General Chemistry

202-SN1-RE

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Office: 5th floor

Covalent Bond Energies and Chemical Reactions

Bond Energies

- Every chemical bond has an energy associated to it.
- Energy varies depending on the molecular environment.
- For example, consider the stepwise decomposition of methane:

Process	**Energy Required (kJ/mol)**
$CH_4(g) \rightarrow CH_3(g) + H(g)$	435
$CH_3(g) \rightarrow CH_2(g) + H(g)$	453
$CH_2(g) \rightarrow CH(g) + H(g)$	425
$CH(g) \rightarrow C(g) + H(g)$	339
	Total = 1652

Average = 1652/4 = 413 kJ/mol

Bond Energies

- C-H bond energies vary amongst different molecules.

Molecule	**Measured C-H Bond Energy (kJ/mol)**
$HCBr_3$	380
$HCCl_3$	380
HCF_3	430
C_2H_6	410

- Despite the variation in bond energies due to the environment, chemists find it useful to use average values.

Bond Energies

Single Bonds						Multiple Bonds	
H—H	432	N—H	391	I—I	149	C=C	614
H—F	565	N—N	160	I—Cl	208	C≡C	839
H—Cl	427	N—F	272	I—Br	175	O=O	495
H—Br	363	N—Cl	200			C=O*	745
H—I	295	N—Br	243	S—H	347	C≡O	1072
		N—O	201	S—F	327	N=O	607
C—H	413	O—H	467	S—Cl	253	N=N	418
C—C	347	O—O	146	S—Br	218	N≡N	941
C—N	305	O—F	190	S—S	266	C≡N	891
C—O	358	O—Cl	203			C=N	615
C—F	485	O—I	234	Si—Si	340		
C—Cl	339			Si—H	393		
C—Br	276	F—F	154	Si—C	360		
C—I	240	F—Cl	253	Si—O	452		
C—S	259	F—Br	237				
		Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

*C=O(CO_2) = 799

Bond Lengths

As the number of shared electrons in a bond increases, the bond length shortens.

Bond	Bond Type	Bond Length (pm)	Bond Energy (kJ/mol)
C—C	Single	154	347
C═C	Double	134	614
C≡C	Triple	120	839
C—O	Single	143	358
C═O	Double	123	745
C—N	Single	143	305
C═N	Double	138	615
C≡N	Triple	116	891

Bond Energies

- Every bond has an energy associated to it.

- To break bonds, energy must be *added* to the system (endothermic).

- To form bonds, energy is *released* (exothermic).

Bond Energies

$$\Delta H = \sum(n * D_{bonds\ broken}) - \sum(n * D_{bonds\ formed})$$

D = the bond energy per mole of bonds (always has a positive sign).

ΔH = sum of the energies required to break old bonds (positive signs) plus the sum of the energies released in the formation of new bonds (negative signs).

Exercise

Predict ΔH for the following reaction:

$$CH_3N \equiv C(g) \rightarrow CH_3C \equiv N(g)$$

Given the following information:

	Bond Energy (kJ/mol)
C–H	413
C–N	305
C–C	347
$C \equiv N$	891

Topic 5c – VSEPR

Structures of Molecules

CH_4

Why does methane have a tetrahedral shape?

VSEPR Model

- VSEPR: Valence Shell Electron-Pair Repulsion.
- Useful in predicting the geometries of molecules formed from nonmetals.
- The structure around a given atom is determined principally by minimizing electron pair repulsions.
- The bonding and nonbonding pairs around a given atom will be positioned as far apart as possible.

Steps to Apply the VSEPR Model

1. Draw the Lewis structure for the molecule.

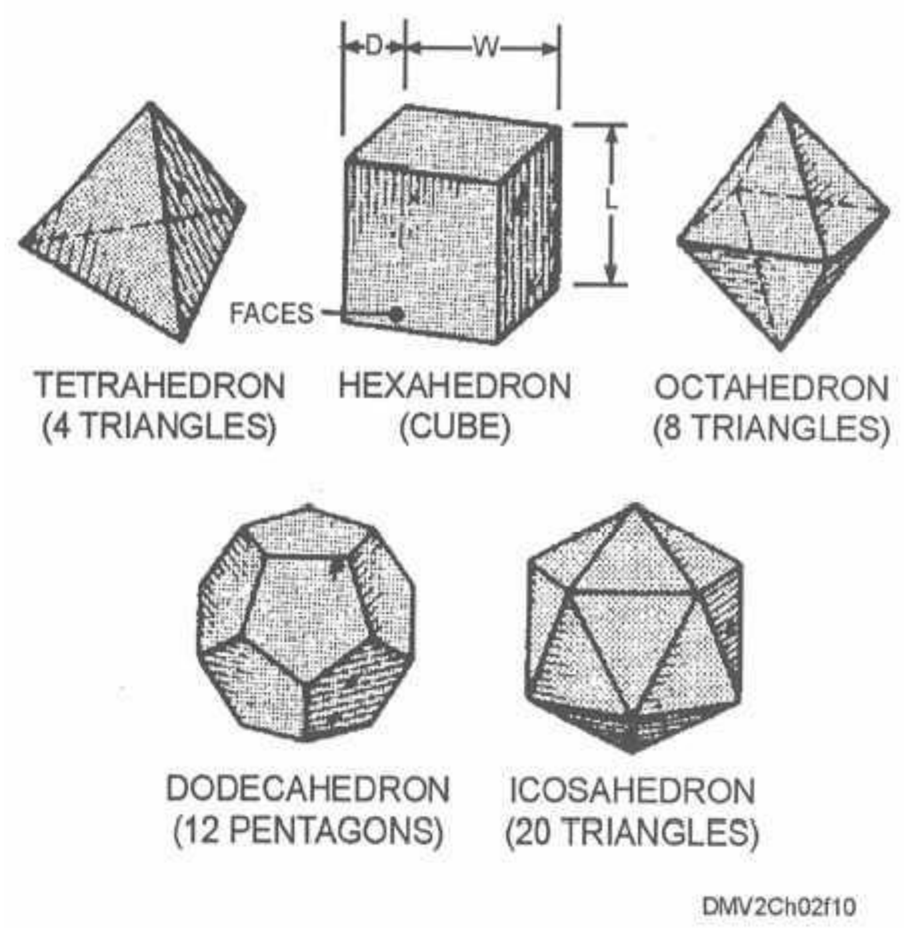
2. Count the electron pairs and arrange them in the way that minimizes repulsion (put the pairs as far apart as possible).

3. Determine the positions of the atoms from the way electron pairs are shared (how electrons are shared between the central atom and surrounding atoms).

4. Determine the name of the molecular structure from positions of the atoms.

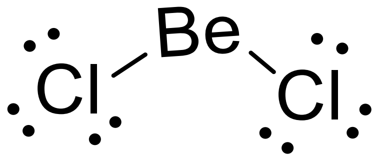
Polyhedra and Naming of Molecular Structure

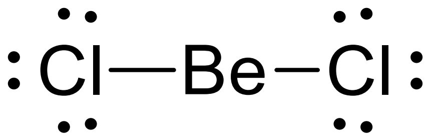
Tetrahedral and octahedral names for molecular shapes are derived from names of polyhedra.



VSEPR Model and Molecular Structure

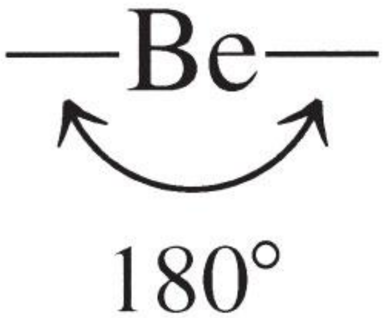
Would you predict $BeCl_2$ is bent or linear?

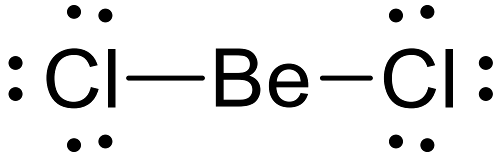




VSEPR model states that the structure around a given atom is determined by minimizing electron-pair repulsion.

