

CHM 101: Introductory Physical Chemistry

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Course Outline

Atoms, molecules and structure

Electronic configuration

Periodicity and building up of the periodic table

ATOMIC STRUCTURE

An atom consists of a nucleus surrounded by electrons.

The nucleus contains two types of particles i.e. proton and neutron, these particles plus the electron surrounding the nucleus are called the fundamental particles.

The electron around the atoms is responsible for its chemical property. An atom contains equal number of protons and electrons therefore an atom is electrically neutral.

The number of proton in the nucleus is equal to the atomic number (Z). When an atom reacts to form a compound, it is the outer electrons which form bonds and determine chemical properties.

Thus the number of protons in the nucleus of an atom controls its chemical properties.

Particle	Symbol	Charge	Mass relative to proton
Electron	e^{-}	-1	$9.11 \times 10^{-31} = \frac{1}{1835}$
Proton	P	+1	$1.672 \times 10^{-24} = 1$
Neutron	N	0	$1.672 \times 10^{-24} = 1$

An atom of particular elements differs from atom of all other elements in the numbers of sub-atomic particles it contains.

An atom of a specific element has a specific number of proton in the nucleus, thus atom with the same number of proton in the nucleus are atoms of the same element.

Atom with different number of proton in the nucleus is atom of different element.

Rutherford model of Atomic structure

It states that electron revolved round the nucleus in an orbit and was held in these orbits by electrostatic attraction to the positively charged nucleus.

This attraction varied inversely as the square of the distance between the electron and the nucleus.

This model failed because the anticipatory radiation of energy by accelerating electron in an orbit which will be eventually collapses into the nucleus according to classical electromagnetic theory did not occur.

Rutherford model laid the foundation of the model picture of the atom. However it did not tell anything as to the position of the electrons and how they were arranged around the nucleus.

Neil-Bohr Model of Atomic structure

In 1913 Neil-Bohr, adopted the quantum theory idea of Plank's and Einstein to account for the spectrum of hydrogen.

He attempted to give an explanation of the emission spectrum of hydrogen atom.

Bohr proposed a new model of the atom based on the modern Quantum theory to explain as to why an orbiting electron did not collapse into the nucleus and how atomic spectra were caused by the radiations emitted when electrons moved from one orbit to the other.

He submitted that the emission spectrum of hydrogen when view through a spectrometer it's seen to be number of separate set of lines or series of lines.

He make use of Quantum theory which states that energy can be absorbed or emitted in certain amount, like separate packet of energy called quanta.

Neil's Bohr made the following assumptions;

- Rutherford's model of the atom is correct
- Each spectral line is caused by an electron
- Electron can exist only in circular orbits of definite quantum energy
- An electron emits energy or radiation when its move from higher orbit to a lower orbit, this will produce a line in the atomic emission spectrum

Bohr suggested that an electron moving in an orbit can have only certain amounts of energy, not an infinite number or values; its energy is quantized.

The energy that an electron needs in order to move in a particular orbit depends on the radius of the orbit.

If the energy of the electron is quantized the radius of the orbit also must be quantized. There are a restricted number of orbits with certain radii not an infinite number of orbits.

An electron moving in one of these orbits does not emit energy. In order to move to an orbit further away from the nucleus the electron must absorb energy to do work against the attraction of the nucleus.

If an atom absorbs a photon a quantum of light energy, it can promote an electron from an inner orbit to an outer orbit. If sufficient photons are absorbed a black line appears in absorption spectrum.

According to the quantum theorem the energy contain in a photon of light of frequency ν is $E = h\nu$, where h is plank's constant and its value is $6.626 \times 10^{-34} \text{ Js}^{-1}$.

For an electron to move from an orbit of energy to one of energy , the light absorbed must have frequency given by plank's equation

$$\Delta E = E_2 - E_1 = h\nu$$

The emission spectrum arises when electrons which have been excited dropped back to orbits of lower energy. Bohr assigned quantum numbers (n) to the orbit. He gave the orbit of the lowest energy the quantum number 1.

An electron in this orbit i.e n= 1is said to be in ground state. The next energy level has quantum number 2 i.e. n = 2 etc. These are equally designated as K, L, M, N, O.....

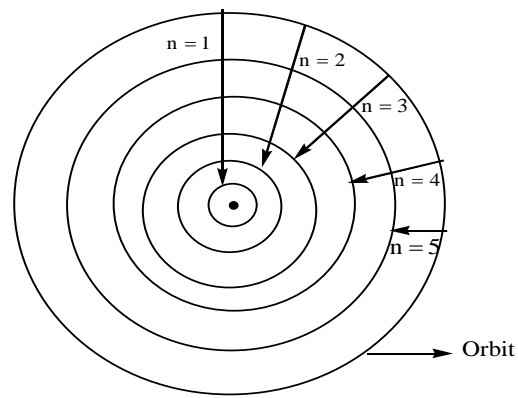
Dropping of electron from higher level to $n = 1$, this line is called Lyman series and is associated with ultraviolet region of electromagnetic radiation.

Electron dropping from higher orbit to $n = 2$, is called Balmer series and is associated with visible region of electromagnetic radiation.

Electron dropping from higher orbit to $n = 3$, is called Paschen series associated with infra-red region of electromagnetic radiation.

Electron dropping from higher orbit to $n = 4$, is called Brackett series and is associated with infra-red region of electromagnetic radiation.

