Chapter 10
Bonding Theories

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Valence Bond Theory

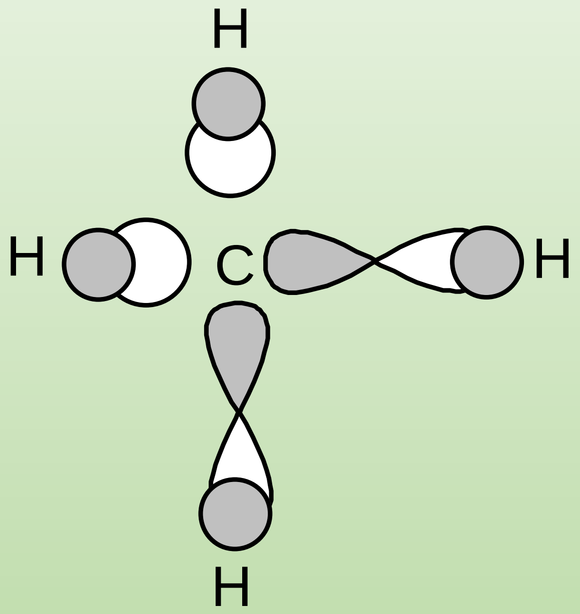
- Valence bond theory is an approximate theory put forth to explain the covalent bond by quantum mechanics.

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

- CH_4
- C is central atom: $1s^2\ 2s^2\ 2p^2$
- Valence electrons for bonding are in the s (spherical) and p (dumbbell) orbitals.
- 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

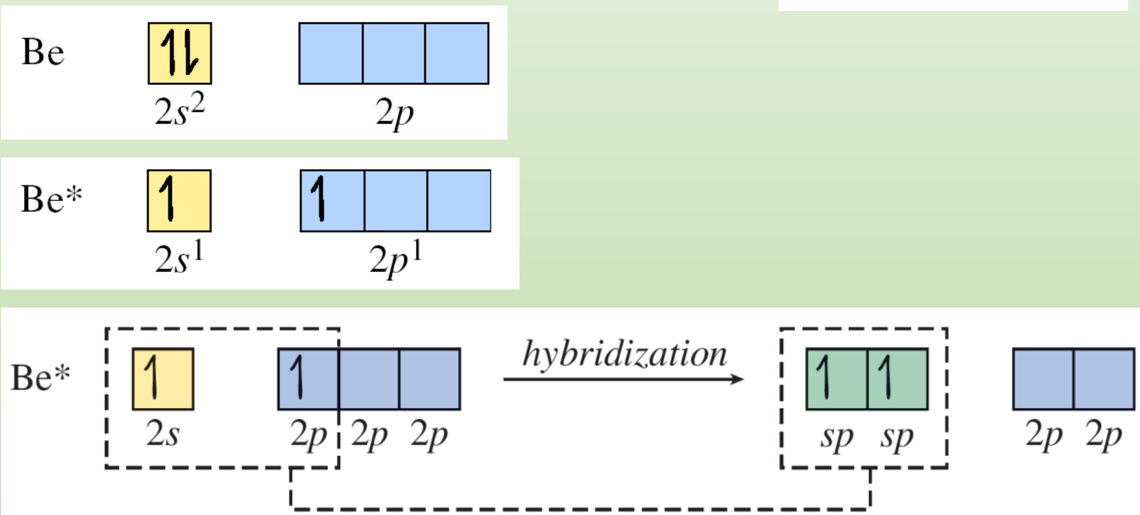
Hybrid orbitals are formed by mixing orbitals, and are named by using the atomic orbitals that combined:

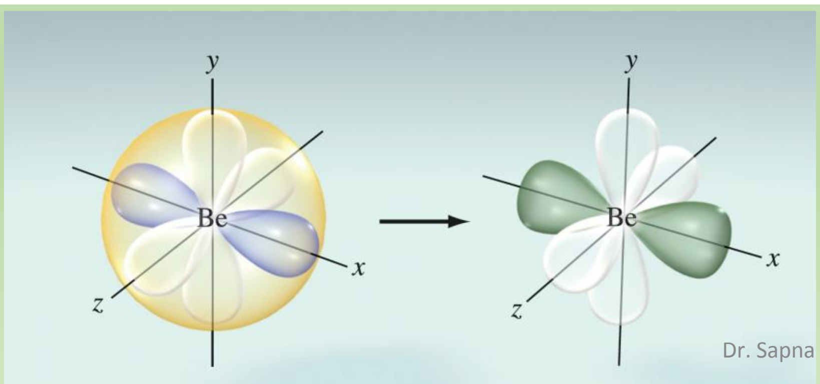
- one *s* orbital + one *p* orbital gives two *sp* orbitals
- one *s* orbital + two *p* orbitals gives three sp^2 orbitals
- one *s* orbital + three *p* orbitals gives four sp^3 orbitals
- one *s* orbital + three *p* orbitals + one *d* orbital gives five sp^3d orbitals
- one *s* orbital + three *p* orbitals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

