Chemistry and the material world

123.102

Lecture 3

- Electronic bookkeeping
  - we need a way of finding out in which proportions two or more atoms make up a molecule – is it CH_3 or CH_4 or CH_5?
  - counting valence electrons – the Octet Rule
  - Step by step construction of a Lewis structure
  - exceptions to the Octet Rule
- Valence Shell Electron Pair Repulsion – VSEPR
  - getting up to shape
  - lone pairs
  - multiple bonds
  - problems and exceptions to VSEPR theory

The Octet Rule

Compounds are most stable if all atoms have filled valence shells

- applies to main group elements (s and p block).
- a filled valence shell can be achieved by either adding **or** removing electrons.
- we are trying to create a *noble gas configuration*.

The elements of group 18 (8th main group) are called noble gases because they will not readily react with any other element to form molecules – including themselves.

- This means that they naturally occur in atomic form.
- Their stability comes from their very stable electron configuration.
- Let's compare:

He: $1s^2$	s^2	[He]
Ne: $1s^2\ 2s^2\ 2p^6$	$s^2\ p^6$	[Ne]
Ar: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$	$s^2\ p^6$	[Ar]

How can other elements achieve a noble gas configuration?

Example 1 – sodium:

Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$	s^1	$[Ne]s^1$	...one electron too many or seven electrons short.
Na^+: $1s^2\ 2s^2\ 2p^6\ 3s^0$	s^0	[Ne]	noble gas configuration

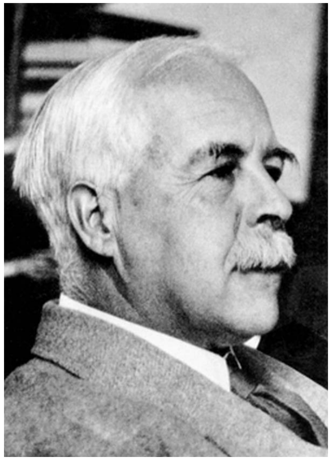
How can other elements achieve a noble gas configuration?

Example 2 – fluorine:

F: $1s^2\ 2s^2\ 2p^5$	$s^2\ p^5$	$[He]2s^2\ 2p^5$	...one electron short or seven too many.
F^-: $1s^2\ 2s^2\ 2p^6$	$s^2\ p^6$	[Ar]	noble gas configuration.

Rules for drawing Lewis structures

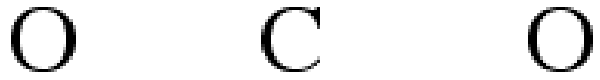
- Write down the chemical symbols of all atoms in the molecule.
- Place one dot for every valence electron around each atom.
- Form bonds by connecting dots until each atom is surrounded by 8 electrons (hydrogen and helium: 2 electrons)
  - The electron count includes all valence electrons of an atom **plus** valence electrons of other atoms which are connected by a bond.



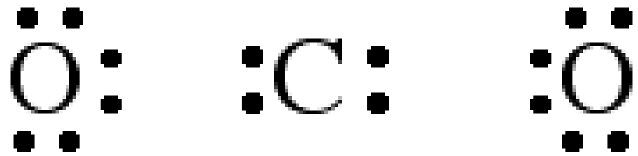
Gilbert N .Lewis
1875 – 1946, United States

