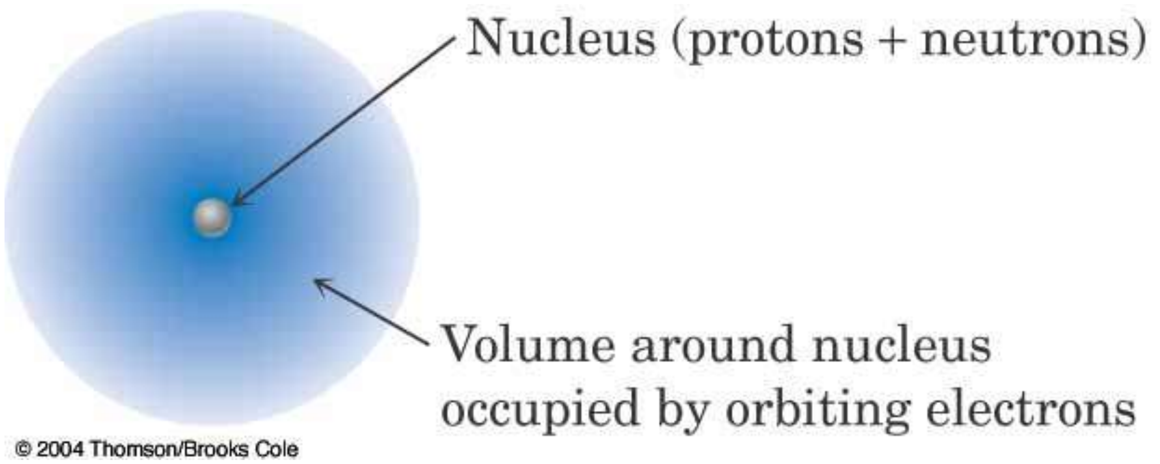
Basics of Organic Chemistry Bonding and Physical Properties

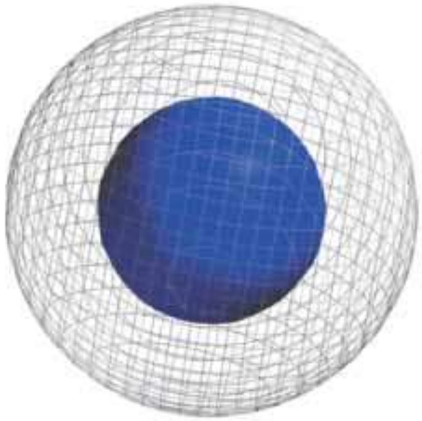
Marks: 20

Organic Chemist's Periodic Table

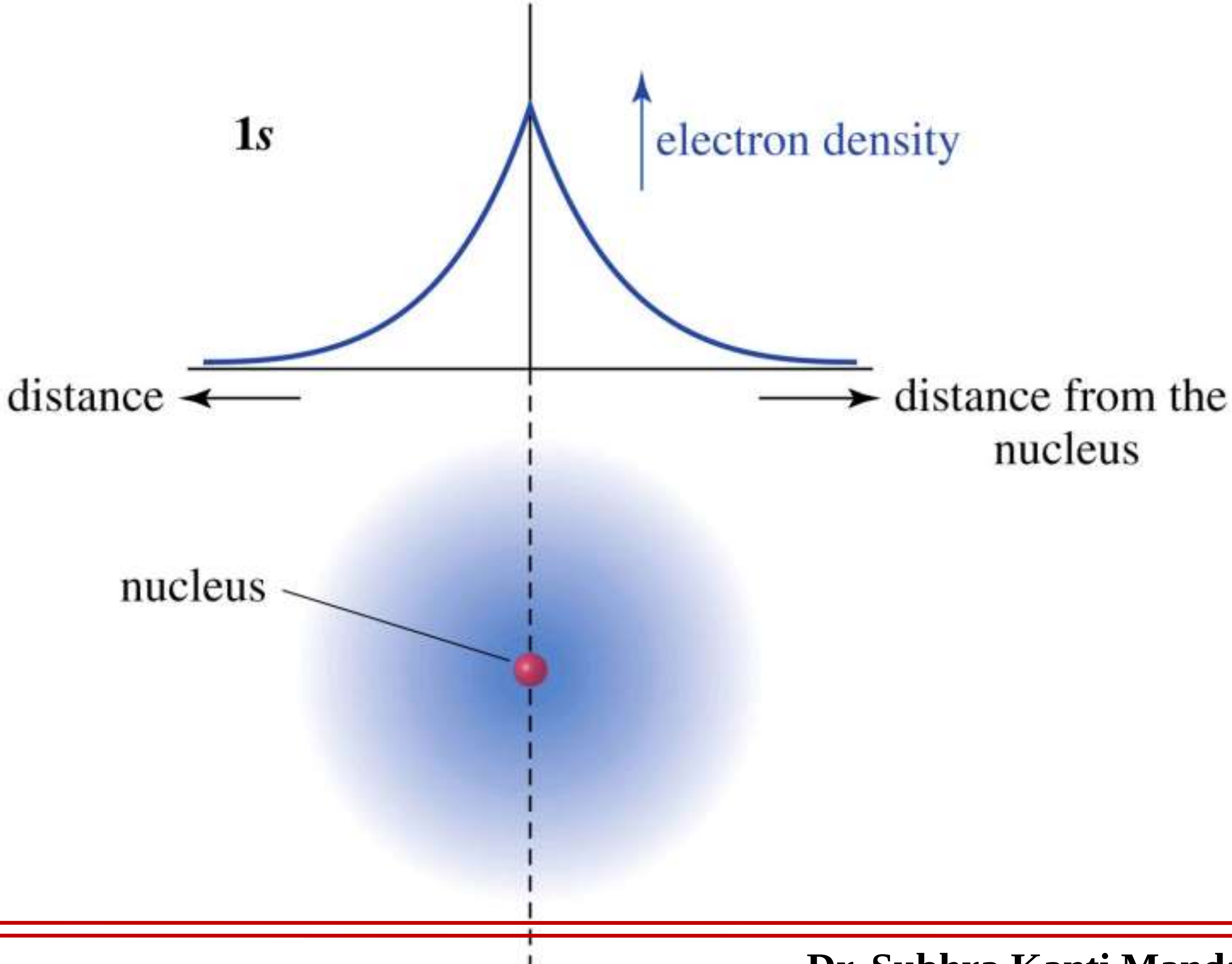
Group 1A	2A											3A	4A	5A	6A	7A	8A
H																	He
Li	Be											B	**C**	**N**	**O**	**F**	Ne
Na	Mg											Al	Si	**P**	**S**	**Cl**	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	**Br**	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	**I**	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Nucleus is a Tiny Fraction of the Volume of an Atom

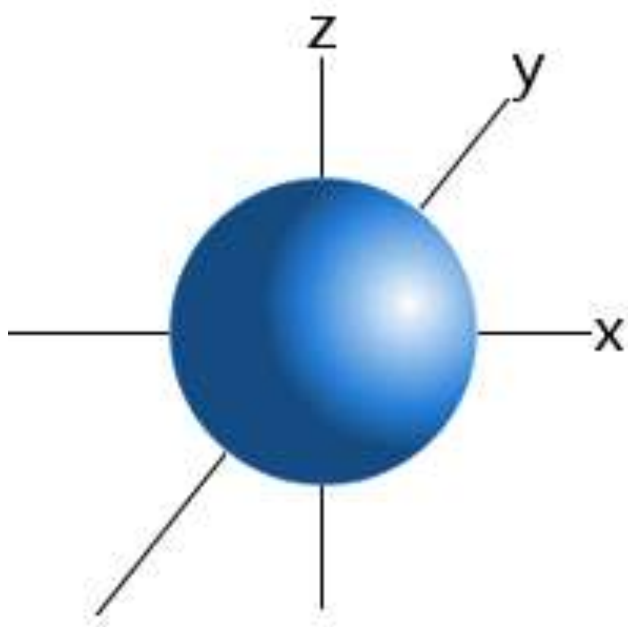




Orbitals are Probabilities



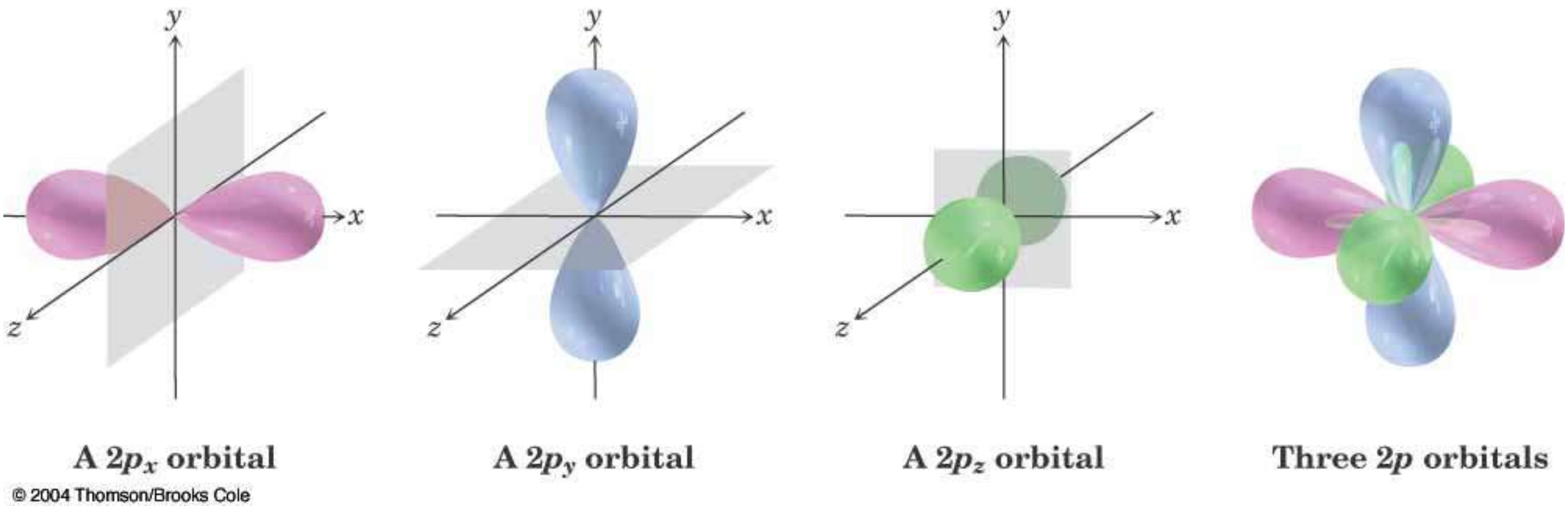
Shape of ‘s’ orbital :



s-orbital is spherical with the nucleus at its centre

Shape of ‘p’ orbitals :

p_x, p_y, p_z



- ❑ *p* orbital has the approximate shape of a pair of lobes on opposite sides of the nucleus, or a somewhat dumbbell shape.

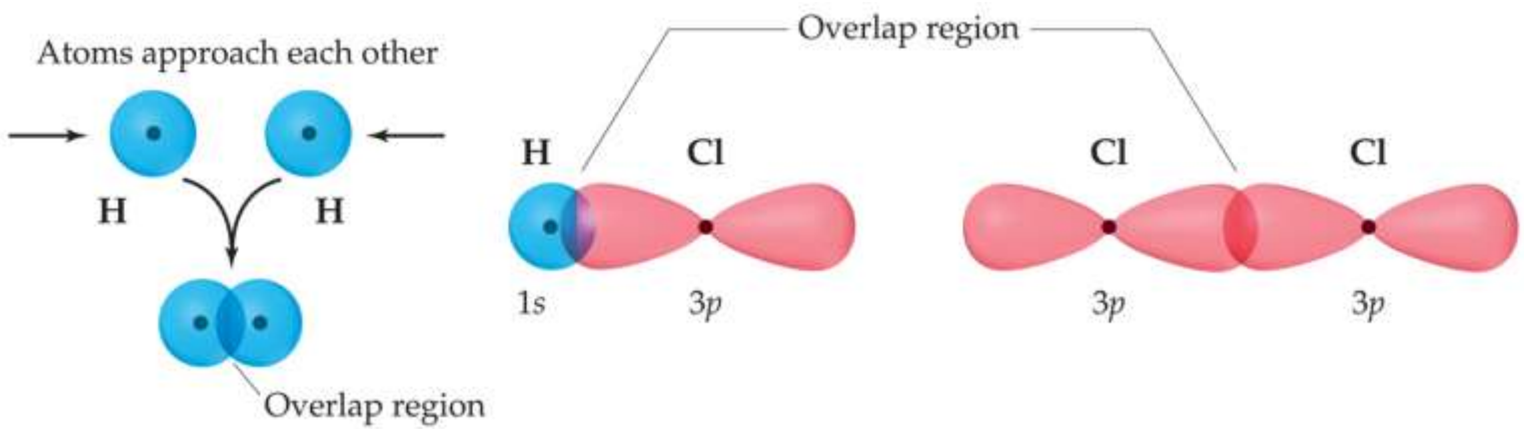
- ❑ Electron in a *p* orbital has equal probability of being in either half.

Valence Bond Theory

- Hybridization is a major player in this approach to bonding.

- There are two ways orbitals can overlap to form bonds between atoms.