sp

- Beryllium Chloride, $BeCl_2$

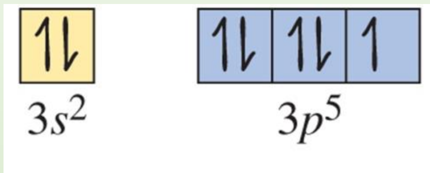
- linear
- both bonds equivalent

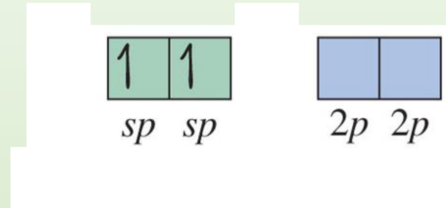




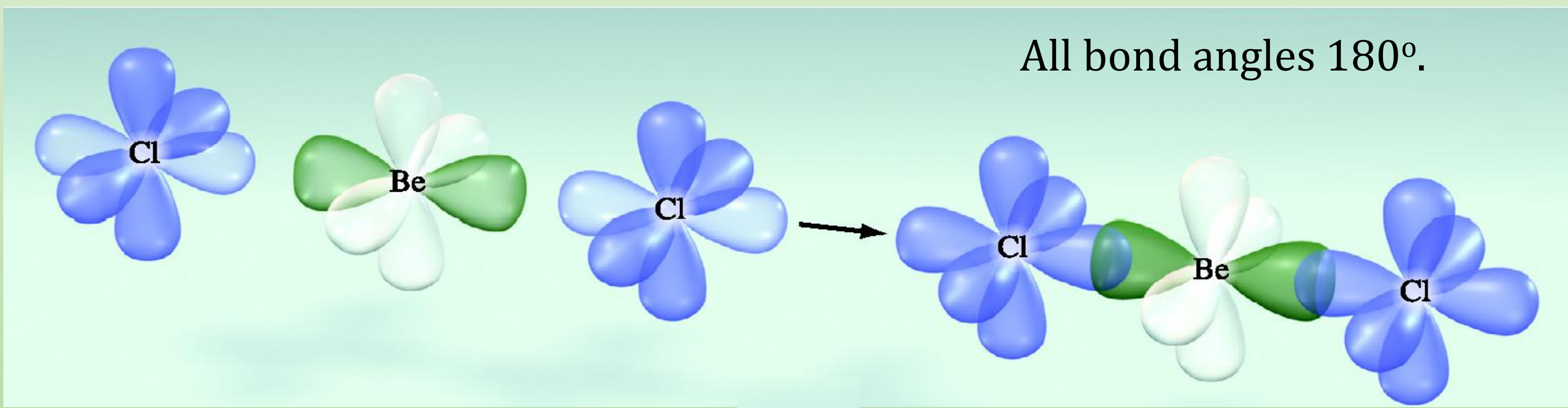
The two *sp* orbitals point in opposite directions inline with one another.

