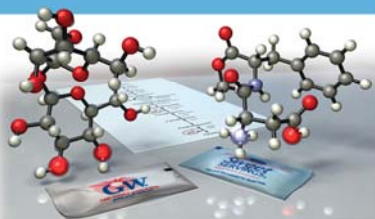


Chemistry: A Molecular Approach, 1st Ed.
Nivaldo Tro

Chapter 10 Chemical Bonding II



Roy Kennedy
Massachusetts Bay Community College
Wellesley Hills, MA
2008, Prentice Hall

Structure Determines Properties!

- properties of molecular substances depend on the structure of the molecule
- the structure includes many factors, including:
 - ✓ the skeletal arrangement of the atoms
 - ✓ the kind of bonding between the atoms
 - ionic, polar covalent, or covalent
 - ✓ the shape of the molecule
- bonding theory should allow you to predict the shapes of molecules

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Molecular Geometry

- Molecules are 3-dimensional objects
- We often describe the shape of a molecule with terms that relate to geometric figures
- These geometric figures have characteristic “corners” that indicate the positions of the surrounding atoms around a central atom in the center of the geometric figure
- The geometric figures also have characteristic angles that we call **bond angles**

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Using Lewis Theory to Predict Molecular Shapes

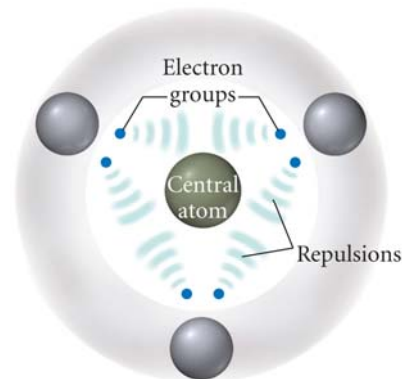
- Lewis theory predicts there are regions of electrons in an atom based on placing shared pairs of valence electrons between bonding nuclei and unshared valence electrons located on single nuclei
- this idea can then be extended to predict the shapes of molecules by realizing these regions are all negatively charged and should repel

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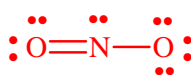
VSEPR Theory

- electron groups around the central atom will be most stable when they are as far apart as possible – we call this **valence shell electron pair repulsion** theory
 - since electrons are negatively charged, they should be most stable when they are separated as much as possible
- the resulting geometric arrangement will allow us to predict the shapes and bond angles in the molecule



Electron Groups

- the Lewis structure predicts the arrangement of valence electrons around the central atom(s)
- each lone pair of electrons constitutes one electron group on a central atom
- each bond constitutes one electron group on a central atom
 - regardless of whether it is single, double, or triple



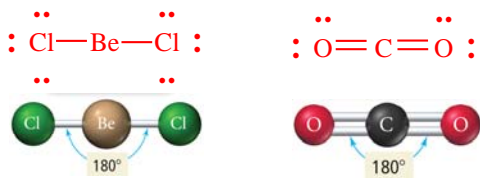
there are 3 electron groups on N
1 lone pair
1 single bond
1 double bond

Molecular Geometries

- there are 5 basic arrangements of electron groups around a central atom
 - based on a maximum of 6 bonding electron groups
 - though there may be more than 6 on very large atoms, it is very rare
- each of these 5 basic arrangements results in 5 different basic molecular shapes
 - in order for the molecular shape and bond angles to be a “perfect” geometric figure, all the electron groups must be on bonds and all the bonds must be equivalent
- for molecules that exhibit resonance, it doesn’t matter which resonance form you use – the molecular geometry will be the same

Linear Geometry

- when there are 2 electron groups around the central atom, they will occupy positions opposite each other around the central atom
- this results in the molecule taking a **linear geometry**
- the bond angle is 180°

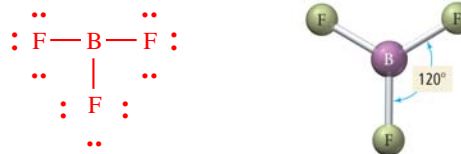


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Trigonal Geometry

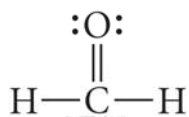
- when there are 3 electron groups around the central atom, they will occupy positions in the shape of a triangle around the central atom
- this results in the molecule taking a **trigonal planar geometry**
- the bond angle is 120°



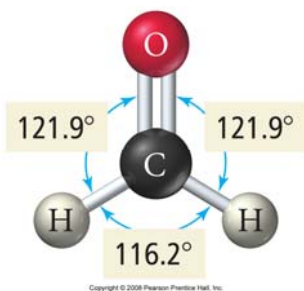
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Not Quite Perfect Geometry



Because the bonds are not identical, the observed angles are slightly different from ideal.



