B.Sc. I

Paper II Organic Chemistry

HYBRIDIZATION

DR. VINITI GUPTA
ASSOCIATE PROFESSOR

ORGANIC CHEMISTRY

SRI TIKA RAM KANYA MAHAVIDYALAYA
ALIGARH

INTRODUCTION

ATOMIC NUMBER OF CARBON = 6

Electronic Configuration = $1s^2$ $2s^2$ [$2p_x^1$ $2p_y^1$ $2p_z^0$] = 2 [GROUND STATE]

Valency =2

Actual Configuration = $1s^2$ [$2s^1$ $2p_x^1$ $2p_y^1$ $2p_z^1$]= 4 [EXCITED STATE]

Valency = 4

CARBON has valency equal to 4 and is called TETRAVALENT.

CARBON ATOM has four half filled orbitals and it can form four bonds with other atoms and groups.

Why does Hybridization take place?

In excited state a carbon atoms has four half filled orbitals .

1 [s orbital]

3 [p orbitals]

All four half filled orbitals are different - either in shape,
energy or
direction.

s orbital is different in shape and energy from p orbitals.

Three p orbitals are similar in shape and energy but different in direction of orientation in space.

p_x is in X axis

p_y in Y axis

p_z is in Z axis

Why does Hybridization take place?

S orbital

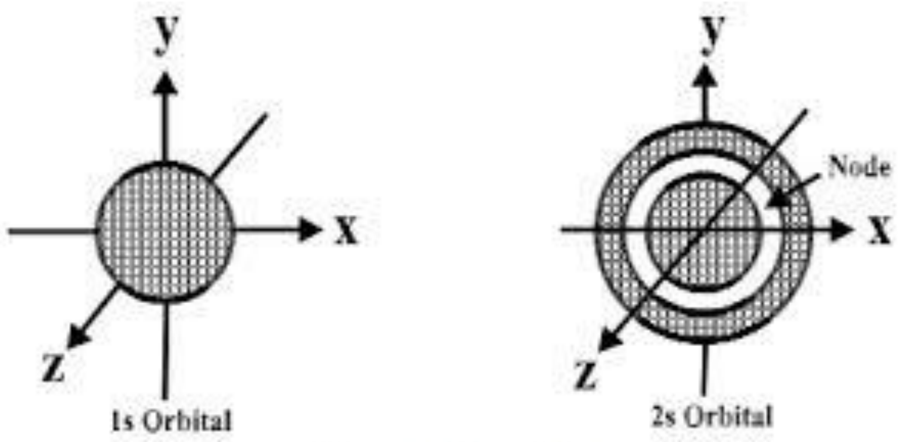
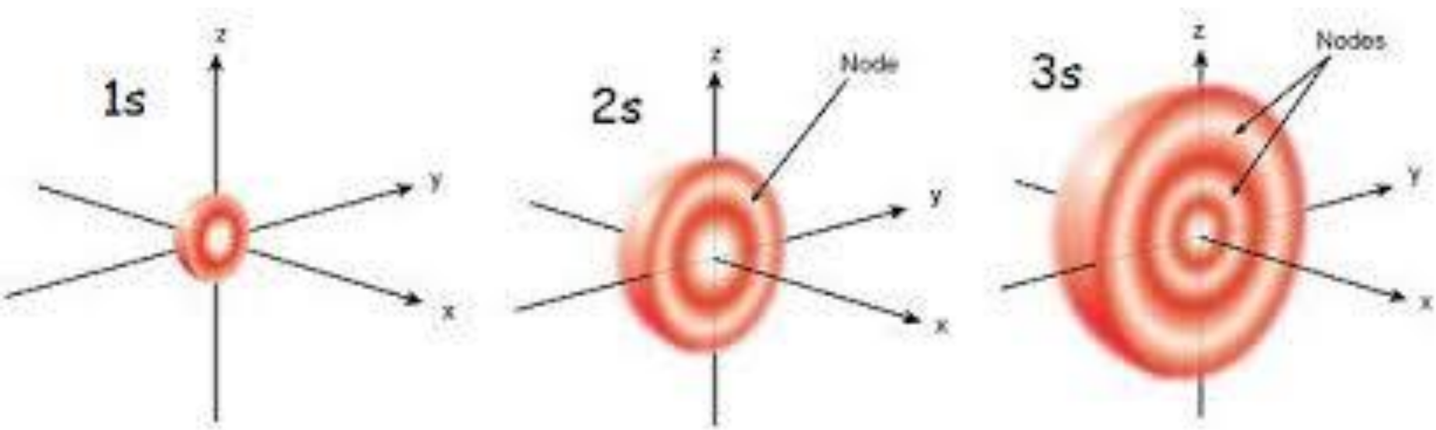
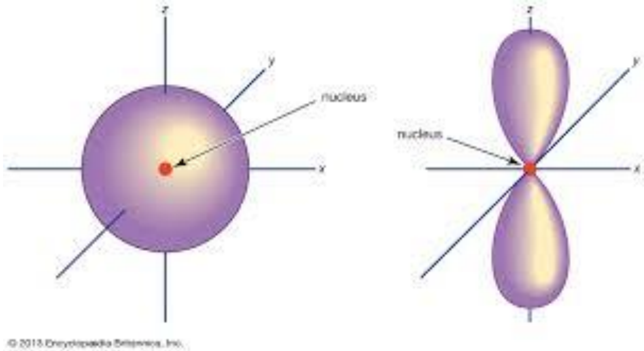
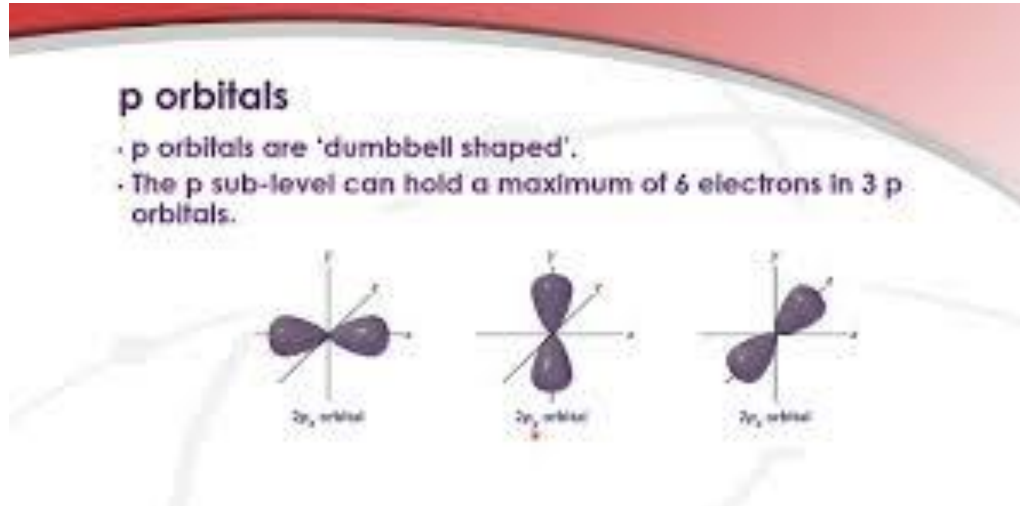


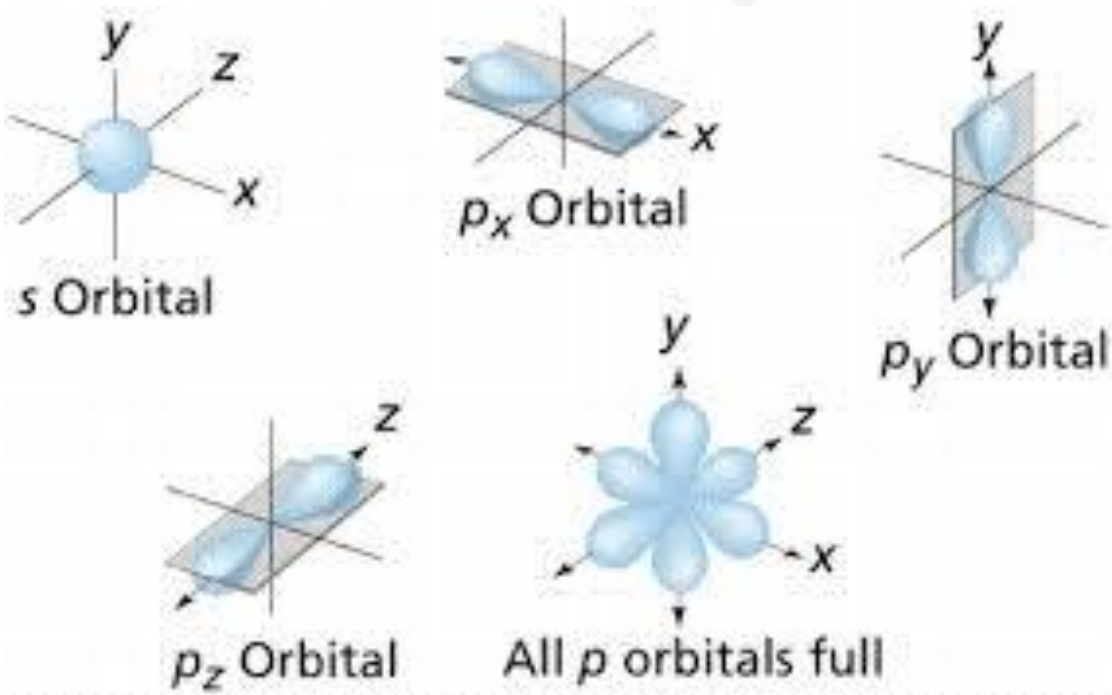
Fig. Shapes of 1s and 2s-orbitals



Why does Hybridization take place?







p orbital

Why does Hybridization take place?

Linus Pauling first developed the hybridisation theory in 1931 to explain the structure of simple molecules such as methane (CH_4), ethylene (C_2H_4), acetylene (C_2H_2).
He explained the structure of organic molecules using atomic orbitals (s, p, d, f)

The valency of carbon is 4.[$1s^2$ **$2s^1$ $2px^1 2py^1 2pz^1$**]
Pauling pointed out that a carbon atom will form four bonds by using one ‘s’ atomic orbital and three ‘p’ atomic orbitals.

Taking the shape and direction of orientation of ‘s’ and ‘p’ atomic orbitals, it is expected that Carbon atom would form three bonds at right angles (dumble shaped in the three directions x, y, z) and a fourth bond using the s orbital (spherical shape) in any arbitrary direction.

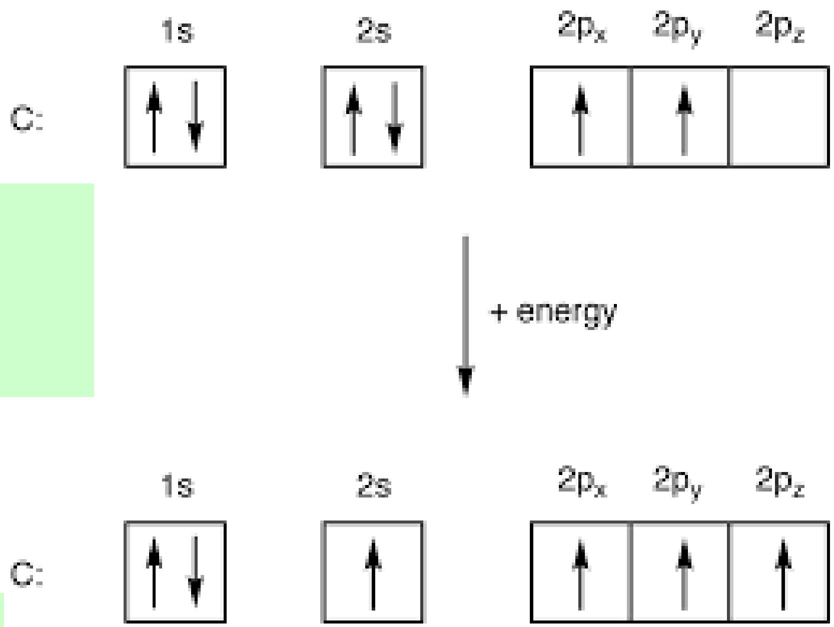
Why does Hybridization take place?

The three bonds of carbon using 'p' orbitals would be stronger (bonds will be formed along the axis) than the single bond of carbon using 's' orbital (s orbital has no direction).
But in reality, all the four bonds of carbon in methane are of equivalent strength.
The geometry of the molecule is tetrahedral.
The bond angle between each molecule is 109°28' (approx. 109.5°).

Pauling explained this by supposing that in the presence of four hydrogen atoms, the one 's' and three 'p' orbitals merge/mix together to form four equivalent combinations or *hybrid* orbitals, each denoted by sp^3 (to indicate its composition) which is directed along the four C-H bonds in the shape of a regular tetrahedron.

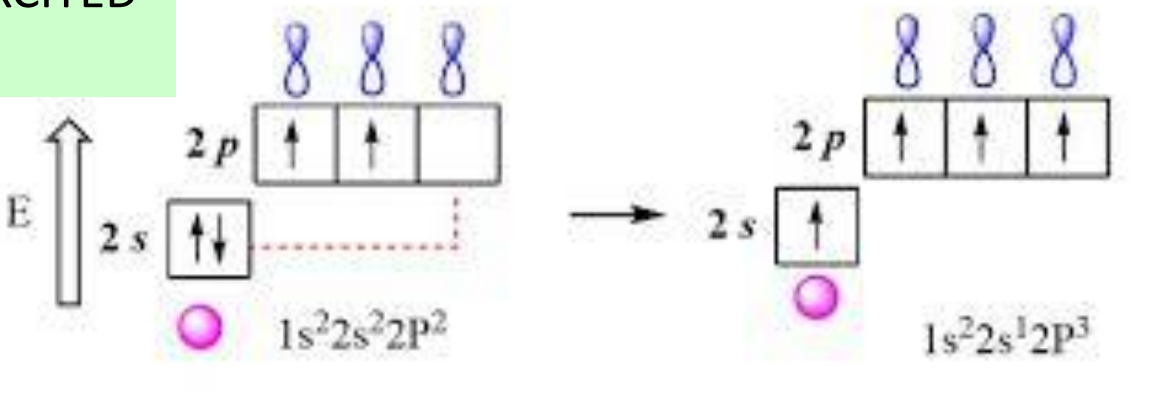
Hybridisation theory is an integral part of organic chemistry.

