

# Lecture B2

## VSEPR Theory

# Covalent Bond Theories

## 1. VSEPR (valence shell electron pair repulsion model).

A set of *empirical* rules for predicting a molecular geometry using, as input, a correct Lewis Dot representation.

## 2. Valence Bond theory.

A more advanced description of orbitals in molecules. We emphasize just one aspect of this theory: Hybrid atomic orbitals.

Works especially well for organic molecules, which is the reason we don't scrap it entirely for MO theory.

## 3. Molecular Orbital theory.

The most modern and powerful theory of bonding. Based upon QM.

# Covalent Bond Theories

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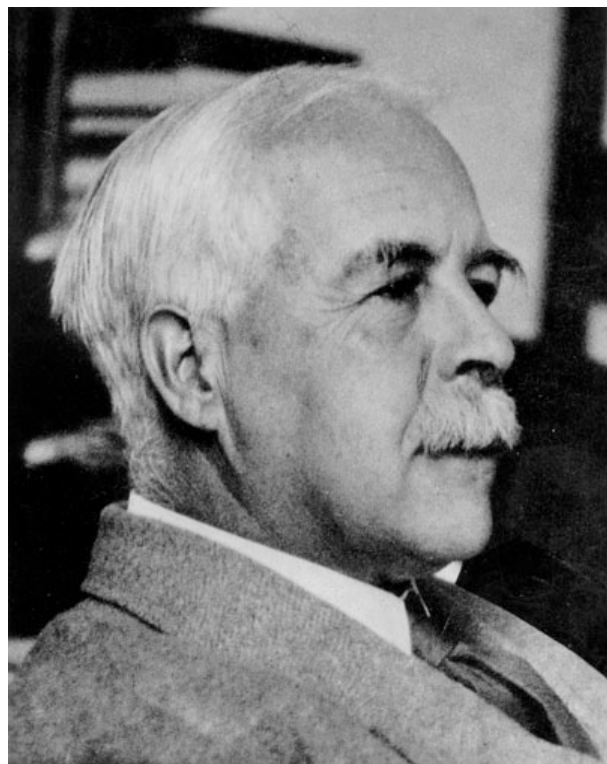
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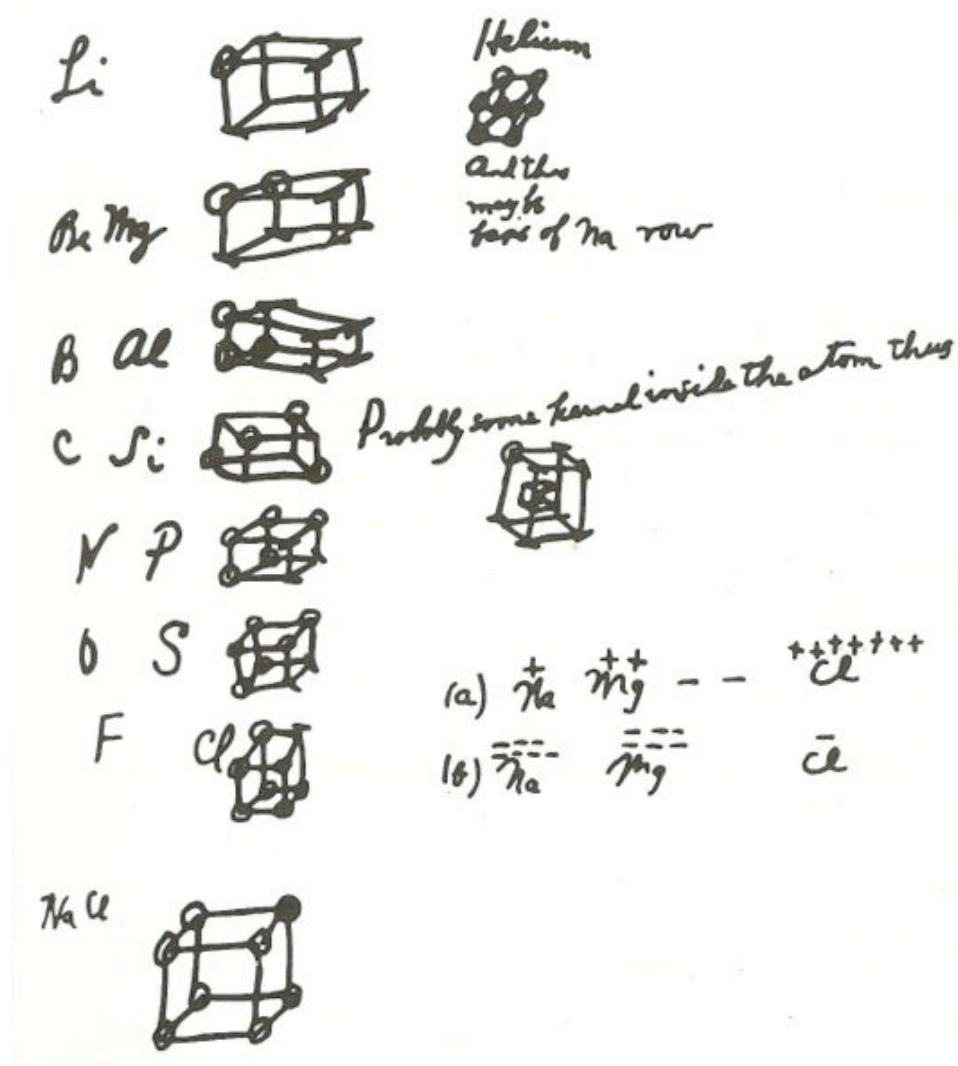
## 3. Molecular Orbital theory.

The most modern and powerful theory of bonding. Based upon QM.

G. N. Lewis tried to develop a geometrical model for atoms and chemical bonding -- but failed.



G. N. Lewis  
1875-1946



Gillespie and Nyholm devised a simple scheme for geometry based on the Lewis dot structure (VSEPR).

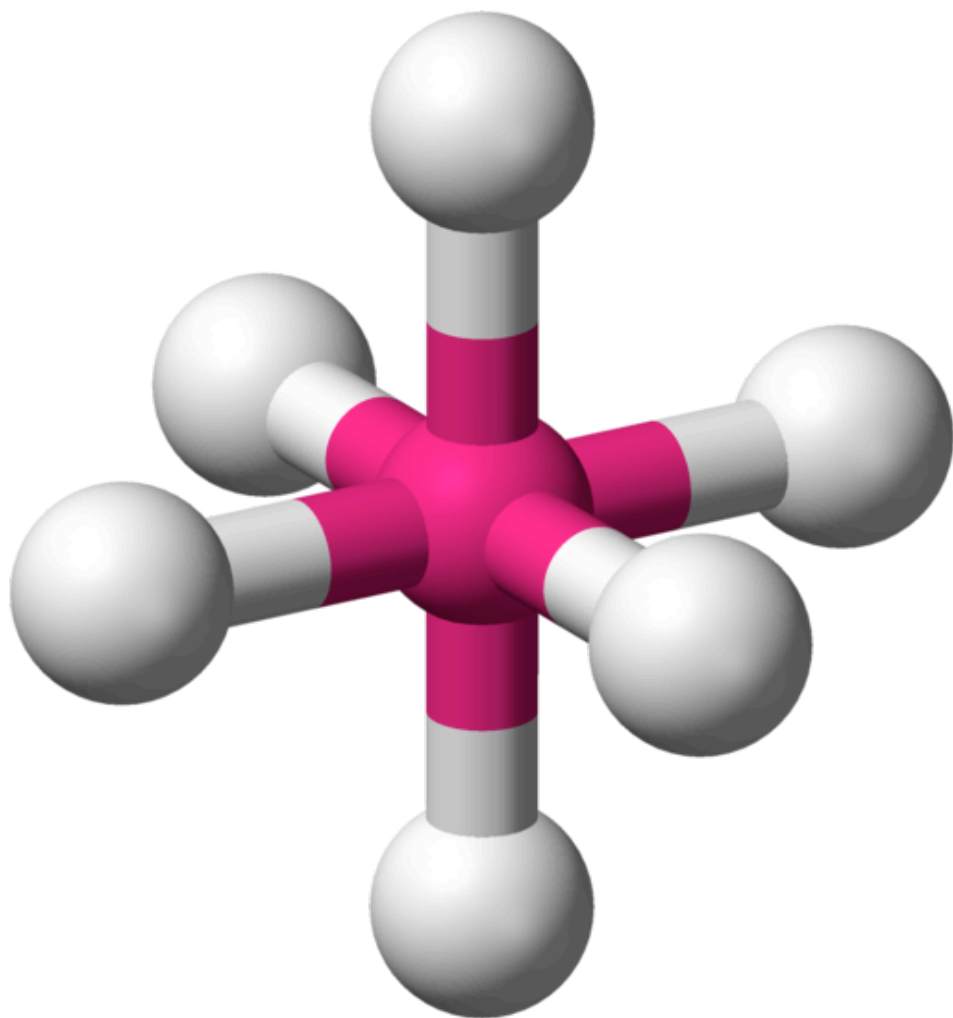
Valence shell electron pair repulsion (VSEPR) theory is a model in chemistry used to predict the shape of individual molecules based upon the extent of electron-pair electrostatic repulsion. It is also named Gillespie-Nyholm\* theory after its two main developers. The acronym "VSEPR" is pronounced "vesper" for ease of pronunciation.



\*Ronald J. Gillespie and Ronald S. Nyholm  
University College, London, 1957.

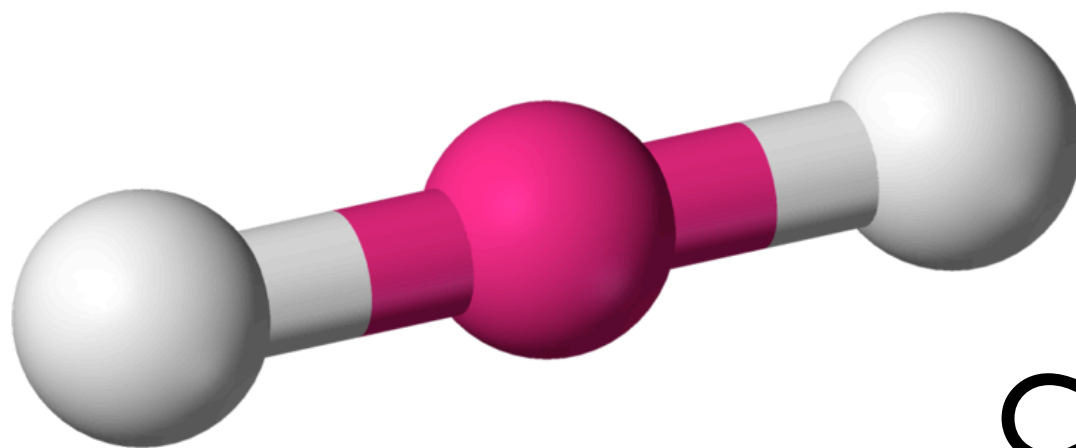
Ronald J. Gillespie  
1924 -

# Living in 3 Dimensions

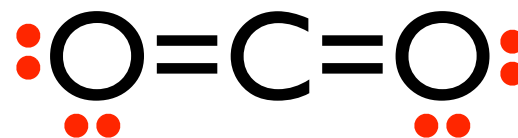


What role does  
geometry play  
in chemical  
structure?

Gillespie and Nyholm looked at the structures of molecules of the form  $AX_n$ :