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

2Cl 

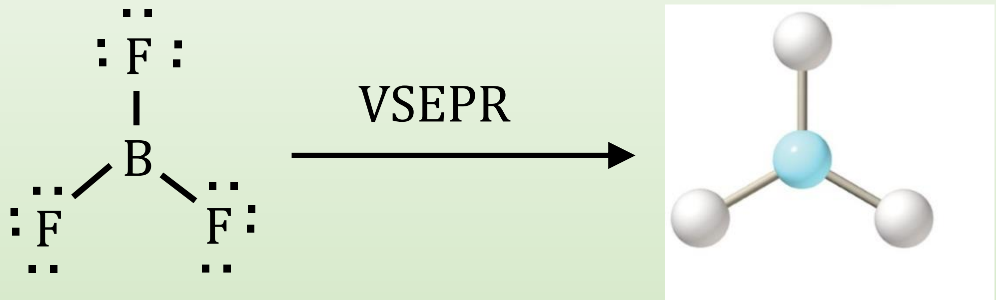
+ **Be** 

$\longrightarrow$ **$BeCl_2$**

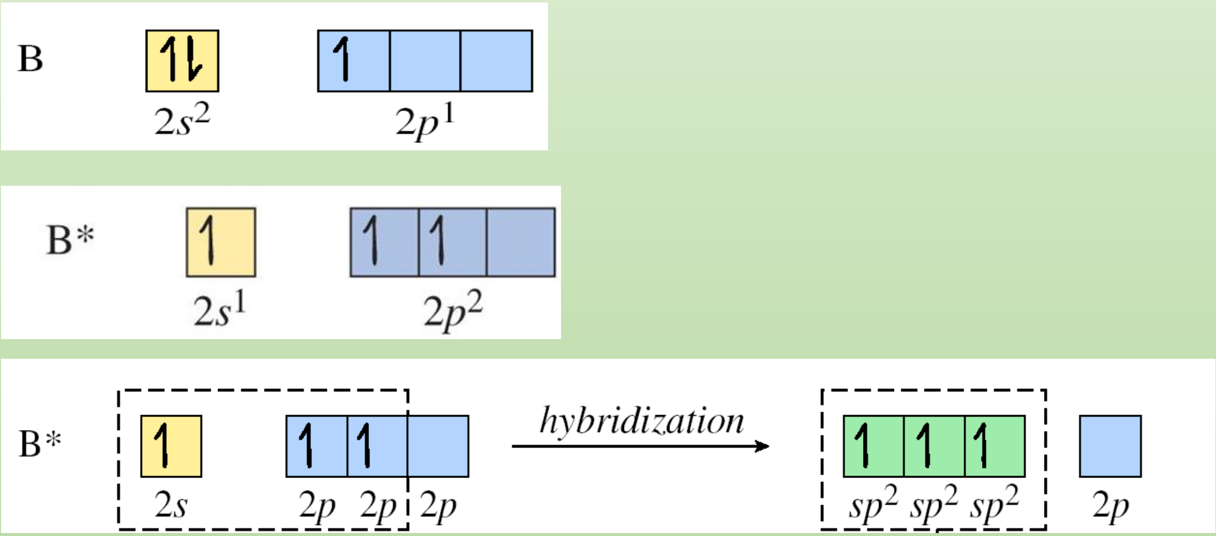


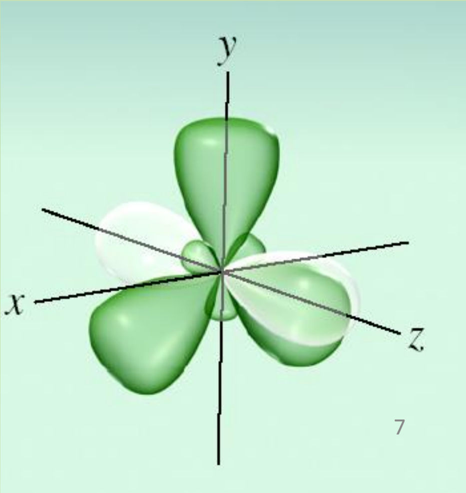
sp^2

- Example: Boron trifluoride, BF_3



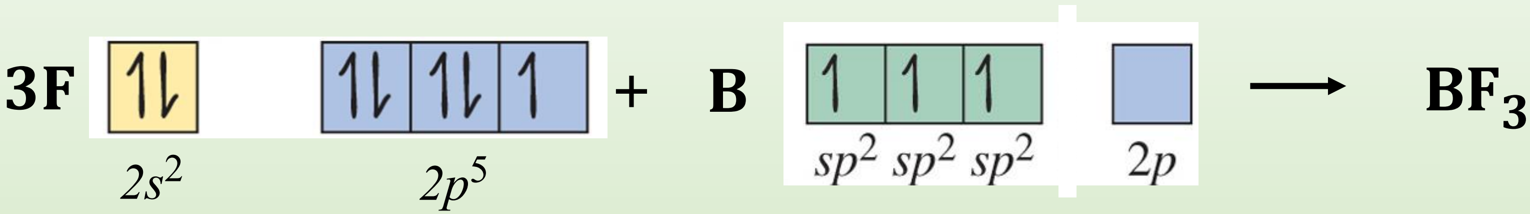
- trigonal planar
- all bonds equivalent