An electron dropping from higher orbit to $n = 5$ is called Pfund series and it is also associated with infra-red region of electromagnetic radiation.



Limitation of Bohr model

Bohr model is outstandingly successful as a model for explaining a spectrum of hydrogen. It was total failure for an atom with more than one electron.

It has the disadvantage that it postulated an electron moving in a circular path creating a changing electromagnetic field and according to Pascal theorem these should result in the loss of energy as radiation, causing the electron to slow down and to be drawn towards the nucleus.

If these were to happen all matter could collapse but fortunately does not.

This led to the replacement of Bohr's model with wave-mechanics model which assume that, the understanding of the nature of the atoms depends on treating the electrons not only as particles but as a wave i.e electrons have dual nature, they could be treated as particle (they have mass) and at the same time as wave (they have wavelength).

The dual nature of electron was reviled by Victor de-Broglie in 1924; he suggested that all matter could exhibit wave-like properties. From wave mechanics we derived the important matter-wave relationship as follows,

$$\lambda = \frac{h}{mV} \quad \text{where } m = \text{mass of the object and } v = \text{velocity.}$$

The wave-like properties of the electrons make it elusive; hence the Uncertainty principle postulated by Heisenberg in 1927, the principle states that, if the momentum of an electron is known accurately then the position of such an electron is certainly not known and vice-versa.

The wave nature of electron gives rise to the concept of orbitals which is defined as a region of high probability of finding an electron with a certain amount of energy. The electron being in an orbital does not mean that it is moving along a path as described by Bohr.

Concept of atomic orbital

According to quantum mechanics an electron is spread out like a wave. The wave that summarizes how the electron is spread out through space is called its wave function (ψ).

This wave function is large in some region and small in others just like a wave in water.

In atoms the wave functions are called atomic orbitals and are defined as a region in space in which there is probability of finding an electron. Each atomic orbital could be specified in three numbers called quantum numbers.

Quantum numbers: - These are index numbers that define the orbital which an electron can occupy. These numbers described the sizes, shape and orientation in space of orbital in an atom.

Principal quantum number (n):- These correspond to the numbering of the energy level. It has values of integers i.e. 1, 2, 3, 4.....

Angular or subsidiary or azimuthal quantum number (l):- These represent a sub-division of space for a given principal quantum number. It ranges from 0 to $n-1$ and it also gives information about the shape of orbital in space e.g. s,p,d,f,g etc. It has values of 0, 1, 2, 3..... etc. It is limited or restricted by the value of n. Thus it is generally given as $l = n - 1$. So for $n = 1, l = 0$. It tells the shape of orbital.

Magnetic quantum number (m):- It depends on l and it ranges from $-l$ to l . i.e. If $l=1$, $m = -1, 0, 1$ and if $l=2$, $m = -2, -1, 0, 1, 2$. It tells the number of orbitals in a sub-shell.

Spin quantum number (s):- The spin quantum number has two values $\pm \frac{1}{2}$. This is used to distinguish between two electrons in an orbital.

Orbital	Angular quantum number (l)	Magnetic quantum number (m)
s	0	0
p	1	-1, 0, 1
d	2	-2, -1, 0, 1, 2
f	3	-3, -2, -1, 0, 1, 2, 3

Example 1:- Describe the allowed combination of the n, l, m quantum numbers when $n = 3$.

Solution:- For $n = 3$, since $l = n - 1, l = 2, 1, 0$.

Also $m = -l$ to $+l, m = 0$, when $l = 0$, when $l = 1, m = -1, 0, 1$ and when $l = 2, m = -2, -1, 0, 1, 2$

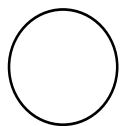
n	l	m	Orbital
3	0	0	s
3	1	-1	p
3	1	0	
3	1	1	
3	2	-2	d
3	2	-1	
3	2	0	
3	2	1	
3	2	2	

Assignment:- Assigned to the 6 – electron in carbon atom the quantum numbers, Hint:- Electronic configuration of carbon is $1s^2, 2s^2, 2p^2$

Types of orbitals

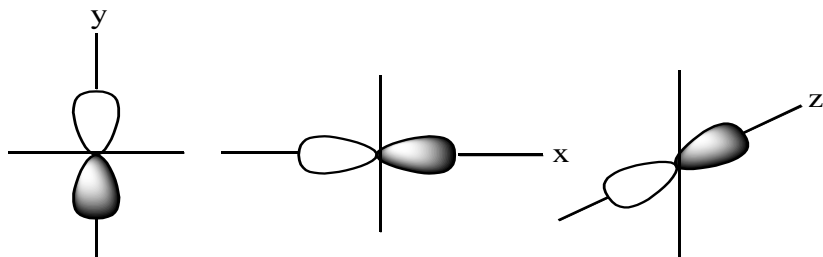
These are some of different orbitals we have namely, s - orbital which represent sap, p - orbital known as penultimate, d - orbital called diffuse and f - orbital stands for fundamental.

s - Orbital has a spherical shape as shown below;



Spherical shape of s - orbital

p - Orbital has a dumbbell shape and it is given below,



Dumbbell shape of p - orbitals

Alt has three degenerate orbitals we the same energy level. The energy of s - orbital is less than energy of p - orbital, hence the energy level sequence of orbitals is as follow $s < p < d < f$.