Ground state and Excited state of atomic orbitals of carbon



Distribution of 6 electrons in GROUND state

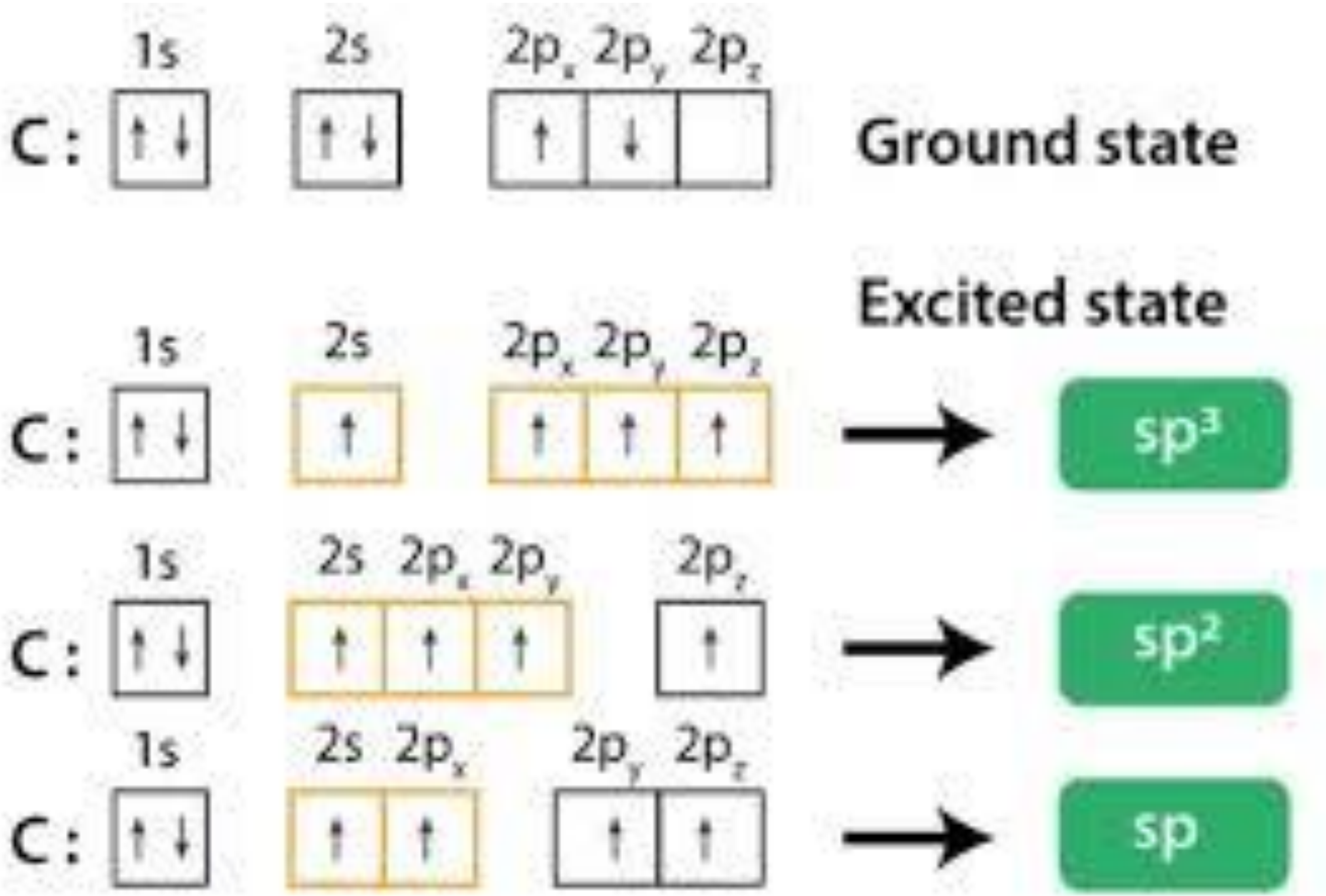
Distribution of 6 electrons in EXCITED state



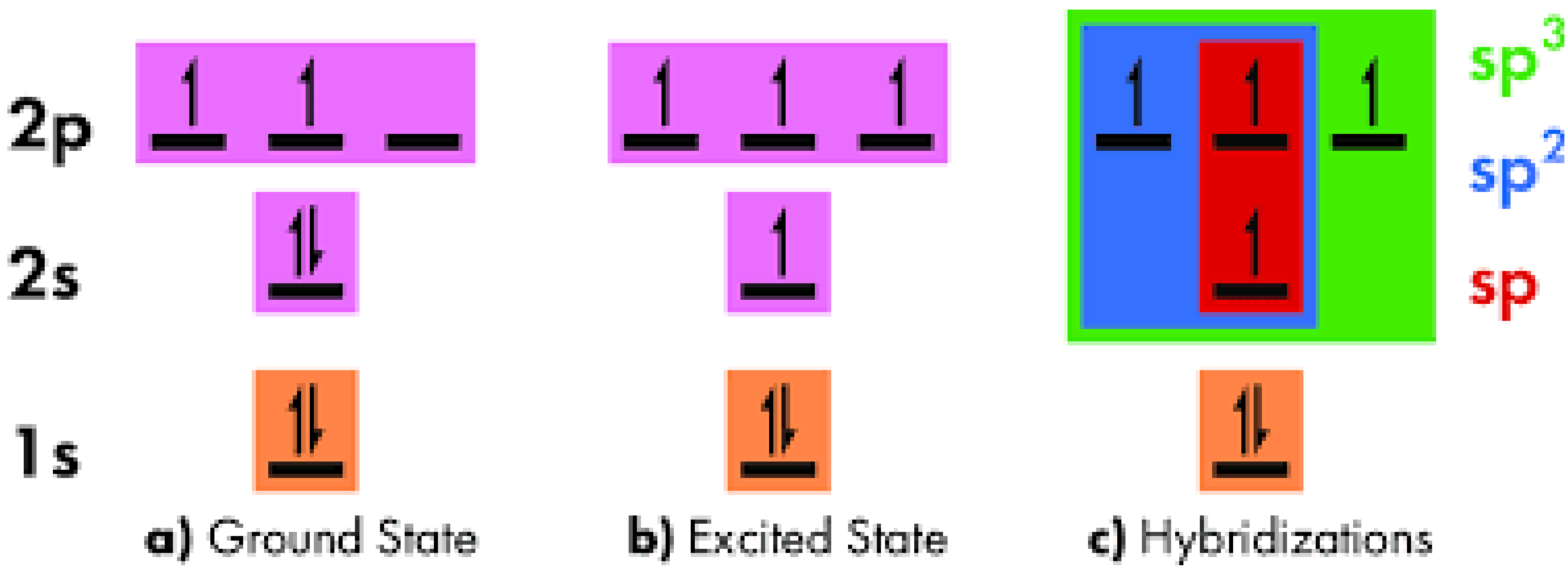
ground state for carbon

excited state for carbon

Hybridization takes place in EXCITED STATE of AO of carbon



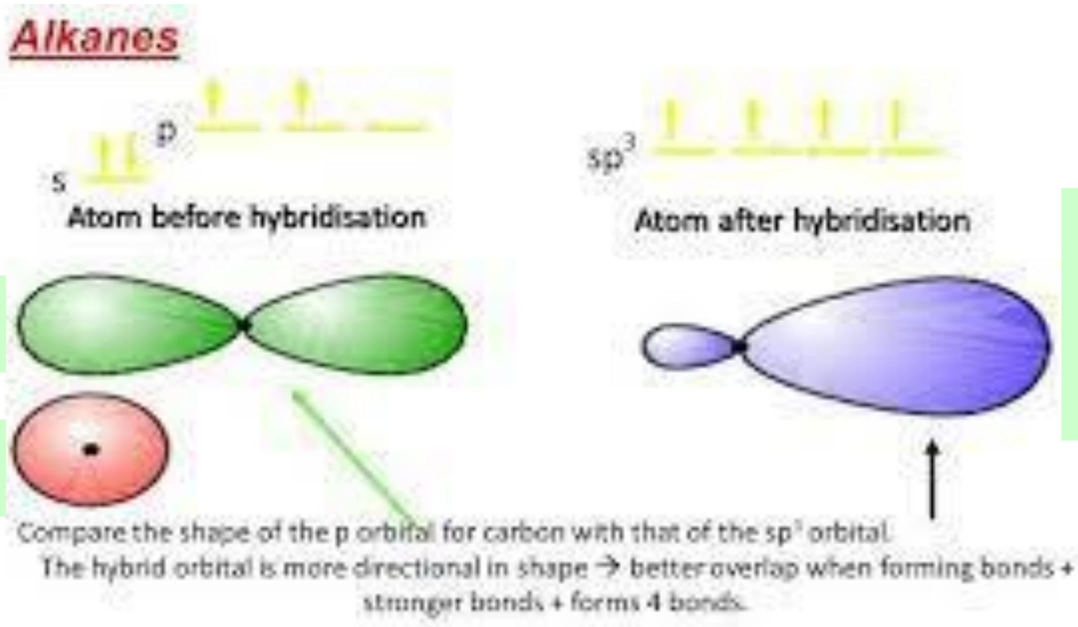
Understanding Types of Hybridization in Carbon Atomic Orbitals



AO before and after Hybridization

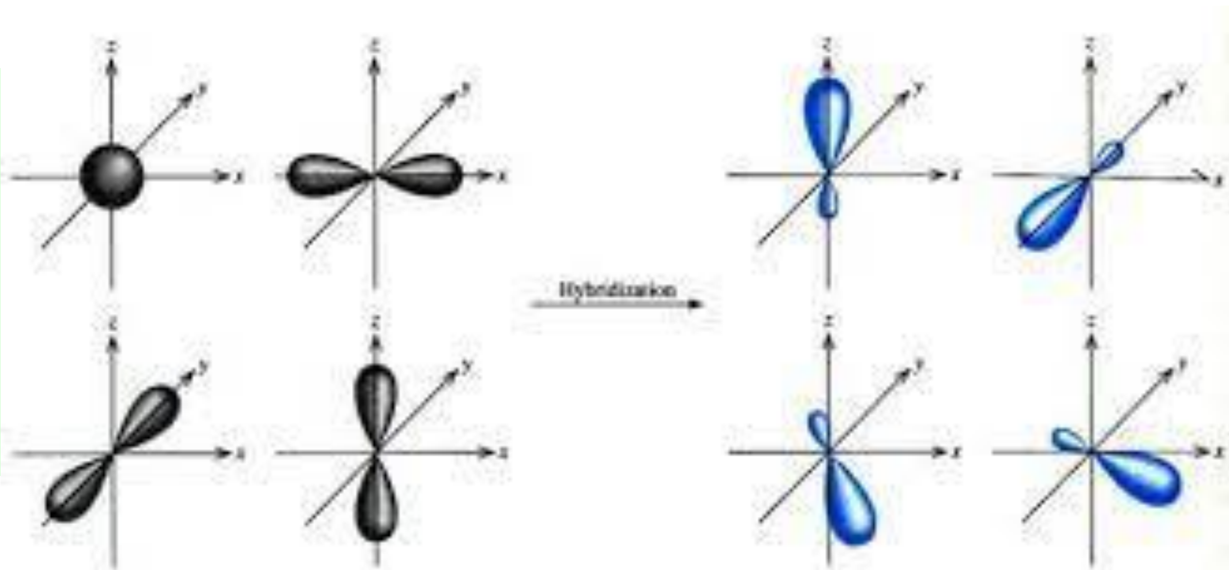
‘p’ ORBITAL

‘s’ ORBITAL



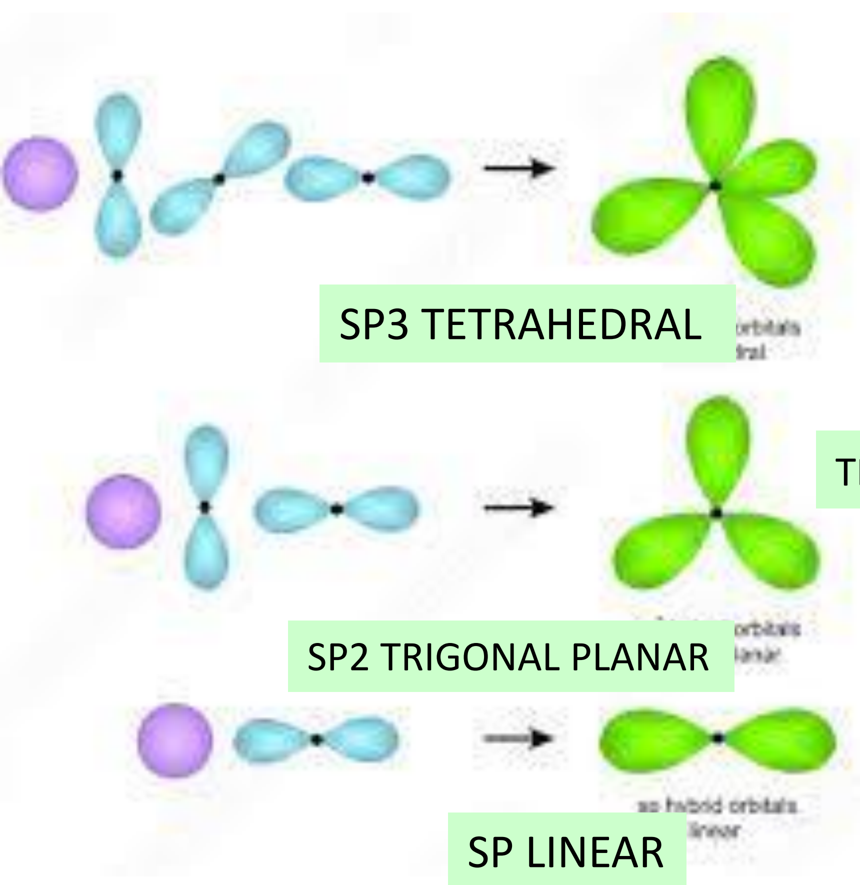
‘sp^3’ ORBITAL
25% s character
75% p charachter

