Molecular Structure
2 - Hybridization

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Valence Bond Theory

The main theory of bonding is the Lewis theory which is explains how sharing electrons in the valence shell creates covalent bonds.

The second main theory is Valence Bond Theory which helps to explain covalent bonding that Lewis theory does not explain, which is that electrons are in orbitals (s, p, d, f).

In general, a covalent bond forms when:

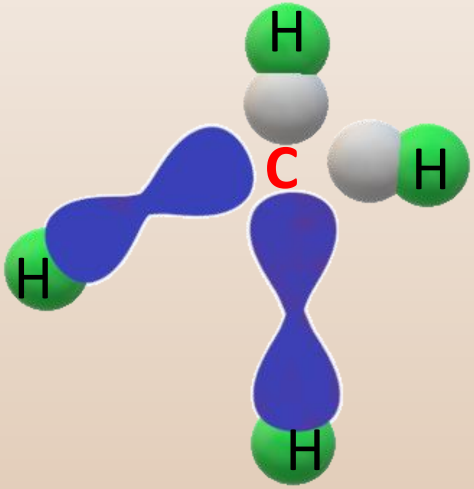
- An orbital on one atom comes to occupy a portion of the same region of space as an orbital on the other atom. The two orbitals are said to overlap.
- The total number of electrons in both orbitals is no more than two. The greater the orbital overlap, the stronger the bond.
- Orbitals (except s orbitals) bond in the direction in which they protrude or point, to obtain maximum overlap.

Methane Molecule According to Lewis Theory

According to Lewis theory the bonding is quite simple: 4 valence electrons (VE) of carbon bond with the 1 VE of hydrogen. The 4 carbon electrons are **$2s^2 2p^2$** configuration and hydrogen is **$1s^1$**. So if we look at the overlaps in methane there will be two s orbitals (spherical) of carbon and two will be p (dumbbell shape) overlapping with s (spherical) of hydrogen. (Shown on the right).

- The orbital overlap required for bonding will be different for the two bonds (s-s and s-p).
- Two bonds will be longer and two shorter and the bond energy will be different too.

Given the above observations there must be a different theory on how covalent bonds are formed otherwise the bonds would look different.



Valence Bond Theory - Hybridization

Hybrid orbitals are formed by mixing orbitals and are named by using the atomic orbitals that combined. This mixing of orbitals creates new “hybrid” orbitals that are equal in energy and have the same shape.

Below are the most common hybridizations possible.

- sp hybridization: one *s* orbital + one *p* orbital gives two *sp* orbitals
- sp^2 hybridization: one *s* orbital + two *p* orbitals gives three sp^2 orbitals
- sp^3 hybridization: one *s* orbital + three *p* orbitals gives four sp^3 orbitals
- sp^3d hybridization: one *s* orbital + three *p* orbitals + one *d* orbital gives five sp^3d orbitals
- sp^3d^2 hybridization: one *s* orbital + three *p* orbitals + two *d* orbitals gives six sp^3d^2 orbitals

Understanding the Next Slides on Hybridization

Here is how to understand the next few slides on hybridization.

1) The Lewis structure of the compound is given first along with the shape and AXE formula.
2) Next is the box configuration of the valence electrons of the central atom in the proper energy level. Ground state is the lowest energy state of any atom. During bonding, energy is supplied to the atom and the electrons jump to occupy any empty orbitals giving the excited state. After this state is when hybridization occurs, hybridized state. The number of electrons mixing (shown by the red dotted line box) will depend on the molecule. In sp^3, one s electron and 3p electrons will mix to give four new equal energy and same shape orbitals (purple box).
3) The next figure shows the shape of new hybridized orbital formed.
4) The last step is for the central atom to form covalent bond with any other atom. If H then s orbital will overlap with the hybridized orbital, and if halogen then a p orbital will overlap with the hybridized orbital.
5) Note that the AXE formula of the compound formed after hybridized orbitals overlap is the same as what we started with.