Rules for assigning electron into orbital

Afbau's principle: - This state that orbital of lowest energy is filled first i.e. the sequence of energy level of an orbital is as follows;

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 6d$$

Hund's rule: - When electrons are placed in a set of orbitals of equal energy i.e. degenerate, they are spread out as much as possible to give the maximum number of unpaired spins.

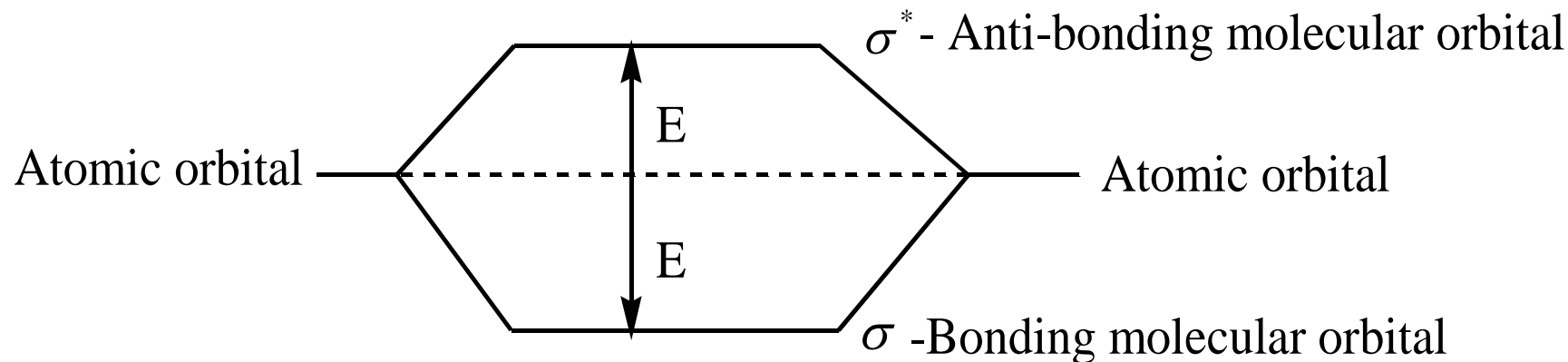
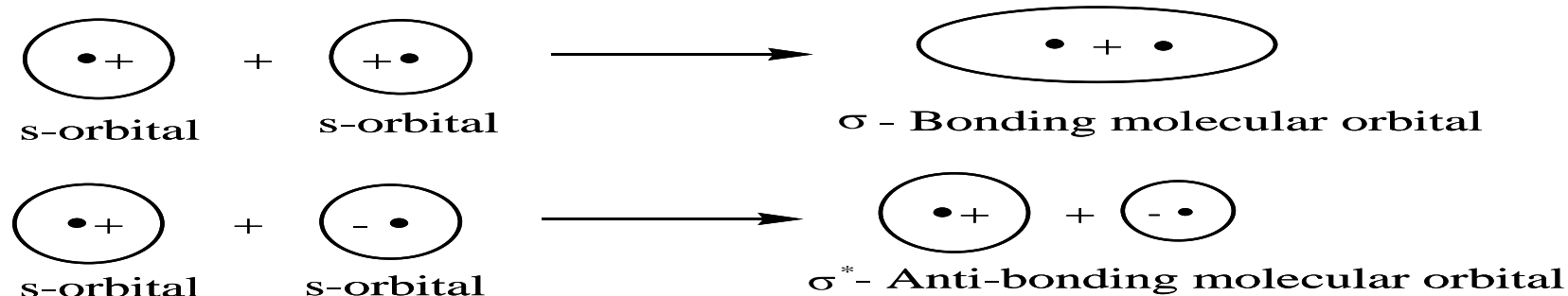
Pauli's exclusive principle: - States that no orbital can contains more than two electrons and the two electrons in the same orbital must have opposite spins i.e. no two electrons in a particular orbital can have the same set of four quantum numbers.

Note that the total number of orbital in a particular energy level is given as n^2 whereas the total number of electron in a particular energy level is given as $2n^2$.

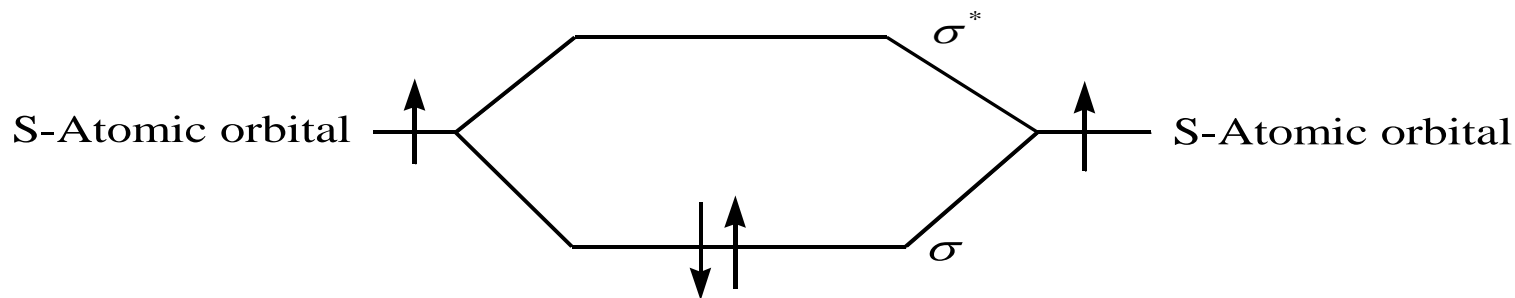
Molecules

Overlap of atomic orbital: - Molecules are formed by the overlapping of two atomic orbital by covalent bond. When a s - orbital overlap with another s - orbitals it will gives rise to two molecular orbitals called bonding and anti-bonding molecular orbitals.