Example 1 – carbon dioxide, CO_2

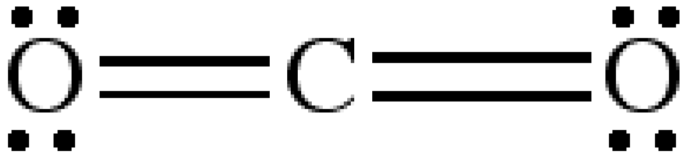
Step 1:
Write down chemical symbols



Step 2:
One dot per valence electron

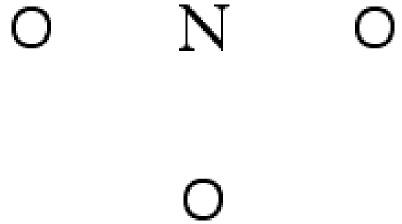


Step 3:
Connect the dots

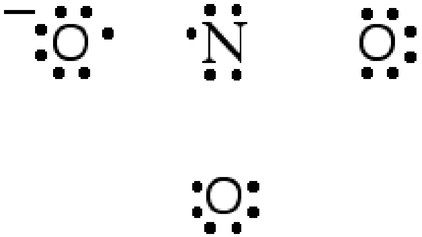


Example 2 – nitrate, NO_3^-

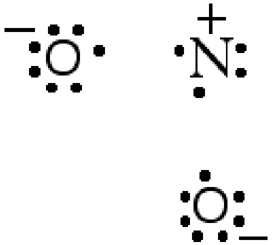
Step 1:
Write down chemical symbols



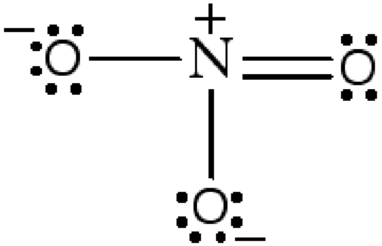
Step 2:
One dot per valence electron



Step 3:
Share the electrons

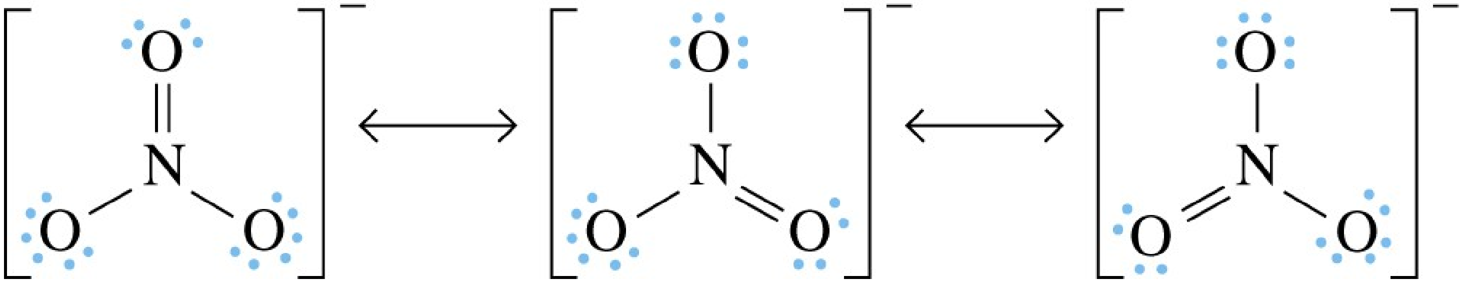


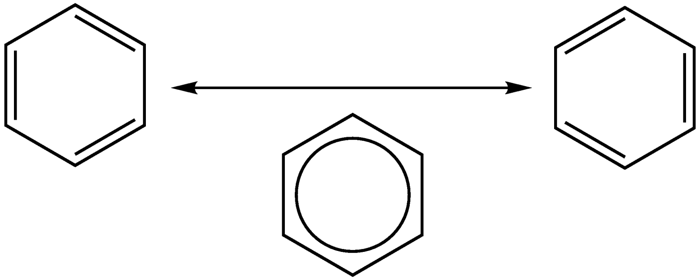
Step 4:
Connect the dots



Intermission – resonance structures

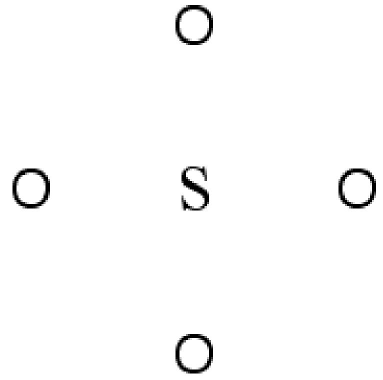
- Often there is more than one way to create a correct Lewis Structure.
- This means that each single Lewis structure is not an accurate representation of the molecule.
- The true structure is a combination of all possible Lewis structures
- These structures are then called *resonance structures*



