Pauli's exclusion principle dictates that a maximum of two electrons may occupy any one orbital. One spin "up" and the other spin "down".

The first energy level n = 1

Holds a maximum of 2 electrons
These go in the 1s orbital
1p and 1d orbitals do not exist

The second energy level n = 2

Holds a maximum of 8 electrons
2 go into the 2s orbital
6 go into the three 2p orbitals
2d orbitals do not exist

The third energy level n = 3

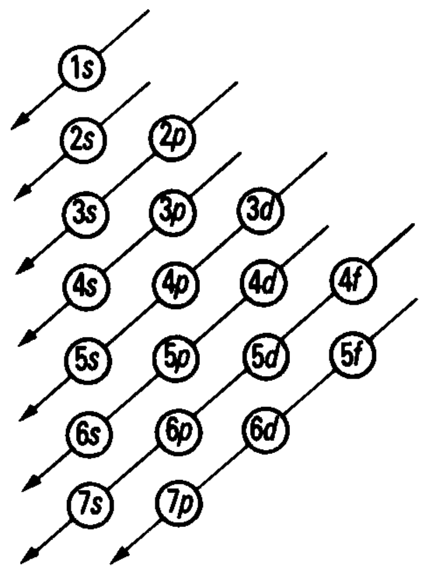
Holds a maximum of 18 electrons
2 go into the 3s orbital
6 go into the three 3p orbitals
10 go into the five 3d orbitals

The Rules of Orbital Filling

The Aufbau Principle

“Electron configurations are built up from the bottom, using the lowest energy orbitals first.”

The Energy of Atomic Orbitals



Hund's rule

“Where orbitals are available in degenerate sets, maximum spin multiplicity is preserved.”

i.e. electrons are not paired until each orbital in a degenerate set has been half-filled

Electronic Configurations

Electronic configurations tell us which orbitals are occupied by the electrons.

Atom	Electronic Configuration
H	$1s^1$
He	$1s^2$
Li	$1s^2\ 2s^1$
Be	$1s^2\ 2s^2$
B	$1s^2\ 2s^2\ 2p_x^1$
C	$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$
N	$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$
O	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$
F	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$
Ne	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$

Chemical Bonding

There are two principal types of non-metallic bonding (metallic bonding will be covered later):

ionic and covalent

Ionic bonding occurs when compounds adopt a regular array of positively and negatively charged ions. The ions are held together by electrostatic forces. *e.g.* NaCl, LiF and $CaCl_2$.

Covalent bonding occurs when two atoms are held together by a pair of shared electrons. e.g. H_2 and C_6H_{12}.

Lewis Structures

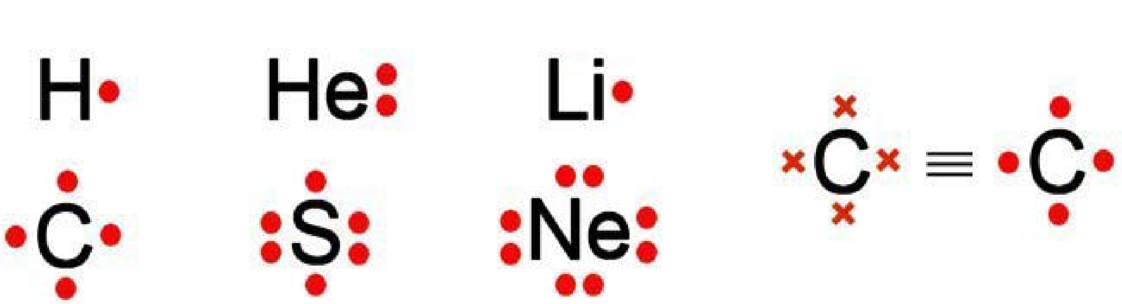
Lewis structure: schematic representation of an atom showing only electrons that are **NOT** core electrons.

Core electrons: all but the outermost shell of electrons corresponding to the electron count of the previous noble gas.

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

The electrons in the outermost shell are often referred to as valence electrons.