This overlapping of this s - orbital with another s - orbital give what is called sigma bond which is strong bond. Bonding molecular orbital has less energy than both the atomic orbital and the anti-bonding molecular orbital.



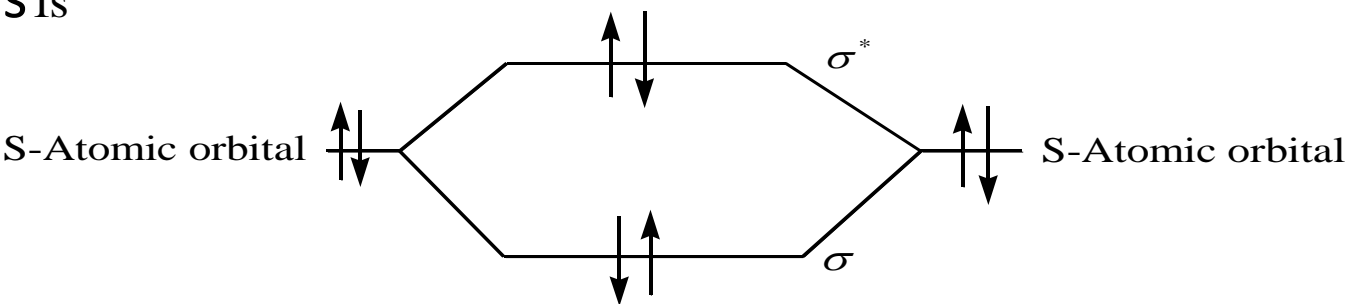
Example 1:- Hydrogen molecule i.e. $\text{H} + \text{H} = \text{H}_2$ Electronic configuration of hydrogen atom is $1s^1$



When two atomic orbital overlap their electron leave and move to the molecular orbital. For a particular orbital we can calculate the bond order which is the number of pair electron in the bonding molecular orbital minus number of electron pair in the anti-bonding molecular orbitals.

Therefore the bond order for hydrogen molecule = $1 - 0 = 1$, Hence the bond in hydrogen molecule is single bond i.e. $\text{H} - \text{H}$.

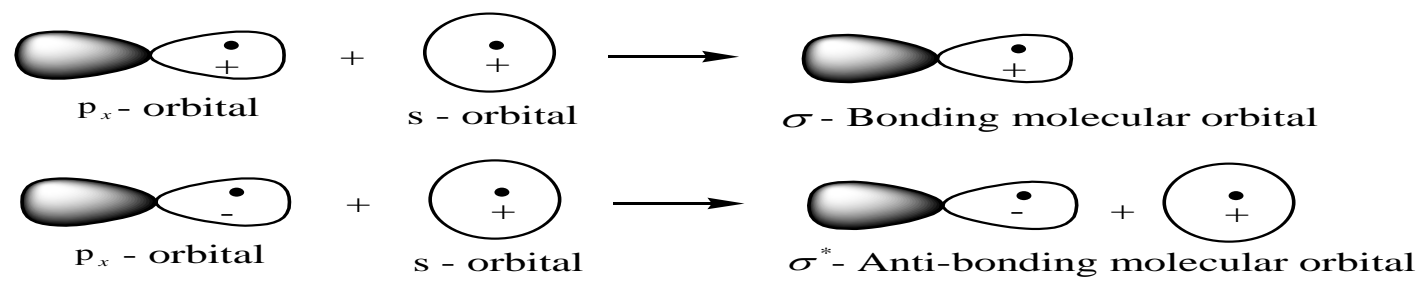
Example 2:- For helium molecule He_2 . Electronic configuration of helium atom is $1s^2$



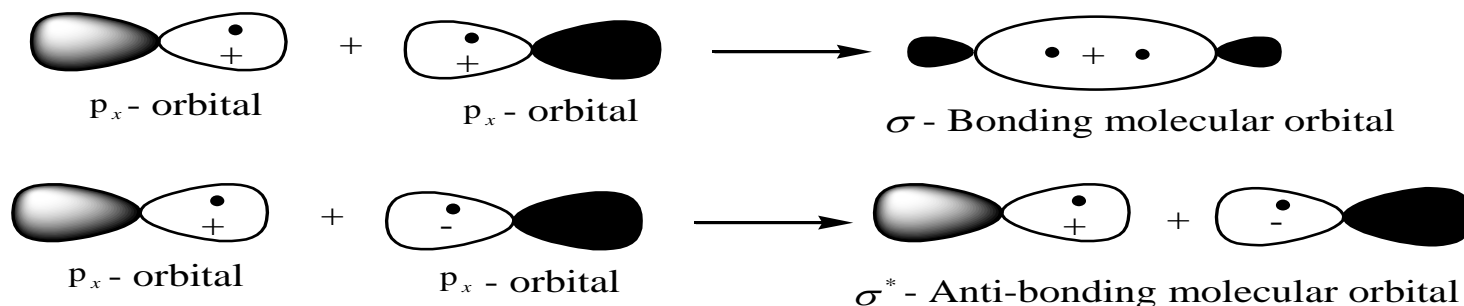
The bond order = $1 - 1 = 0$, this confirmed the non-existence of the helium molecule.

