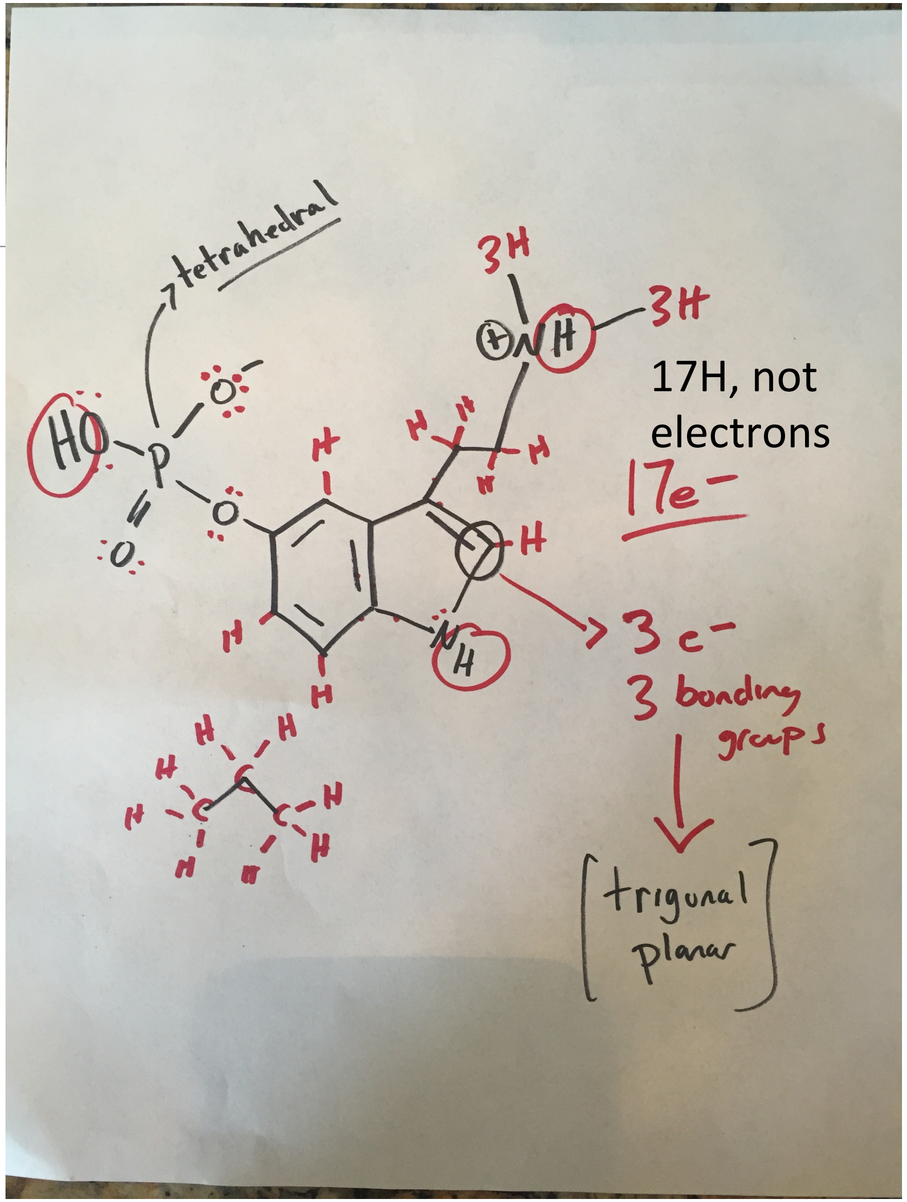
Organic Molecules

How many Hydrogen atoms exist on this molecule?



