

Hybridization

Dr. Sapna Gupta

Valence Bond Theory

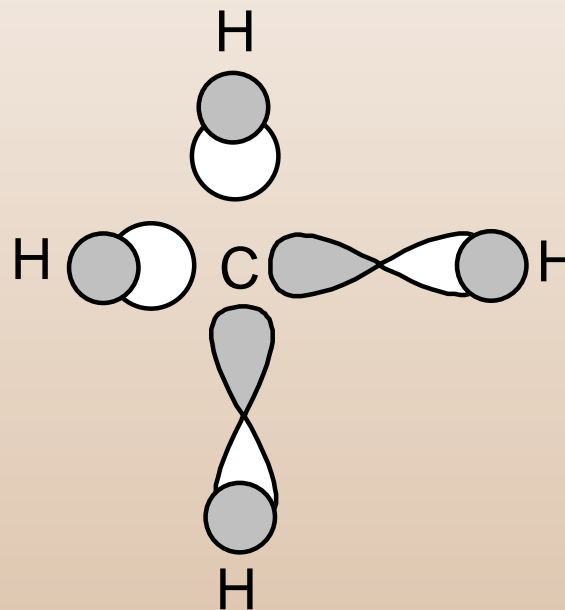
- The 1st theory of bonding is the Lewis theory which is about sharing electrons in the valence shell.
- The second theory is Valence Bond Theory which helps to explain some points that Lewis theory does not explain.

A 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, so as to obtain maximum overlap.

Methane Molecule According to Lewis Theory

- In Lewis theory two orbitals of carbon will be s (spherical) and two will be p (dumbbell shape).
- The orbital overlap required for bonding will be different for the two bonds.
- Two bonds will be longer and two shorter and the bond energy will be different too.
- Therefore there must be a different theory on how covalent bonds are formed.



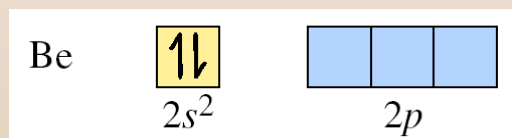
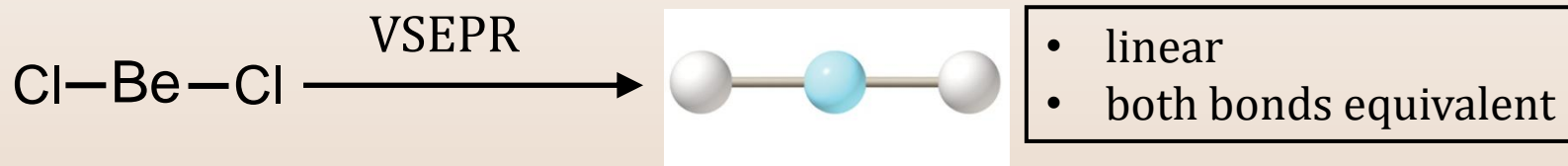
Valence Bond Theory - Hybridization

Hybrid orbitals are formed by mixing orbitals, and are named by using the atomic orbitals that combined:

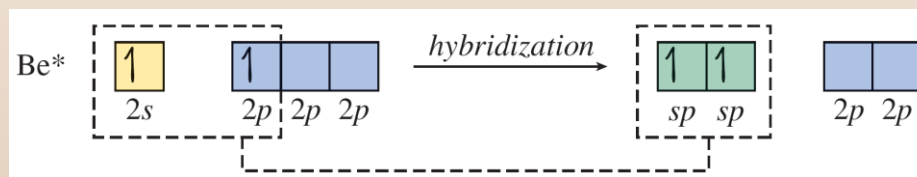
- one s orbital + one p orbital gives two sp orbitals
- one s orbital + two p orbitals gives three sp^2 orbitals
- one s orbital + three p orbitals gives four sp^3 orbitals
- one s orbital + three p orbitals + one d orbital gives five sp^3d orbitals
- one s orbital + three p orbitals + two d orbitals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