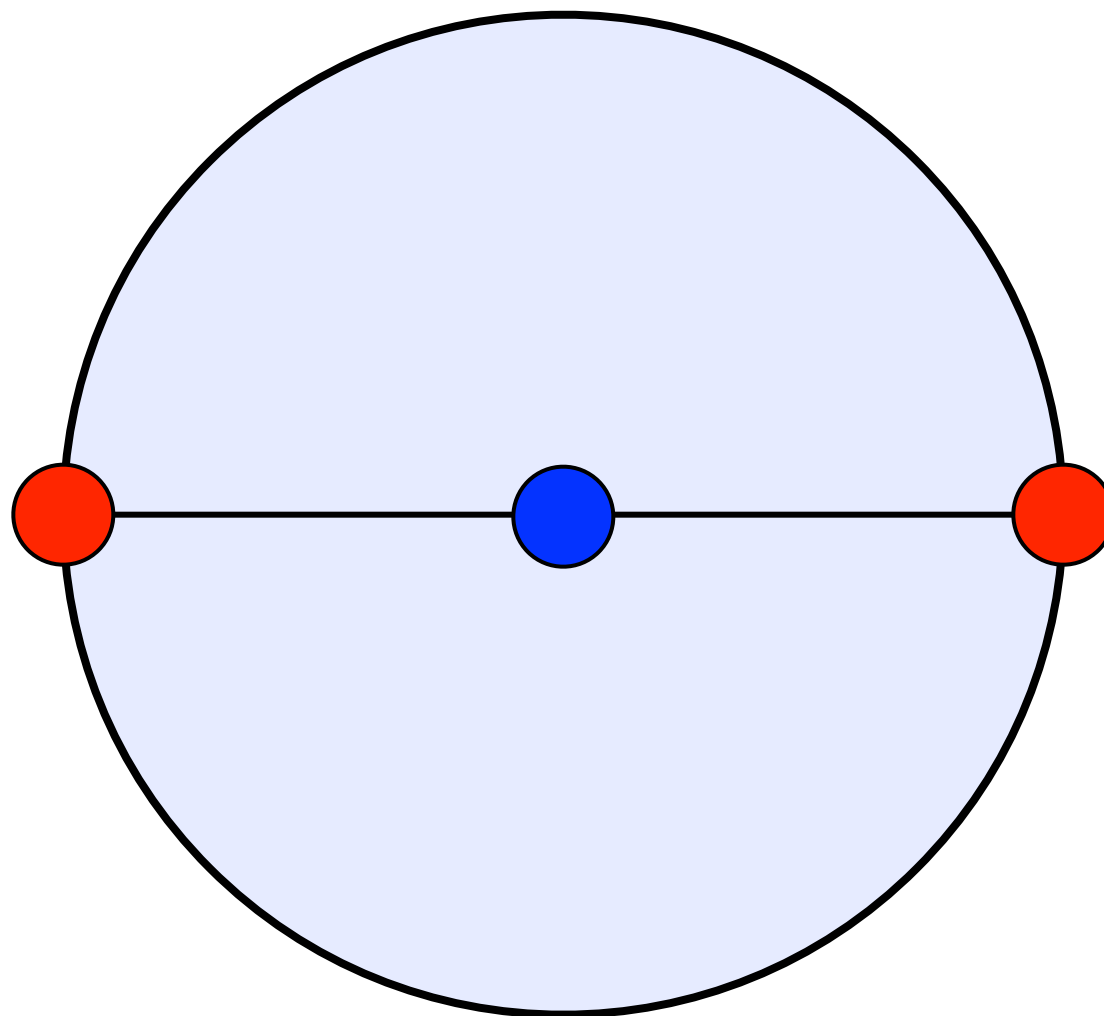
16 electrons



O-C-O angle:  $180^\circ$

Linear Geometry

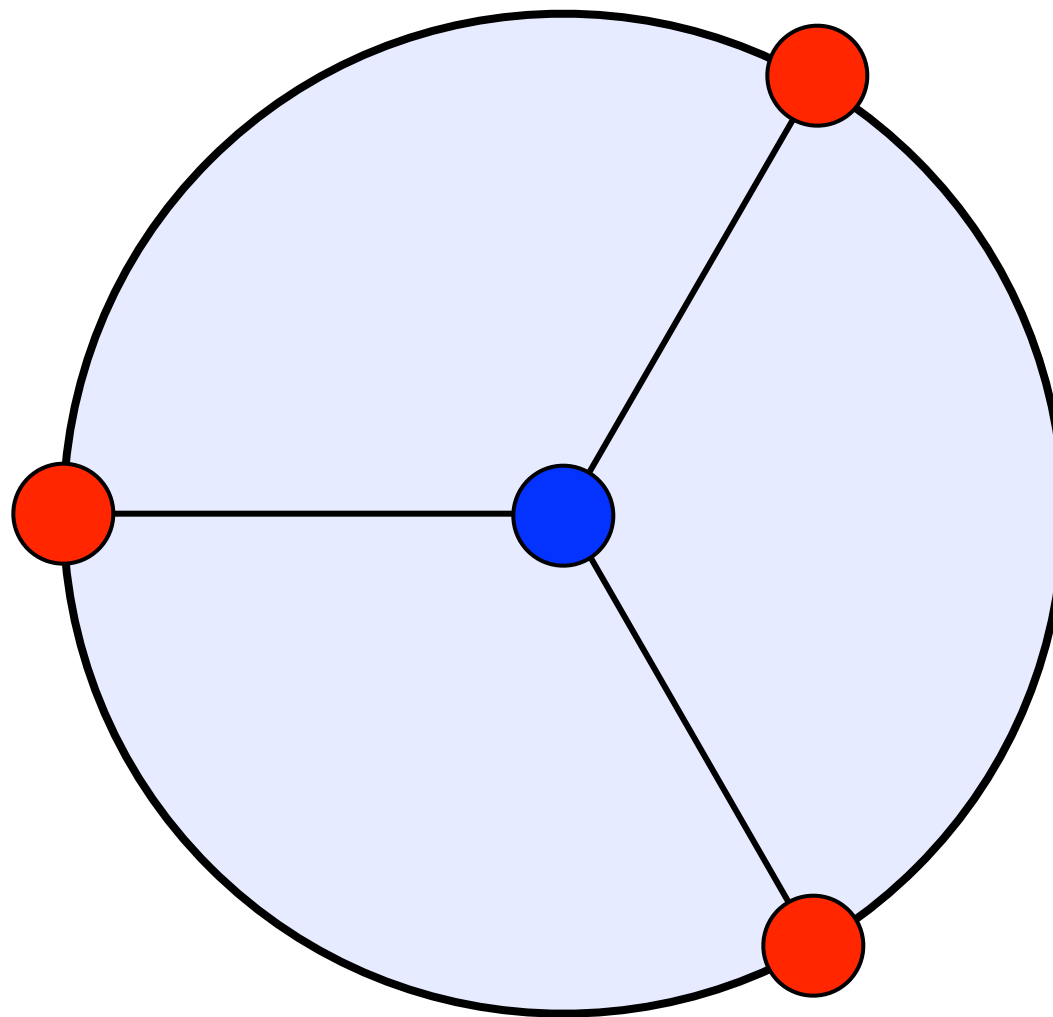
$AX_2$



X-A-X angle:  $180^\circ$

Linear Geometry





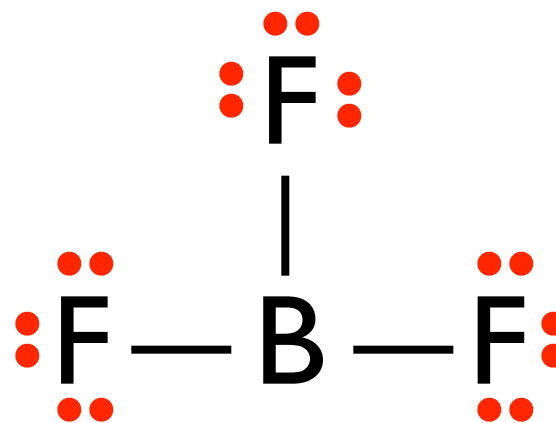
$AX_3$

X-A-X angle:  $120^\circ$

Trigonal Geometry

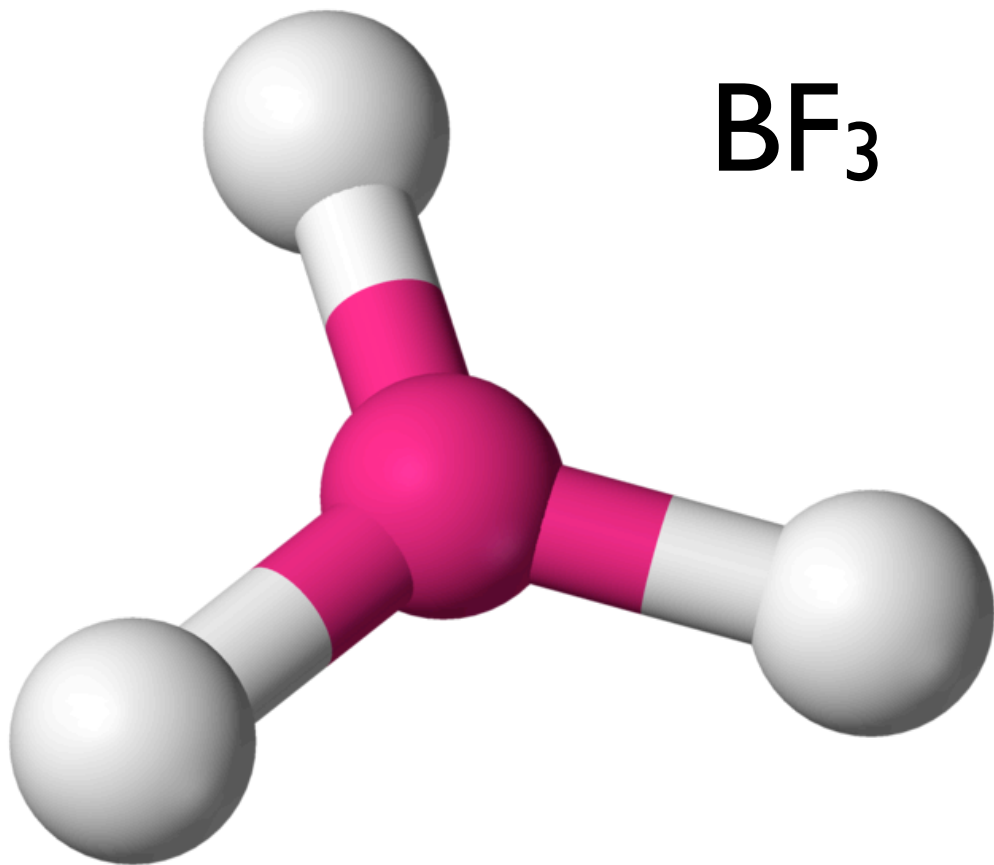


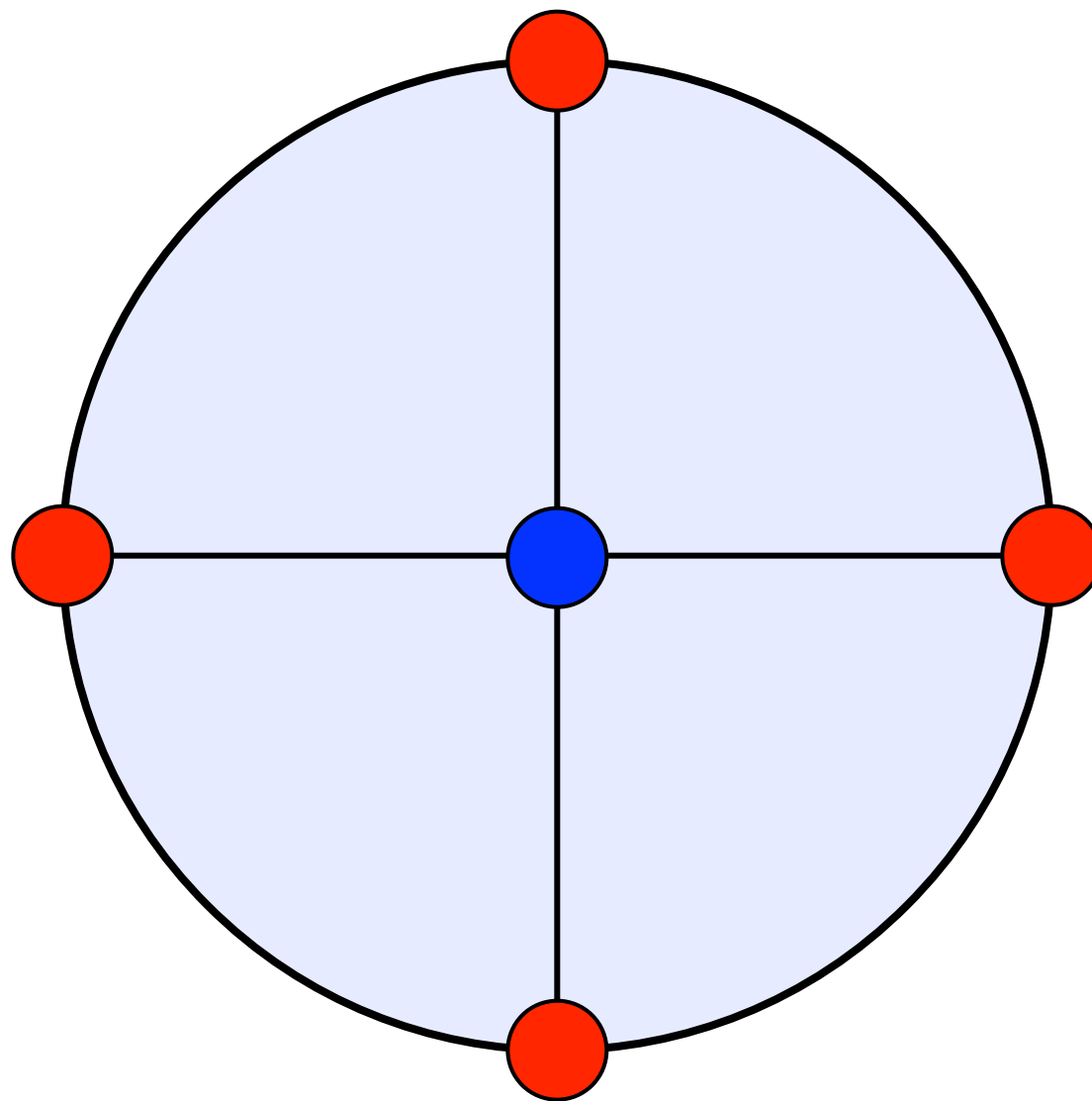
24 electrons



F-B-F angle:  $120^\circ$

Trigonal Planar Geometry

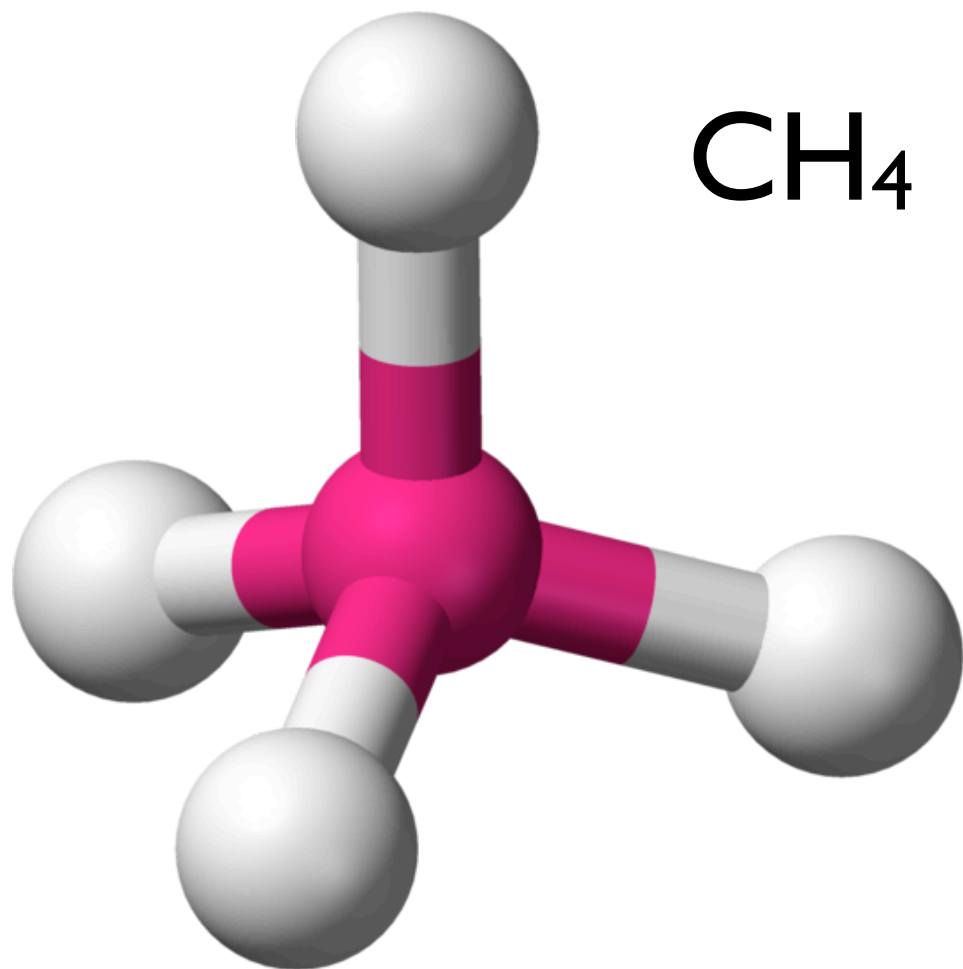




$AX_4$

X-A-X angle:  $90^\circ$

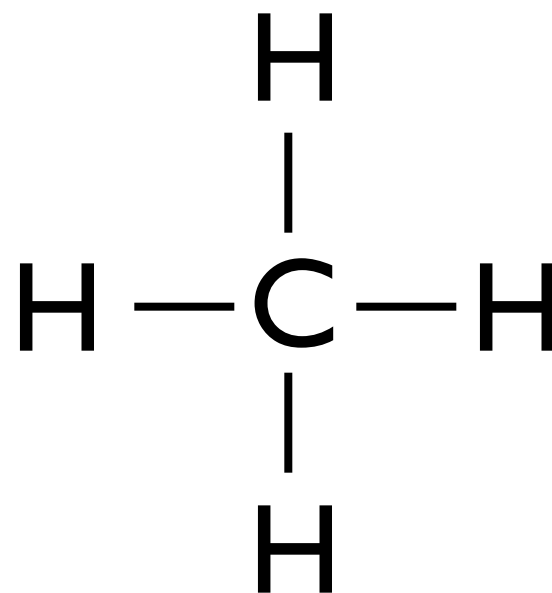
Square Planar Geometry?



$\text{CH}_4$

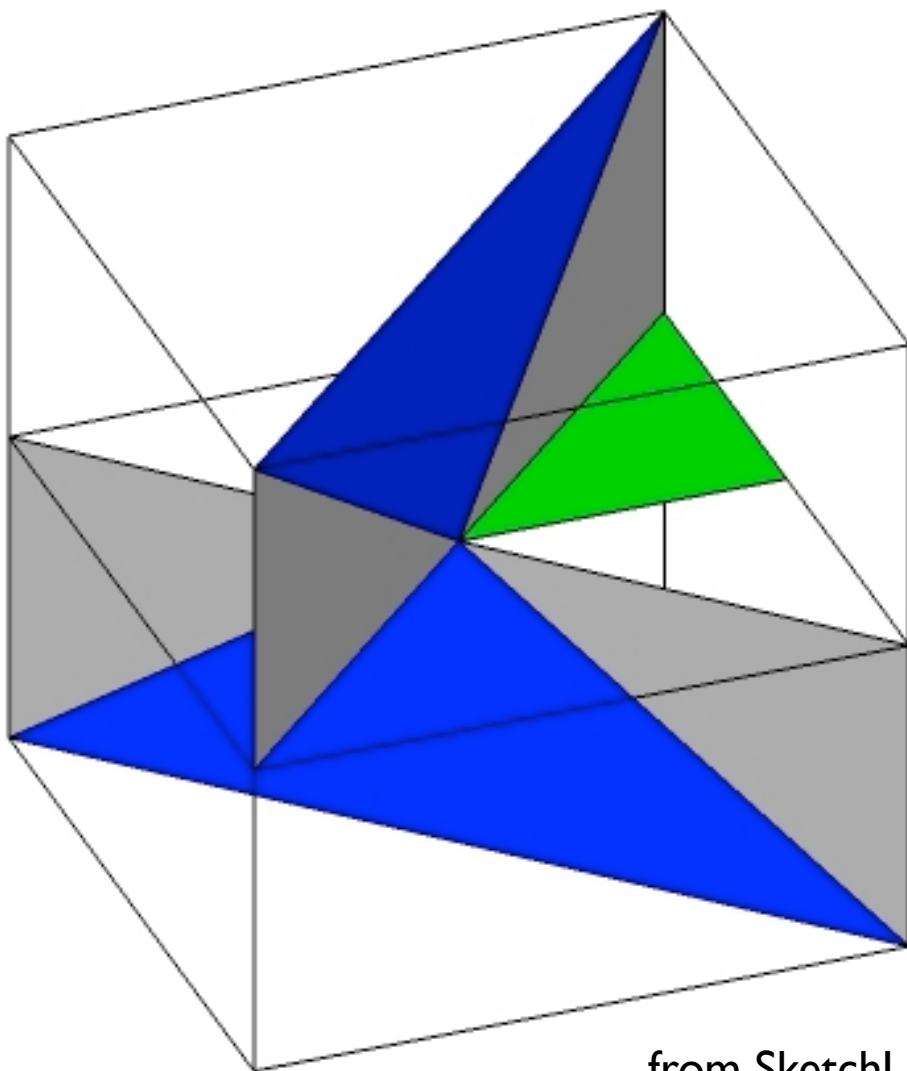
$\text{AX}_4$

8 electrons



H-C-H angle: ?

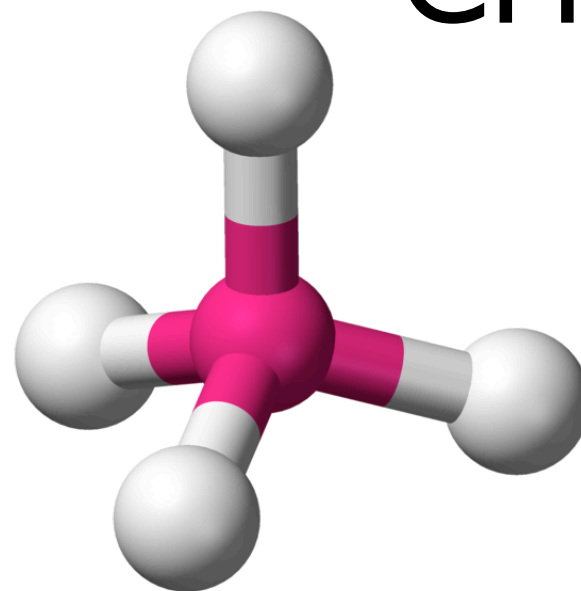
Tetrahedral Geometry



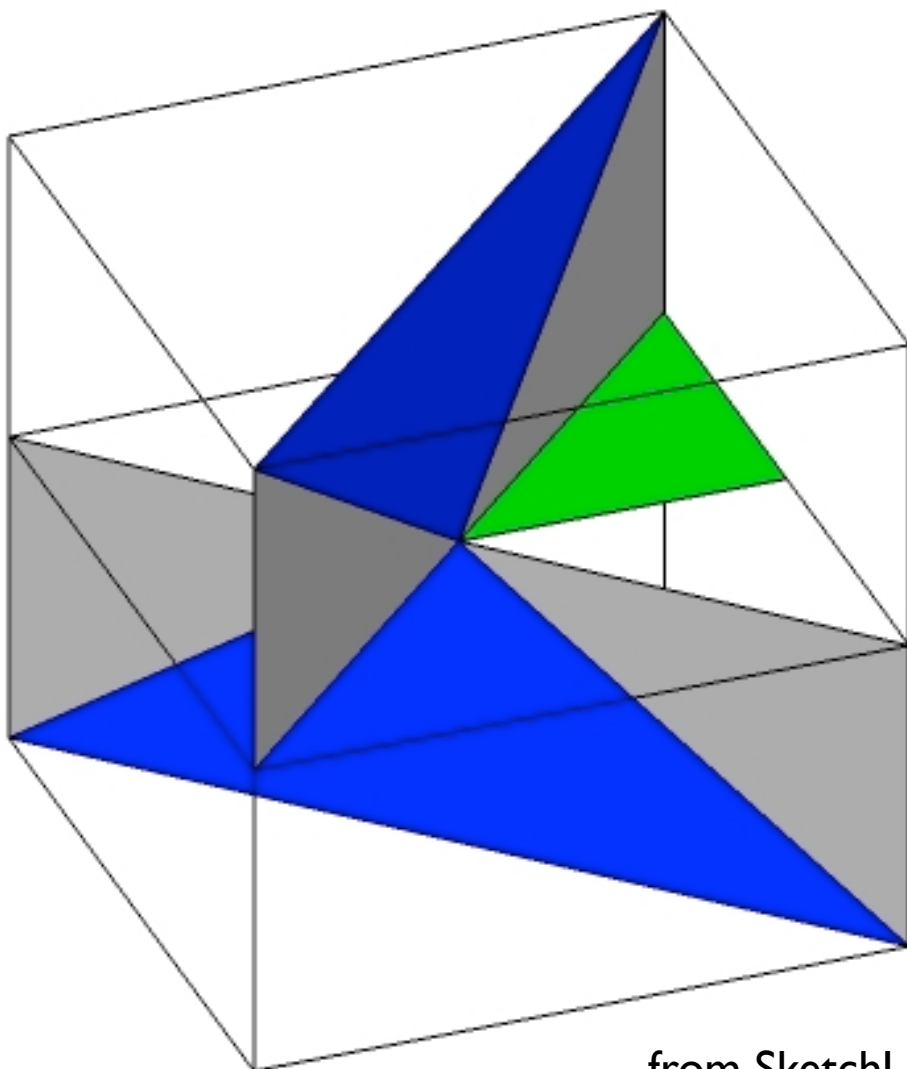
H-C-H angle: **109.47°**

$AX_4$

$CH_4$



Tetrahedral Geometry



$AX_4$

Green Triangle:

$$1 + 1 = 2$$

$$\text{Hypotenuse} = \sqrt{2}$$

Gray Triangle:

$$2 + 1 = 3$$

$$\text{Hypotenuse} = \sqrt{3}$$

$$\text{Grey Angle} = \cos^{-1}(\sqrt{2}/\sqrt{3})$$

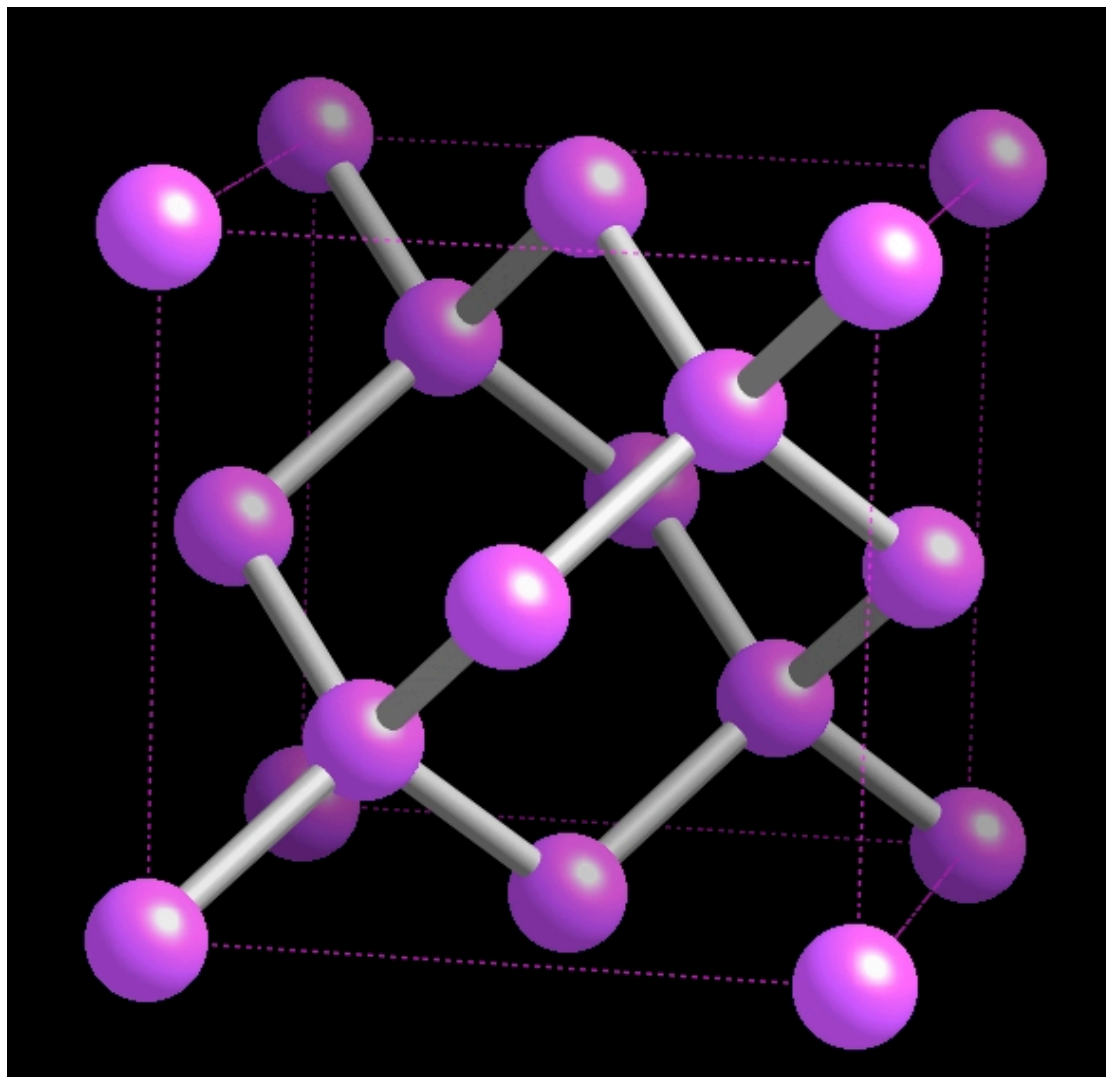
Blue Triangle:

$$\text{Blue Angle} = 180 - 2 \times \text{GA}$$

H-C-H angle:  $109.47^\circ$

Tetrahedral Geometry

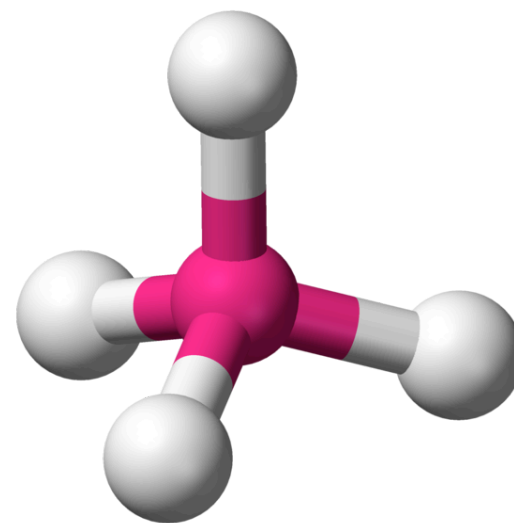
# VSEPR in Solids: Diamond Structure



From CrystalMaker

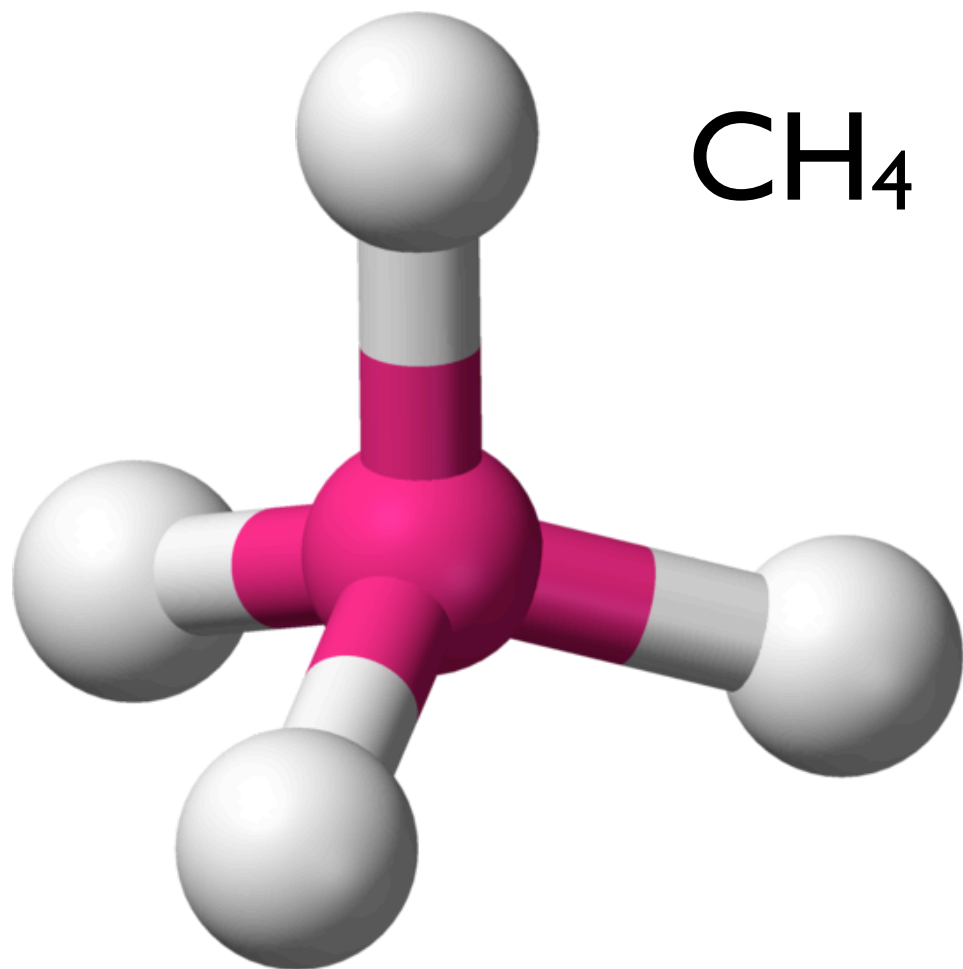
Diamond

Also ZnS



C-C-C angle: **109.47°**

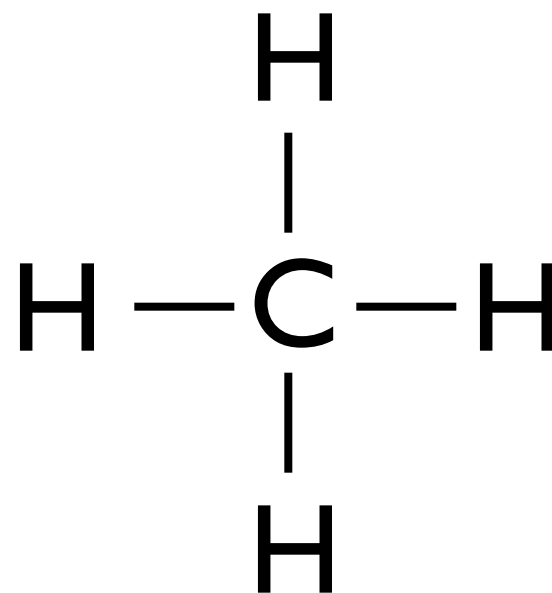
Tetrahedral Site Symmetry



H-C-H angle:  $109.47^\circ$

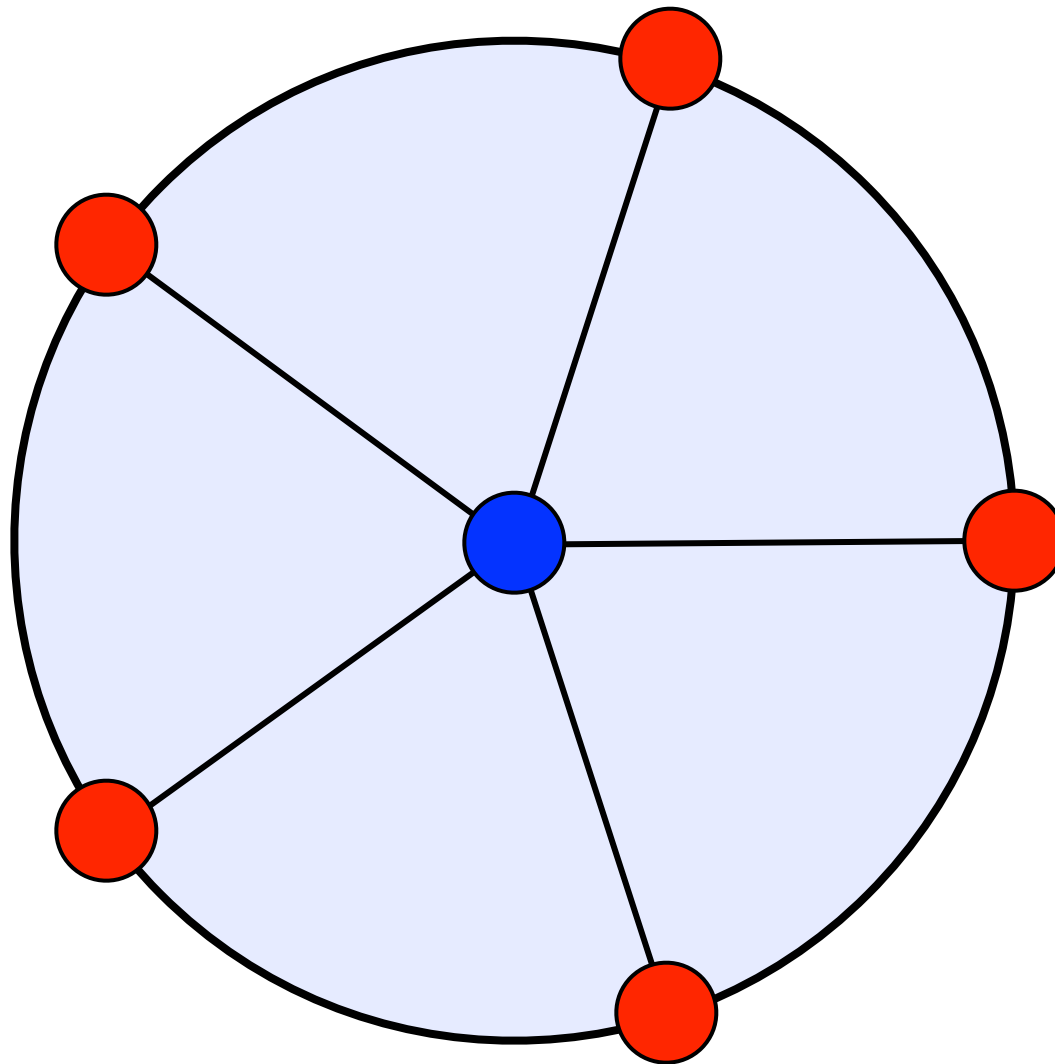
$\text{AX}_4$

8 electrons



Tetrahedral Geometry

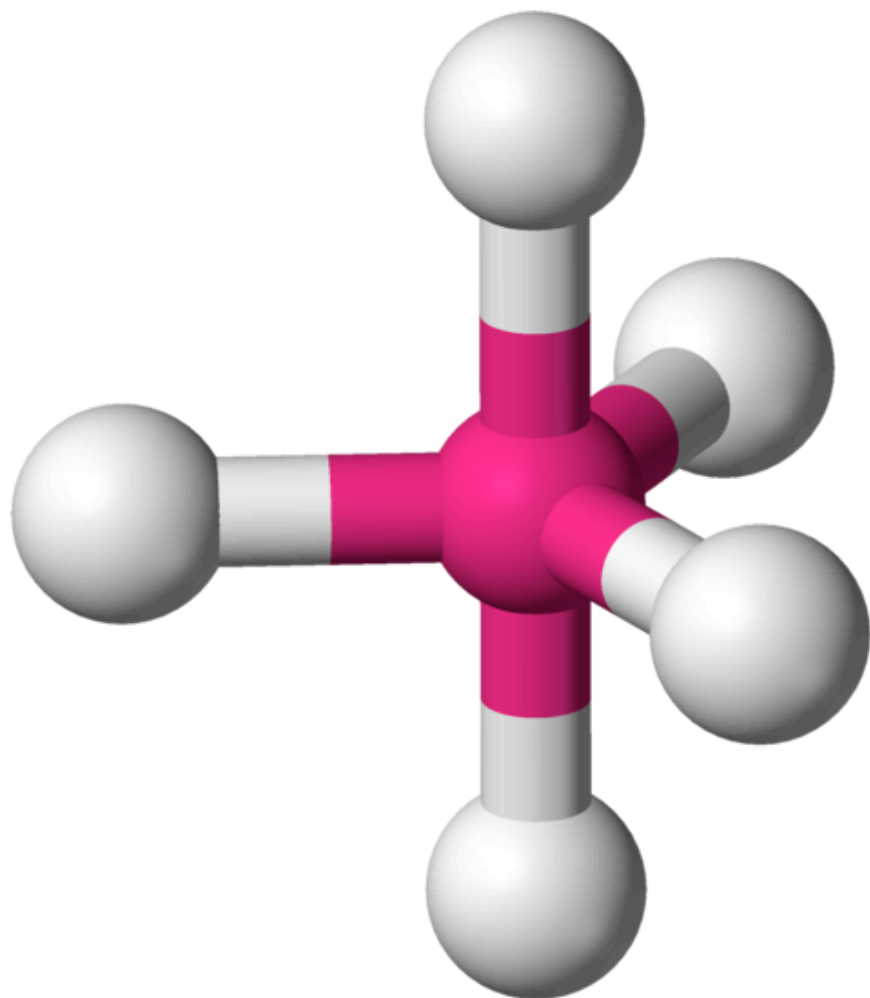




$AX_5$

X-A-X angle:  $72^\circ$

Pentagonal Planar Geometry?



$AX_5$

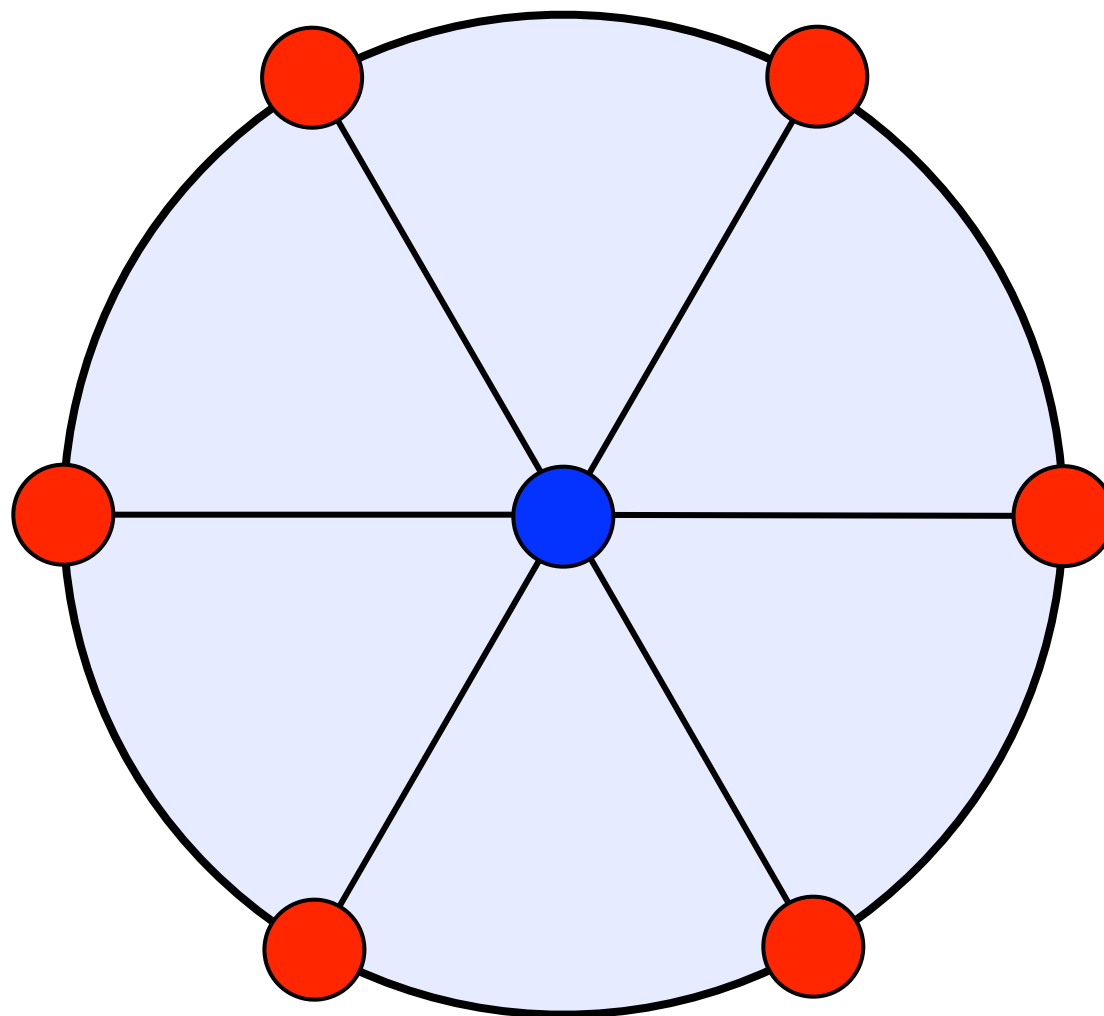
$PCl_5$

40 electrons

Cl-P-Cl angles:  $90, 120^\circ$

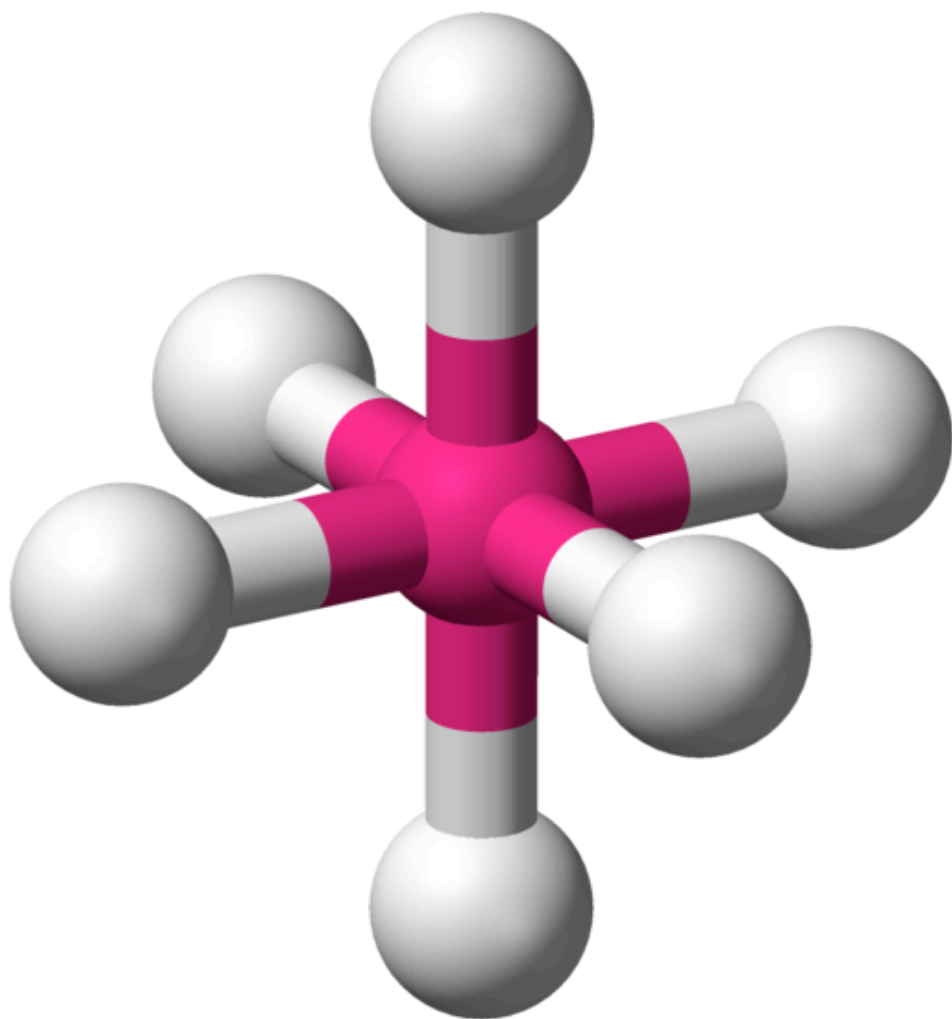
Trigonal Bipyramidal  
Geometry

$AX_6$



X-A-X angle:  $60^\circ$

Hexagonal Geometry?



$AX_6$

$SF_6$

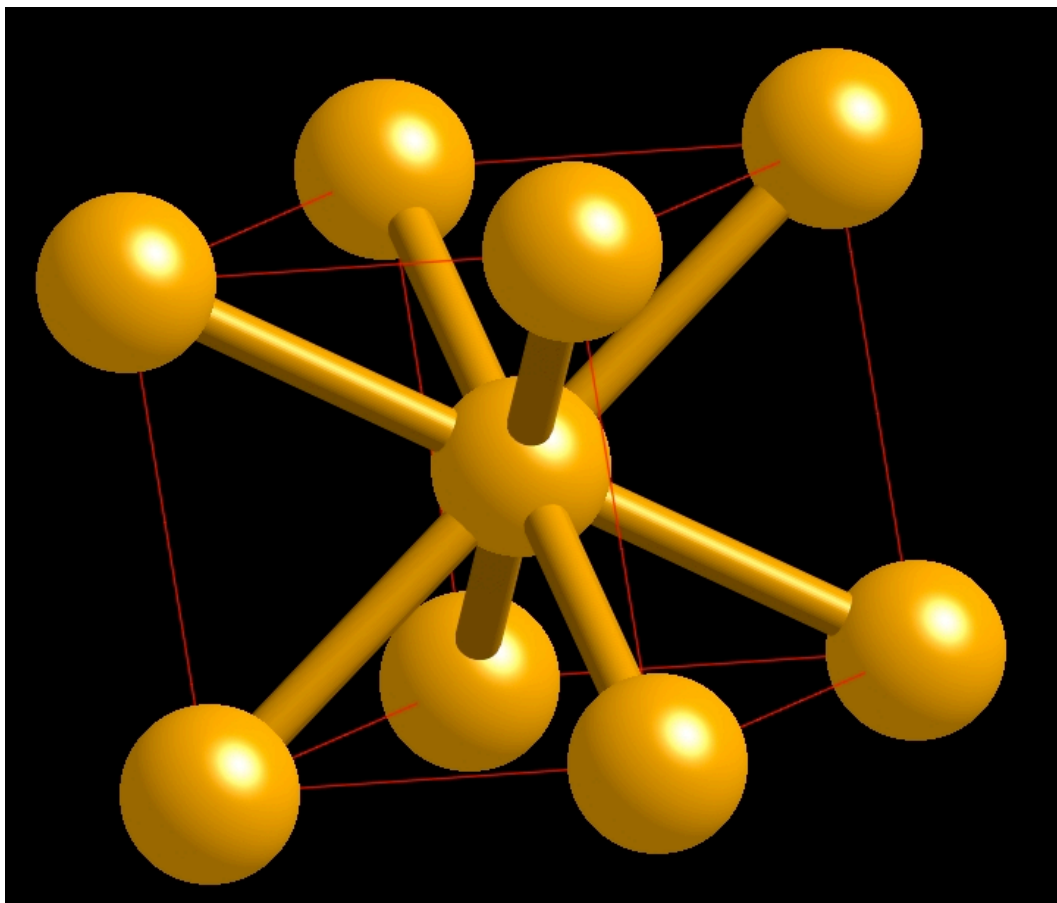
48 electrons

F-S-F angle:  $90^\circ$

Octahedral Geometry

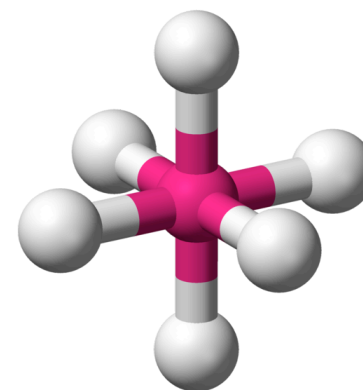
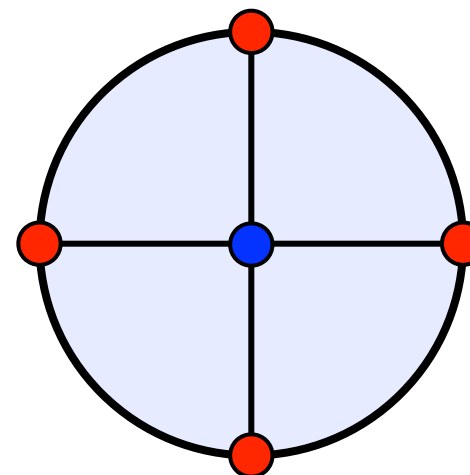
# VSEPR in Solids: Body Centered Cubic Structure

$AX_6$



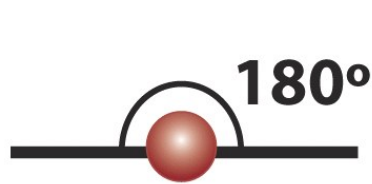
From CrystalMaker

C-C-C angle:  $90^\circ$

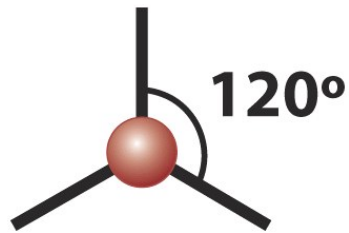


Octahedral Site Symmetry

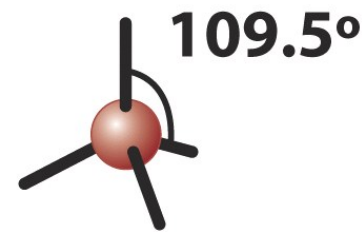
Gillespie and Nyholm realized that the covalent bonds were arranged so as to minimize overlap:



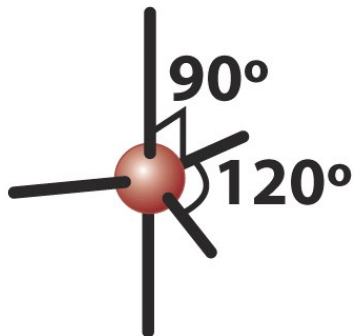
**Linear**



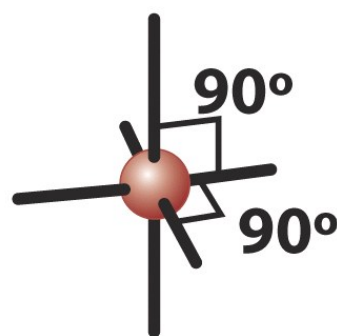
**Trigonal planar**



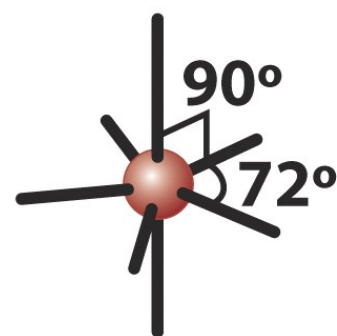
**Tetrahedral**



**Trigonal  
bipyramidal**

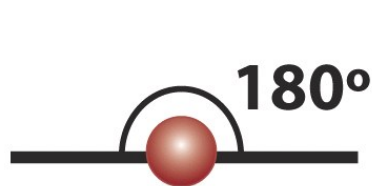


**Octahedral**

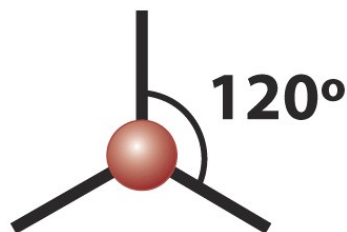


**Pentagonal  
bipyramidal**

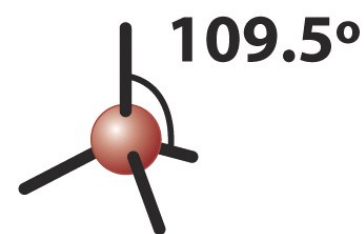
They also realized that **non-bonding electron pairs** on the central atom **ALSO** needed to be included, and actually required **MORE** relief from overlap.



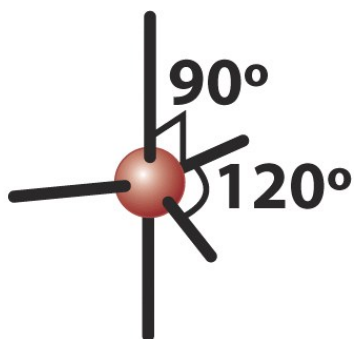
**Linear**



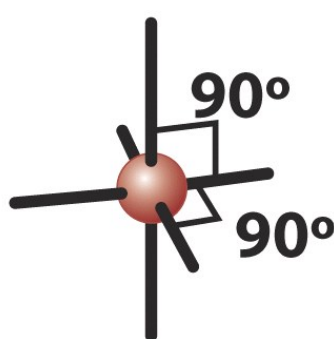
**Trigonal planar**



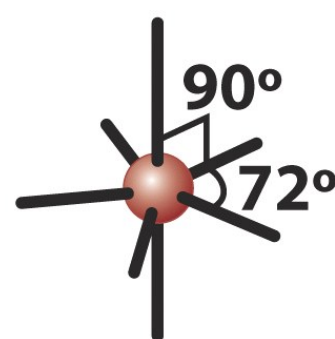
**Tetrahedral**



**Trigonal  
bipyramidal**

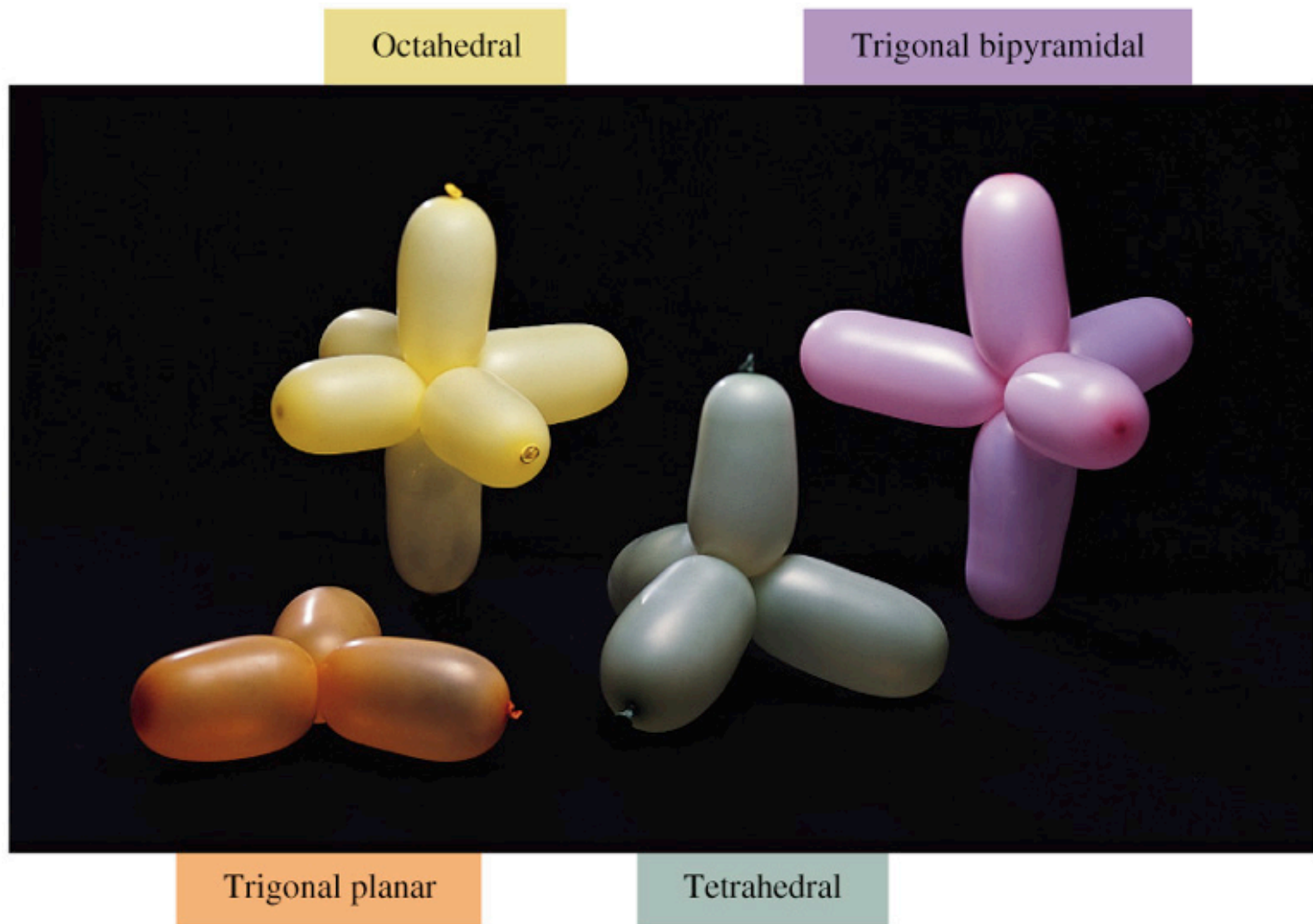


**Octahedral**



**Pentagonal  
bipyramidal**

Thus, the electron pairs around each atom in a molecule tend to be arranged to minimize repulsion - *it doesn't matter whether these electron pairs are in bonds, or are non-bonding lone pairs.*





