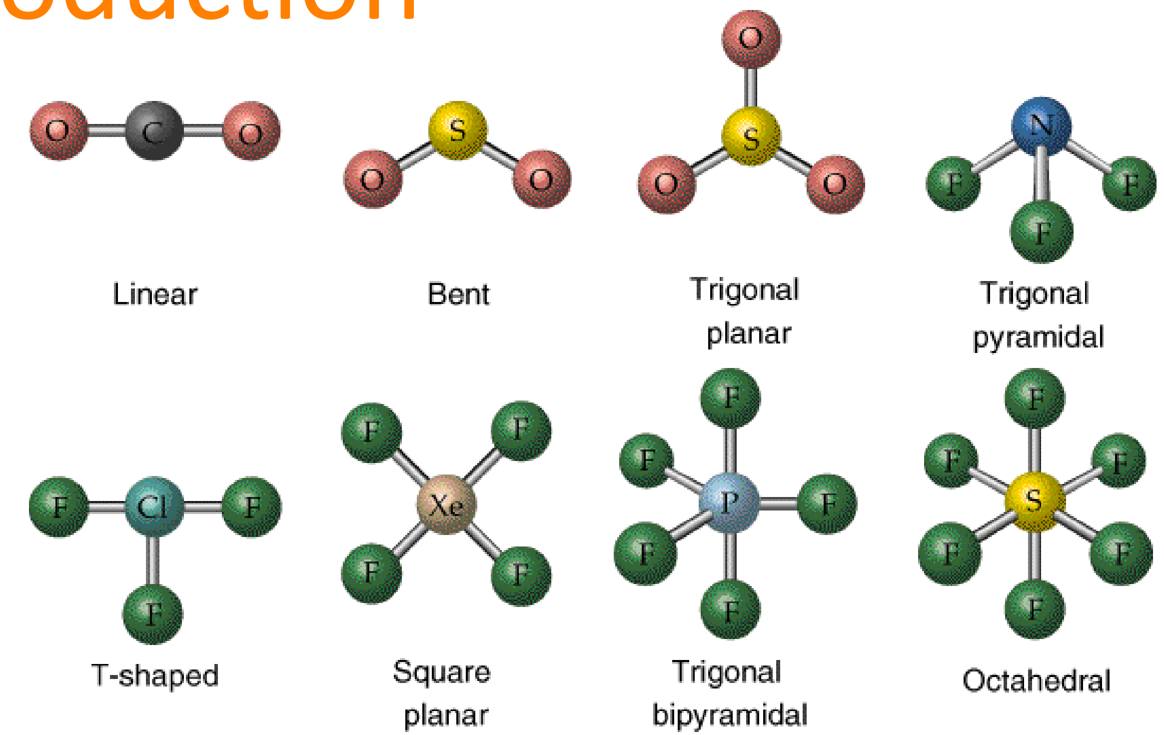
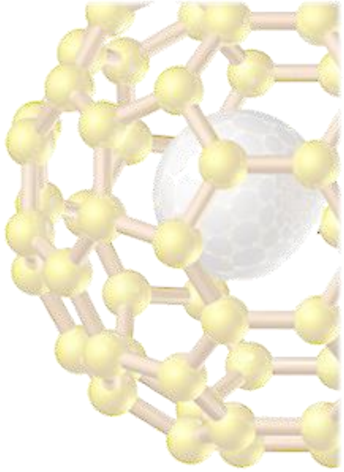
AH Chemistry – Unit 1

