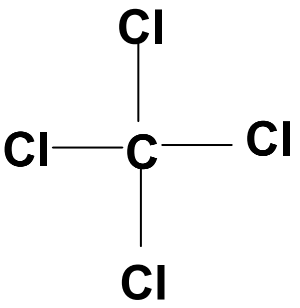
Molecular Shapes

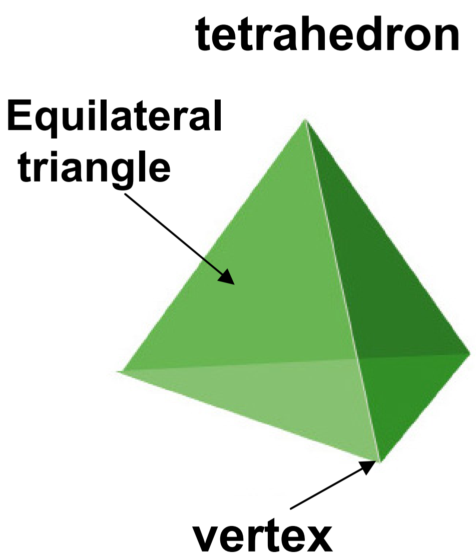
- Lewis structures give <u>atomic connectivity</u>: they tell us which atoms are physically connected to which, as well as <u>types of covalent bonds</u>, number of <u>lone pairs</u>, <u>formal charges</u>, <u>resonance structures</u>.

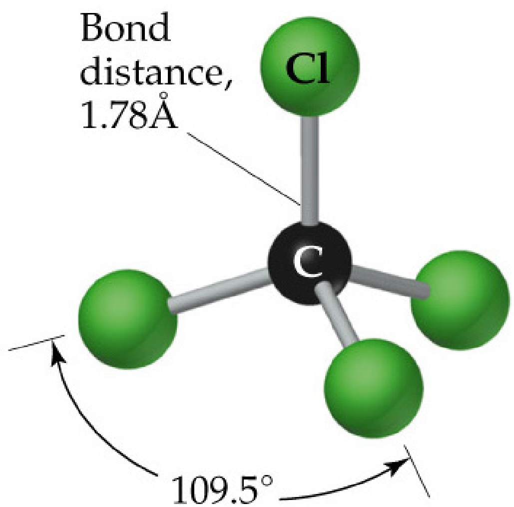
- Lewis structure does not provide the 3-dimentional shape of a molecule

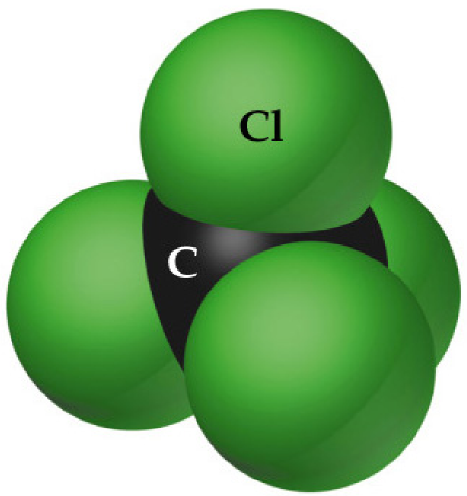
- The shape of a molecule is determined by its bond angles.

- Consider CCl_4: experimental Cl-C-Cl bond angles are 109.5°.
  - Therefore, the molecule cannot be planar.