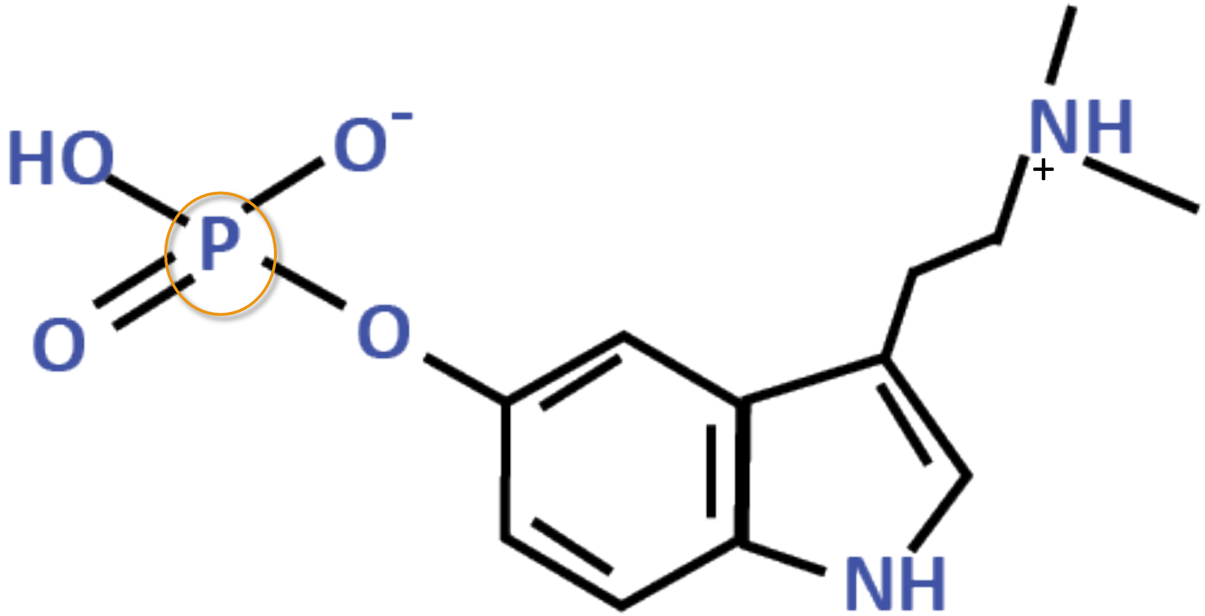
Organic Molecules

How many Hydrogen atoms exist on this molecule?



Organic Molecules

What is the molecular and electronic geometry of the circled central atom?



Organic Molecules

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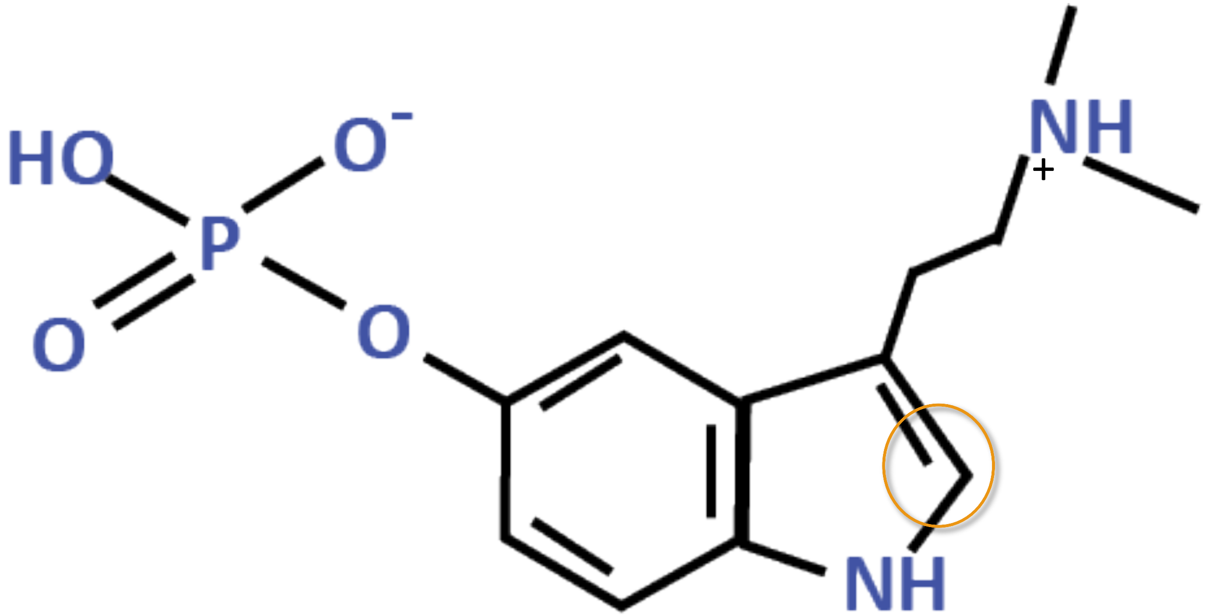