VSEPR Model and Molecular Structure

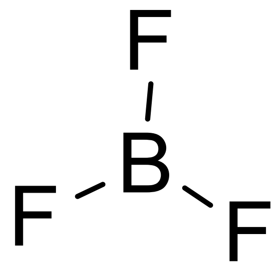


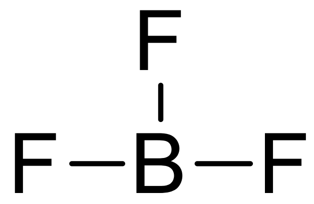


$BeCl_2$ adopts a linear structure to minimize electron pair repulsion.

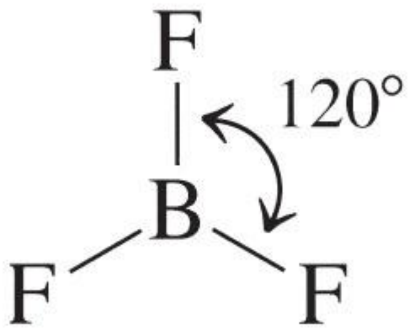
VSEPR Model and Molecular Structure

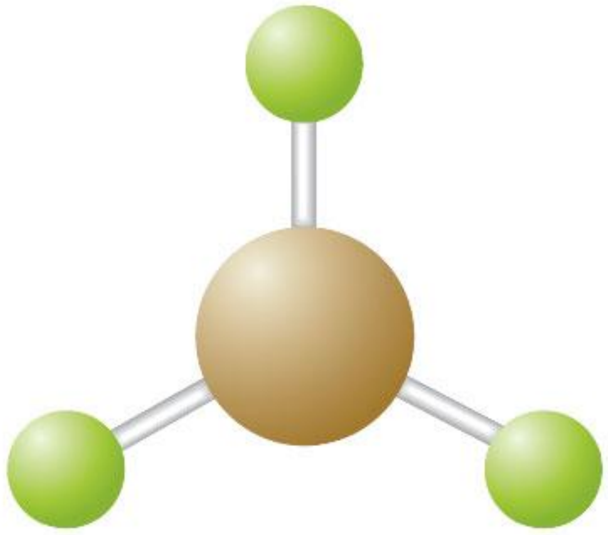
What structure should boron trifluoride have?





VSEPR Model and Molecular Structure

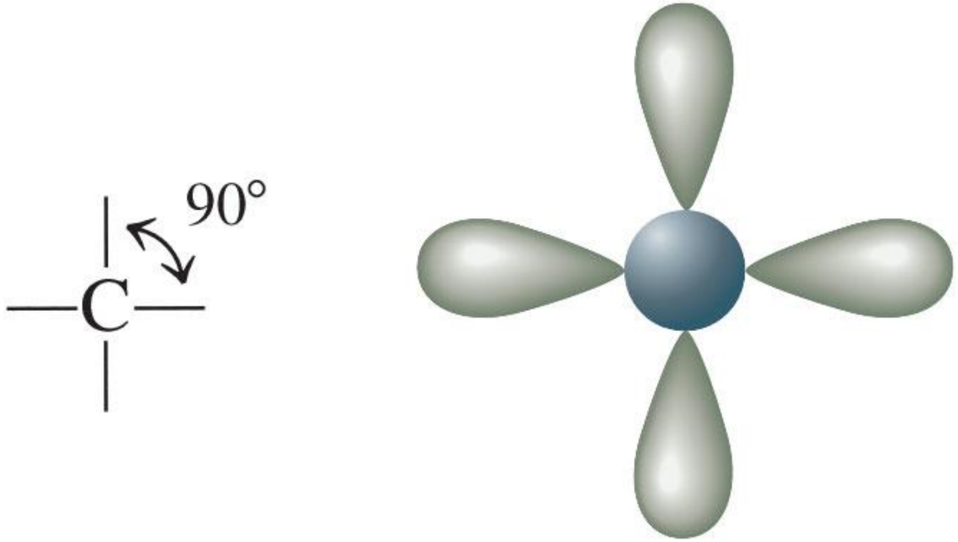




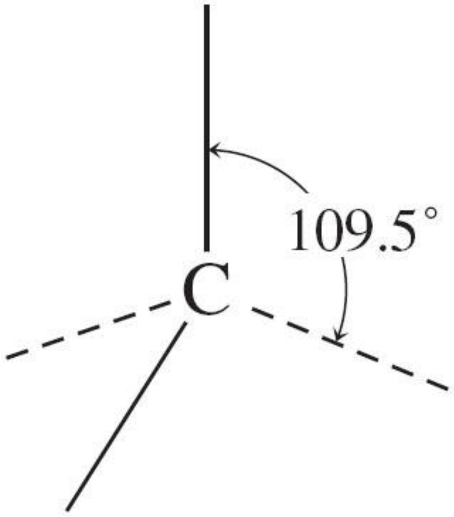
BF_3 has a trigonal planar molecular structure.

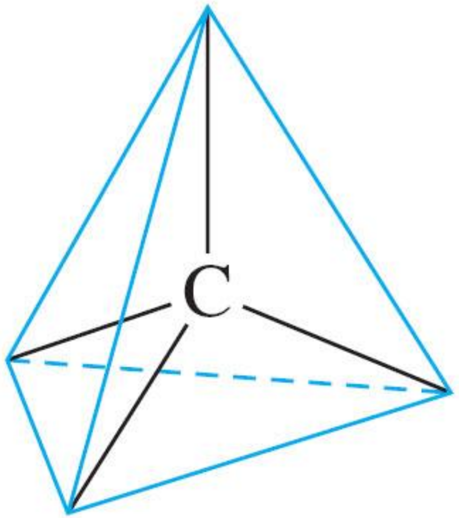
VSEPR Model and Molecular Structure

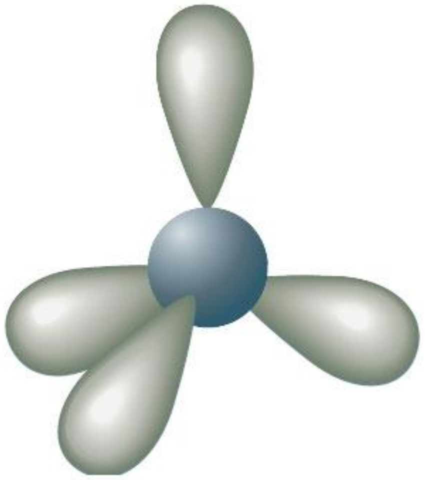
Why does methane have a tetrahedral shape?



VSEPR Model and Molecular Structure



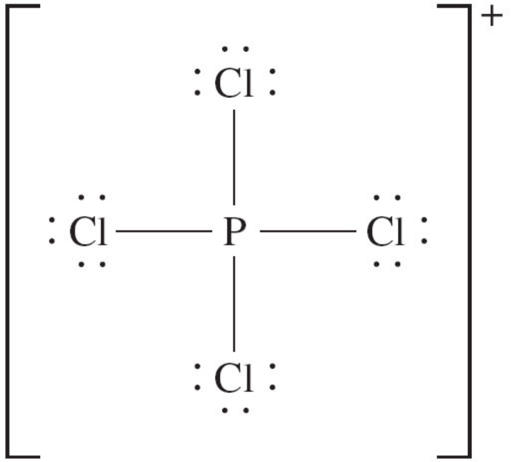


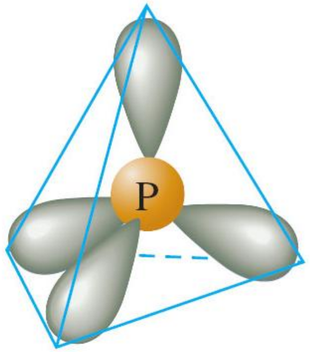


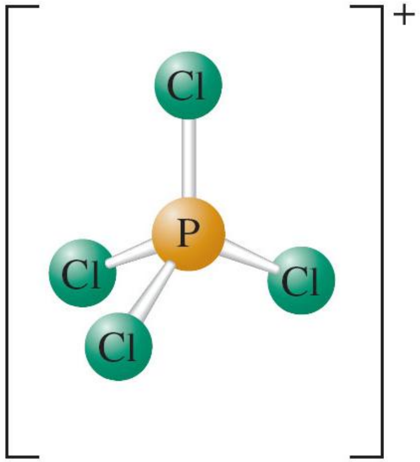
Methane adopts a tetrahedral shape to minimize electron pair repulsion.