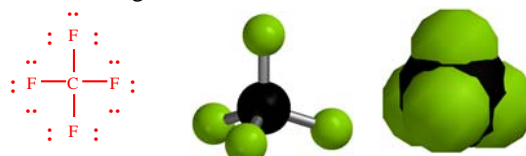
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Tetrahedral Geometry

- when there are 4 electron groups around the central atom, they will occupy positions in the shape of a tetrahedron around the central atom
- this results in the molecule taking a **tetrahedral geometry**
- the bond angle is 109.5°



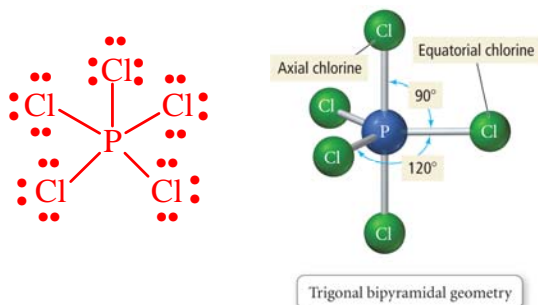
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Trigonal Bipyramidal Geometry

- when there are 5 electron groups around the central atom, they will occupy positions in the shape of two tetrahedra that are base-to-base with the central atom in the center of the shared bases
- this results in the molecule taking a **trigonal bipyramidal geometry**
- the positions above and below the central atom are called the **axial** positions
- the positions in the same base plane as the central atom are called the **equatorial** positions
- the bond angle between equatorial positions is 120°
- the bond angle between axial and equatorial positions is 90°

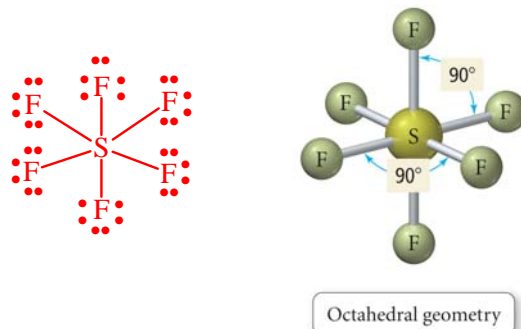
Trigonal Bipyramidal Geometry



Octahedral Geometry

- when there are 6 electron groups around the central atom, they will occupy positions in the shape of two square-base pyramids that are base-to-base with the central atom in the center of the shared bases
- this results in the molecule taking an **octahedral geometry**
 - ✓ it is called octahedral because the geometric figure has 8 sides
- all positions are equivalent
- the bond angle is 90°

Octahedral Geometry



The Effect of Lone Pairs

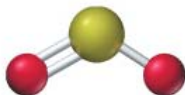
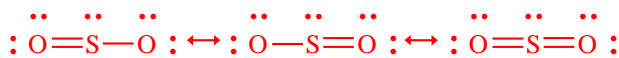
- lone pair groups “occupy more space” on the central atom
 - ✓ because their electron density is exclusively on the central atom rather than shared like bonding electron groups
- relative sizes of repulsive force interactions is:
Lone Pair – Lone Pair > Lone Pair – Bonding Pair > Bonding Pair – Bonding Pair
- this effects the bond angles, making them smaller than expected

Derivative Shapes

- the molecule’s shape will be one of basic molecular geometries if all the electron groups are bonds and all the bonds are equivalent
- molecules with lone pairs or different kinds of surrounding atoms will have distorted bond angles and different bond lengths, but the shape will be a derivative of one of the basic shapes