Organic Molecules

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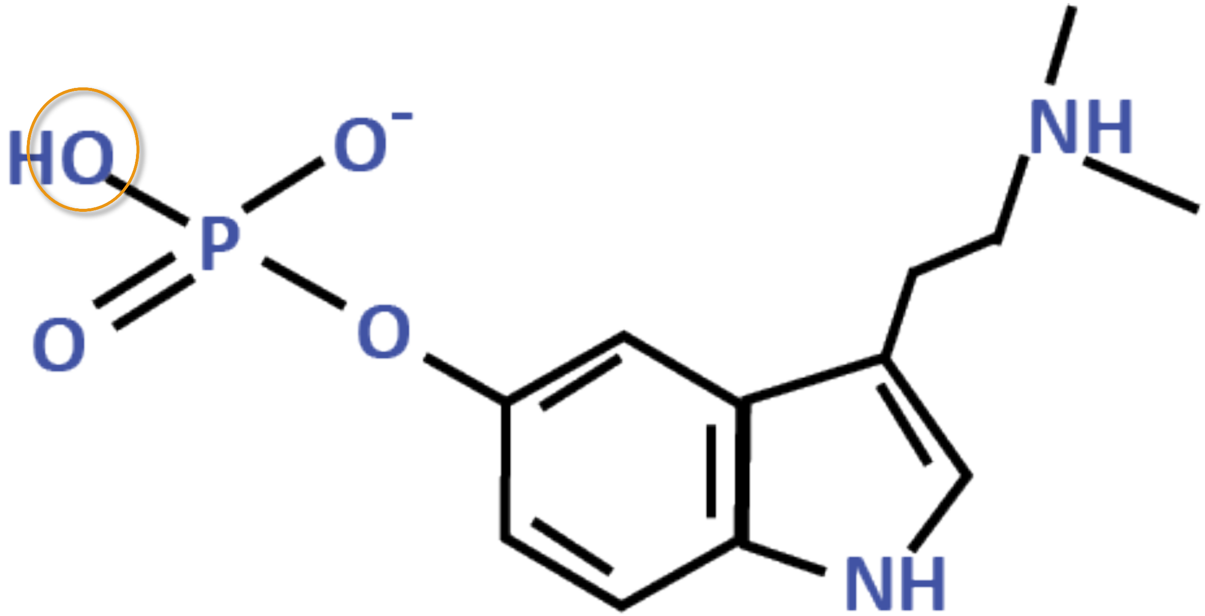
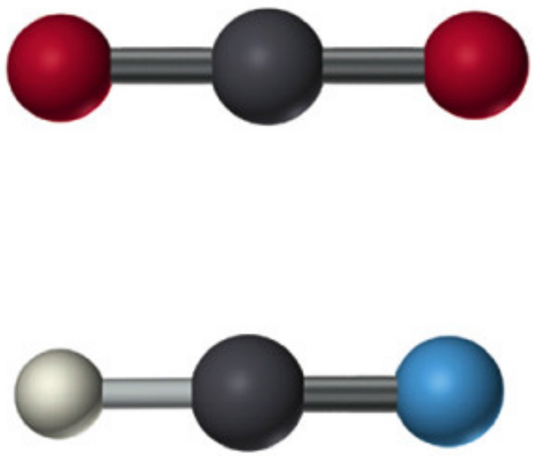