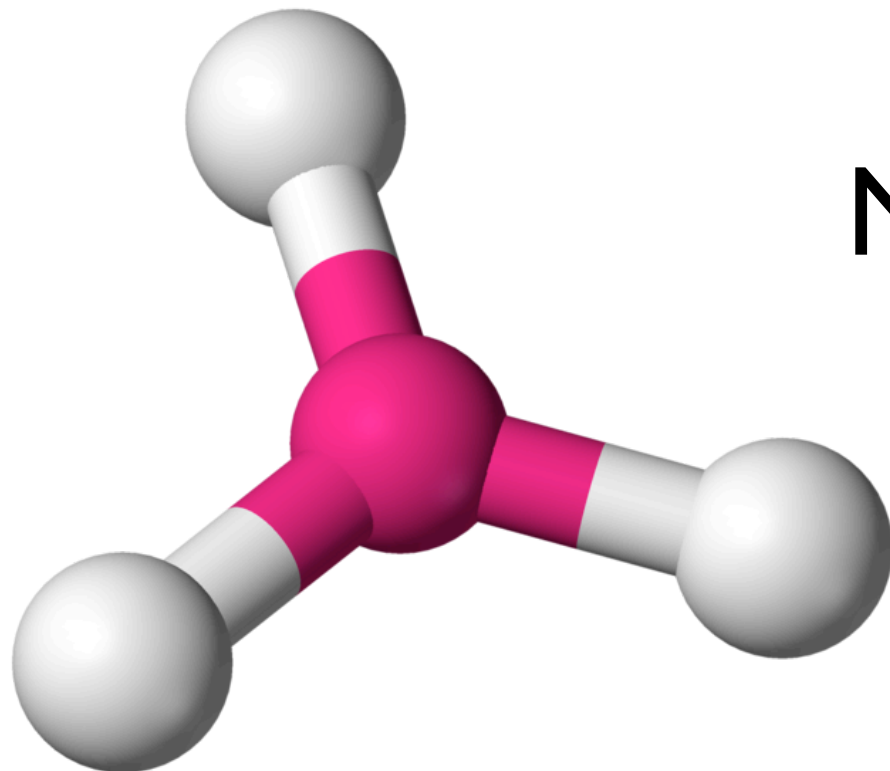
For example:



$$s = 3$$

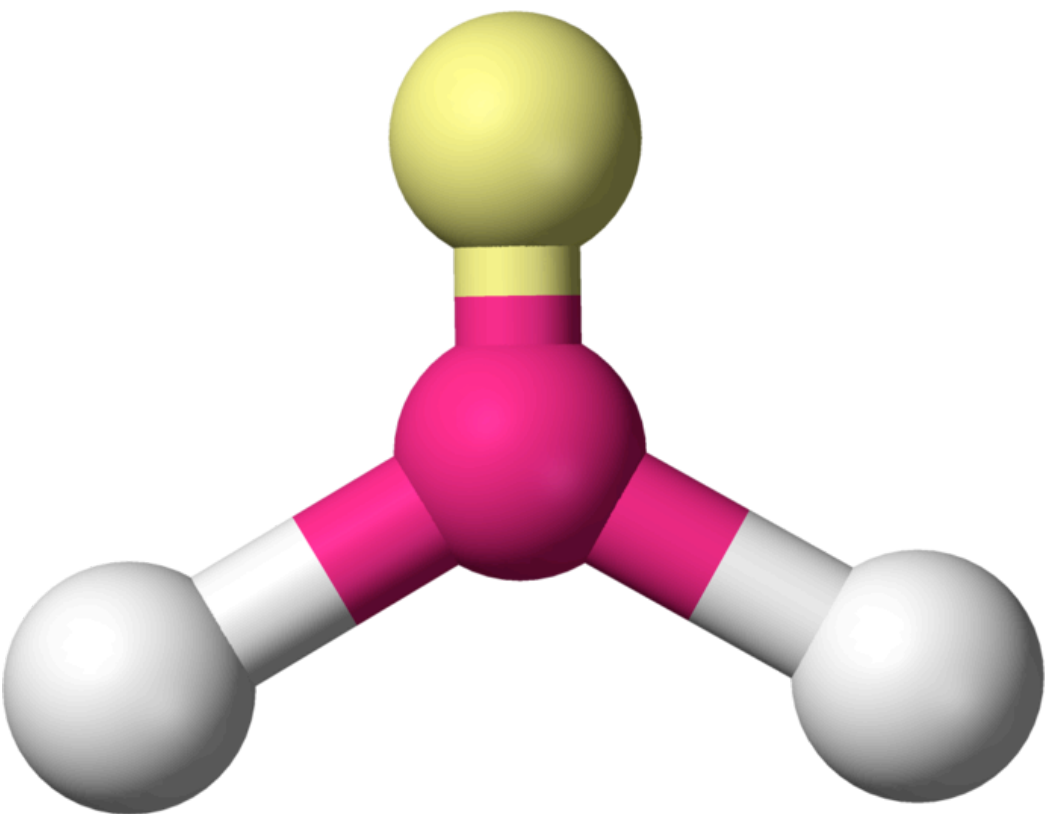
$$n = 3$$

$$m = 0$$

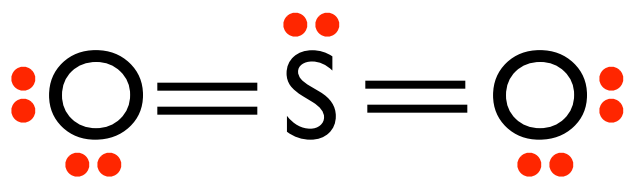


$s$  is the total number of bonds ( $n$ ) and lone pairs ( $m$ ).

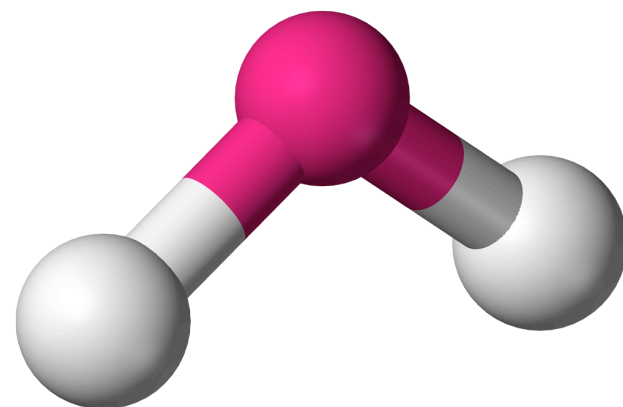
Trigonal Planar Geometry

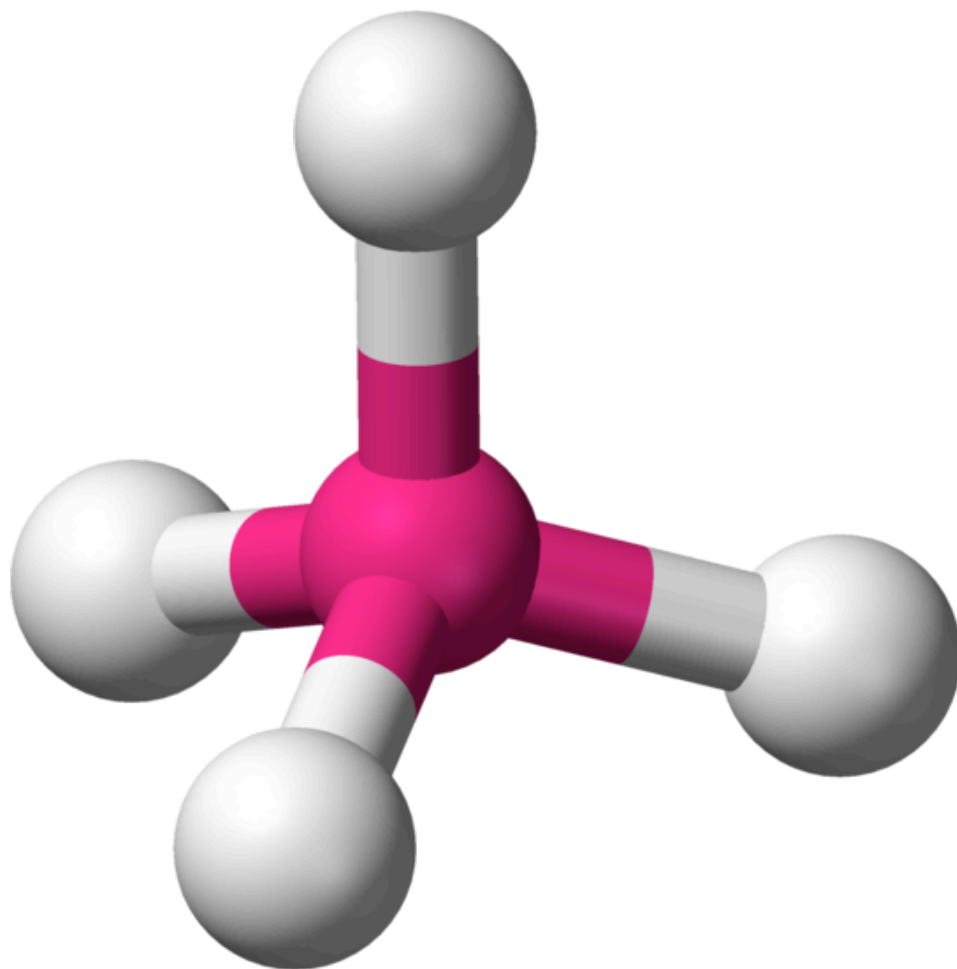


$$\begin{aligned} s &= 3 \\ n &= 2 \\ m &= 1 \end{aligned}$$



18 electrons





$$s = 4$$

$$n = 4$$

$$m = 0$$



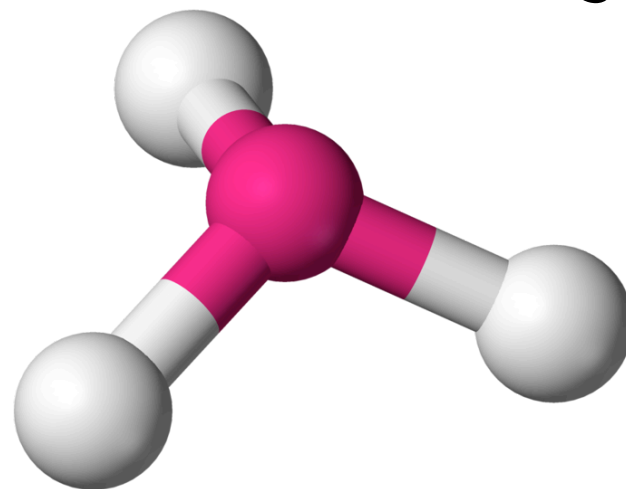
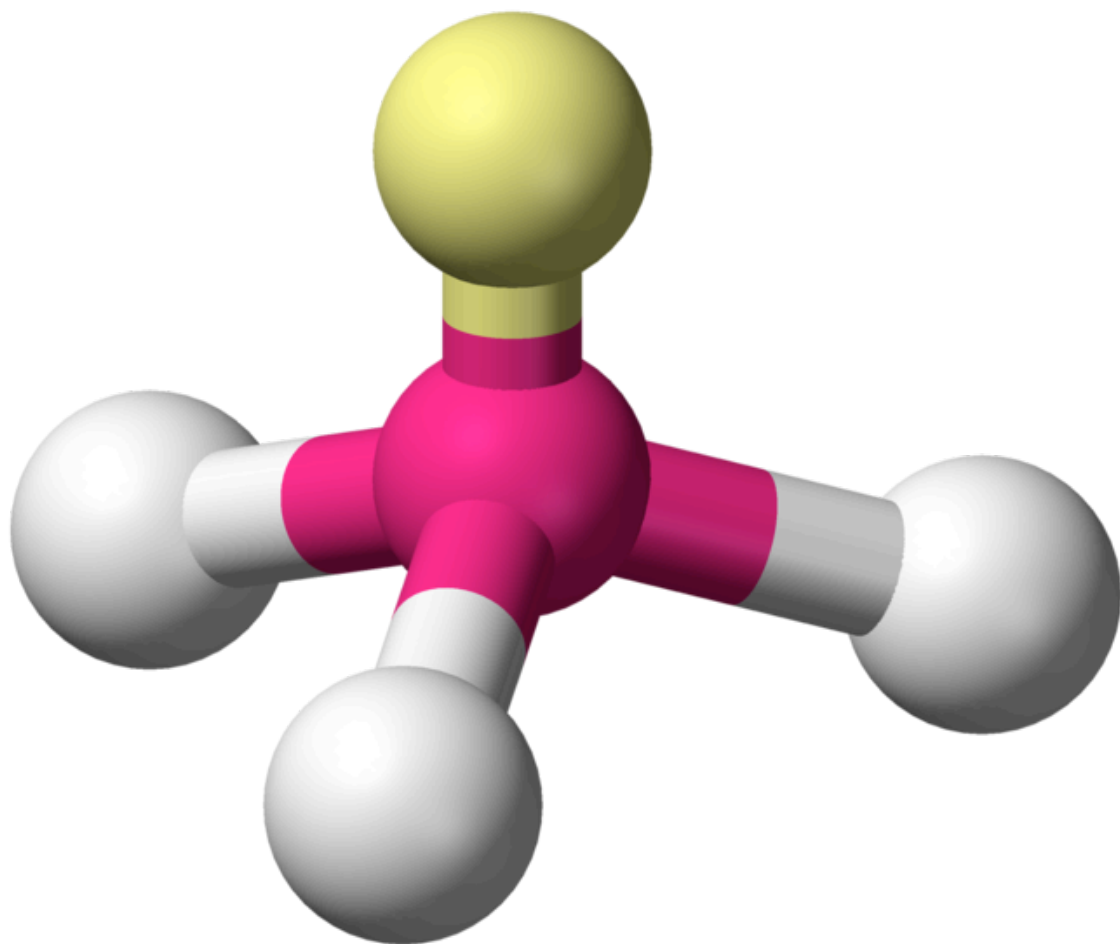
Tetrahedral Geometry



$$s = 4$$

$$n = 3$$

$$m = 1$$



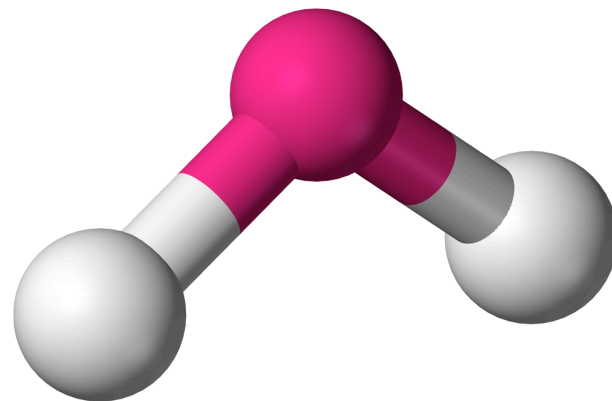
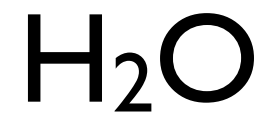
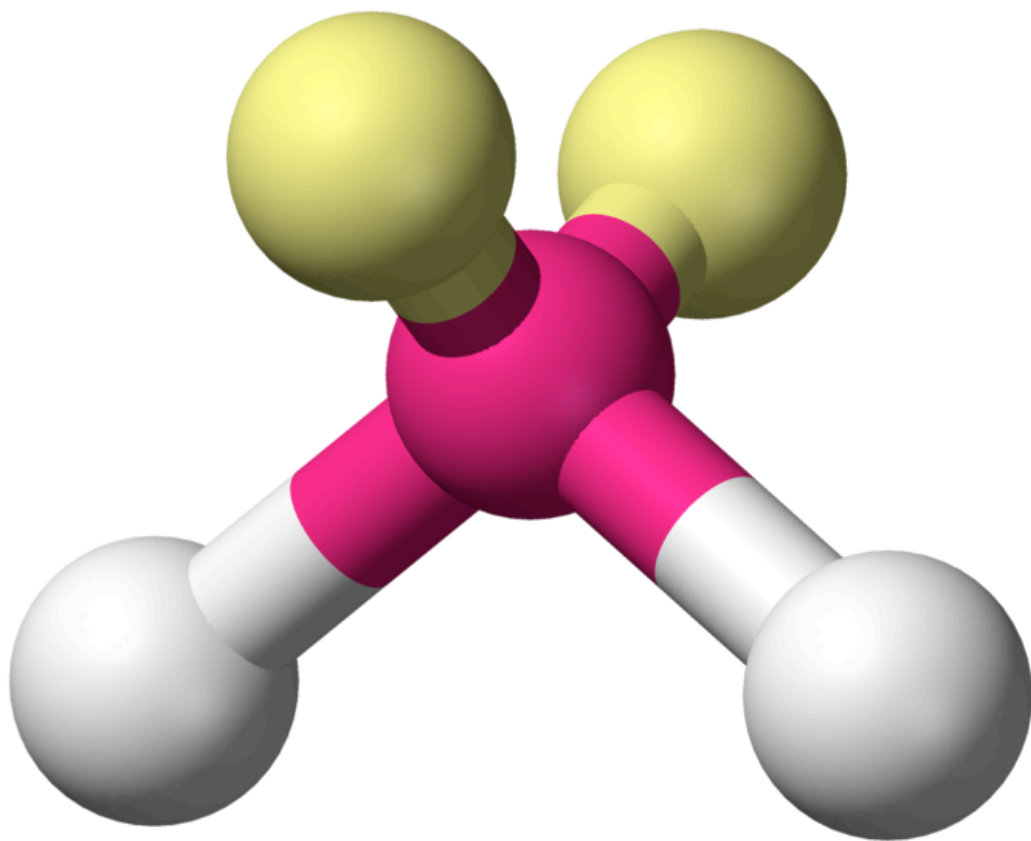
Trigonal Pyramidal Geometry



$$s = 4$$

$$n = 2$$

$$m = 2$$





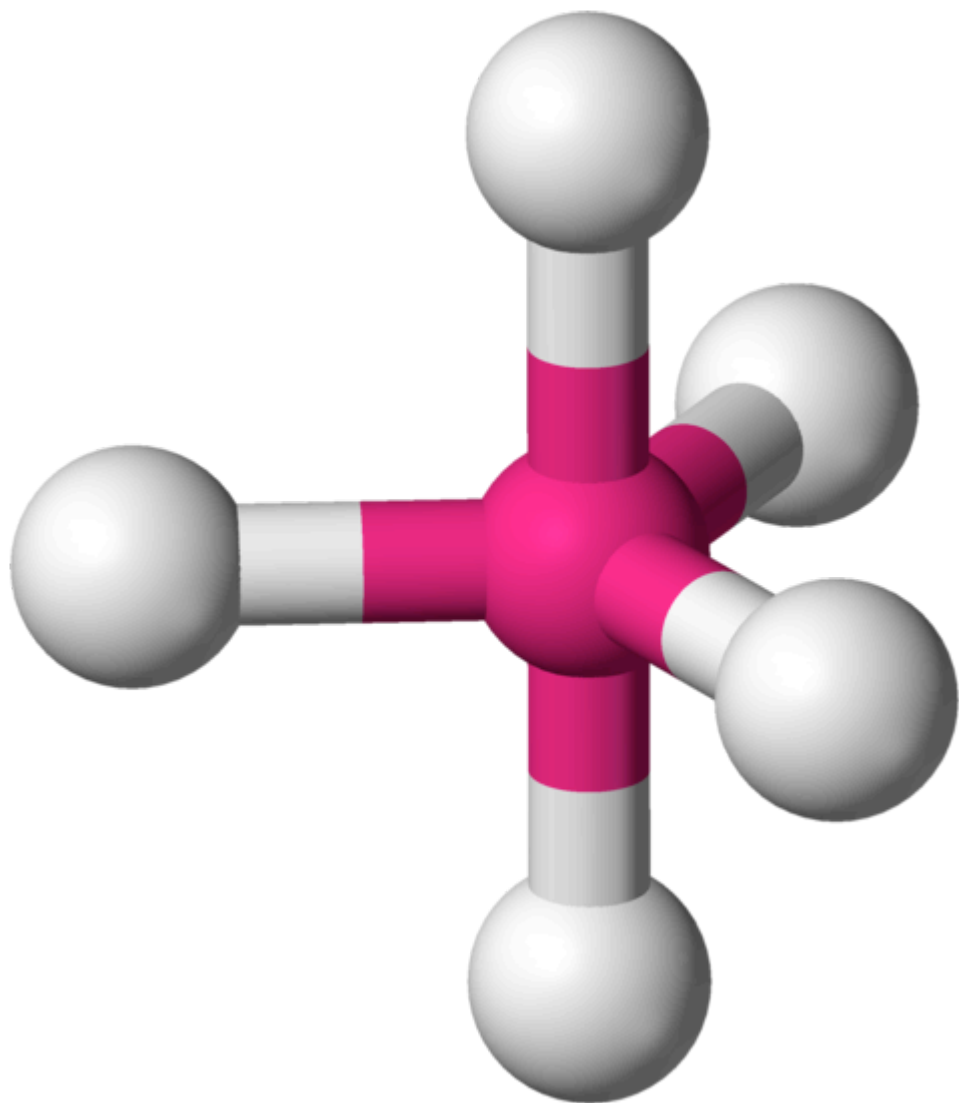
$$s = 5$$

$$n = 5$$

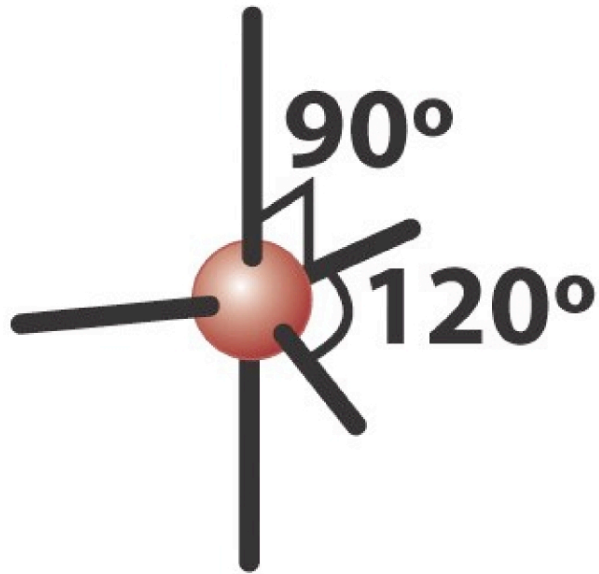
$$m = 0$$



Trigonal Bipyramidal  
Geometry

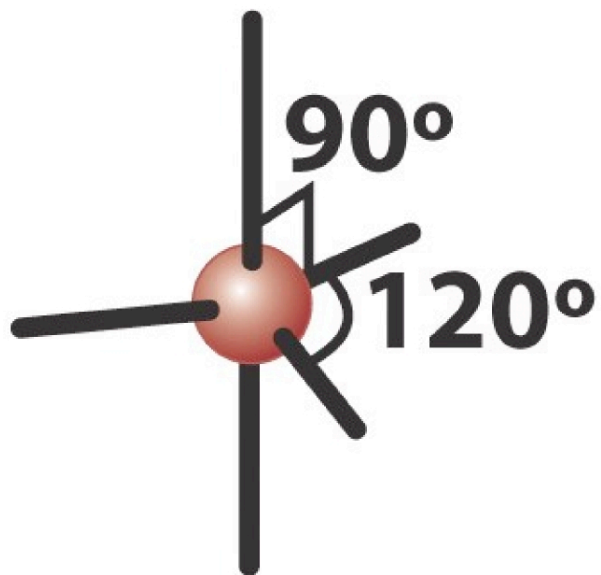


Two different positions.  
Where do the lone pairs go?