sp

- Beryllium Chloride, BeCl_2

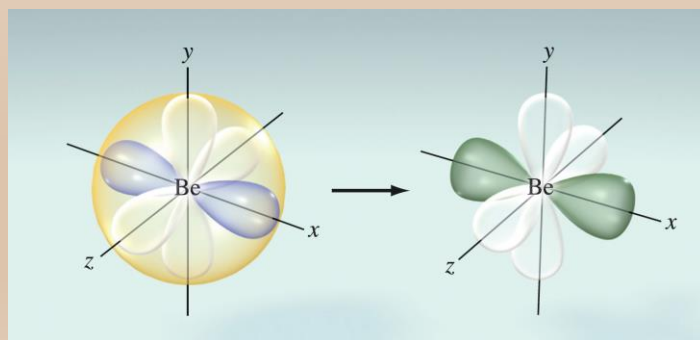


Ground state



Excited State

Hybridized State

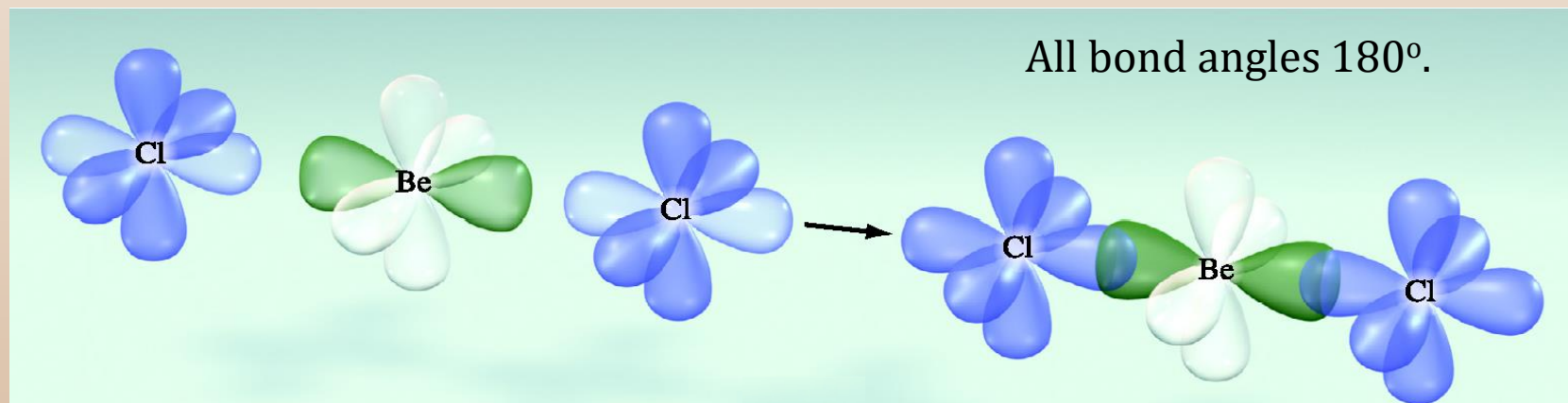


The two sp orbitals point in opposite directions inline with one another.

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

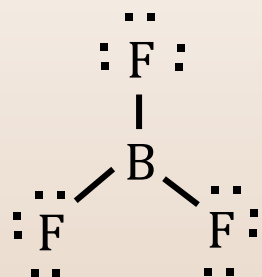


All bond angles 180° .