Electrons are symbolised by either • or x

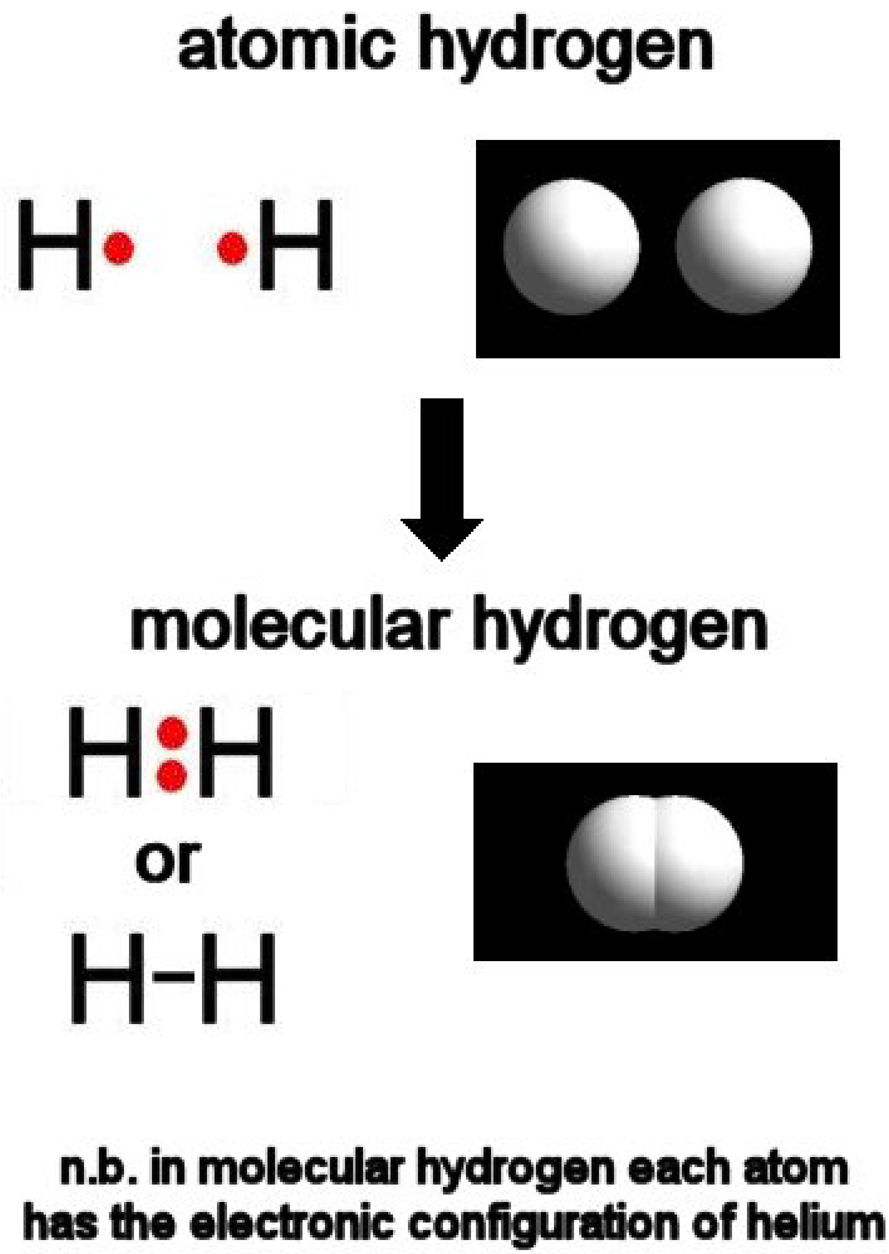


The basic principle of covalent bonding is that all atoms involved in covalent bonds should attain the electronic configuration of the next noble gas.

The Noble Gases

Gas	Configuration
He	$1s^2$
Ne	$[He]\ 2s^2 2p^6$
Ar	$[Ne]\ 3s^2 3p^6$
Kr	$[Ar]\ 4s^2 3d^{10} 4p^6$
Xe	$[Kr]\ 5s^2 4d^{10} 5p^6$

Simple models of the covalent bond can be generated using Lewis structures.



The Lewis representation tells us that:

1) There are two electrons lying between the hydrogen nuclei.
2) These two electrons form a covalent bond.