Shapes of Molecules and Polyatomic Ions

Introduction

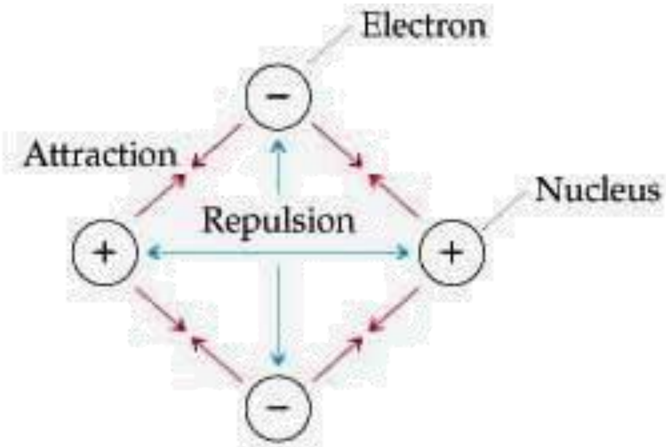


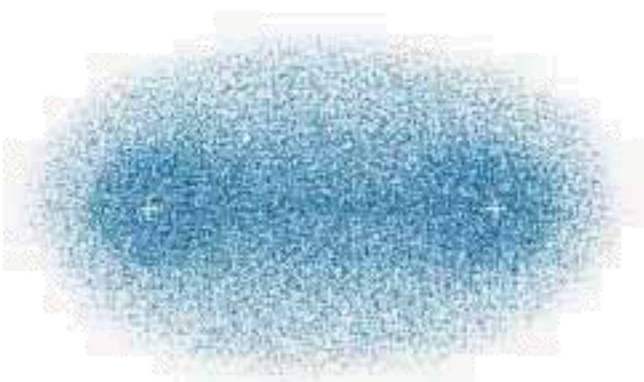


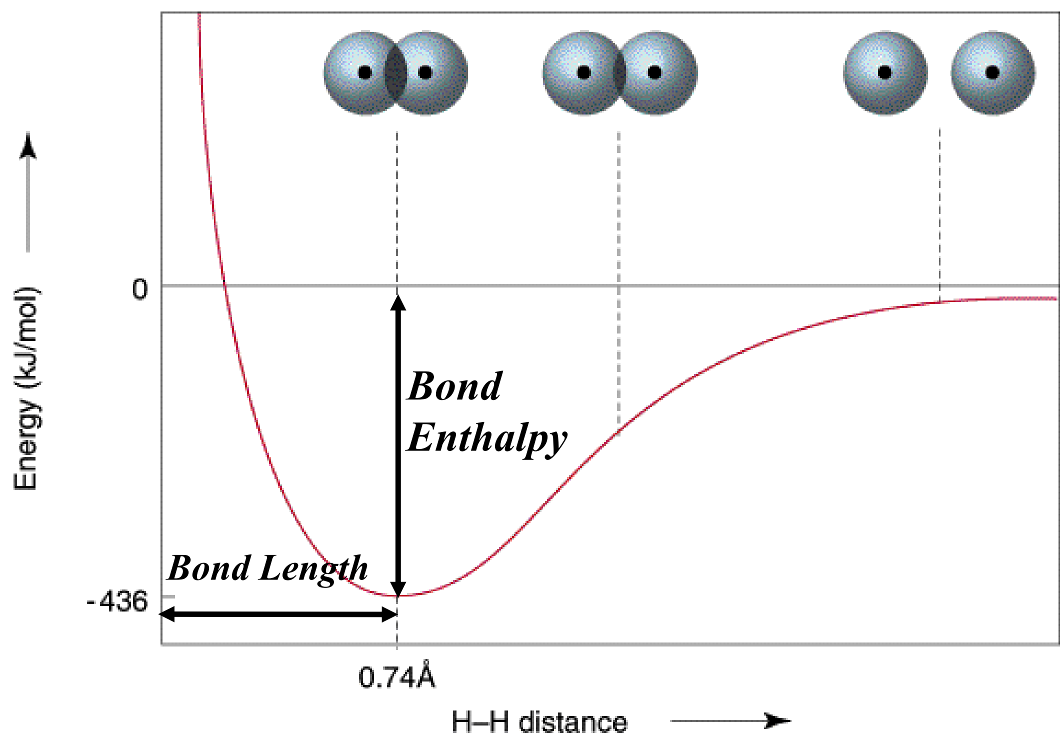
This topic explores further aspects of ***Covalent Bonding***, leading to an understanding of the ***Shapes*** of molecules & polyatomic ions

Covalent Bonding

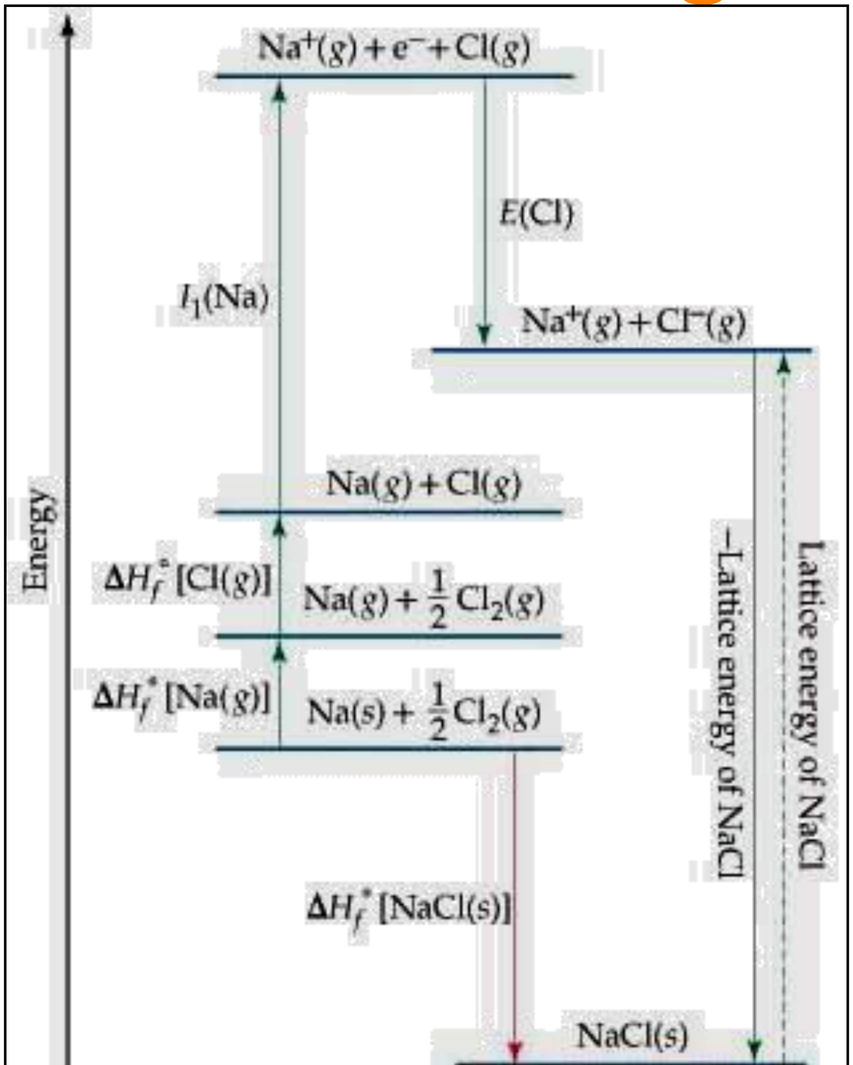
A ***Covalent Bond*** will form when atoms can rearrange their electrons (by ***sharing***) to produce an arrangement of ***lower energy***.