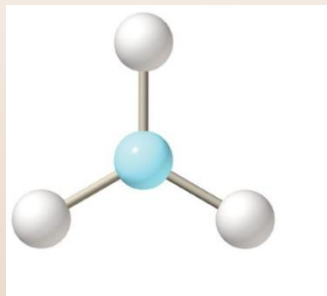


sp²

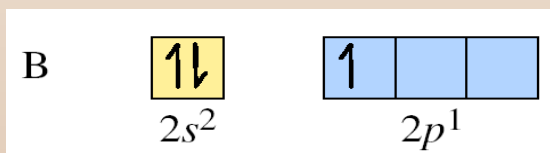
- Example: Boron trifluoride, BF₃



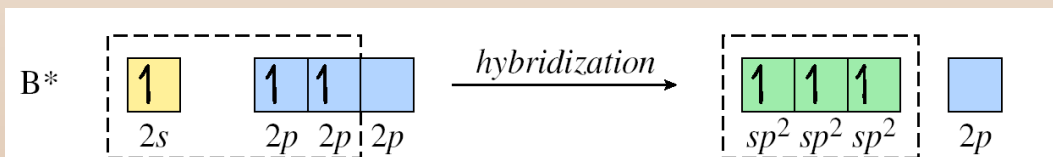
VSEPR



- trigonal planar
- all bonds equivalent

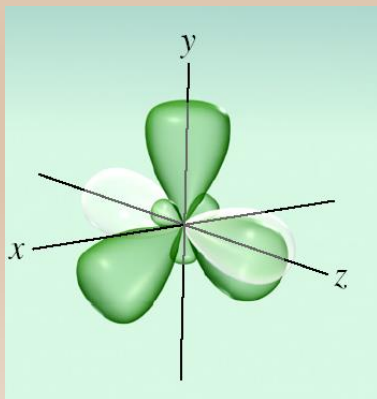


Ground state



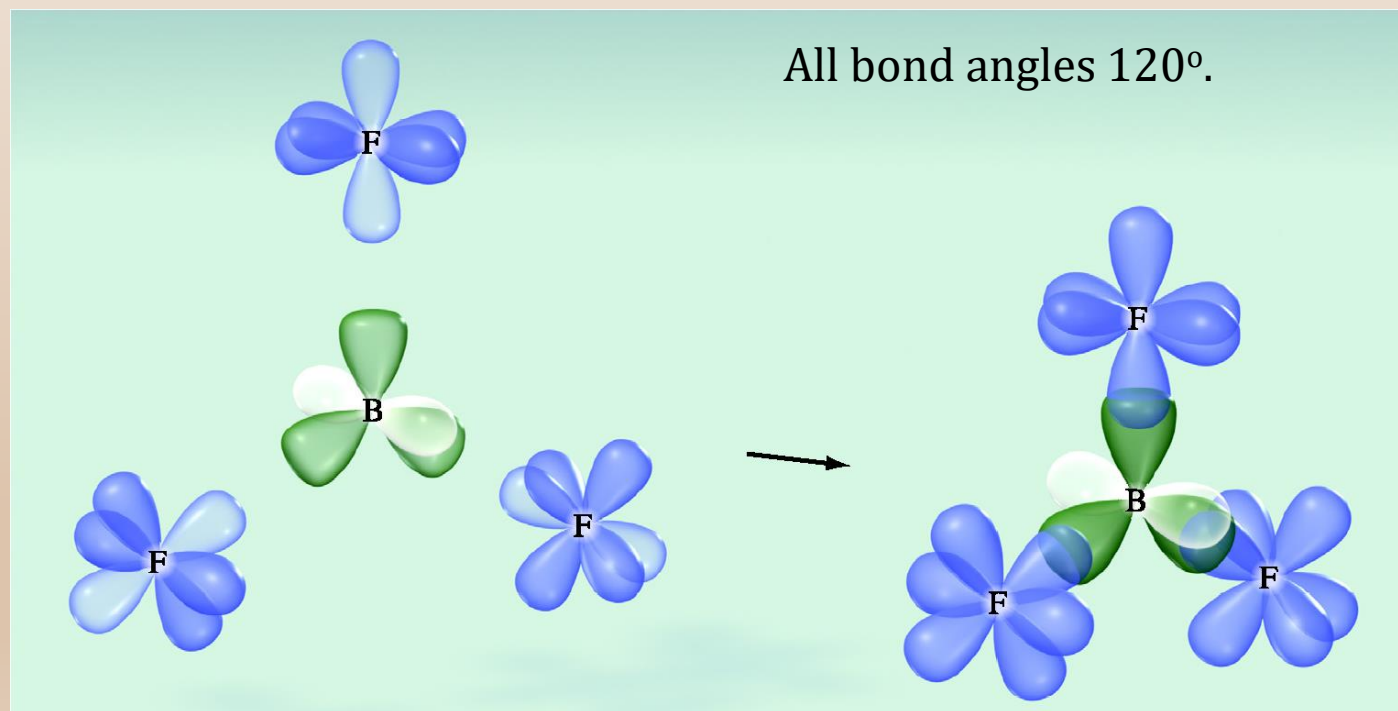
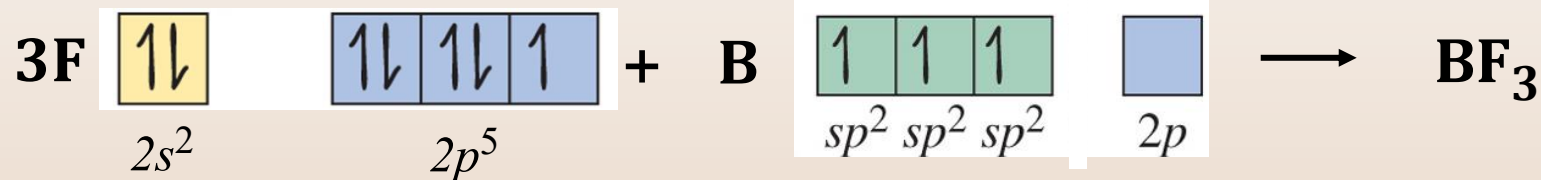
Excited State

Hybridized State



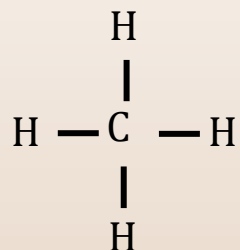
The three sp² orbitals point to the corners of an equilateral triangle.