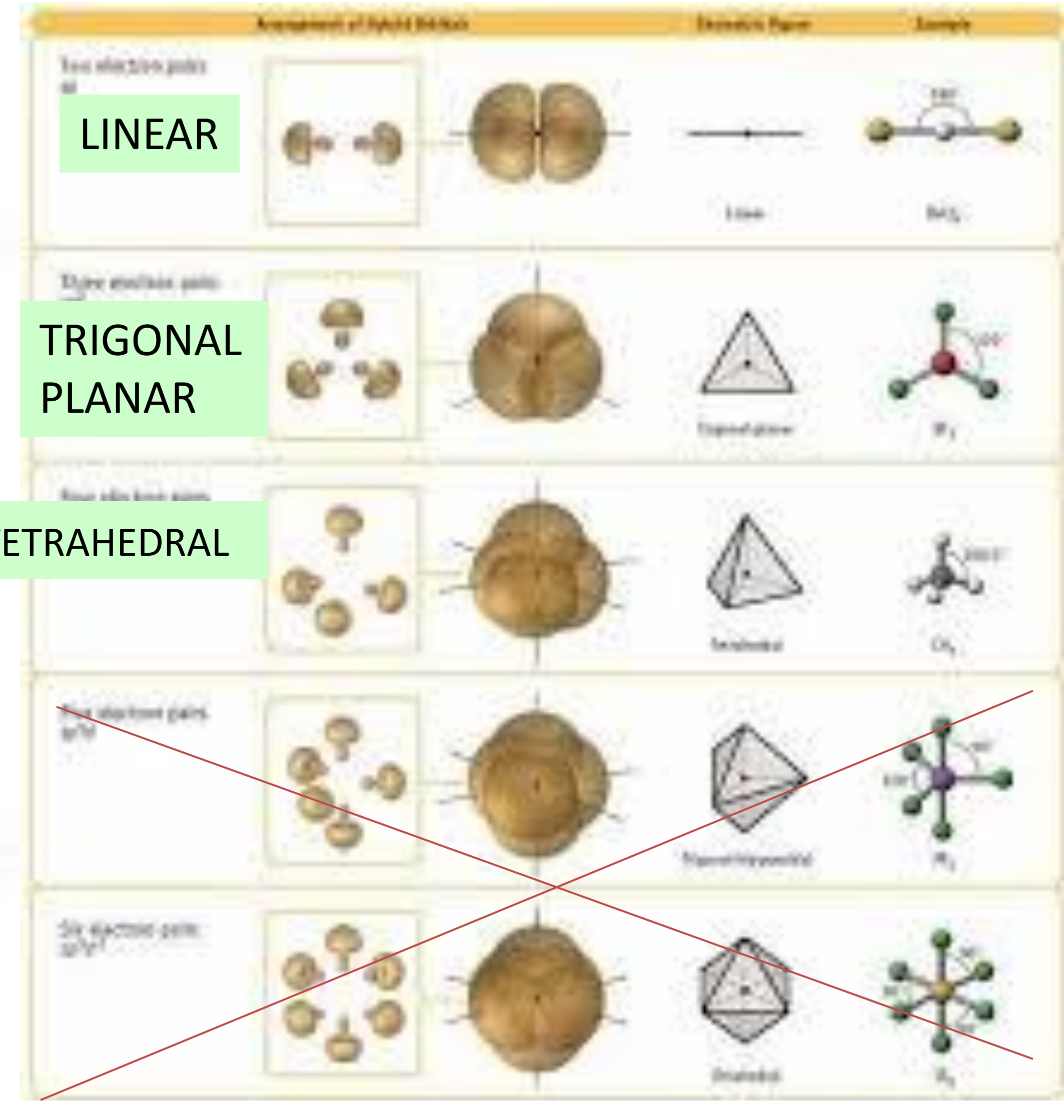
1s + 3p combine to form 4 new orbitas



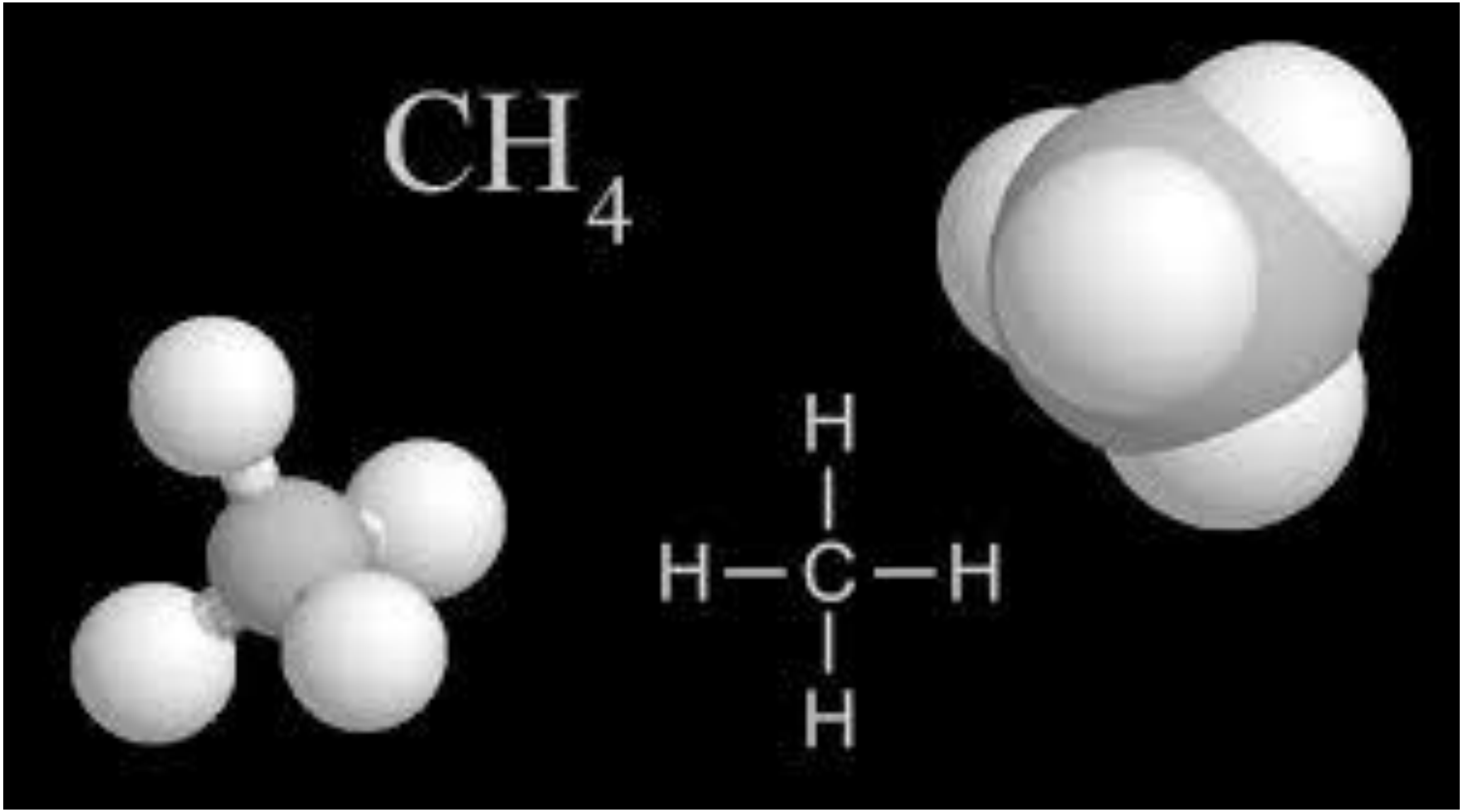
4 sp3 hybrid orbitals

Hybridization brings about change in shape and bond angle of molecule





Hybridization Type is sp^3



1s + 3 p orbitals = 4 sp3 orbitals

Hybridization Type is sp^3

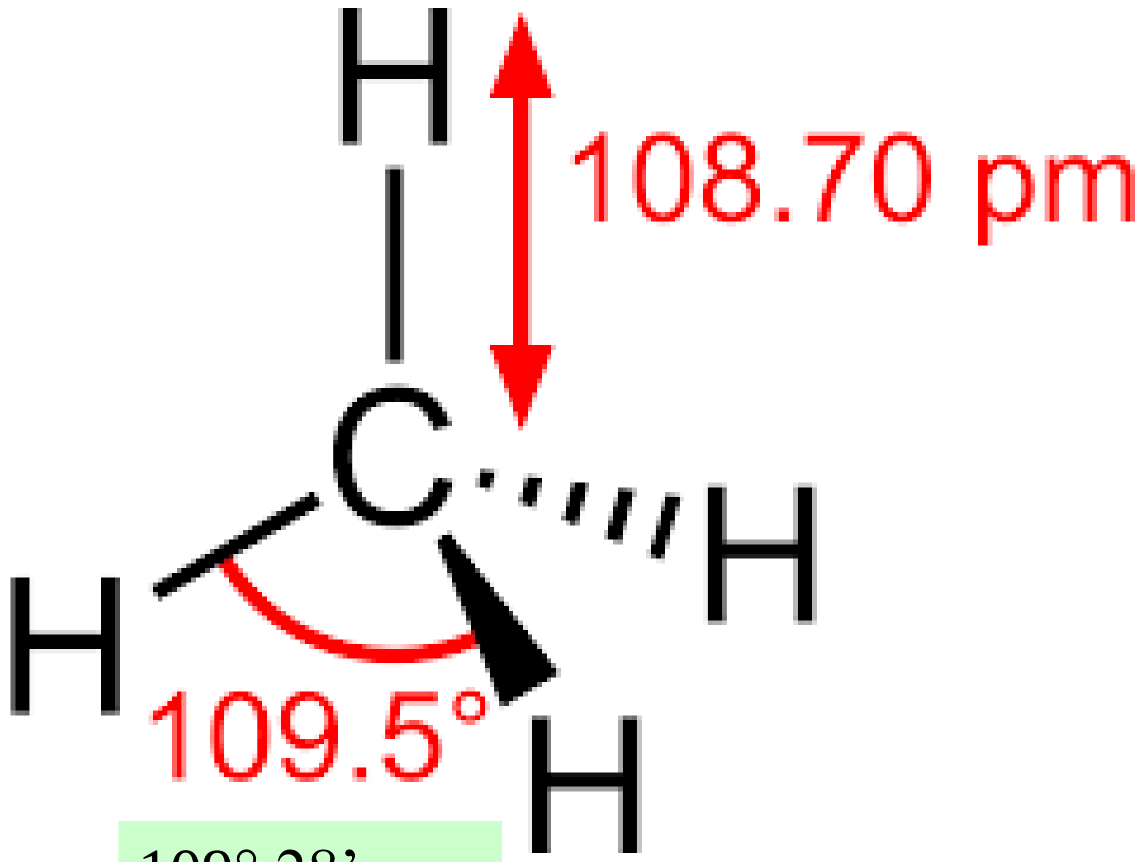
SINGLE BOND IS A SIGMA ELECTRON BOND

THESE ARE CALLED SATURATED MOLECUES

THE SHAPE OT THE MOLECULE IS THREE DIMENSIONAL

GEOMETRY OF MOLECULE IS TETRAHEDRAL

BOND ANGLE 109.5°



109° 28’