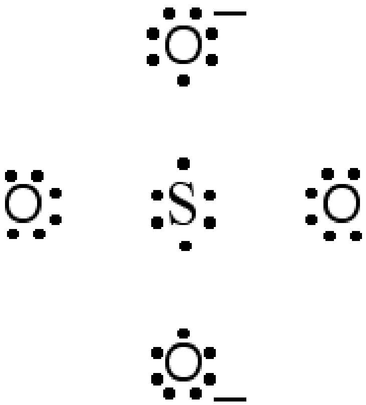


Example 3 – sulfate, SO_4^{2-}

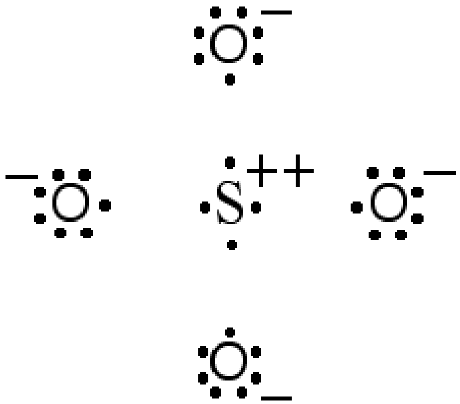
Step 1:
Write down chemical symbols



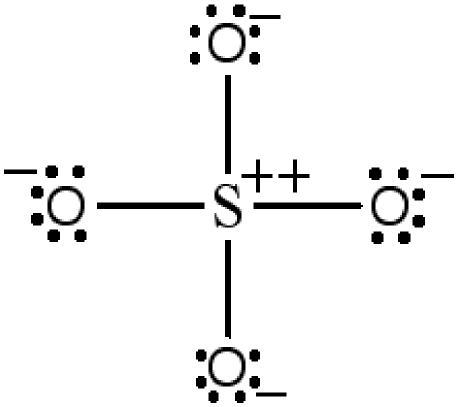
Step 2:
One dot per valence electron



Step 3:
Share the electrons



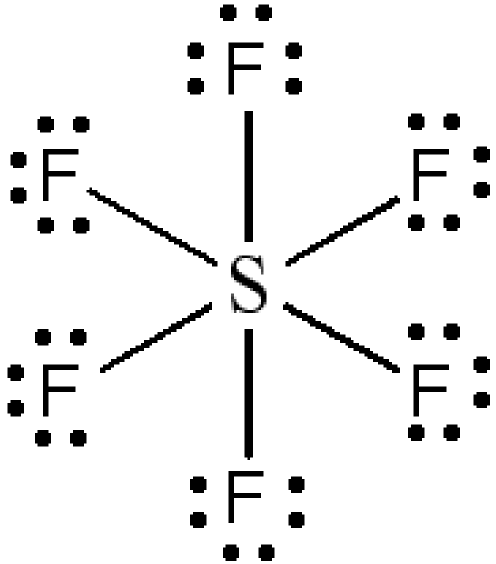
Step 4:
Connect the dots



The octet rule is not without exception!

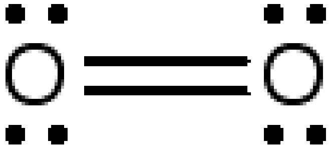
SF_6 is a good example:

- Each fluorine atom has 7 electrons.
- The sulphur atom has 6 electrons.
- By bonding each fluorine atom to the central sulphur atom it seems as though there are 12 electrons in the valence shell of the S atom.
- This type of bonding is more complicated than Lewis Structures allow for.
- Molecules like SF_6 are called *hypervalent* or, more recently, *hypercoordinated*.



The octet rule is not without exception!

another good example is O_2:



- The Lewis Structure is very simple.
- All electrons are paired, either in bonds or in lone pairs.
- Magnetic measurements confirm that O_2 has a magnetic moment.
- Two electrons are actually unpaired!

Lewis structures tell us how the valence electrons are distributed among the atoms, but they not tell us how the atoms are arranged in three-dimensional space – the shape of the molecule.

Valence Shell Electron Pair Repulsion – VSEPR

- The molecular shape is primarily determined by the repulsion between electron pairs in the molecule.
- To minimize this repulsion atoms will be situated in a way that electron pairs are as far apart as possible.
- Lone Pairs, electron pairs that reside exclusively at one atom, take up more space than electron pairs engaged in a bond.

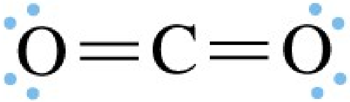
Regular patterns emerge when one tries to maximize the space between electron pairs:

# of connected atoms (incl. lone pairs)	No lone pairs	One lone pair	Two lone pairs
2	linear		
3	trigonal planar	bent (~120°)	
4	tetrahedral	trigonal pyramidal	bent (~109°)
5	trigonal bipyramidal	saw horse	T shaped
6	octahedral	square pyramidal	square planar

2 sets of bonds, no lone pair

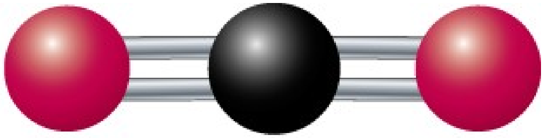
In CO_2 there are two sets of bonds connecting the central atom (C) with the oxygen atoms (O).

The arrangement which maximizes the distance between those sets of bonds is shown below – linear.



$O=C=O$

two sets of electron pairs around the C atom

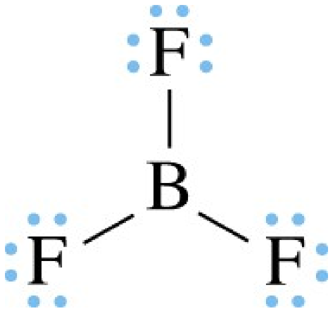


linear shape
bond angle = 180°

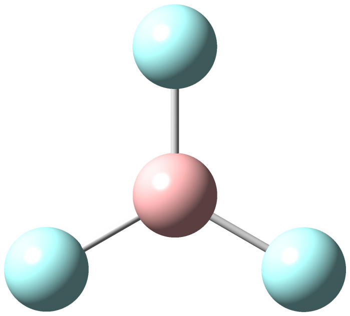
3 sets of bonds, no lone pair

In BF_3 there are three sets of bonds connecting the central atom (B) with the fluorine atoms (F).

The arrangement which maximizes the distance between those sets of bonds is shown below – trigonal planar.