Ionic Bonding

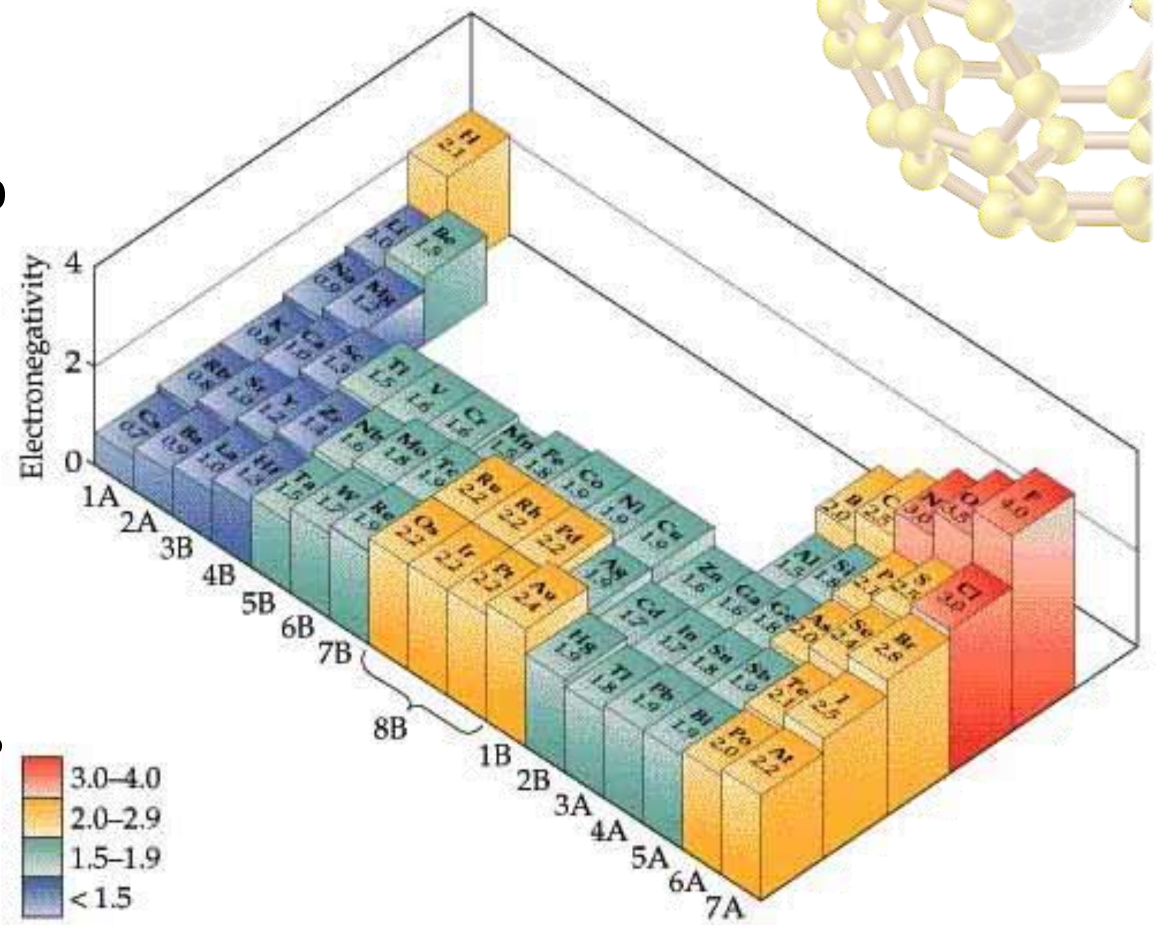


An ***Ionic Bond*** will form when atoms can rearrange their electrons (***transfer***) to produce an arrangement of ***lower energy***.

Despite the advantage gained by achieving a ***'stable octet'*** , the real driving force behind ionic bonding is the stability of the ***Ionic Lattice*** formed.

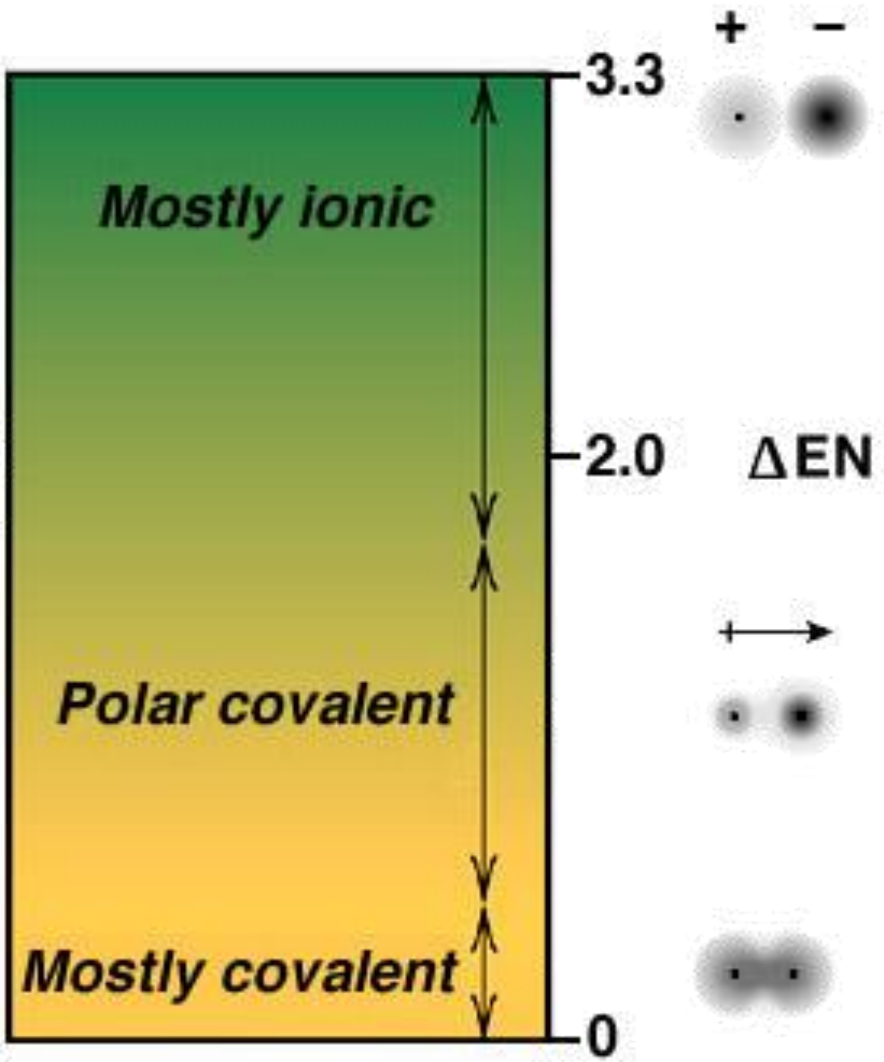
Electronegativity 1

Ionic and Covalent are, in fact, rather arbitrary labels and it is no longer enough to simply look to see if a metal element is involved or not.



Electronegativity values are a useful guide but properties will still need to be studied to provide confirmation.