s – Orbital overlap with p – orbital and p – orbital overlap with p - orbital

When s - orbital overlap with p_x - orbital, it gives sigma bonding molecular orbital and sigma anti-bonding molecular orbital as follows;

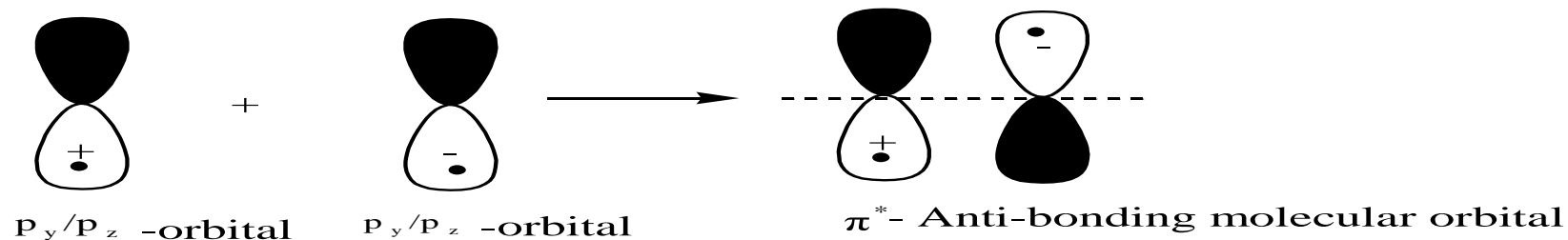
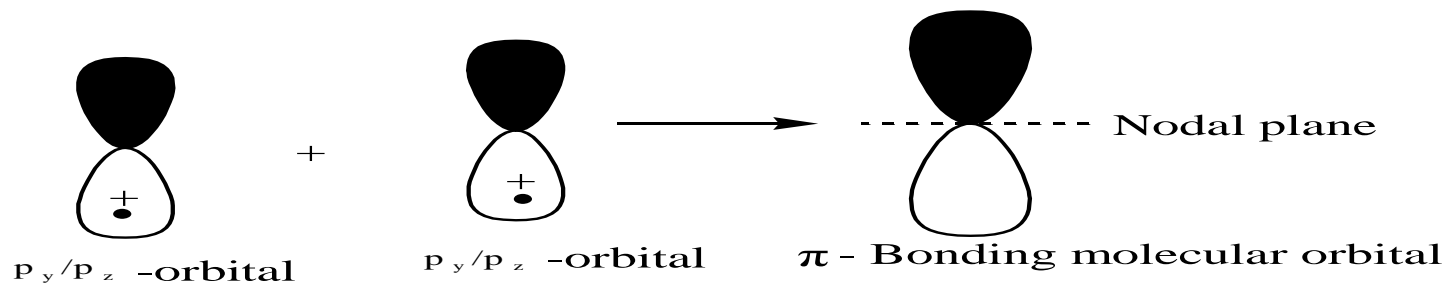


Head to head overlap of two p_x - orbital give sigma bonding and sigma anti-bonding molecular orbitals as thus;

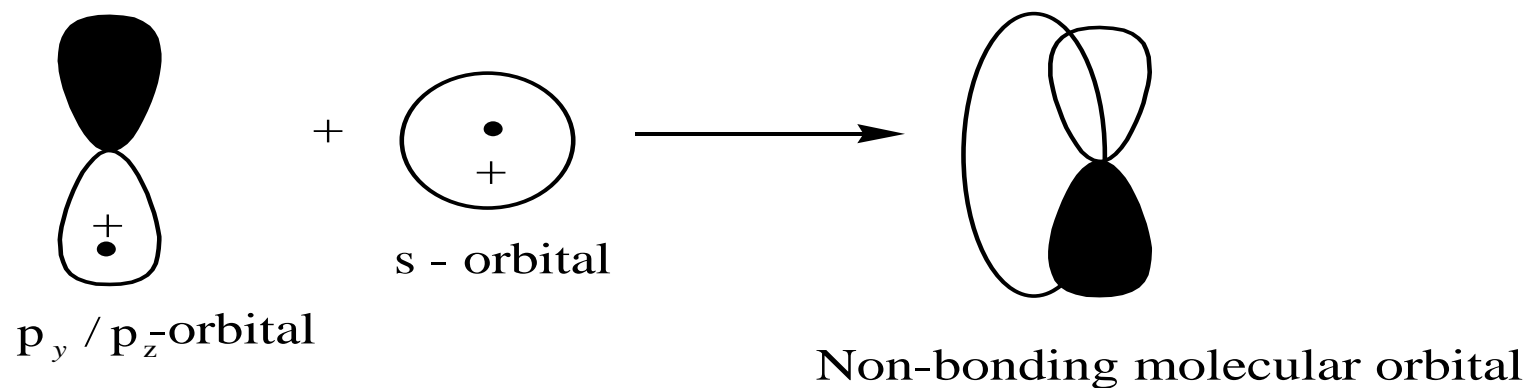


But lateral overlap (side to side overlap) of either p_y & p_z since they are perpendicular to p_x they will not be able to overlap head to head, this lateral overlap of p_y & p_z result in the formation pie (π) bonding and anti-bonding molecular orbital.