Sigma (σ) Bonds

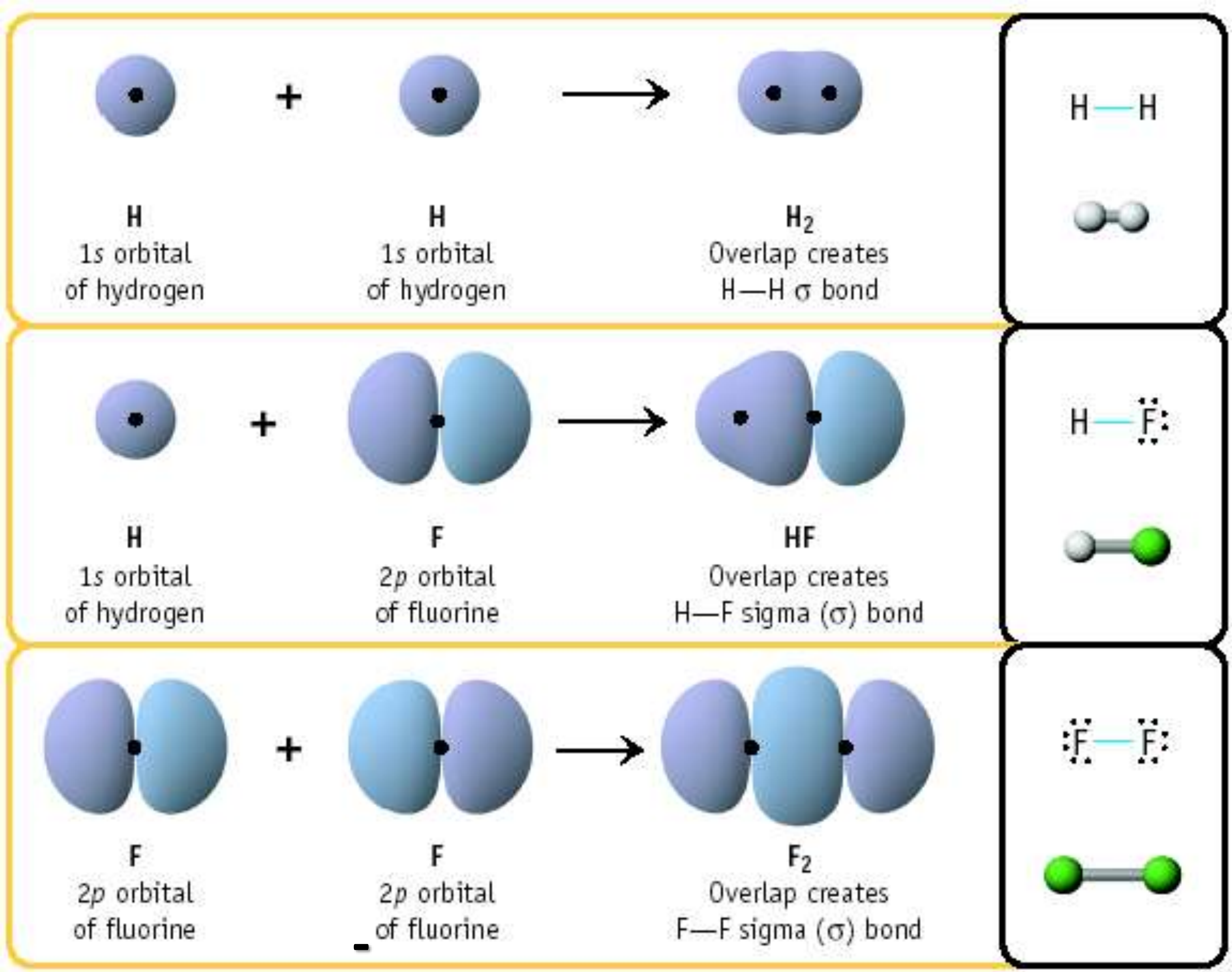


- Sigma bonds are characterized by
  – Head-to-head overlap.
  – Cylindrical symmetry of electron density about the internuclear axis.

σ (sigma) bond

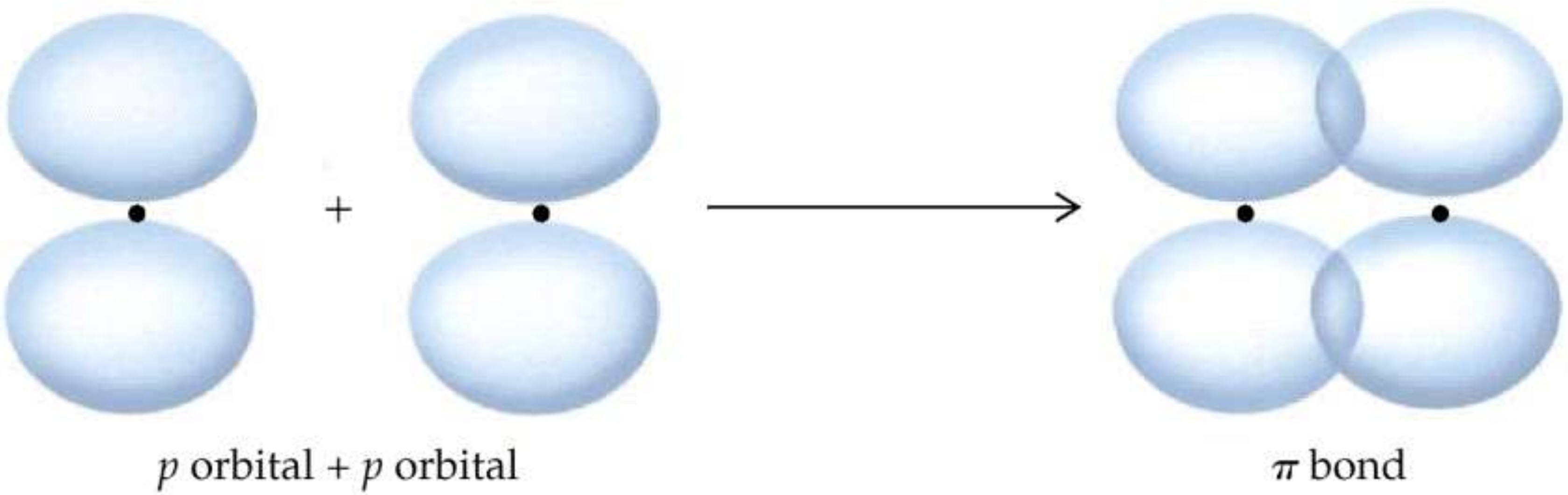
- A sigma bond can be formed by the overlap of:
  - s and p orbitals
  - two p orbitals
  - two s orbitals
  - two hybrid orbitals
  - an s orbital and a hybrid orbital

Sigma Bond Formation



π (pi bond)

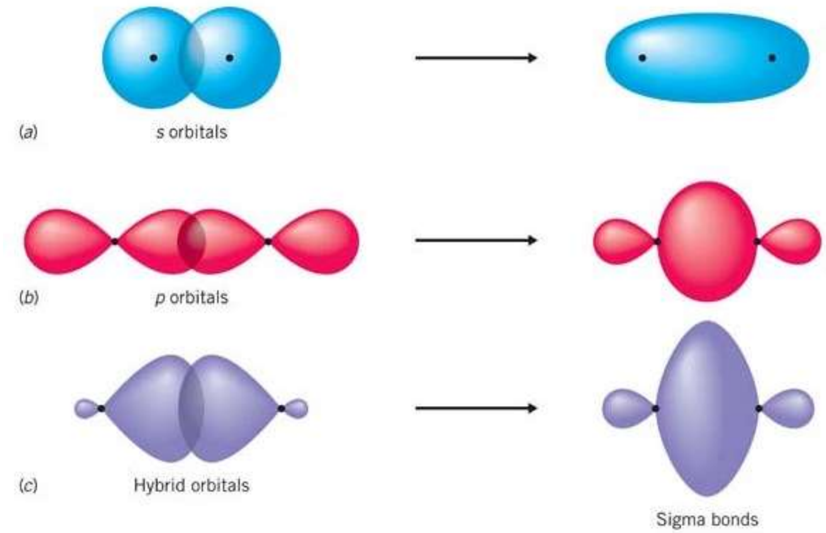
- A covalent bond formed by the parallel (side by side) overlap of two **p** orbitals.



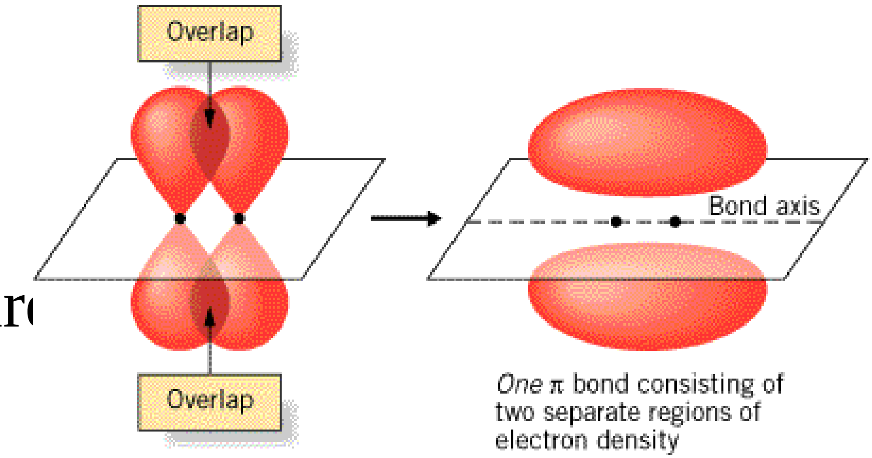
π bonds are characterized by electron density above and below the inter-nuclear axis.

Bonding Types

- Two types of bonds result from orbital overlap:
- sigma (σ) bonds
  – from head-on overlap
  – lie along the bond axis
  – account for the first bond

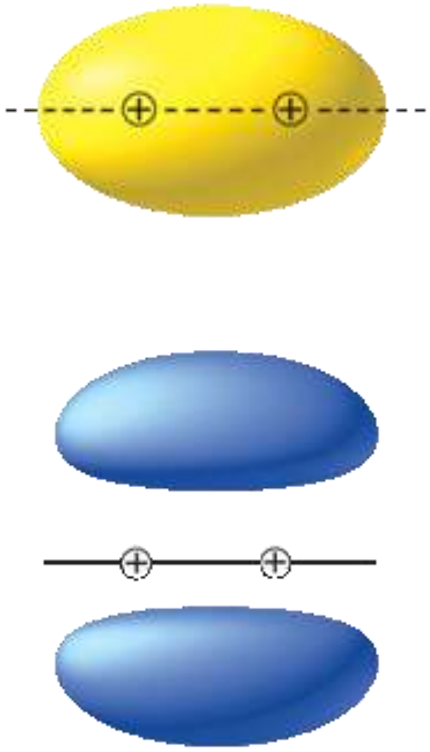


- pi (π)bonds
  – pi bonds are perpendicular to bond axis
  – account for the second and thir bonds in a multiple bond



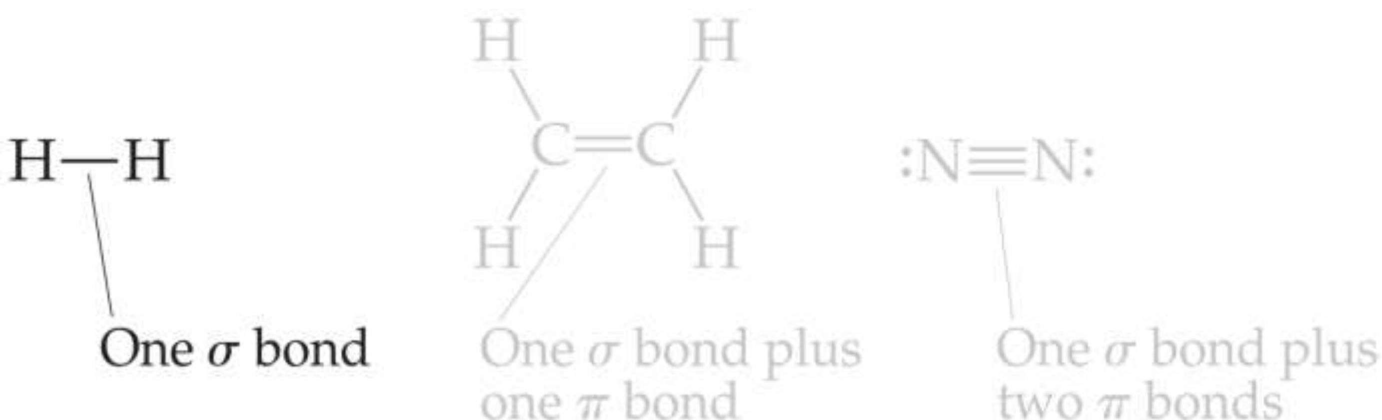
How can a drawing show where an electron is most likely to be found?

Drawings can show molecular orbitals, which are the areas where bonding electrons are most likely to be found.



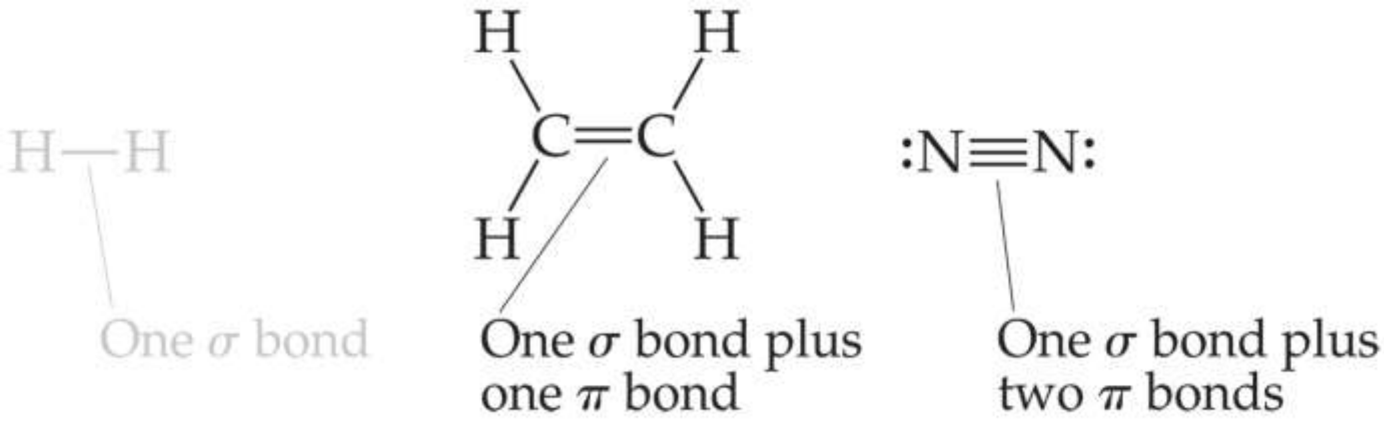
Single Bonds

Single bonds are always σ bonds, because σ overlap is greater, resulting in a stronger bond and more energy lowering.