Electronegativity 2

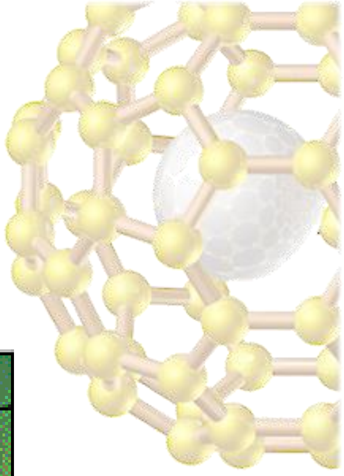


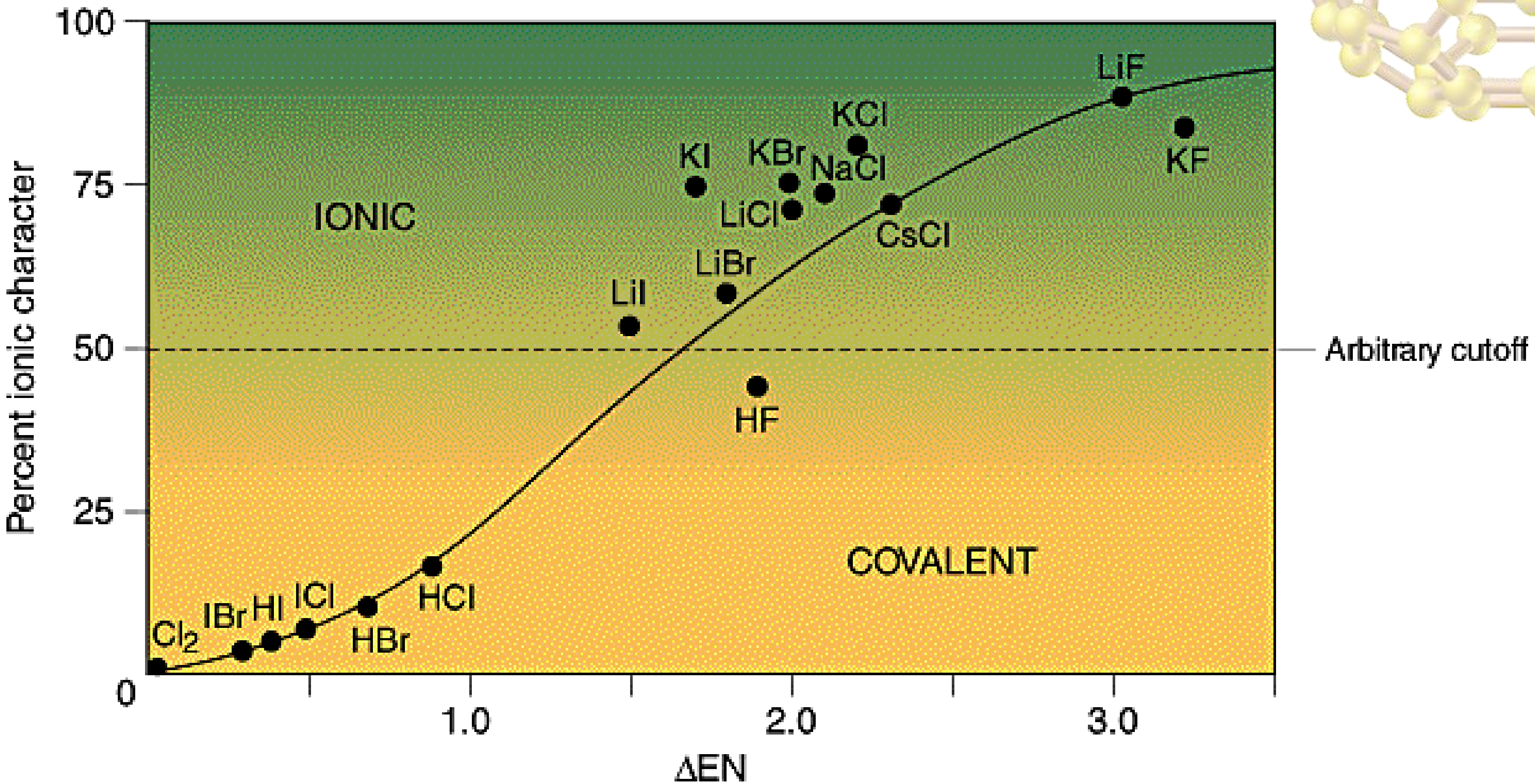
Ionic and Covalent are just opposite ends of a ***bonding continuum***

Most bonds lie between these two extremes.

ΔEN	IONIC CHARACTER
>1.7	Mostly ionic
0.4-1.7	Polar covalent
<0.4	Mostly covalent
0	Nonpolar covalent

Electronegativity 3





Bonding Diagrams

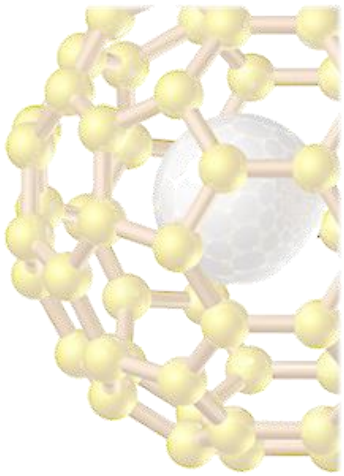


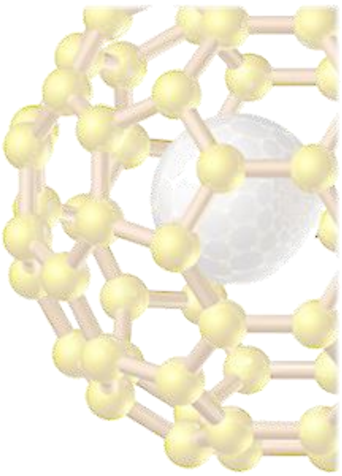
TABLE 8.1 Electron-Dot Symbols

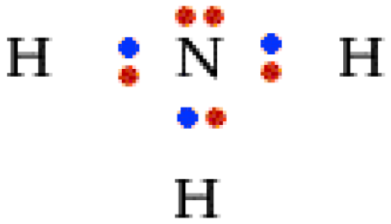
Element	Electron Configuration	Electron-Dot Symbol
Li	[He]$2s^1$	Li•
Be	[He]$2s^2$	•Be•
B	[He]$2s^2 2p^1$	•Ḃ•
C	[He]$2s^2 2p^2$	•Ċ̣•
N	[He]$2s^2 2p^3$	•Ṇ̇:
O	[He]$2s^2 2p^4$	:Ọ̇:
F	[He]$2s^2 2p^5$	•F̤̈:
Ne	[He]$2s^2 2p^6$	:N̤̈e:

Various methods (***models***) can be used to explain the properties associated with covalent bonding.