Three sets of electron pairs around the B atom

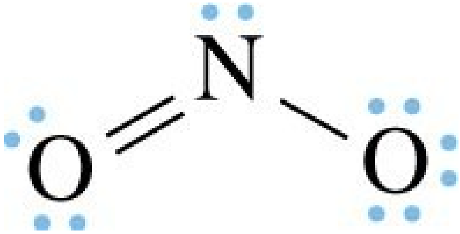


trigonal planar shape
bond angle = 120°

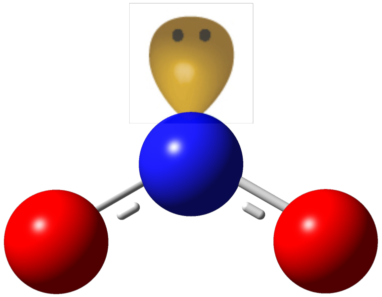
2 sets of bonds and one lone pair

In NO_2 there are two sets of bonds connecting the central atom (N) with the oxygen atoms (O). There is also one lone pair on the central nitrogen atom.

The arrangement which maximizes the distance between those sets of bonds is shown below – bent.



Three sets of electron pairs incl. a lone pair around the N atom

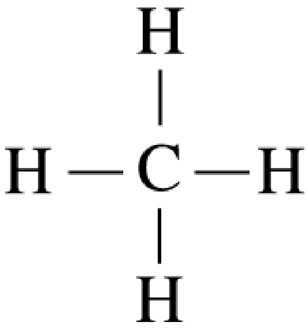


bent shape
bond angle < 120°

4 sets of bonds, no lone pair

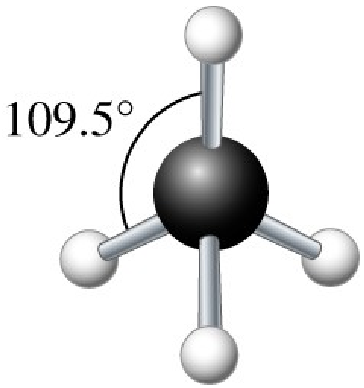
In CH_4 there are four sets of bonds connecting the central atom (C) with the hydrogen atoms (H).

The arrangement which maximizes the distance between those sets of bonds is shown below – tetrahedral.



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Four sets of electron
pairs around the C atom

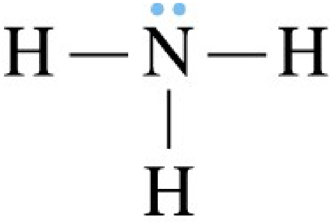


tetrahedral shape
bond angle = 109.5°

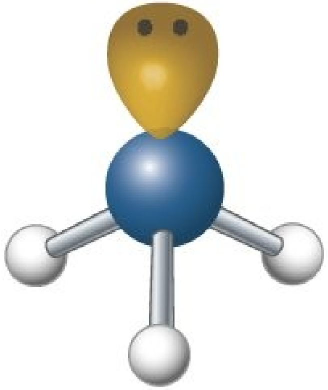
3 sets of bonds and one lone pair

In NH_3 there are three sets of bonds connecting the central atom (N) with the hydrogen atoms (H). There is also one lone pair on the central nitrogen atom.

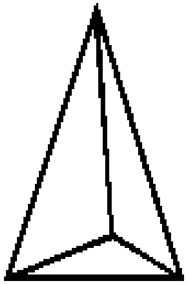
The arrangement which maximizes the distance between those sets of bonds is shown below – trigonal pyramidal.



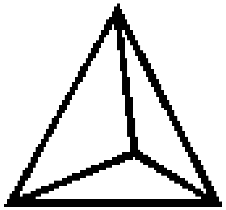
Four sets of electron pairs incl. one lone pair around the N atom



trigonal pyramidal
bond angle < 109.5°



trigonal pyramid:
a pyramid on a
trigonal base.

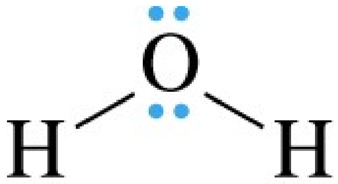


tetrahedron:
all sides are identical

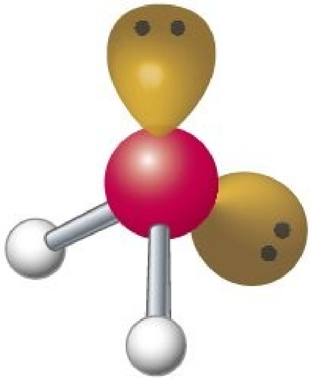
2 sets of bonds and two lone pairs

In OH_2 (usually written as H_2O) there are two sets of bonds connecting the central atom (O) with the hydrogen atoms (H). There are also two lone pairs on the oxygen atom.

The arrangement which maximizes the distance between those sets of bonds is shown below – bent.