VSEPR Model and Molecular Structure

Predict the molecular structures of PCl_4^+, PCl_5 and PCl_6^-





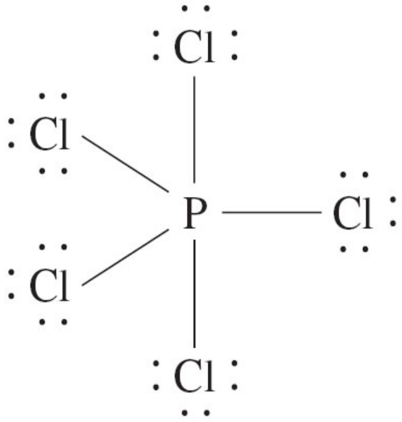


PCl_4^+

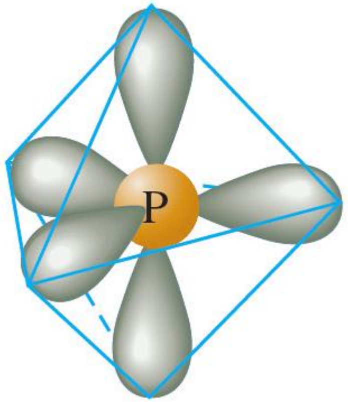
tetrahedral

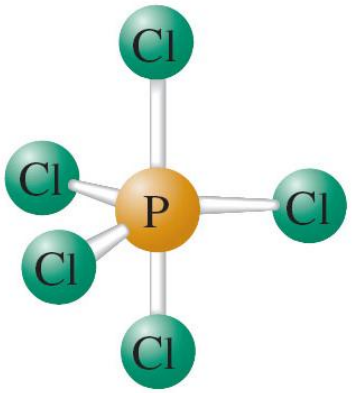
VSEPR Model and Molecular Structure

Predict the molecular structures of PCl_4^+, PCl_5 and PCl_6^-



PCl_5



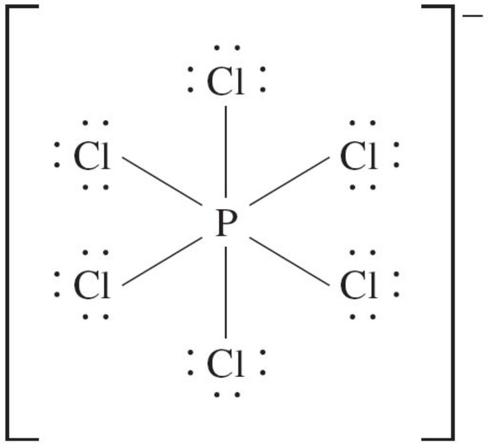


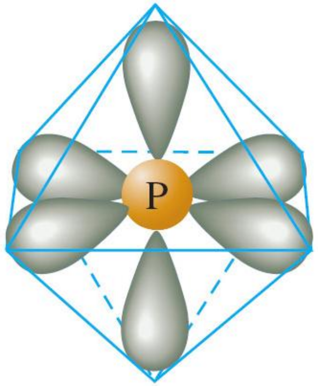
Trigonal bipyramidal

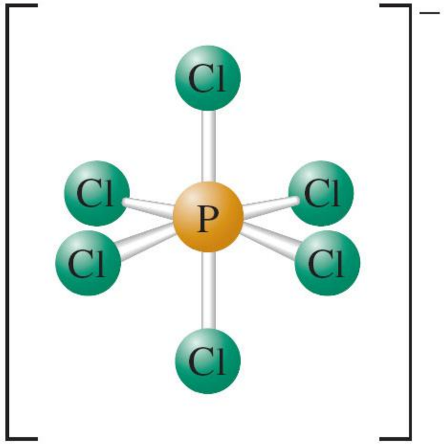
Start by drawing the Lewis structure and see how many electron pairs are around it.

VSEPR Model and Molecular Structure

Predict the molecular structures of PCl_4^+, PCl_5 and PCl_6^-



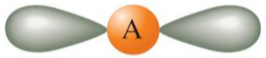
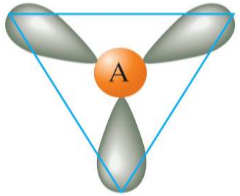
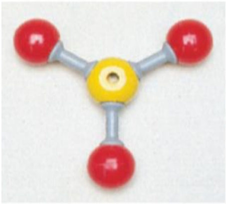
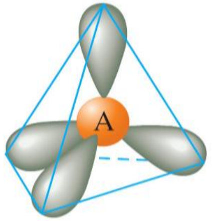
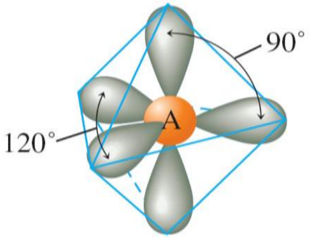
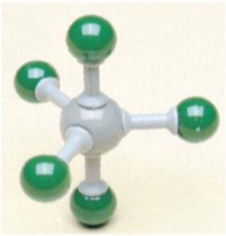
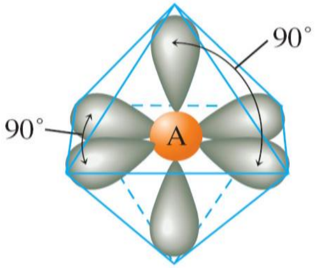
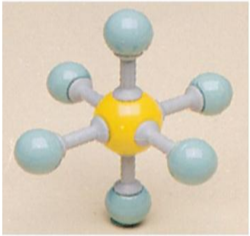




PCl_6^-

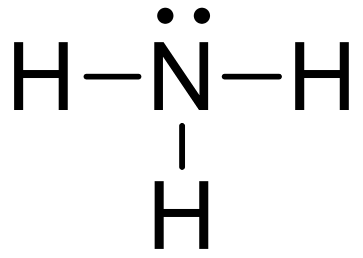
Octahedral

Geometries that minimize repulsion.

Number of Electron Pairs	Arrangement of Electron Pairs		Example
2	Linear		
3	Trigonal planar		
4	Tetrahedral		
5	Trigonal bipyramidal		
6	Octahedral		

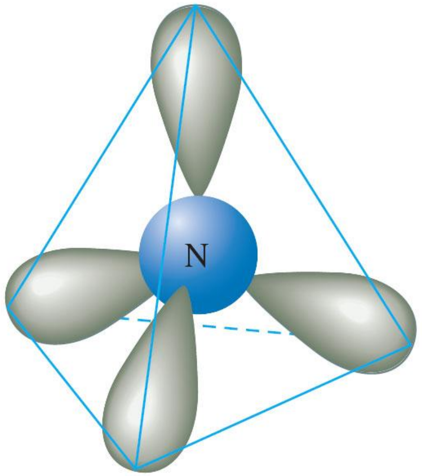
VSEPR Model and Molecular Structure

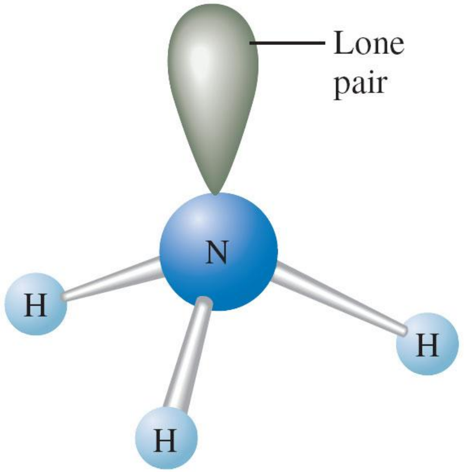
Predict the molecular structure of ammonia