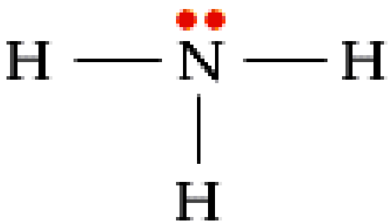
One useful model positions electrons (both bonding and non-bonding) around atoms at 'four corners'. These are sometimes called ***Lewis Diagrams***

Bonding Structures

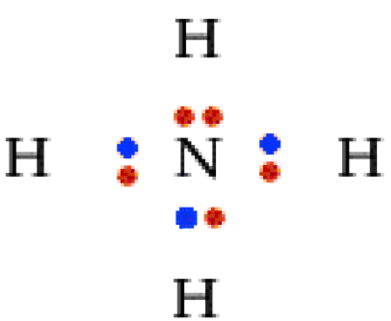




In Ammonia the central nitrogen atom has 4 electron pairs, the ***'stable octet'***

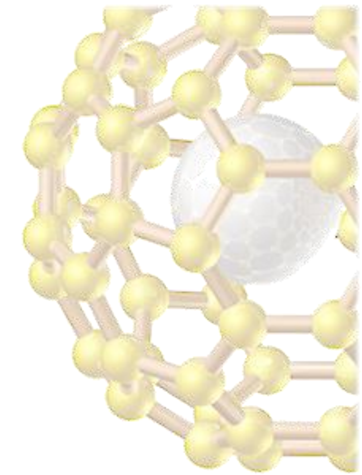


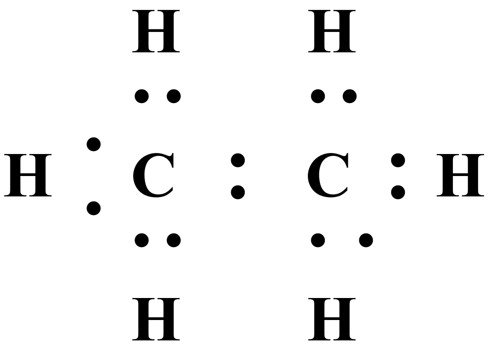
There are 3 ***'bonding pairs'*** and 1 ***'non-bonding pair'*** - often referred to as a ***'lone pair'***



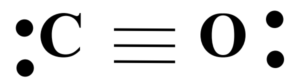
Sometimes atoms will use a lone pair as a bonding pair to form a ***Dative*** or ***Coordinate*** Covalent bond, as in the Ammonium ion, NH_4^+

More Bonding Structures

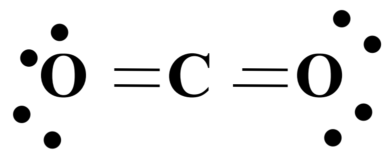




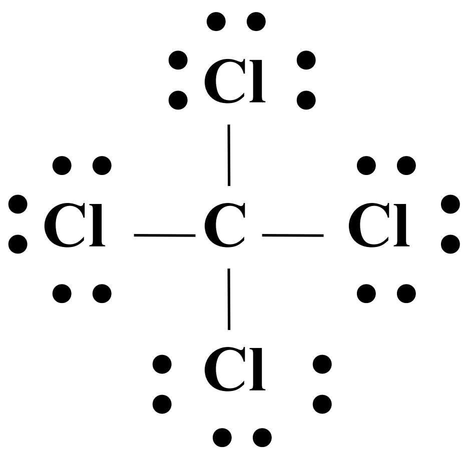
Ethane



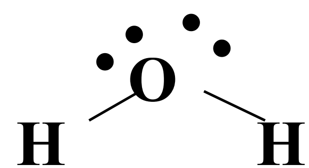
CO Carbon Monoxide



CO_2 Carbon Dioxide

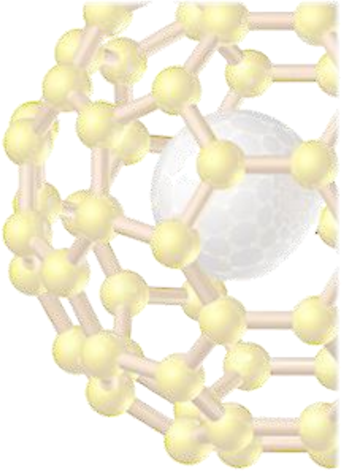


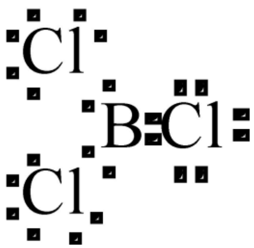
CCl_4 Carbon Tetrachloride



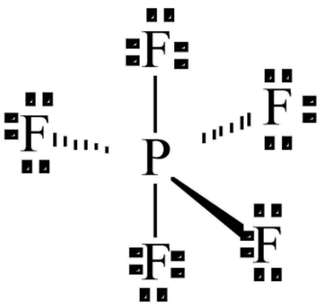
H_2O Water
Hydrogen Oxide

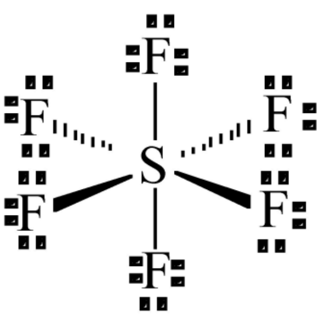
Unusual Bonding





In both these molecules, the Be and B atoms do not achieve a '***stable octet***'. The resulting molecules are, predictably, very reactive (unstable).



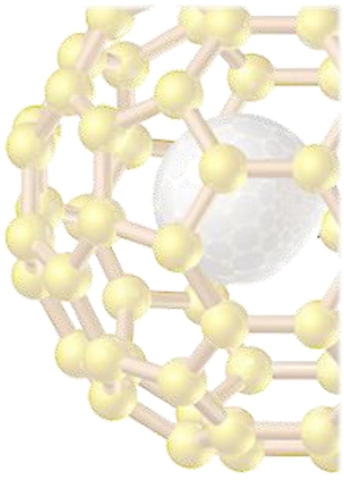


In both these molecules, the P and S atoms have in excess of a 'stable octet'.

The extra orbitals needed, to cope with more than 8 electrons, come from the empty ***d-orbital*** set.