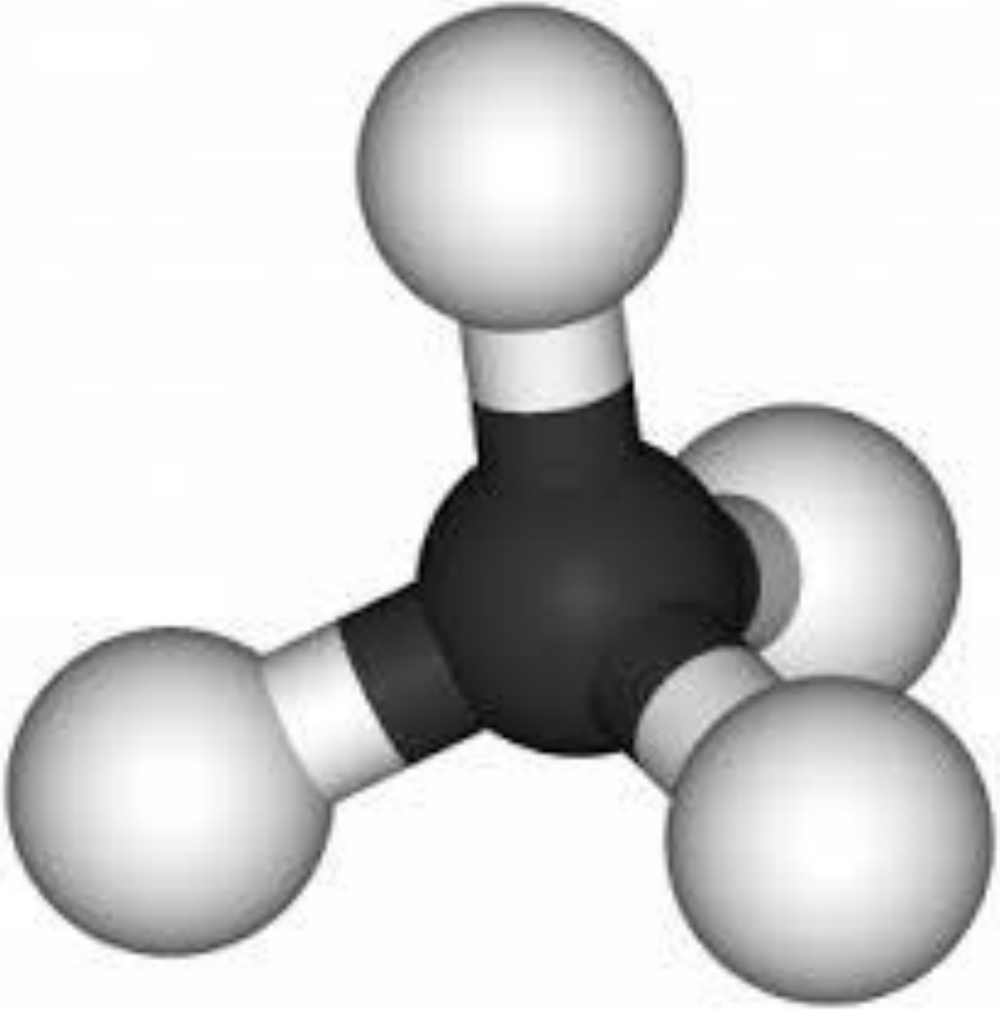
Hybridization Type is sp^3

THE SHAPE OT THE MOLECULE IS THREE DIMENSIONAL

GEOMETRY OF MOLECULE IS TETRAHEDRAL

25% OF S CHARACTER AND 75% OF P CHARACTER

BOND ANGLE 109.5°



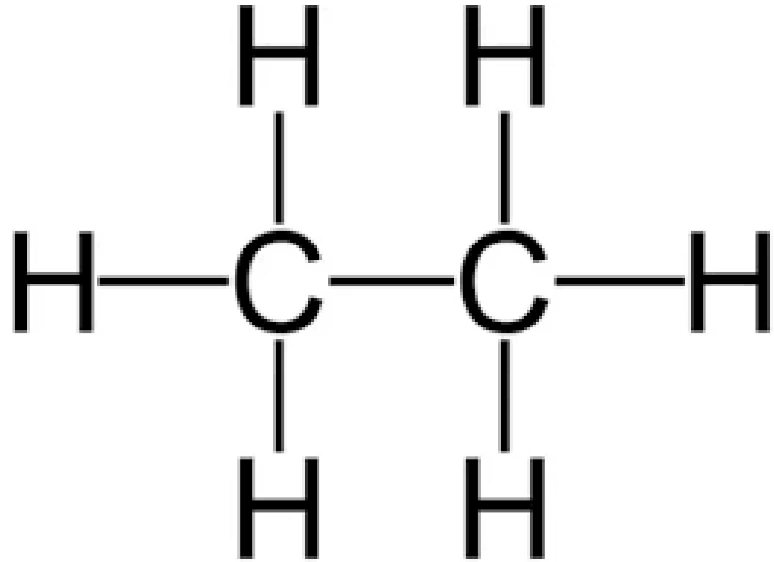
Tetrahedral Molecule of Ethane

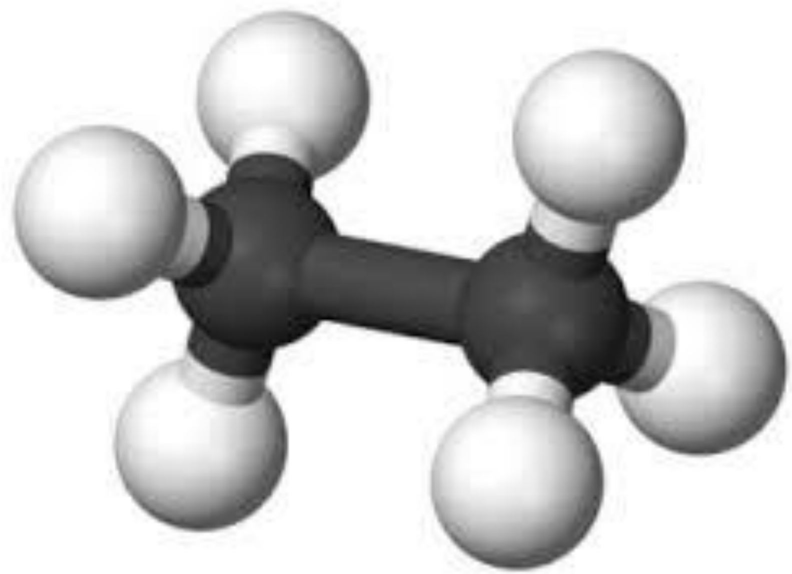
THE SHAPE OT THE MOLECULE IS THREE DIMENSIONAL

GEOMETRY OF MOLECULE IS TETRAHEDRAL

25% OF S CHARACTER AND 75% OF P CHARACTER

BOND ANGLE 109.5°





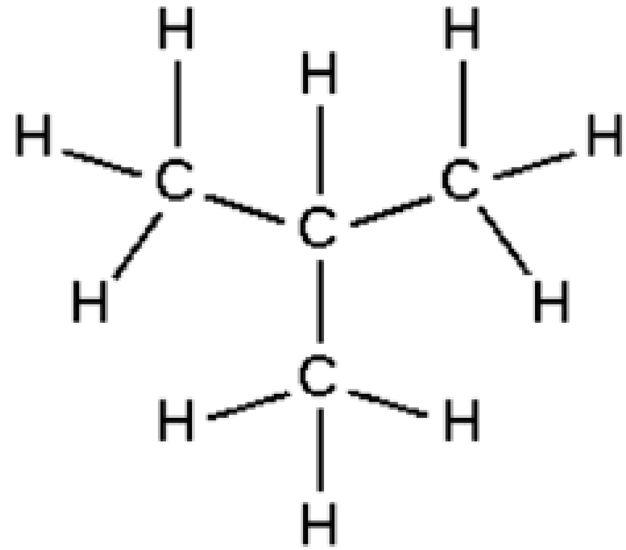
Tetrahedral Molecule of Butane and Isobutane

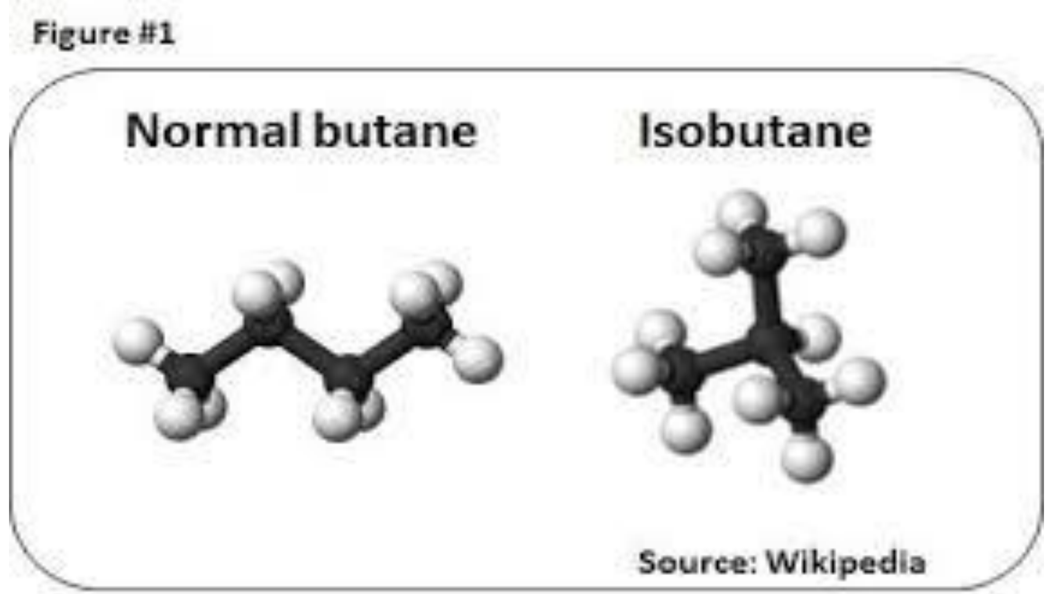
THE SHAPE OT THE MOLECULE IS THREE DIMENSIONAL

GEOMETRY OF MOLECULE IS TETRAHEDRAL

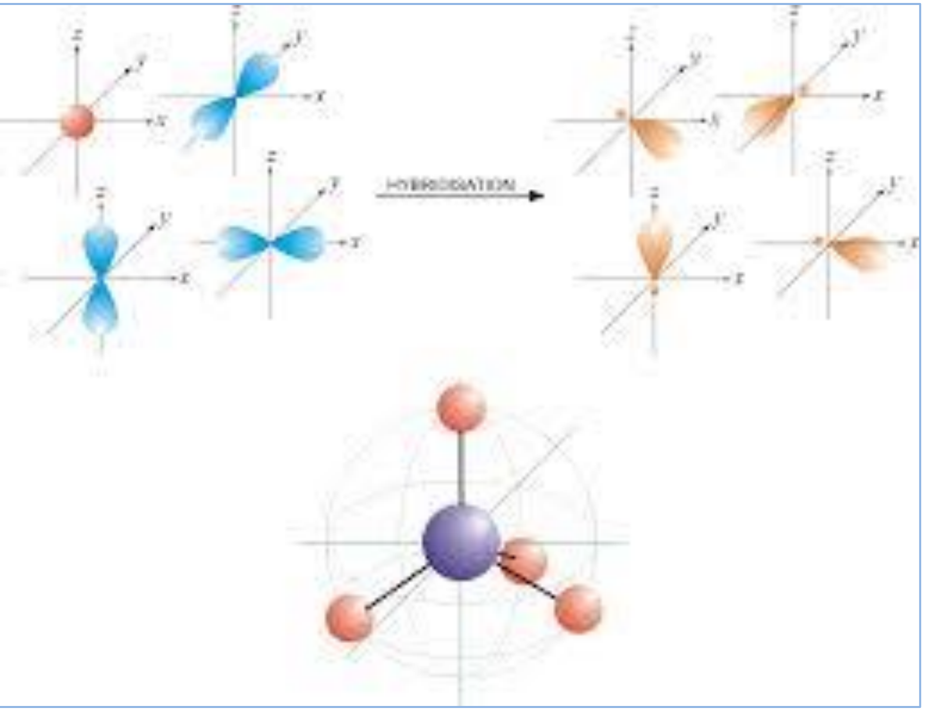
25% OF S CHARACTER AND 75% OF P CHARACTER

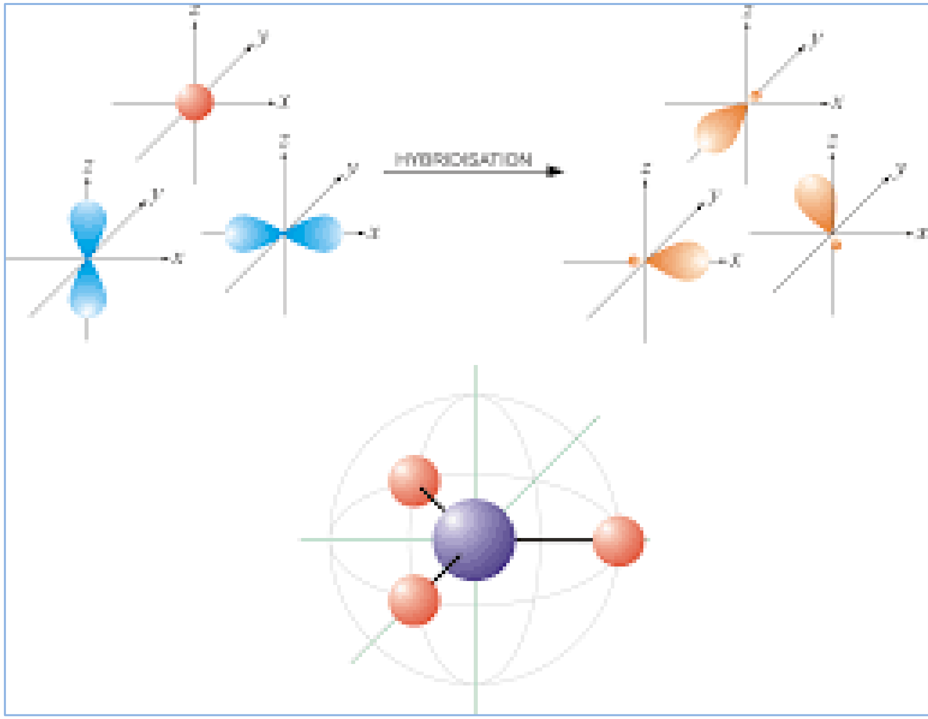
BOND ANGLE 109.5°





Hybridization Type is sp^2





THIS IS sp^3 HYBRIDIZED MOLECULE

The four sp3 orbitals will form 4 sigma bonds. The 4 sp3 orbitals are not arranged in a single plane. The shape of molecule is three dimensional.