VSEPR Model and Molecular Structure

Predict the molecular structure of ammonia

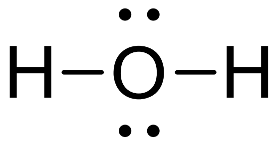


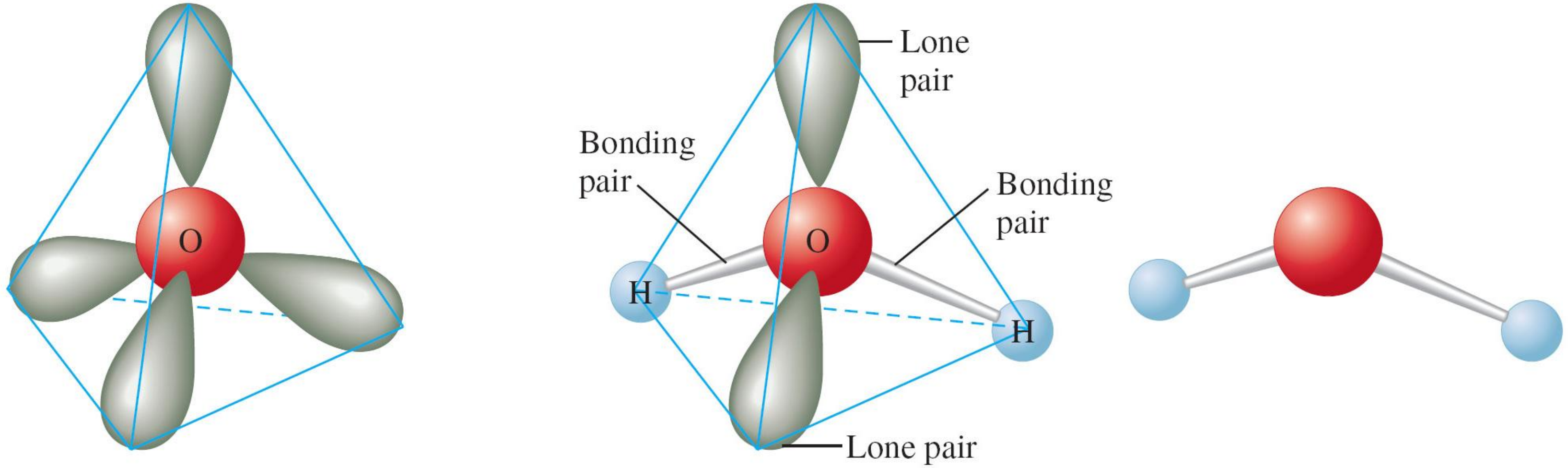


- Electron pair arrangement of ammonia is tetrahedral, but one electron pair is a lone pair.
- Molecular structure is based on the positions of the atoms. Ammonia has a trigonal pyramidal shape.

VSEPR Model and Molecular Structure

Predict the molecular structure of water



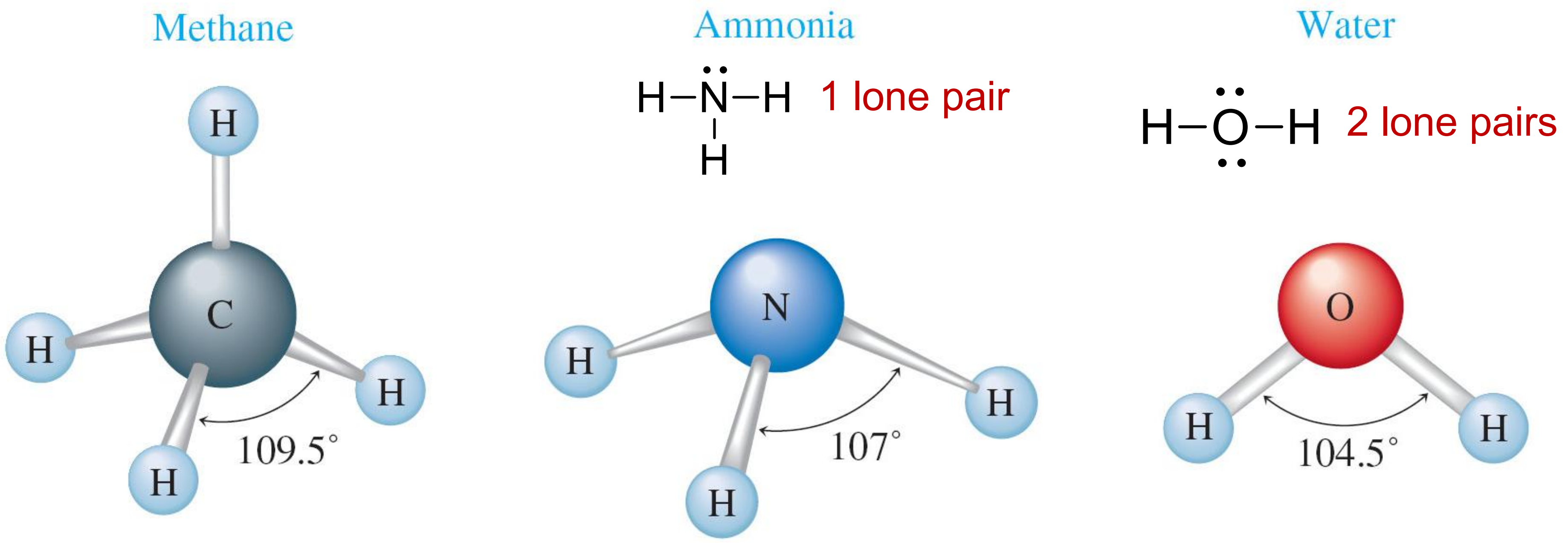


(a) (b) (c)

Bent (v-shaped)

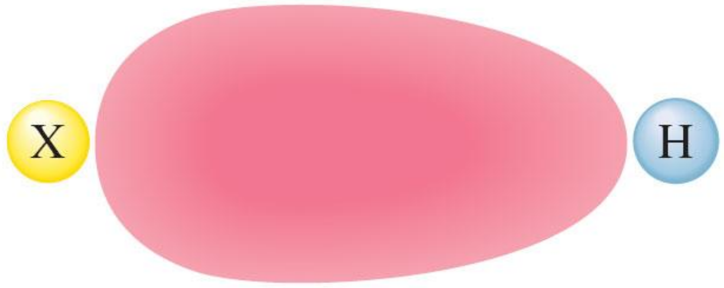
Lone pairs are arranged in a way to minimize repulsions.

VSEPR Model and Molecular Structure



- Actual bond angles in ammonia and water are less than ideal bond angle of 109.5°.
- Lone pair electrons cause more repulsion than bonding electrons and tend to compress the bond angles between bonding pairs.