1

sp^3

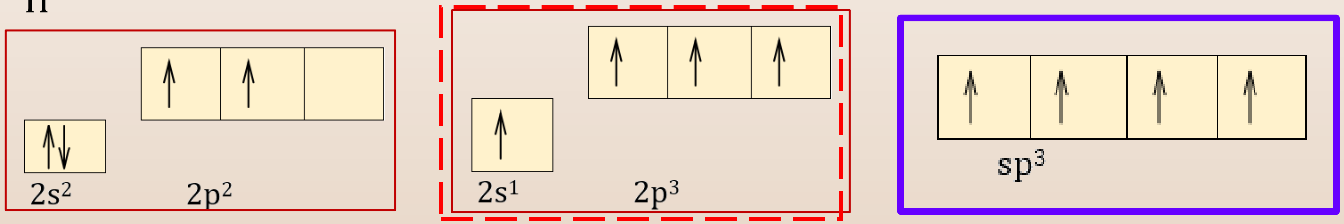
Example: Methane, CH_4

- tetrahedral
- all bonds equivalent

AX_4

2

C
$4e^-$

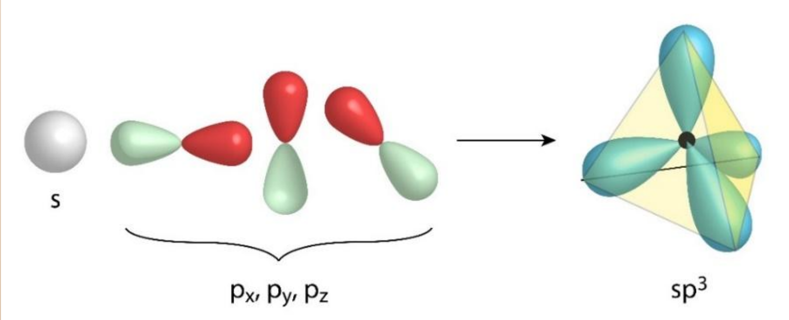


Ground State

Excited State

Hybridized State

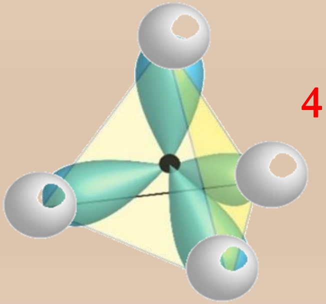
3



The sp^3 hybrid orbitals point to the corners of a tetrahedron.

Each C $2sp^3$ orbital overlaps a H $1s$ orbital to yield CH_4.

4



4 σ bonds

Bond angles 109.5°.