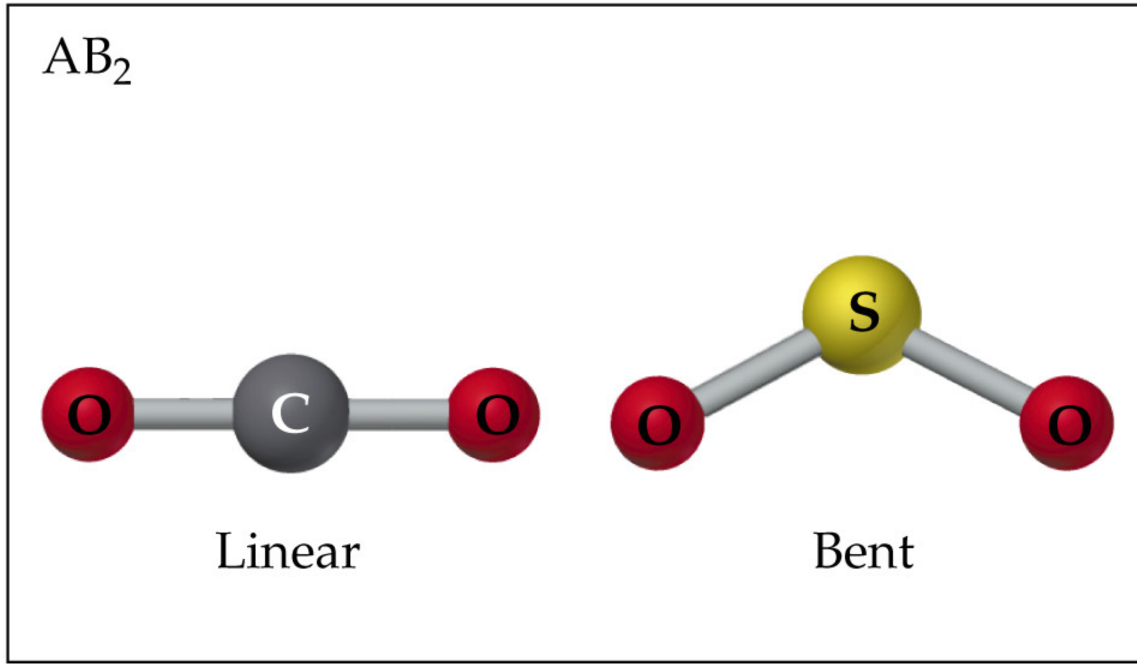


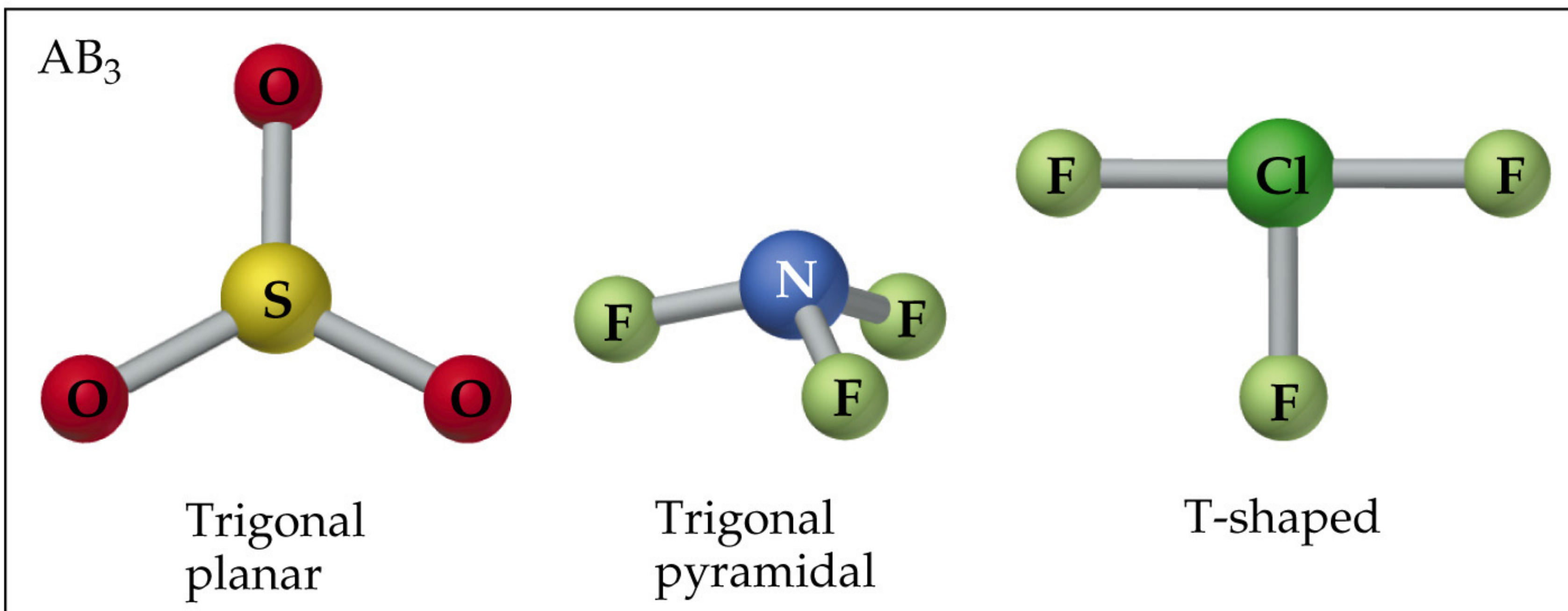
- In order to predict molecular shape, we assume the valence electron shells of atoms in molecules repel each other.
- Therefore, the molecule adopts 3D geometry that minimized this repulsion.
- We call this process **V**alence **S**hell **E**lectron **P**air **R**epulsion (**VSEPR**)