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

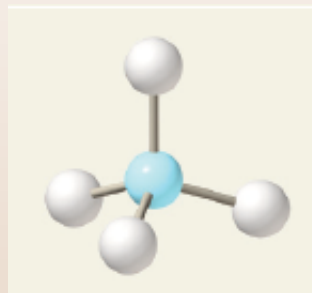


sp^3

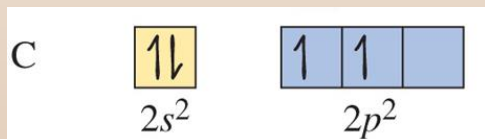
- Example: Methane, CH_4



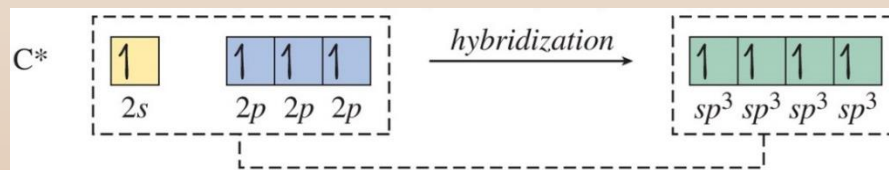
VSEPR



- tetrahedral
- all bonds equivalent

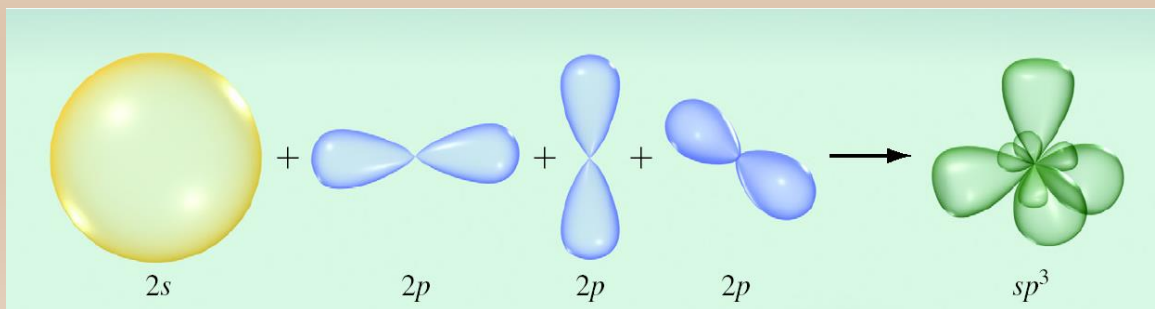


Ground state



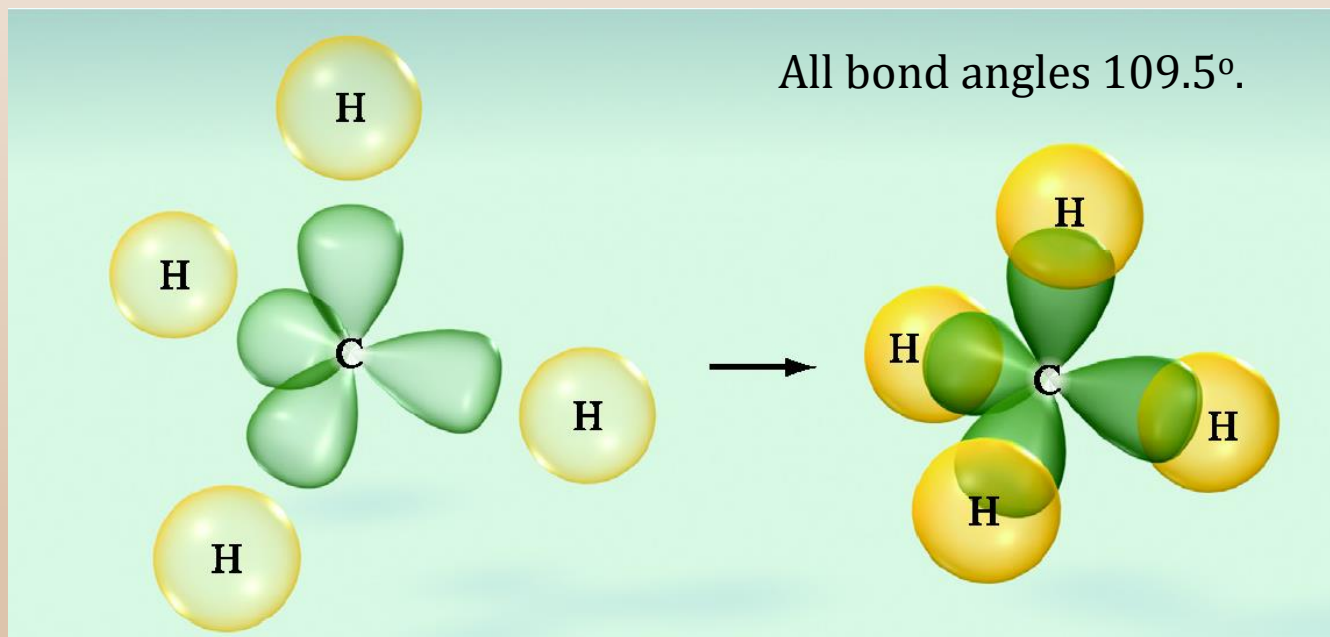
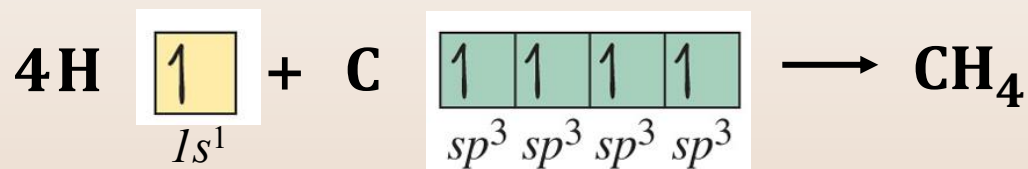
Excited State