Four sets of electron pairs incl. to lone pairs around the O atom

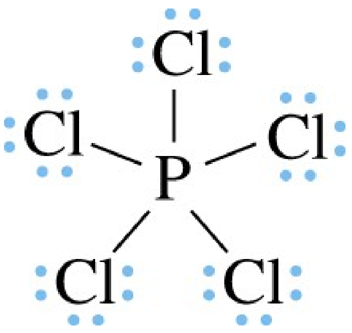


bent shape
bond angle < 109.5°

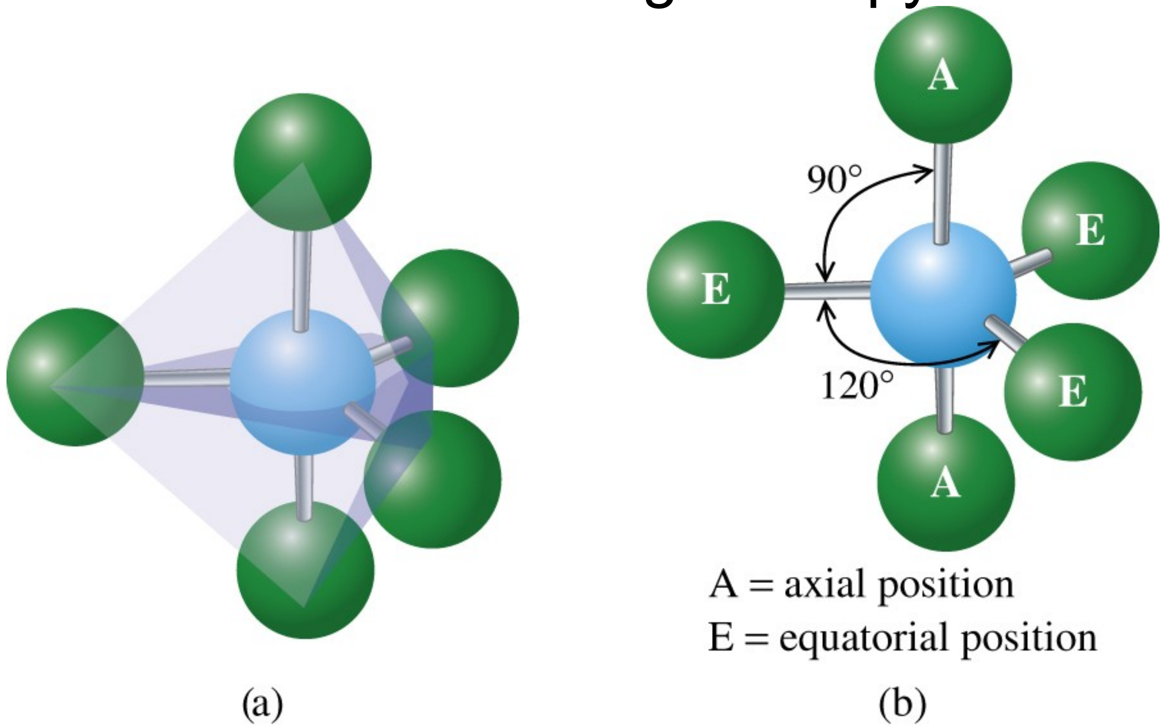
5 sets of bonds, no lone pair

In PCl_5 there are five sets of bonds connecting the central phosphorous atom (P) with the chlorine atoms (Cl).

The arrangement which maximizes the distance between those sets of bonds is shown below – trigonal bipyramidal.