1

sp^2

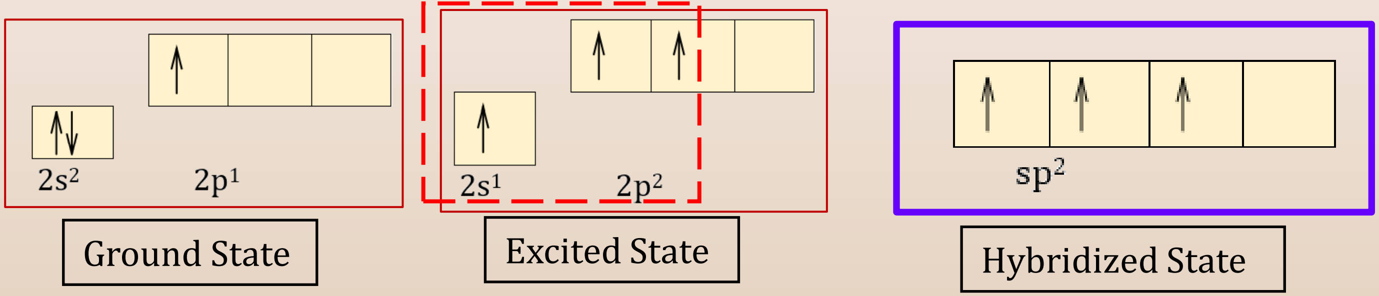
Example: Boron trifluoride, BF_3

- trigonal planar
- all bonds equivalent

AX_3

2

B
$3e^-$


$2s^2$ $2p^1$

Ground State

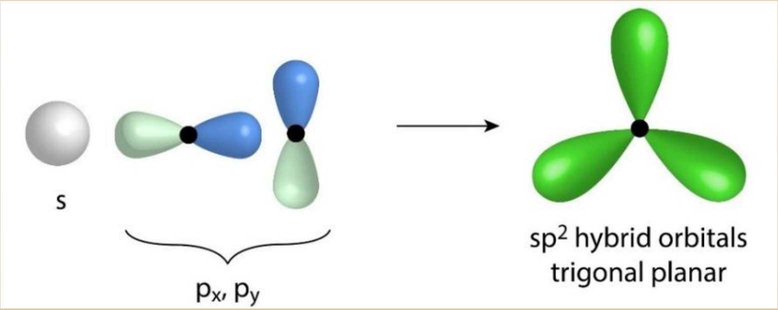
$2s^1$ $2p^2$

Excited State

sp^2

Hybridized State

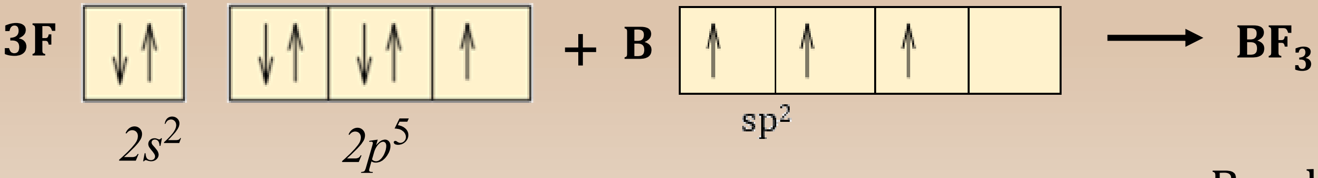
3

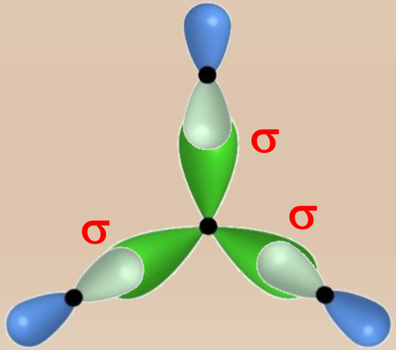


The three sp^2 orbitals point to the corners of an equilateral triangle.

Each B sp^2 orbital overlaps a F $2p$ orbital to yield BF_3.

4


3F $2s^2$ $2p^5$ + B sp^2 → BF_3



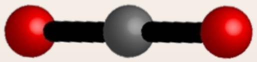
Bond angles 120°.

1

sp

Example: Beryllium Chloride, $BeCl_2$

$\text{Cl—Be—Cl} \xrightarrow{\text{VSEPR}}$

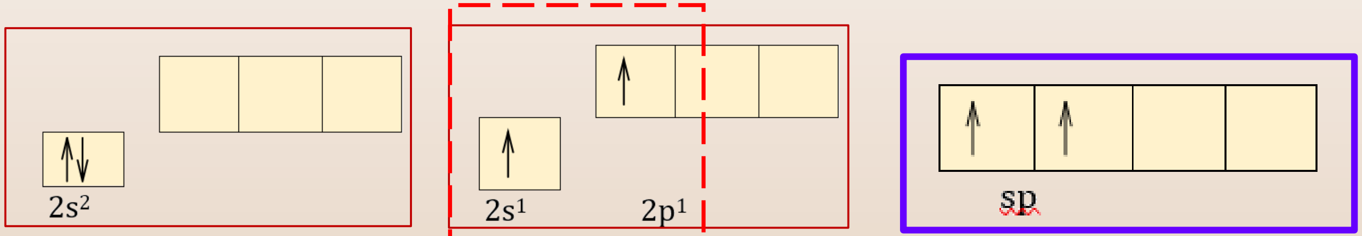


- linear
- both bonds equivalent

AX_2

2

Be
2e⁻

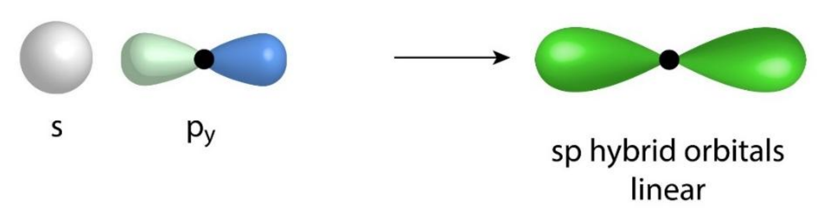


Ground State

Excited State

Hybridized State

3



The two *sp* orbitals point in opposite directions inline with one another.

