INTRODUCTION TO ENGG. CHEMISTRY

PART A:ATOMS TO MOLECULES TO MATERIALS FOR ENGINEERS

PART B: STRUCTURE & STEREOSTRUCTURE OF MOLECULES

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PART A: ATOMS TO MOLECULES TO MATERIALS FOR ENGINEERS

1. VALENCE BOND THEORY

a)HYBRIDIZATION

b) SIGMA & Pi BOND

2. MOLECULAR ORBITAL THEORY

To rationalize how the shapes of atomic orbitals are transformed into the orbitals occupied

in covalently bonded species,

we need the help of two bonding theories:

Valence Bond (VB) Theory

Molecular Orbital (MO) Theory

Valence Bond (VB) Theory,

The theory describes

- **the placement of electrons into bonding orbitals located around**
- **the individual atoms from which they originate.**

Molecular Orbital (MO) Theory

places all electrons from atoms involved into molecular orbitals spread out over the entire species.

This theory works well for excited species, and molecules like O_2.

VALENCE BOND THEORY [text]

Developed in 1927 by HEITLER and LONDON

For maximum electron density and overlapping *i.e.stable bond formation-*

i) The electrons should have opposite spins and

ii) The greater overlapping of the electron clouds.

VALENCE BOND THEORY [text]

P-2

Linus Pauling and J.C. Slater extended this theory:

a) Extent of overlapping of the electron wave functions determine the strength of a bond [maximum overlap=strongest bond]

b) Out of two orbitals of identical stability or energy the one with more *directionally concentrated* would form a stronger bond.

VALENCE BOND THEORY [text]

P-2

Linus Pauling and J.C. Slater extended this theory:

a) Extent of overlapping of the electron wave functions determine the strength of a bond

[maximum overlap=strongest bond]

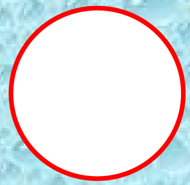
b) Out of two orbitals of identical stability or energy the one with more directionally concentrated would form a stronger bond.

c) s-spherically symmetrical

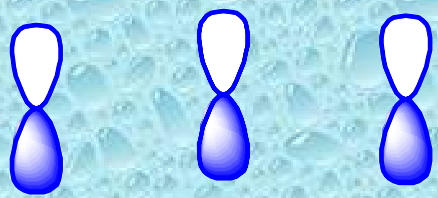
d) The direction of bond forming orbitals will decide the direction. e.g. Px – Px overlap will be in x direction.

e) When a bond is formed along x-direction, P_y , P_z orbitals wil remain as it is.

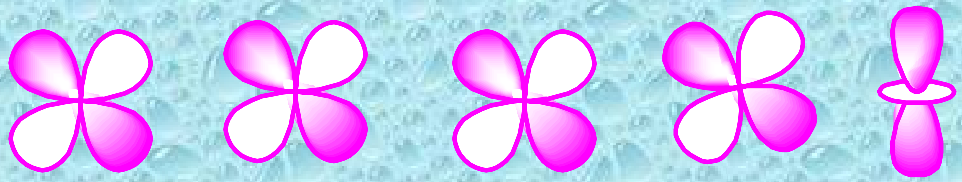
Orbital shapes, Individual (“isolated”) Atoms



all s orbitals



all p orbitals



d orbitals

COVALENT BOND FORMATION (Valence Bond Theory) P-2

- In order for a **covalent bond** to form between

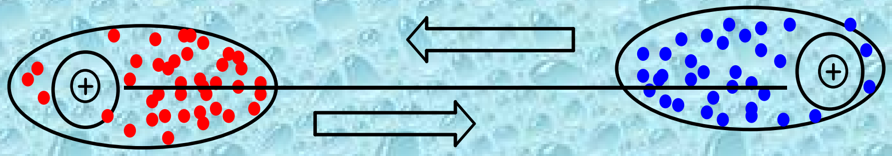
- **two atoms,** **overlap** must occur between the orbitals containing the **valence electrons.**

- **The** **best overlap** occurs when two orbitals are allowed to meet **"head on"** **in a straight line.**

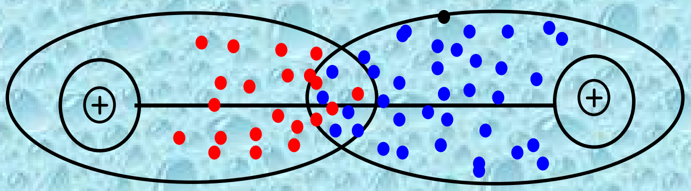
- When this occurs, the atomic orbitals merge to form **a single bonding orbital and a**

- **"single bond"** **is formed, called a** **sigma (σ) bond**.

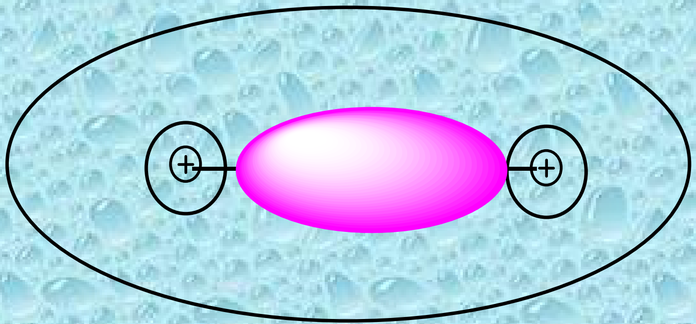
e.g. H_2 ,F_2



Dotted areas: representation of "electron cloud" for one electron



"Head-on Overlap"

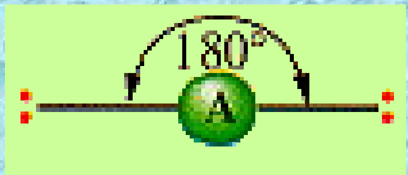


Sigma Bond: merged orbital, 2 e's

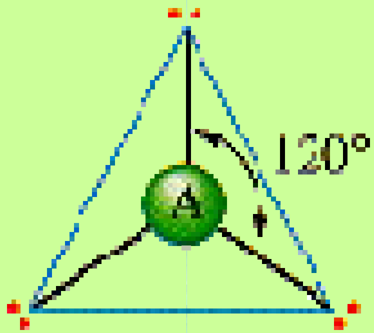
Valence Bond Theory:

- **H_2 forms due to overlap of two 1s orbitals.**
- **F_2** : **Electron densities from p-subshell** electrons overlap to produce a bond **in F_2.**
- **CH_4: The 1s orbital** of hydrogen must overlap with **the 2s and 2p orbitals of carbon.**

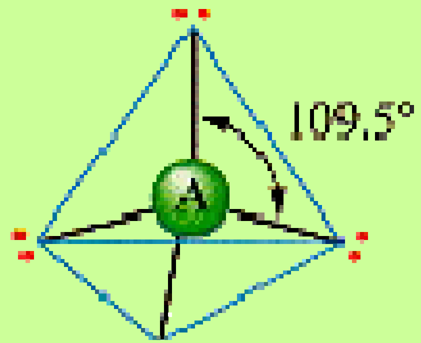
Effect of the number of electron pairs around the central atom



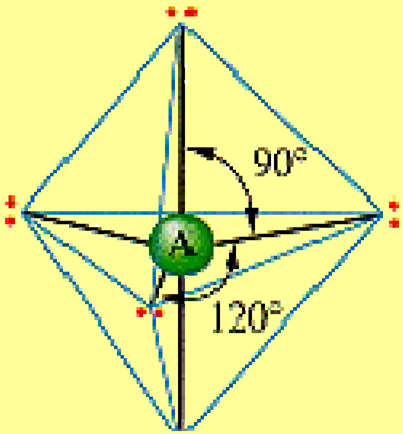
2 charge clouds, linear



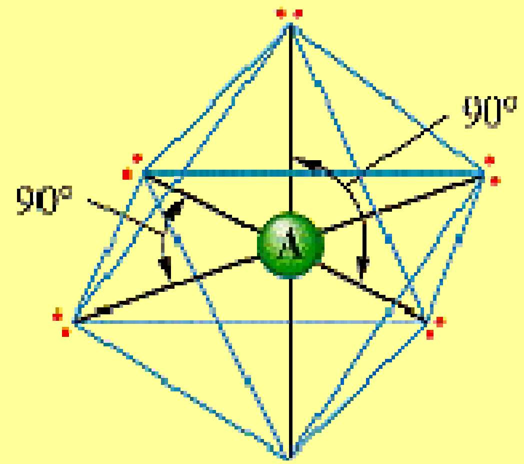
3 charge clouds, trigonal planar



4 charge clouds, tetrahedral



5 charge clouds, trigonal bipyramidal



6 charge clouds, Octahedral

LIMITATIONS of VALENCE BOND THEORY [text]

P-3

VBT doesn't explain :

a] the formation of coordinate bond

b] The formation of odd electron molecules e.g. H_2^+, NO, O_3 etc. where no electron pairing takes place.

c] the paramagnetic nature of Oxygen.

d] structure of molecules involving resonance and hybridization.

HYBRIDISATION

- Carbon in its GS and Excited state as per VBT

- Three out of four substitutes should be different which is not so. e.g. **CH_4 and CCl_4**
- To explain this the **concept of hybridization** came forward

HYBRIDISATION

- Hybridization is the phenomenon of **intermixing and redistribution** of two or more orbitals of slightly different energies to give
- a **new set of orbitals of equivalent energy and shape.**
- The new orbitals are called **Hybrids or Hybridized orbitals.**

HYBRIDISATION

- **Points to note:**

1) Hybridization is a theoretical concept.