H:H is termed the Lewis representation

H-H is the conventional representation

A bond in which only one pair of electrons is shared is called a σ-bond

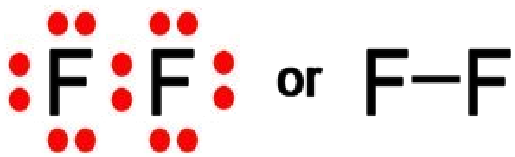
The Octet Rule

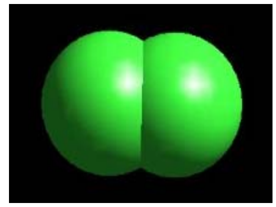
Lewis realised that many elements are surrounded by eight electrons in covalent compounds. He called this the octet.

8 is a special number as all the outer or valence orbitals are filled:
e.g. Ne - $2s^2 2p^6$ and Ar - $3s^2 3p^6$

Fluorine has electronic configuration: $1s^2 2s^2 2p^5$
It has a Lewis configuration: $[He]2s^2 2p^5$
i.e. F has seven valence electrons

It needs only one more electron to attain the electronic configuration of neon and complete the octet. It achieves this octet by forming a covalent bond with another F atom:



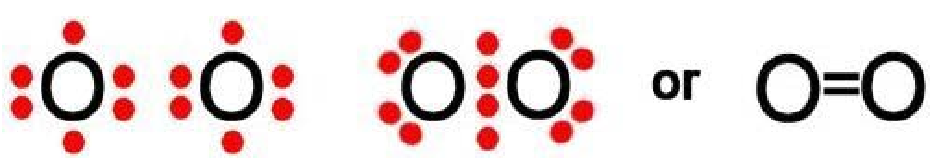


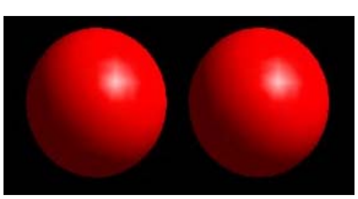
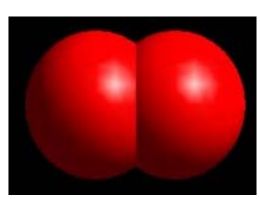
Now consider oxygen...

Oxygen has electronic configuration: $1s^2 2s^2 2p^4$
It has a Lewis configuration: $[He]2s^2 2p^4$
i.e. O has six valence electrons

Q How can oxygen attain an octet when the formation of a covalent bond will only give it one extra electron?

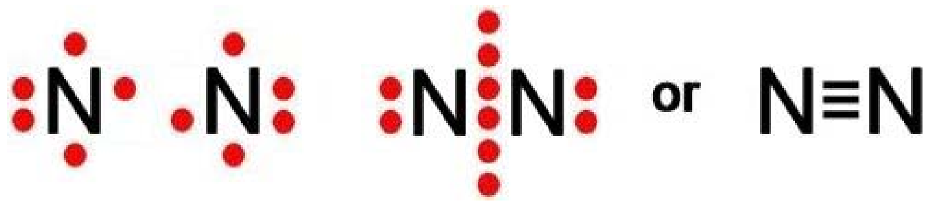
A By forming a double bond instead of a single one. This consists of a σ bond and an additional π bond.



Nitrogen has electronic configuration: $1s^2 2s^2 2p^3$
It has a Lewis configuration: $[He]2s^2 2p^3$
i.e. N has five valence electrons

It achieves the octet by forming a triple bond. This consists of a σ bond and two additional π bonds.



The triple bond present in molecular nitrogen is the strongest known covalent bond. We are very fortunate that this is so...

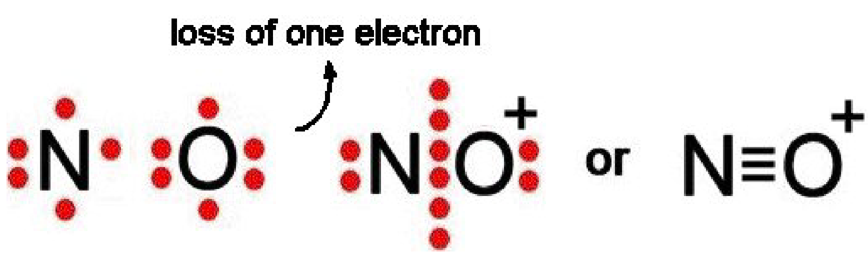
Why is the strength of the nitrogen triple covalent bond so important to the human race?