**Trigonal  
bipyramidal**

This geometry is the  
strange one...



## Trigonal bipyramidal

Two different positions.  
Where do the lone pairs go?

**Axial position:**

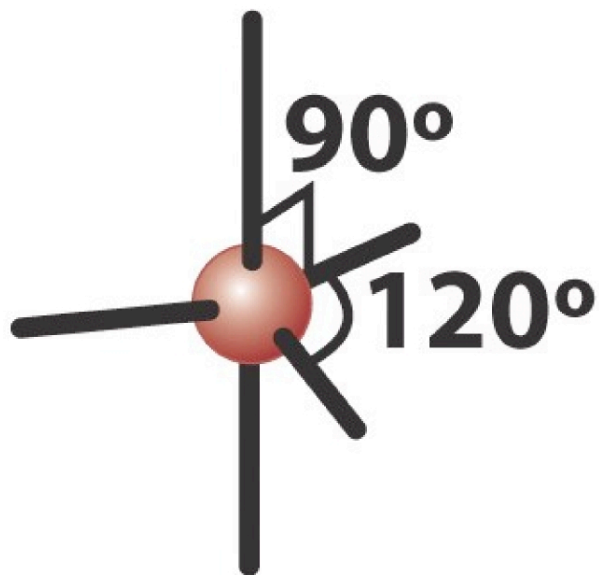
Three  $90^\circ$  angles and

One  $180^\circ$  angle:

Average =  $(3 \times 90 + 180) / 4$

Average =  $112.5^\circ$





## Trigonal bipyramidal

Two different positions.  
Where do the lone pairs go?

### Axial position:

Three 90° angles and

One 180° angle:

$$\text{Average} = (3 \times 90 + 180) / 4$$

$$\text{Average} = 112.5^\circ$$

### Equatorial position:

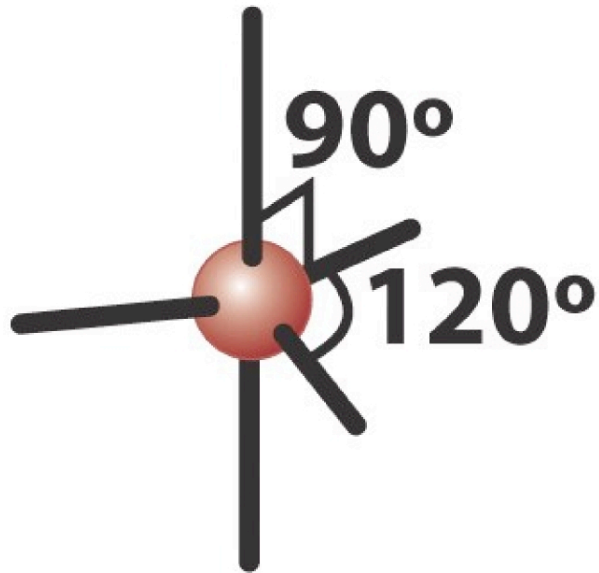
Two 90° angles and

Two 120° angles:

$$\text{Average} = (2 \times 90 + 2 \times 120) / 4$$

$$\text{Average} = 105^\circ$$

Equatorial is observed even though its average angle is smaller!!!



**Trigonal  
bipyramidal**

**Axial position:**

Three 90° angles and

One 180° angle:

Average =  $(3 \times 90 + 180) / 4$

Average = 112.5°

**Equatorial position:**

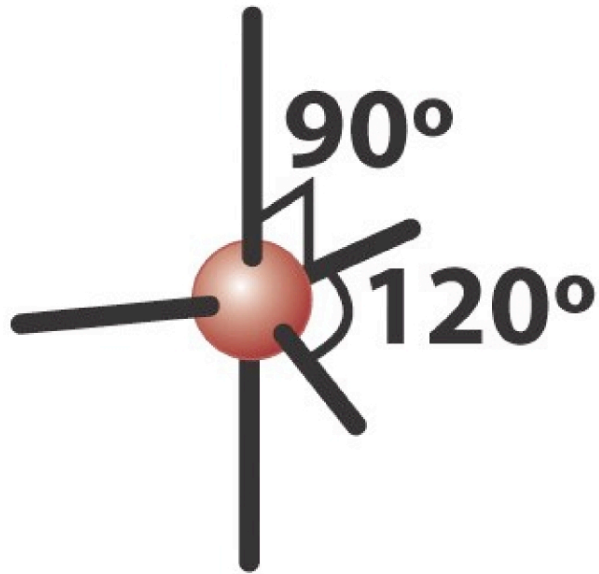
Two 90° angles and

Two 120° angles:

Average =  $(2 \times 90 + 2 \times 120) / 4$

Average = 105°

Equatorial is observed even though its average angle is smaller!!!



## Trigonal bipyramidal

Conclusion: electron overlap is a nonlinear function of distance.

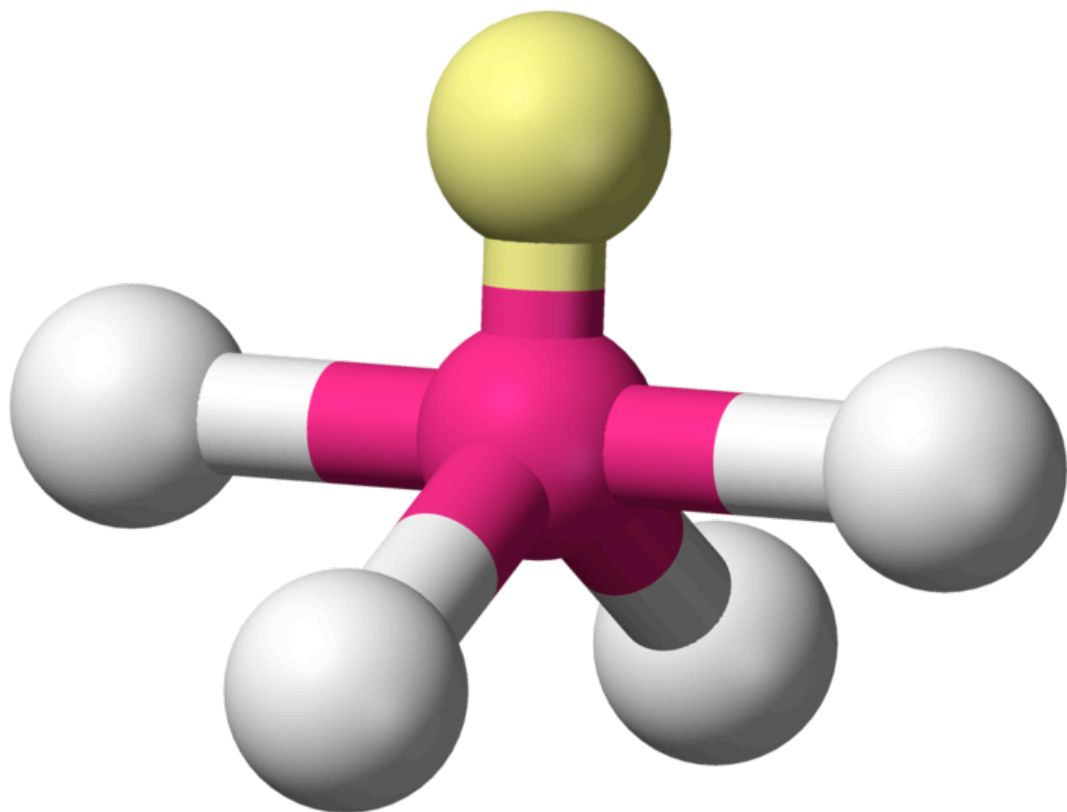
Equatorial position:

Two 90° angles and

Two 120° angles:

Average =  $(2 \times 90 + 2 \times 120) / 4$

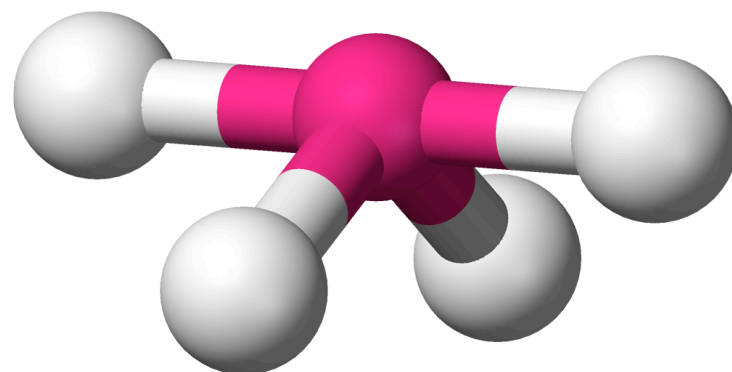
Average = 105°



$$s = 5$$

$$n = 4$$

$$m = 1$$



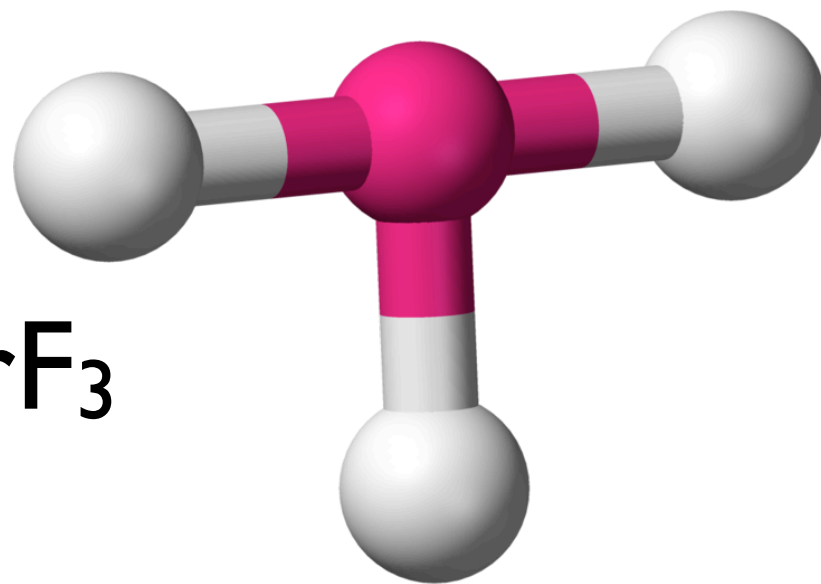
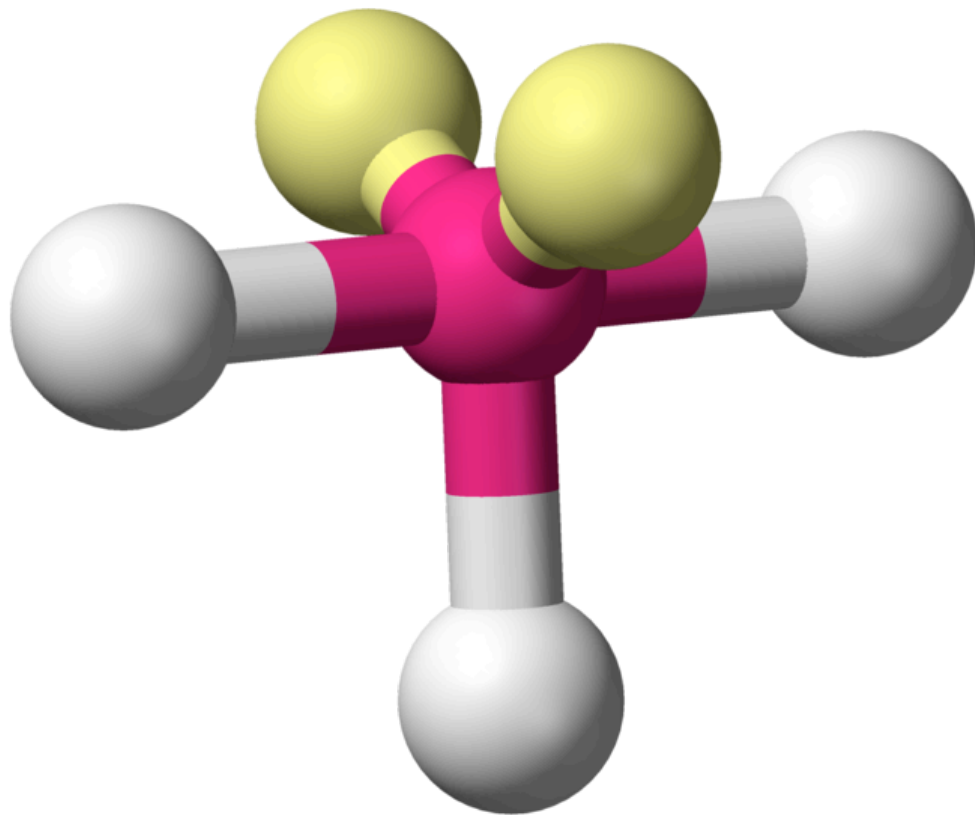
Seesaw Geometry



$$s = 5$$

$$n = 3$$

$$m = 2$$



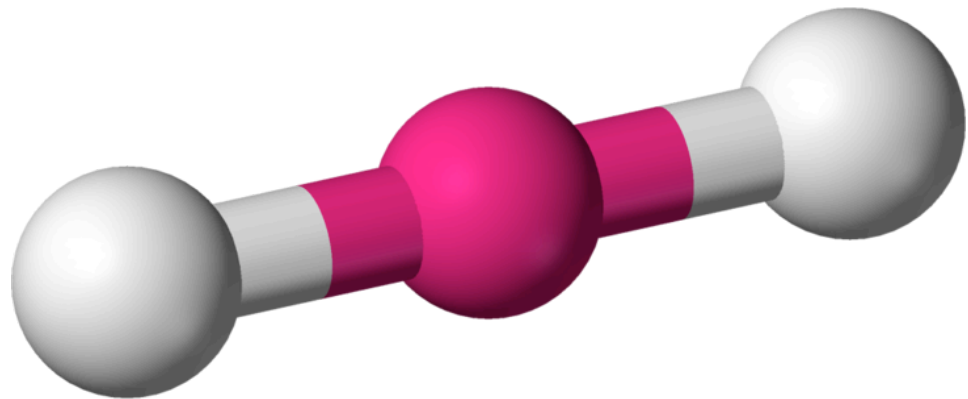
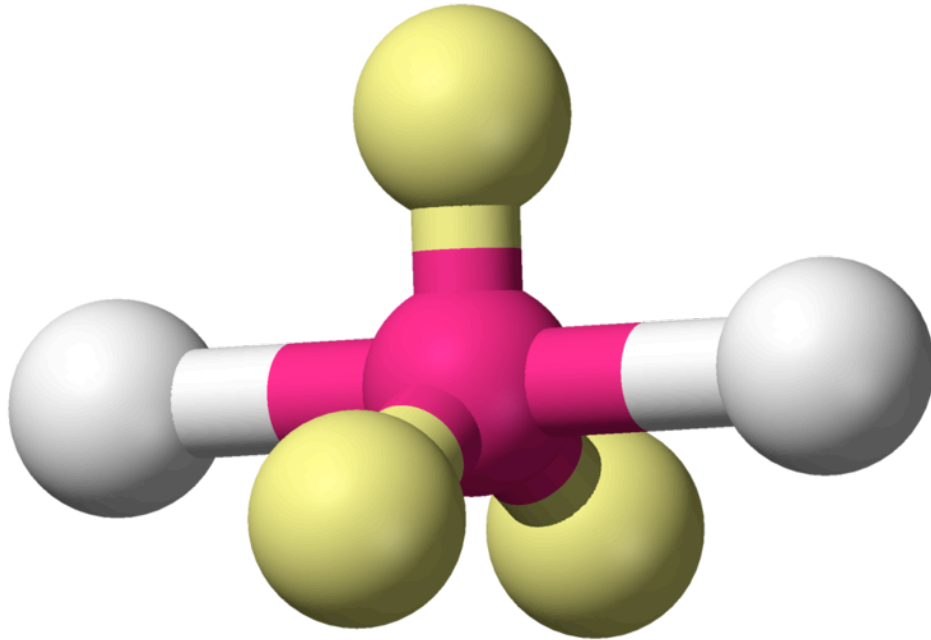
Tee-Shape Geometry



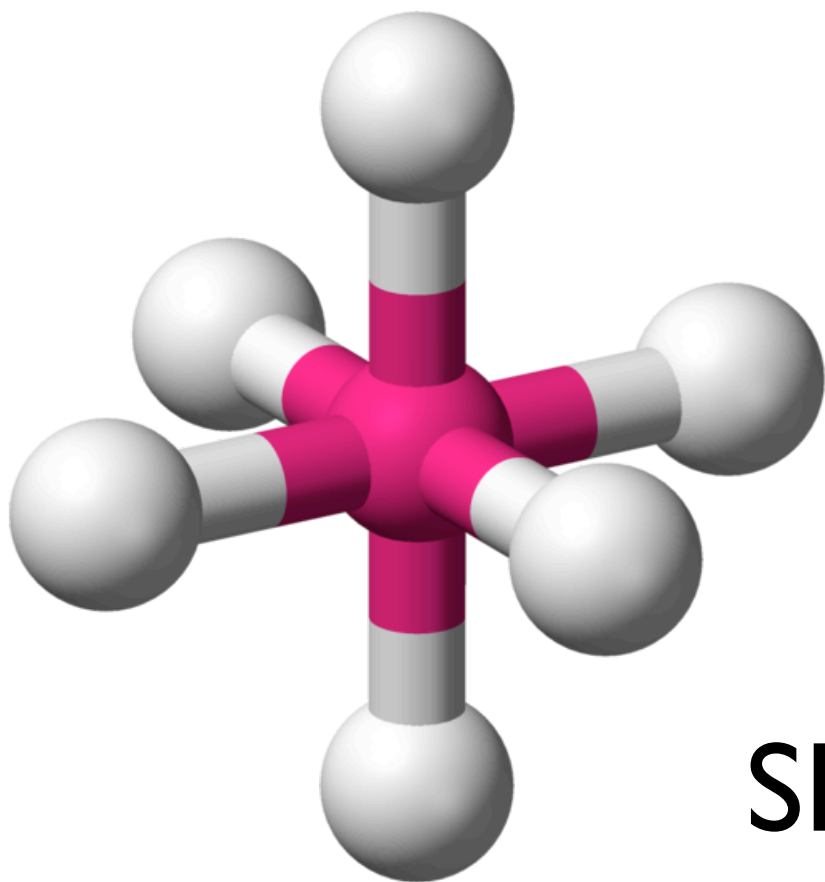
$$s = 5$$

$$n = 2$$

$$m = 3$$



Linear Geometry



$s = 6$

$n = 6$

$m = 0$

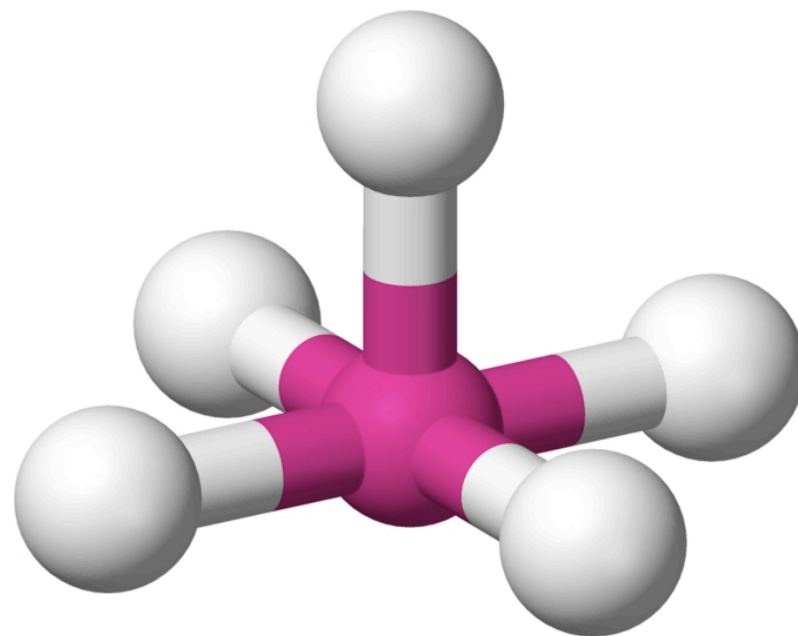
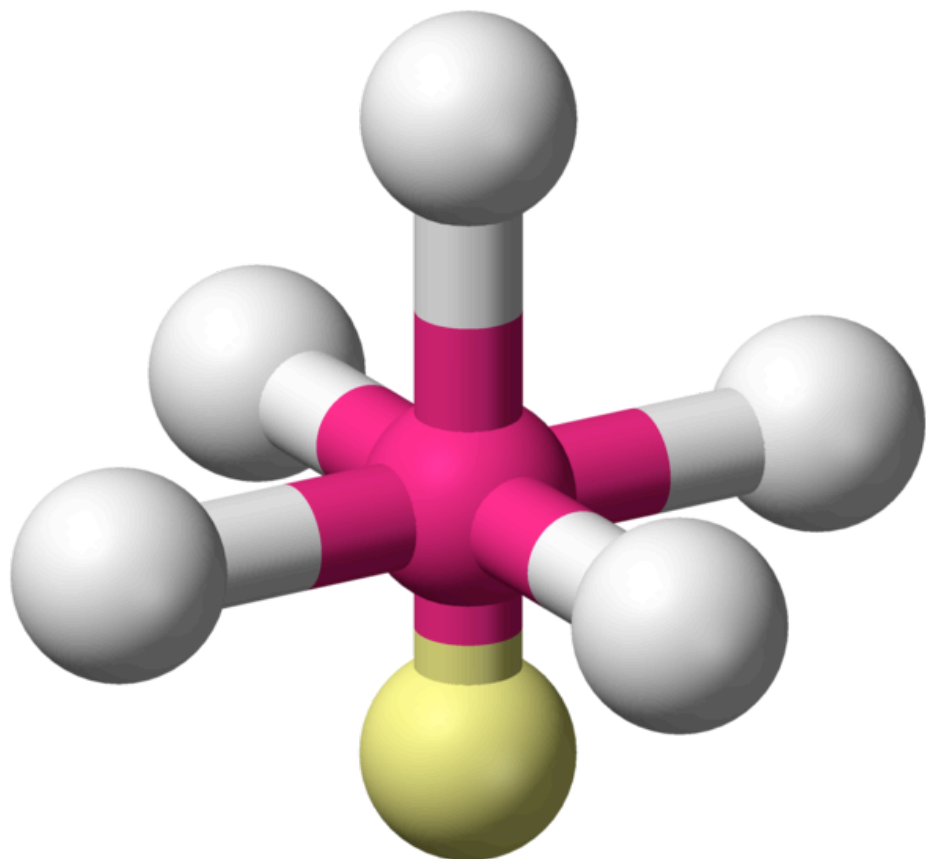
Octahedral Geometry