THIS IS sp^2 HYBRIDIZED MOLECULE

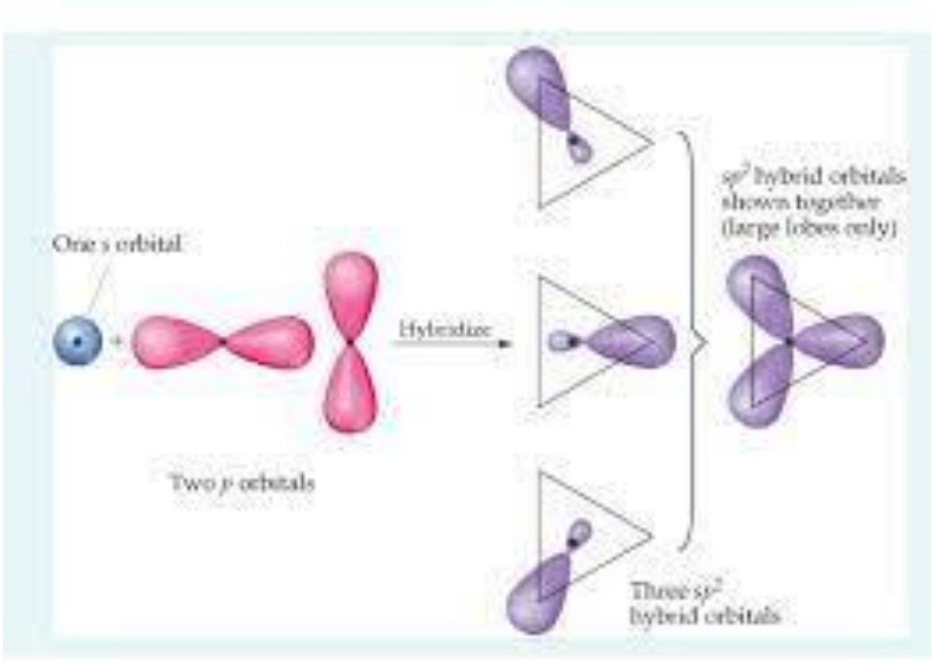
The three sp2 orbitals will form 3 sigma bonds. The 3 sp2 orbitals are arranged in a single plane. The shape of a molecule is two dimensional. The bond angle is 120°

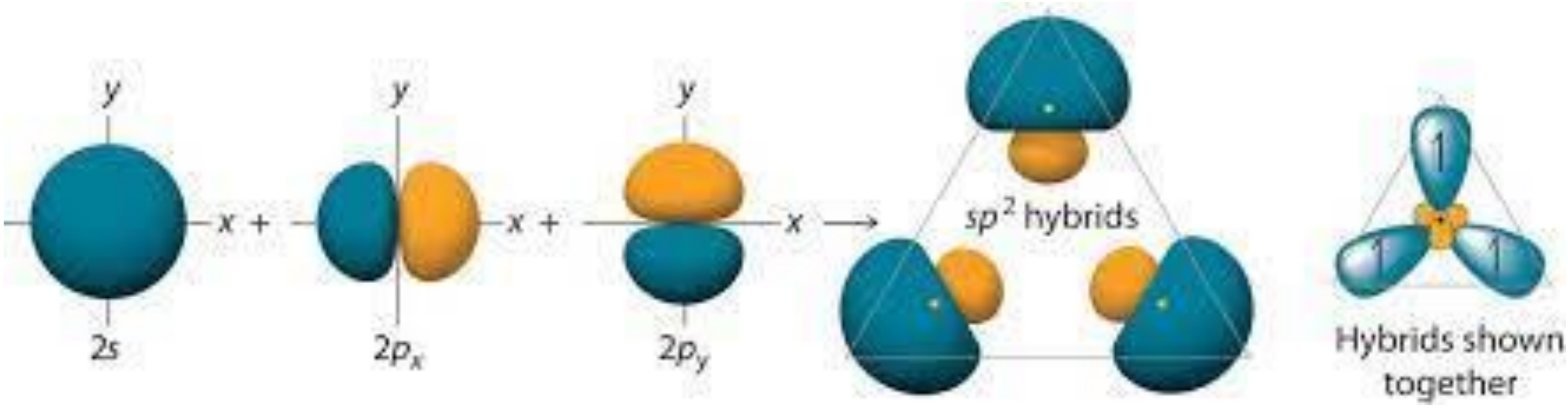
Hybridization Type is sp^2

THESE PICTURES SHOW ONLY THE 3 sp2 HYBRID AOMIC ORBITALS WHICH ARE SIGMA BONDS.

THESE PICTURES DO NOT SHOW THE PRESENCE OF A PI BOND.

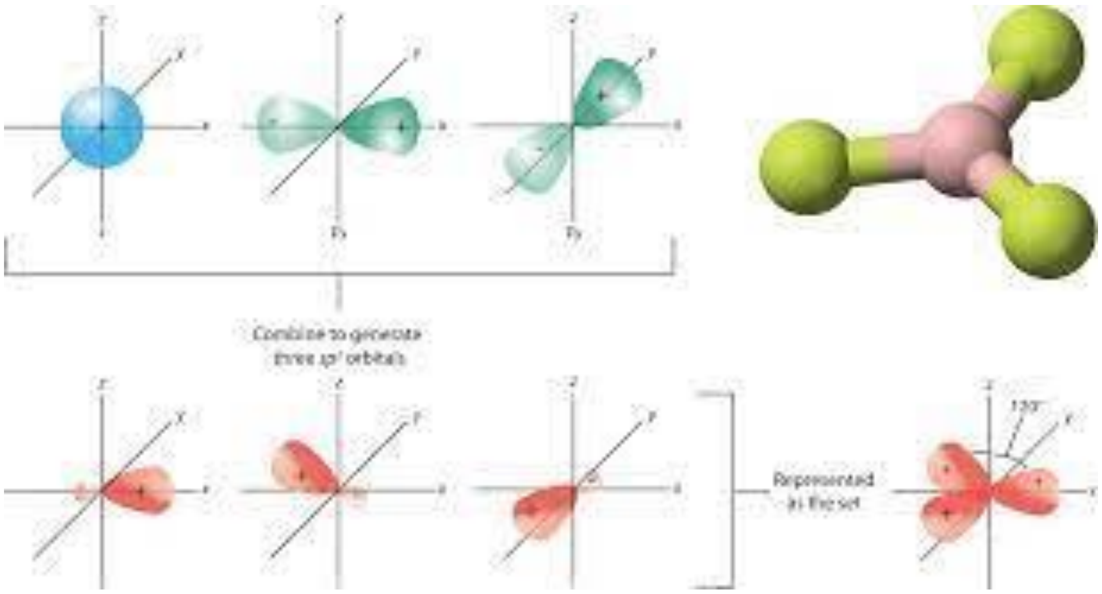
THESE PICTURES DO NOT SHOW THE PLACEMENT OF THE REMAINING PZ ORBITAL WITH ONE ELECTRON

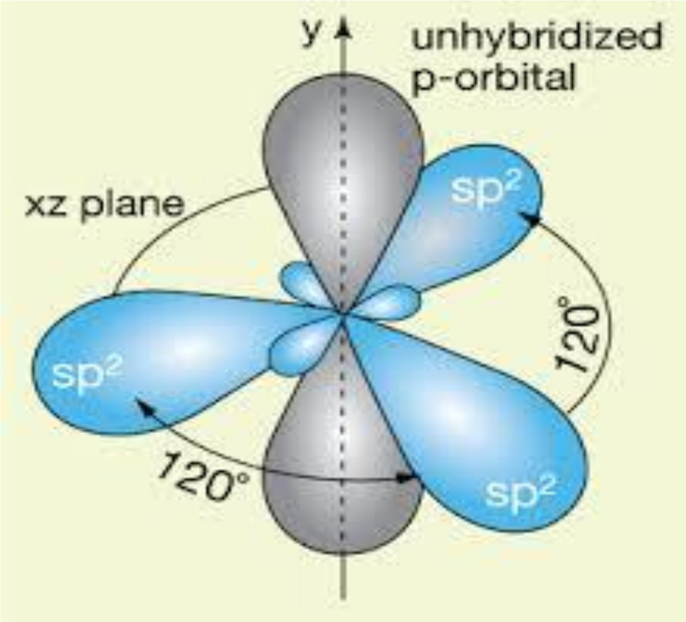




Hybridization Type is sp^2

THIS PICTURE SHOWS THE 3 SP2 HYBRID ATOMIC ORBITALS WHICH ARE SIGMA BONDS AND DIRECTED TO THE THREE CORNERS OF AN EQUILATERAL TRIANGLE.



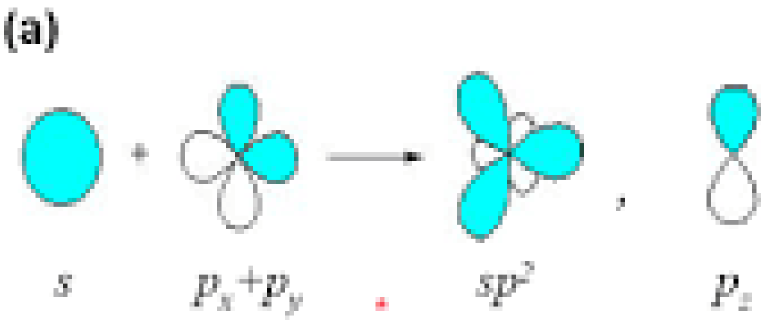


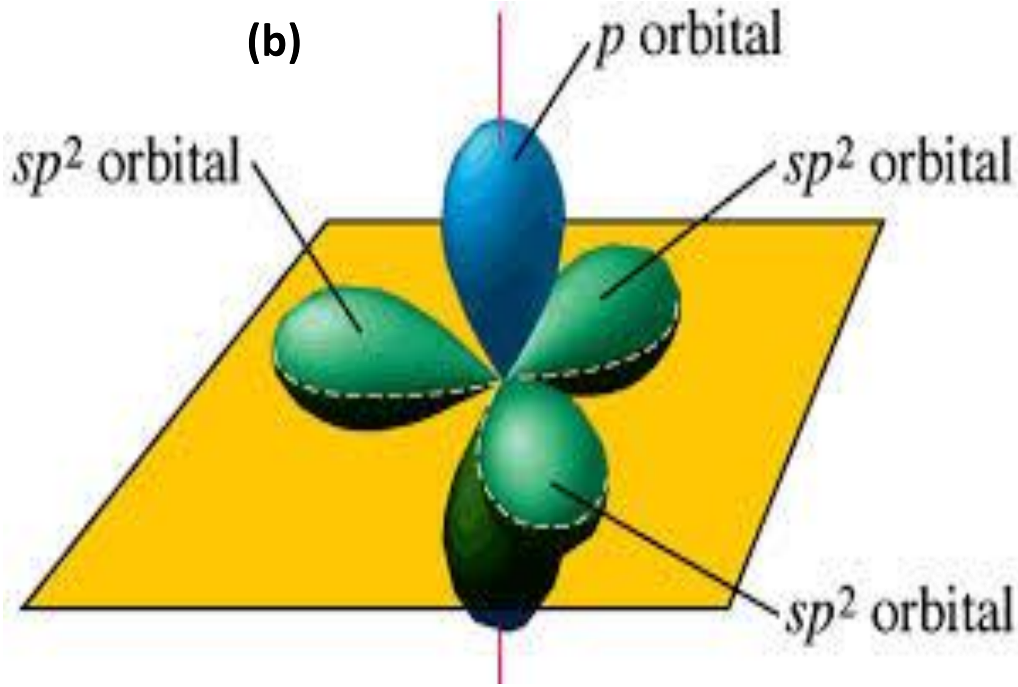
Hybridization Type is sp^2

PICTURE (A) SHOWS THE PRESENCE OF AN UNHYBRIDIZED PZ AO.

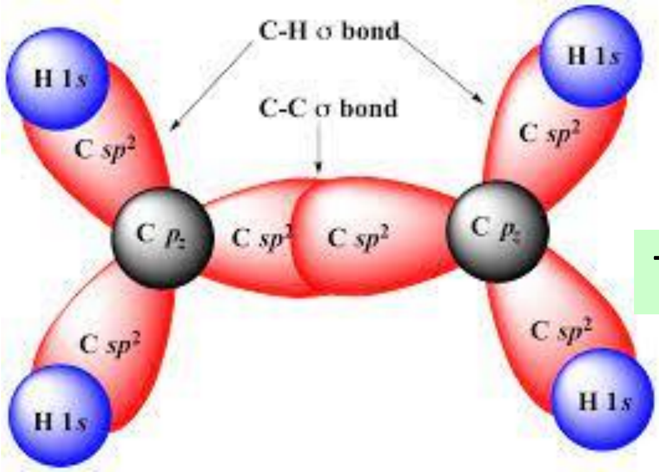
PICTURE (B) SHOWS THE PLACEMENT OF THE PZ ORBITAL HAVING ONE ELECTRON WITH RESPECT TO THE THREE HYBRID ORBITALS.

THE UNHYBRID PZ IS PERPENDICULAR TO THE PLANE OF THE HYBRIDIZED ORBITALS.