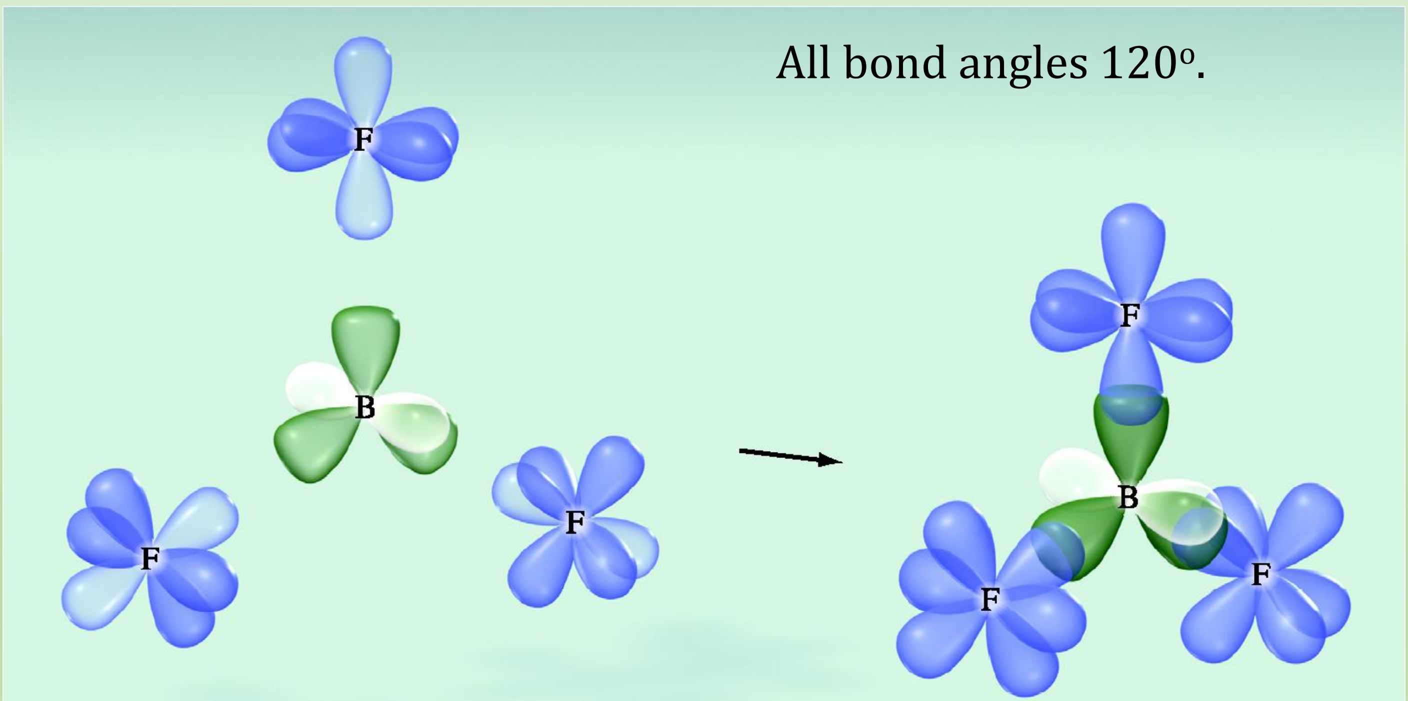




The three sp^2 orbitals point to the corners of an equilateral triangle.

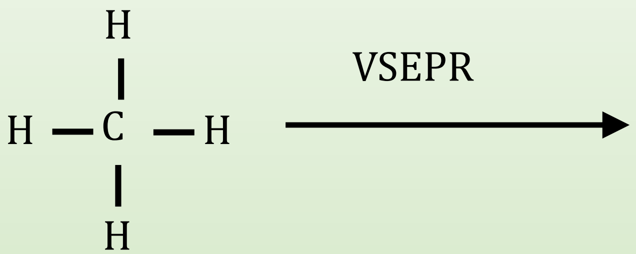
Each B sp^2 orbital overlaps a F 2p orbital to yield BF_3.