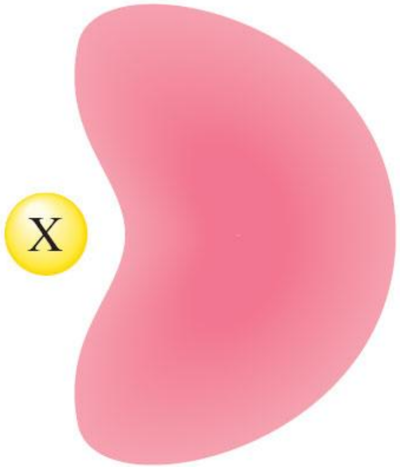
VSEPR Model and Molecular Structure



Bonding pair electrons

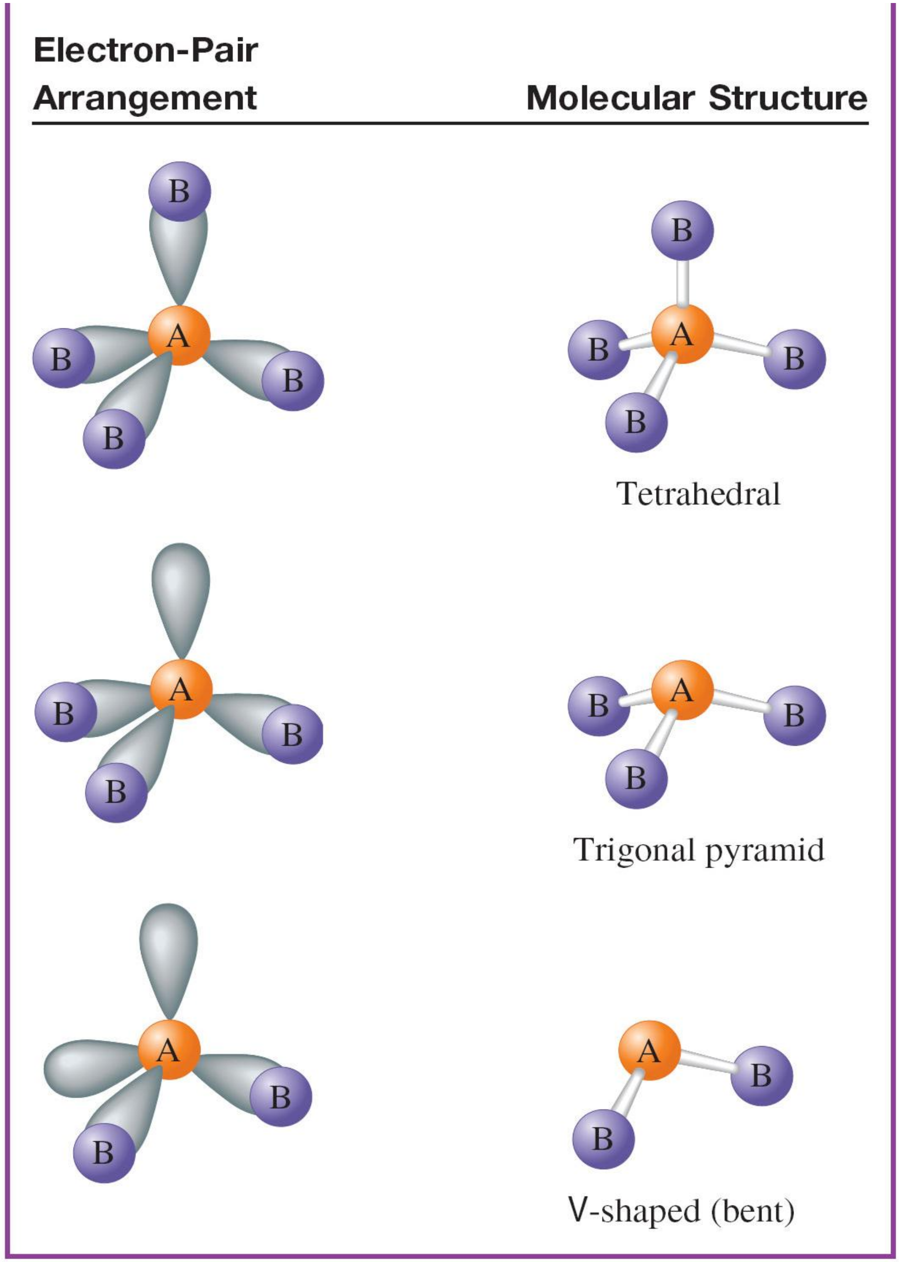
- Lone pair electrons want to be close to the single nucleus and tend to spread out and take up more space.

- Lone pairs require more room than bonding pairs and tend to compress the angles between the bonding pairs.