$$s = 6$$

$$n = 5$$

$$m = 1$$



Square Pyramidal Geometry

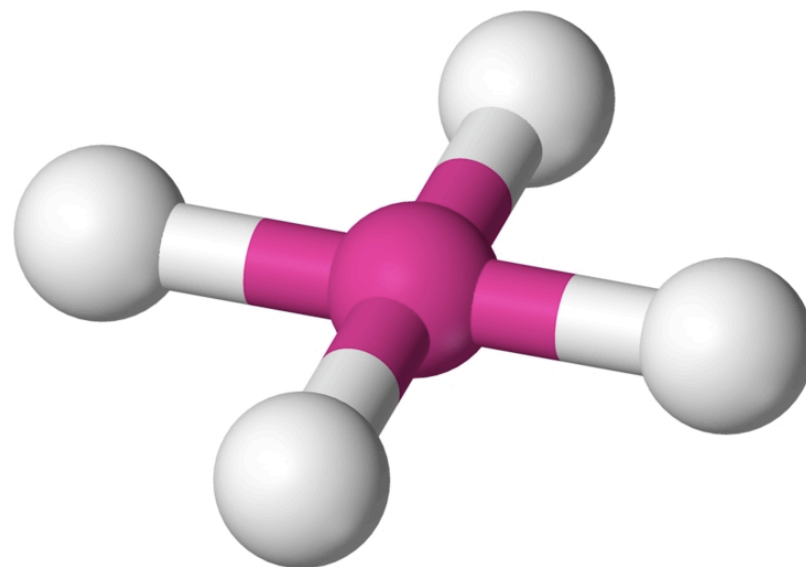
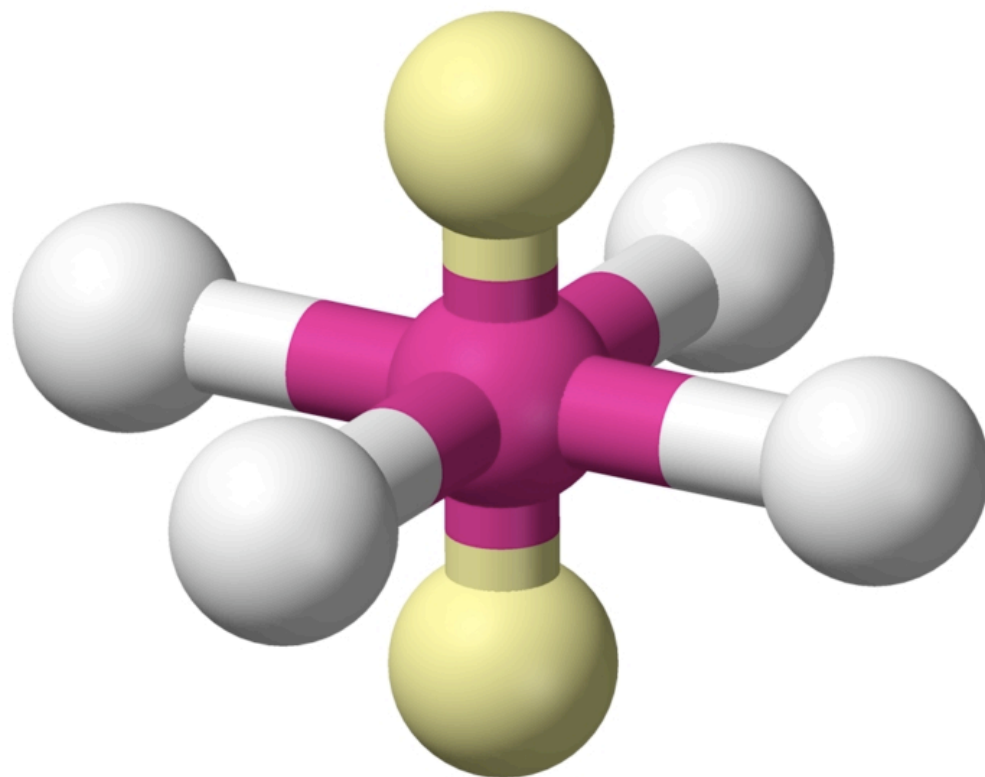




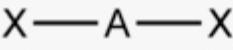
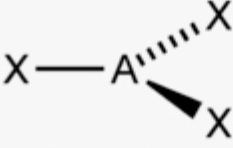
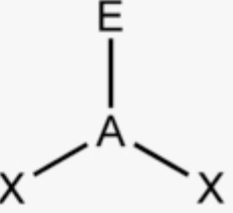


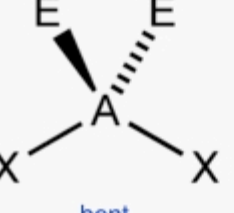



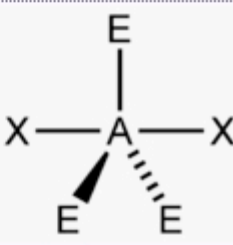


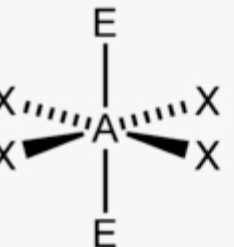
$$s = 6$$

$$n = 4$$

$$m = 2$$

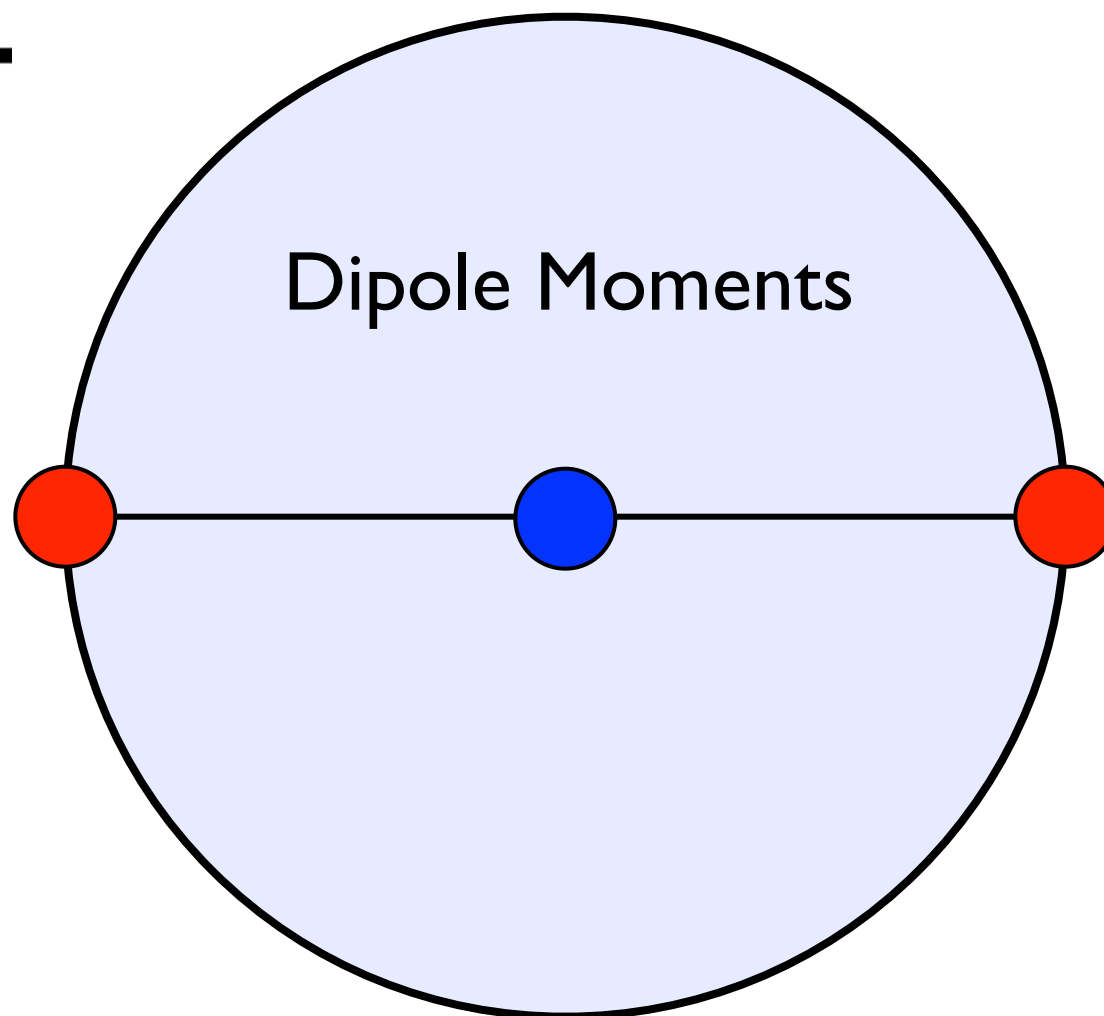


Square Planar Geometry

Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs
2	 linear			
3	 trigonal planar	 bent		
4	 tetrahedral	 trigonal pyramid	 bent	
5	 trigonal bipyramid	 seesaw	 T-shaped	 linear
6	 octahedral	 square pyramid	 square planar	



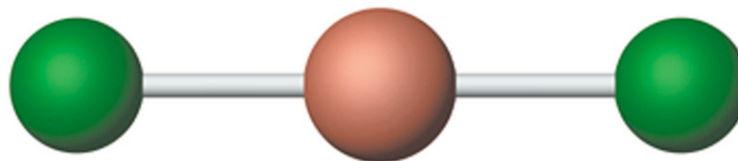
$AX_2$



X-A-X angle:  $180^\circ$

Linear Geometry

Two examples:  $\text{BeCl}_2$  and  $\text{CO}_2$



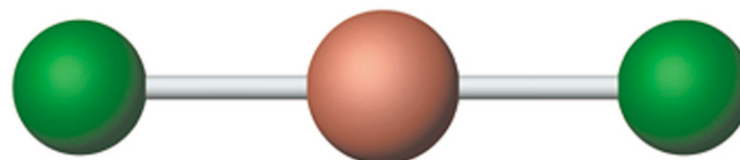
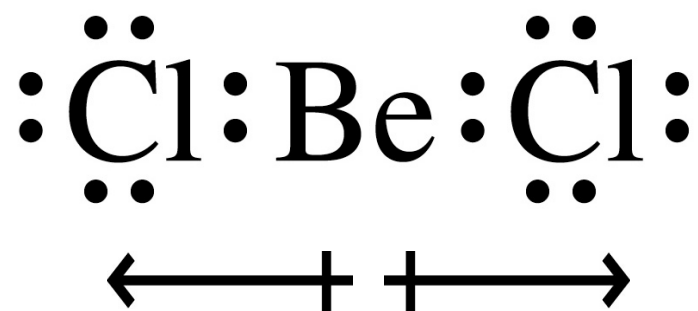
Both of these are of the  $\text{AX}_2\text{E}_0$  format - linear geometry. Note that single and double bonds both count as one for VSEPR geometries.

We can also predict the existence of a molecular dipole moment from the molecular geometry, and the electronegativities of each element:



1											13	14	15	16	17	
H 2.1											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Li 1.0	Be 1.5											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
Na 0.9	Mg 1.2	3	4	5	6	7	8	9	10	11	12	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Cs 0.8	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 2.4	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9					
Fr 0.7	Ra 0.9	Ac <sup>†</sup> 1.1	* Lanthanides: 1.1–1.3 † Actinides: 1.3–1.5													

We can also predict the existence of a molecular dipole moment from the molecular geometry, and the electronegativities of each element:

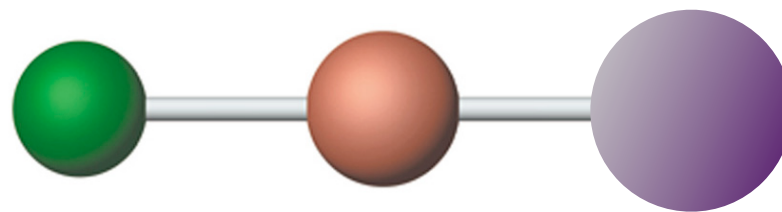


the two bond dipoles in  $\text{BeCl}_2$  cancel  
(they are equal in magnitude, and opposite in direction)

$\text{BeCl}_2$  has no net molecular dipole.

$\text{CO}_2$  has no net molecular dipole as well.

What about the molecule: BeClBr?



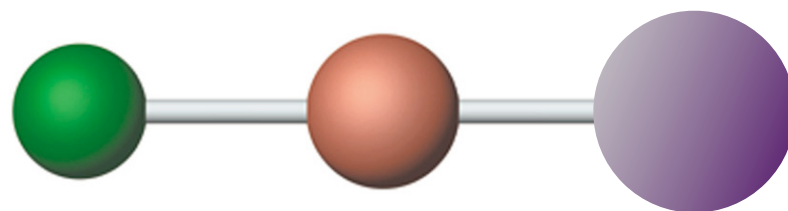
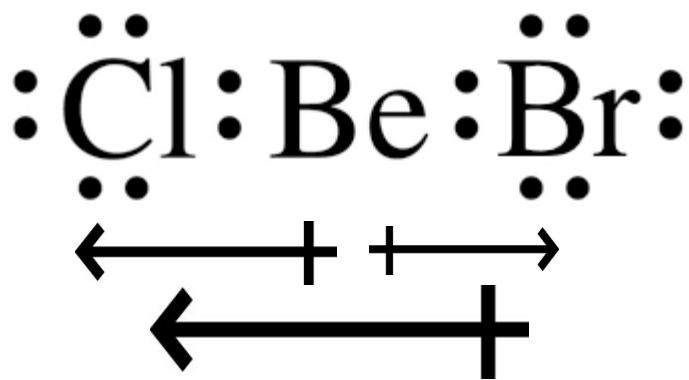
# What about the molecule: BeClBr?



1													13	14	15	16	17
H 2.1													B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Li 1.0	<b>Be 1.5</b>																
Na 0.9	Mg 1.2												Al 1.5	Si 1.8	P 2.1	S 2.5	<b>Cl 3.0</b>
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	<b>Br 2.8</b>	
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	
Cs 0.8	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 2.4	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9	Ac† 1.1	* Lanthanides: 1.1–1.3 † Actinides: 1.3–1.5														



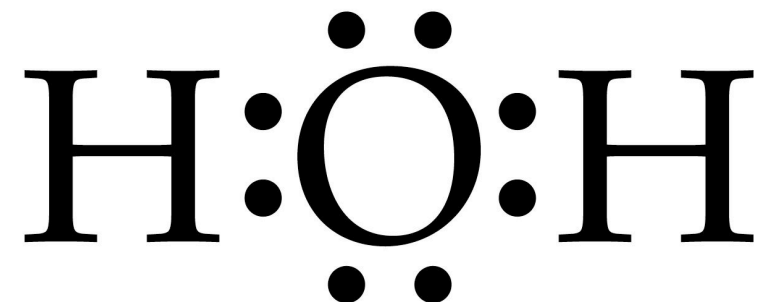
What about the molecule: BeClBr?



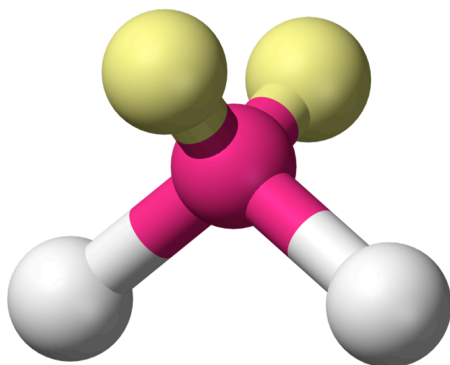
the two bond dipoles in BeClBr do not cancel.

BeClBr has a small molecular dipole oriented along the molecular axis, and directed towards the Cl.

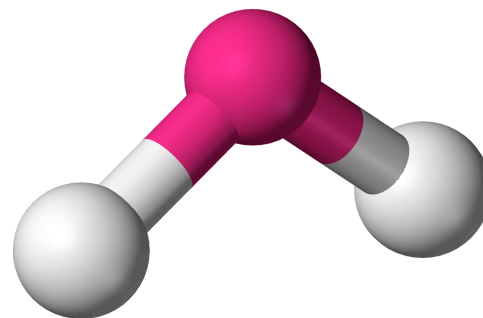
Another example: H<sub>2</sub>O



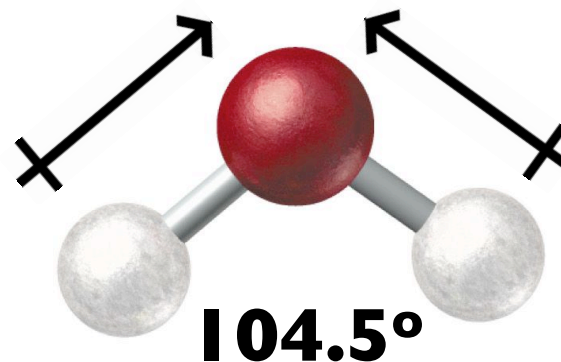
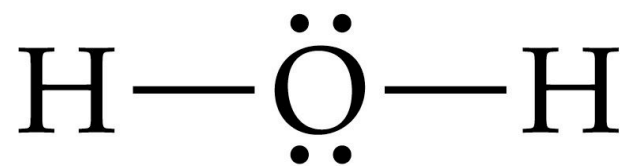
The oxygen is surrounded by four electron pairs, two in sigma bonds and two in lone pairs. The VSEPR group is **AX<sub>2</sub>E<sub>2</sub>** -- bent geometry.



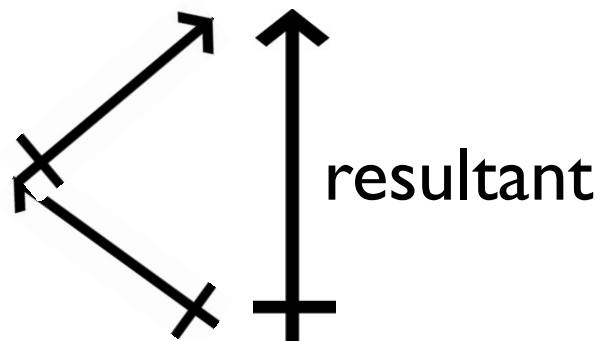
or



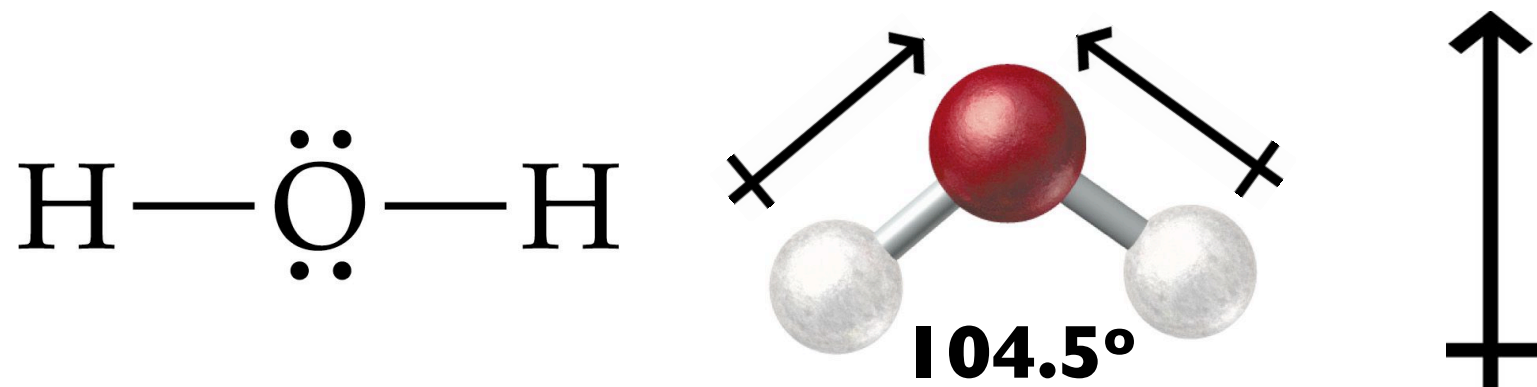
Does H<sub>2</sub>O have a dipole moment?



we perform this vector addition  
in our heads:



H<sub>2</sub>O has a dipole moment of 1.85D



the tetrahedral **electron group geometry** requires that the **molecular geometry** is bent.

The molecular dipole moment bisects the H-O-H bond and is directed towards the oxygen.

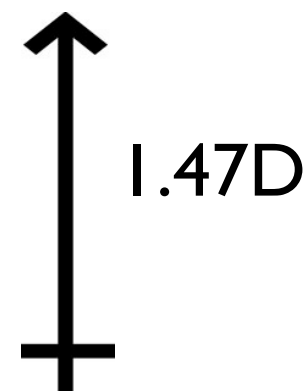
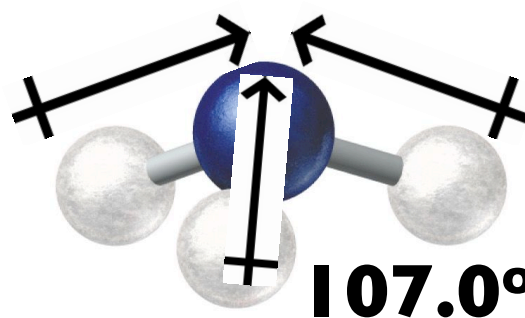
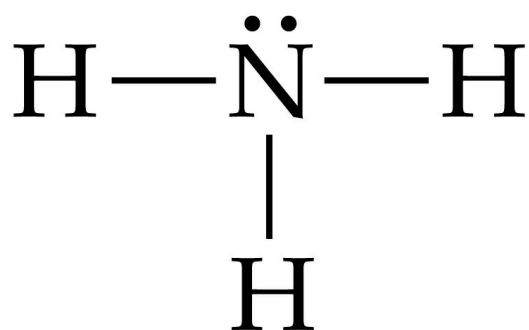
Both Electronegativity differences and Geometry determine the dipole moment of a molecule:

**TABLE 3.1** Dipole Moments of Selected Molecules

Molecule	Dipole moment (D)	Molecule	Dipole moment (D)
HF	1.91	PH <sub>3</sub>	0.58
HCl	1.08	AsH <sub>3</sub>	0.20
HBr	0.80	SbH <sub>3</sub>	0.12
HI	0.42	O <sub>3</sub>	0.53
CO	0.12	CO <sub>2</sub>	0
ClF	0.88	BF <sub>3</sub>	0
NaCl*	9.00	CH <sub>4</sub>	0
CsCl*	10.42	<i>cis</i> -CHCl=CHCl	1.90
H <sub>2</sub> O	1.85	<i>trans</i> -CHCl=CHCl	0
NH <sub>3</sub>	1.47		

\*For pairs of ions in the gas phase, not the bulk ionic solid.

A second molecule with tetrahedral electron group symmetry about the central atom is  $\text{NH}_3$  (ammonia):

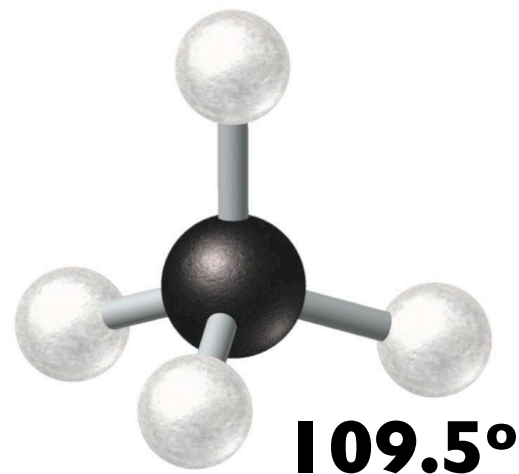
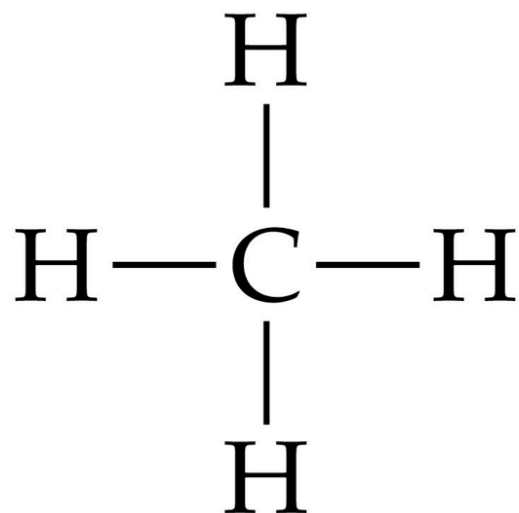


VSEPR class:  $\text{AX}_3\text{E}_1$ .

molecular geometry = trigonal pyramidal.