The methodology is not limited to homodinuclear molecules such as H_2, F_2 and O_2. It can be readily applied to mixed systems, e.g. carbon monoxide:

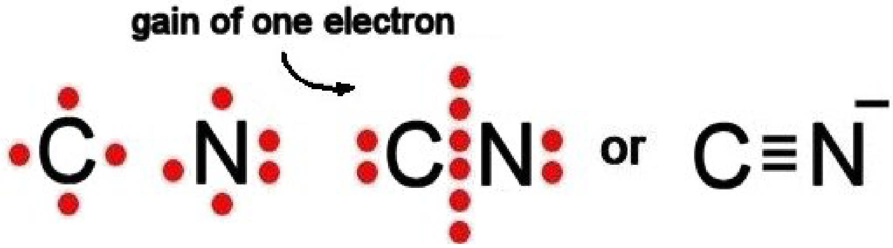
Note the similarity between N_2 and CO. The molecules are said to be isoelectronic.

For N and O there is a problem. There are 11 valence electrons.

Q How can nitrogen and oxygen produce a molecule with shared electron pairs and no single electron?



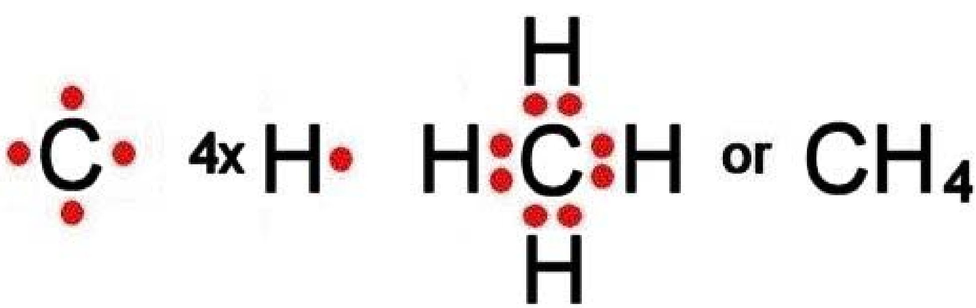
Similarly for carbon and nitrogen there are only 9 valence electrons.

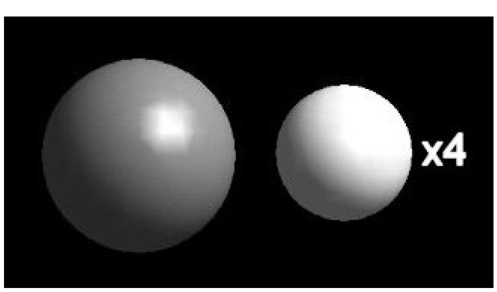


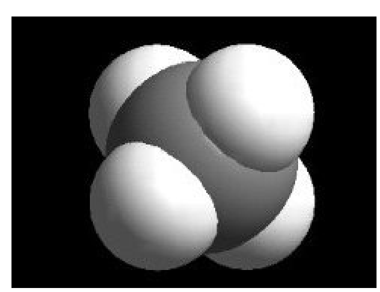
The Application of Lewis Structures to Polyatomic Molecules

1) Calculate the number of valence electrons for all of the atoms in a molecule.
2) Make any necessary compensation for charge.
3) Arrange electrons around component atoms so that the octet rule is satisfied.

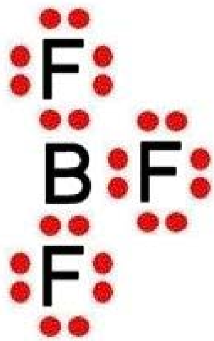
N.B. for hydrogen, the duplet rule applies.