Five sets of electron pairs around the P atom

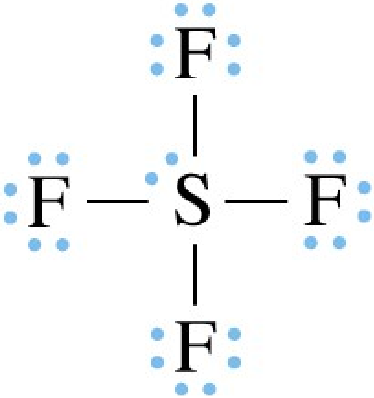


trigonal bipyramidal shape
bond angles = 90° and 120°

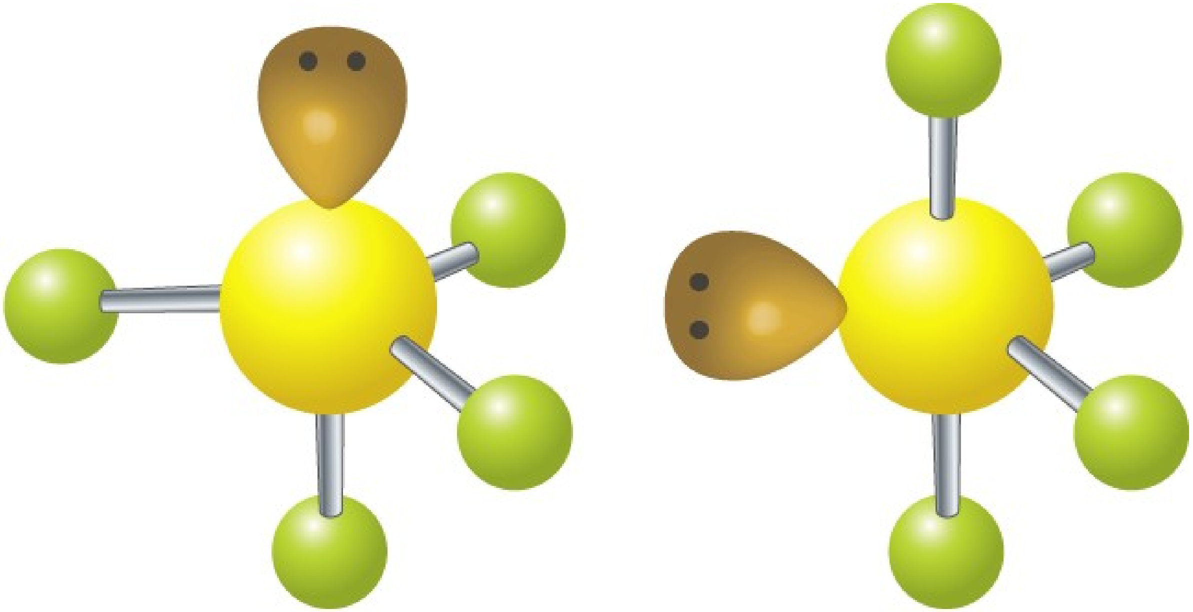
4 sets of bonds and one lone pair

In SF_4 there are four sets of bonds connecting the central sulfur atom (S) with the chlorine atoms (F). There is also one lone pair on the central sulfur atom.

The arrangement which maximizes the distance between those sets of bonds is shown below – seesaw



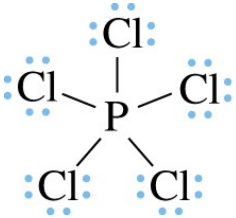
Five sets of electron pairs incl. one lone pair around the S atom



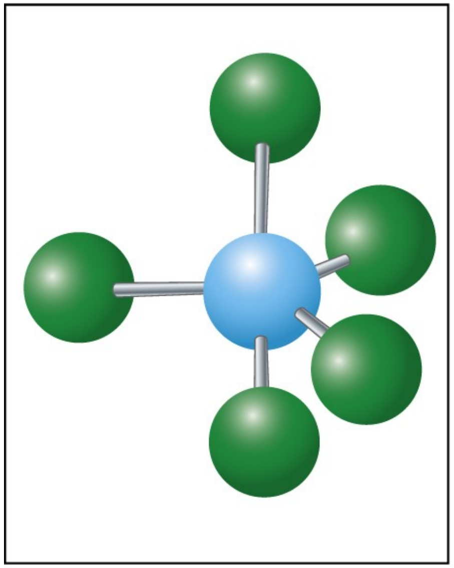
trigonal pyramid

seesaw

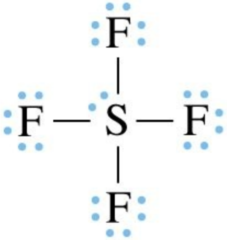
lone pairs always occupy equatorial positions