The molecular dipole moment is coincident with the 3-fold axis of the molecule and is directed towards the N.

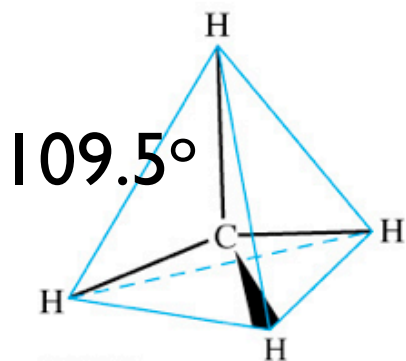
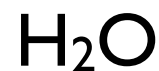
A third molecule with tetrahedral electron group symmetry about the central atom is  $\text{CH}_4$  (methane):



VSEPR group:  $\text{AX}_4\text{E}_0$   
molecular geometry = tetrahedral.

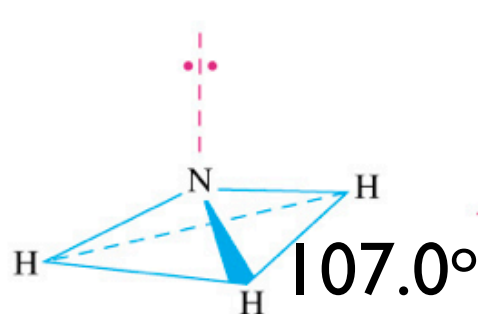
methane is non-polar.

Lone pairs actually need more room, and cause bond angle compression in  $\text{NH}_3$  and  $\text{H}_2\text{O}$ :



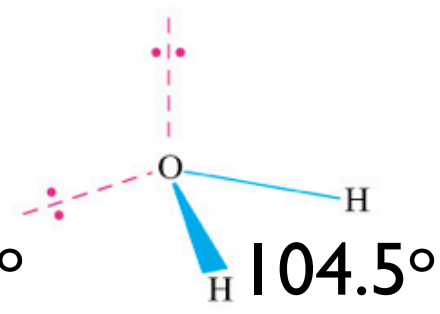
VSEPR  
notation:  $\text{AX}_4$   
(a)

a perfect  
tetrahedron



$\text{AX}_3\text{E}$   
(b)

1 lone pair



$\text{AX}_2\text{E}_2$   
(c)

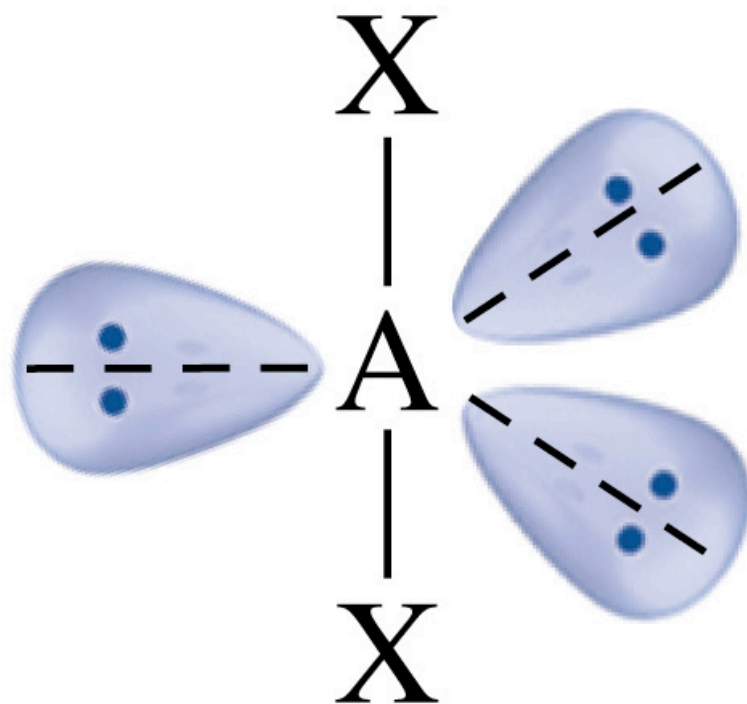
2 lone pairs



Given the formula for a molecule, you should be able to:

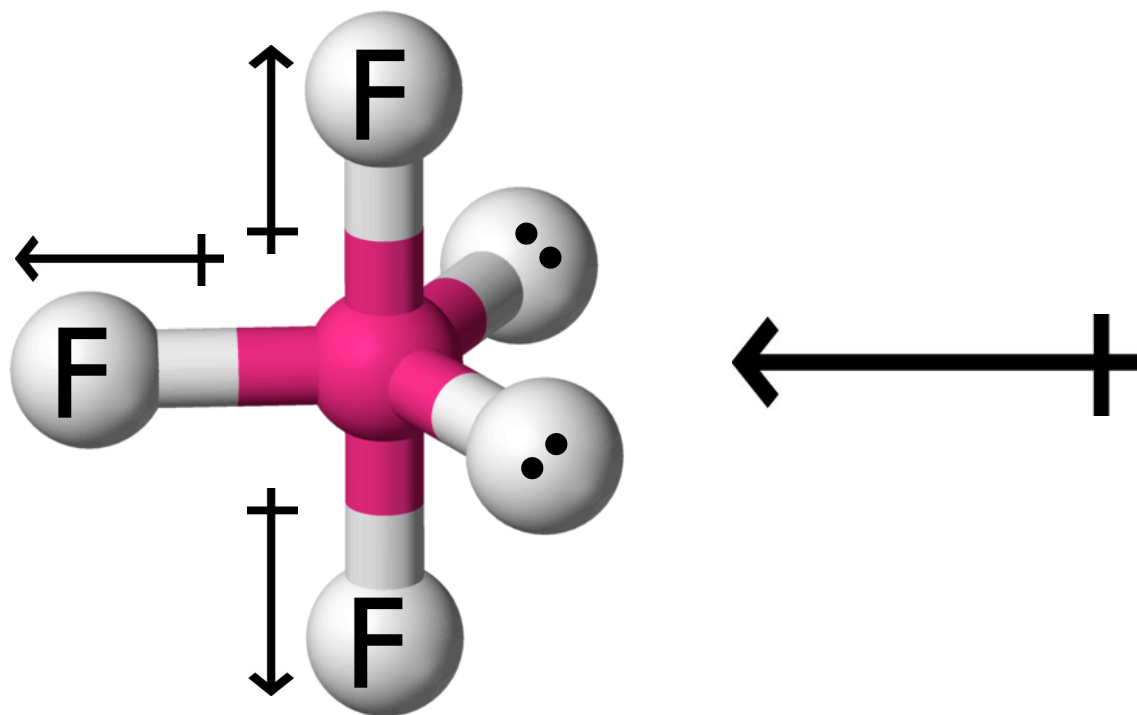
1. Produce the best Lewis Dot representation for that molecule, include resonance structures.
2. Determine the formal charge on each atom of your structure(s).
3. Indicate its molecular geometry.
4. Determine whether it is polar or nonpolar.
5. Specify the direction of the dipole moment.

Dipole moments for trigonal bipyramidal geometries:



Linear

**VSEPR group:  $AX_2E_3$**  = trigonal bipyramidal  
**molecular geometry** = linear and no dipole moment  
**example:**  $XeF_2$

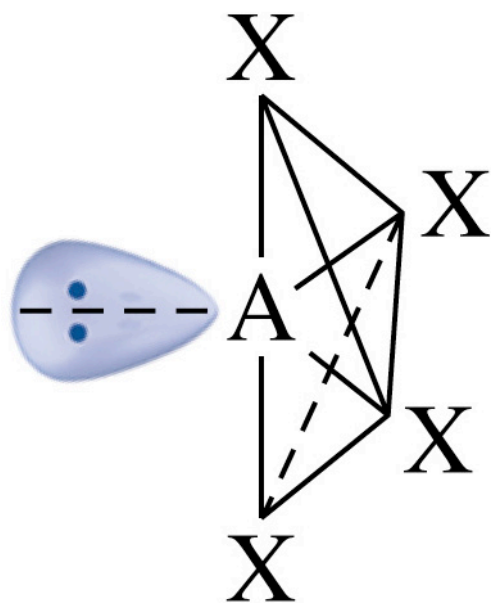


**VSEPR group:  $AX_3E_2$**  = trigonal bipyramidal  
**molecular geometry** = t-shaped  
**example:** IF<sub>3</sub>

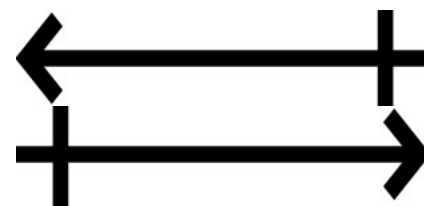
Dipole bisects lone pair and is directed towards F.

what about a SINGLE single lone pair - does it choose an equatorial or axial position within a molecule having a trigonal bipyramidal electron group geometry?

answer: equatorial



Seesaw

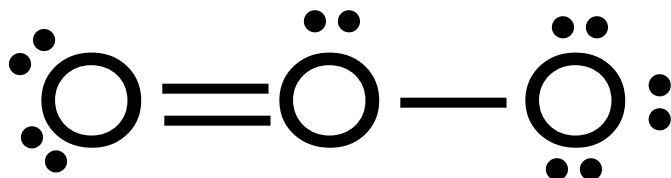
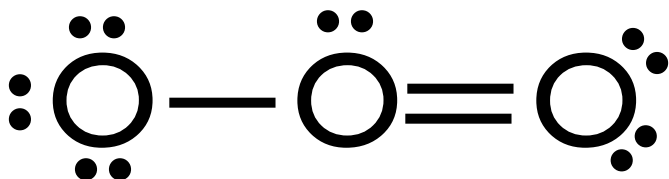


dipole directed  
along lone-pair-A  
axis.

**VSEPR group:  $AX_4E_1$  = trigonal bipyramidal**  
**molecular geometry = see-saw**

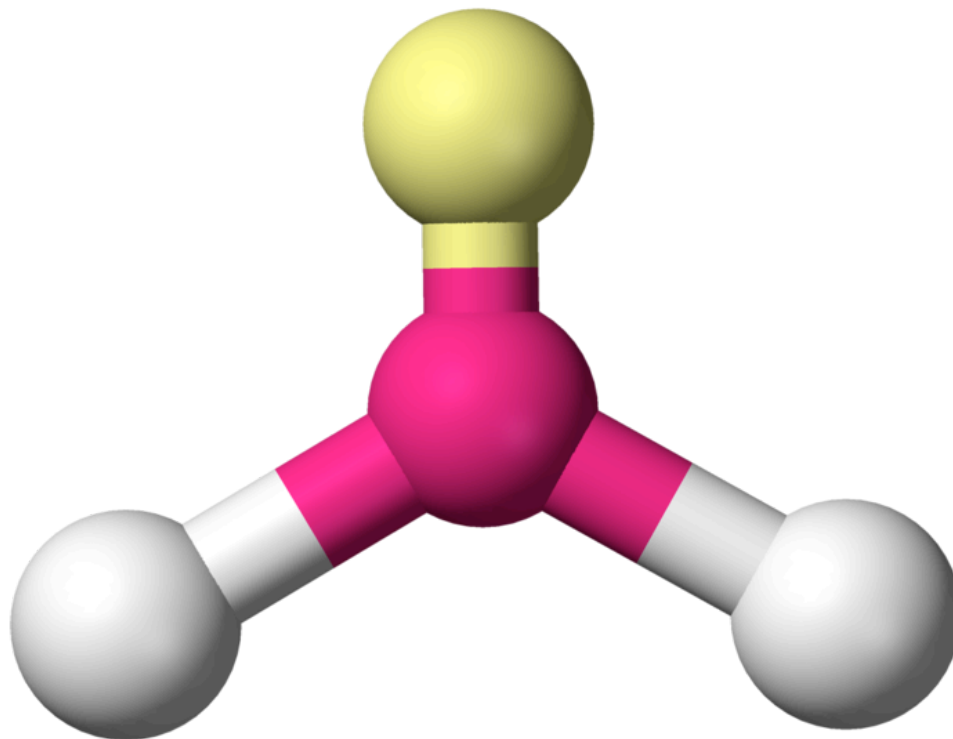
And remember to include resonance structures!

An example: ozone, O<sub>3</sub> (18 electrons):



two resonance structures

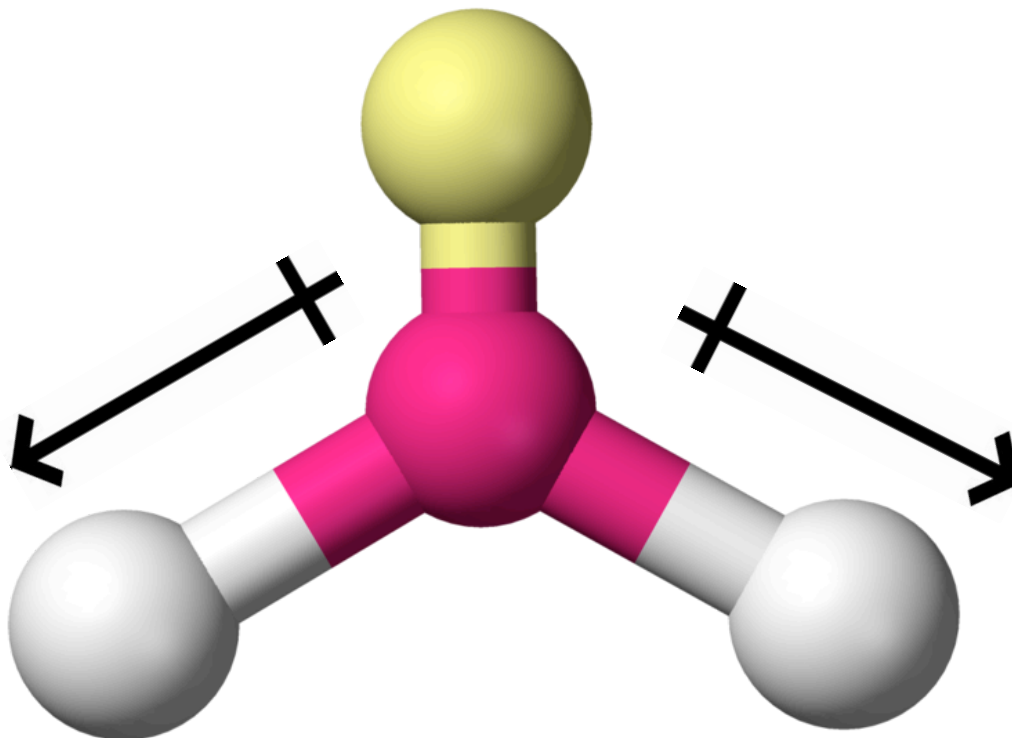
Ozone, O<sub>3</sub> (18 electrons):



**VSEPR group: AX<sub>2</sub>E<sub>1</sub>** = trigonal  
**molecular geometry** = bent

Bond angle = 116°

Ozone, O<sub>3</sub> (18 electrons):

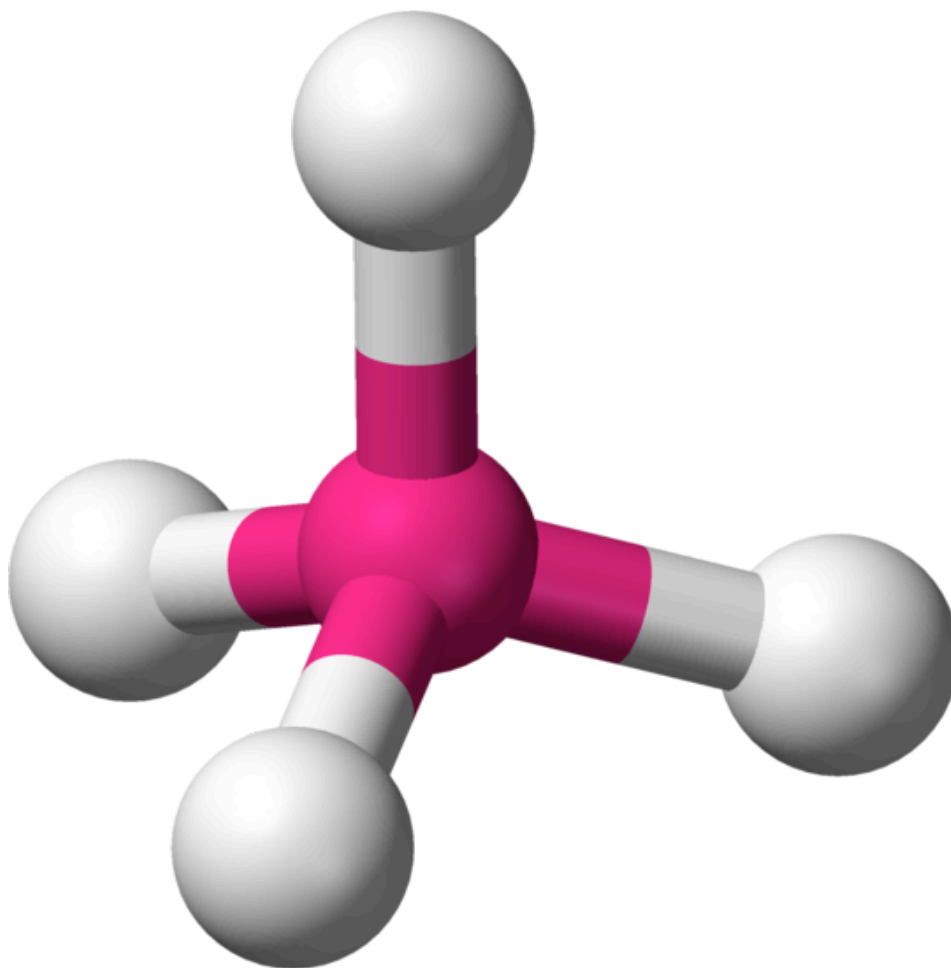


**VSEPR group: AX<sub>2</sub>E<sub>1</sub>** = trigonal  
**molecular geometry** = bent

Bond angle = 116°

Small dipole moment (0.53D), because it's all oxygen.