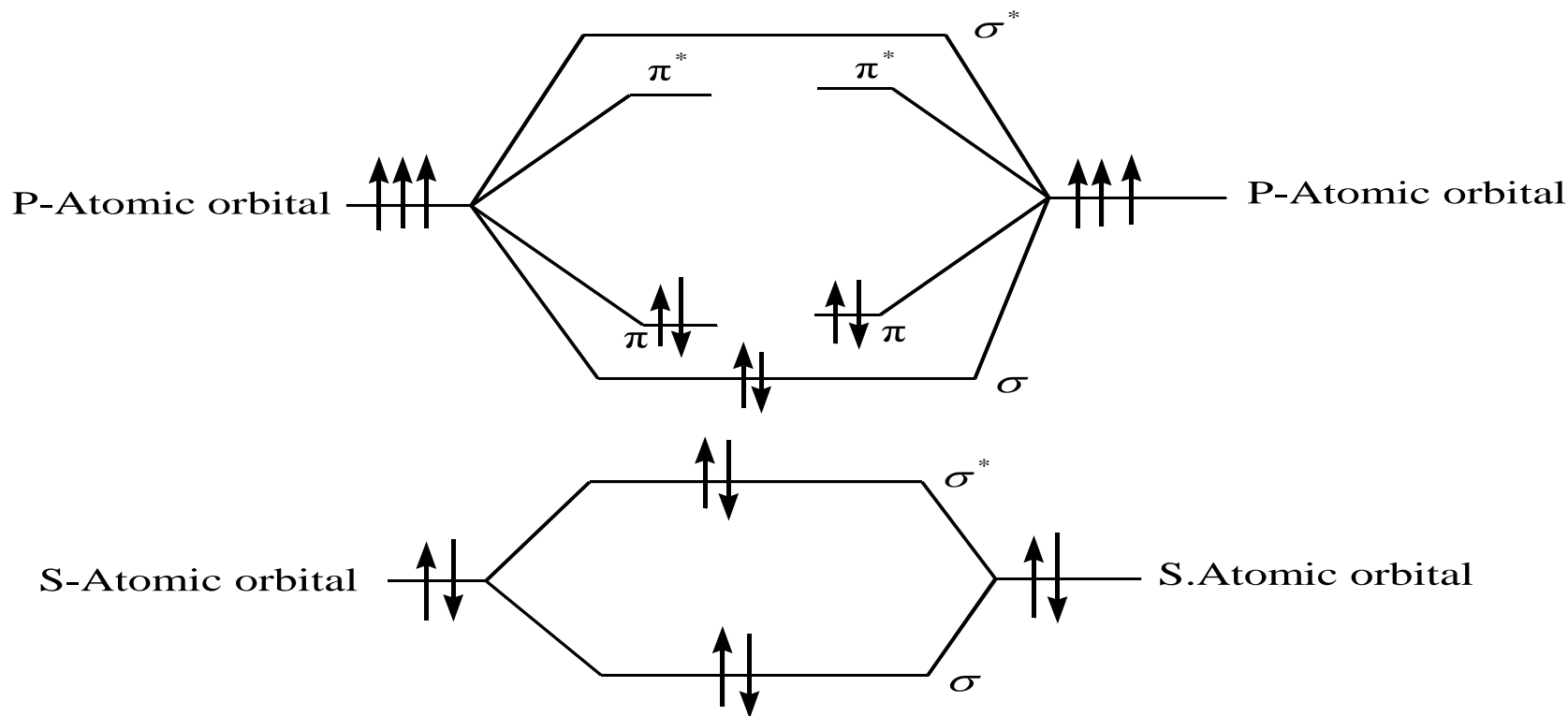
But pie bond is weaker than sigma bond which mean that pie bond is more higher in energy than sigma bond i.e. the lower the energy the higher the stability of the orbital.



When s - orbital overlap with p_y & p_z - orbital it gives non-bonding molecular orbital.



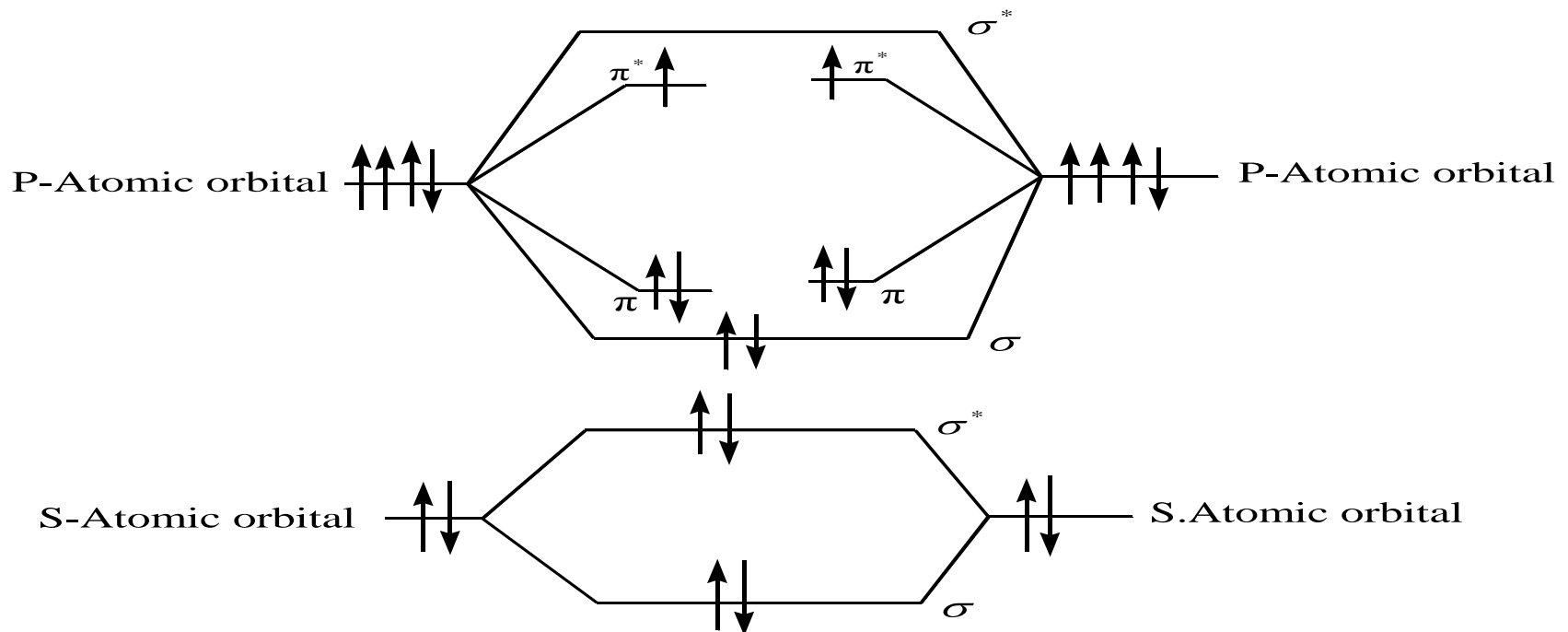
Example 3:- For nitrogen molecule N_2 Electronic configuration for N is $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$. Generally chemical bonding involves valency electrons therefore the formation of can be represented thus;