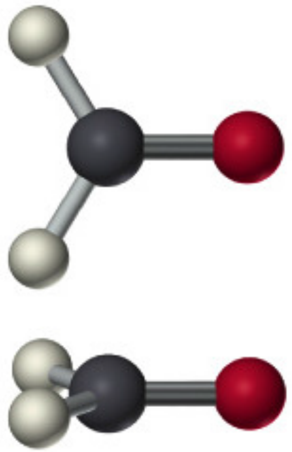
Extra Slides

VSEPR Theory: Simple Geometries

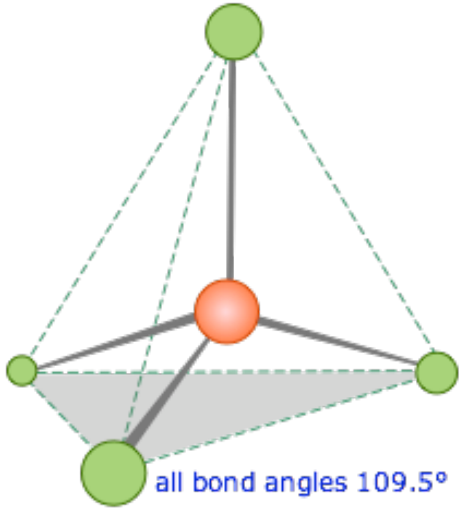
- VSEPR Theory electronic geometries are named after the shape you observe if you enclose your electron-dense regions in a 3D structure.



Linear



Trigonal Planar

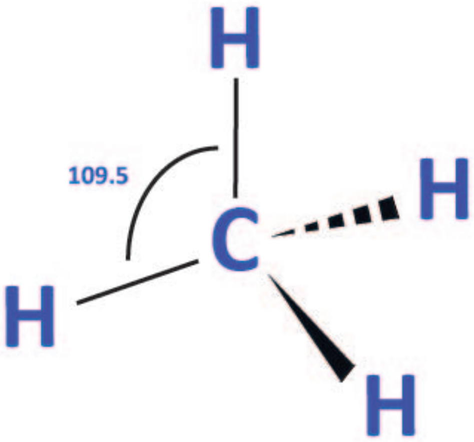


Tetrahedral

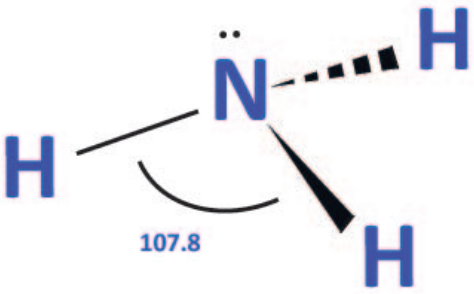
Note: these examples have the same electronic and molecular geometries because there are no lone pairs (the number of electron-dense regions is equal to the number of bonding regions).

VSEPR Geometries: 4 e^- Regions

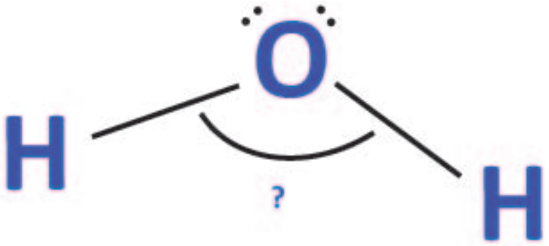
- What happens when we have fewer bonding regions than total electron-dense regions?
- In other words, what happens when we replace a bond with a lone-pair region?
  - Your molecular geometry is determined by looking first at the number of electron-dense regions and then at the number of bonding regions.