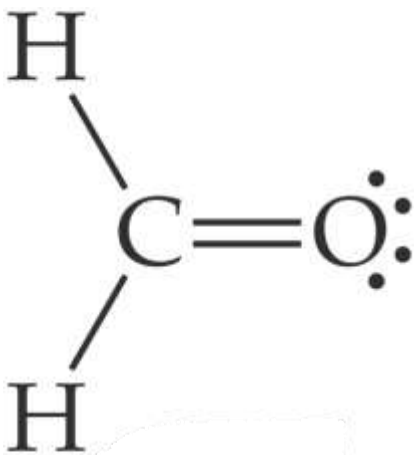


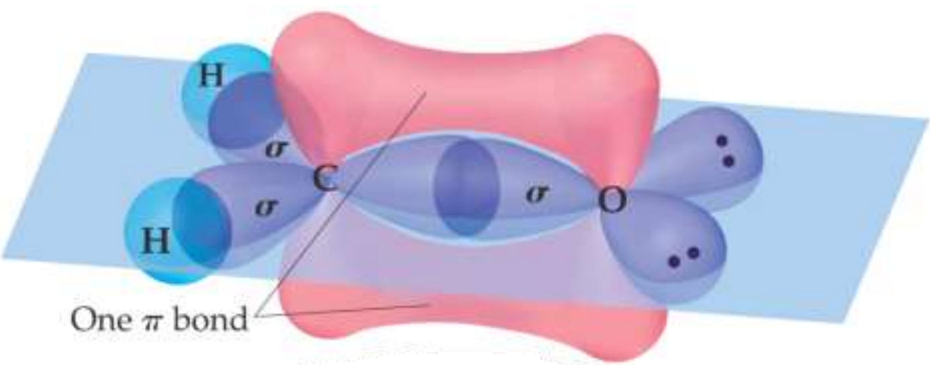
Multiple Bonds

In a multiple bond one of the bonds is a σ bond and the rest are π bonds.



Multiple Bonds

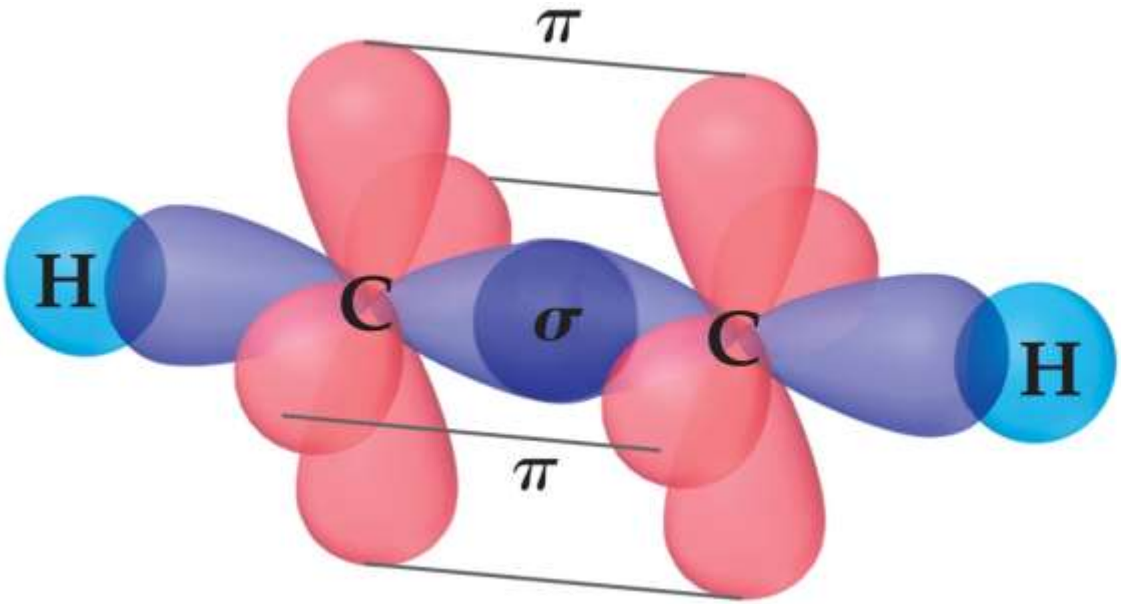




- In a molecule like formaldehyde (shown at left) an *sp*^{2} orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.
- The unhybridized *p* orbitals overlap in π fashion.

Multiple Bonds

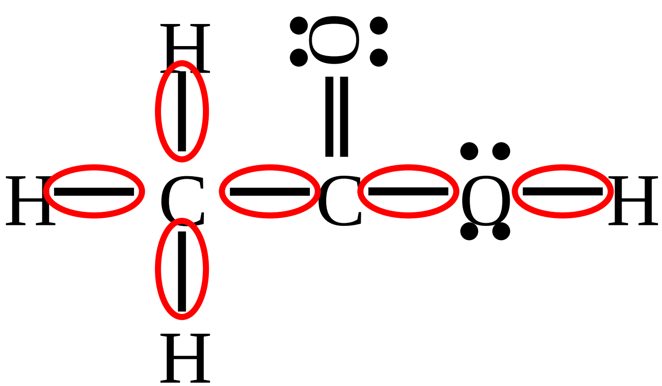
In triple bonds, as in acetylene, two *sp* orbitals form a σ bond between the carbons, and two pairs of *p* orbitals overlap in π fashion to form the two π bonds.



Sigma (σ) and Pi Bonds (π)

Single bond	1 sigma bond
Double bond	1 sigma bond and 1 pi bond
Triple bond	1 sigma bond and 2 pi bonds

How many σ and π bonds are in the acetic acid (vinegar) molecule CH_3COOH?



σ bonds = 6+ 1 = 7

π bonds = 1

Hybridization

- Experimentally, we observe that the four bonds in methane (CH_4) are equivalent and point towards the four corners of a tetrahedron
  - This does not correspond to the notion that we have one 2s orbital and three 2p orbitals on the C as we would expect to have one bond (involving the 2s orbital of C) different from the other three
  - Also, we need to have orbitals that point to all four corners of a tetrahedron rather than lying along the x, y, and z axes
  - We use the concept of hybridization to explain the tetrahedral geometry around the C
- Hybridization is the combination of atomic orbitals within an atom to form a new set of hybrid orbitals
- In the Valence Bond model, hybrid orbitals (those orbitals obtained when two or more non-equivalent orbitals of the same atom combine) form lone pairs or covalent bonds with other atoms

Hybridization in VB Theory

- Atomic orbitals are mixed to allow formation of bonds that have realistic bond angles

- The newly mixed orbitals that result are called "hybrid orbitals" with specified shapes:

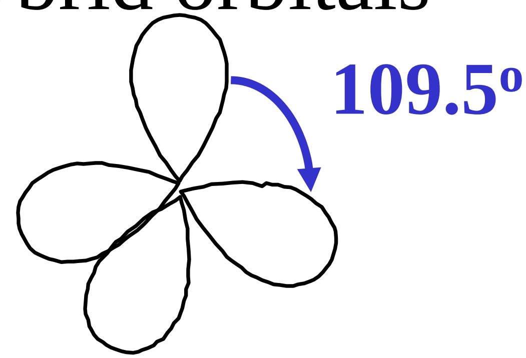
Hybridization	Bond Angles
sp	180^o
sp^2	120^o
sp^3	109.5^o

How are sp^3 hybrid orbitals formed?

p

s

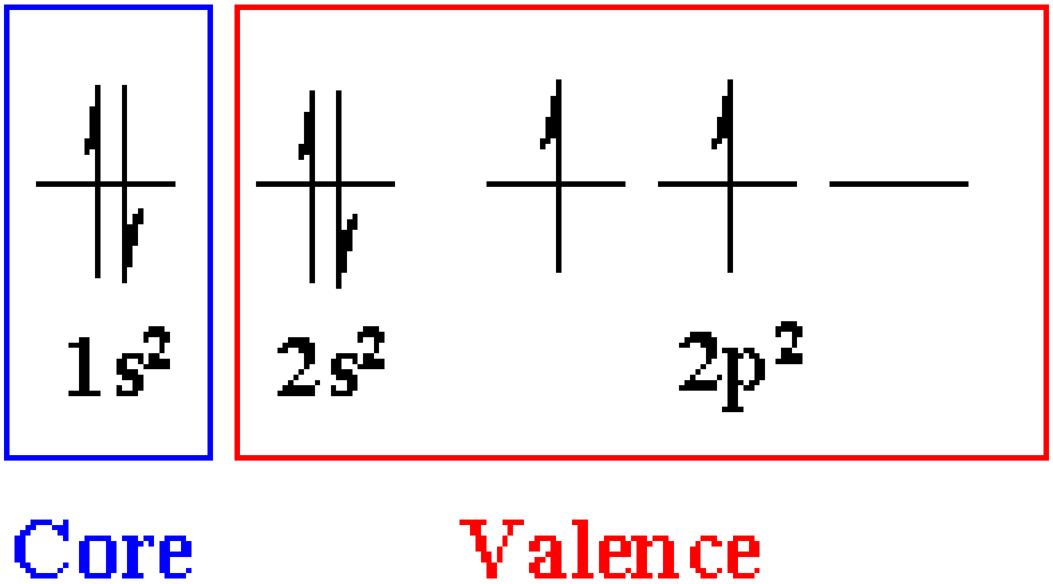
four sp^3 hybrid orbitals



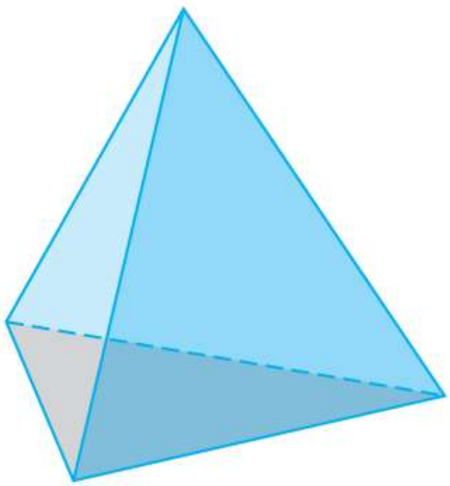
If we take s and all three p we form four sp^3 hybrid.

These hybrid orbitals are "degenerate." That is, they are of the same E, higher than s but lower than p.