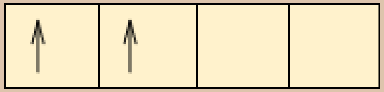
Each Be *sp* orbital overlaps a Cl 3*p* orbital to yield $BeCl_2$.

4

2Cl

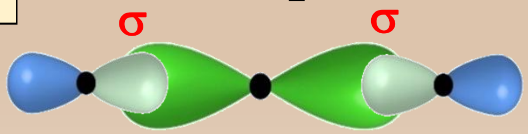
$3s^2$ $3p^5$

Be



sp

$BeCl_2$



Bond angle 180°.

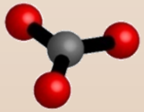
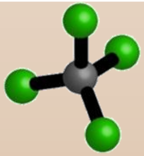
How to Know the Hybridization

Follow the steps below to determine the hybridization on the central atom in a molecule:

1) Write the Lewis electron-dot formula.
2) Write the AXE formula to determine the electron geometry of the central atom.
3) From the electronic geometry deduce the hybridization.
4) Overlap the hybridized orbitals singly first with the atoms. Any remaining electrons are either lone pair of electrons or double or triple bonds.

Determining Hybridization

Lewis structure → Number of electron domains → Type of hybridization

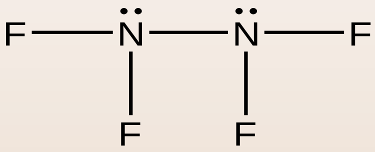
Electron groups	Hybrid orbitals	Electronic Geometry	3D shape
2	Sp	Linear	
3	Sp^2	Trigonal planar	
4	Sp^3	Tetrahedral	
5	Sp^{3}d	Trigonal bipyramidal	
6	Sp^{3}d^2	Octahedral	

Hybridized Orbital Characteristics

Electron Groups	**AXE formula**	**Bond Angle**	**E.g.**	**Electronic Geometry**	**Hybridization**	**Shape of Molecule**
2	AX_2	180°	$BeCl_2$	Linear	sp	Linear
3	AX_3	120 °	BF_3	Trigonal planar	sp^2	Trigonal planar
3	AX_2E	120 °	SO_2	Trigonal planar	sp^2	Bent
4	AX_4	109.5 °	CH_4	Tetrahedral	sp^3	Tetrahedral
4	AX_3E	109.5 °	NH_3	Tetrahedral	sp^3	Trigonal Pyramidal
4	AX_2E_2	109.5 °	H_2O	Tetrahedral	sp^3	Bent
5	AX_5	90 °, 120 °, 180 °	PCl_5	Trigonal bipyramidal	sp^3d	Trigonal Bipyramidal
6	AX_6	90 °, 180 °	SF_6	Octahedral	sp^3d^2	Octahedral

Solved Problem: Determining hybridization type

Use hybridization to give the hybridization and shape of N atom in N_2F_4.



Answer:

1) The Lewis electron-dot structure shows three bonds and one lone pair around each N atom.
2) This is four electron groups (accurately: AX_3E) for central atom.
3) Therefore, a tetrahedral electron geometry.
4) A tetrahedral arrangement has sp^3 hybrid orbitals.
5) The shape will be trigonal pyramidal for both nitrogen atoms.

Understanding Multiple Bond Hybridization

Double Bond: The Lewis structure of CO_2 molecule is as follows:

- It has carbon as central atom and two oxygen atoms as terminal atoms.
- The electronic geometry is AX_2.
- The hybridization on carbon therefore is sp.

Triple Bond: The Lewis structure of HCN molecule is as follows:

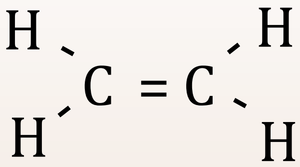
- The carbon is still central with H and N as terminal atoms.
- The electronic geometry is AX_2.
- The hybridization on carbon is still sp.