- **Cant be detected spectroscopically.**
- Energy cannot be measured only can be calculated theoretically.

2) The concept is **not applicable to isolated atoms.**

3) **Shape of the molecules** are not due to the hybrids but for **lower energy.**

Characteristics of Hybridization

1) **The no. of hybrids orbitals = no. of Atomic Orbitals.**
2) Hybridization **requires energy** which is **recovered during bond formation.**
3) **All hybrid orbitals are equal in energy and shape.**
4) **All are directed in preferred direction.**
5) **More effective due to better overlapping.**

A.O.s are not symmetrical.

Characteristics of Hybridization

6) **More effective due to better overlapping. A.O.s are not symmetrical.**

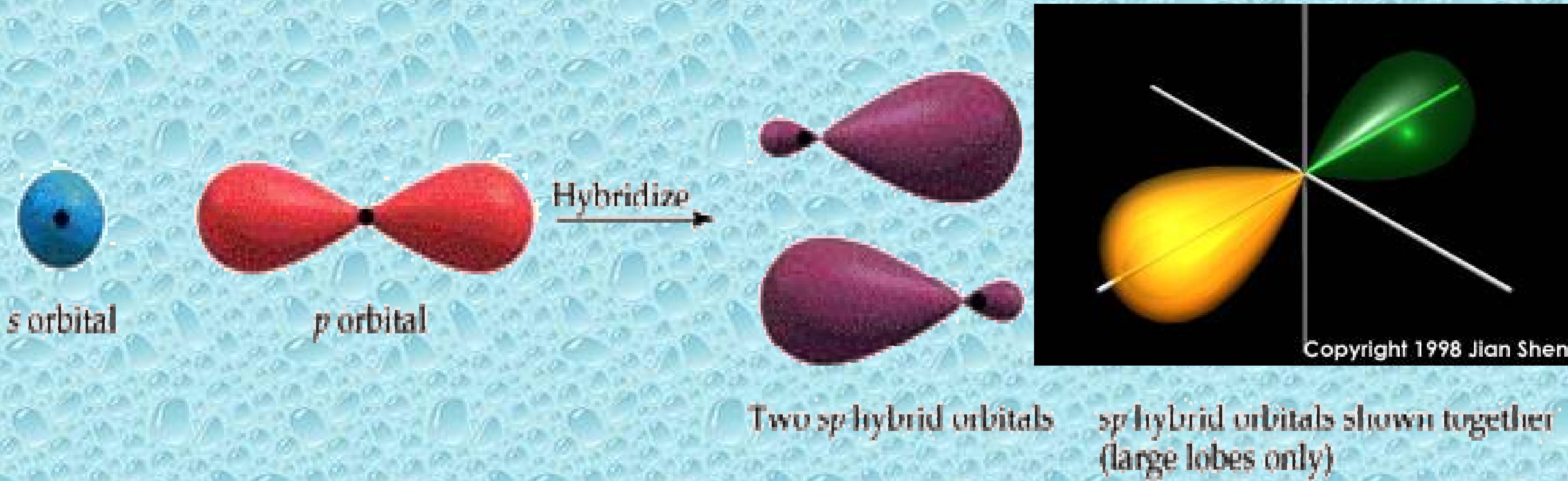
7) Due to **directional nature indicates the geometry of the molecule**

8) Like A.O. the **hybrid orbitals can accommodate maximum two electrons of opposite spins**

Formation of sp hybrid orbitals

The combination of an s orbital and a p orbital produces 2 new orbitals called sp orbitals.

2s



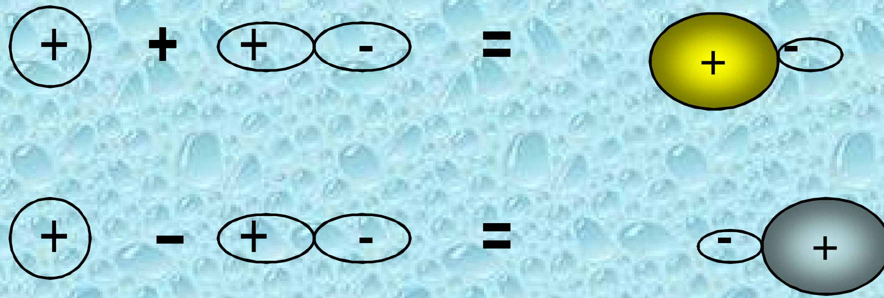
These new orbitals are called hybrid orbitals

The process is called hybridization

What this means is that both the s and one p orbital are involved in bonding to the connecting atoms

The *sp* Hybrid Orbitals

The sp hybrid orbitals: formation of two sp hybrid orbitals



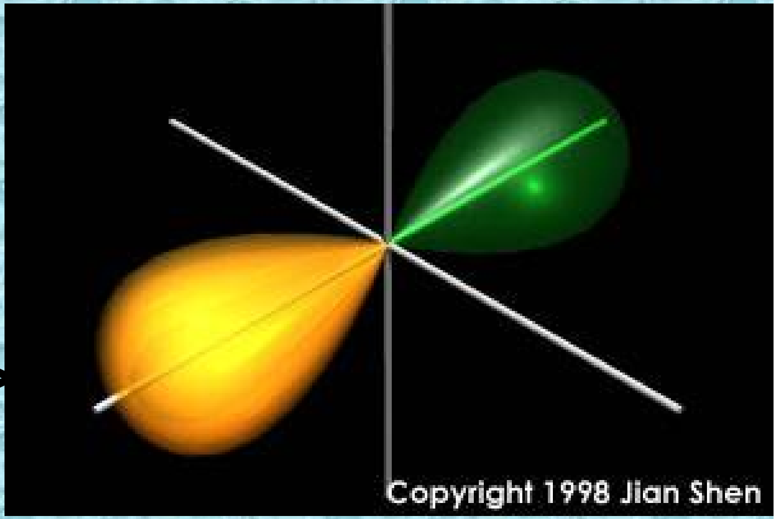
hybridization of s and *p* orbitals = 2 *sp* hybrid orbitals

E S ↑_ ↑_ __ __

G S ↑↓ __ __ __

Two states of Be

Two sp hybrid orbitlas =>



Bonds with *sp* Hybrid Orbitals

Formations of bonds in these molecules are discussed during the lecture. Be prepared to do the same by yourself.

Cl–Be–Cl H–C≡C–H H–C≡N : O=C=O

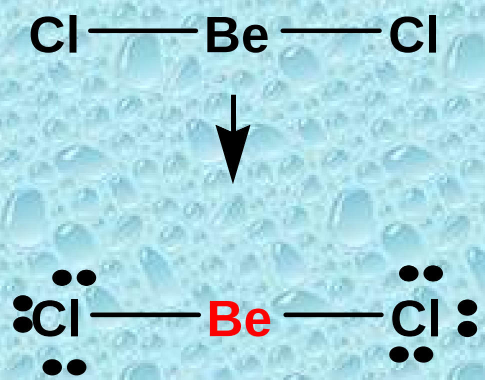
Double and triple bonds involve pi π bonding, and the the application of valence bond method to π bonds will be discussed.

You are expected to be able to draw pictures to show the π bonding.

BeF_2 , $BeCl_2$ [‘sp’]

“sp” Hybridization

$BeCl_2$

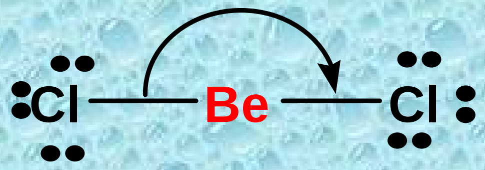


Be	2
2Cl	14

16 e's/2= 8 prs

Octet violator

Number of regions around CENTRAL ATOM: 2



shape : LINEAR
bond angles: 180^{o}

- H^1 He^2
- Li^3 Be^4 B^5

- Be^4 - $1s^2$, $2s^2$ (G.S.)
- Be^4 - $1s^2$, $2s^1$, $2p^1$ (Excited State)
- Make sp hybrid