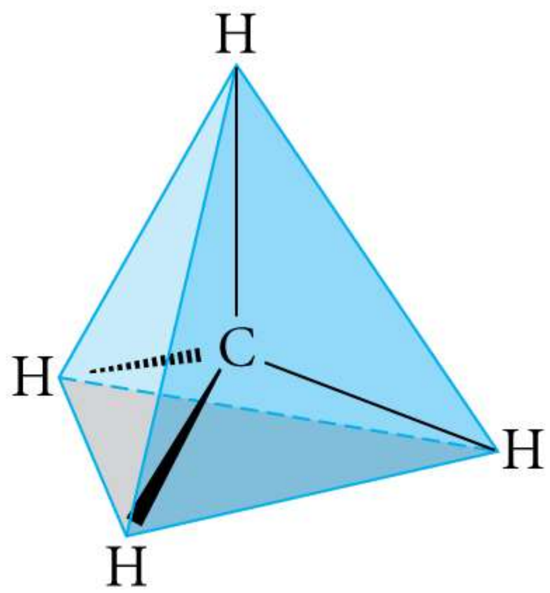
Electron Configuration of Carbon

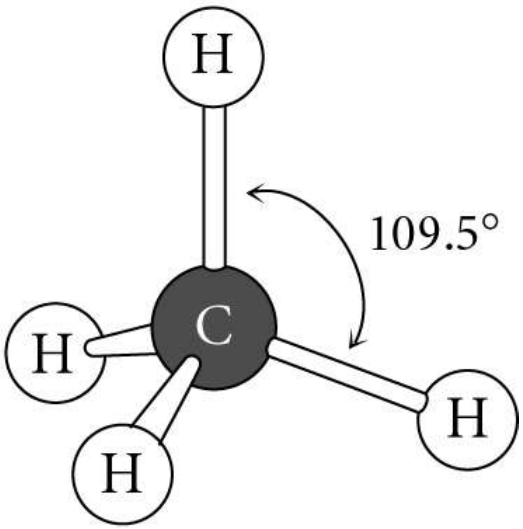


Tetrahderal Geometry



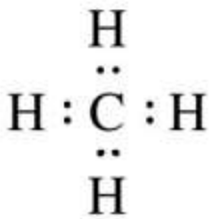
a regular tetrahedron



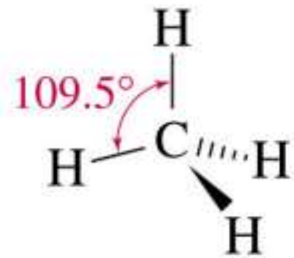


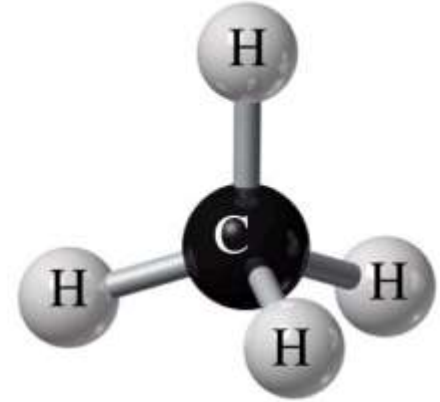
methane

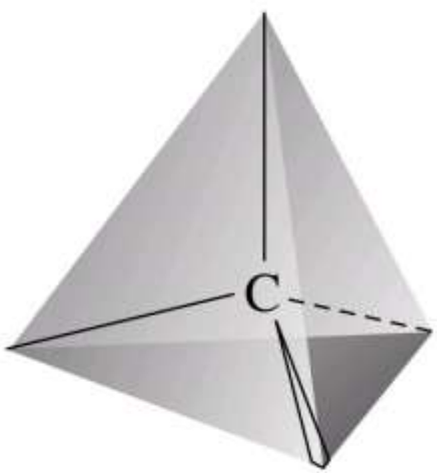
Methane Representations

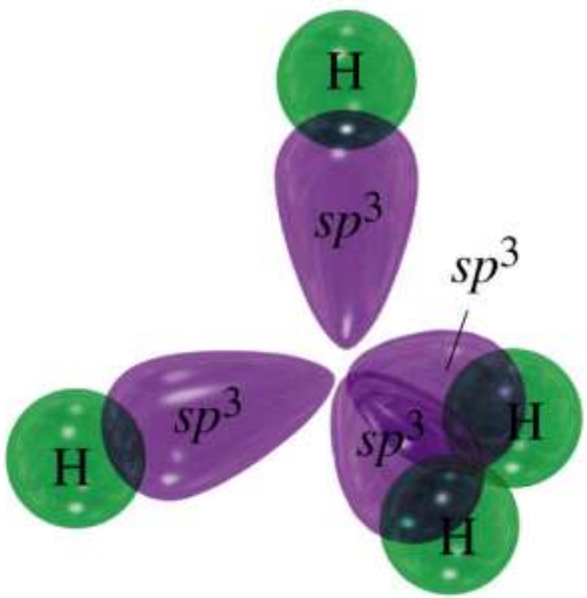


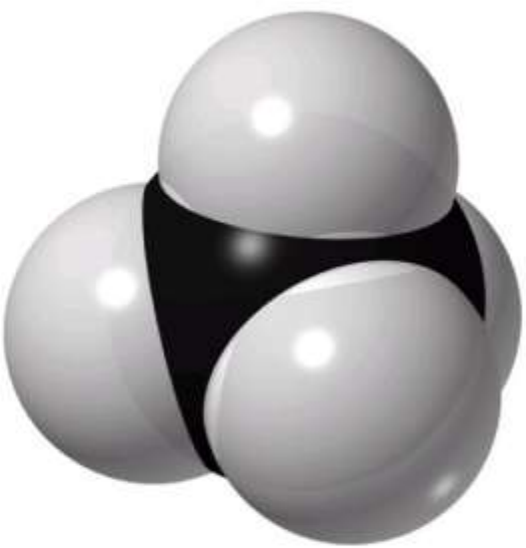
methane







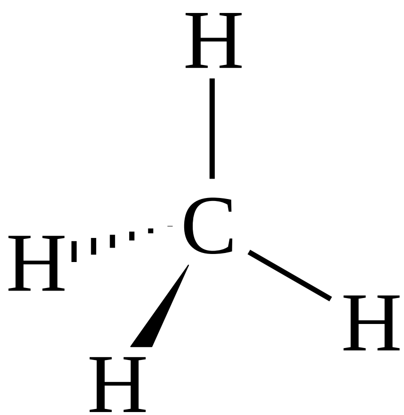


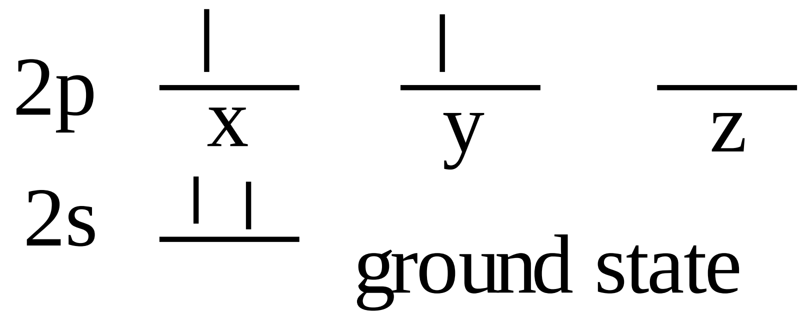


In Ground State

2 bonding sites, 1 lone pair

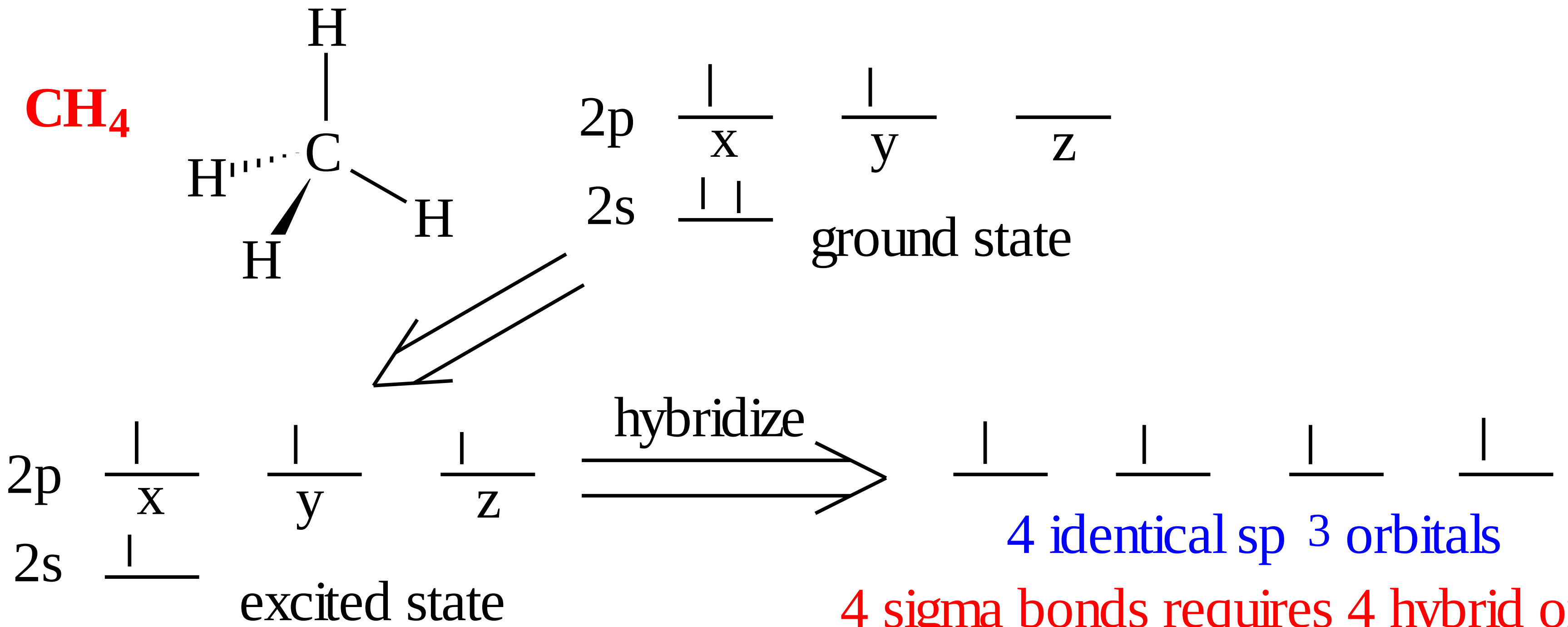
CH_4





sp^3 Hybridization

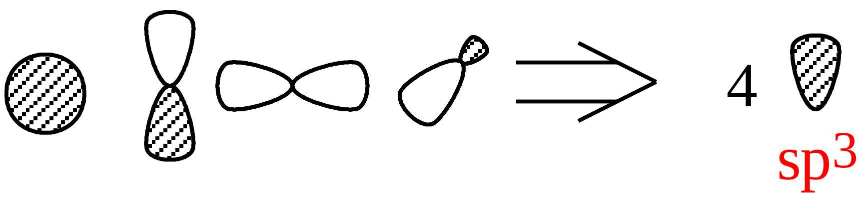
CH_4



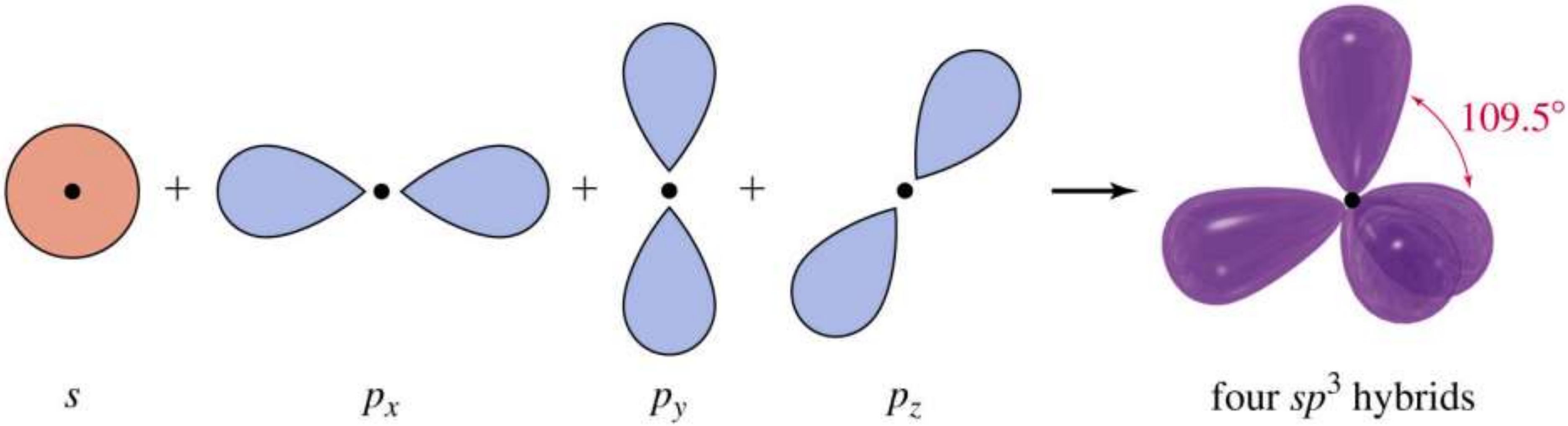
4 identical sp^3 orbitals

4 sigma bonds requires 4 hybrid orbitals

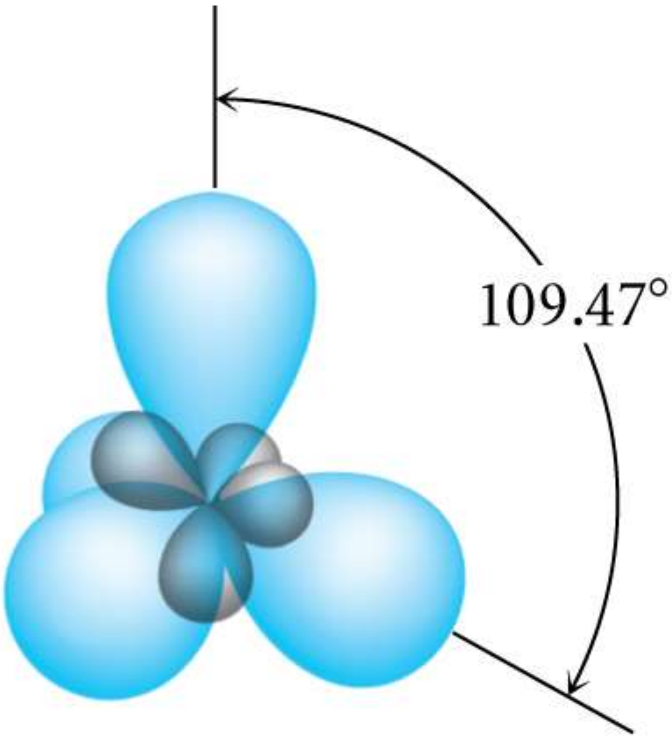
tetrahedral geometry



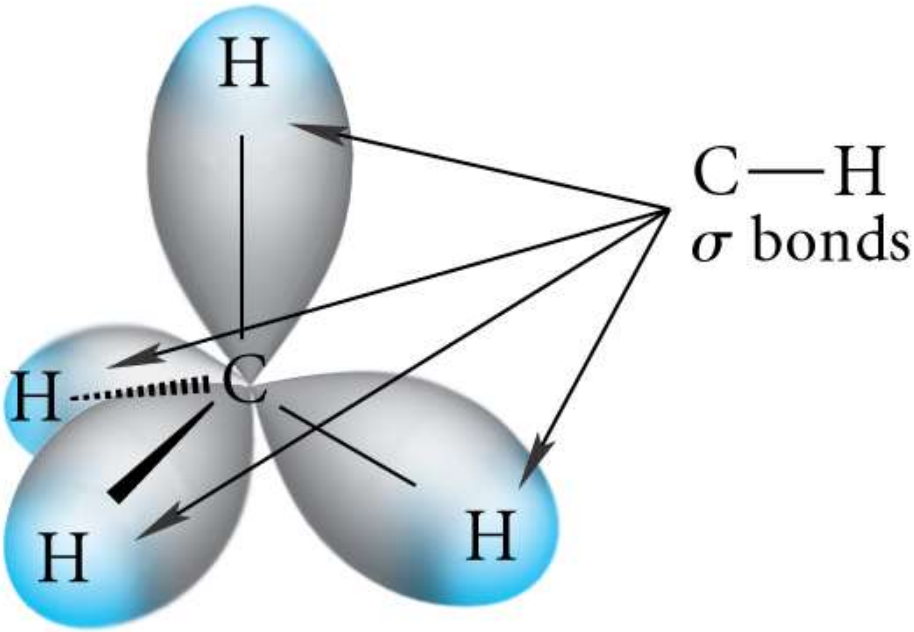
Hybridization of 1s and 3p Orbitals – sp^3



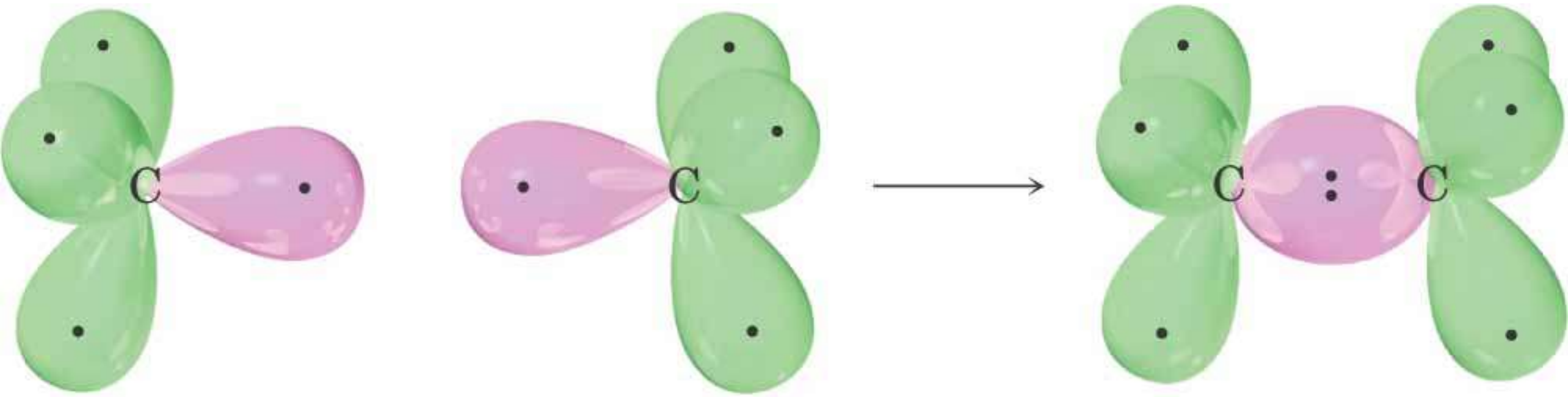
sp^3 is Tetrahedral Geometry
Methane



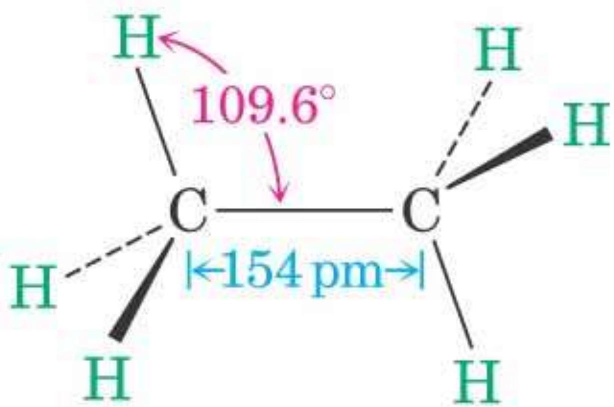
(c)