This 'mixing' of orbitals is called ***hybridisation***

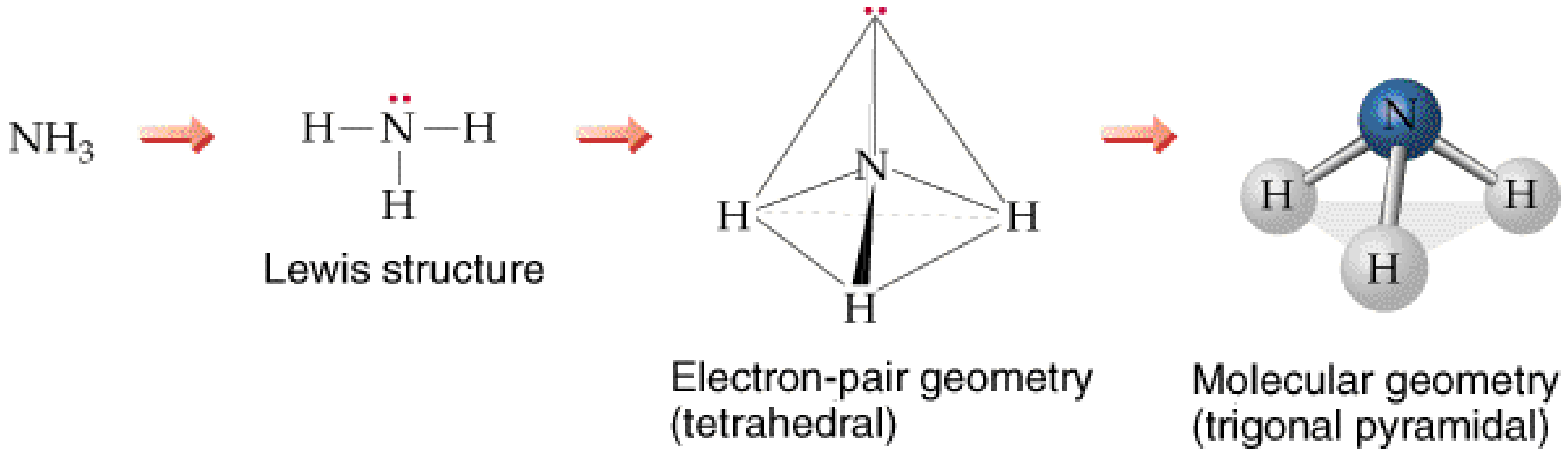
Shapes of Molecules



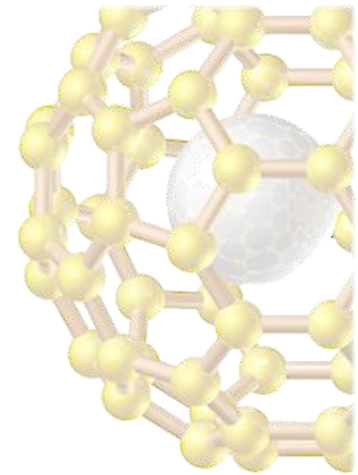
In order to predict molecular shape, we consider that ***all*** outer shell electrons (***valence electrons***) of the central atom repel each other. Therefore, the molecule adopts whichever 3D geometry ***minimizes this repulsion***.

Both ***bonding*** and ***non-bonding*** electron pairs must be considered.

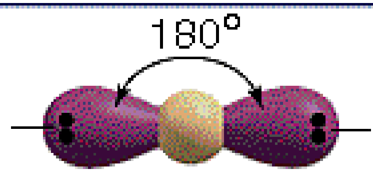
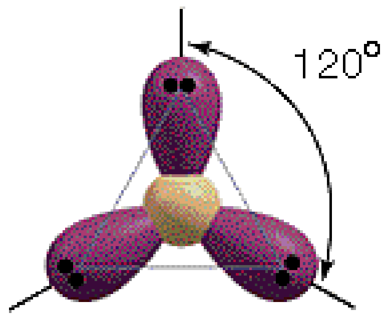
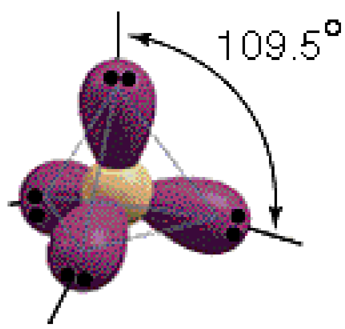
We call this process the *Valence Shell Electron Pair Repulsion* (***VSEPR***) theory.



Electron Pair Geometry 1

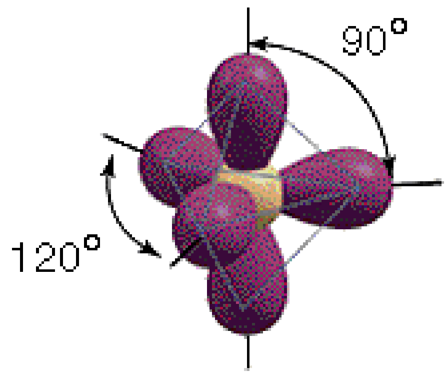
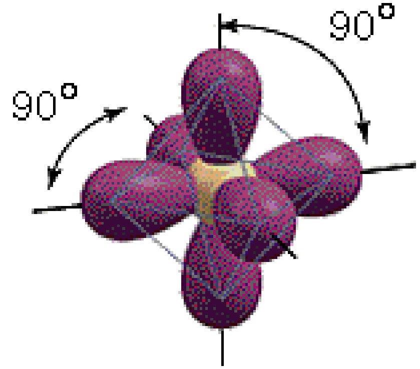


ELECTRON-PAIR GEOMETRIES AS A FUNCTION OF THE NUMBER OF ELECTRON PAIRS

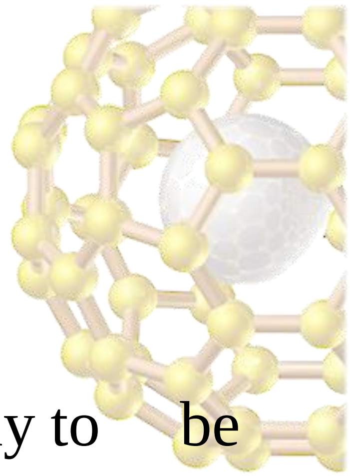
Number of Electron Pairs	Arrangement of Electron Pairs	Electron-Pair Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°

Electron Pair Geometry 2

ELECTRON-PAIR GEOMETRIES AS A FUNCTION OF THE NUMBER OF ELECTRON PAIRS

Number of Electron Pairs	Arrangement of Electron Pairs	Electron-Pair Geometry	Predicted Bond Angles
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90° 180°

Counting Electron Pairs



It is important not to confuse the ***number of atoms*** with the ***number of electron pairs***.