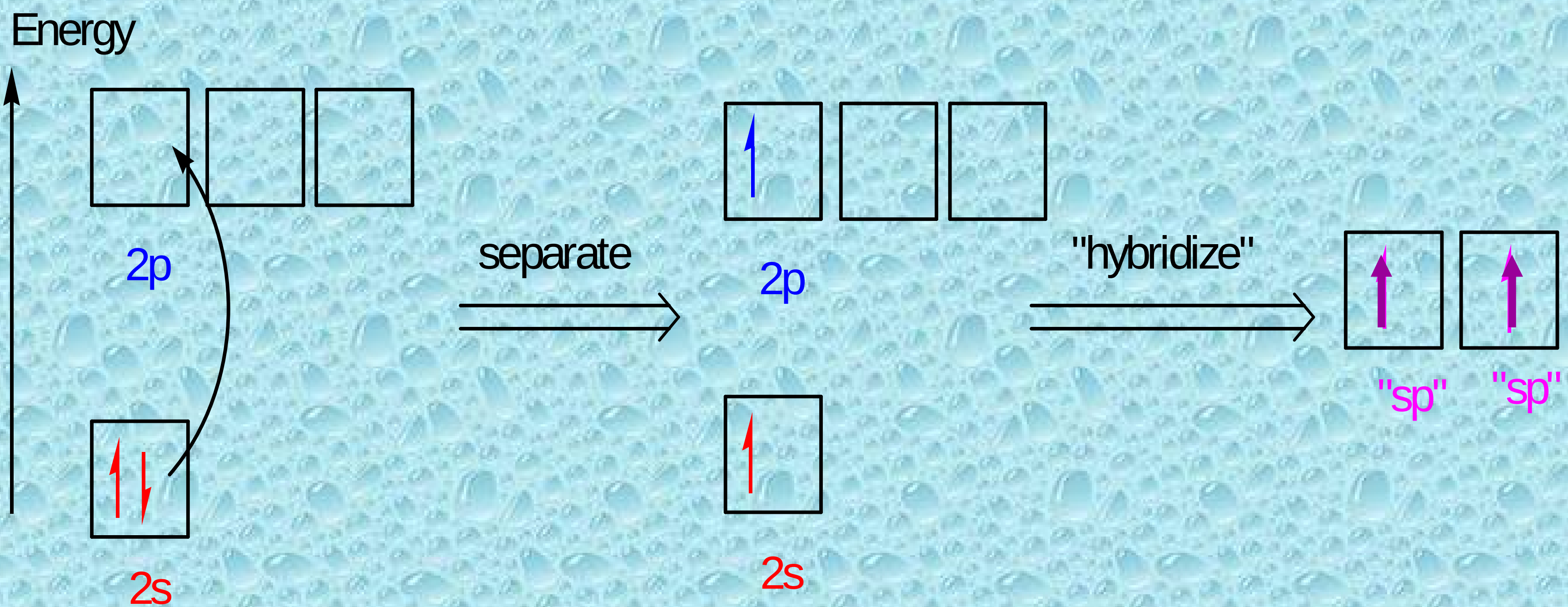
- **Chlorine atom, $1s^2$,$2s^2 2p^6$,$3s^2 3p^5$**

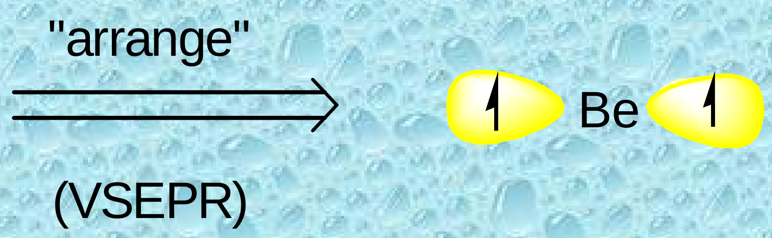
Hybridization of Be in $BeCl_2$

Valence e's

Hybrid sp orbitals:
1 part s, 1 part p

Atomic Be: $1s^2$ $2s^2$





Be is said to be "sp hybridized"

FORMATION OF $BeCl_2$:

- **Each Chlorine atom, $1s^22s^22p^63s^23p^5$, has one unshared electron in a p orbital.**

- **The half filled p orbital overlaps head-on with a**
- **half full hybrid sp orbital of the beryllium to form a sigma bond.**

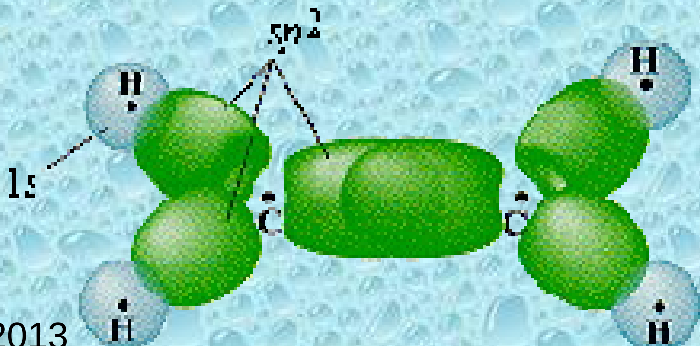
Multiple bonds

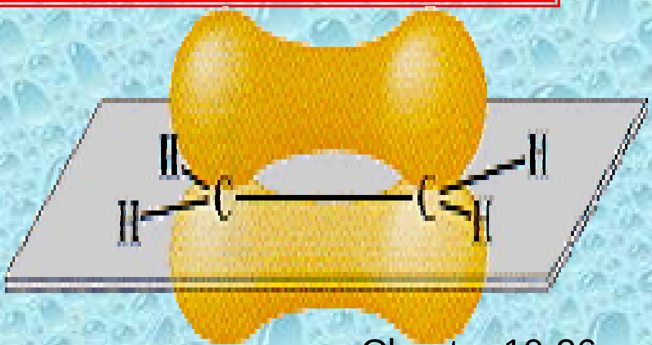
ETHYLENE C_2 H_4 [sp^2]

Ethylene:C_2H_4 planar with a trigonal geometry = sp^2 hybridization for each of the carbon atoms and they form σ bonds with hydrogen.

- Each carbon has 4 orbitals in its valence shell. This means **one of the p-orbitals for each C is not hybridized.**

- **Charge distribution resembling a cloud which is above and below the plane of the molecule and called a π –bond .**



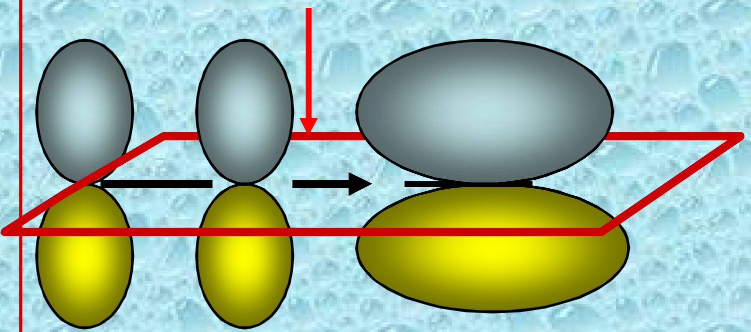


A π Bond

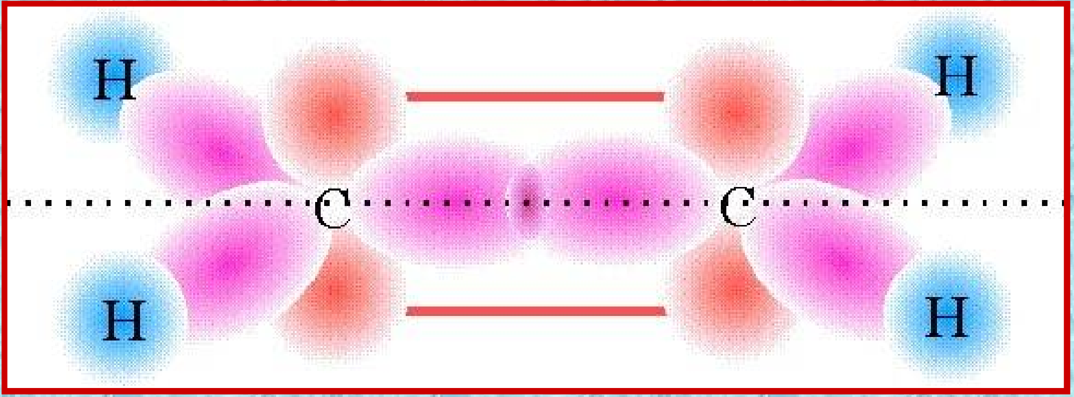
How are pi bonds formed?

Sigma (σ) bond is symmetric about axis.

Pi (π) electron distribution above and below axis with a nodal plane, on which probability of finding electron is zero; π bond is not as strong as sigma - less overlap.