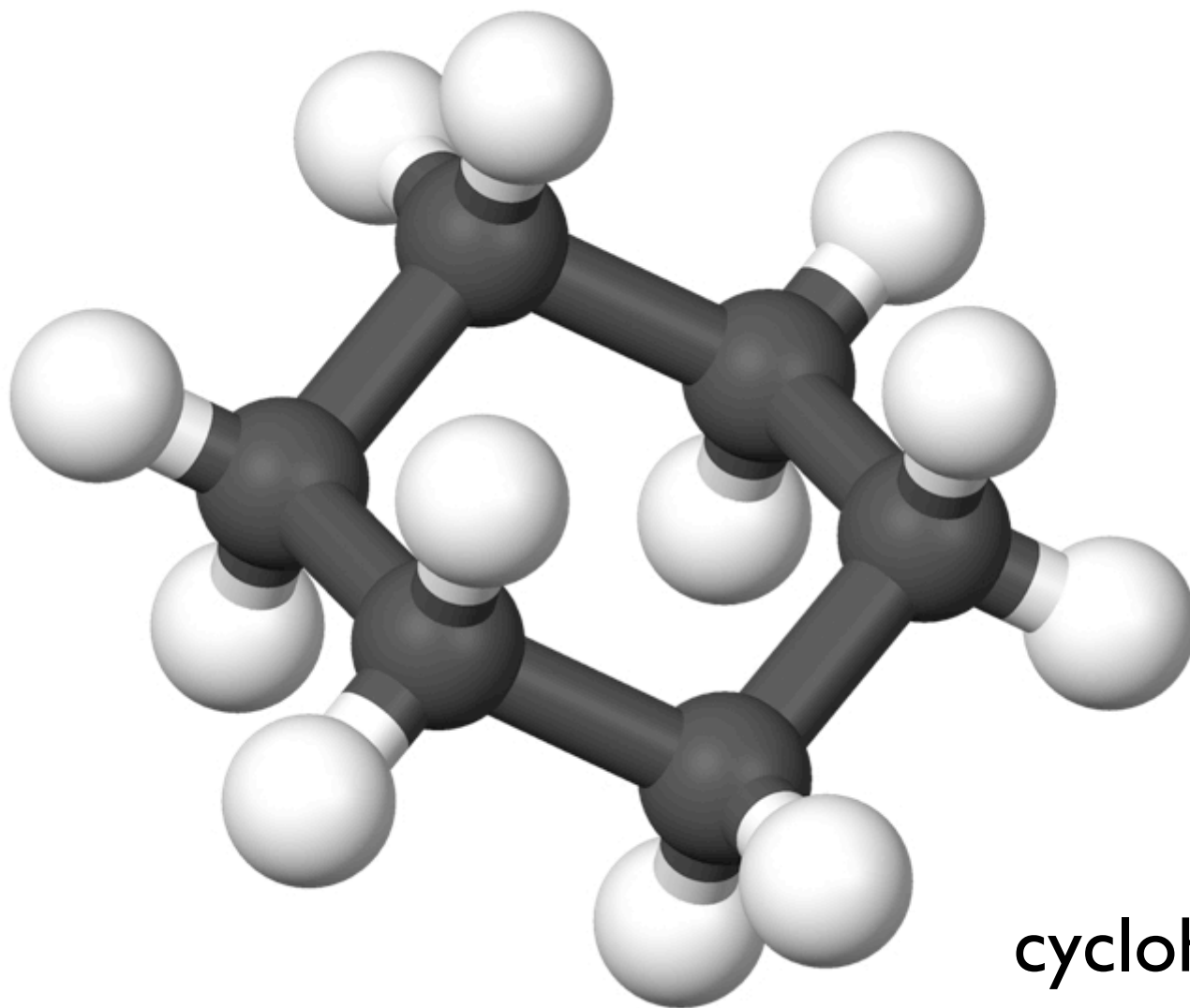
# Hydrocarbons



methane

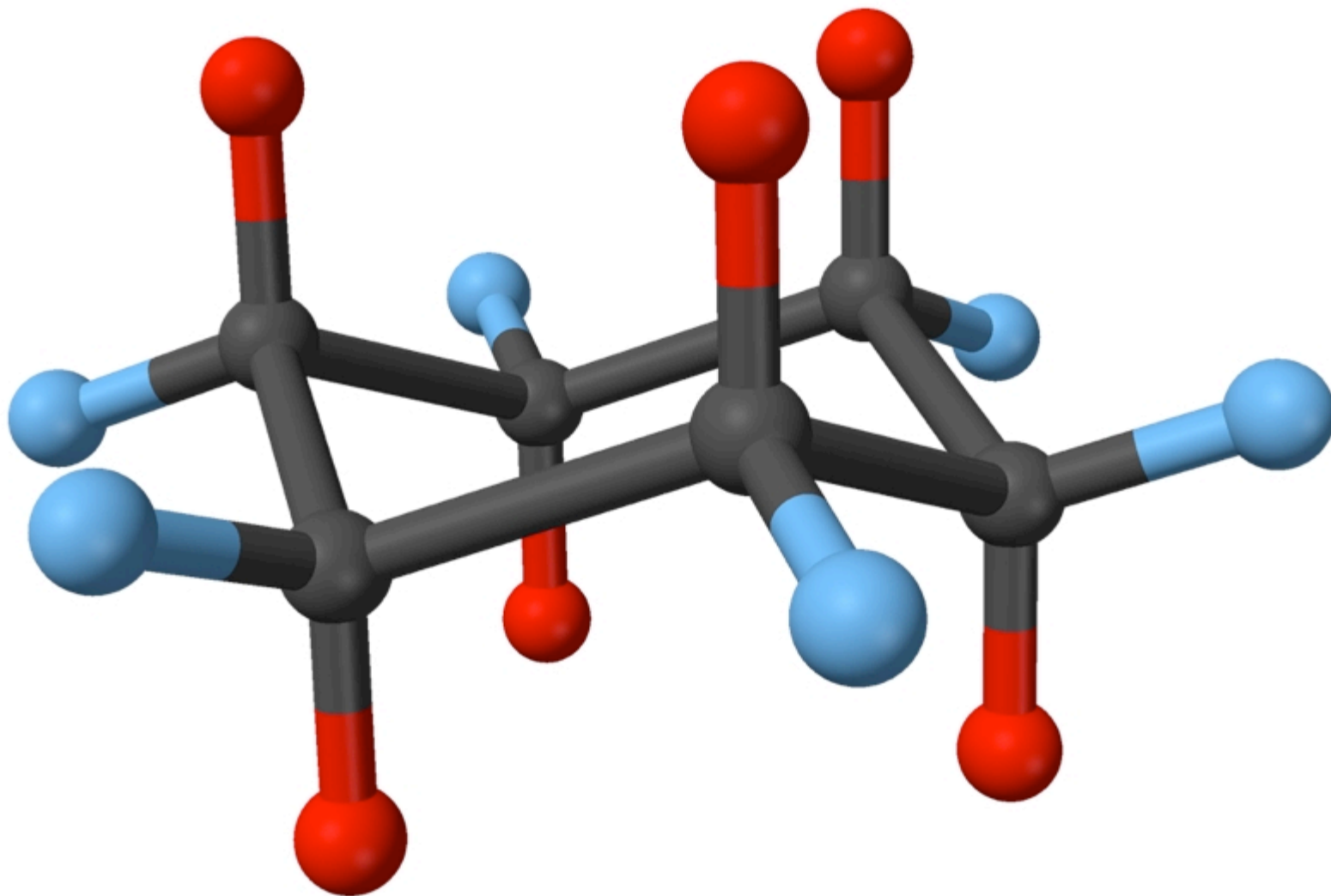


# Hydrocarbons



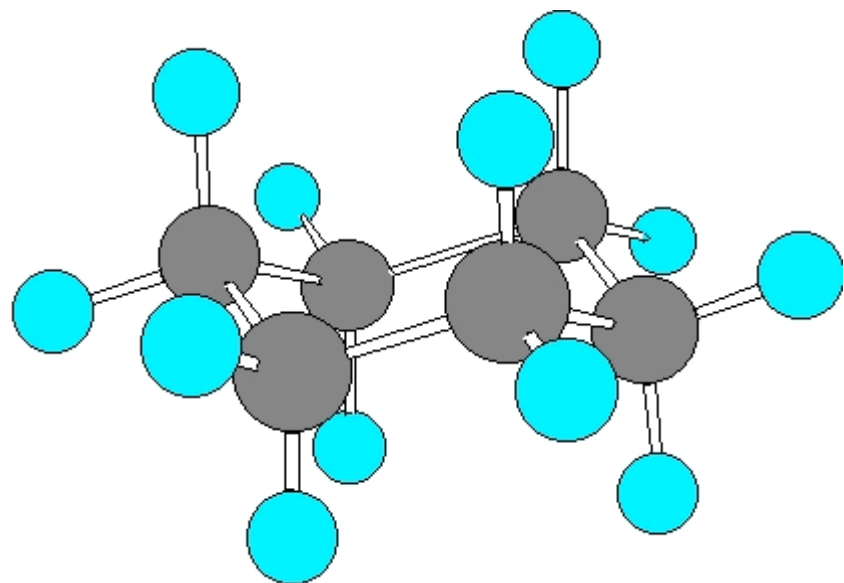
cyclohexane  
 $C_6H_{12}$

# Hydrocarbons



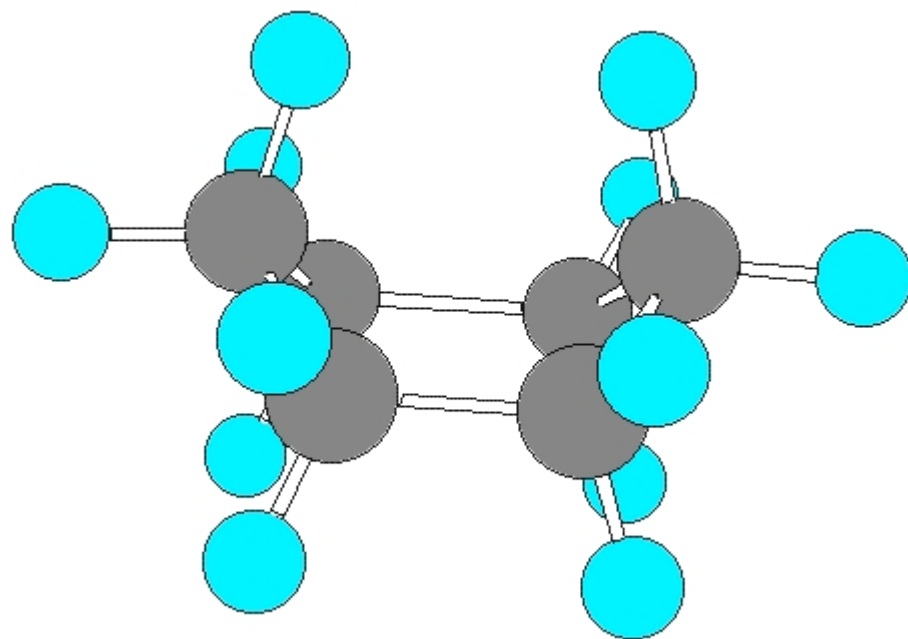
axial and equatorial  
hydrogens

# Hydrocarbons



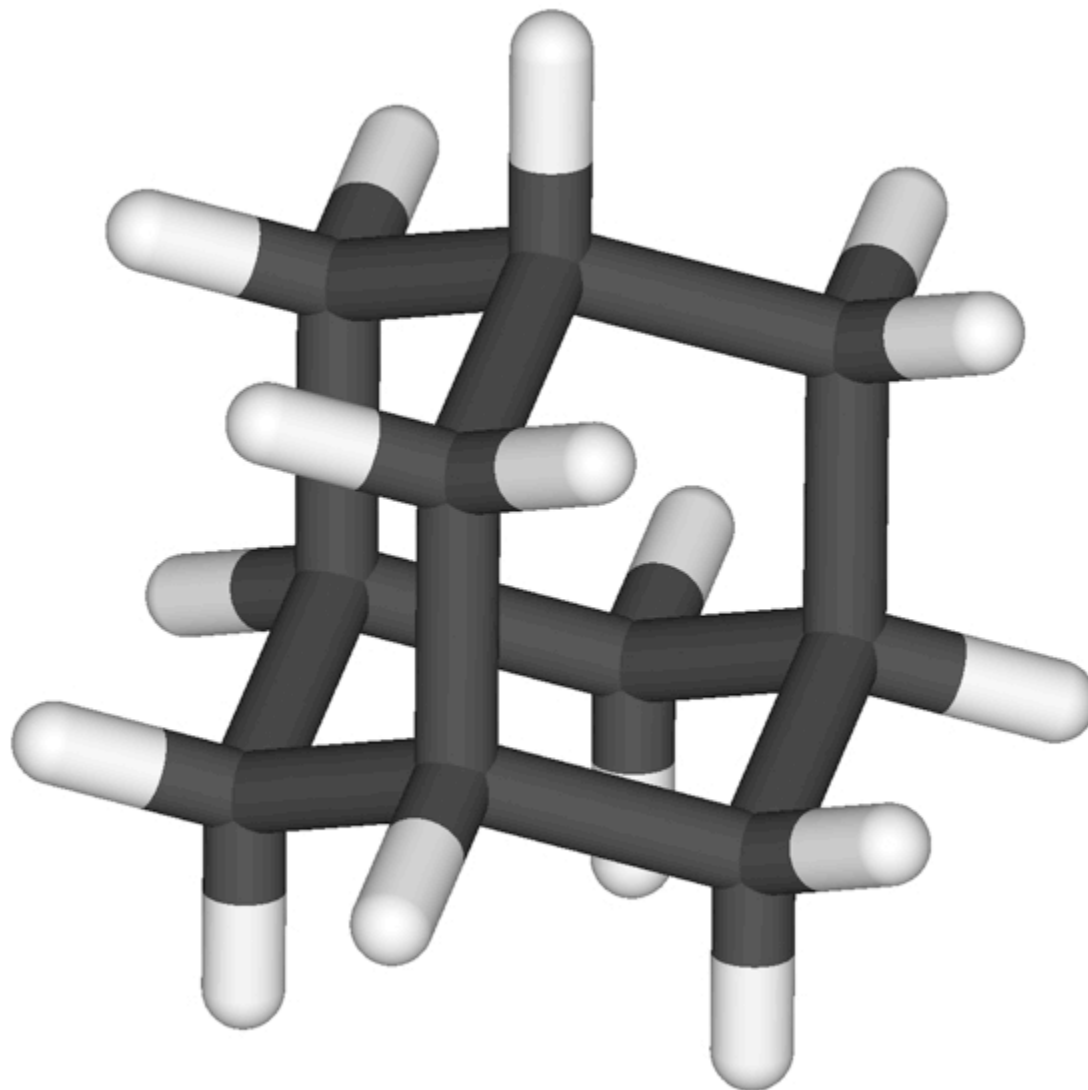
chair

two conformations  
of cyclohexane

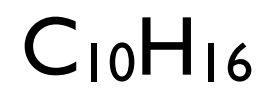


boat

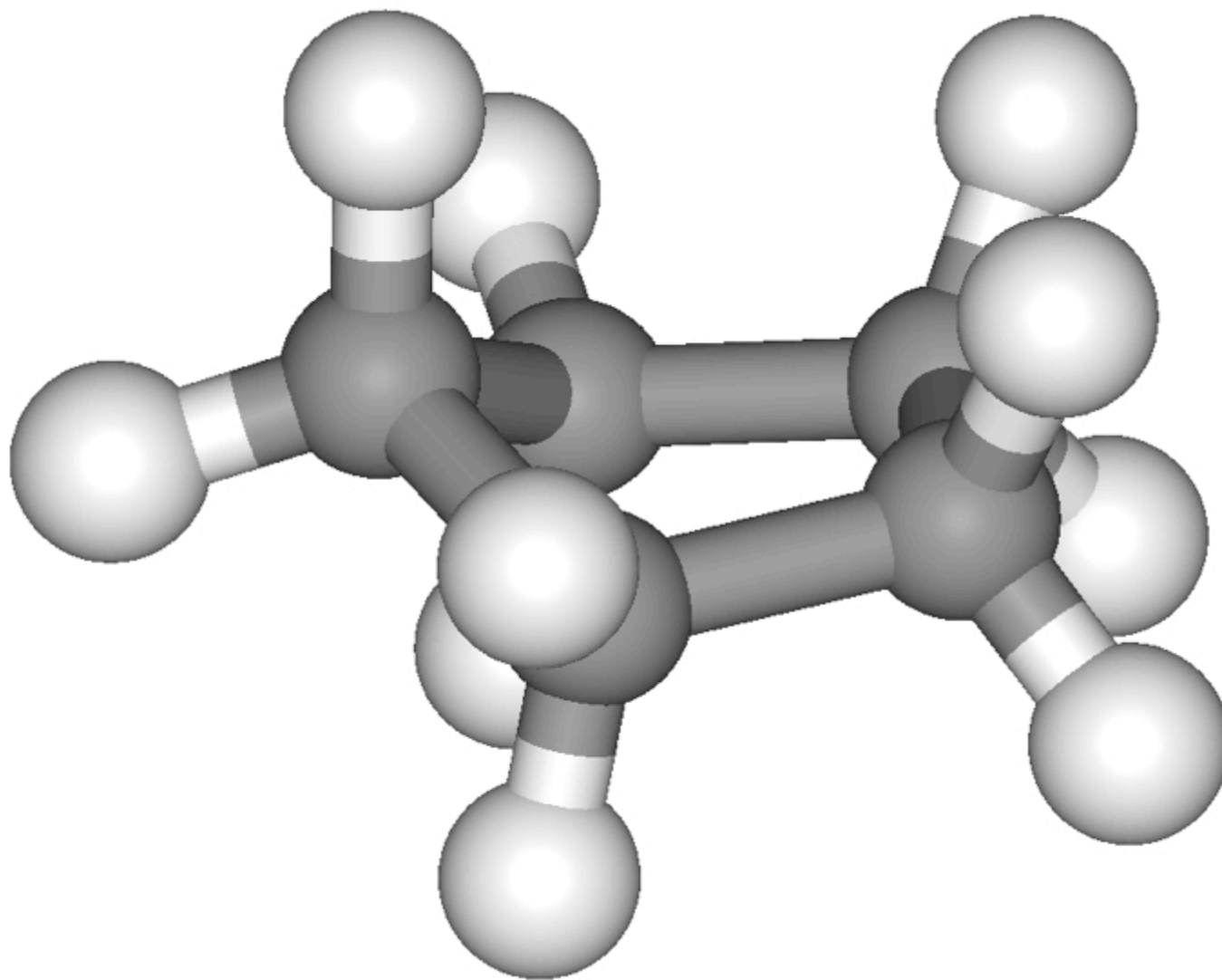
# Hydrocarbons



adamantane

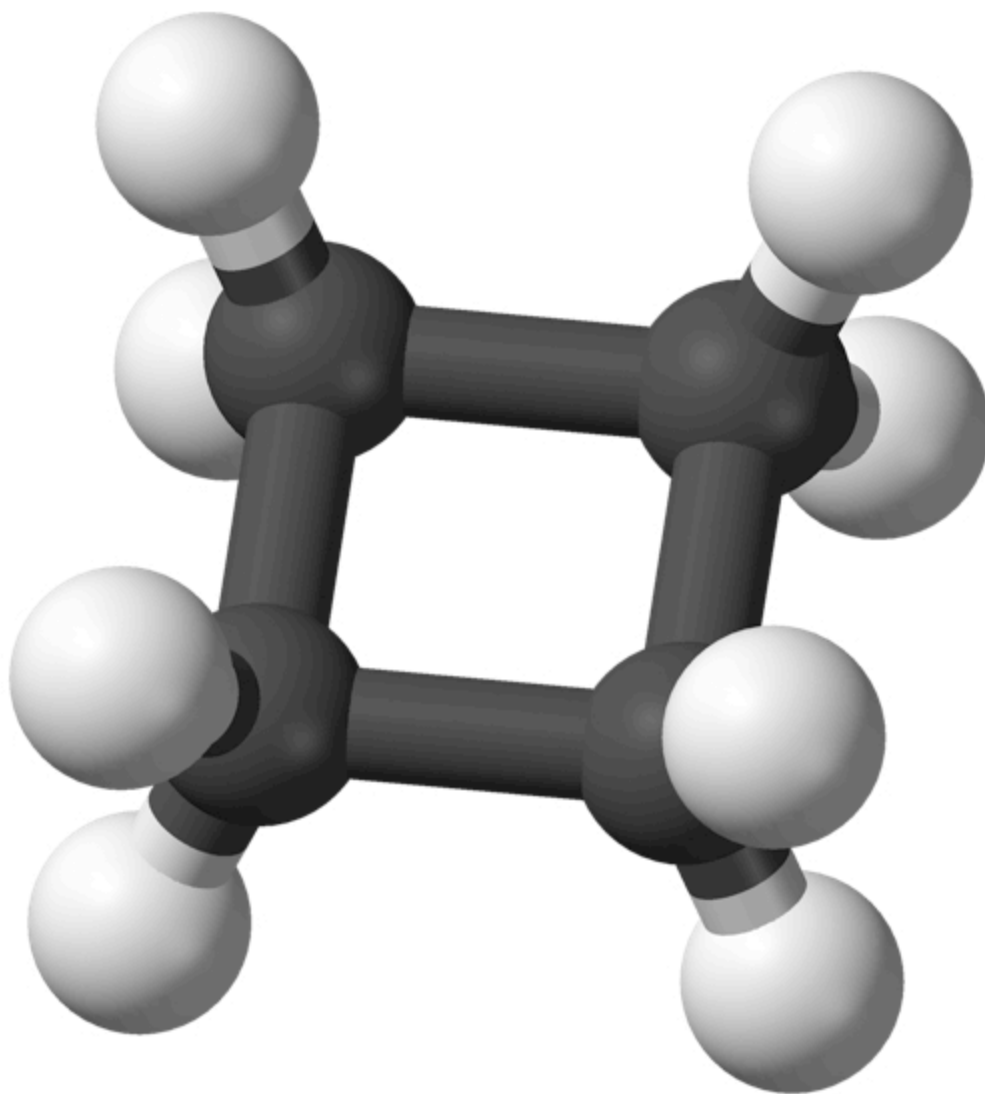


# Hydrocarbons



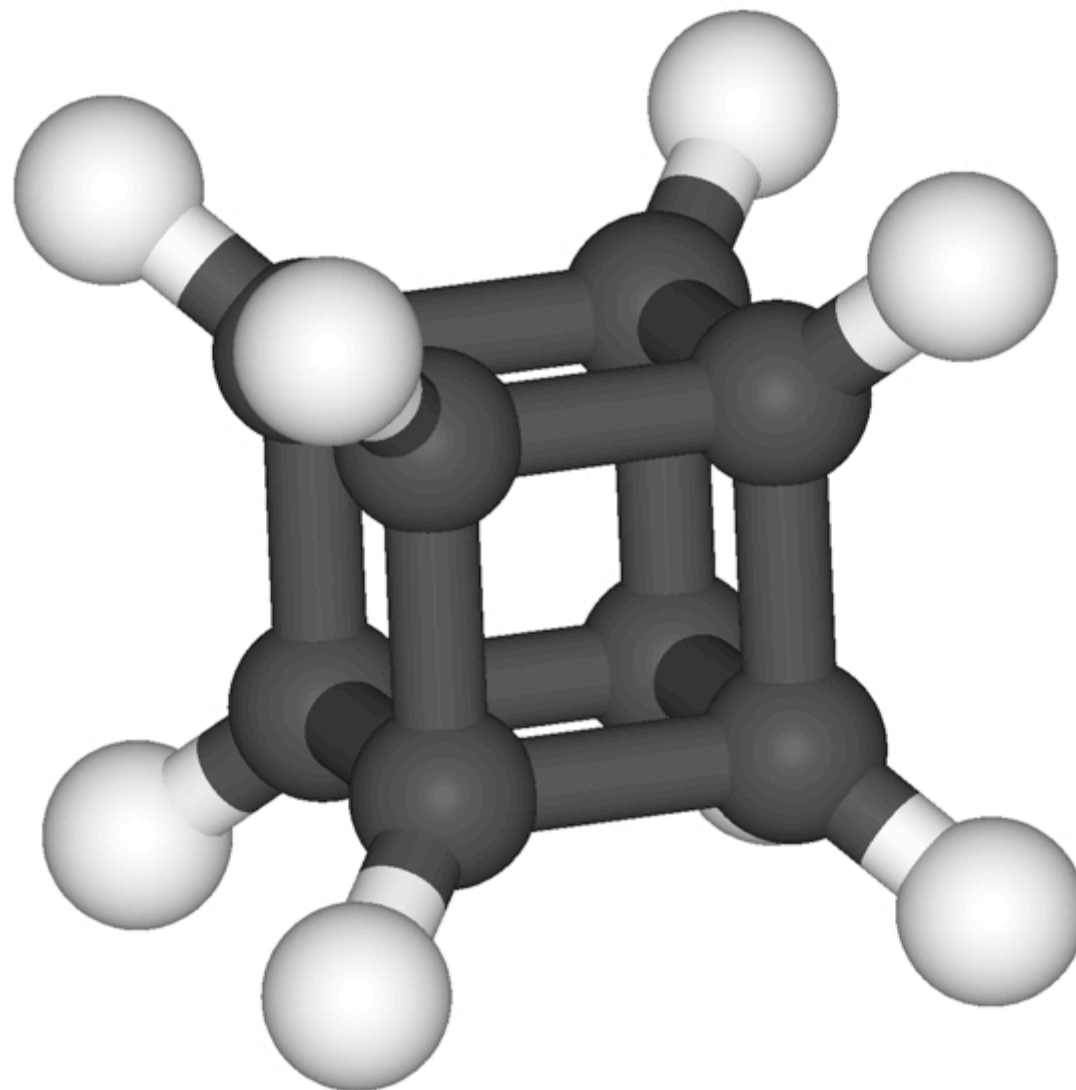
cyclopentane  
 $C_5H_{10}$

# Hydrocarbons



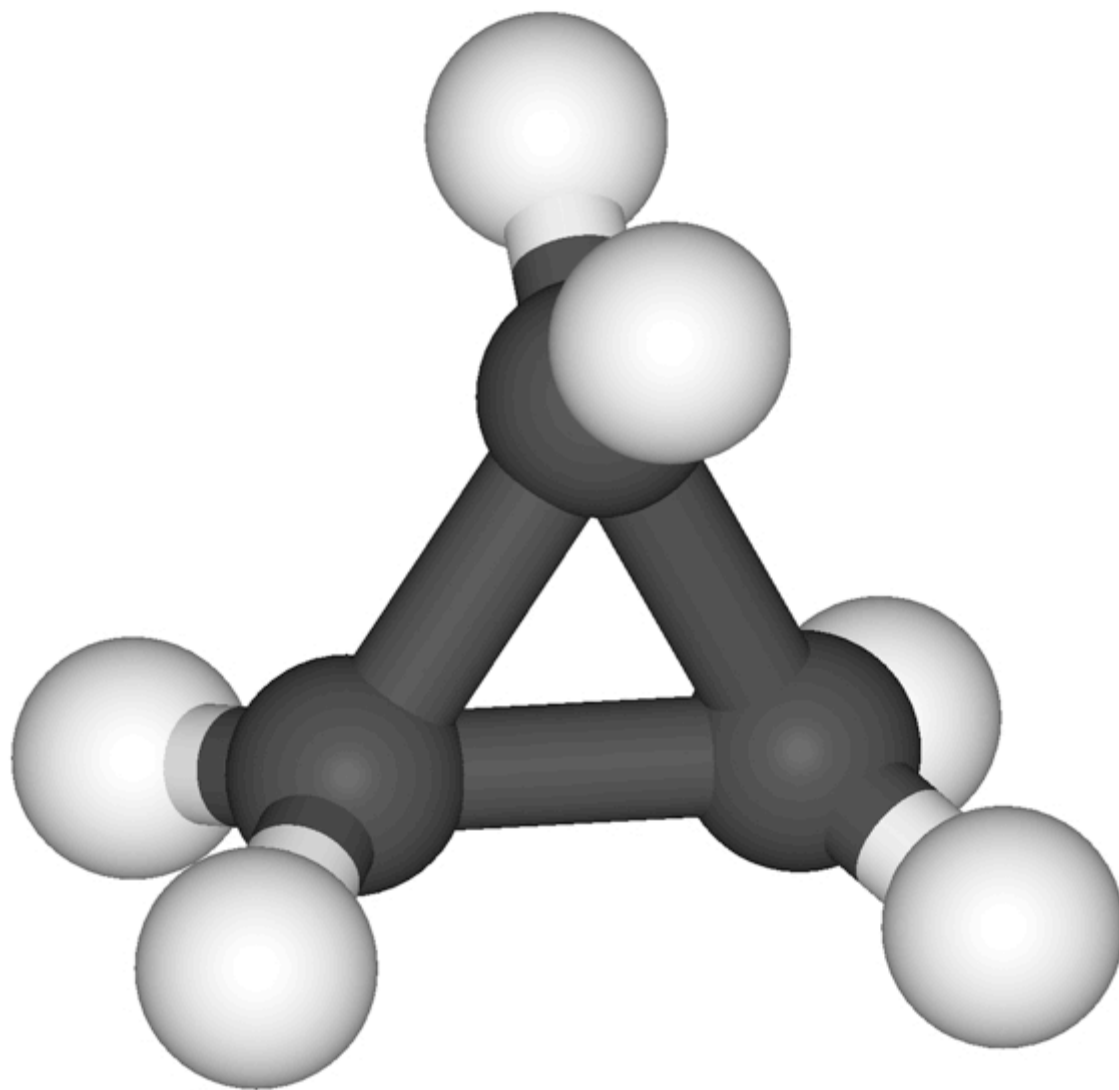
cyclobutane  
 $C_4H_8$

# Hydrocarbons



cubane  
 $C_8H_8$

# Hydrocarbons



cyclopropane  
 $C_3H_6$