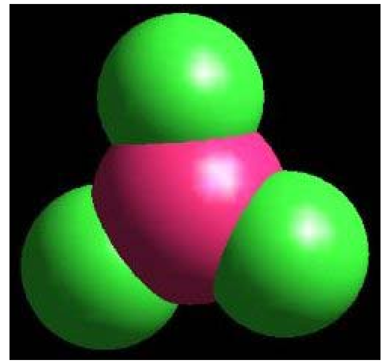






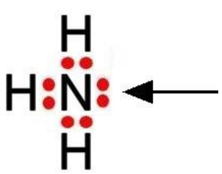
Exceptions to the Octet Rule



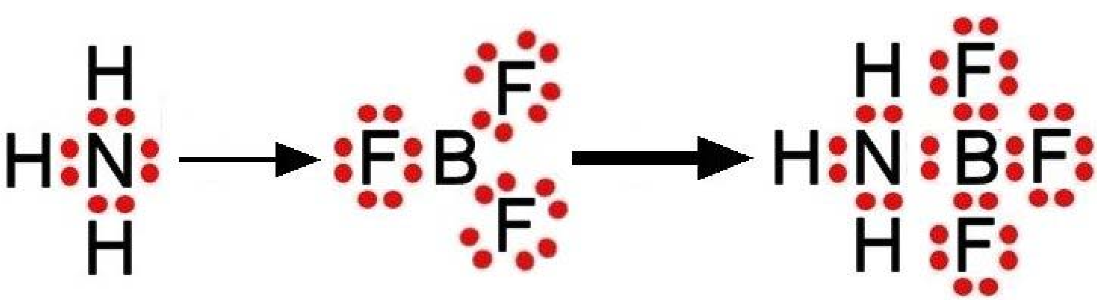


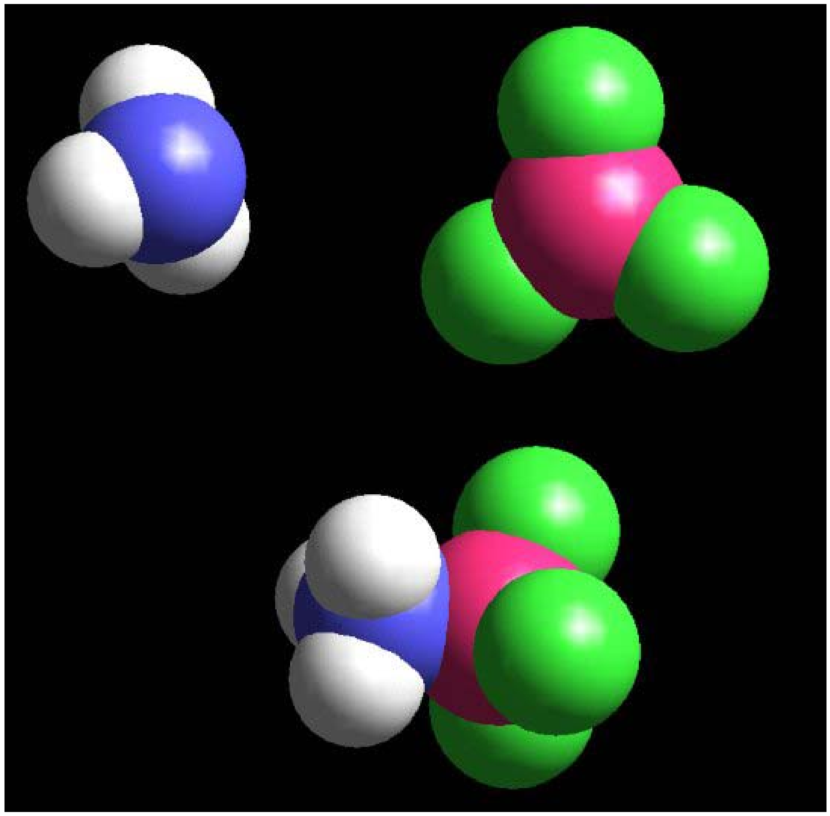
Boron trifluoride, BF_3, exists yet it does not obey the octet rule. The three fluorine atoms obey the octet rule but the boron atom is surrounded by only six electrons. The boron is said to be electron defficient.

It will achieve the octet of electrons very readily in the presence of a species capable of donating a lone pair of electrons.



The nitrogen atom has a pair of electrons that are not involved in covalent bonding. This is a called a lone pair.





Now both boron and nitrogen obey the octet rule.

The nitrogen atom donates a lone pair of electrons to the boron atom filling its valence shell. The bond thus formed is called a dative covalent bond.

Dative covalent bonds are defined as bonds in which both bonding electrons originate from the same atom.

BF_3 is capable of accepting a pair of electrons. Such species are known as Lewis acids.
NH_3 is capable of donating a pair of electrons. Such species are known as Lewis bases.

Molecular Shape and VSEPR

VSEPR – Valence Shell Electron Pair Repulsion

http://www.shef.ac.uk/chemistry/vsepr/

A method for predicting molecular shape around a central atom from Lewis structures. The method assumes:

1) Atoms in a molecule are joined by electron pairs - termed bonding pairs.