Derivative of Trigonal Geometry

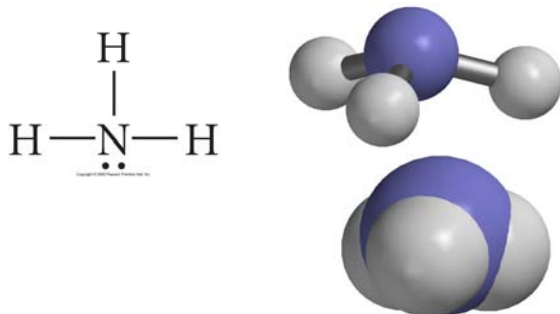
- when there are 3 electron groups around the central atom, and 1 of them is a lone pair, the resulting shape of the molecule is called a **trigonal planar - bent shape**
- the bond angle is $< 120^\circ$



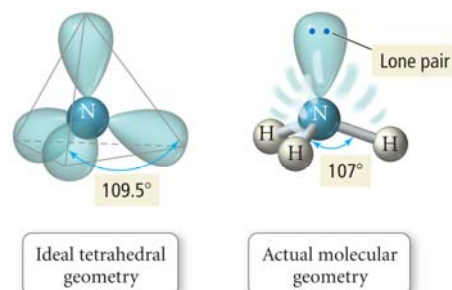
Derivatives of Tetrahedral Geometry

- when there are 4 electron groups around the central atom, and 1 is a lone pair, the result is called a **pyramidal shape**
 - ✓ because it is a triangular-base pyramid with the central atom at the apex
- when there are 4 electron groups around the central atom, and 2 are lone pairs, the result is called a **tetrahedral-bent shape**
 - ✓ it is planar
 - ✓ it looks similar to the trigonal planar-bent shape, except the angles are smaller
- for both shapes, the bond angle is $< 109.5^\circ$

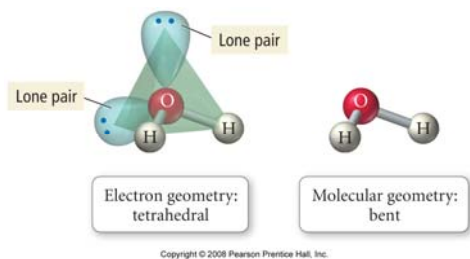
Pyramidal Shape



Bond Angle Distortion from Lone Pairs



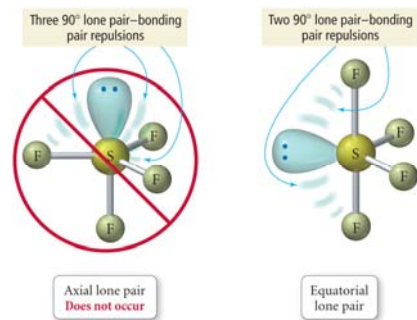
Tetrahedral-Bent Shape



Derivatives of the Trigonal Bipyramidal Geometry

- when there are 5 electron groups around the central atom, and some are lone pairs, they will occupy the equatorial positions because there is more room
- when there are 5 electron groups around the central atom, and 1 is a lone pair, the result is called **see-saw shape**
✓ aka **distorted tetrahedron**
- when there are 5 electron groups around the central atom, and 2 are lone pairs, the result is called **T-shaped**
- when there are 5 electron groups around the central atom, and 3 are lone pairs, the result is called a **linear shape**
- the bond angles between equatorial positions is $< 120^\circ$
- the bond angles between axial and equatorial positions is $< 90^\circ$
✓ linear = 180° axial-to-axial

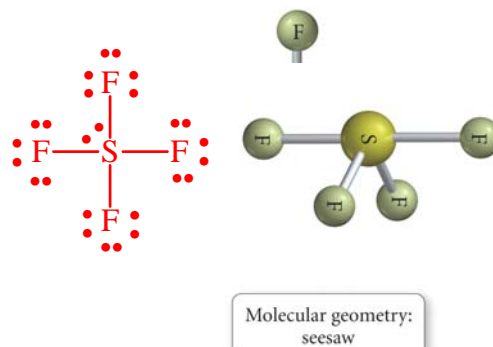
Replacing Atoms with Lone Pairs in the Trigonal Bipyramid System