For example, CF_4 and XeF_4 may, at first sight, appear likely to be the same shape.

Electron pairs = electrons of central atom + no. of atoms attached

divided by 2

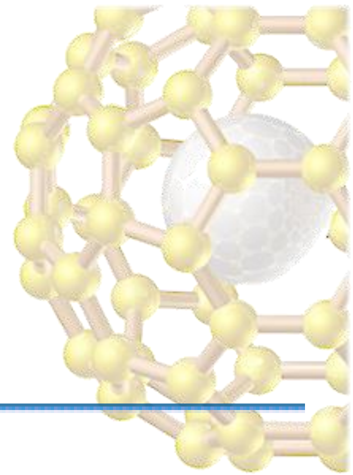
$$CF_4 = \frac{4 + 4}{2}$$

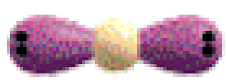
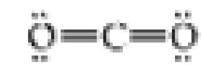
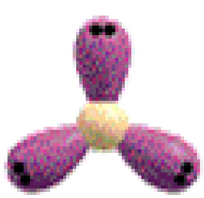
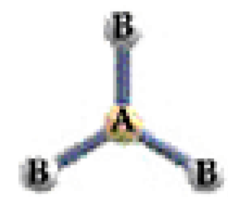
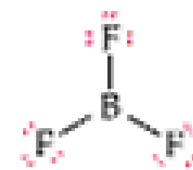
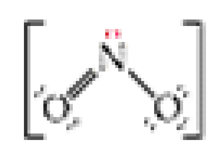
= ***4 electron pairs***

$$XeF_4 = \frac{8 + 4}{2}$$

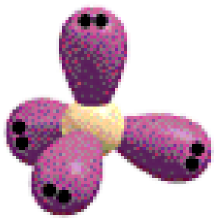
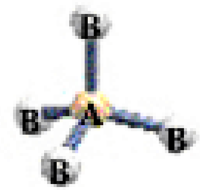
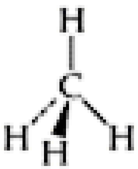
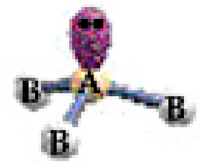
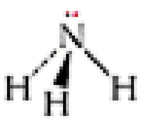
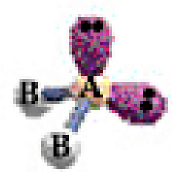
= ***6 electron pairs***

Molecular Geometry 1

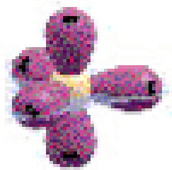
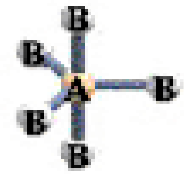
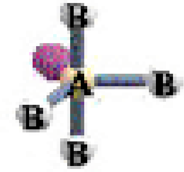
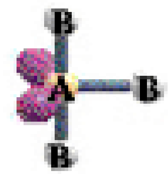


Total Electron Pairs	Electron-Pair Geometry	Bonding Pairs	Nonbonding Pairs	Molecular Geometry	Example
2 pairs	 Linear	2	0	 Linear	
3 pairs	 Trigonal planar	3	0		
		2	1	 Bent	

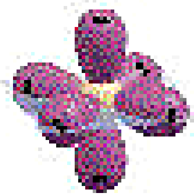
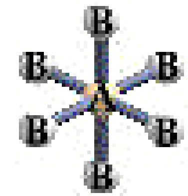
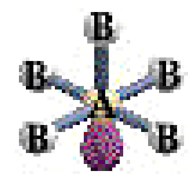
Molecular Geometry 2

Total Electron Pairs	Electron-Pair Geometry	Bonding Pairs	Nonbonding Pairs	Molecular Geometry	Example
4 pairs	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramid	
		2	2	 Bent	

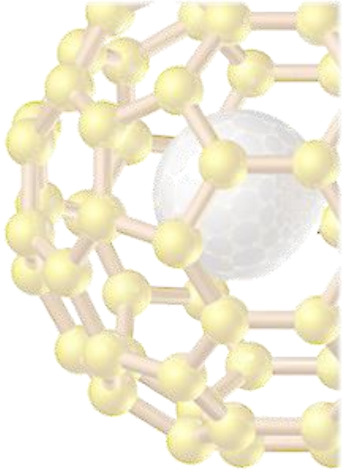
Molecular Geometry 3

Number of Electron Pairs	Electron-Pair Geometry	Bonding Pairs	Nonbonding Pairs	Molecular Geometry	Example
5 pairs	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2

Molecular Geometry 4

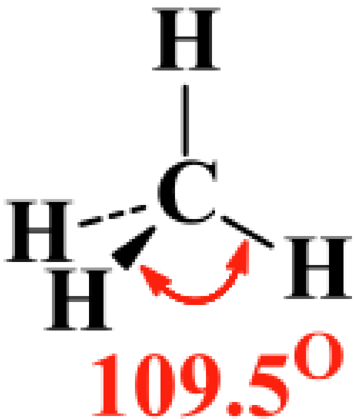
Number of Electron Pairs	Electron-Pair Geometry	Bonding Pairs	Nonbonding Pairs	Molecular Geometry	Example
6 pairs	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

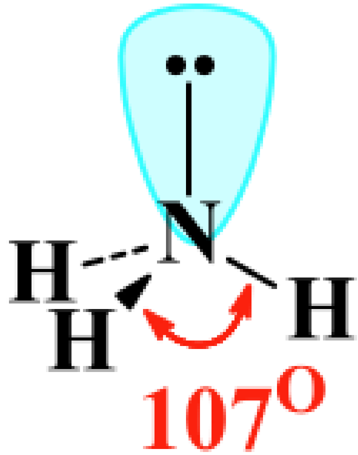
Repulsive Forces 1

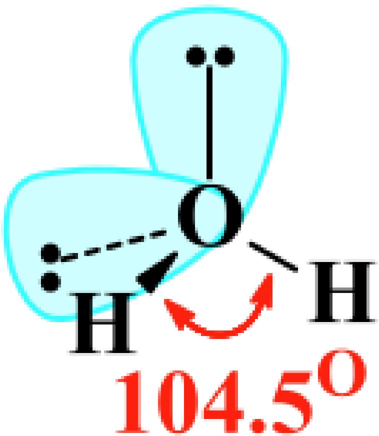


Bonding electrons, because they are attracted by two nuclei, do not repel as much as non-bonding electrons.