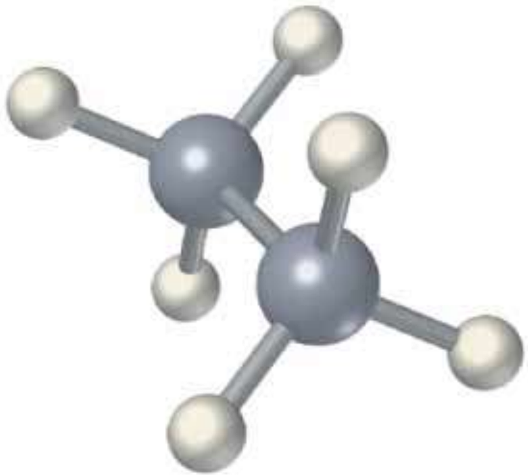


(d)

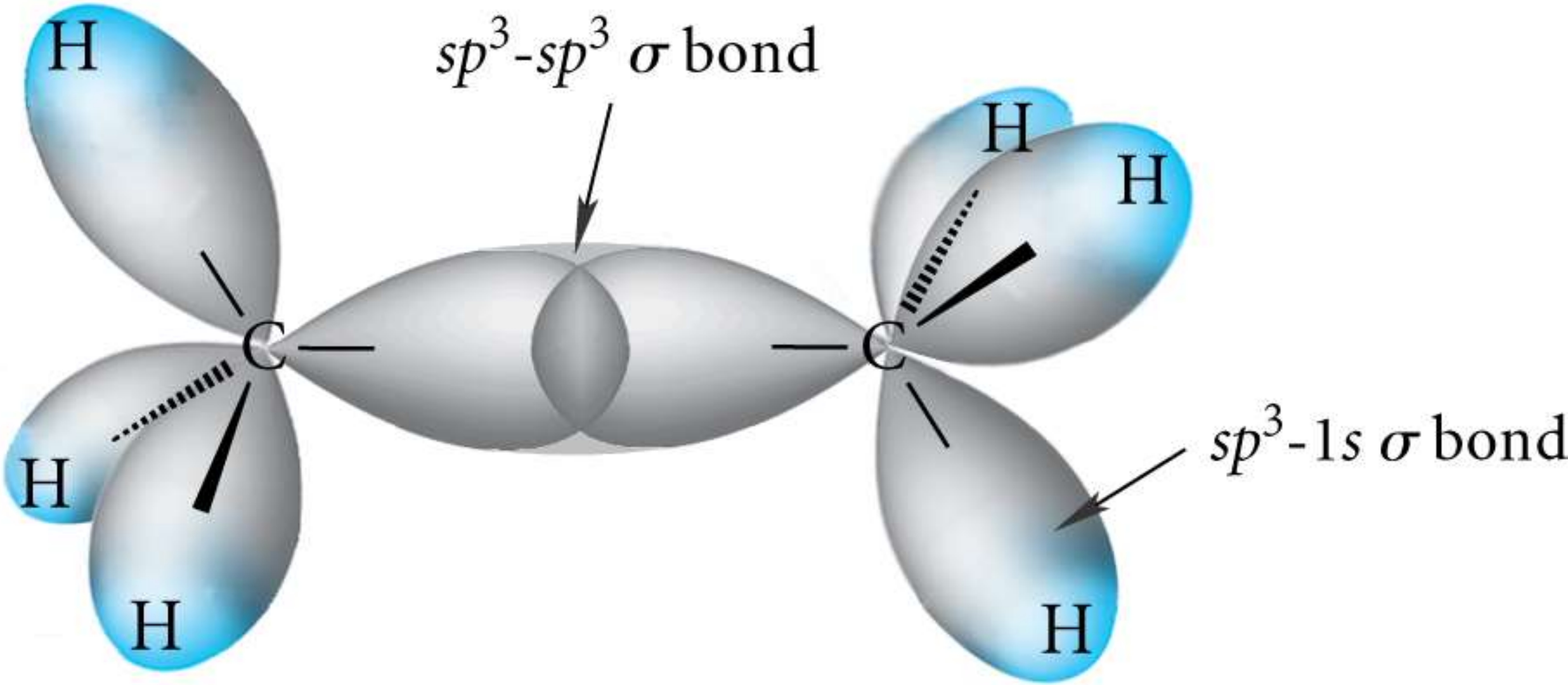


sp^3 **carbon** *sp*^{3} **carbon** *sp*^{3}–*sp*^{3} σ **bond**

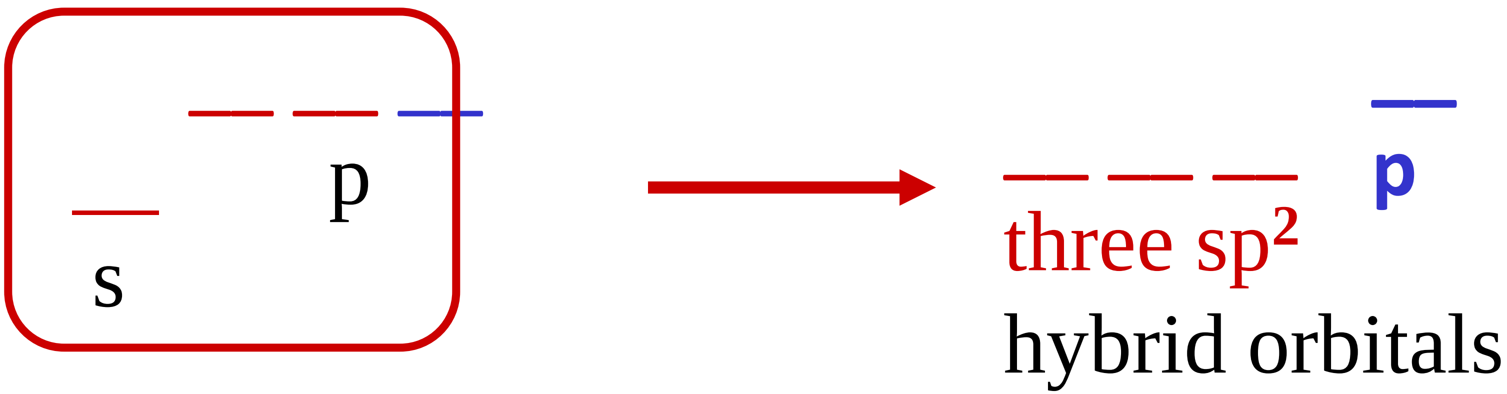




Orbital Depiction of Ethane, C_2H_6 , the σ bond



How are sp^2 hybrid orbitals formed?



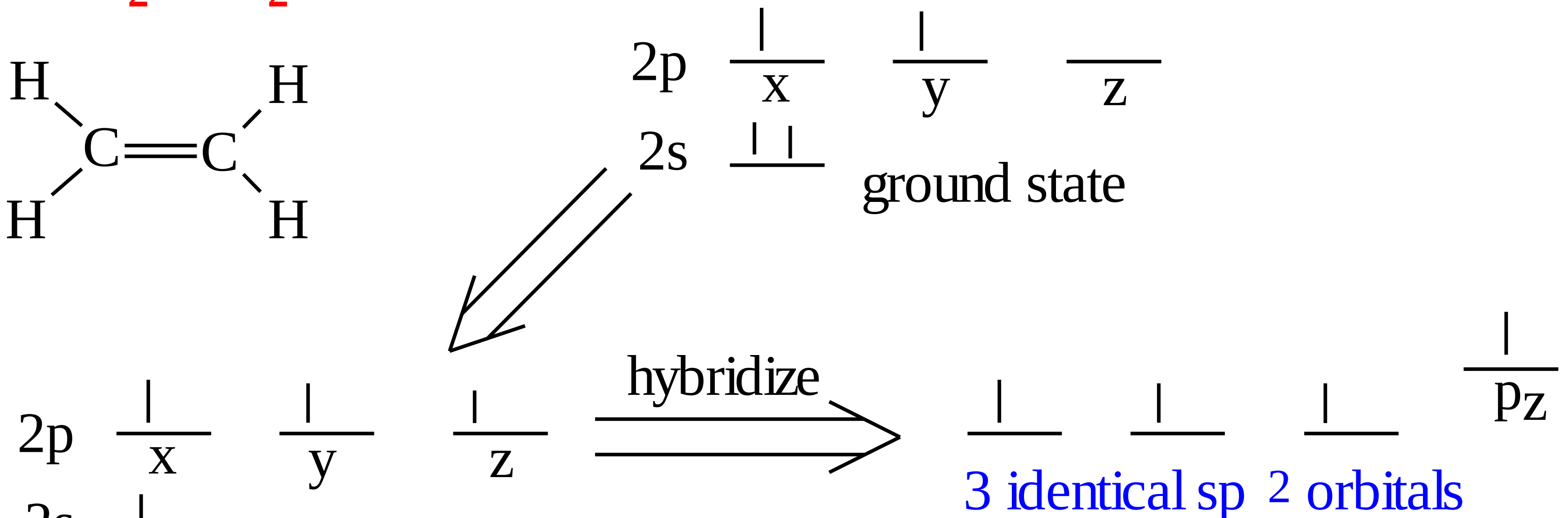
If we take s and just two p orbitals,
we form three sp^2 hybrid orbitals leaving one pure **p** untouched.

These three sp^2 hybrid orbitals are planar with angles of 120^o.

The un-hybridized p (pure p) are used in double and triple bonds.

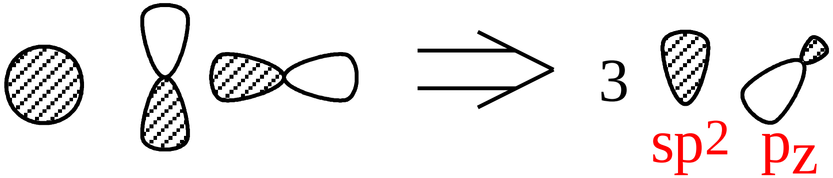
sp^2 Hybridization

$CH_2{=}CH_2$

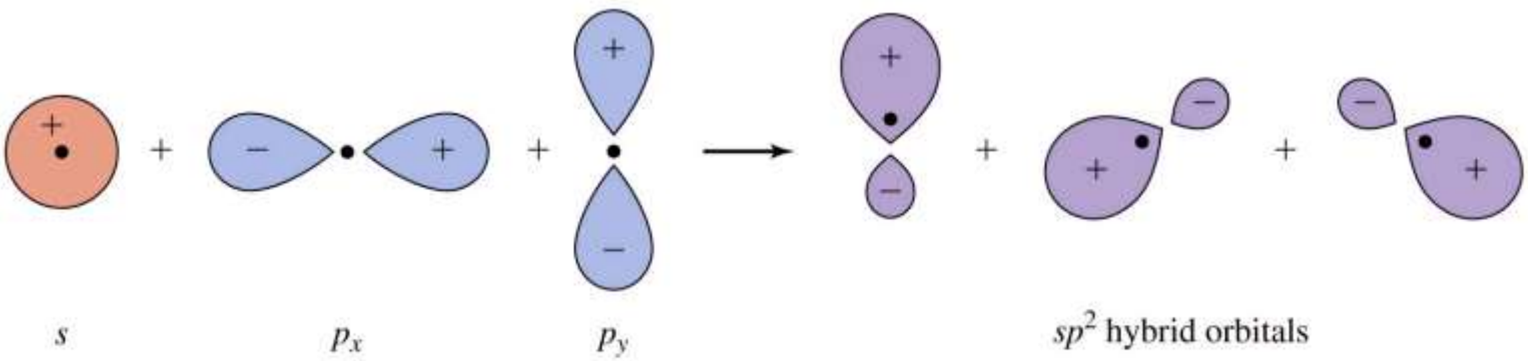


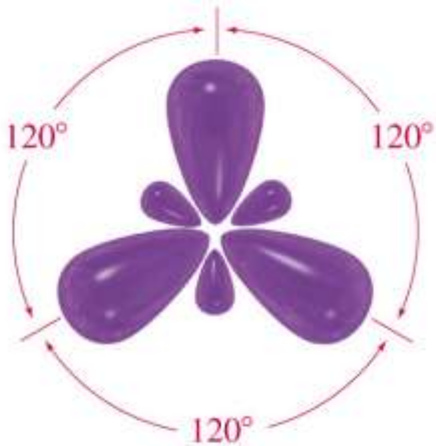
3 sigma bonds requires 3 hybrid orbitals