Tetrahedral



Trigonal Pyramid

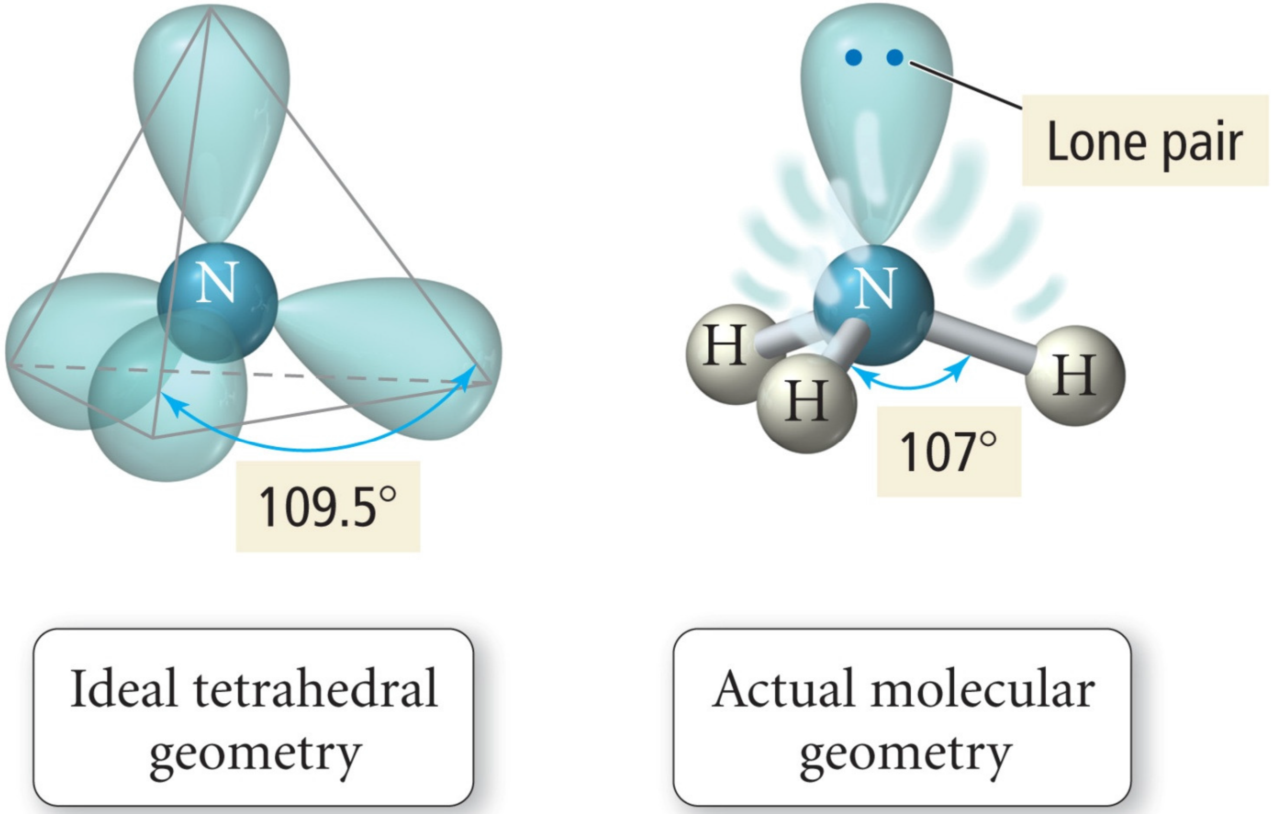


Bent

All of the above have tetrahedral electronic geometry

VSEPR Geometries: 4 e^- Regions

- Lone pairs occupy more space on the central atom than a bonding pair of electrons
- 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

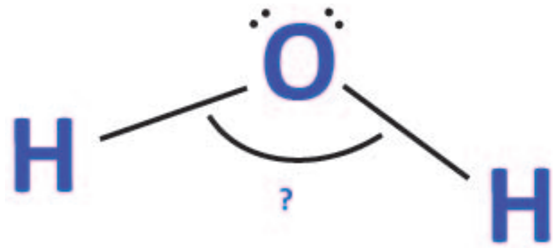


Polling Question

What are the approximate bond angles around the central atom of water (H_2O) in 3D space?