Bond order = $4 - 1 = 3$, therefore nitrogen molecule can be represented thus $N \equiv N$. To use Lewis structure to denote nitrogen molecule we have; $\ddot{N} :: :: \ddot{N}$

From the Lewis structure we can conclude that p_x^1, p_y^1 & p_z^1 are involved in bonding, so we have lone pair (electron that does not involve in bonding). Nitrogen molecule is diamagnetic because it does not have unpaired electron.

Example 4:- For oxygen molecule O_2 . Electronic configuration of oxygen atom is $1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$



Bond order = $4 - 2 = 2$, therefore oxygen molecule can be represented thus $O=O$, its Lewis structure is $:\ddot{O}::\ddot{O}:$

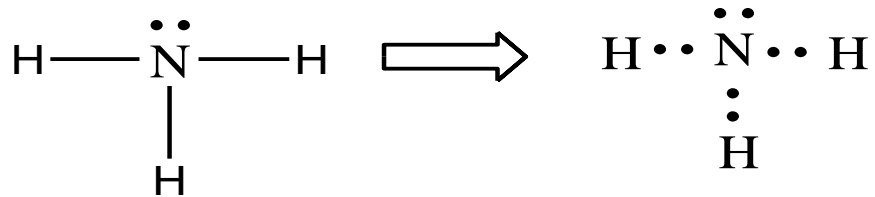
From the Lewis structure we observed that oxygen has two lone pair electrons and two unpaired electrons which involved in the bond formation. Since oxygen molecule contains unpaired electron it can be classified as paramagnetic.

Assignment: - Consider the following molecules fluorine molecule F_2 and neon molecule Ne_2 , calculate the bond order and predict whether the molecule will exist or not.

Note that all the above examples are homonuclear diatomic molecules

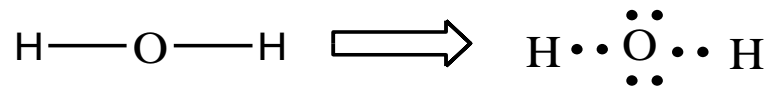
Note that all the above examples are homonuclear diatomic molecules.

Heteronuclear molecule e.g. Ammonia NH_3 , Electronic configuration for N is $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ and that of hydrogen atom is $1s^1$;



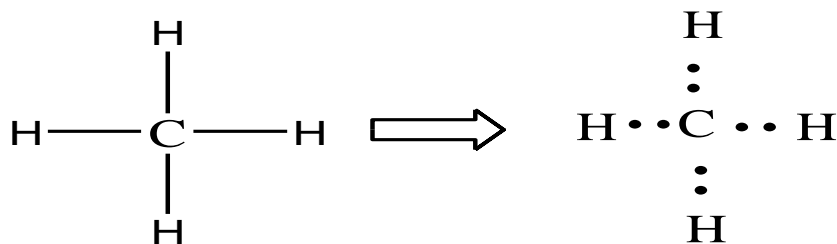
From the structure written above we could see that ammonia has three bond electron and one lone pair electron.

For water molecule H_2O , Electronic configuration of oxygen atom is $1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$ and that of hydrogen is $1s^1$



From the structure above oxygen have two lone pair electron and two bond pair electron. In a heteronuclear molecule, the central atom tends to attain octet configuration.

For methane, the ground state electronic configuration of carbon is $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$ and the excited state electronic configuration is $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$. Carbon will form excited state by hybridization (mixing of orbital) result in the formation of sp^3 - hybrid orbital in methane.



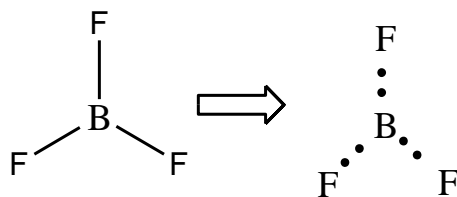
In the methane molecule all the electron are bond pair. It has no lone pair electron as it was found in nitrogen and oxygen above. The lone pair and bond pair electrons determine the structure of the molecule. The difference in their structure is as a result of repulsion between those pair electron.