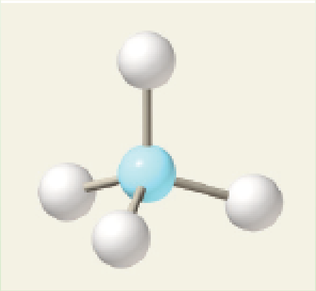




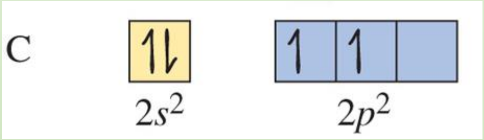
sp^3

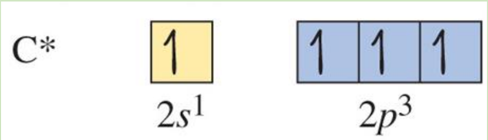
- Example: Methane, CH_4

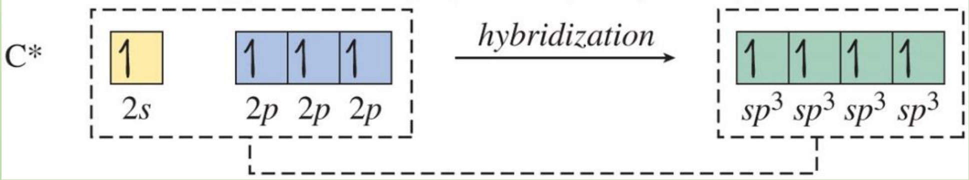


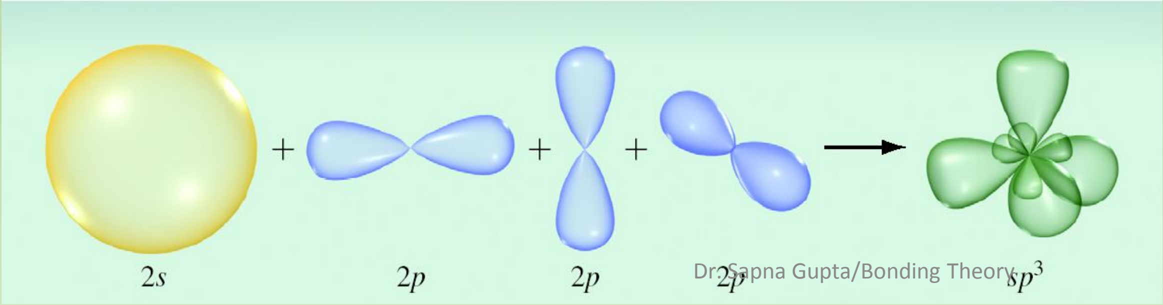


- tetrahedral
- all bonds equivalent



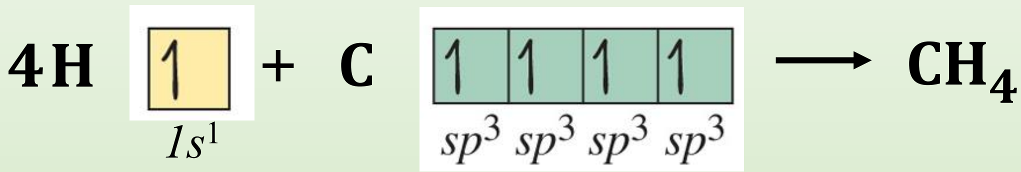


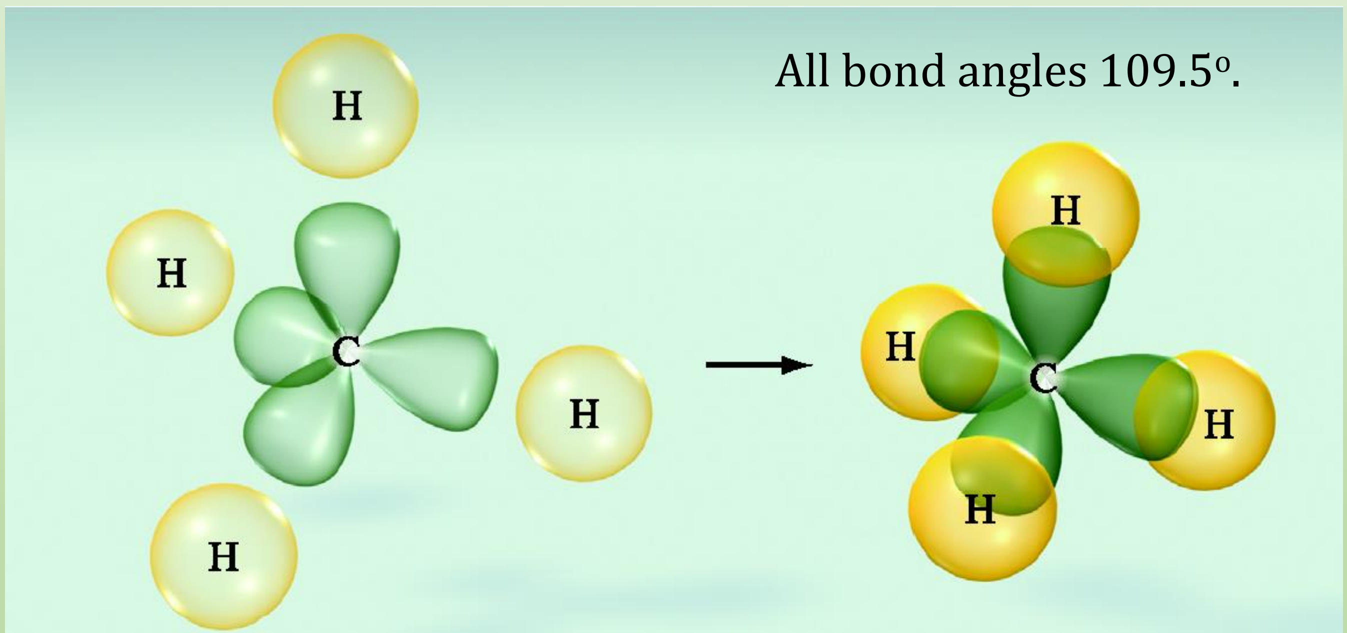




The sp^3 hybrid orbitals point to the corners of a tetrahedron.

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





Working out Hybridization

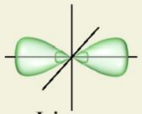
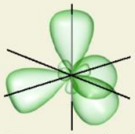
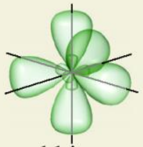
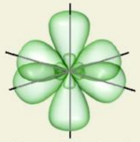
To figure out hybridization on the central atom in a molecule:

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.