Hybridized State



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 .



Working out Hybridization

To figure out hybridization on the central atom in a molecule:

1. Write the Lewis electron-dot formula.
2. Use VSEPR to determine the electron geometry about the atom.
3. From the electronic geometry deduce the hybrid orbitals.
4. Assign the valence electrons to the hybrid orbitals one at a time, pairing only when necessary.
5. Form bonds by overlapping singly occupied hybrid orbitals with singly occupied orbitals of another atom.

Determining Hybridization

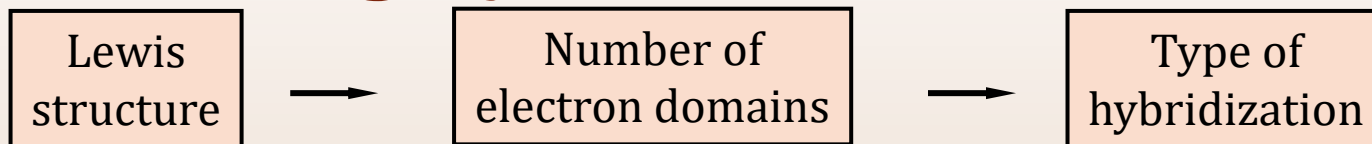
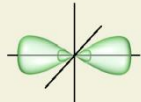

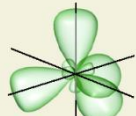

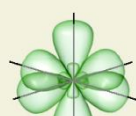
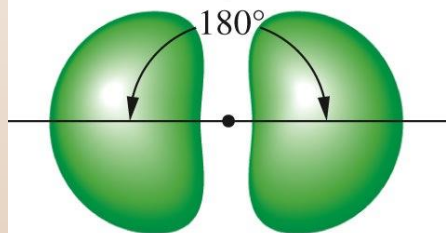


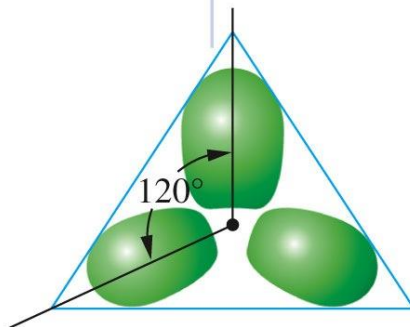
TABLE 9.4 Number of Electron Domains and Hybrid Orbitals on Central Atom		
Number of Electron Domains on Central Atom	Hybrid Orbitals	Geometry
2	sp	 Linear
3	sp^2	 Trigonal planar
4	sp^3	 Tetrahedral
5	sp^3d	 Trigonal bipyramidal
6	sp^3d^2	 Octahedral

Shapes of the Hybridized Orbitals

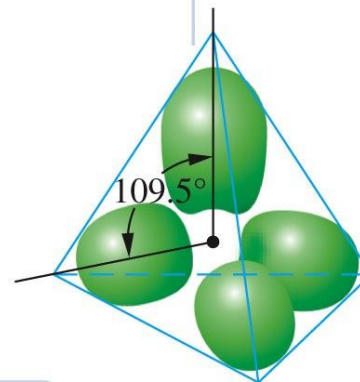
Linear arrangement:
 sp hybrid orbitals



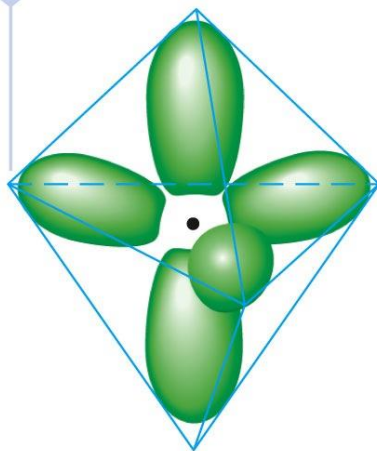
Trigonal planar arrangement:
 sp^2 hybrid orbitals