Overlap of 2 2*p* orbitals for the formation of π bond

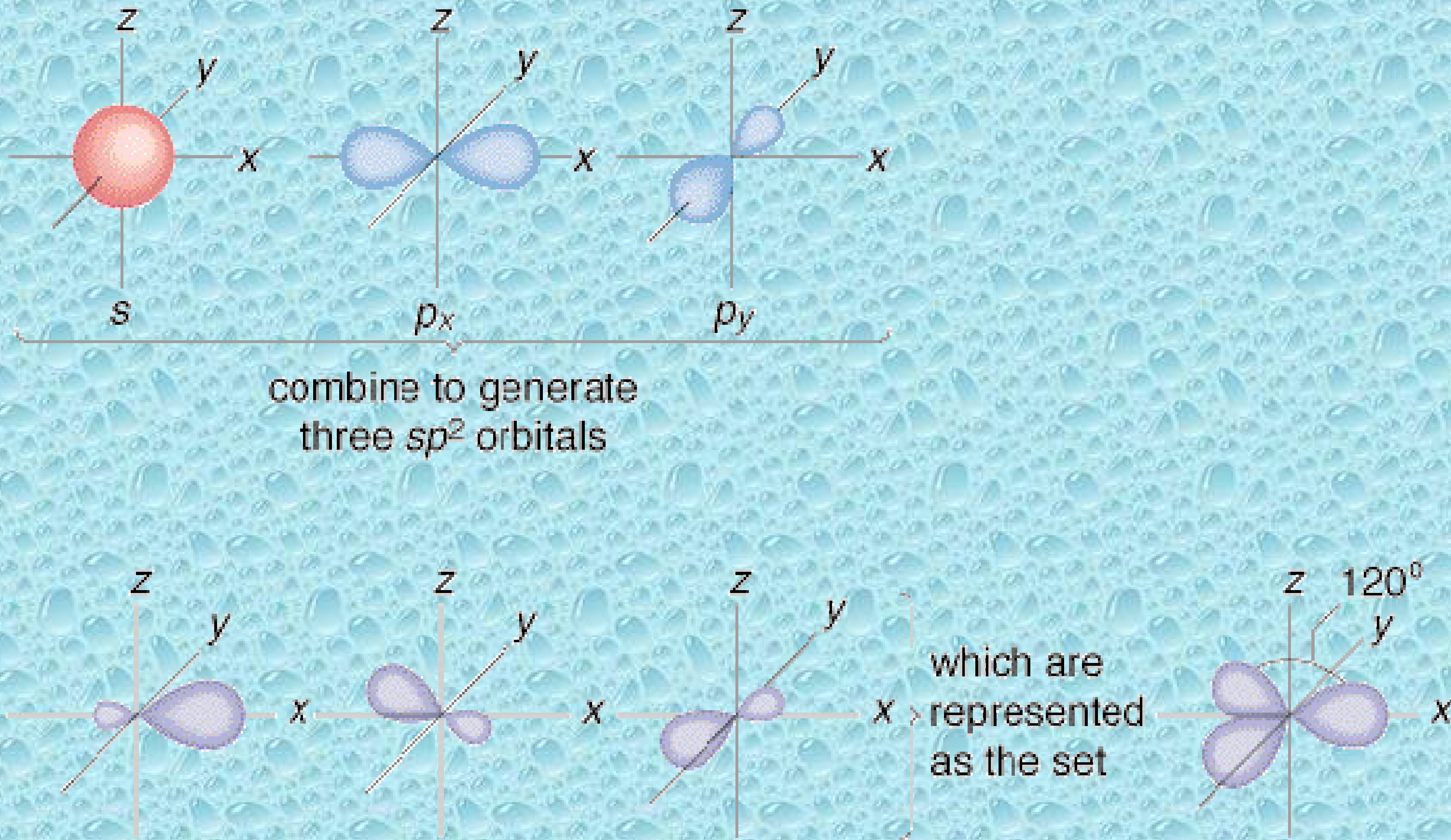


Bonding of C_2H_4

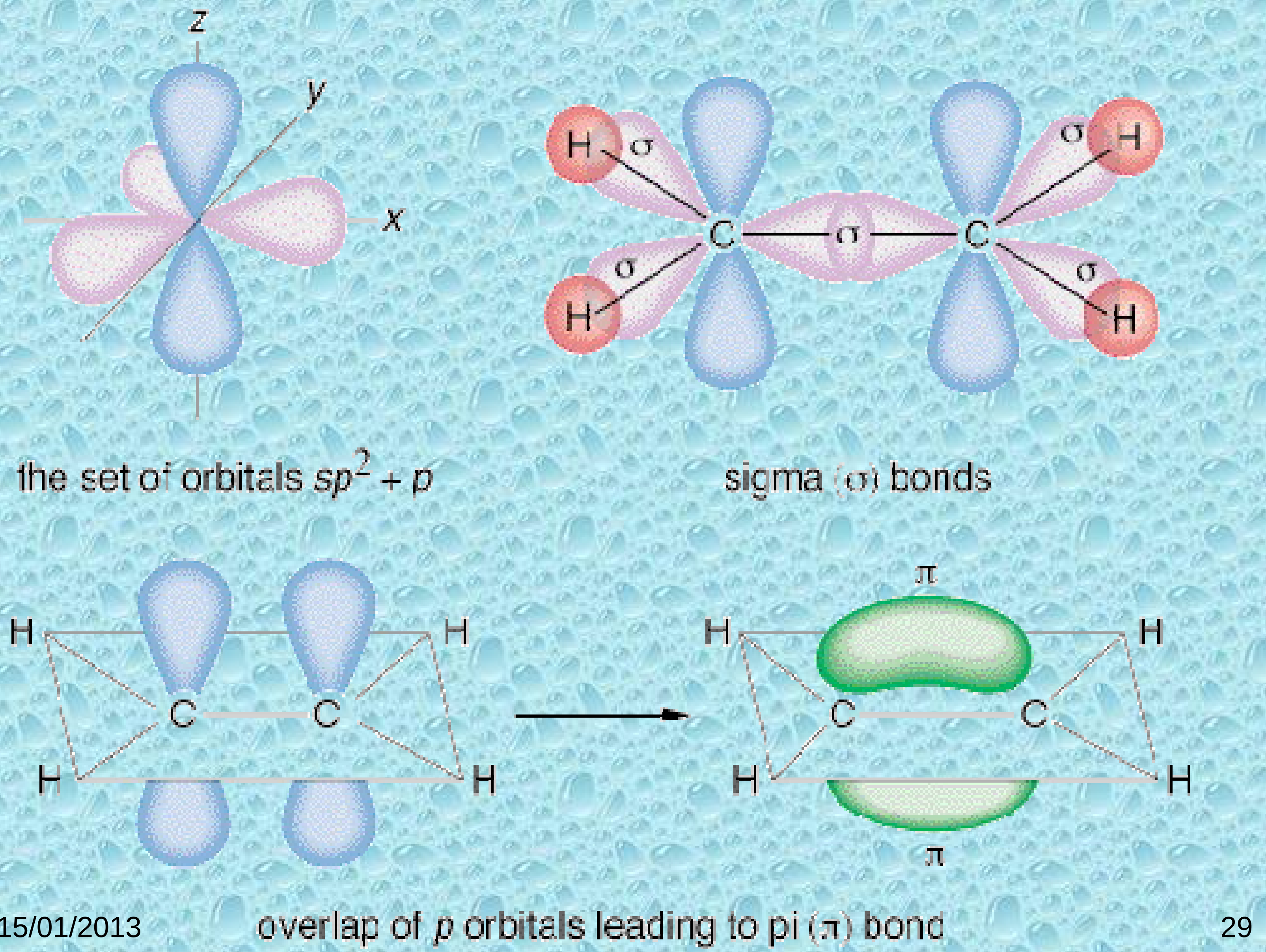
C
2s 2p 2p 2p
sp^2 sp^2 sp^2 2p

Formation of sp^2 hybrid orbitals

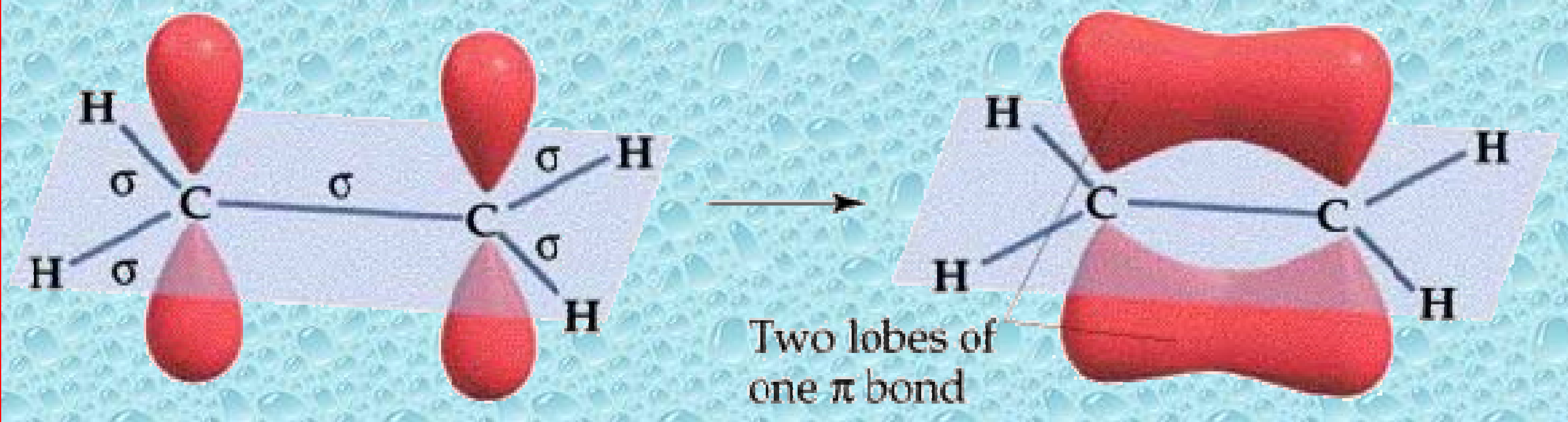
P-6



Example: $H_2C{=}CH_2$



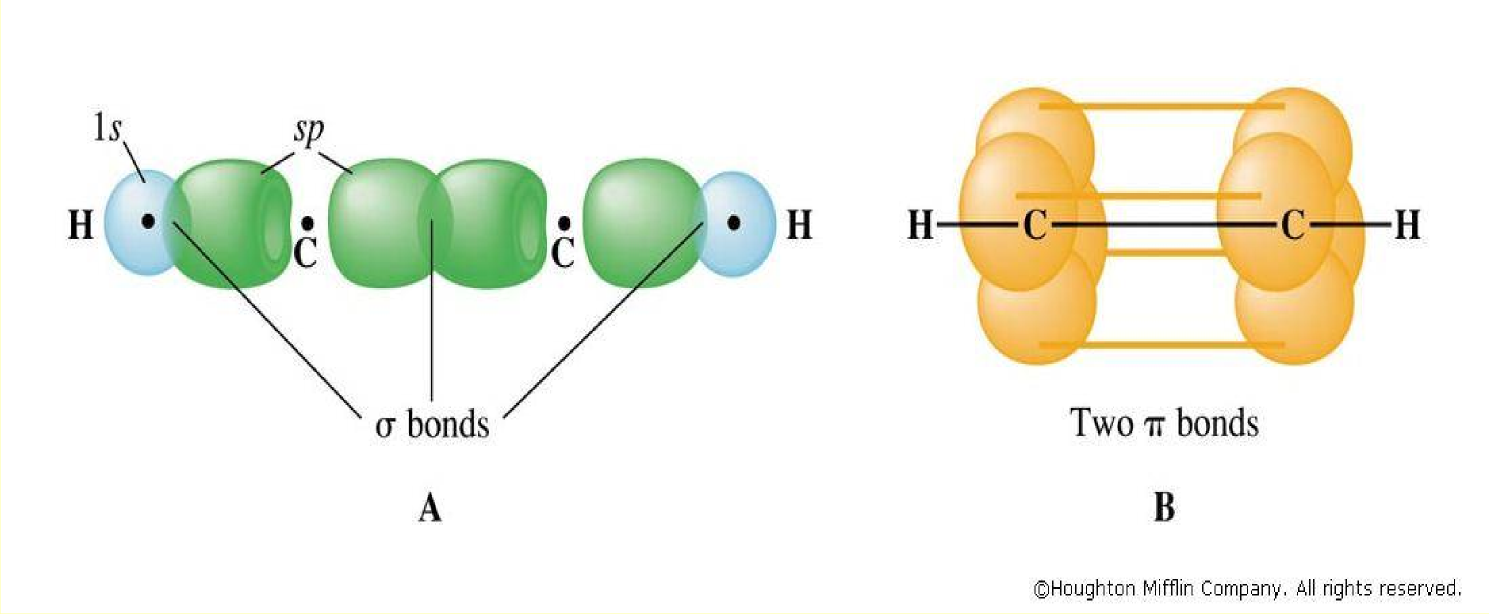
Example: $H_2C{=}CH_2$



Multiple bonds | **ACETYLENE C_2 H_2 ['sp']** | **P-5**