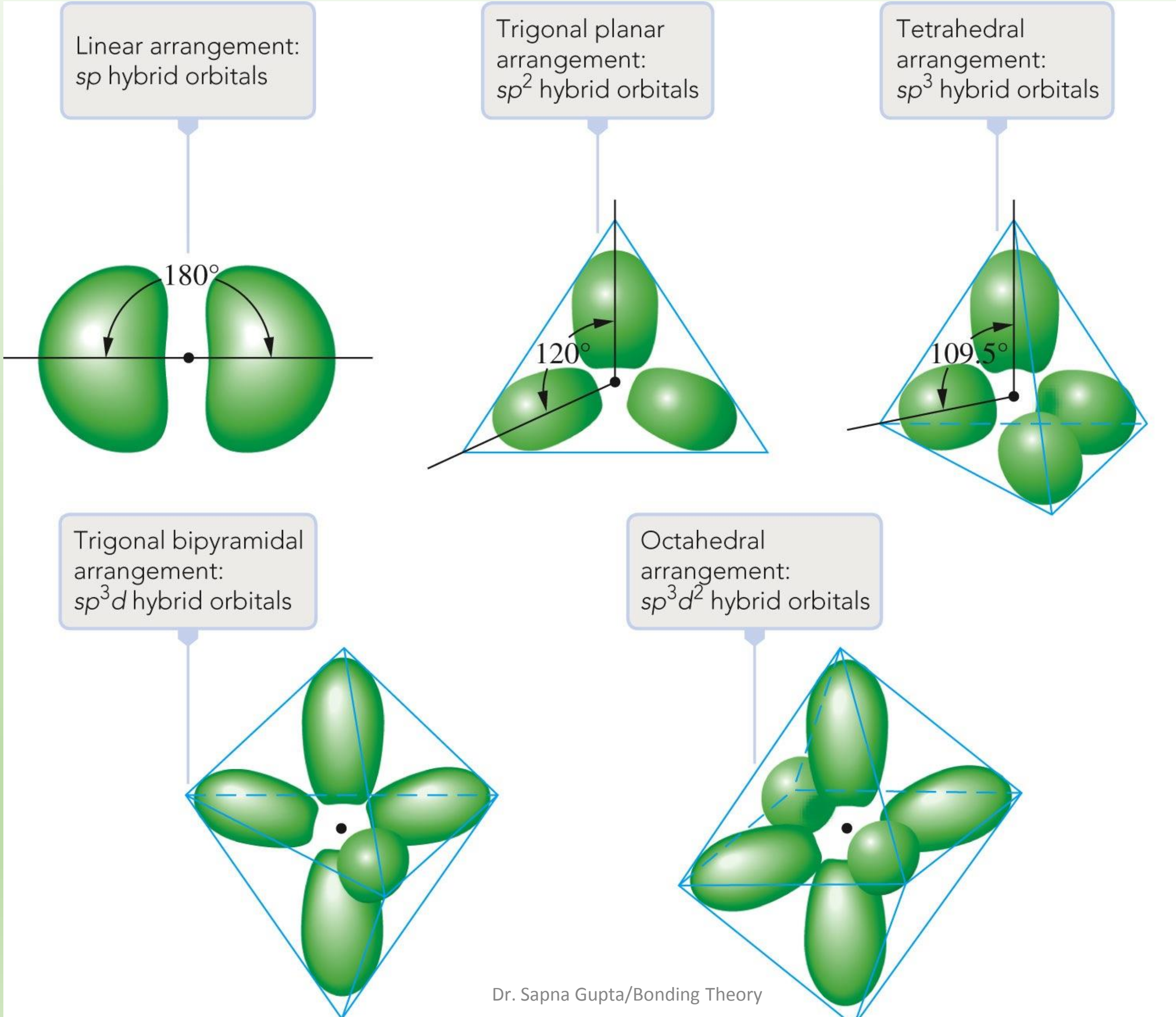
Determining Hybridization

Lewis structure → Number of electron domains → Type of 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

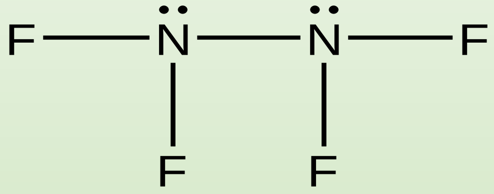


Hybridized Orbital Characteristics

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
5	AX_4E	90°, 120°, 180°	SF_4	Trigonal bipyramidal	sp^3d	Seesaw
5	AX_3E_2	90°, 180°	CIF_4	Trigonal bipyramidal	sp^3d	T – shape
5	AX_2E_3	180°	XeF_2	Trigonal bipyramidal	sp^3d	Linear
6	AX_6	90°, 180°	SF_6	Octahedral	sp^3d^2	Octahedral
6	AX_5E	90°	BrF_5	Octahedral	sp^3d^2	Square Pyramidal
6	AX_4E_2	90°	XeF_4	Octahedral	sp^3d^2	Square Planar
6	AX_3E_3	90°, 180°		Octahedral	sp^3d^2	T – Shape
6	AX_2E_4	180°		Octahedral	sp^3d^2	Linear

Solved Problem

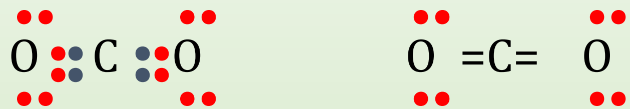
Use valence bond theory to describe the bonding about an N atom in N_2F_4.



1. The Lewis electron-dot structure shows three bonds and one lone pair around each N atom
2. So that is four electron groups (accurately: AX_3E) on central atom
3. Therefore a tetrahedral arrangement
4. A tetrahedral arrangement has sp^3 hybrid orbitals

Explaining Multiple Bonds

- Consider CO_2 molecule. The Lewis structure 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.