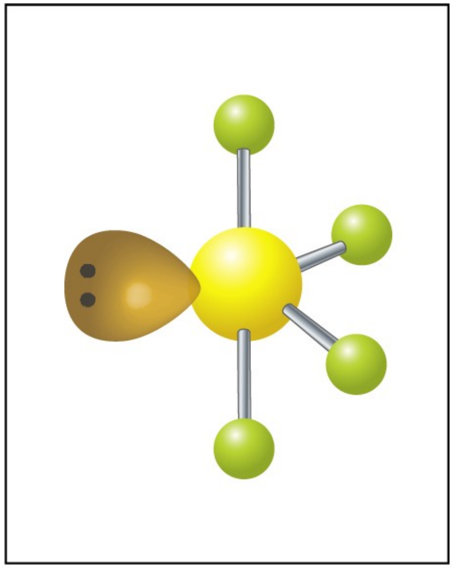
trigonal bipyramidal



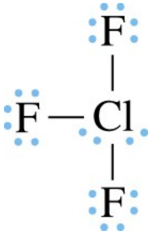
PCl_5
lone pairs = 0



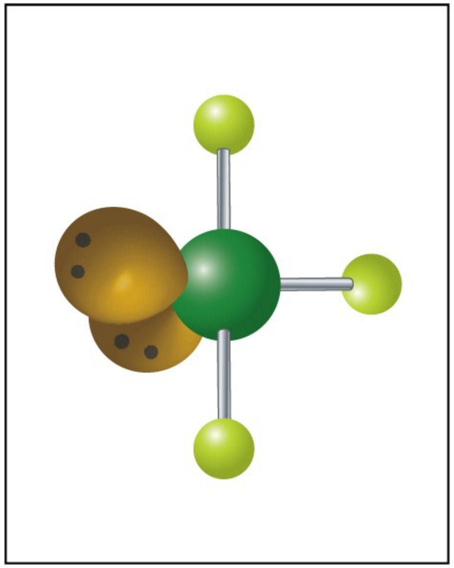
seesaw



SF_4
lone pairs = 1

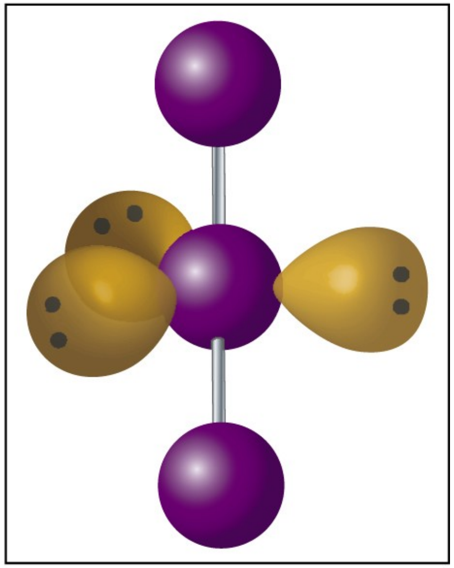


T-shaped



ClF_3
lone pairs = 2

linear

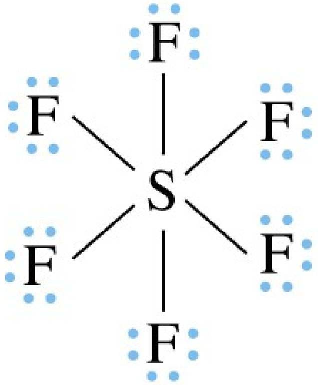


I_3^-
lone pairs = 3

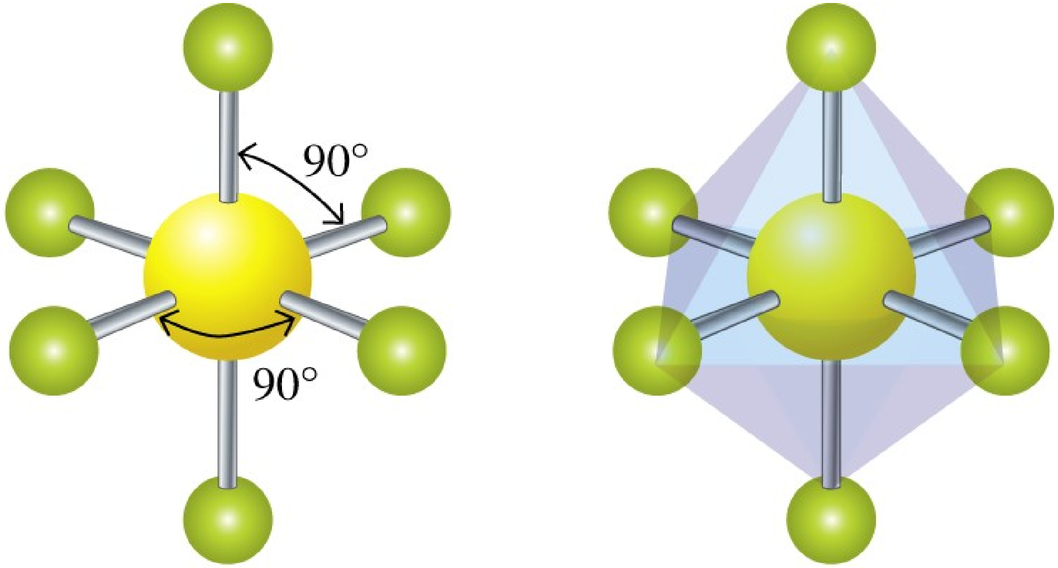
6 sets of bonds, no lone pairs

In SF_6 there are six sets of bonds connecting the central sulfur atom (S) with the fluorine atoms.

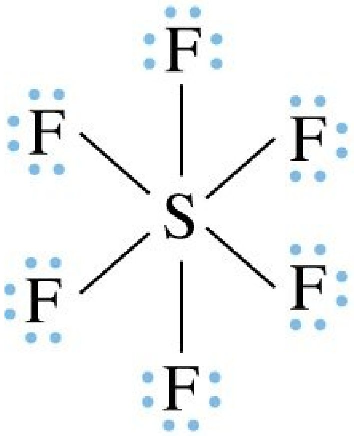
The arrangement which maximizes the distance between those sets of bonds is shown below – octahedral