trigonal planar geometry

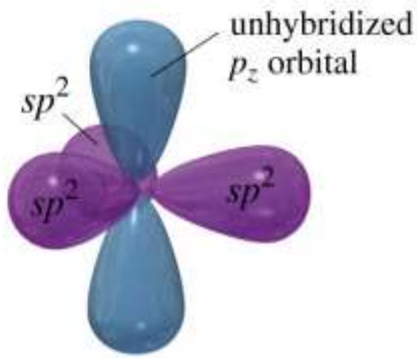


Hybridization of 1s and 2p Orbitals – sp^2



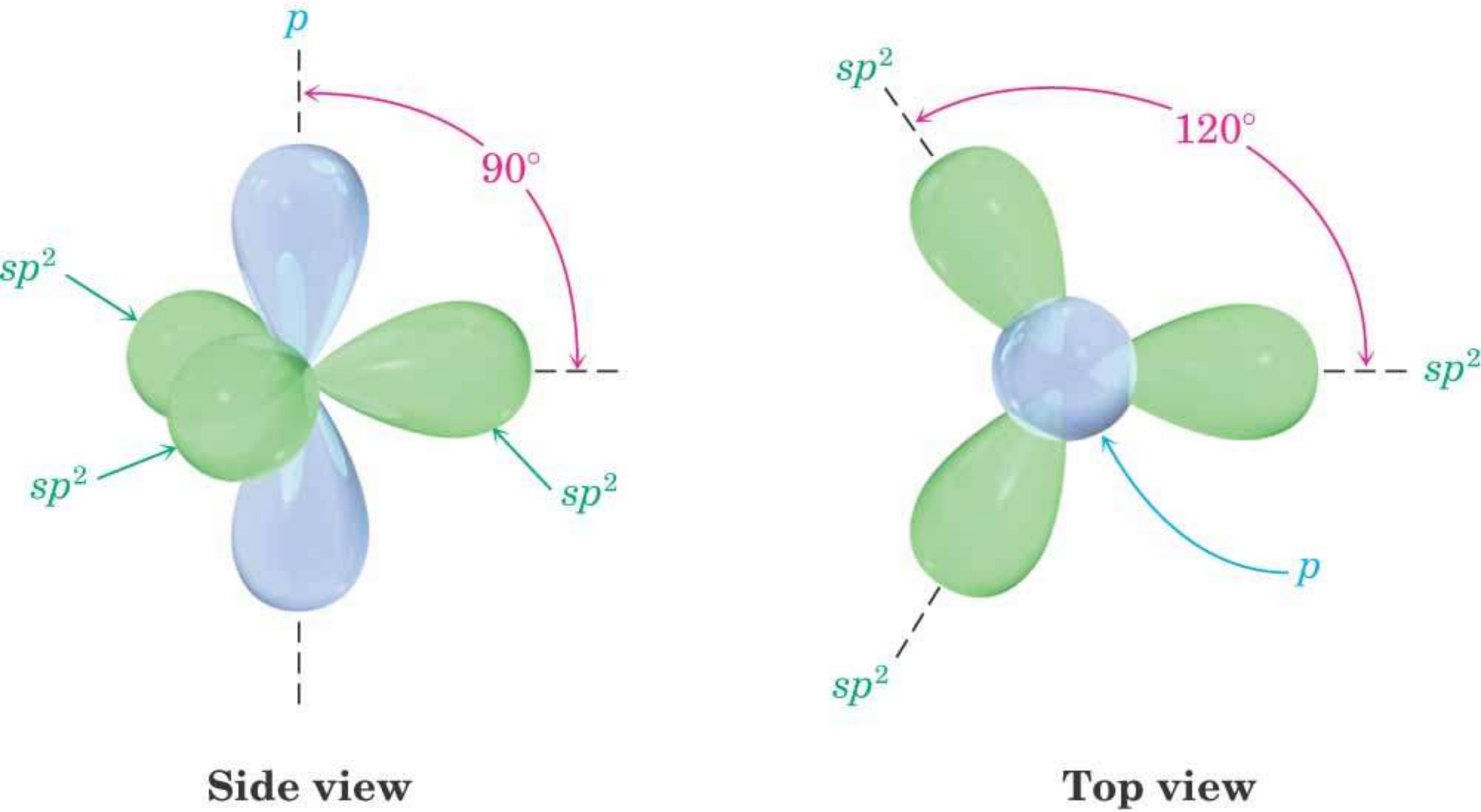


three sp^2 hybrid orbitals superimposed

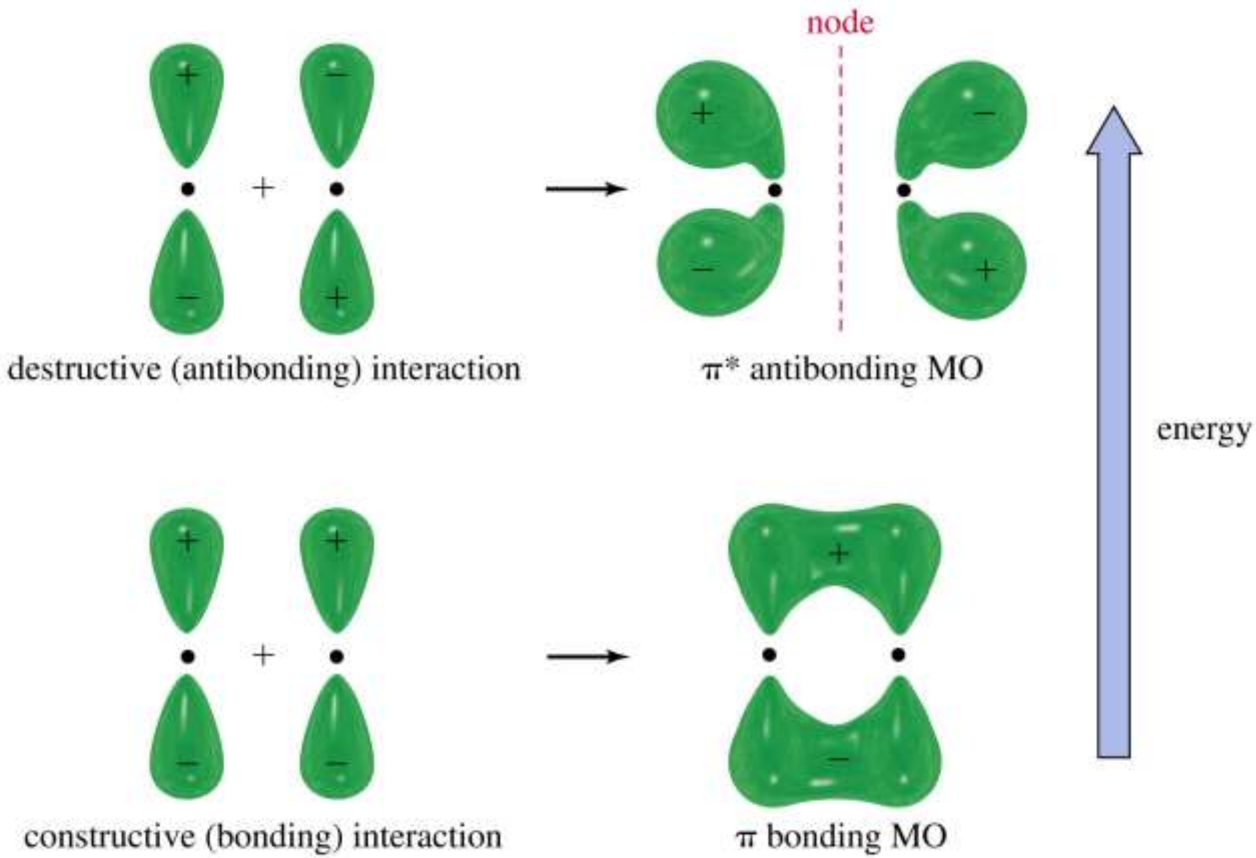


sp^2 hybrid carbon atom
(viewed from the side)

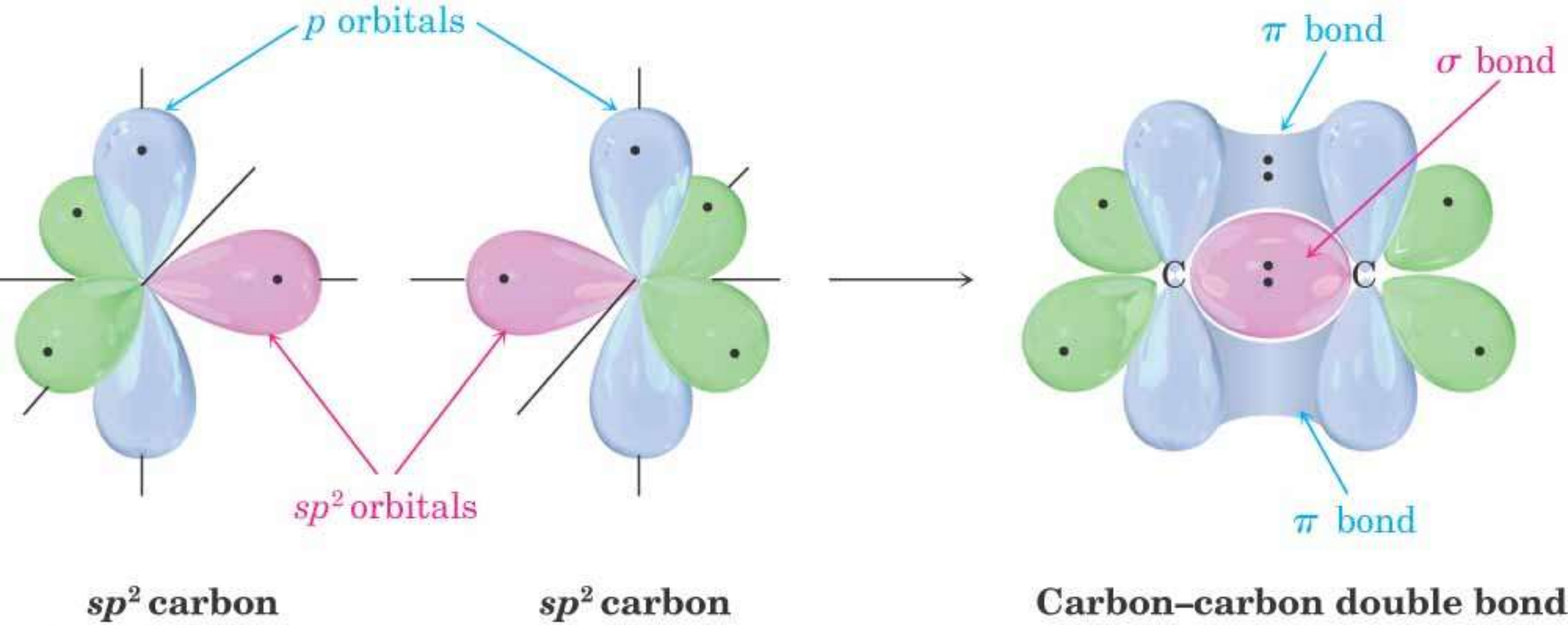
An sp^2 hybridized atom



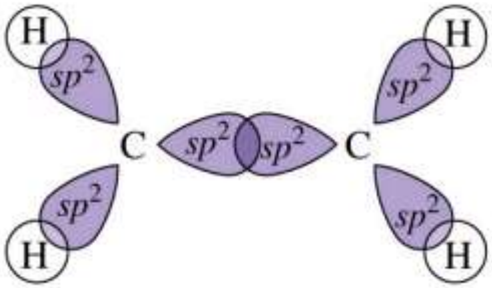
The π bond
Overlap of 2 parallel p Orbitals



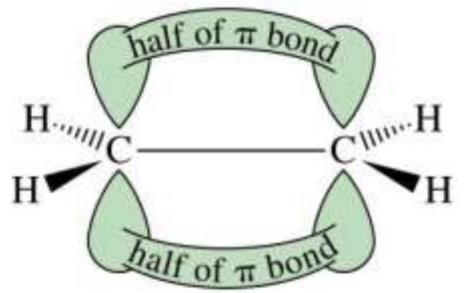
Ethylene $CH_2{=}CH_2$



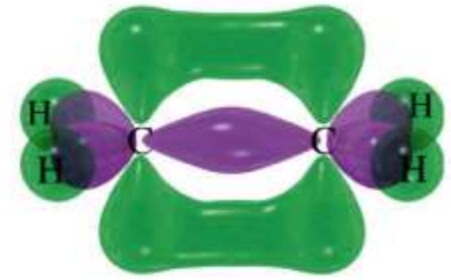
Views of Ethylene, C_2H_4



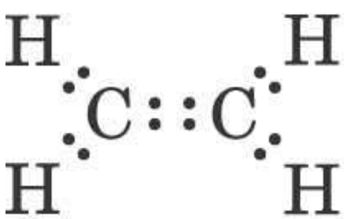
σ bond framework
(viewed from above the plane)

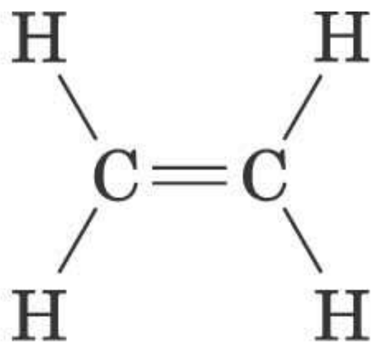


π bond
(viewed from alongside the plane)