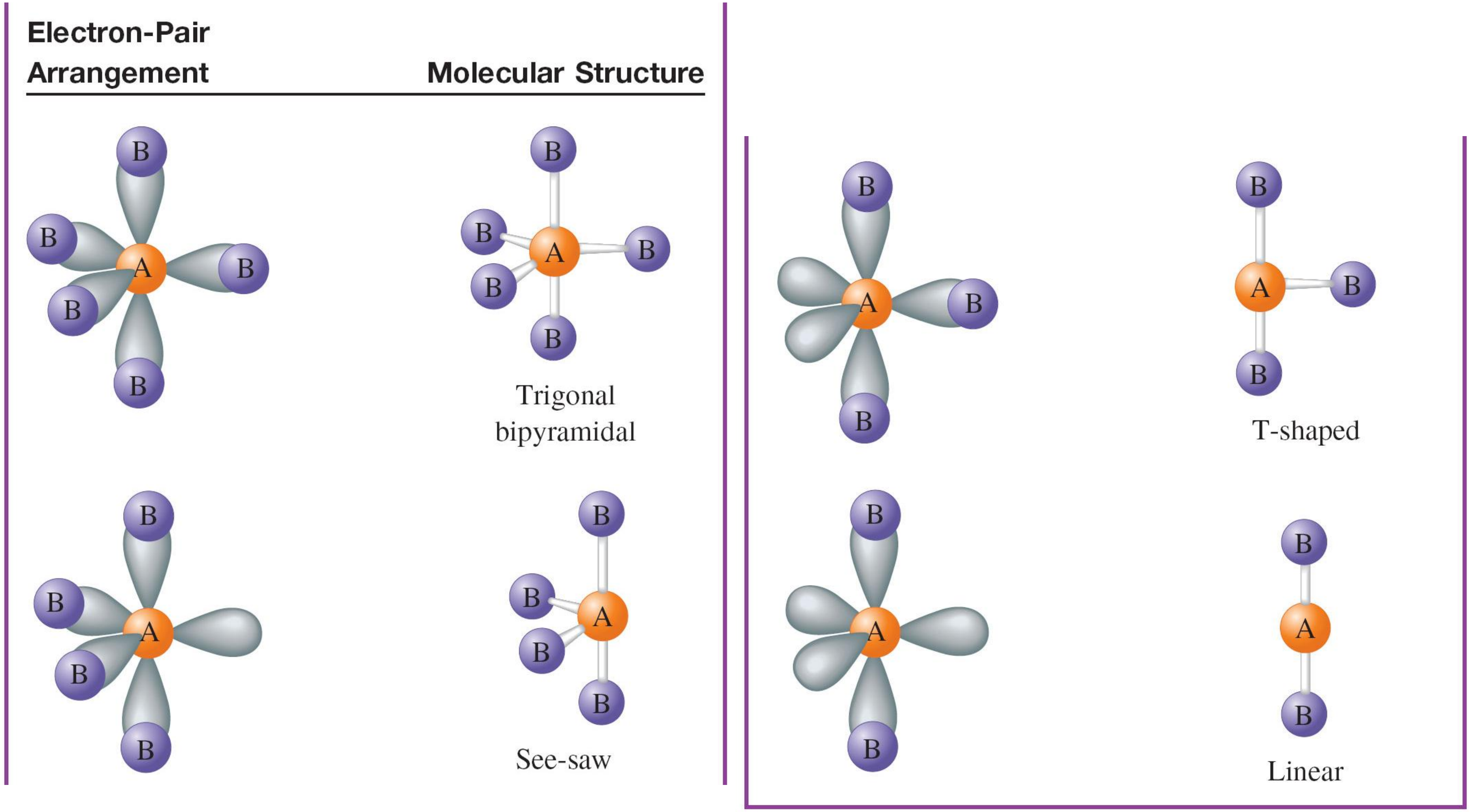


Lone pair electrons

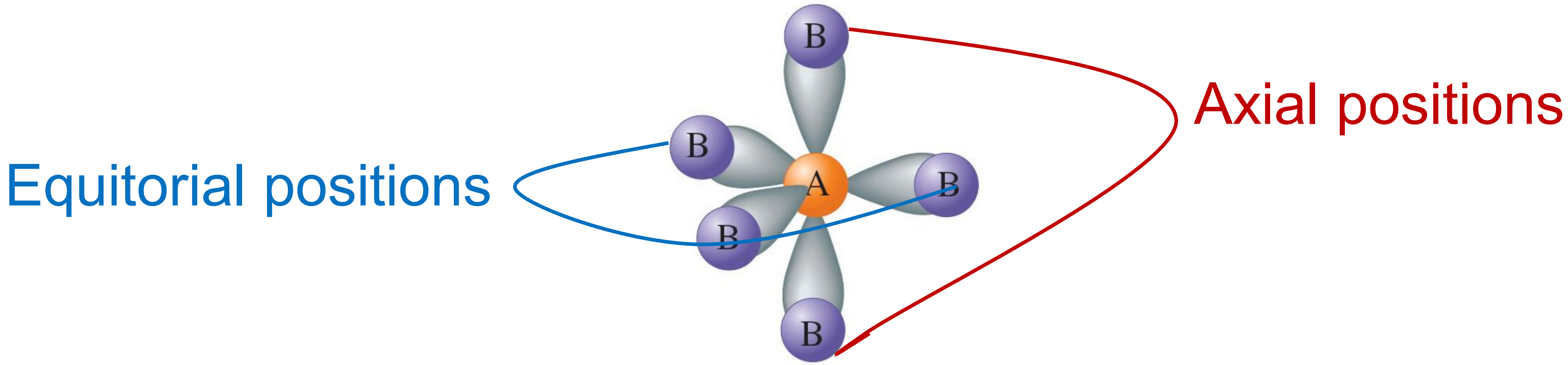
Structures of Molecules That Have Four Electron Pairs Around the Central Atom



Structures of Molecules That Have Five Electron Pairs Around the Central Atom

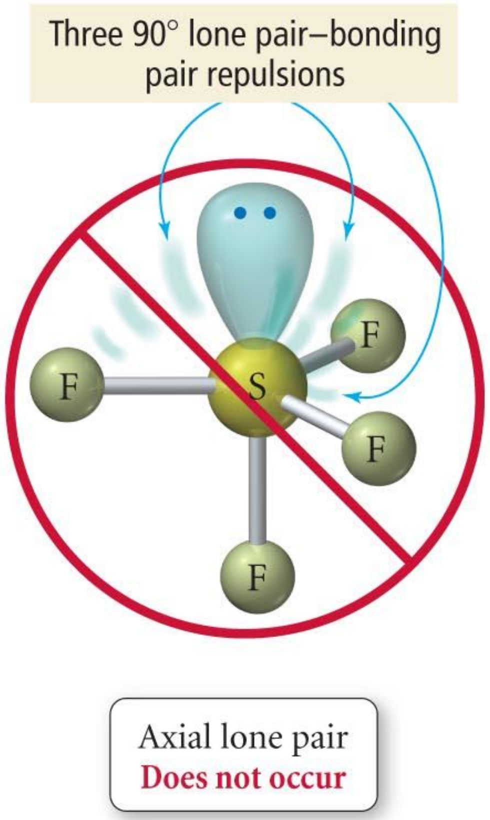


Lone Pair Geometry in Trigonal Bipyramid



- Lone pair electrons will only be found in the equitorial positions in the trigonal bipyramidal geometry.

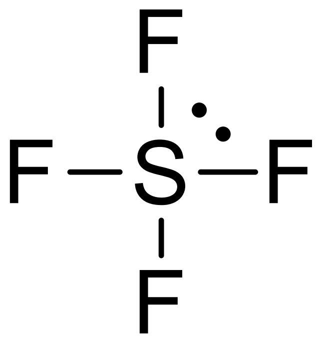
Lone Pair Geometry in Trigonal Bipyramid

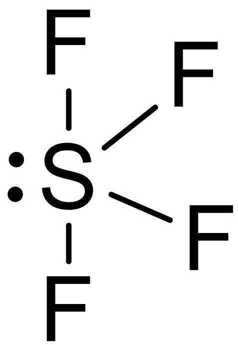


- This geometry results in less 90° interactions with the bonding pairs (and other lone pairs).