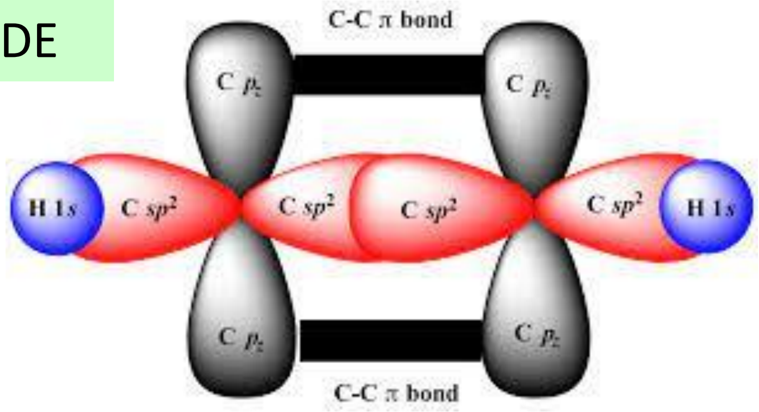


Hybridization Type is sp^2



THIS IS AN ETHYLENE MOLECULE AS SEEN FROM ABOVE

THIS IS AN ETHYLENE MOLECULE AS SEEN FROM SIDE



Hybridization Type is sp^2

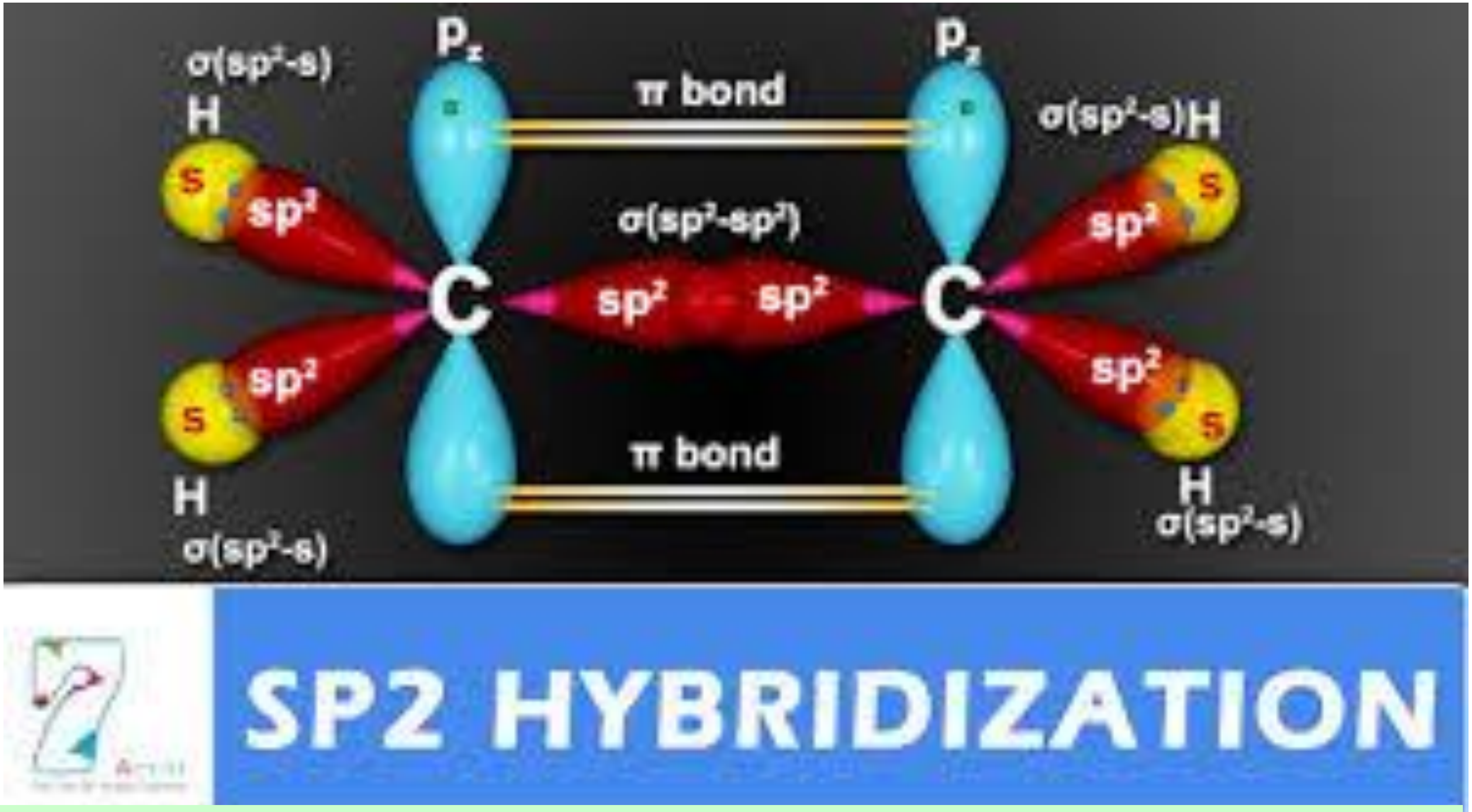
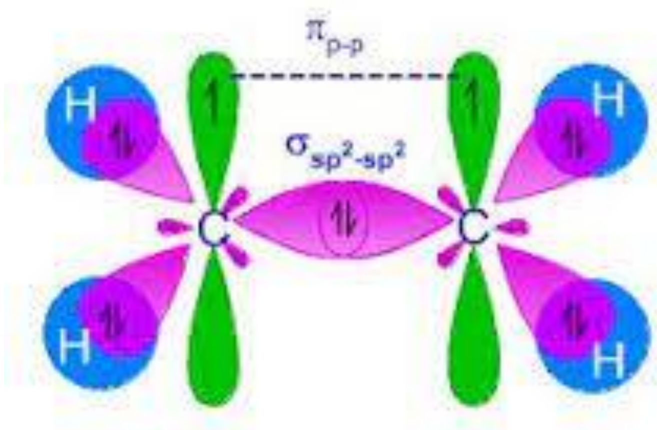
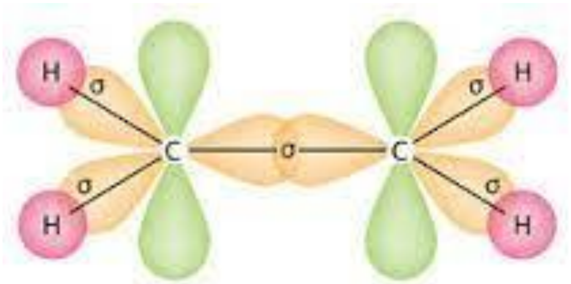


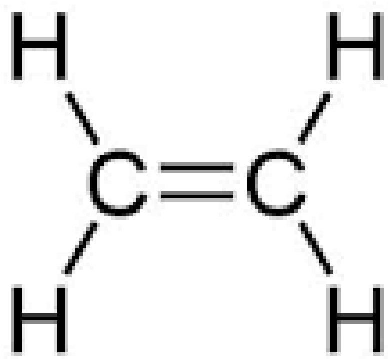
DIAGRAM AS YOU DRAW ON PAPER

Hybridization Type is sp^2



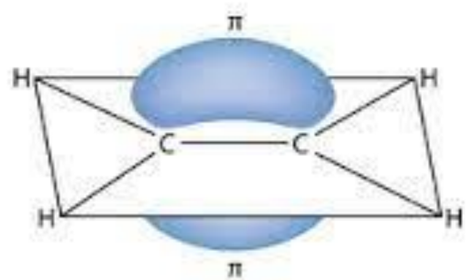


Sigma (σ) bond

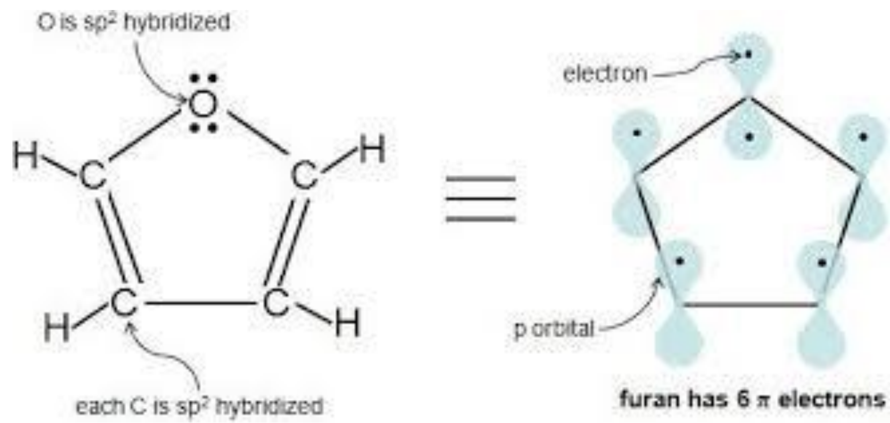


ethylene

methylene

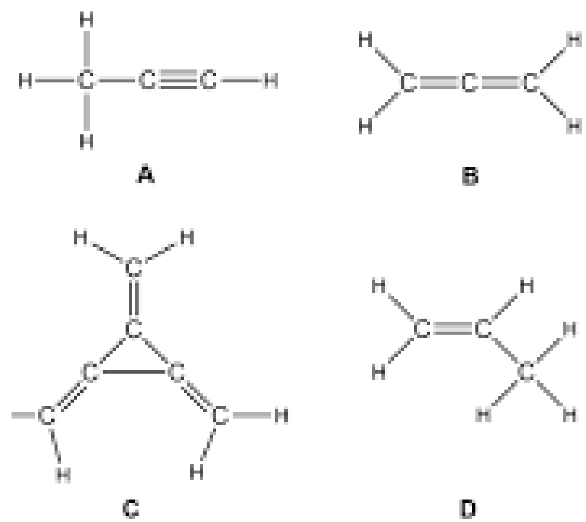


Hybridization Type is sp^2

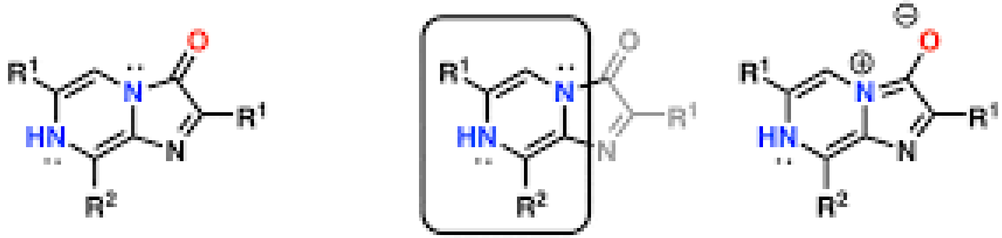


furan has 6 π electrons

Which molecule has carbon atoms that are sp^2 and sp^3 hybridized?



An exception to the exception



Coelenterazine

8 pi electrons ("antiaromatic")

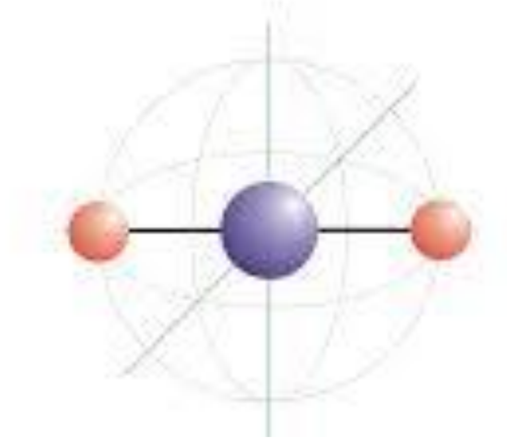
Resonance form with 10 pi electrons (aromatic)

if both nitrogens are sp^2 hybridized, the six-membered ring qualifies as anti-aromatic

Hybridization Type is sp

THIS IS sp HYBRIDIZED MOLECULE

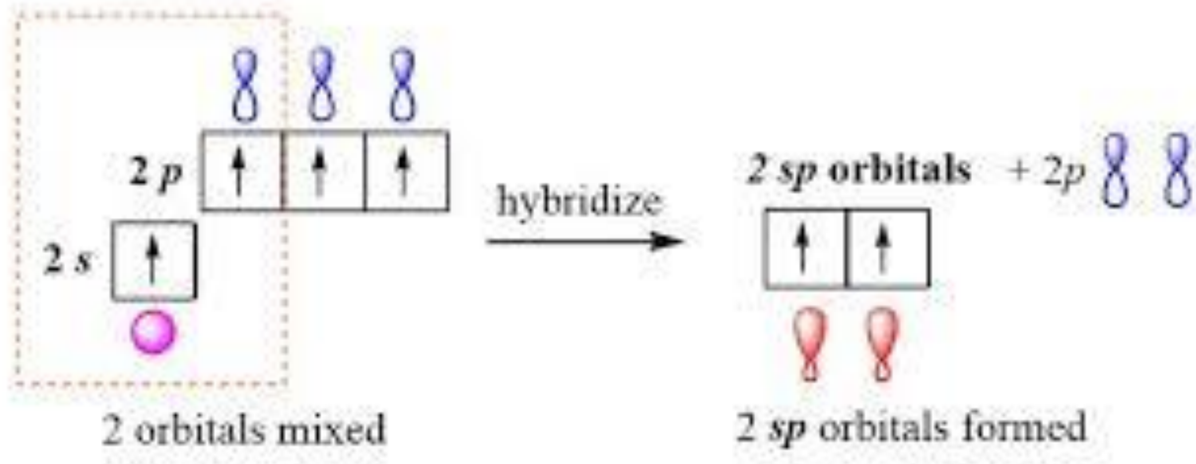
The two sp orbitals will form 2 sigma bonds. The 2 sp orbitals are arranged in a straight line. The shape of a molecule is one dimensional/linear. The bond angle is 180°

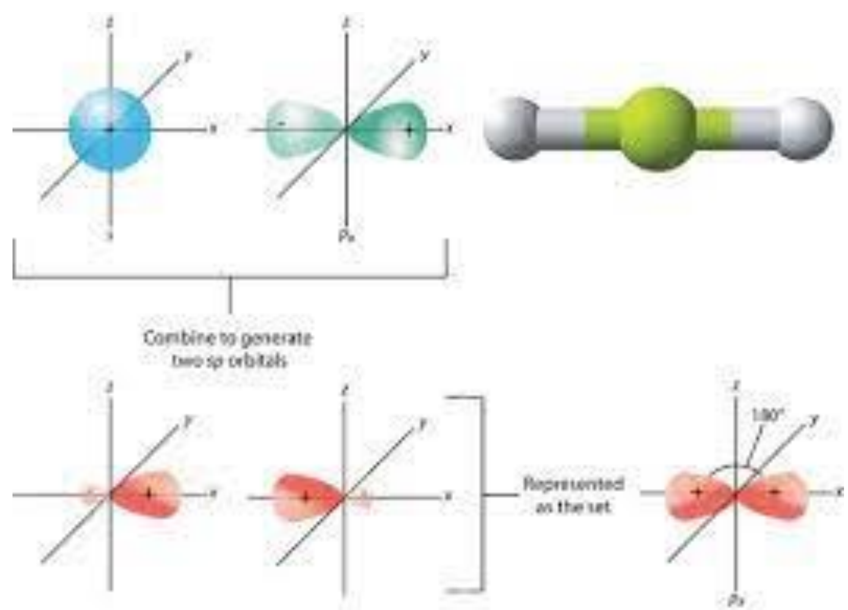


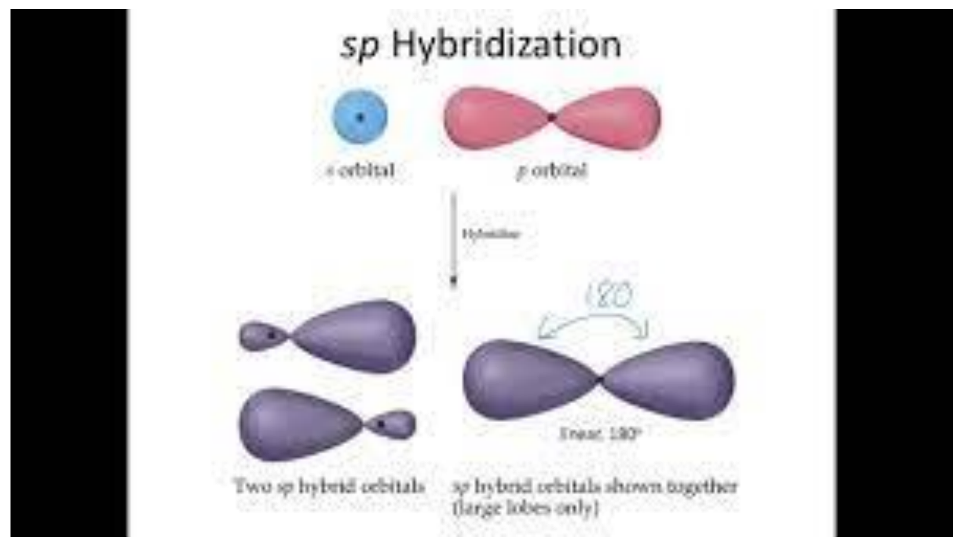
Hybridization Type is sp

THE TWO HYBRID sp ORBITALS ARE ORIENTED OPPOSITE TO EACH OTHER

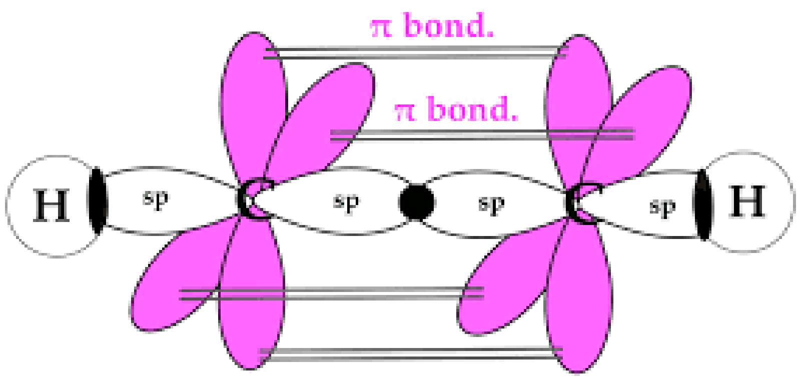
THEY MAKE AN ANGLE OF 180° WITH RESPECT TO EACH OTHER.