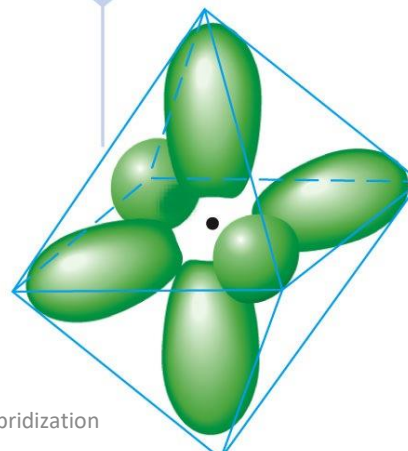
Tetrahedral arrangement:
 sp^3 hybrid orbitals



Trigonal bipyramidal arrangement:
 sp^3d hybrid orbitals

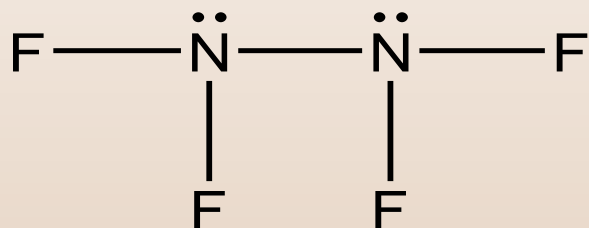


Octahedral arrangement:
 sp^3d^2 hybrid orbitals



Solved Problem

Use valence bond theory to describe the bonding about an N atom in N_2F_4 .



The Lewis electron-dot structure shows three bonds and one lone pair around each N atom. So that is AX_3E , four electron groups on central atom have a tetrahedral arrangement.

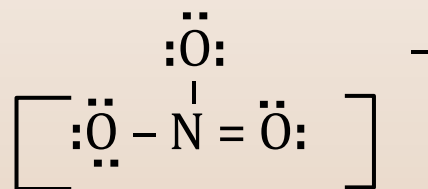
A tetrahedral arrangement has sp^3 hybrid orbitals

Solved Problem

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

Answer:

- Lewis structure is



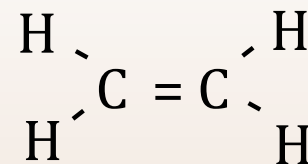
- Electronic geometry of N is AX₃

- Hybridization of a three electron group atom is sp²

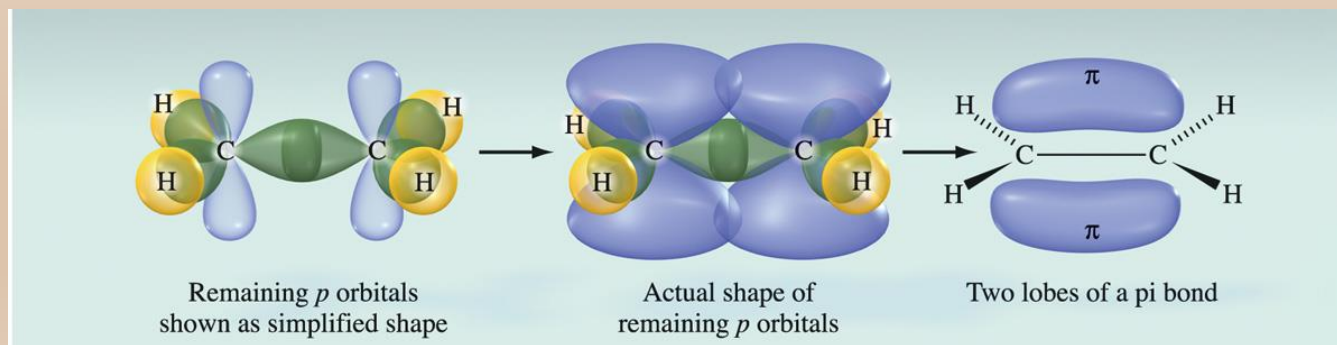
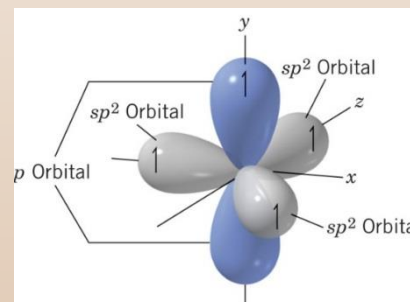
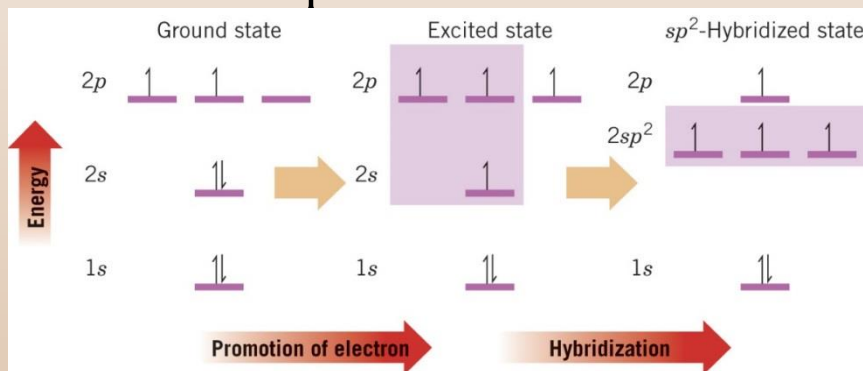
Hybridization of Multiple Bonds