Hybridization of Multiple Bonds

Single bonds are formed by simple orbital overlap e.g. in H-H bond it is a s-s overlap.

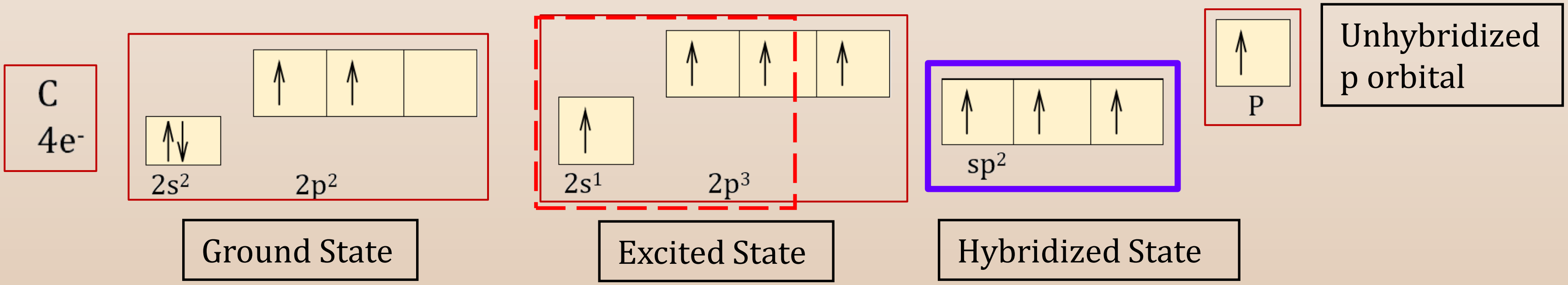
- Some single bonds are hybridized (as discussed in previous slides). These are called sigma bonds.
- In a double bond there is a sigma and a pi bond.
- The pi bond is unhybridized orbital overlap of p orbitals.
- In a triple bond there is one sigma and two pi bonds.

Ethylene – $CH_2=CH_2$



AX_3

- Number of e- domains are 3 hence hybridization = sp^2 (shape = trigonal planar, bond angle = 120°)
- There are two central atoms; both carbon.
- Each carbon will mix 1 of s and 2 of p orbitals; 1e- of p is left over and this forms the pi bond.