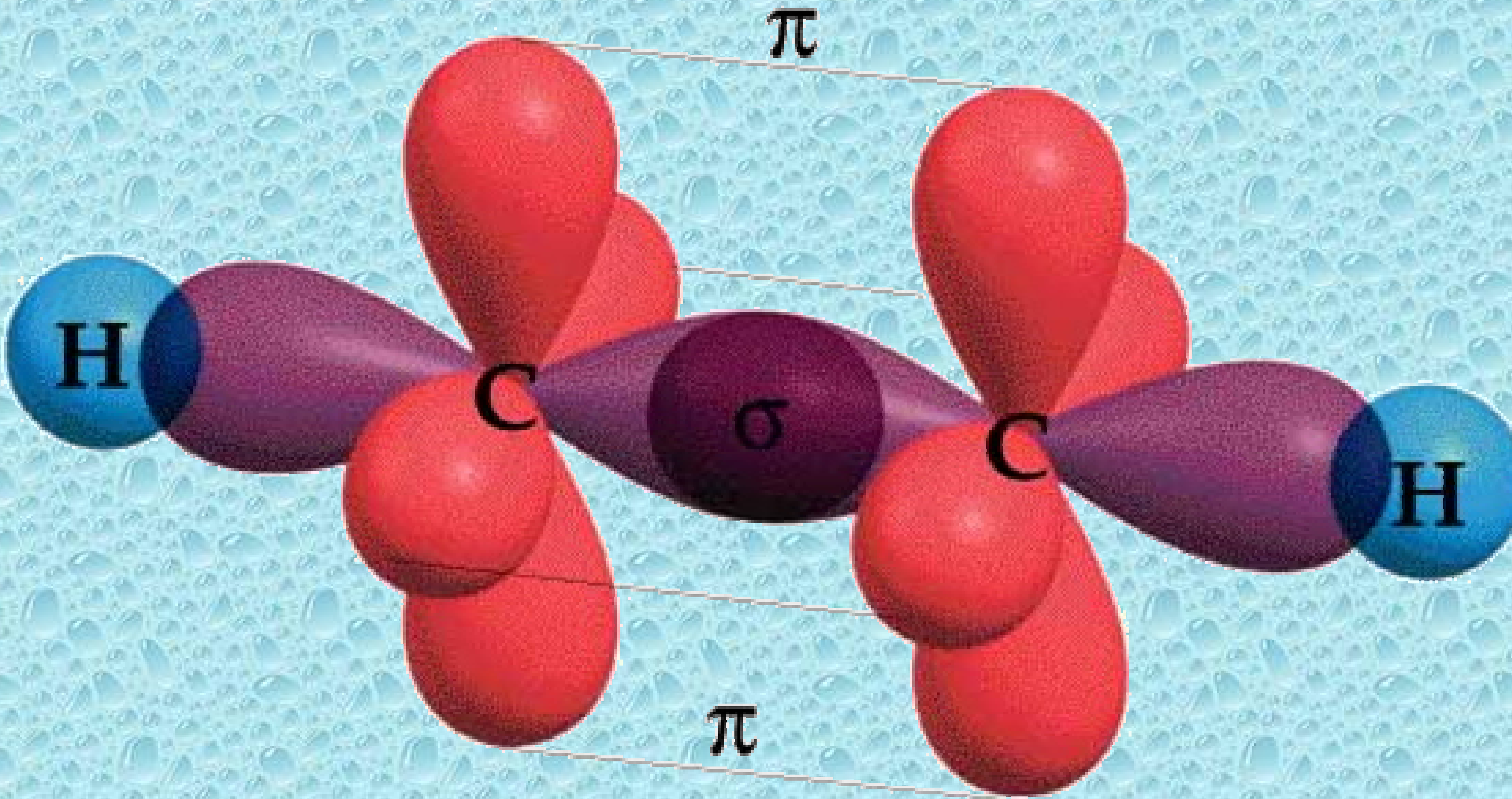
Overlap above and below makes rotation of carbon atoms difficult.

- **E.g. C_2H_2: sp (linear) hybridized. Leads to the existence of a σ bond as well as two π bonds.**

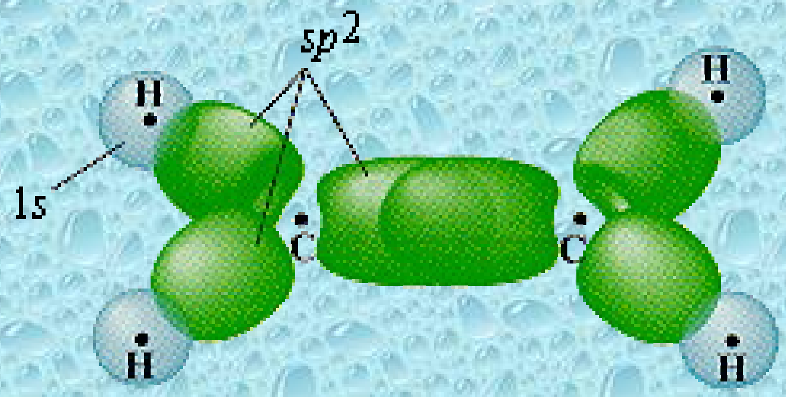


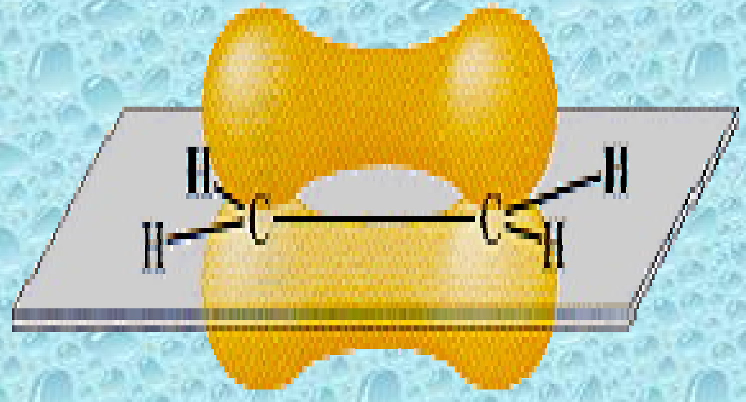
- **single bond is a σ bond,**
- **double bond is a σ bond and a π bond,**
- **triple bond is a σ bond and 2 π bonds.**