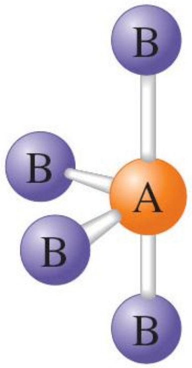
VSEPR Model and Molecular Structure

Predict the molecular shape of SF_4





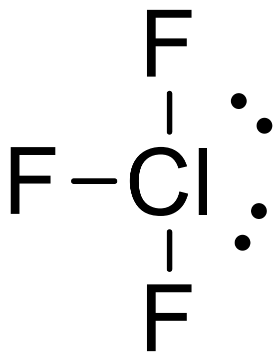
See-saw

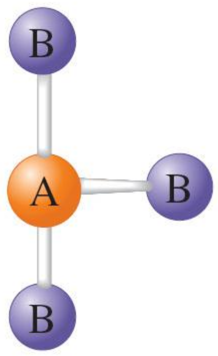


See-saw

VSEPR Model and Molecular Structure

Predict the molecular shape of ClF_3

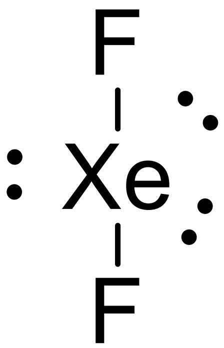




T-shaped

VSEPR Model and Molecular Structure

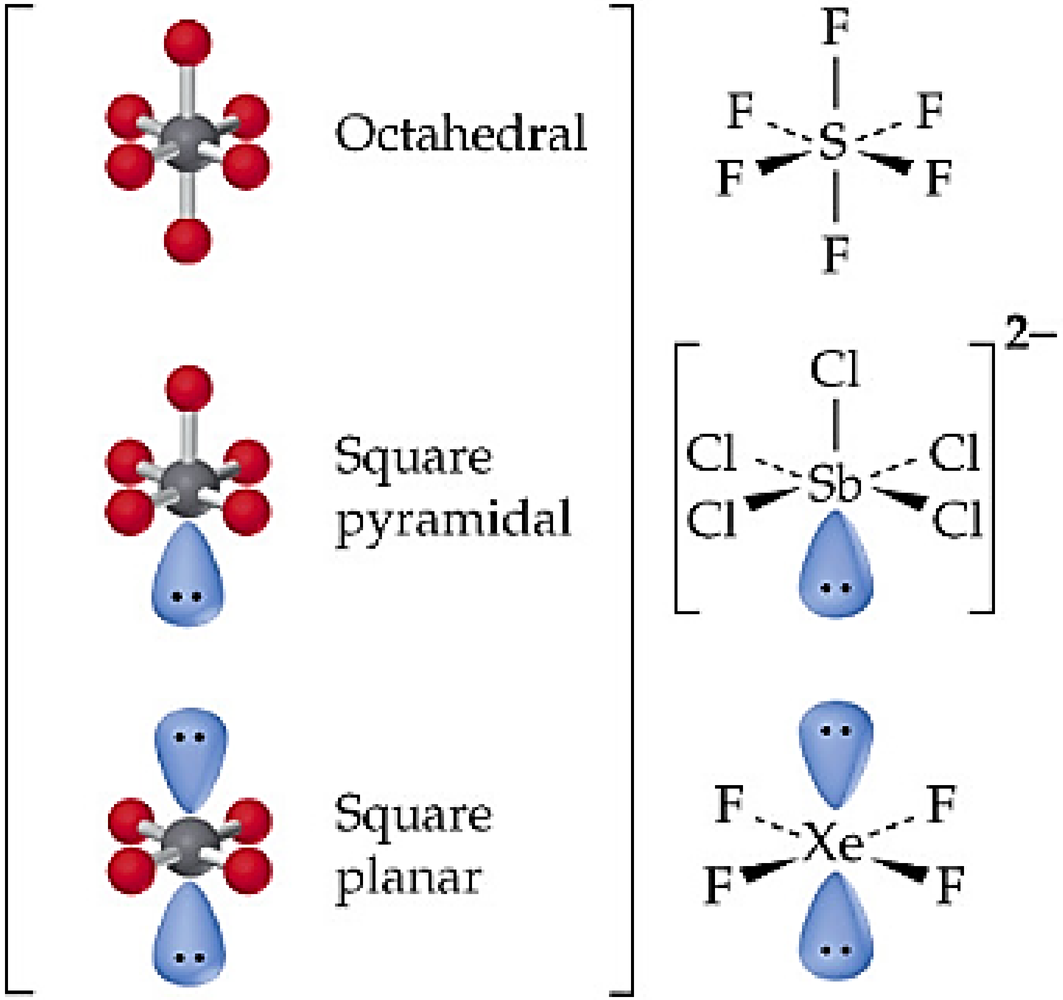
Predict the molecular shape of XeF_2



linear

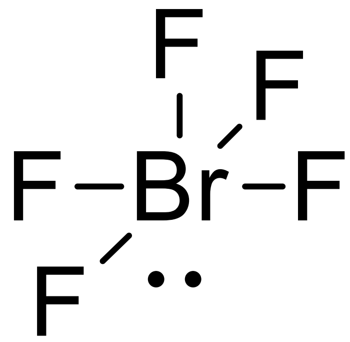
VSEPR Model and Molecular Structure

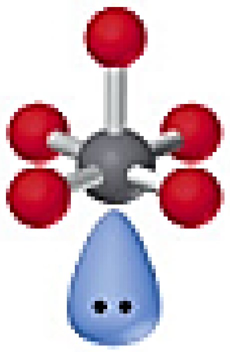
Structures of Molecules That Have Six Electron Pairs Around the Central Atom



VSEPR Model and Molecular Structure

Predict the molecular shape of BrF_5

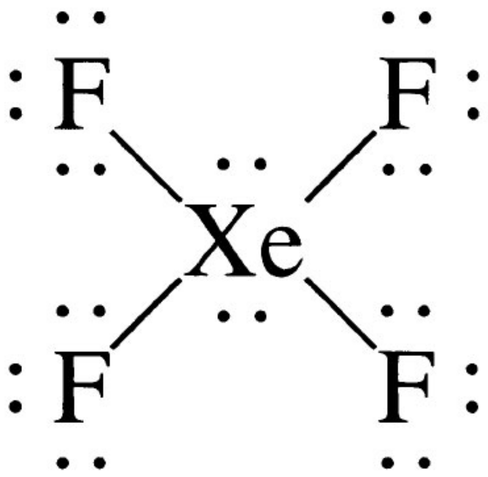




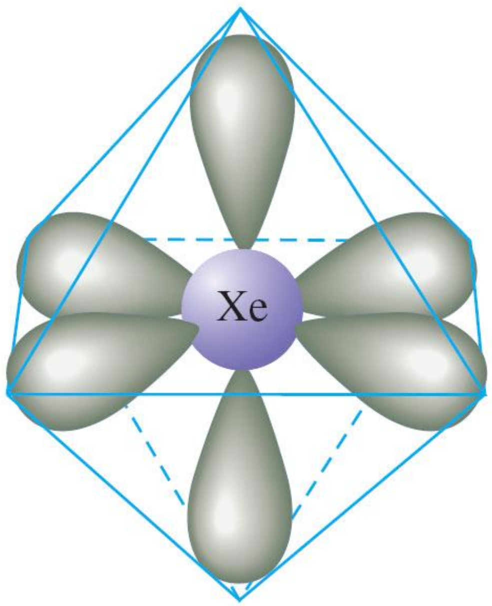
Square pyramidal

VSEPR Model and Molecular Structure

Predict the molecular shape of XeF_4



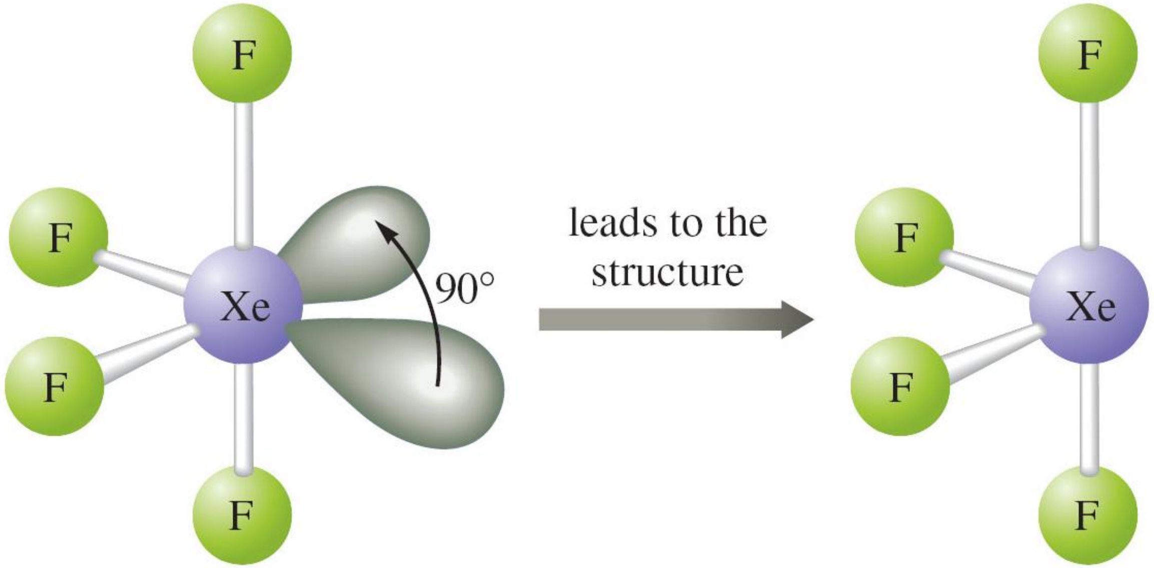
Lewis Structure



Octahedral arrangement

VSEPR Model and Molecular Structure

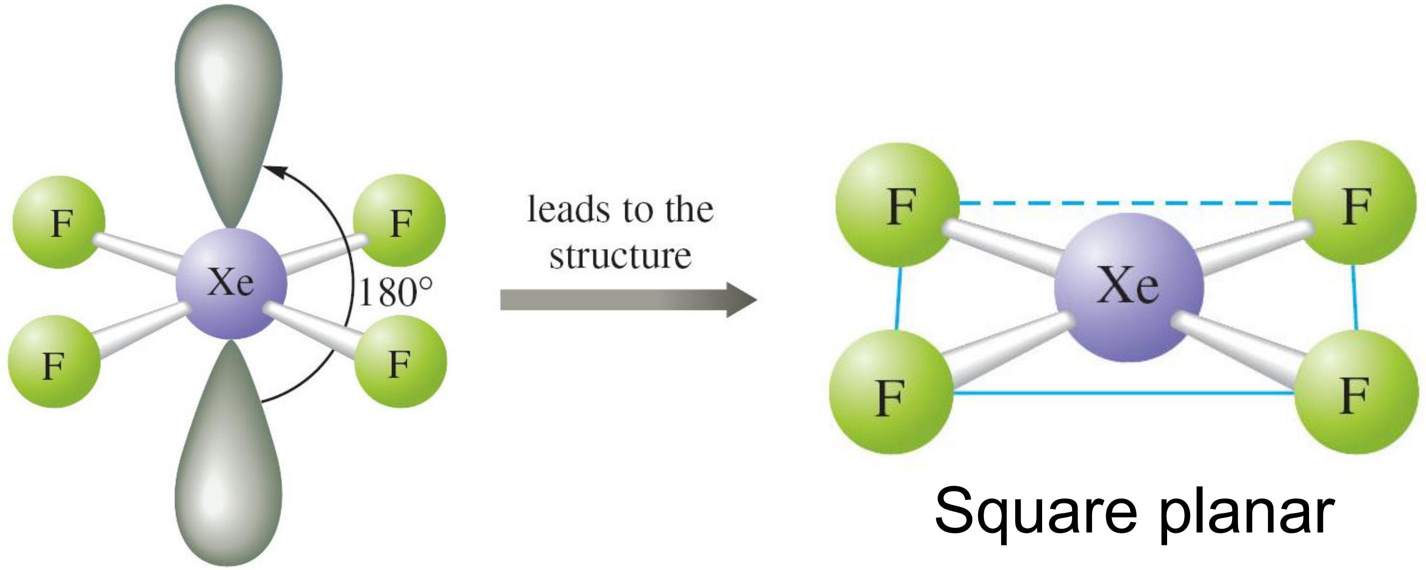
Predict the molecular shape of XeF_4



Lone pair electrons are only separated by 90° so this geometry is high in energy (it's NOT preferred).