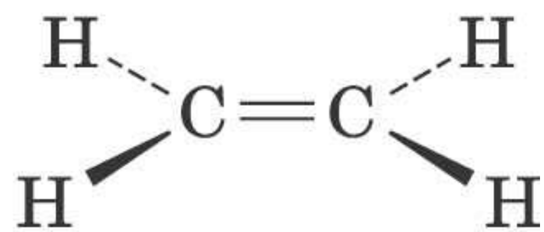


ethylene





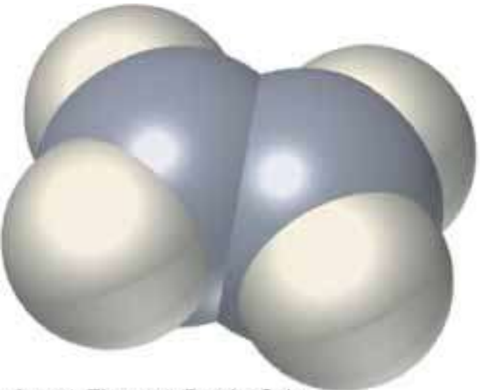
Top view

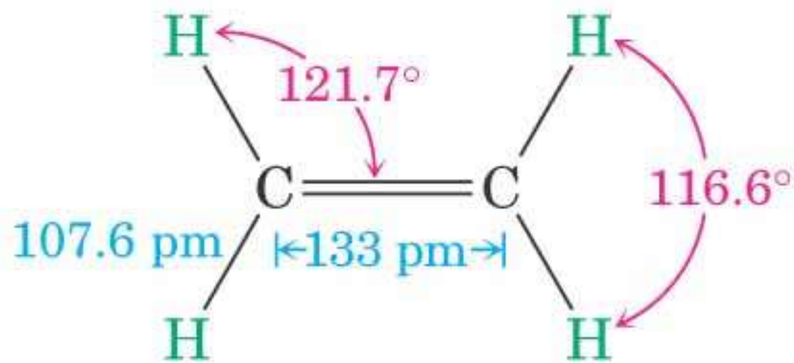


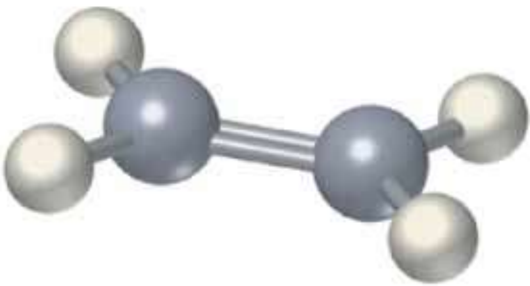
Side view

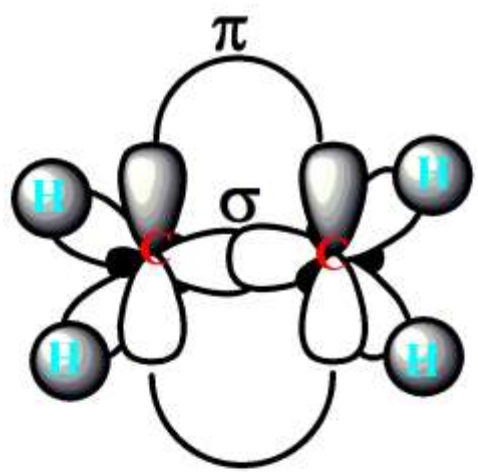
Ethylene

Ethylene



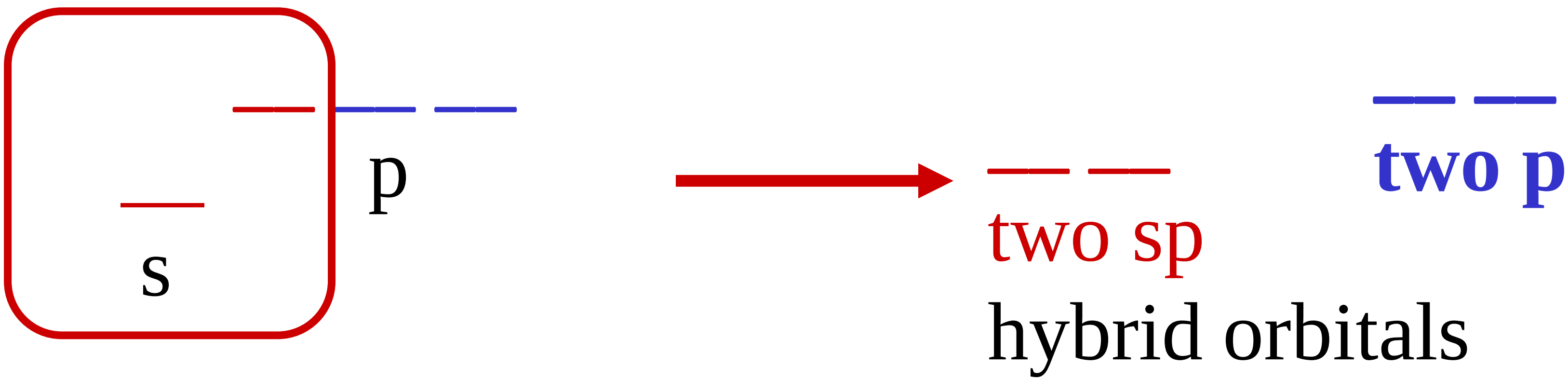






Orbital diagram of ethylene

How are sp hybrid orbitals formed?



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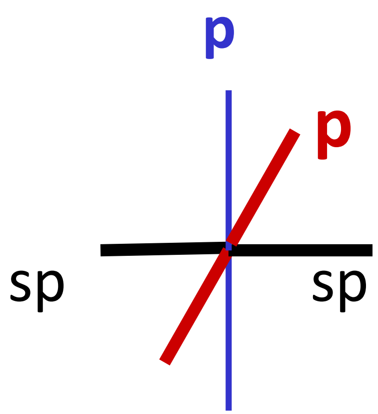


These two sp hybrid orbitals are linear with angles of 180^{o}

sp hybridization

$H-C\equiv C-H$

2p x y z

2s

ground state

2p x y z

2s

excited state

hybridize

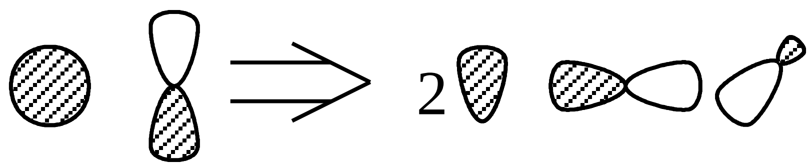
$\Longrightarrow$

2 identical sp orbitals

py pz

2 sigma bonds requires 2 hybrid orbitals

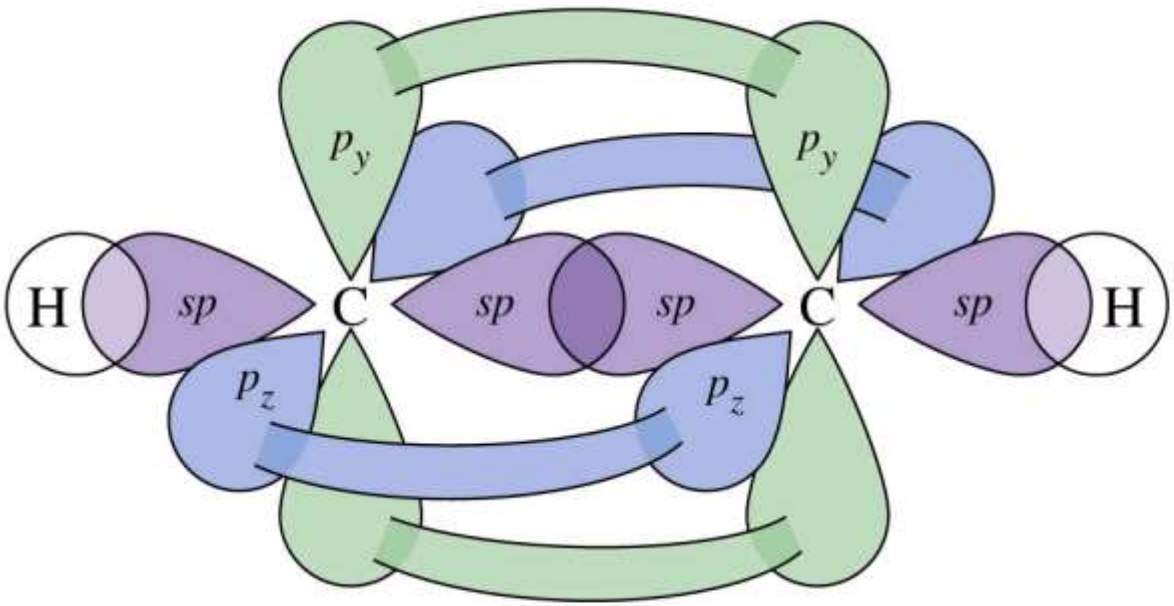
linear geometry



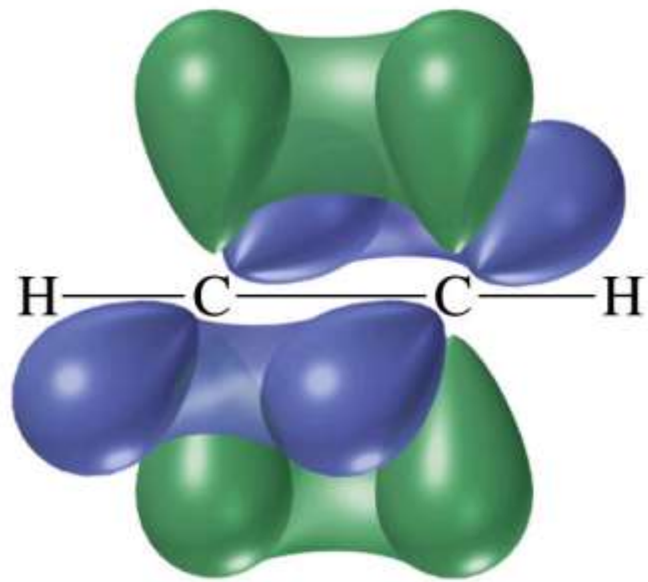
Acetylene, C_2H_2,

1 s bond

2 perpendicular p bonds

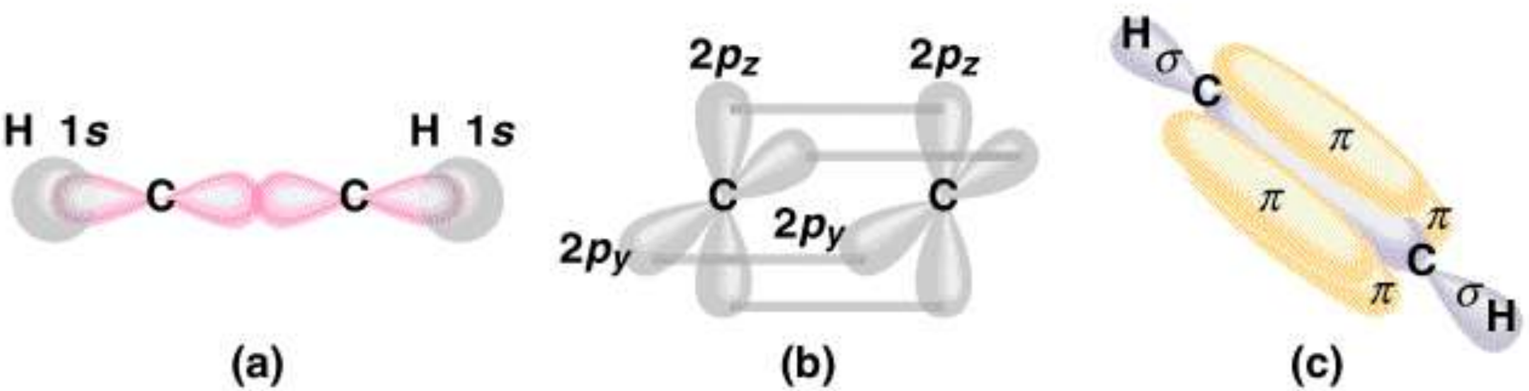


acetylene



acetylene

Bonding in Acetylene



- The sp hybridized orbitals form a σ C-C bond and two σ C-H bonds
- The $2p_y$ and $2p_z$ orbitals form two π bonds between the two carbons

Hybridization around Carbon

	Hybridization
4 σ bond	sp3
3 σ bond + 1 π bond	sp^2
2 σ bond + 2 π bond	sp

Orbital picture diagram of acetonitrile

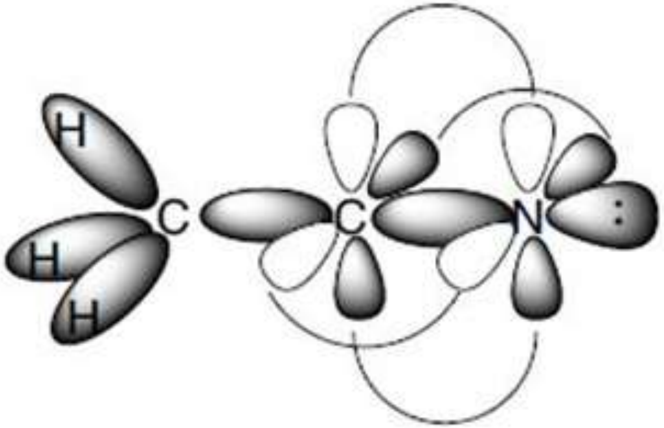
What is the hybridization of each non-hydrogen atom in acetonitrile? Draw the bonding orbitals (leaving out the small back lobes).

$H_3C{-}C{\equiv}N{:}$
a b

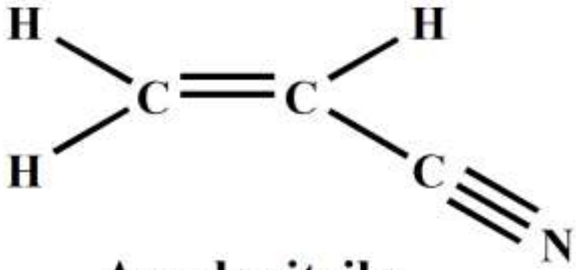
C_a: ***sp***^{3} (4 σ-bonds)

C_b: ***sp*** (2 σ-bonds)

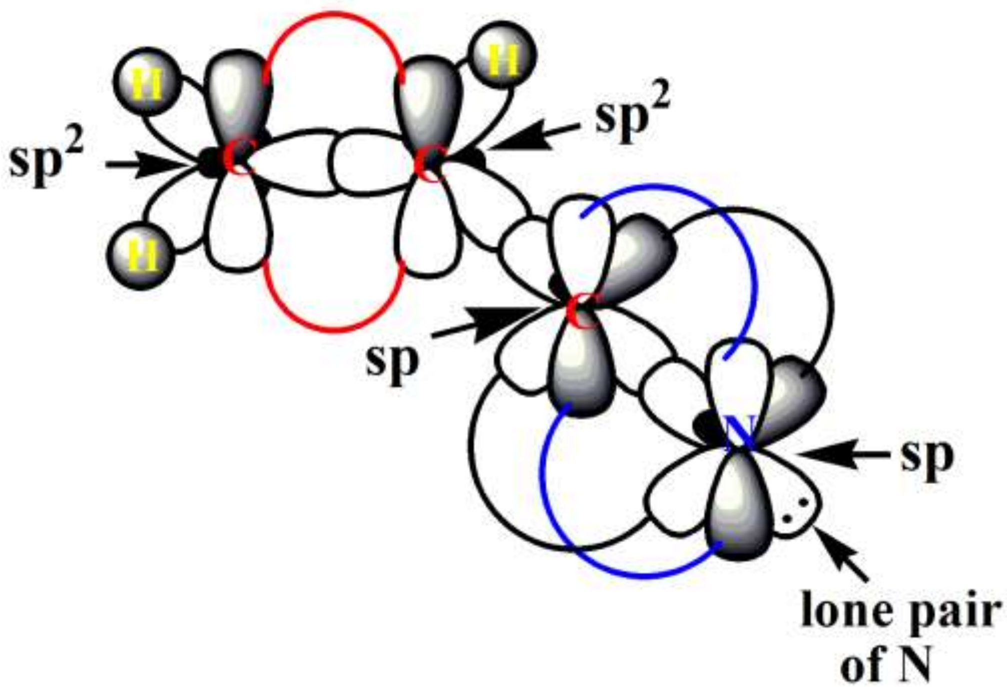
N: ***sp*** (1 σ-bond, 1 lone pair)