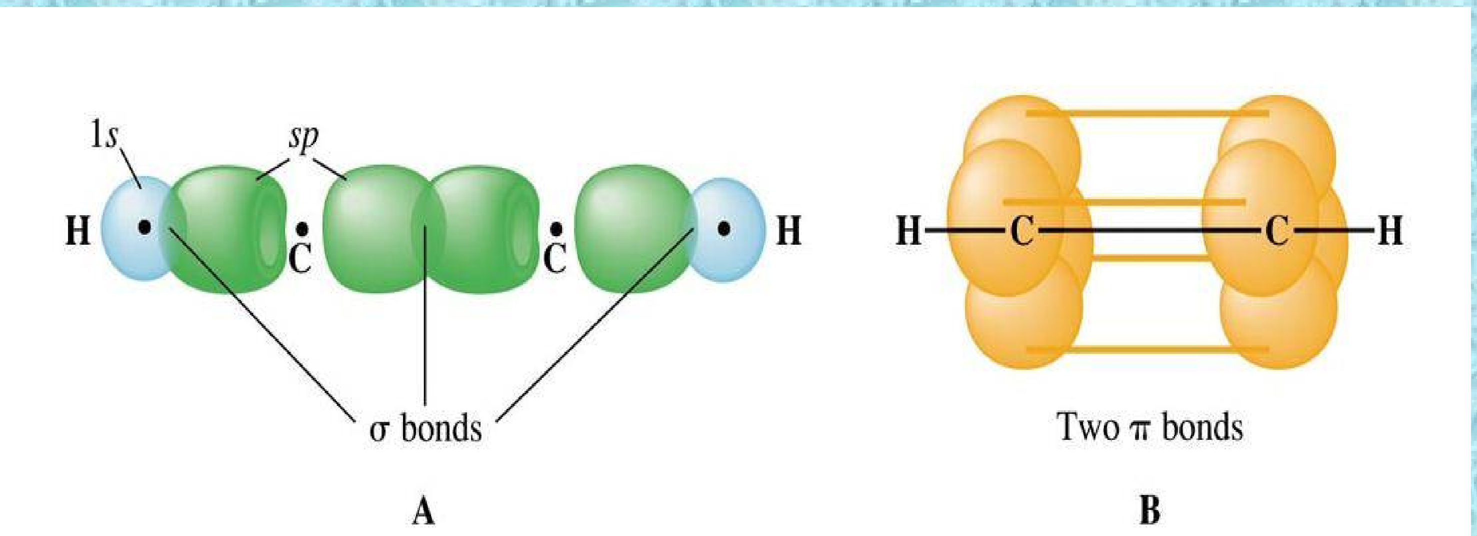
Example: HC≡CH



VBT: Multiple bonds

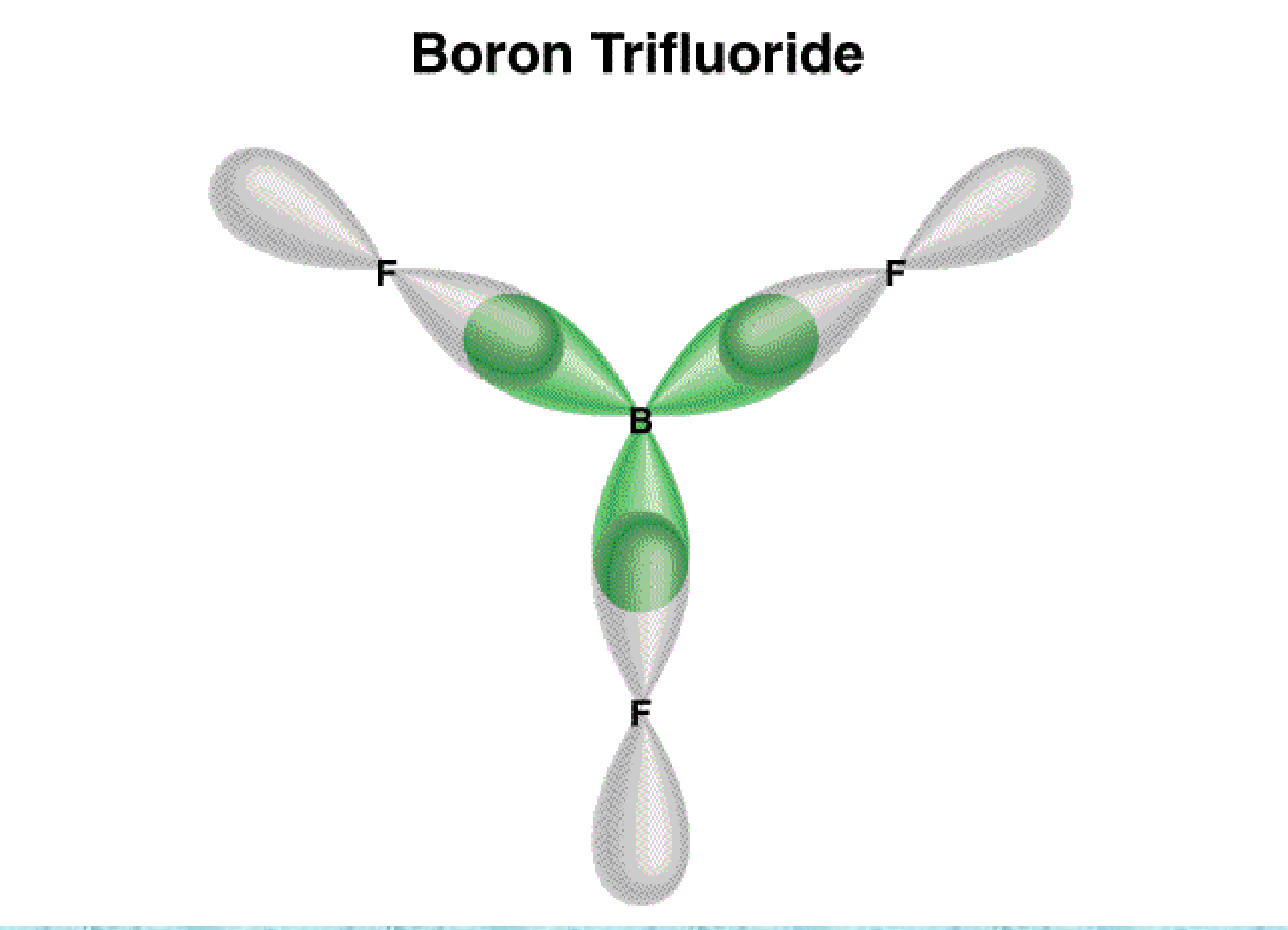






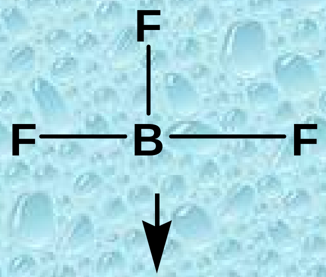
An example of using *sp*^{2} hybrid orbitals

BORON TRIFLORIDE BF_3 [***sp***^{2} **]**



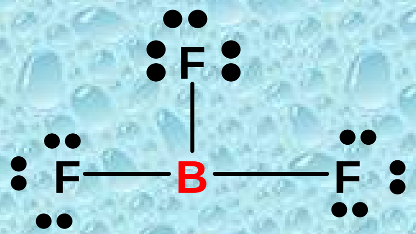
"sp^2" Hybridization

BF_3



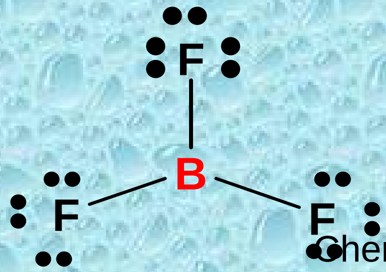
B 3
3F 21

24 e's/2= 12 prs



Octet violator

Number of regions around CENTRAL ATOM: 3



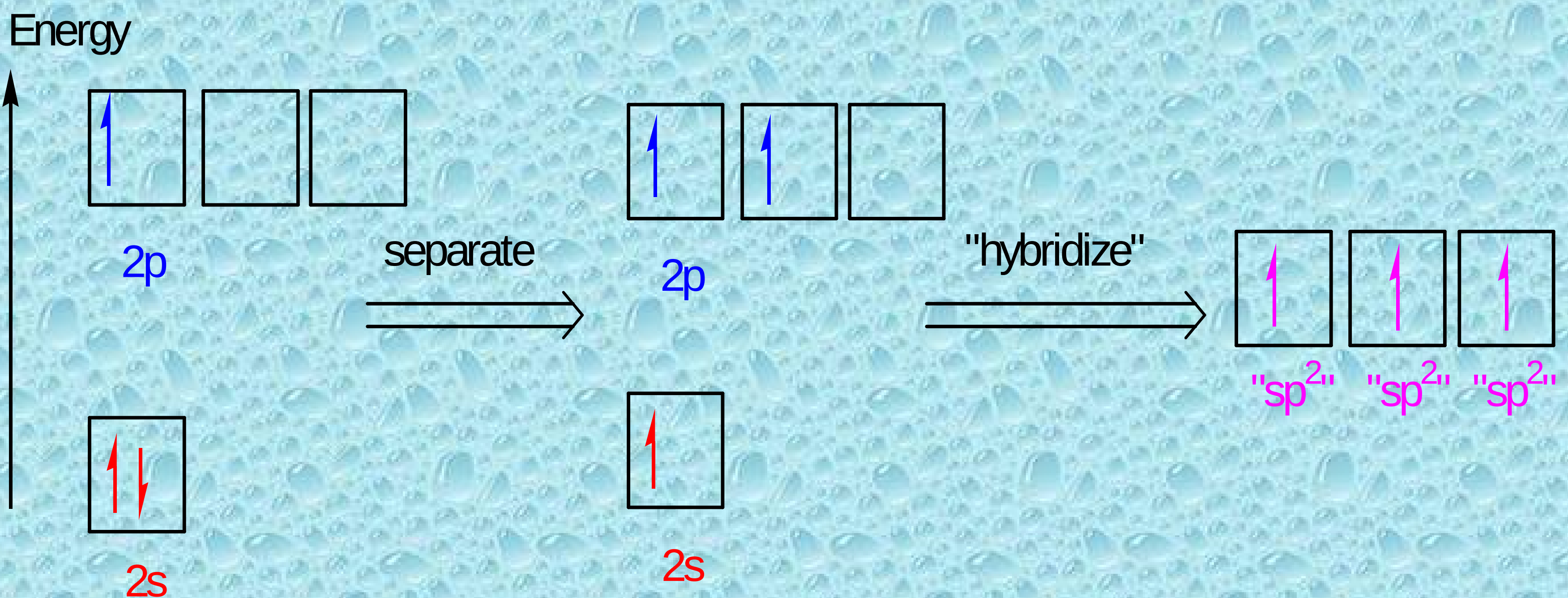
shape : TRIGONAL PLANAR
bond angles: 120^{o}