C
$4e^-$

$2s^2$ $2p^2$

Ground State

$2s^1$ $2p^3$

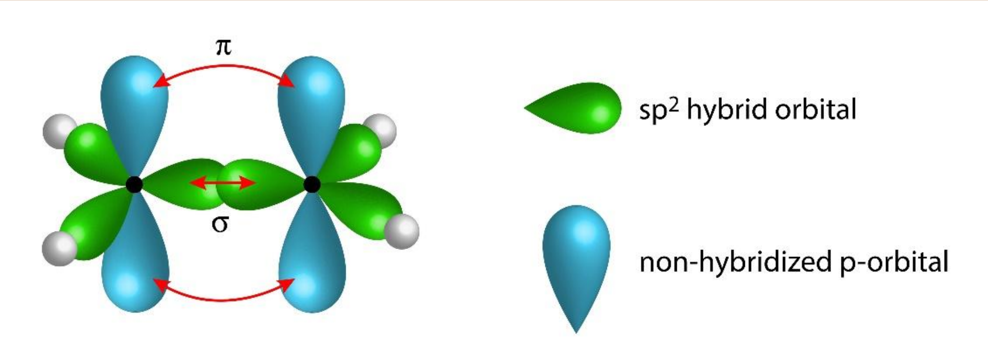
Excited State

sp^2

Hybridized State

P

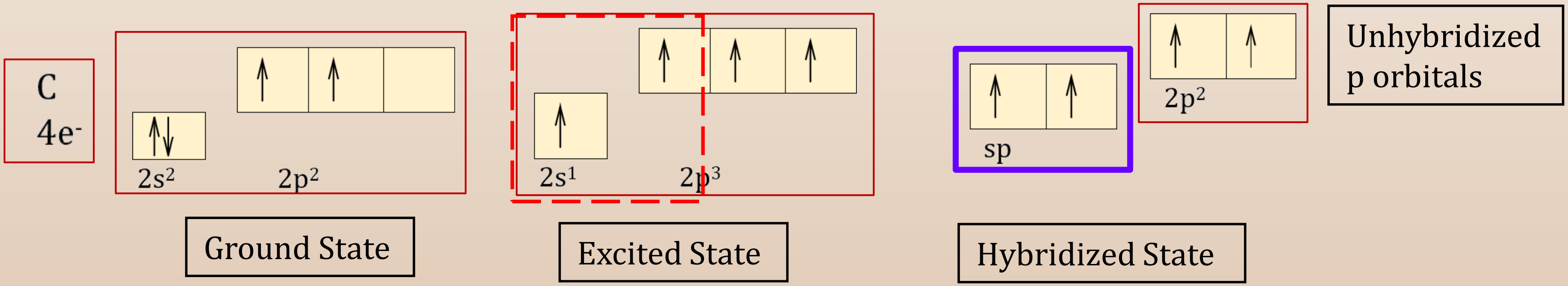
Unhybridized p orbital

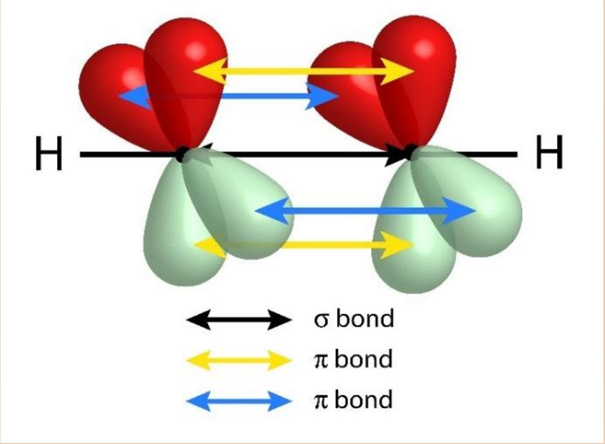


Double bond = 1 σ bond + 1 π bond

Acetylene C_2H_2 $H-C{\equiv}C-H$ AX_2

- Number of e- domains = 2 hence hybridization = **sp** (shape = linear, bond angle = 180°)
- There are two central atoms; both carbon.
- Each carbon will mix 1 of s and 1 of p orbitals; 2e- of p orbitals are left over and this form two pi bonds.



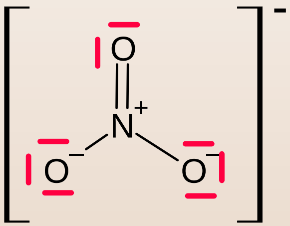


Triple bond = 1 σ bond + 2 π bonds

Solved Problem: Predicting hybridization of multiple bonds

What is the hybridization on the central atom in nitrate ion?

1) Lewis structure is



2) Electronic geometry of N is AX_3
3) Hybridization of a three electron group atom is sp^2.

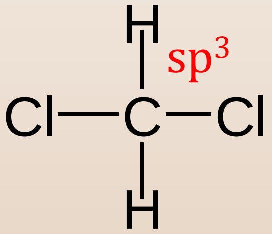
Bond Lengths of Ethyne, Ethene and Ethane

- The carbon-carbon bond length is shorter as more bonds hold the carbons together.
- The carbon-hydrogen bond lengths also get shorter with more *s* character of the bond.