- 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 - $\text{CH}_2=\text{CH}_2$

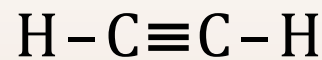


- Number of e- domains = 3
- Hybridization = sp^2 (shape = trigonal planar, bond angle = 120°)
- There are two central atoms; both carbon.
- Each carbon will mix 1 of s and 2 of p orbitals; 1 of p is left over and this forms the pi bond.

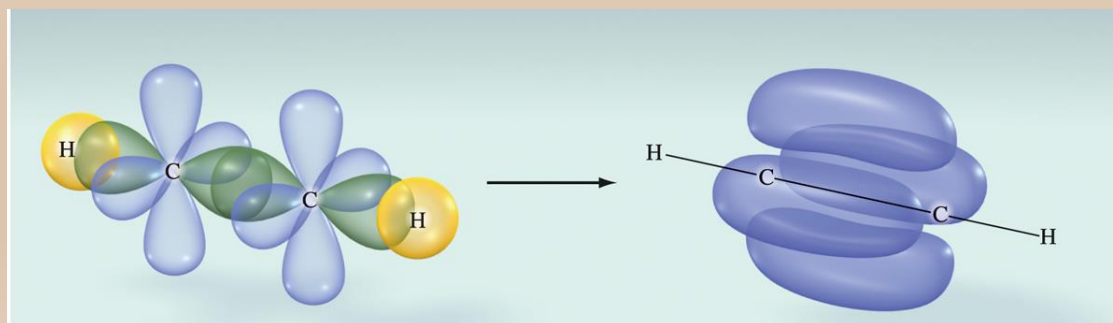
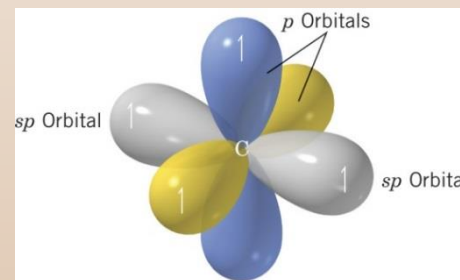
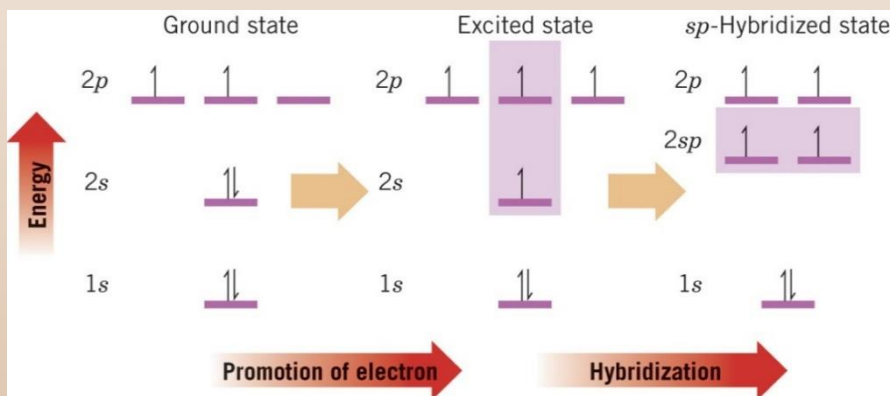


Double bond = 1 σ bond + 1 π bond

Acetylene C_2H_2



- Number of e- domains = 2
- 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; 2 of p orbitals are left over and this form two pi bond.