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See-Saw Shape

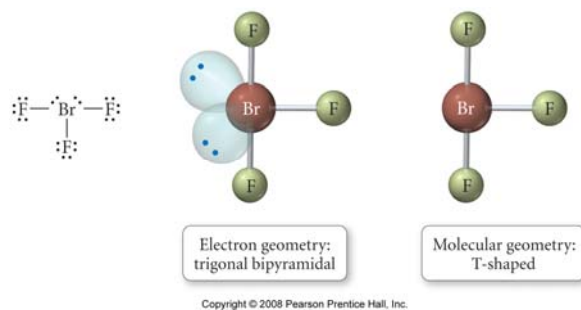


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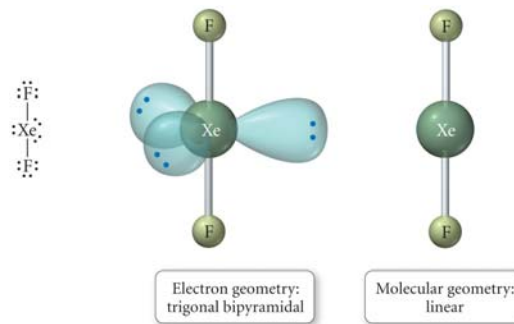
T-Shape



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Linear Shape



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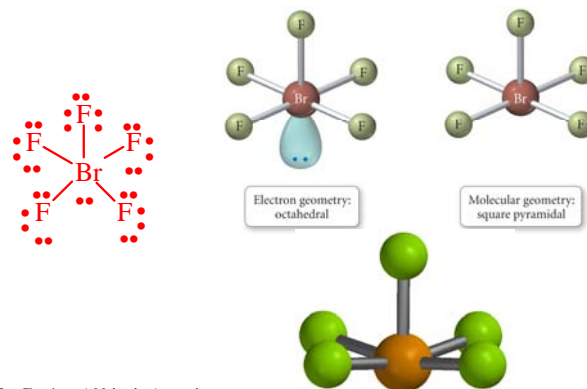
Derivatives of the Octahedral Geometry

- when there are 6 electron groups around the central atom, and some are lone pairs, each even number lone pair will take a position opposite the previous lone pair
- when there are 6 electron groups around the central atom, and 1 is a lone pair, the result is called a **square pyramidal shape**
 - ✓ the bond angles between axial and equatorial positions is $< 90^\circ$
- when there are 6 electron groups around the central atom, and 2 are lone pairs, the result is called a **square planar shape**
 - ✓ the bond angles between equatorial positions is 90°

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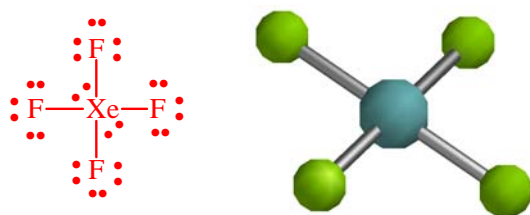
Square Pyramidal Shape



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Square Planar Shape



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TABLE 10.1 Electron and Molecular Geometries

Electron Groups*	Bonding Groups	Lone Pairs	Electron Geometry	Molecular Geometry	Approximate Bond Angles	Example
2	2	0	Linear	Linear	180°	$\text{:}\ddot{\text{O}}=\text{C}=\ddot{\text{O}}\text{:}$
3	3	0	Trigonal planar	Trigonal planar	120°	$\text{:}\ddot{\text{B}}\text{:}$ $\text{H}-\text{B}-\text{H}$ $\text{:}\ddot{\text{F}}\text{:}$
3	2	1	Trigonal planar	Best	$< 120^\circ$	$\text{:}\ddot{\text{O}}=\text{S}=\ddot{\text{O}}\text{:}$
4	4	0	Tetrahedral	Tetrahedral	109.5°	H $\text{H}-\text{C}-\text{H}$ H
4	3	1	Tetrahedral	Trigonal pyramidal	$< 109.5^\circ$	H $\text{H}-\text{N}-\text{H}$ H
4	2	2	Tetrahedral	Best	$< 109.5^\circ$	$\text{H}-\ddot{\text{O}}-\text{H}$

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