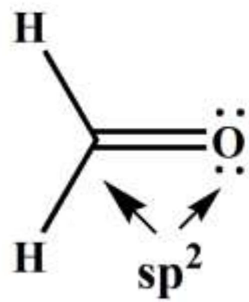
Orbital picture diagram of acrylonitrile

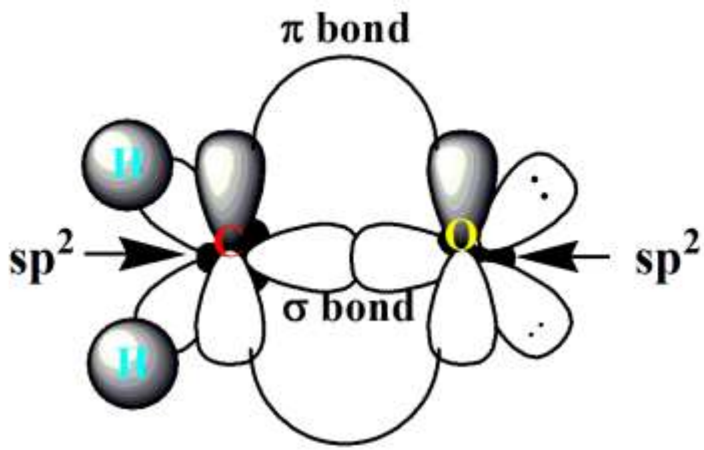


Acrylonitrile

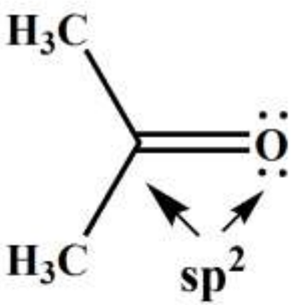


Orbital picture diagram of carbonyl compounds

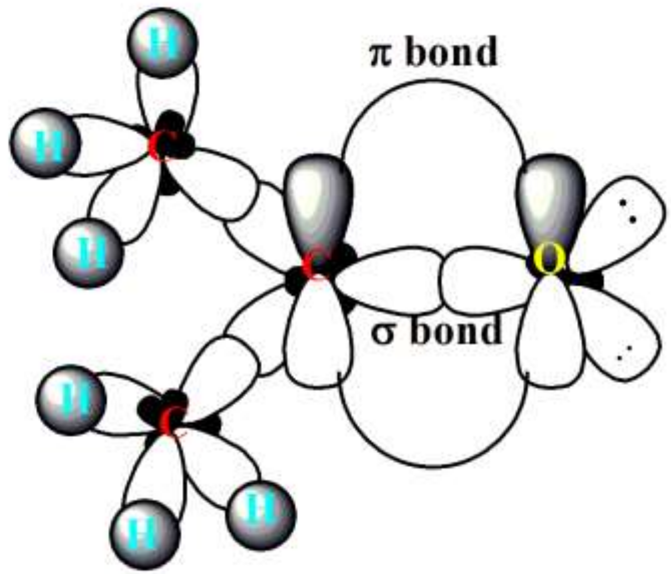


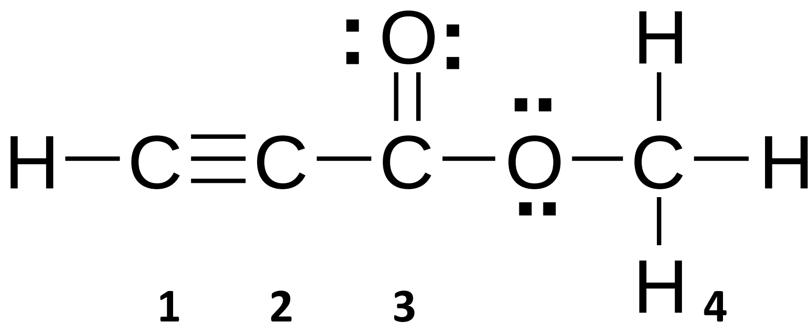


Formaldehyde



Acetone





Always start with hybridization.

Give the hybridization of each C and each O.

Give the bond angles.

How many σ bonds are there?

How many π bonds are there?

9 σ bonds

3 π bonds

Ans. C1 = sp   C2 = sp   C3 =sp^2 C4 = sp^3 O = sp^3

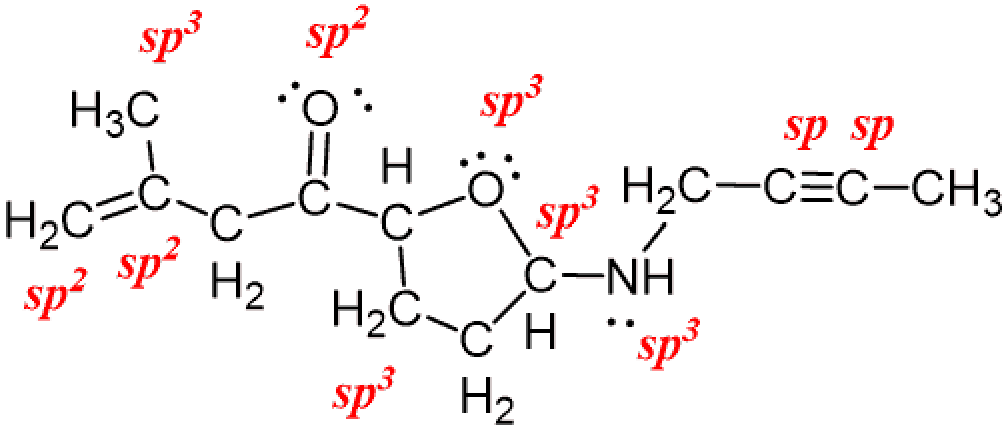
C1-C2-C3 = 180^o

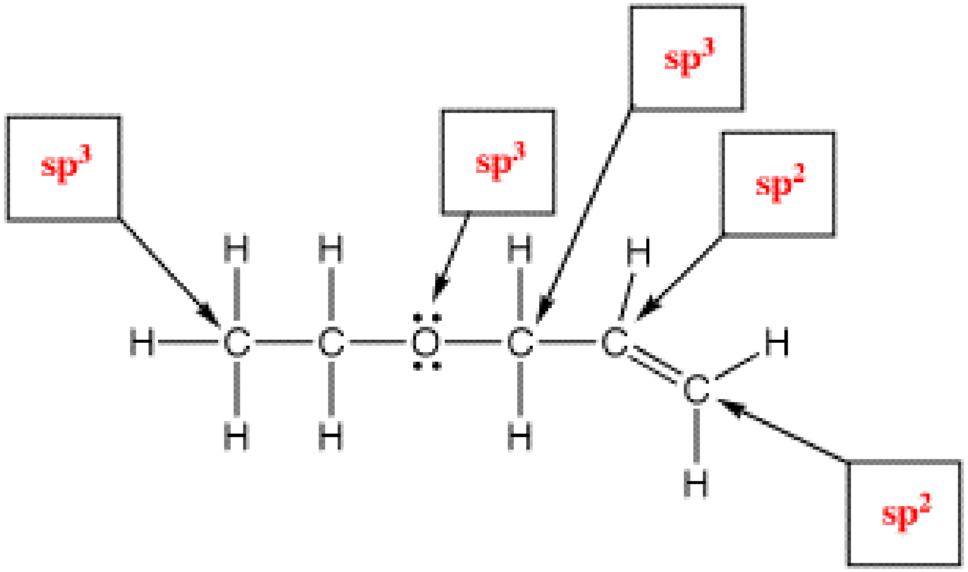
C2-C3-O = 120^o

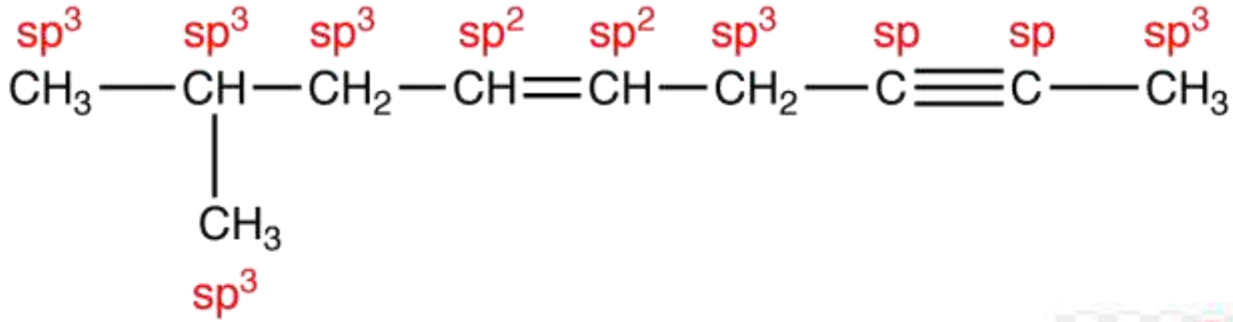
C2-C3=O = 120^o

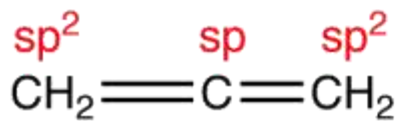
O-C4-H = 109.5^o

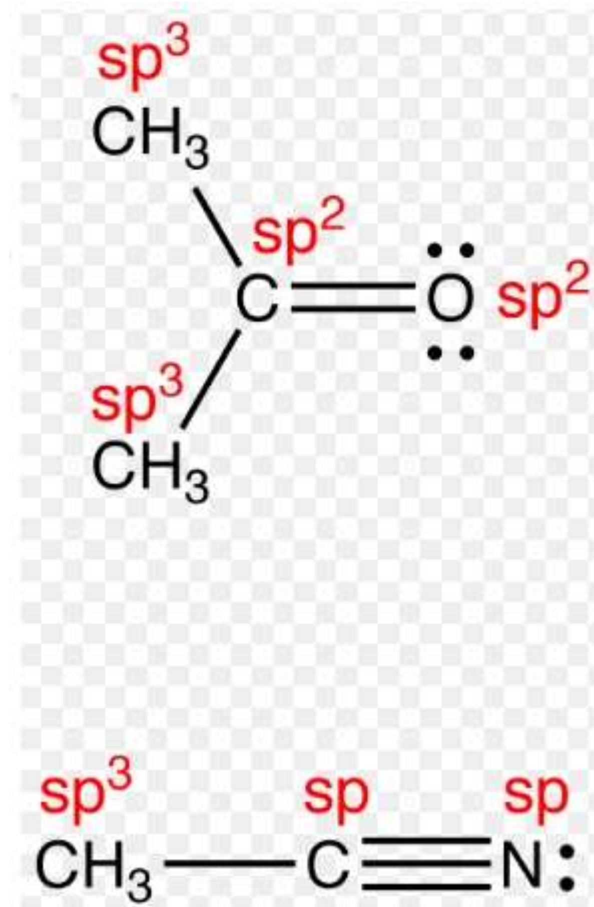
Hybridization: Examples



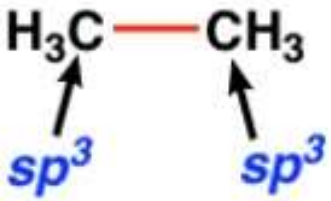



sp3 sp3 sp3 sp2 sp2 sp3 sp sp sp3
CH3—CH—CH2—CH=CH—CH2—C≡C—CH3
CH3
sp3

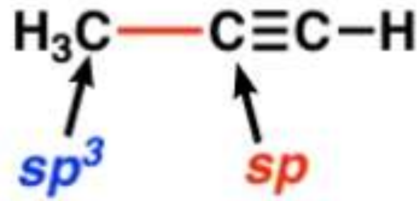

sp2 sp sp2
CH2=C=CH2


sp3
CH3
sp2
C=O
sp2
sp3
CH3
sp3 sp sp
CH3—C≡N:

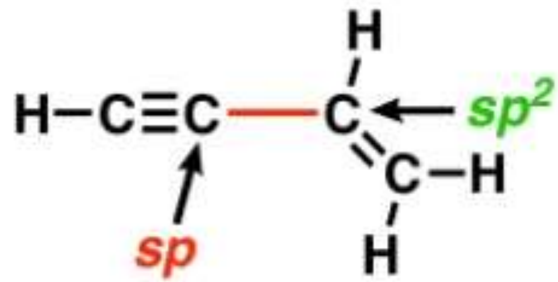
sp^3–sp^3 σ-bond



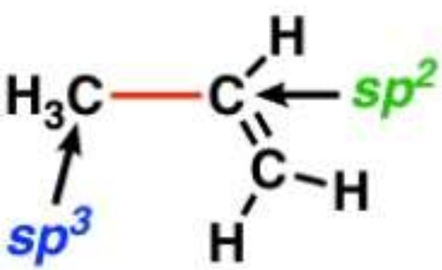
sp^3–sp σ-bond



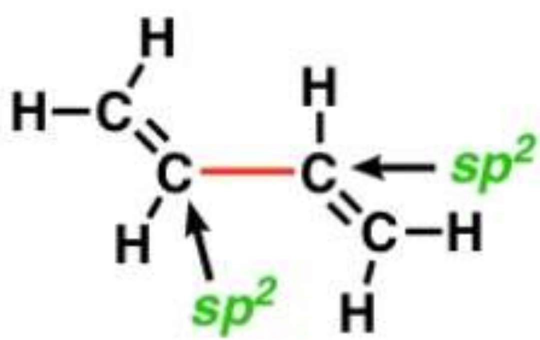
sp–sp^2 σ-bond



sp^3–sp^2 σ-bond



sp^2–sp^2 σ-bond



sp–sp σ-bond