This can cause ‘distortions’ in the shapes of molecules:







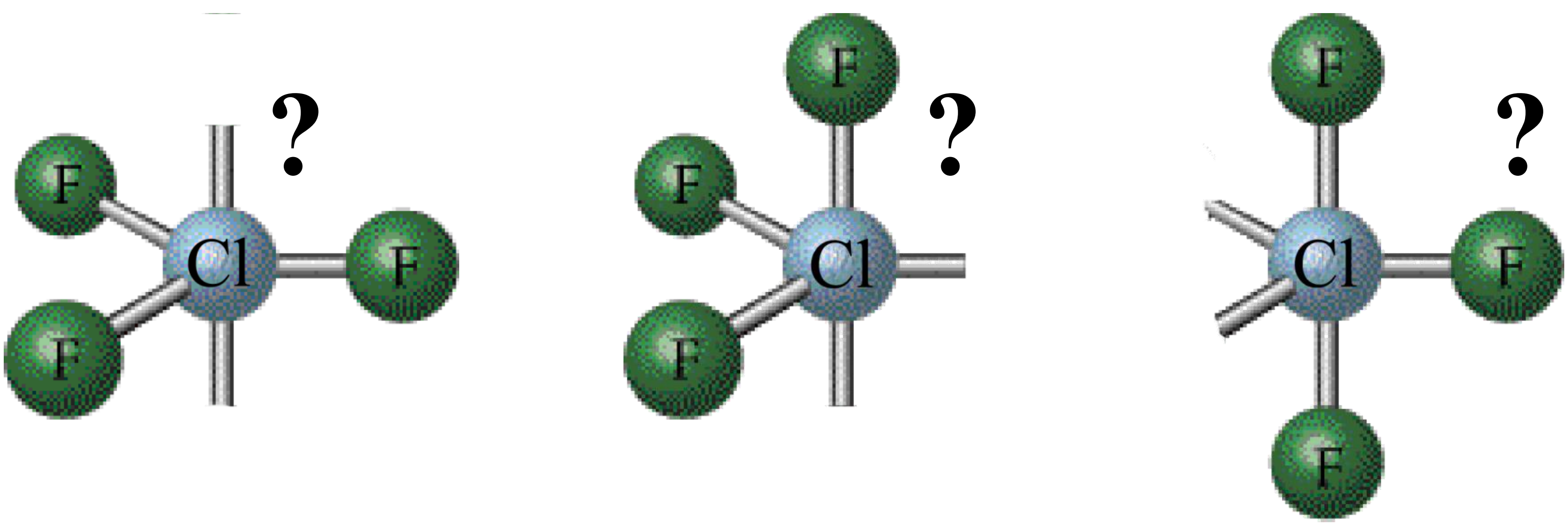
Repulsive Forces 2

Electron pair repulsions decrease in strength in the order:

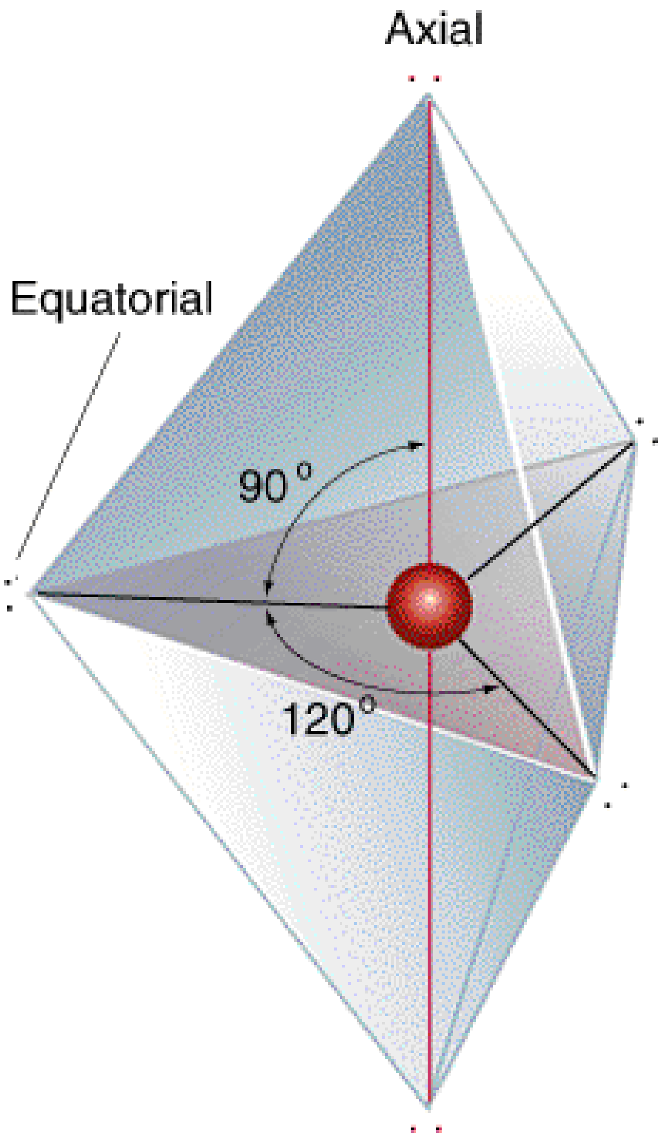
non-bonding/non-bonding

non-bonding/bonding

bonding/bonding



Repulsive Forces 3



Placing the non-bonding lone pairs at the Axial positions would appear to give least repulsion but they would only be 90° away from the 3 bonding pairs.

To minimize e^{-}– e^{-} repulsion, lone pairs are always placed in equatorial positions, so …