We can have the following repulsion between each electron in the structure of a molecules (i) lone pair and lone pair (ii) lone pair and bond pair (iii) bond pair and bond pair

The repulsion is greatest between lone pair - lone pair, then followed by lone pair - bond pair and the least repulsion is when we have bond pair - bond pair. Therefore the repulsion will be greatest in water and the least will be in methane, hence their structure differs.

Note that all N_2 , O_2 & F_2 are not electron deficient but both N_2 & O_2 are unsaturated because of the presence of triple bond and double bond respectively in their structure while F_2 is saturated.

But for boron trifluoride BF_3 Electronic configuration of boron is $1s^2, 2s^2, 2p_x^1$ and that of fluorine is $1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$. Its structure is represented thus;



Because boron atom has not attained the octet structure and all electron deficient atoms are called Lewis acid since it can accept two electrons. But ammonia is called Lewis base because it can donate or loses two electrons or pair's electron.

The structures of molecules are represented in a Lewis diagram which represents the arrangement of atom and the location of all valency electrons within the structure. Bond pair electrons are represented by line.

In the heteronuclear molecules the structure shows the position of the atoms whether central or peripheral. In the diagram, the configuration of the valency electrons of the atom involved in the bonding is revealed. In most cases atoms involved attain octet configuration while hydrogen if it is involved it attain duplet configuration.

For many molecules, the number of valence electrons is just sufficient to provide an octet for the atoms involved while in some molecules it is not e.g. BF_3 .

For molecules especially those involving second row atoms of the periodic table the octet rule is not necessary applies e.g. PCl_5 .

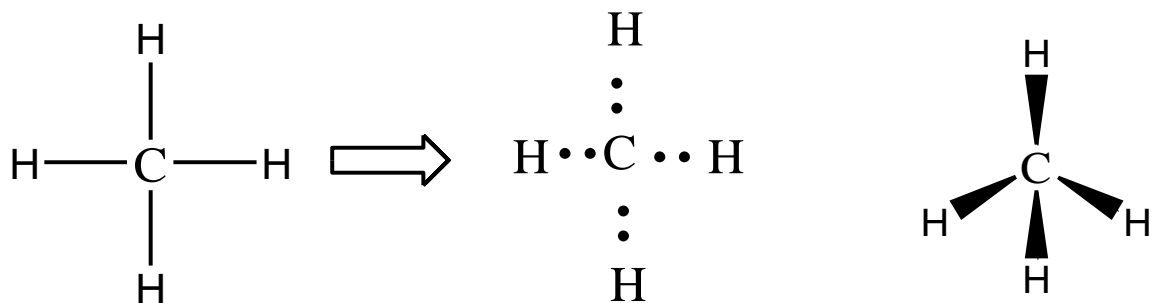
The species that are electron deficient e.g. BF_3 is referred to as a Lewis acid while molecules that are electron sufficient e.g. NH_3 are referred to as a Lewis base.

Once the Lewis diagram of a molecule is correctly written hybridization theory and valence shell electron pair repulsion (VSEPR theory) can be used to account for the geometry or shape of the molecule. In a molecule there are two types of electron, (i) non-bonding or lone pair of electron (ii) bonding or bond pair electron.

This group of negatively charged electrons will repel each other and also determine the geometry or shape of the molecule.

Note that the most stable arrangement is one which repelling electron group are far away from each other as possible this is to minimize repulsion, it is known as valence shell electron pair repulsion theory.

For instance methane has tetrahedral structure and bond angle of 109°



Guides towards predicting the shape of the molecule

Write the Lewis structure of the molecule, consider the central atom in the molecule and determine its occupancy.

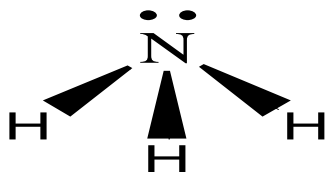
Occupancy = $x + y$, where x is the number of bond pair electron or number of atom bonded to the central atom while y is the number of lone pair electron.

When the occupancy is 2, the shape of the molecule will be linear. For example BeF_2 , electronic configuration of Be is $1s^2, 2s^2$ and that of fluorine is $1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$. Lewis structure is $\text{F} \cdot \text{Be} \cdot \text{F}$

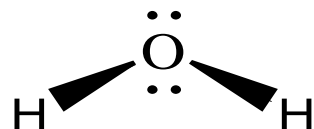
So the occupancy = $2 + 0 = 2$, hence the molecule of BeF_2 is linear in shape $\text{F} - \text{Be} - \text{F}$.

Occupancy	Shape
2	Linear 180°
3	Trigonal planar e.g. BF_3 , 120°
4	Tetrahedral e.g. CH_4 , 109°
5	Trigonal bipyramidal e.g. PCl_5
6	Octahedral e.g. common among complex compound $[\text{Cu}(\text{NH}_3)_6]^{2+}$

Since ammonia has occupancy of 4 and it said to be tetrahedral but due to the lone pair of electron present which lead to repulsion makes it to be pyramidal in shape.



Also in water molecule which has the structure H – O – H and 4 occupancy. The repulsion is greater and its bond angle is 104° with a bent shape.



As the occupancy increases the bond angle decreases.