a. 90 degrees

c. 88 degrees



b. 109.5 degrees

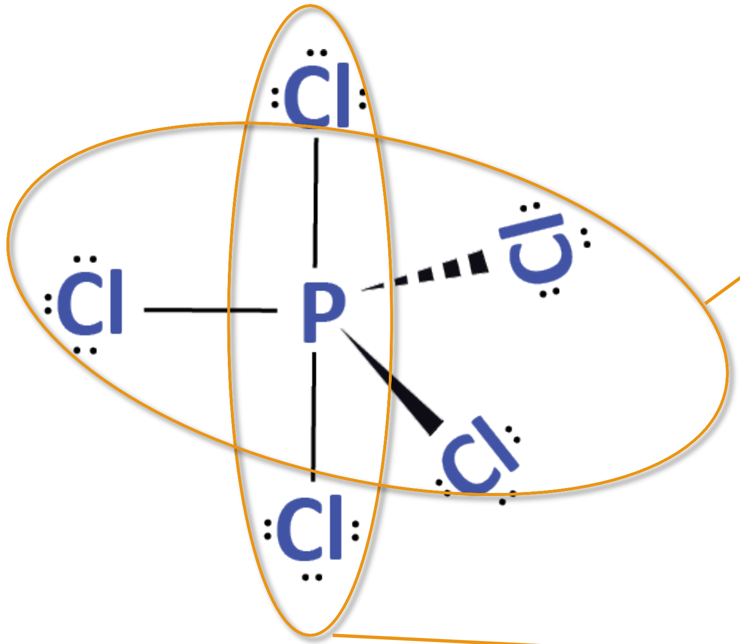
d. 104.5 degrees

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



The Equatorial Position bonds look like a trigonal planar structure

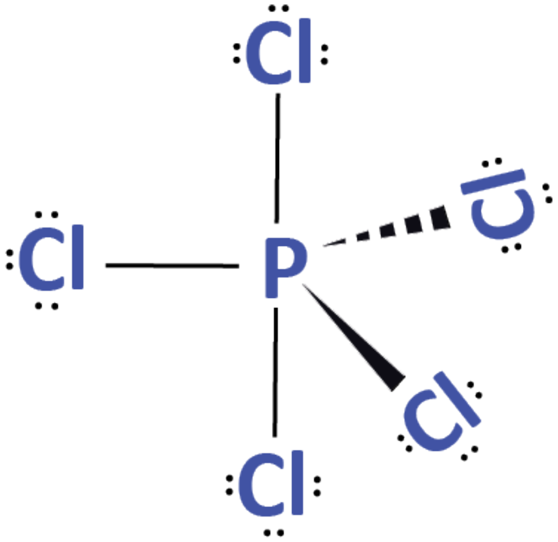
The Axial position bonds are linear

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



Equatorial Position

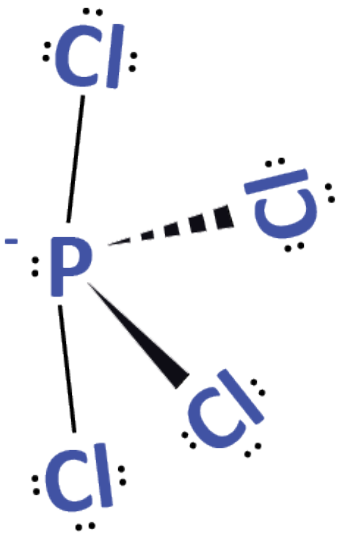
Axial Position

VSEPR Geometries: 5 e- Regions

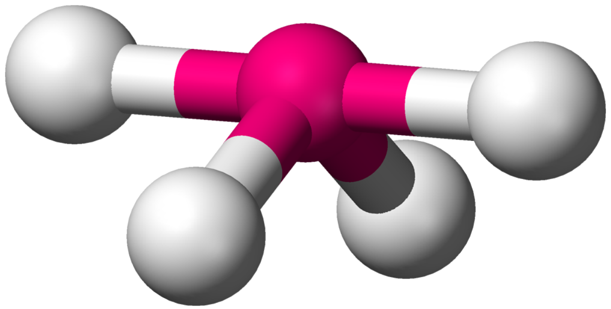
- The equatorial and axial positions have differing stability.
- If you want to replace a bond with a lone pair in the trigonal bipyramidal electronic geometry, you must remove an equatorial bond.
- **It is more stable to add lone pairs to the equatorial position**
- Notice the effect of the lone pair