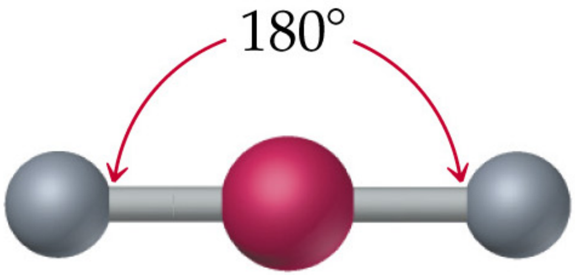
We can predict shapes using VSEPR theory.

- There are simple shapes for AB_2 and AB_3 molecules.

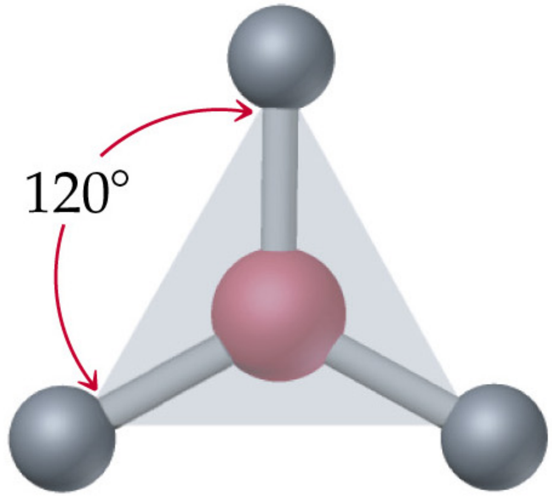
The most symmetric structure is called fundamental