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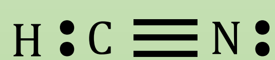
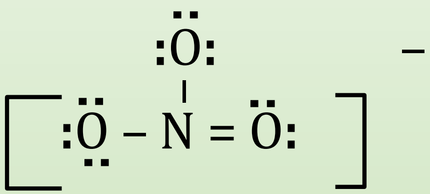
- Now consider the HCN molecule. The Lewis structure is as follows:



- 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.

Solved Problem

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



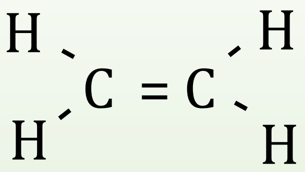
Answer:

- Lewis structure is
- Electronic geometry of N is AX_3
- Hybridization of a three electron group atom is sp^2

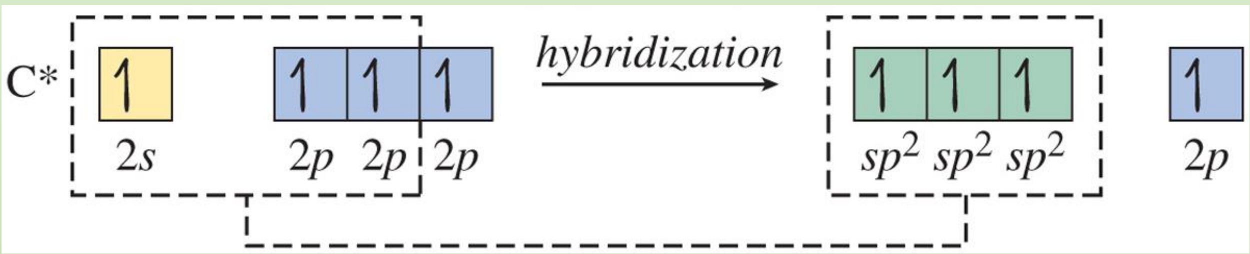
Hybridization of Multiple Bonds

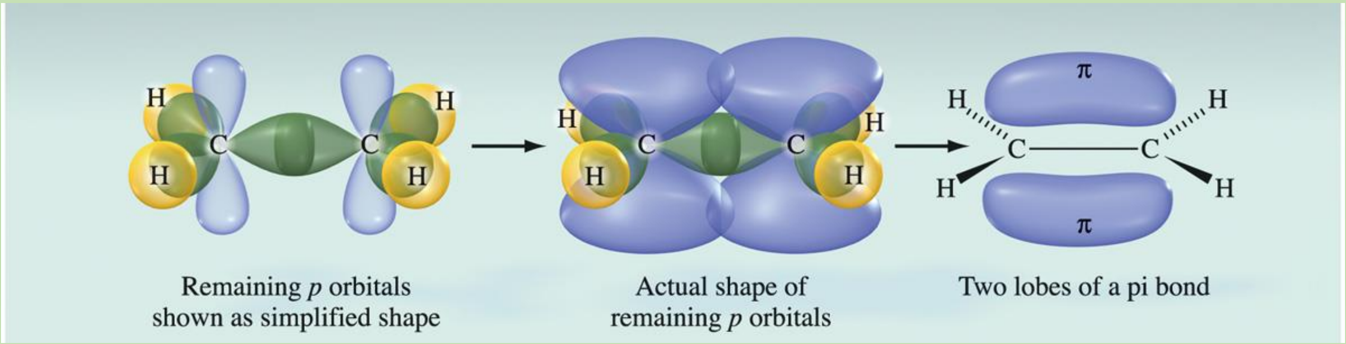
- Single bonds are formed by simple orbital overlap e.g. in H-H bond it is a s-s overlap.
- Some single bonds are hybridized (as discussed in previous slides). These are called sigma bonds.
- In a double bond there is a sigma and a pi bond.
- The pi bond is unhybrized orbital overlap of p orbitals.
- In a triple bond there is one sigma and two pi bonds.

Ethylene – $CH_2{=}CH_2$



- 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.