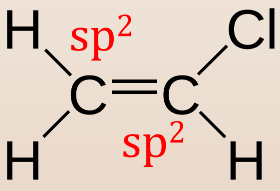
Property	**sp^3**	**sp^2**	**sp**
Shape	Tetrahedral	Trigonal planar	Linear
Bond Length	1.54 °A	1.34 °A	1.20 °A
Angle	109°	120°	180°
New hybrid bonds called	Sigma	Sigma	Sigma
Bonds in organic compounds	Sigma All single	Sigma and pi Double bonds	Sigma and 2 pi Triple bonds
Examples	CH_4	BH_3	BeH_2
Organic examples	All alkanes	Alkenes (C=C) Carbonyls (C=O) Carbon-nitrogen (C=N)	Alkynes Nitriles (C≡ N)
Bond Strength	439 kJ/mol	728 kJ/mol	965 kJ/mol

Solved Problem: Counting pi and sigma bonds

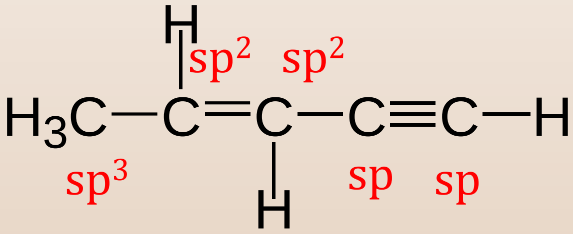
How many pi bonds and sigma bonds are in each of the following molecules? Describe the hybridization of each C atom.



(a)



(b)



(c)

(a) 4 sigma bonds

(b) 5 sigma bonds,
1 pi bond

(c) 10 sigma bonds,
3 pi bonds

Molecular Orbital Theory

All atoms have atomic orbitals (AO), which when bond and overlap with other atomic orbitals will form molecular orbitals (MO).

The number of AO combining will form the same number of MO. Two atomic orbitals will combine to form two molecular orbitals. (4 AO will give 4 MO etc.)

How the orbitals are combining depends on energy and orientation. (Wavefunctions - + and – regions)

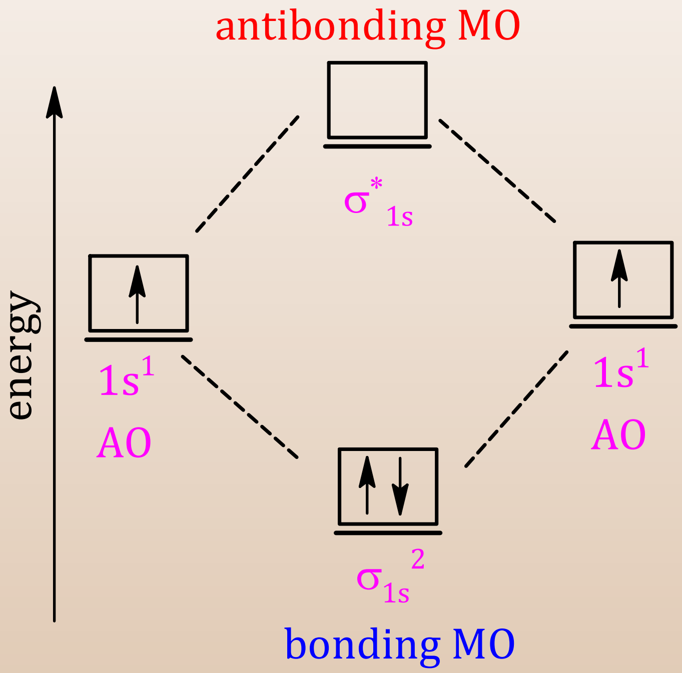
- Half the of MO are bonding with low energy and half will be antibonding at a higher energy level. Electrons usually will be found in the bonding MO.
- Bonding MO are obtained by adding atomic orbitals of similar wavefunction (e.g. ψ+ and ψ+).
- Antibonding MO are obtained by subtracting or opposite wavefunction atomic orbitals (e.g. ψ+ and ψ-).

(read more at: chem.libretexts.org)

Molecular Orbital Theory

$$\begin{array}{ccccc} H & + & H & \rightarrow & H_2 \\ 1s^1 & & 1s^1 & & \sigma_{1s}^{\;2} \end{array}$$

Two atomic orbitals, both s^1 with one electron each, form 2 MO. These new MO are sigma bonds, one is higher in energy, antibonding, while the other is bonding MO at a lower energy. The two electrons are found in the bonding MO.



Key Words/Concepts

- Valence bond theory
- Hybridization of atomic orbitals
  - *s* and *p*
  - *s*, *p,* and *d*
- Hybridization involving multiple bonds
- Molecular orbital theory
  - Bonding and antibonding orbitals