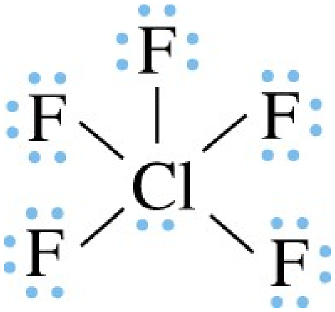
Six sets of electron pairs around the central S atom



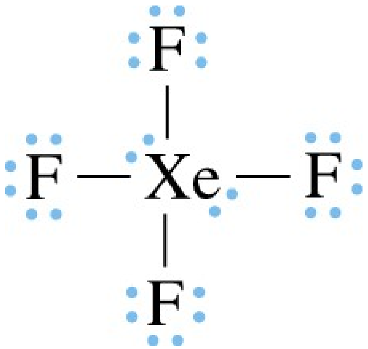
octahedral shape – all bond angles = 90°



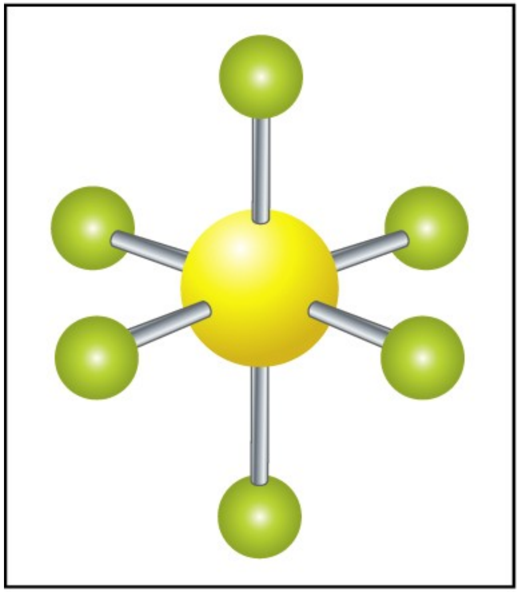
octahedral



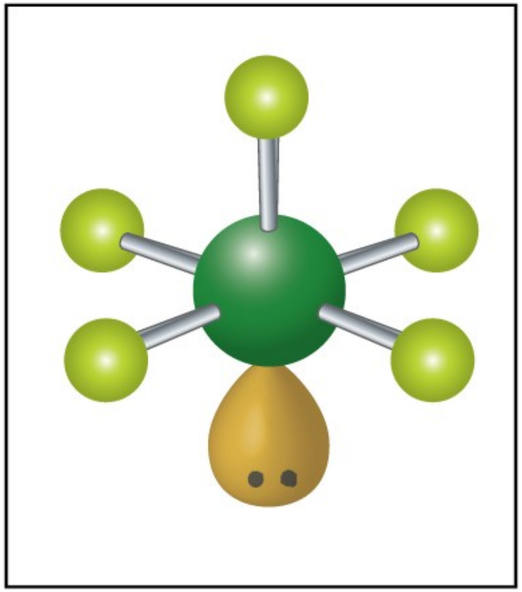
square pyramidal



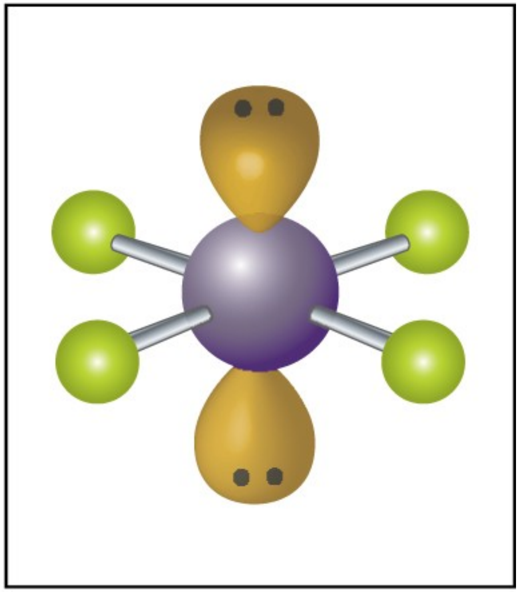
square planar



SF_6
lone pairs = 0



ClF_5
lone pairs = 1



XeF_4
lone pairs = 2

VSEPR theory does have exceptions

The fluorides of the alkaline earth metals BeF_2, MgF_2, CaF_2, SrF_2 and BaF_2 are all predicted to be linear by VSEPR.

Unfortunately SrF_2 and BaF_2 were confirmed to be bent by gas phase experiments.

Today we covered:

- The octet rule and how it relates to the electron configuration of noble gases.
- How to construct a Lewis Structure step by step.
- How sometimes resonance structures occur.
- Exceptions to the octet rule – like SF_6 and O_2.
- How to predict the three dimensional shape of a molecule with Valence Shell Electron Pair Repulsion theory (VSEPR).
- How the molecular shape can be derived from simple geometrical figures if we know the valence configuration.
- Exceptions to VSEPR theory.