Electronic: Trigonal Bipyramid

Molecular: Seesaw



Equatorial Position



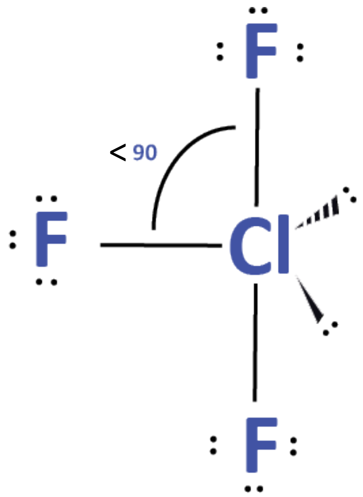
Axial Position

VSEPR Geometries: 5 e- Regions

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

Electronic: Trigonal Bipyramid

Molecular: Linear

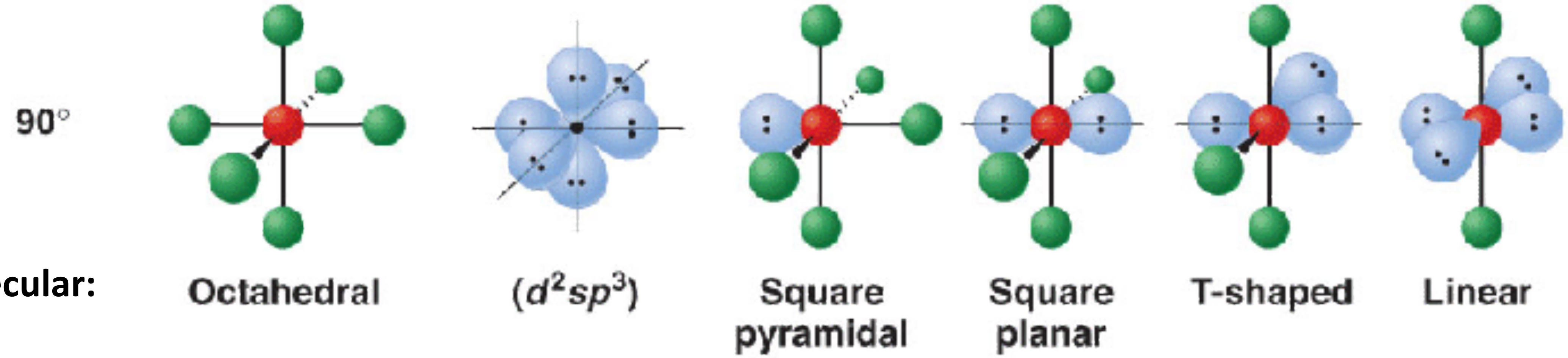
- When we remove the last equatorial bond, we end up in a linear geometry with only the most stable axial bonds remaining.

Equatorial Position

Axial Position

VSEPR Geometries: 6 e- Regions

- The octahedral molecular geometry is completely symmetrical, so there is no axial/equatorial preference.
- The one rule when replacing bonds with lone pairs is that you must always remove electrons from the opposite position as the last.

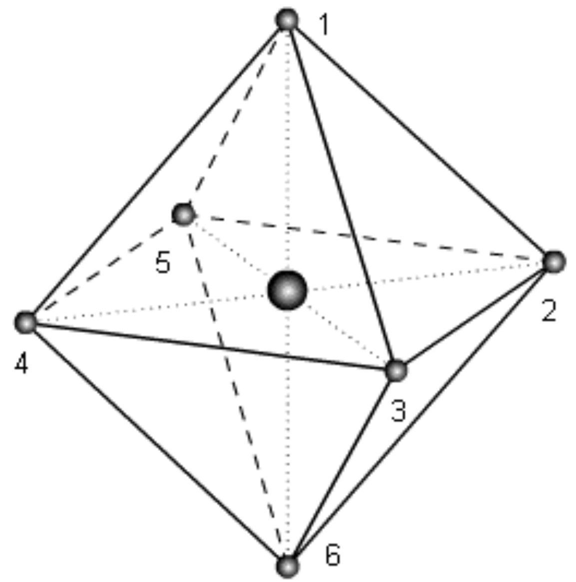


Molecular:

Electronic: Octahedral

VSEPR Geometries: 6 e- Regions

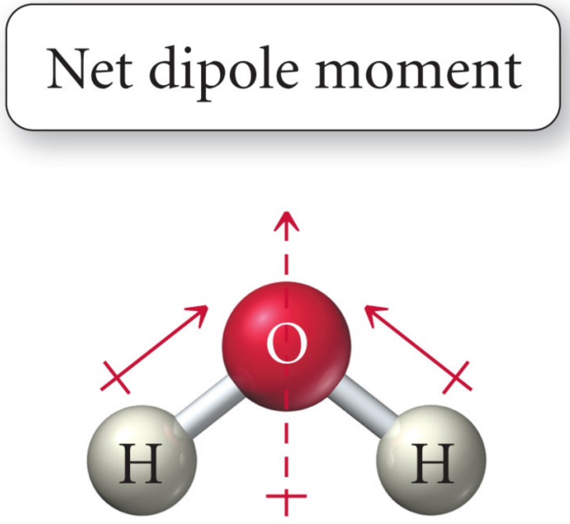
- Why is the geometry called “Octahedral” if it has six peripheral atoms?
- Remember: VSEPR geometries are named after the geometry of the **enclosure**
  - **An octahedral prism has 6 vertices**