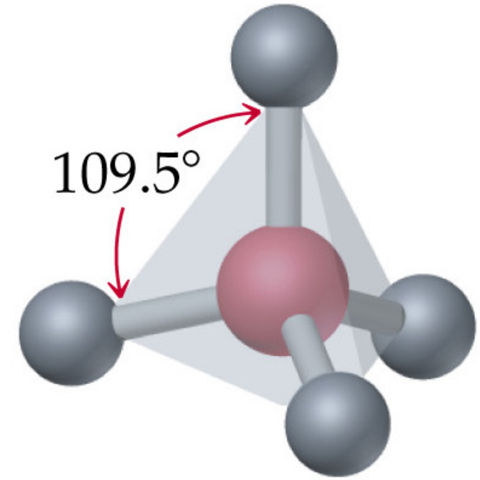




Linear

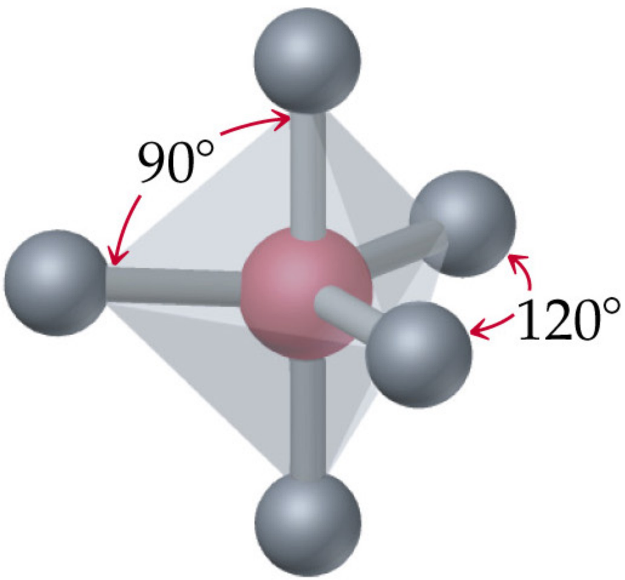


Trigonal planar

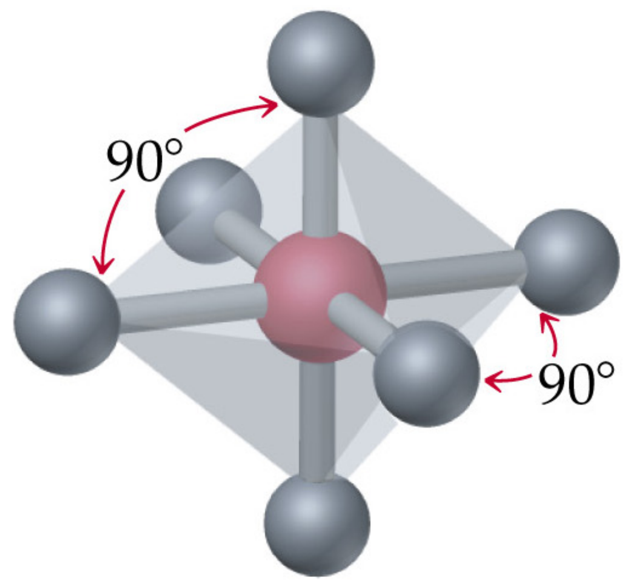


Tetrahedral

•There are five fundamental geometries for molecular shape:



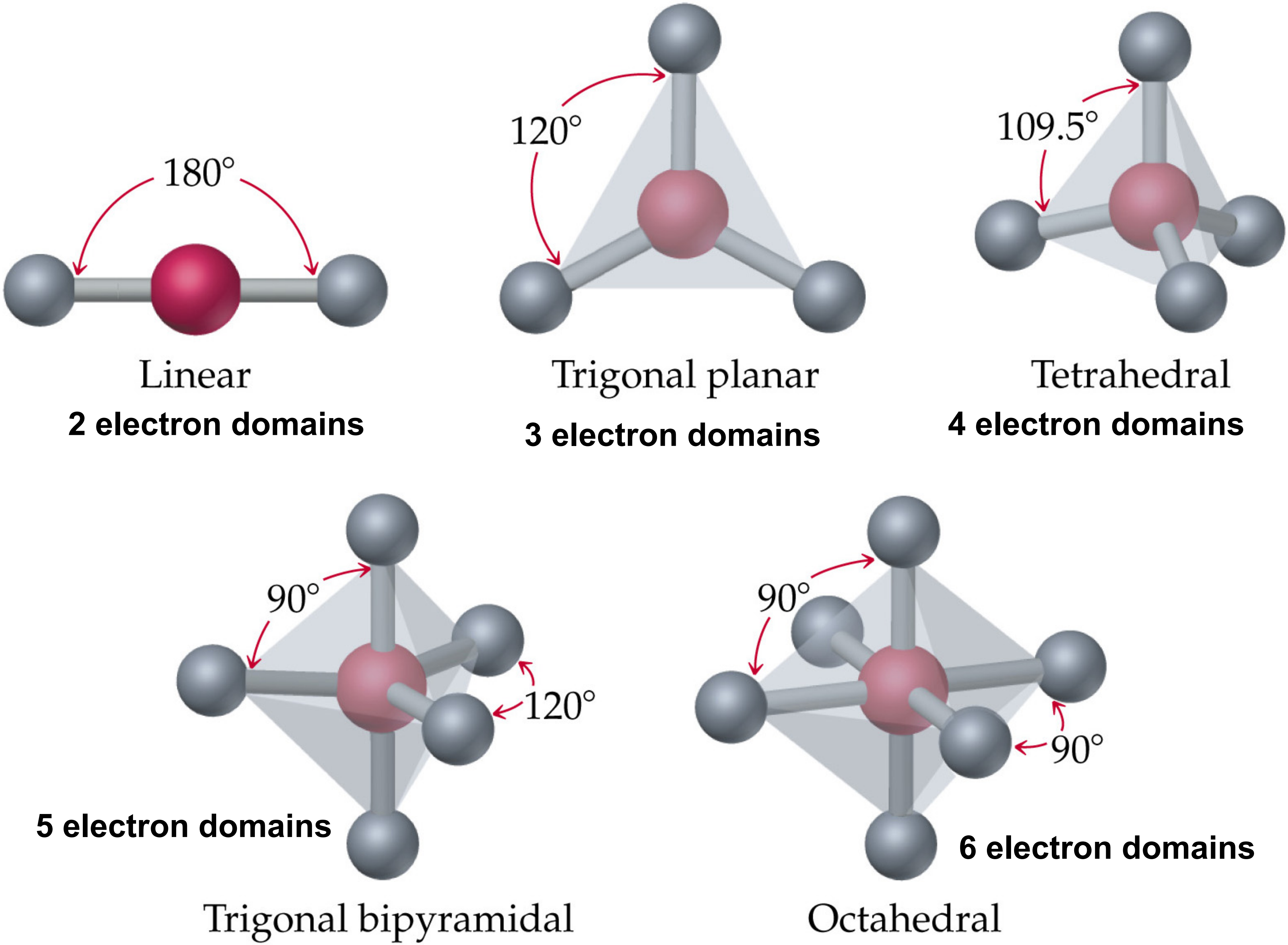
Trigonal bipyramidal



Octahedral

VSEPR Model

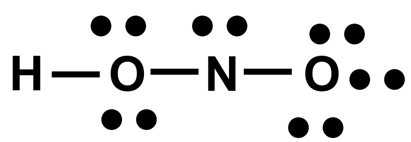
- To determine the shape of a molecule, draw Lewis structure and find
- (a) lone pairs (or non-bonding pairs) of electrons and
- (b) bonding pairs (covalent bonds).
- (c) all e-pairs (lone and bonding) are electron domains. E-domains repel each other.
- (d) 3D geometry: place in 3D space *ALL* electron domains, in a way to minimize the e^--e^- repulsion

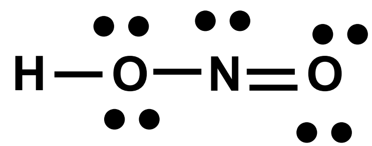


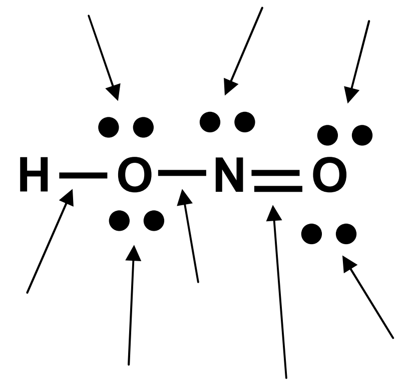
180°
Linear
2 electron domains
120°
Trigonal planar
3 electron domains
109.5°
Tetrahedral
4 electron domains
90°
120°
5 electron domains
Trigonal bipyramidal
90°
90°
6 electron domains
Octahedral

Example:

HNO_2 **18e (9 pairs)**





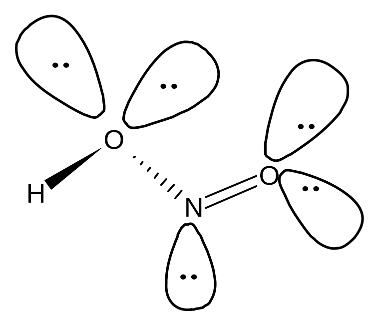


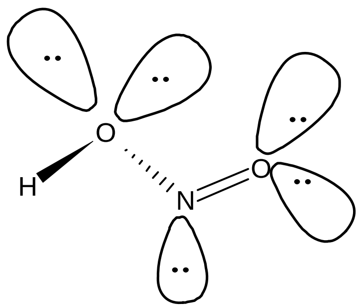
Central O: 4 domains, tetrahedral electron domain structure

Double bond is one domain

Central N: 3 domains, trigonal planar electron domain structure

Terminal O: 3 domains, trigonal planar electron domain structure





Molecular geometry: ignore lone pairs

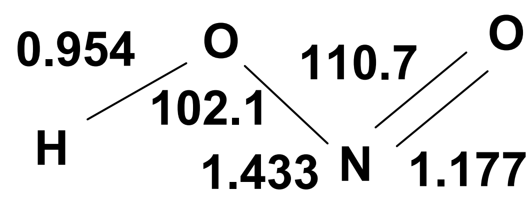
Central O: electron domain structure: tetrahedral