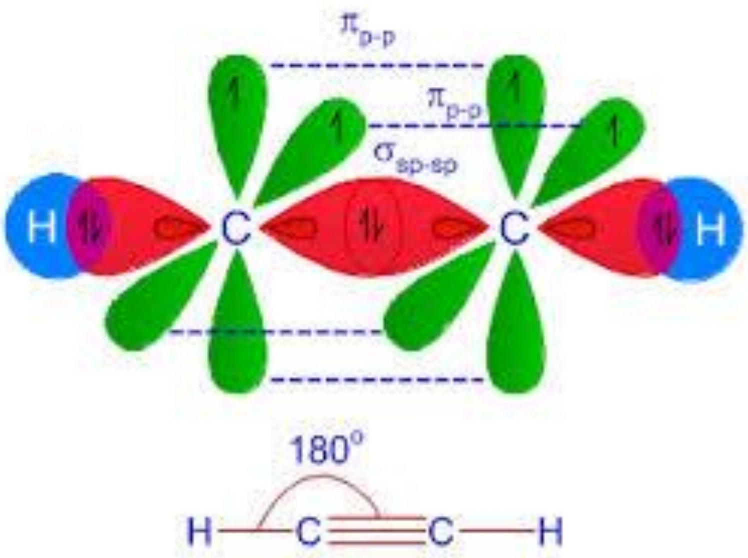


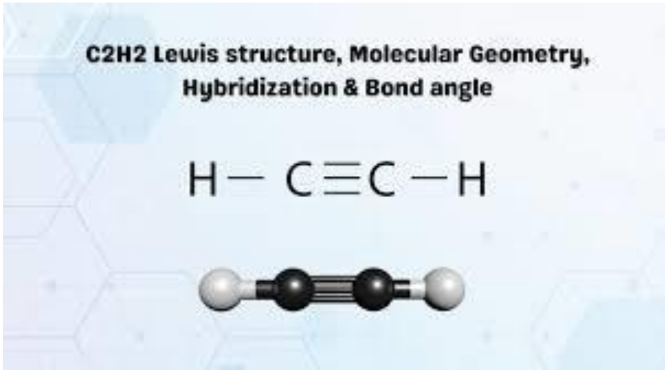


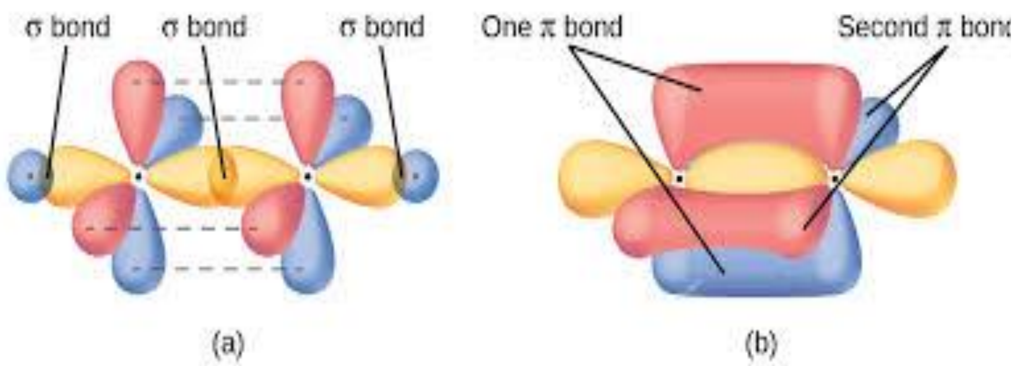


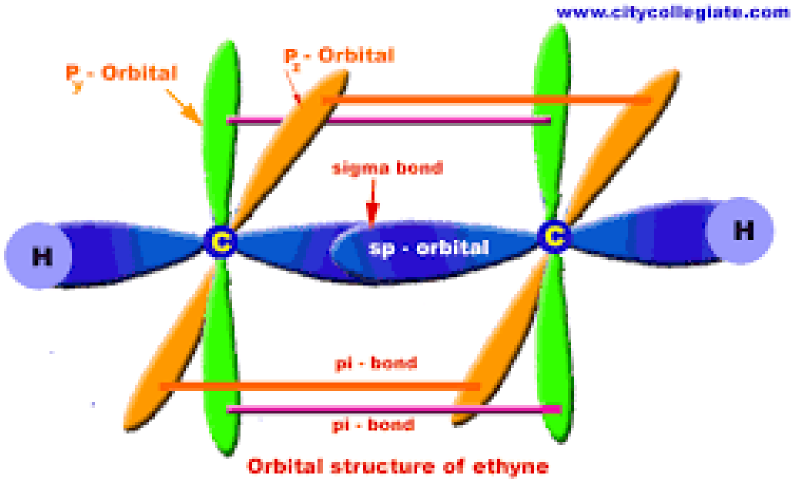
Hybridization Type is sp in ACETYLENE or ETHYNE



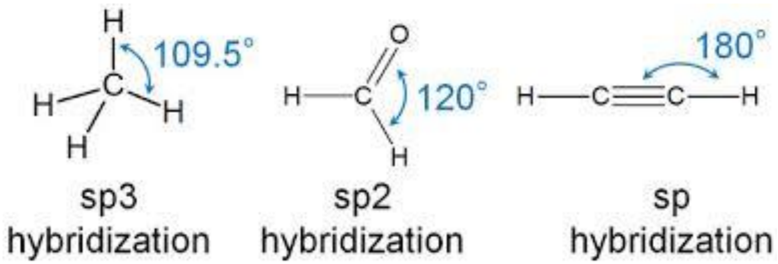


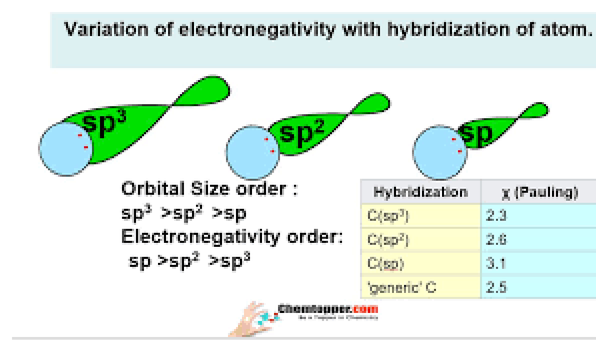


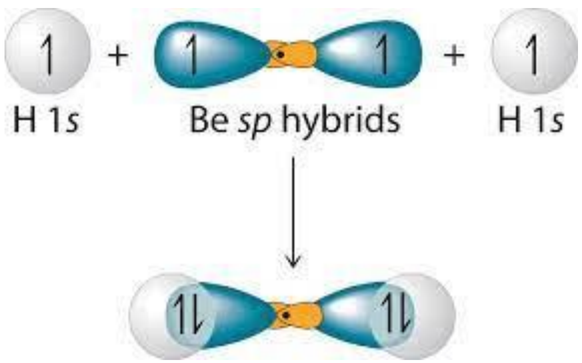


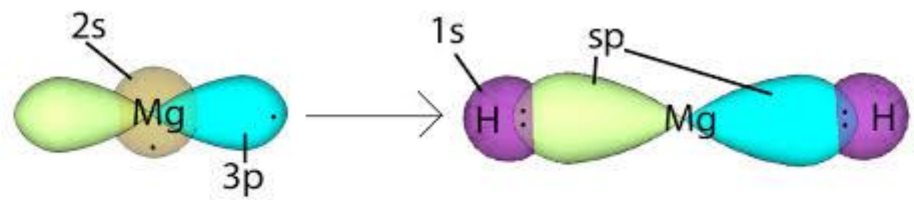


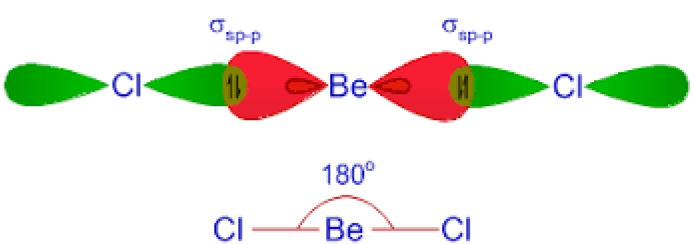
Hybridization Type is sp – all these molecules are linear in shape

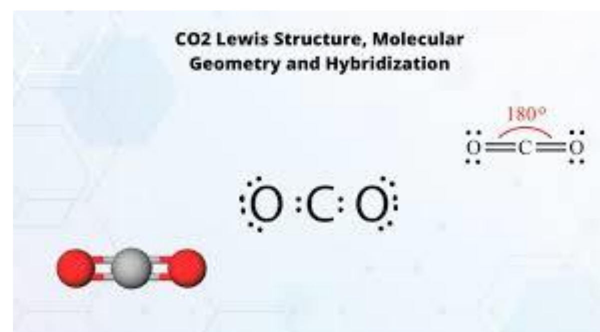








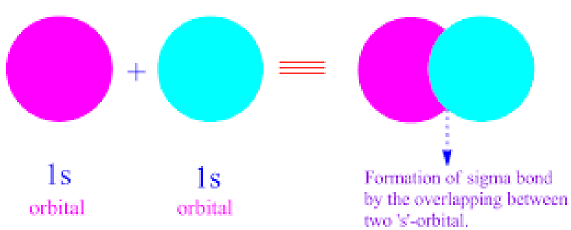


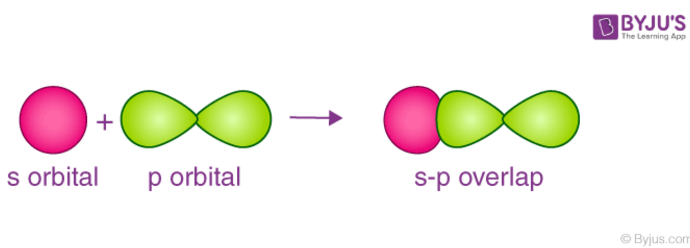


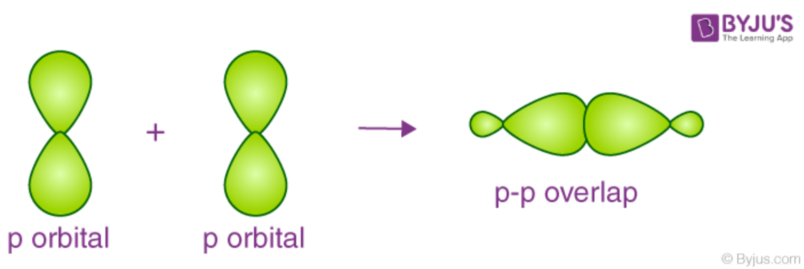
SIGMA (σ) AND PI (π) BONDS

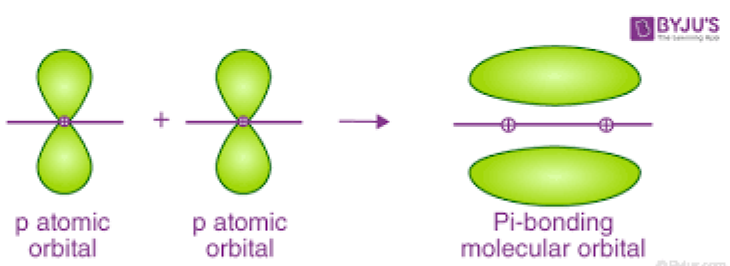
Covalent bonds are formed by the overlapping of atomic orbitals.
Sigma and pi bonds are types of covalent bonds that differ in the overlapping of atomic orbitals.
Sigma bonds are formed due to head-to-head / 180 ° overlapping of atomic orbitals.
Pi bonds are formed by the lateral/sideways overlap of two atomic orbitals.

Various bond parameters such as bond length, bond angle, and bond enthalpy depend on the way the atomic orbital overlap.
This overlap gives rise to two primary types of covalent bonds, i.e. sigma and pi bonds.
Electrons of sigma bond are called sigma electrons and those of pi bond are called pi electrons.