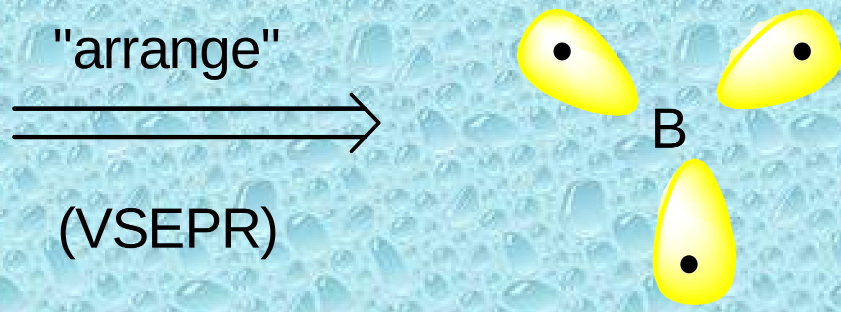
Hybridization of B in BF_3

Hybrid sp^2 orbitals:
1 part s, 2 parts p

Valence e's

Atomic B : $1s^2\ 2s^2\ 2p^1$





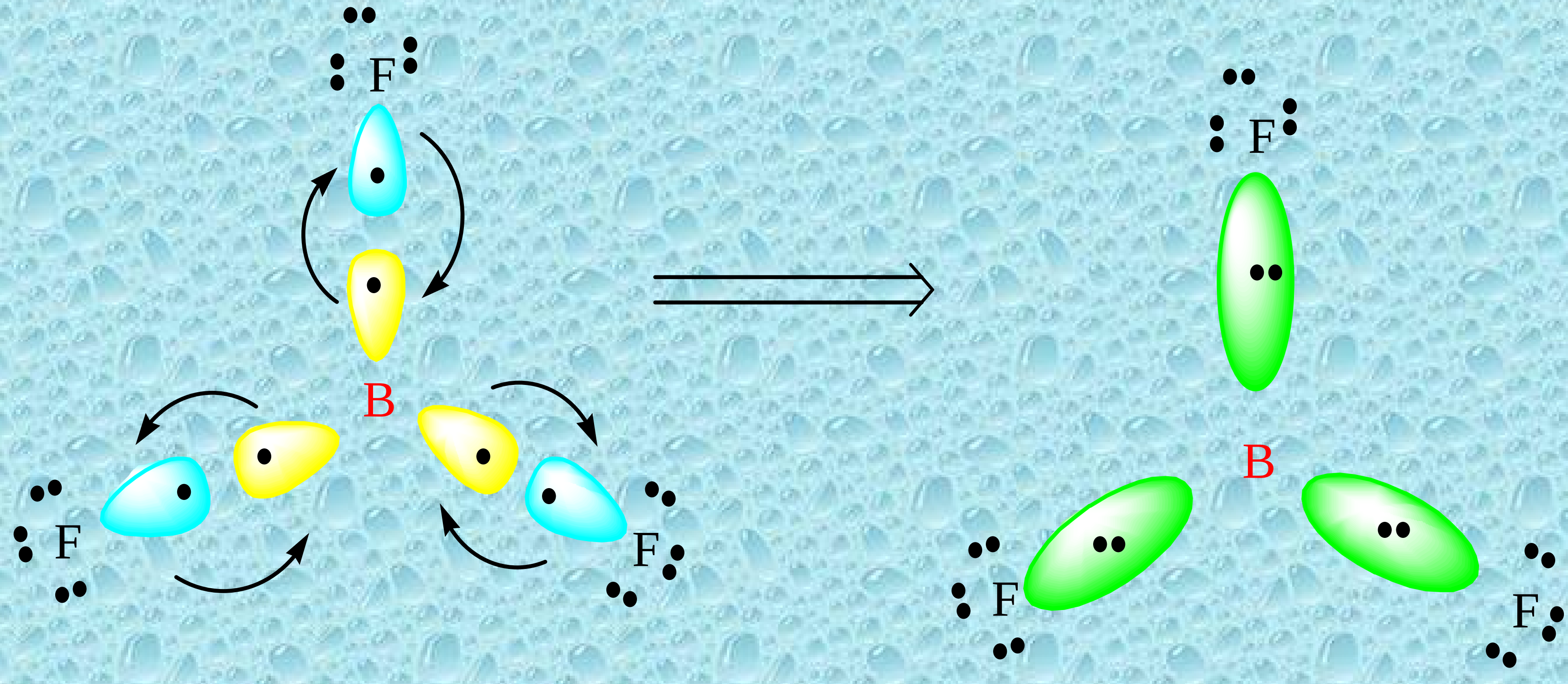
B is said to be "sp^2 hybridized"

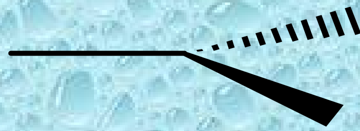
FORMATION OF BF_3:

- **Each fluorine atom, $1s^2 2s^2 2p^5$, has one unshared electron in a p orbital.**

- **The half filled p orbital overlaps head-on with a**
- **half full hybrid sp^2 orbital of the boron to form a sigma bond.**

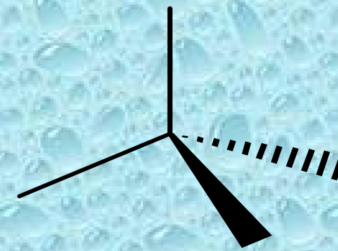
sp^2 hybridized, TRIGONAL PLANAR, 120^o bond angles





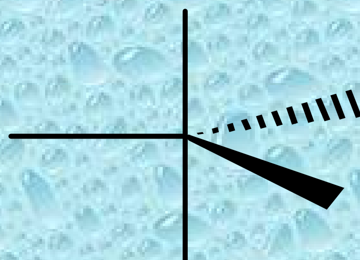
sp^2

trigonal



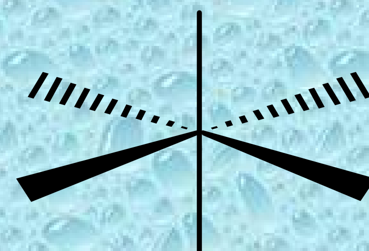
sp^3

tetrahedral



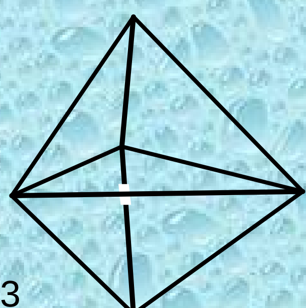
sp^3d

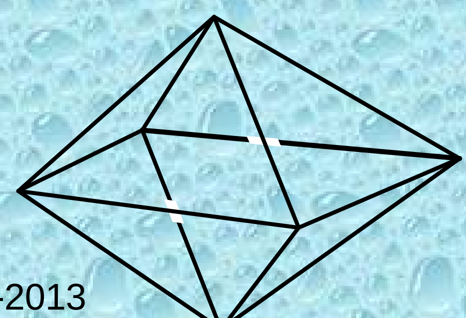
trigonal-bipyramidal



sp^3d^2

octahedral





CH_4 , CCl_4 [sp^3]