Triple bond = 1 σ bond + 2 π bonds

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
 - *2s* orbitals are held more closely to the nucleus than *2p* orbitals
 - A hybridized orbital with more percent *s* character is held more closely to the nucleus than an orbital with less *s* character
 - The *sp* orbital of ethyne has 50% *s* character and its C-H bond is shorter
 - The *sp*³ orbital of ethane has 25% *s* character and its C-H bond is longer

Molecule	Bond	Bond strength		Bond length (pm)
		(kJ/mol)	(kcal/mol)	
Methane, CH ₄	(<i>sp</i> ³) C—H	439	105	109
Ethane, CH ₃ CH ₃	(<i>sp</i> ³) C—C (<i>sp</i> ³)	377	90	154
	(<i>sp</i> ³) C—H	421	101	109
Ethylene, H ₂ C=CH ₂	(<i>sp</i> ²) C=C (<i>sp</i> ²)	728	174	134
	(<i>sp</i> ²) C—H	464	111	109
Acetylene, HC≡CH	(<i>sp</i>) C≡C (<i>sp</i>)	965	231	120
	(<i>sp</i>) C—H	558	133	106

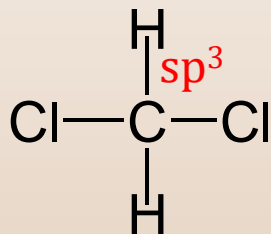
Hybridization Summary

On the web: <http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/hybrv18.swf>

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)

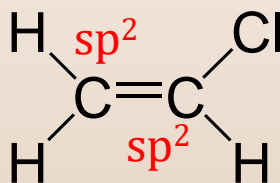
Solved Problem

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



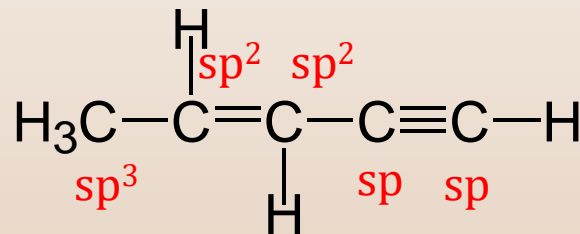
(a)

(a) 4 sigma bonds



(b)

(b) 5 sigma bonds,
1 pi bond



(c)

(c) 10 sigma bonds,
3 pi bonds

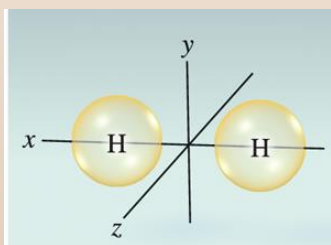
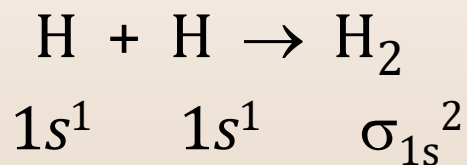
Molecular Orbital Theory

As atoms approach one another, their atomic orbitals overlap and form molecular orbitals.

Molecular orbitals concentrated in regions between nuclei are called **bonding orbitals**. They are obtained by adding atomic orbitals.

Molecular orbitals having zero values in regions between nuclei (and are in other regions) are called **antibonding orbitals**. They are obtained by subtracting atomic orbitals.

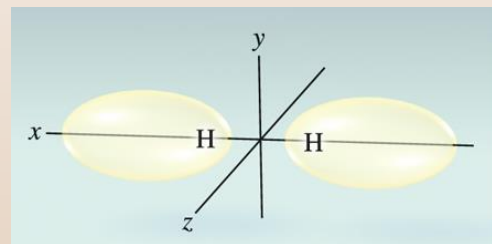
Molecular Orbital Theory



$1s \quad 1s$
H atomic orbitals

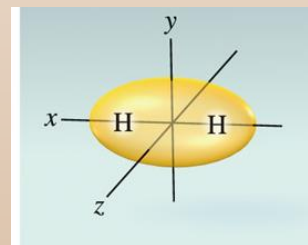
difference

antibonding orbital



σ_{1s}^*

bonding orbital



σ_{1s}

sum

H_2 molecular orbitals

Key Words/Concepts

- Valence Bond Theory
- Hybridization
- Sp, sp^2 and sp^3 hybridization
- Properties of all the hybridizations (bond angles, shapes etc)
- Molecular Orbital Theory