Central O: molecular structure: bent

Central N: electron domain structure: trigonal planar

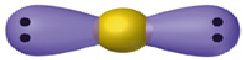
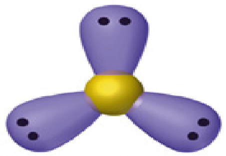
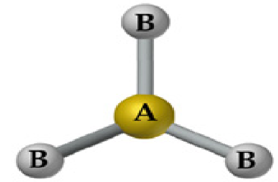
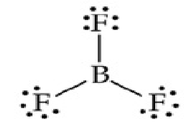
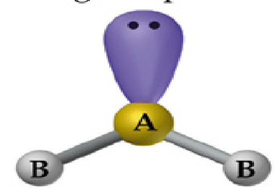
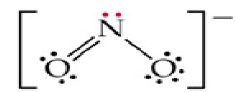
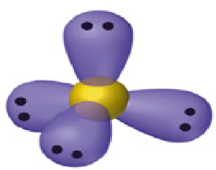
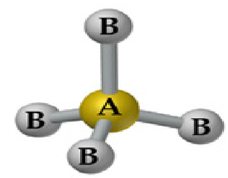
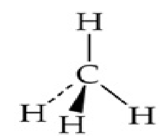
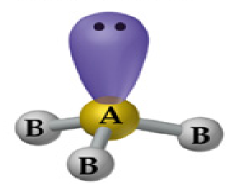
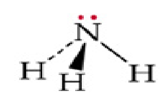
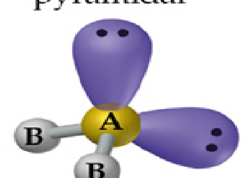
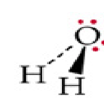
Central N: molecular structure: bent

Molecular structure: trans-, cis- or gauche?



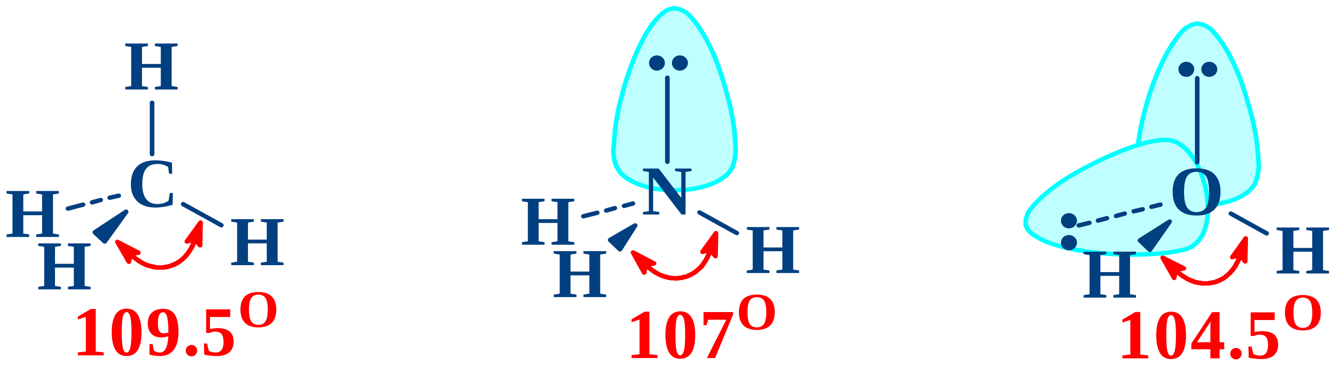
(trans- is 2.3 kJ/mol lower in energy than cis-)

Electron Domains Around the Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

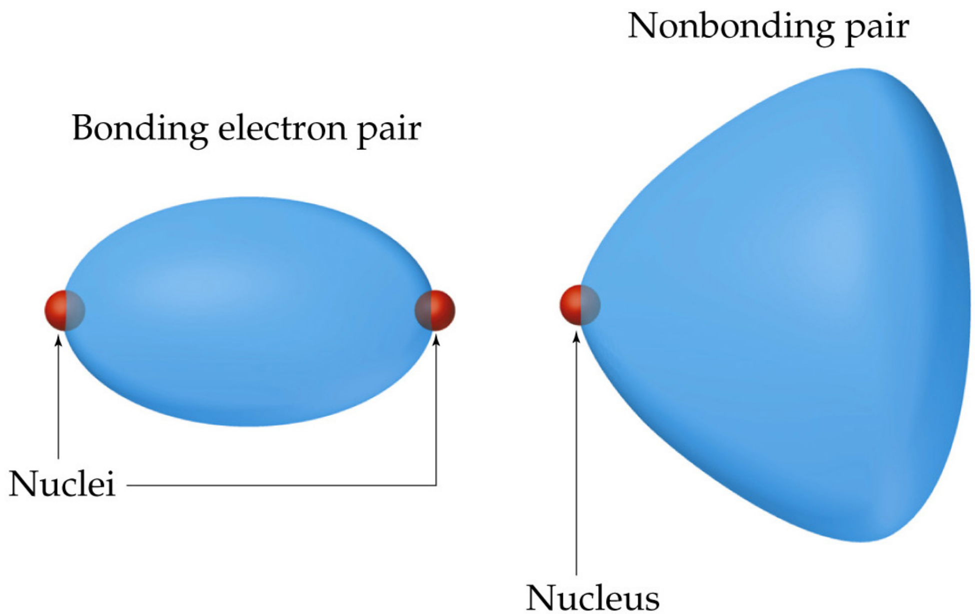
- By experiment, the H-X-H bond angle decreases on moving from C to N to O:



- Since electrons in a bond are attracted by two nuclei, they do not repel as much as lone pairs. Lone pairs occupy larger space.

- Therefore, the bond angle decreases as the number of lone pairs increase.

The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles



- Similarly, electrons in multiple bonds repel more than electrons in single bonds. Double bond occupies larger space.

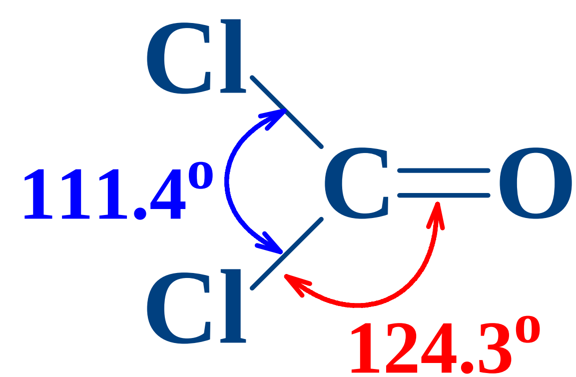
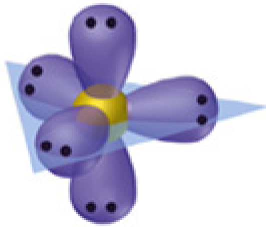
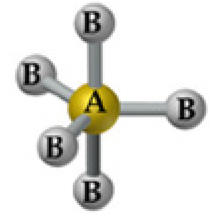
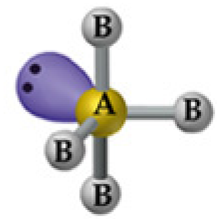
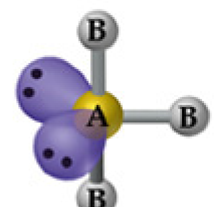
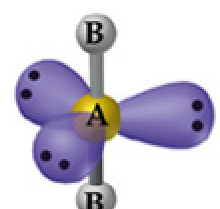


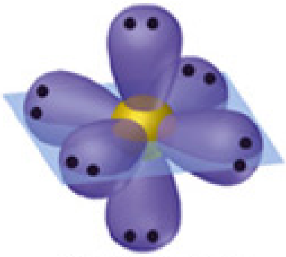
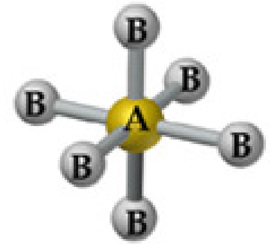
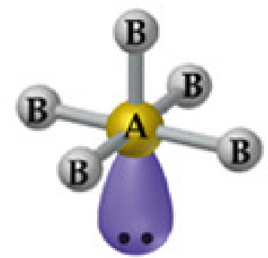
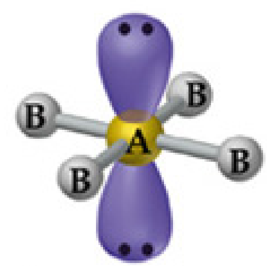
TABLE 9.3 Electron-Domain Geometries and Molecular Shapes for Molecules with Five and Six Electron Domains Around the Central Atom

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2

- **Atoms that have expanded octets have AB_5 (trigonal bipyramidal) or AB_6 (octahedral) electron pair geometries.**

- **For trigonal bipyramidal structures there is a plane containing three electrons pairs. The fourth and fifth electron pairs are located above and below this plane.**

TABLE 9.3 Electron-Domain Geometries and Molecular Shapes for Molecules with Five and Six Electron Domains Around the Central Atom

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

- For octahedral structures, there is a plane containing four electron pairs. Similarly, the fifth and sixth electron pairs are located above and below this plane.

Molecules with Expanded Valence Shells

- To minimize e^--e^- repulsion, lone pairs are always placed in equatorial positions. (ClF_3)