VSEPR Model and Molecular Structure

Predict the molecular shape of XeF_4

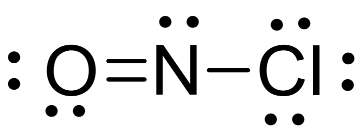


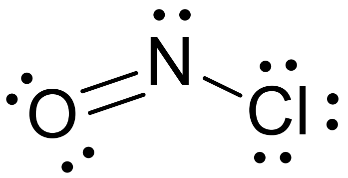
Square planar

XeF_4 has a square planar shape.

VSEPR Model and Molecular Structure

Predict the molecular shape of NOCl

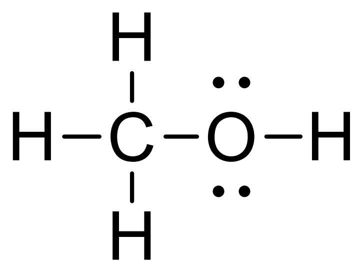




Bent (v-shaped)

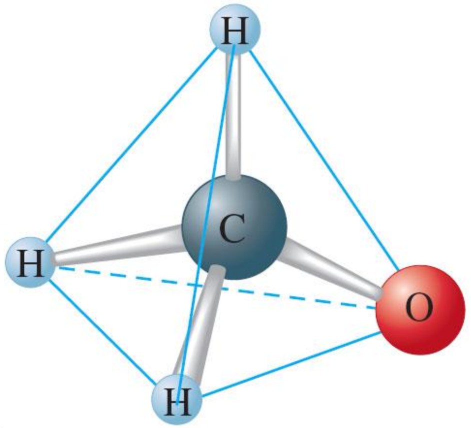
In VSEPR, double (and triple) bonds are counted as one "effective" electron pair for geometry purposes.

Molecules With Multiple Central Atoms



What is the molecular geometry of methanol?

Molecules With Multiple Central Atoms

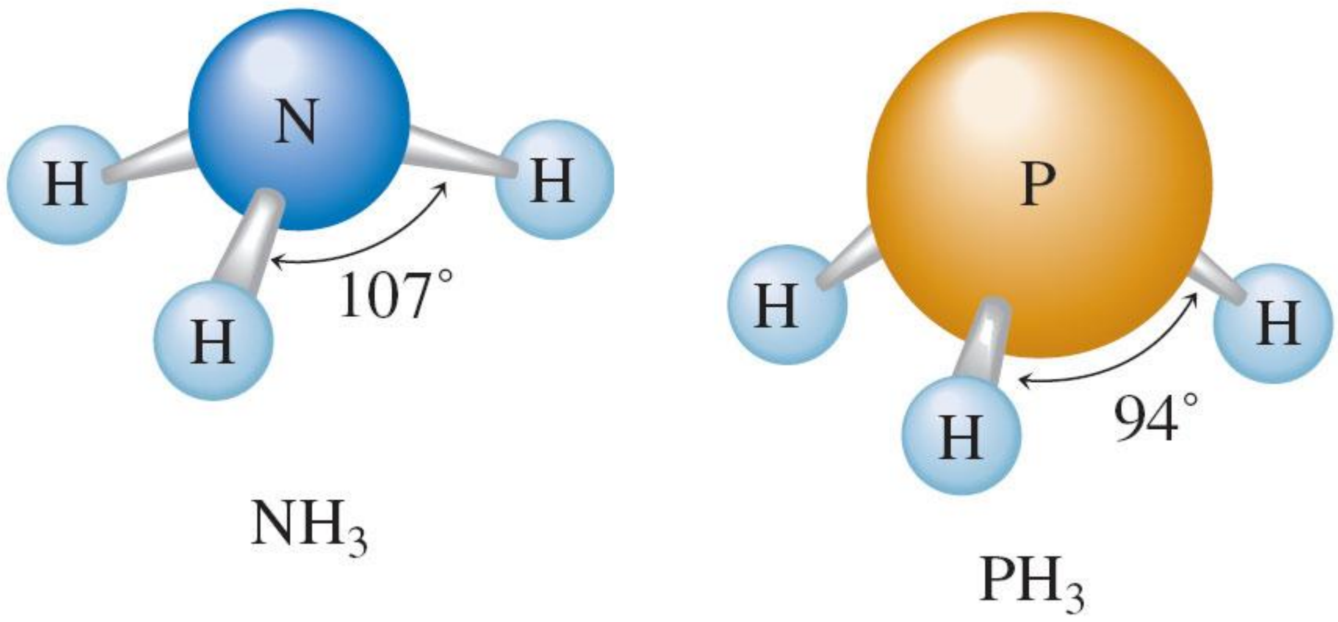


(a)

Tetrahedral
around C

There is a molecular geometry around every central atom!

Limitations to VSEPR Model



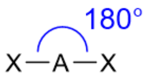
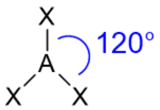
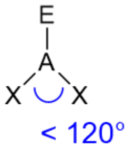
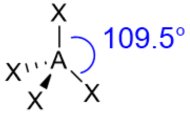
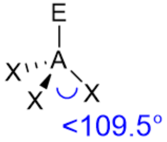
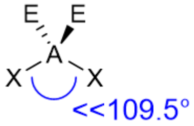
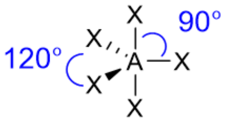
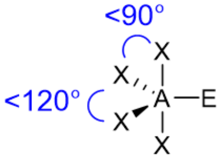
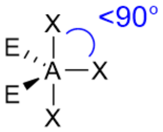
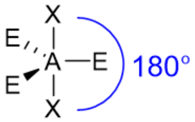
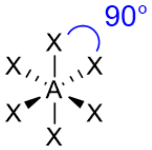
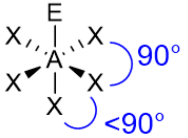
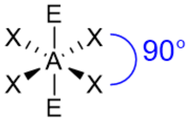
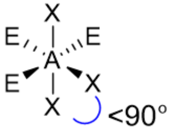
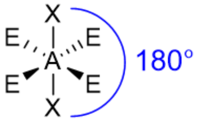
- Ammonia (NH_3) and phosphine (PH_3) have the same Lewis structure. But actual structure is different as PH_3 has reduced bond angles.
- Thus, VSEPR has some limitations and exceptions.

Review

The rules for using the VSEPR model to predict molecular structure:

- Determine the Lewis Structure(s) for the molecule.
- For molecules with resonance structures, use any of the structures to predict the molecular structure.
- Sum the electron pairs around the central atom.
- In counting pairs, count each multiple bond as a single effective pair.
- The arrangement of the pairs is determined by minimizing electron-pair repulsions (Table on slide 16).
- Lone pairs require more space than bonding pairs do. Choose an arrangement that gives the lone pairs as much room as possible.

VSEPR Geometries

Steric Number	Basic Geometry (0 lone pairs)	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal pyramidal	 Bent or Angular		
5	 Trigonal bipyramidal	 Seesaw	 T-Shape	 Linear	
6	 Octahedral	 Square Pyramidal	 Square Planar	 T-Shape	 Linear

- Important terminology:
  - Electron Geometry
  - Molecular Geometry/Shape

Exercise

Determine the shape for each of the following molecules, and include bond angles:

HCN

NO_3^-

SF_4

O_3