2) More than one set of bonding pairs may join two atoms.

3) Some atoms possess pairs of electrons not involved in bonding - termed lone pairs.

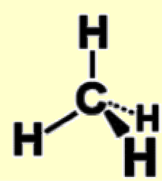
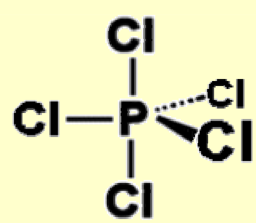
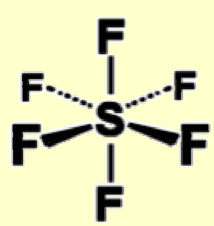
4) The bonding and lone electron pairs adopt a position about an atom such that their interactions are minimised.

5) Lone pairs occupy more space than bonding pairs

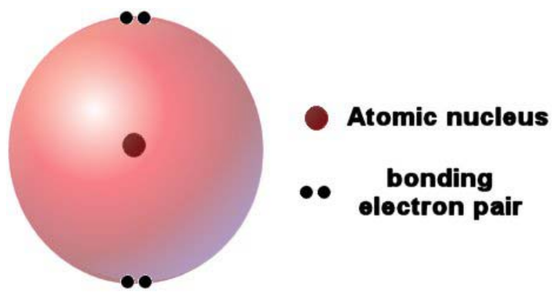
6) Single, double and triple bonds occupy progressively more space.

VSEPR theory relies on the calculation of the number of σ electron pairs about an atom.

For each number of σ electron pairs there is a preferred geometry about the central atom.

σ Pairs	***Geometry***	***3D representation***
2	Linear	
3	Trigonal Planar	
4	Tetrahedral	
5	Trigonal Bipyramidal	
6	Octahedral	

The shapes are calculated from simple geometrical constructions. The atomic nucleus is situated at the centre of a sphere and the electron pairs are situated on the surface of the sphere, as far apart as possible.



Assessing VSEPR Molecular Shapes

1) Draw a Lewis structure of the central atom taking into account any charges present. Draw ALL valence electrons.
2) Double bonds comprise ONE σ electron pair and one π electron pair.
3) Triple bonds comprise ONE σ electron pair and TWO π electron pairs.
4) DISCOUNTING any π electron pairs, count the total number of electron pairs around the central atom.
6) Look up the corresponding geometry in the previous table.
7) Slight adjustments may be made to the geometry to account for lone pair interactions.

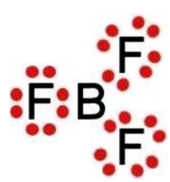
Water H_2O

Lewis structure

Central atom: Oxygen (O)
Valence electrons on O = 6
2x hydrogen contribute 1 electron each = 2
Total = 8
Valence electron pairs = 4
Geometry is therefore tetrahedral

Boron trifluoride BF_3

Lewis structure



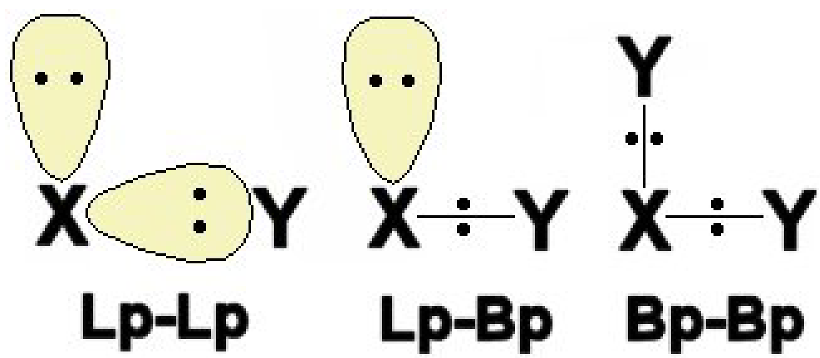
Central atom: Oxygen (B)
Valence electrons on B = 3
3x fluorine contribute 1 electron each = 3
Total = 6
Valence electron pairs = 3
Geometry is therefore trigonal planar

Interactions Between Electron Pairs

There are three possible interactions:

1) lone pair - lone pair (Lp-Lp)
2) lone pair - bonding pair (Lp-Bp)
3) bonding pair - bonding pair (Bp-Bp)

Q Of the three possible electron pair interactions which is the greatest and why?