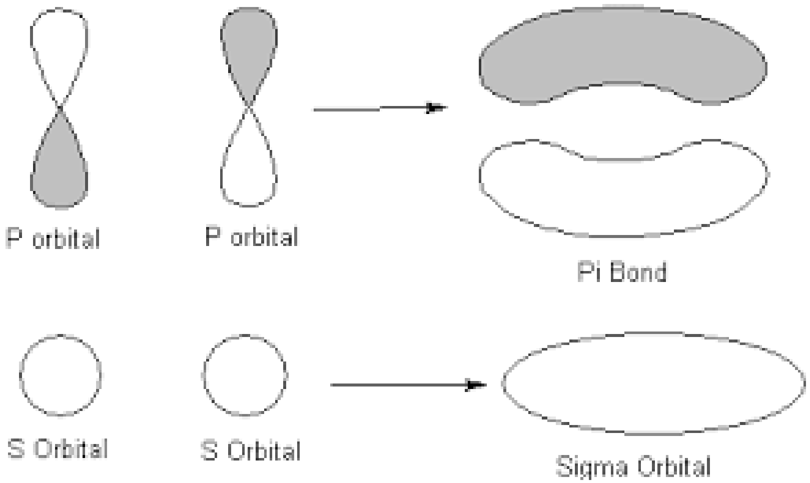


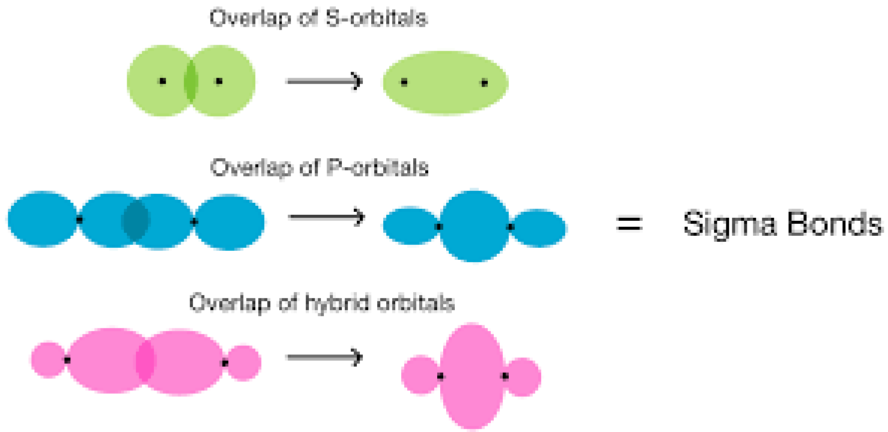


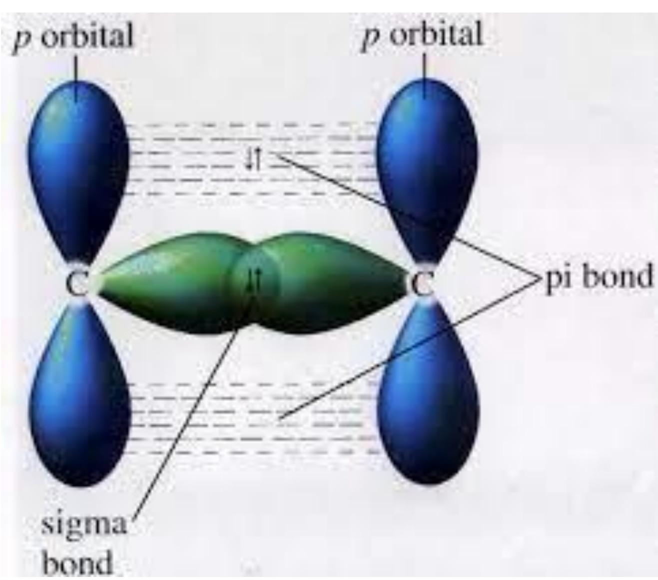


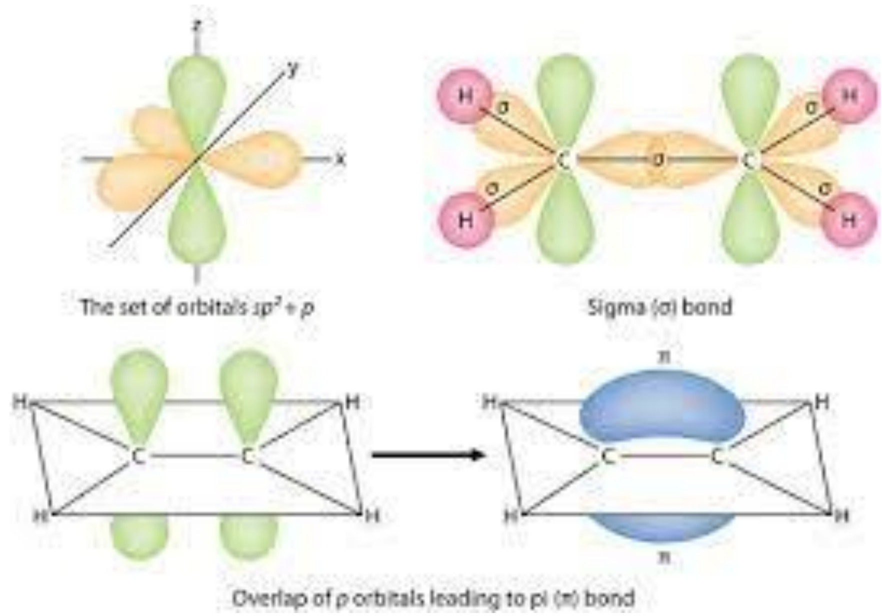


SIGMA (σ) AND PI (π) BONDS









THE SIGMA (σ) BONDS

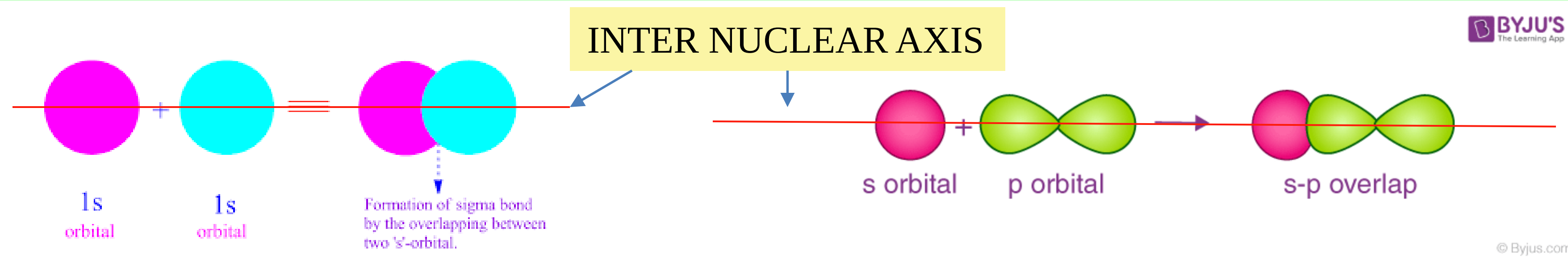
This type of covalent bond is formed by head-on overlap of atomic orbitals along the nuclear axis.

Sigma bonds are the strongest covalent because the orbitals overlap directly.

The electrons participating in a σ bond are commonly referred to as σ electrons.

Actually, all single bonds are sigma bonds.

Sigma bods can be formed via the following combinations of atomic orbitals.



1. S-S Overlapping

One 's' orbital of one carbon atom undergoes head-on overlapping with the 's' orbital of the second carbon atom along the internuclear axis.

An 's' orbital must be half-filled (has only one electron) before it overlaps with another.

This type of overlap occurs in H_2 molecules, where each hydrogen atom has a half-filled s orbital.

2. S-P Overlapping

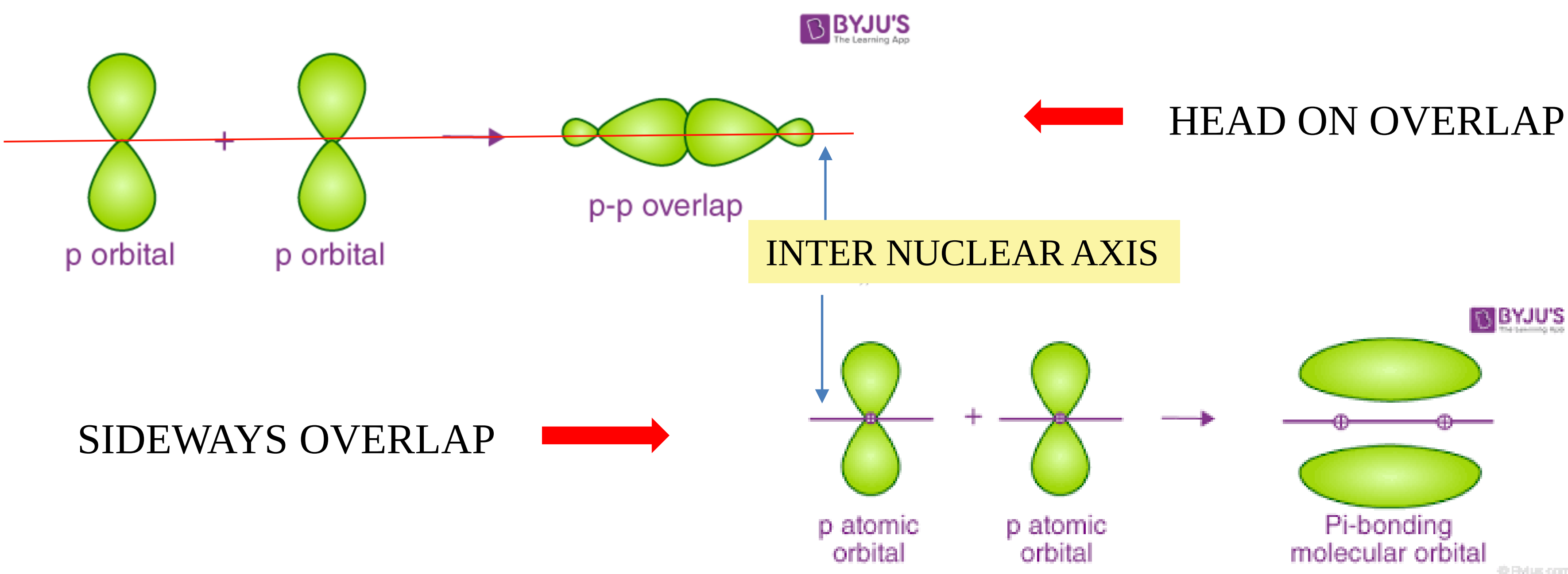
One half filled 's' orbital overlaps with one half-filled 'p' orbital along the internuclear axis, forming a covalent bond.

This type of overlapping can be observed in ammonia. An NH_3 molecule features 3 sigma bonds, formed by the overlap of the $2p_x$, $2p_y$, and $2p_z$ orbitals belonging to the nitrogen atom and the 1s orbitals of the three hydrogen atoms.

THE SIGMA (σ) BONDS

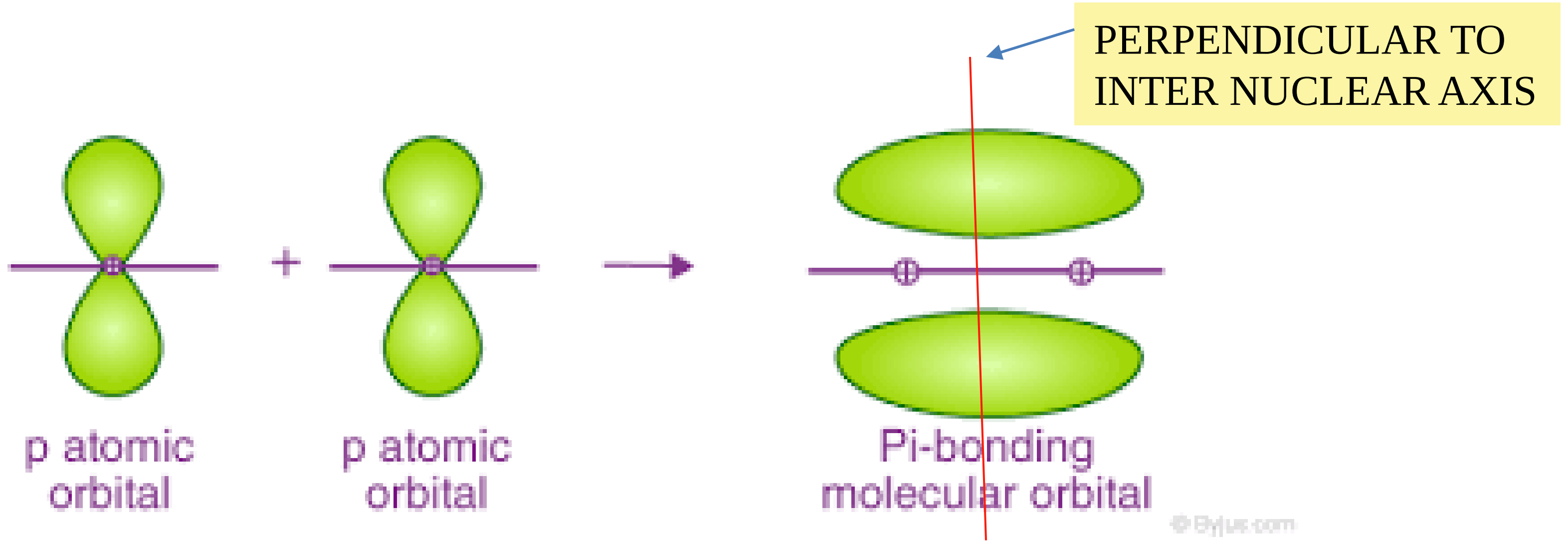
3. P-P overlapping

One half-filled 'p'orbital from each participating atom undergoes head-on overlapping along the internuclear axis. This type of overlapping is illustrated below.
A Cl_2 molecule features a p-p overlap of the $3p_z$ orbitals of two chlorine atoms.
It is important to note that the head-to-head overlapping of two p orbitals gives a sigma bond whereas the lateral/sideways/parallel overlap of these orbitals leads to the formation of pi bonds.



THE PI (π) BONDS

Pi bonds are formed by the sidewise overlap of atomic orbitals along a direction perpendicular to the internuclear axis.
During the formation of π bonds, the axis of the atomic orbitals are parallel to each other whereas the overlapping is perpendicular to the internuclear axis.
Pi Bonds are generally weaker than sigma bonds, owing to the significantly lower degree of overlapping. Generally, double bonds consist of one sigma and one pi bond, whereas a typical triple bond is made up of two π bonds and one σ bond.
It is important to note that a combination of sigma and pi bonds is always stronger than a single sigma bond.



DIFFERENCE BETWEEN SIGMA AND PI BONDS

Sigma Bond	Pi Bond
The overlapping orbitals can be pure or hybrid	The overlapping orbitals must be unhybridized
These bonds are strong and have high bond energies.	These bonds are relatively weak.
Can exist independently	Must exist along with a sigma bond.
Has an impact on the shape of molecules	Has no role in determining the shape of molecules

Identify the hybridization Types sp^3, sp^{2}, sp