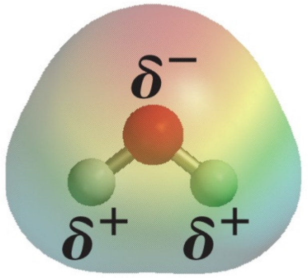


VSEPR Theory: Molecular Polarity

- 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 always be polar, as long as there is a single polar bond.
  - Lone pairs are generally an indication that the molecule is polar, except in the sp^3d and sp^3d^2 linear conformations.





Summary for Today

- **Advanced Lewis Structures**
  - **Expanded Valence:**
    - if a central atom have an atomic number greater than 13, it is possible to have an expanded valence. You can draw the structures by knowing how many available electrons must be in your valence and by minimizing formal charge.
  - **Incomplete Octet:**
    - Be and B are electron-poor compounds that are stable without filling their octets.
  - **Radicals:**
    - Radicals are molecules with unpaired electrons in the valence

Summary for Today

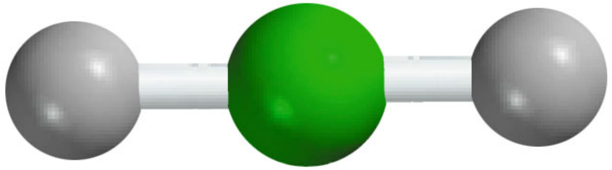
- **Valence Shell Electron Pair Repulsion (VSEPR)**
  - **What is the electronic and molecular geometry of a molecule in three dimensional space?**
    - Electronic geometry depends on the number of bonding regions and lone pair regions
    - Molecular geometry depends on the electronic geometry and the number of bonding regions
  - **What is the relationship between geometry, lone pair electrons, and bond angles?**
    - Lone pairs decrease the “pure” ideal bond angles of a given geometry
  - **How does the geometry relate to molecular polarity?**
    - Molecular polarity is indicated by a net asymmetry in your molecular structure with the condition that your molecule contains polar bonds

Incomplete Octet

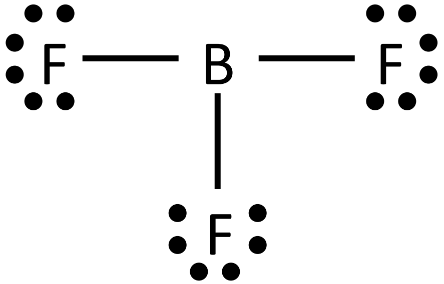
Exam Tip: there are only a few good examples of the incomplete octet: BeX_2 and BX_3, where X is either Hydrogen or a Halogen.

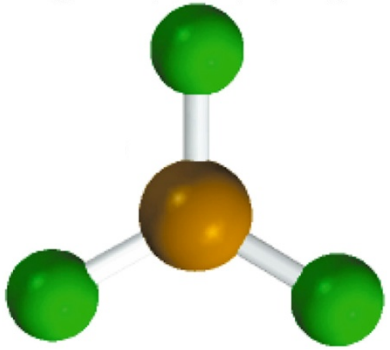
- The octet rule will also be useless for central atoms with fewer than 4 valence electrons (ex: **Boron** and **Beryllium**).
- Beryllium (Be) is satisfied making **2 bonds** (4 valence e^-).
- Boron is satisfied making **3 bonds** (6 valence e^-)
- Boron and beryllium don't have many valence electrons and they have low electronegativies, so we consider them to be **electron-poor** elements with little desire to fill their octets.

H—Be—H



Be (2 e^-) + 2H (1e^-) = 4 total e^-





B (3 e^-) + 3F (7e^-) = 24 total e^-

Incomplete Octet: Radicals

- There are a few compounds that are stable with an odd number of valence electrons
- **Radicals** are compounds with an unpaired electron in their molecular structure
- The famous of these highly reactive compounds are the nitrogen oxides (NO_x), which are heavily regulated automobile emissions
- A radical compound will always have an **odd number of available electrons**, and will not follow the S = N – A rule.
- Notice how in the drawing from Nitric Oxide (right) the nitrogen has an incomplete octet.