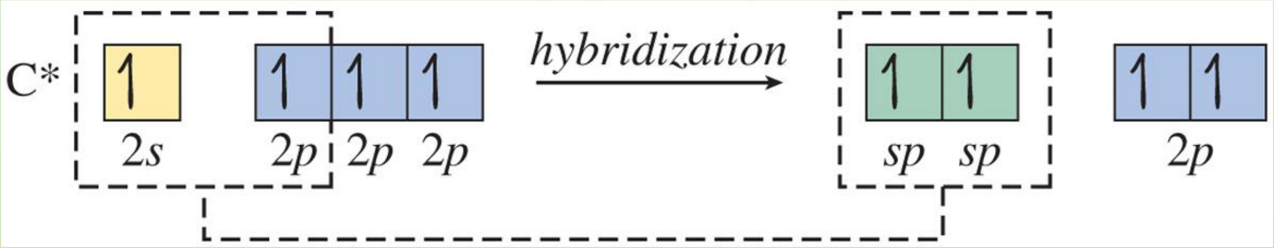


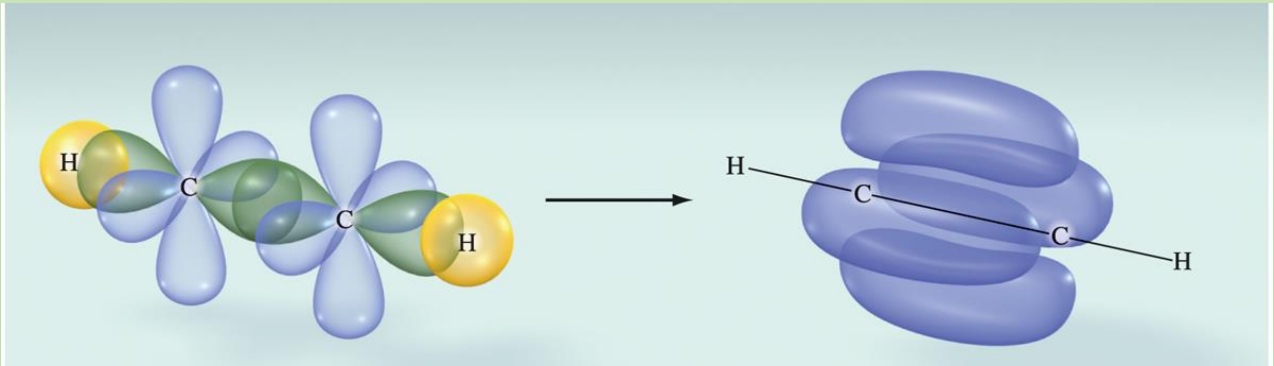
Double bond = 1 σ bond + 1 π bond

Acetylene C_2H_2

$H-C\equiv C-H$

- 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.

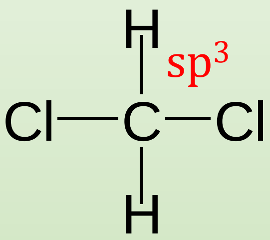




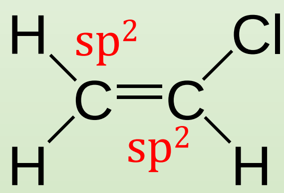
Triple bond = 1 σ bond + 2 π bonds

Solved Problem

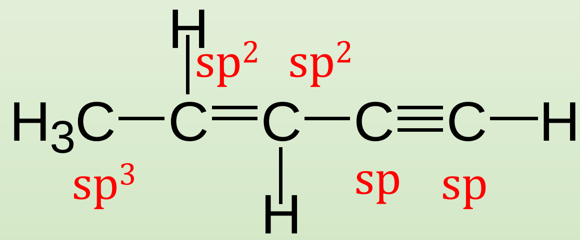
How many pi bonds and sigma bonds are in each of the following molecules? Describe the hybridization of each C atom.



(a)



(b)



(c)

(a) 4 sigma bonds

(b) 5 sigma bonds,
1 pi bond

(c) 10 sigma bonds,
3 pi bonds

Molecular Orbital Theory

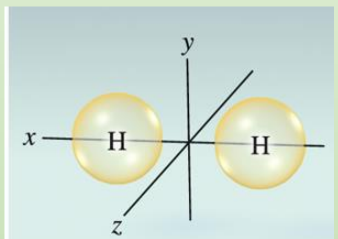
- As atoms approach one another, their atomic orbitals overlap and form molecular orbitals.
- Two atomic orbitals combine to form two molecular orbitals. (4 AO will give 4 MO etc.) (*Half the of MO are bonding and half will be antibonding*.)
- How the orbitals are combining depends on energy and orientation. (Wavefuntions - + and – regions)
- Molecular orbitals concentrated in regions between nuclei (center of orbital) are called **bonding orbitals.** They are obtained by adding atomic orbitals (e.g. ψ+ and ψ+).
- 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 (e.g. ψ+ and ψ-).

- (read more at: Chemwiki – UCDavis)

Molecular Orbital Theory

$$H + H \rightarrow H_2$$

$1s^1$ $1s^1$ $\sigma_{1s}{}^2$

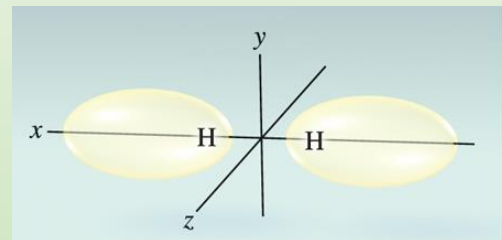


$1s$ $1s$

H atomic orbitals

difference

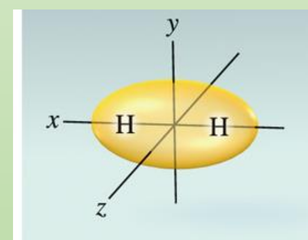
antibonding orbital



σ^*_{1s}

sum

bonding orbital



σ_{1s}

H_2 molecular orbitals

Key Points

- Molecular geometry
  - VSEPR model
- Molecular geometry and polarity
- 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