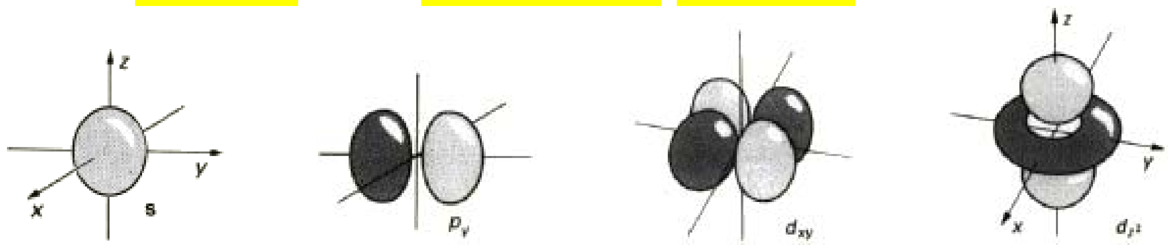
A Lone pairs are bigger than bonding pairs, consequently:

Lp-Lp > Lp-Bp > Bp-Bp

Using VSEPR rules we find that Lewis structures give good predictions of molecular structure…

Limitations of VSEPR Theory

Electrons are known to have wave particle duality and do not exist simply as point charges but in atomic and molecular orbitals.



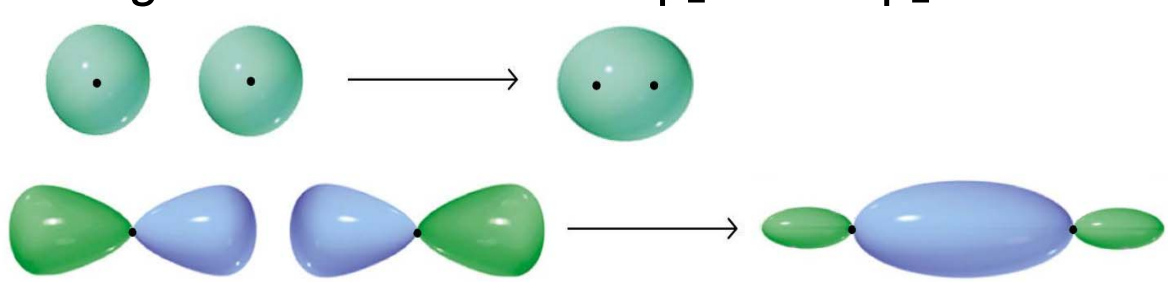
Mixing of atomic orbitals on two atoms produces a molecular orbital. This is the quantum mechanical description of a bond.

For bonding interactions orbitals must overlap with the same wavefunction sign (see orbital shading) – light with light and dark with dark

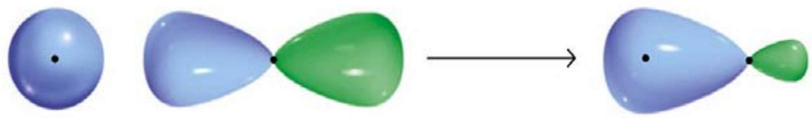
Single bonds

These can occur in two ways:

1) Overlap of like orbitals
   e.g. an s with an s or a p_z with a p_z



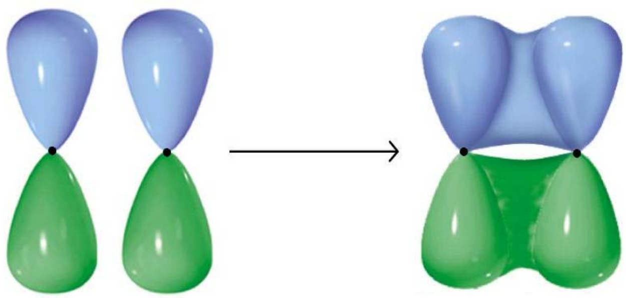
2) Overlap of different orbitals
e.g. an s with a p_z



By convention p_z orbitals form σ-bonds.

Double Bonds

π-bonds result from p_x-p_x and p_y-p_y interactions



But there are problems...

e.g. For BeH_2 VSEPR theory predicts a linear structure.

The ground state of Be is $[He]2s^2$. But the 2s orbital is spherical and therefore non-directional.

Q How can we describe two bonds arranged at 180° from this orbital description?

A We must develop a new type of orbital... This is done through hybridisation.