METHANE, CARBON TETRACHLORIDE

The sp^3 Hybridized Orbitals

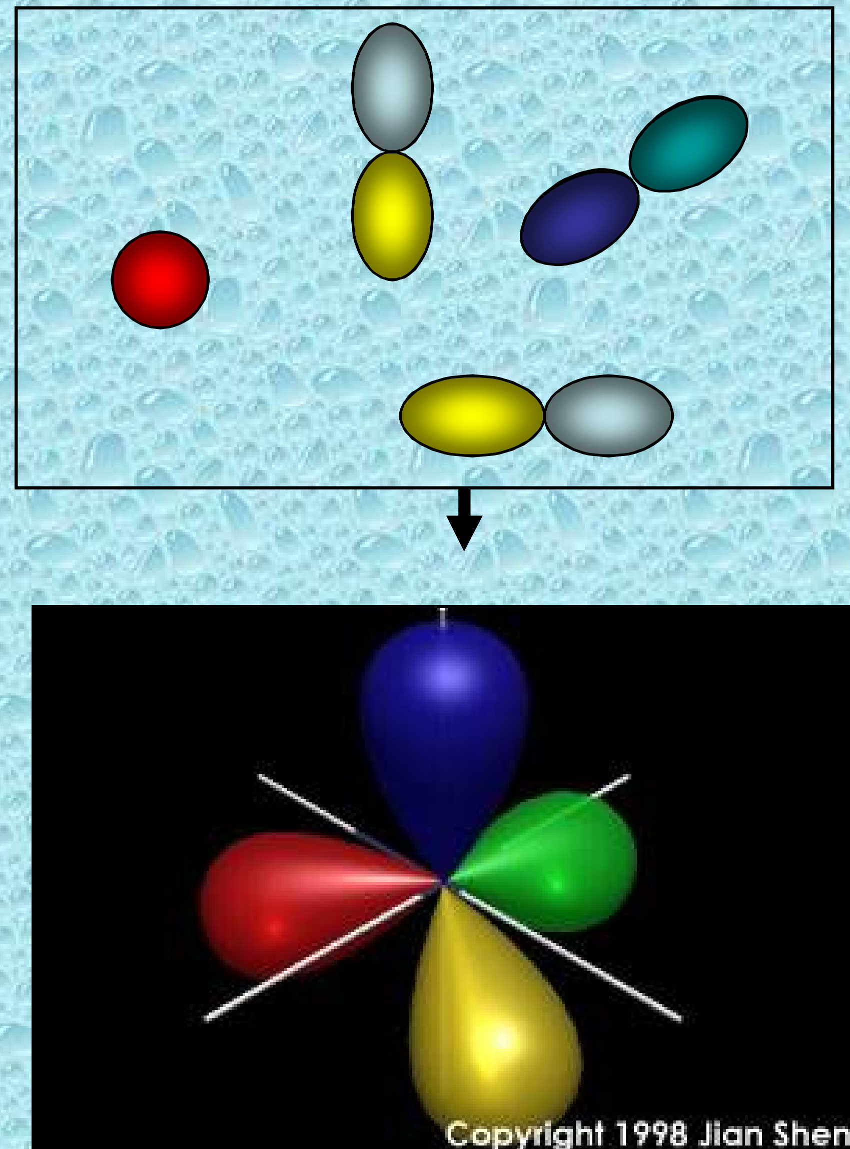
Ground state and excited state electronic configuration of C

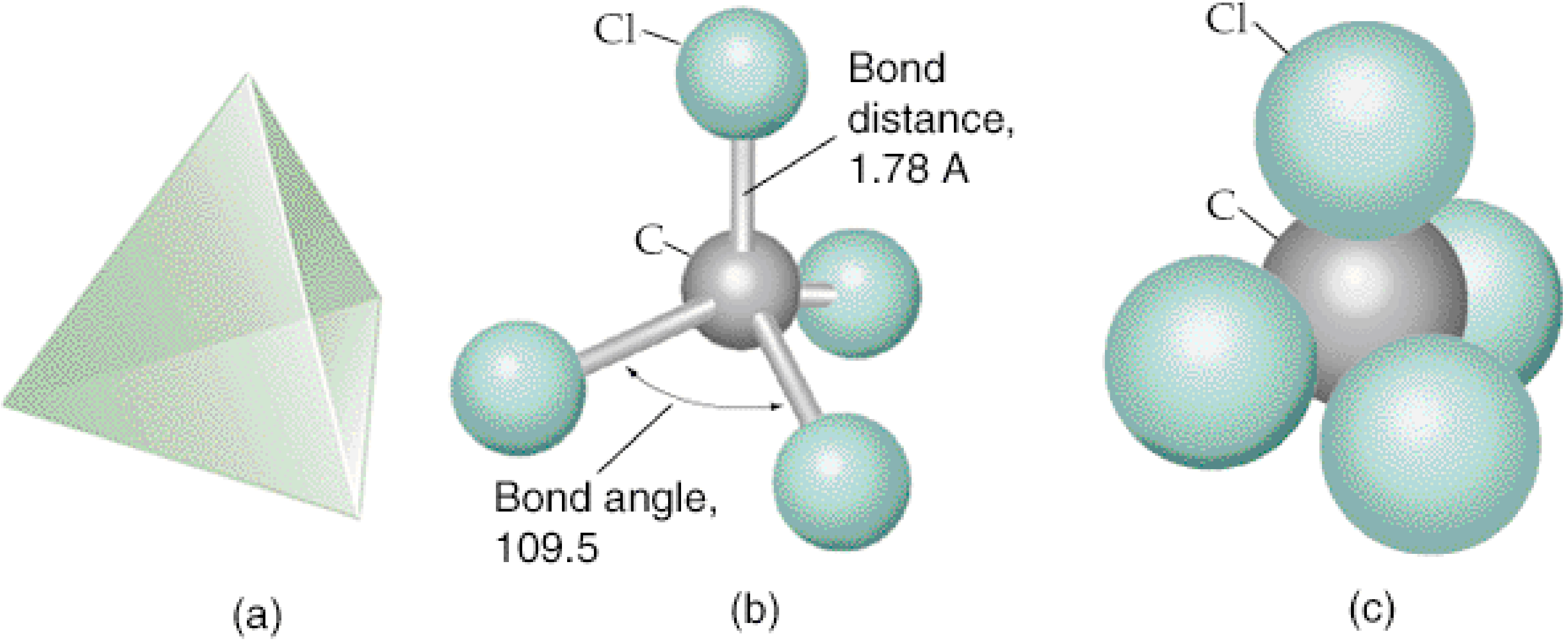
↑_ ↑_ ↑_ ↑_

↑↓ ↑_ ↑_ __

The hybridization of a *s* and three *p* orbitals led to **4 sp^3 hybrid orbitals** for bonding.

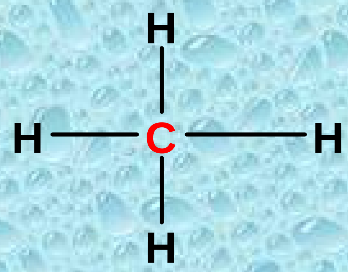
Compounds involving sp^3 hybrid orbitals: **CF_4, CH_4, :NH_3, H_2O::, SiO_4^{4-}, SO_4^{2-}, ClO_4^-, etc**




Cl
Bond
distance,
1.78 A
C
Bond angle,
109.5
Cl
C
(a)
(b)
(c)

"sp^3" Hybridization 4 region species

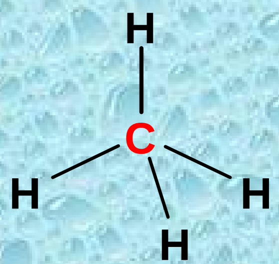
CH_4



C 4
4H 4

8
8 e's /2 = 4 pr

Number of regions around CENTRAL ATOM: 4



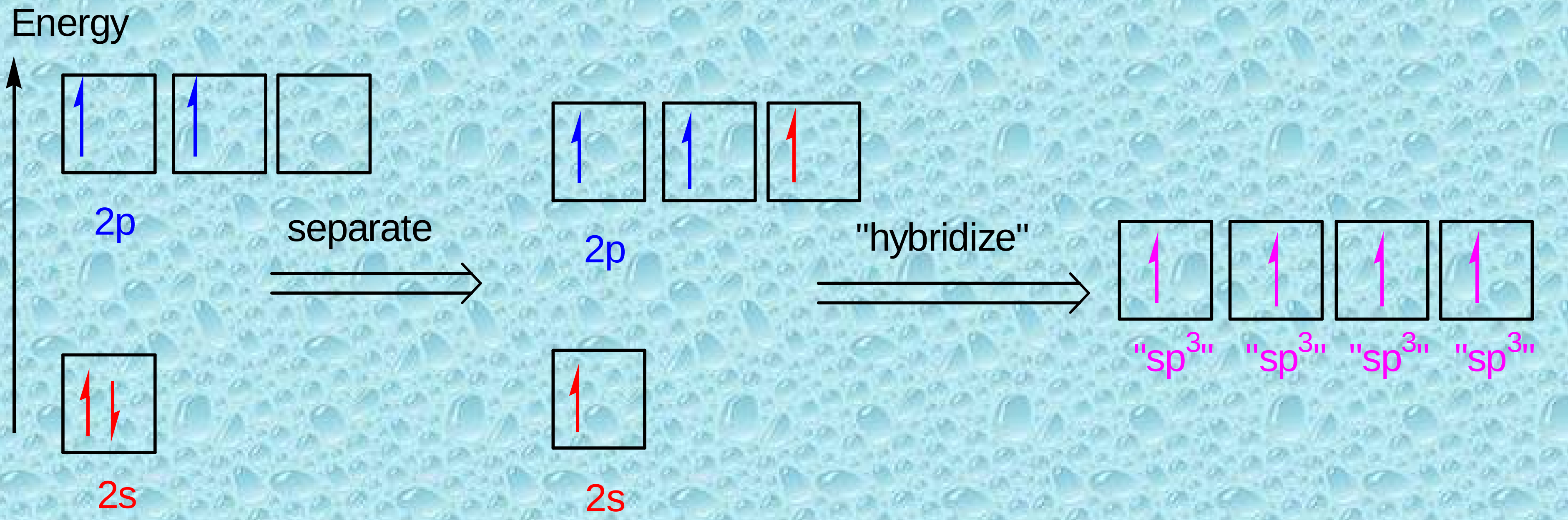
shape : TETRAHEDRAL
bond angles: 109.5^o

Hybridization of C in CH_4

Valence e's

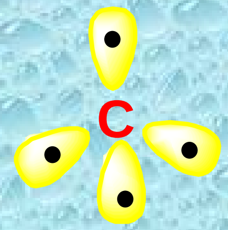
Hybrid sp^3 orbitals: 1 part s, 3 parts p

Atomic C : $1s^2\ 2s^2\ 2p^2$



"arrange"

(VSEPR)



C is said to be "sp^3 hybridized"

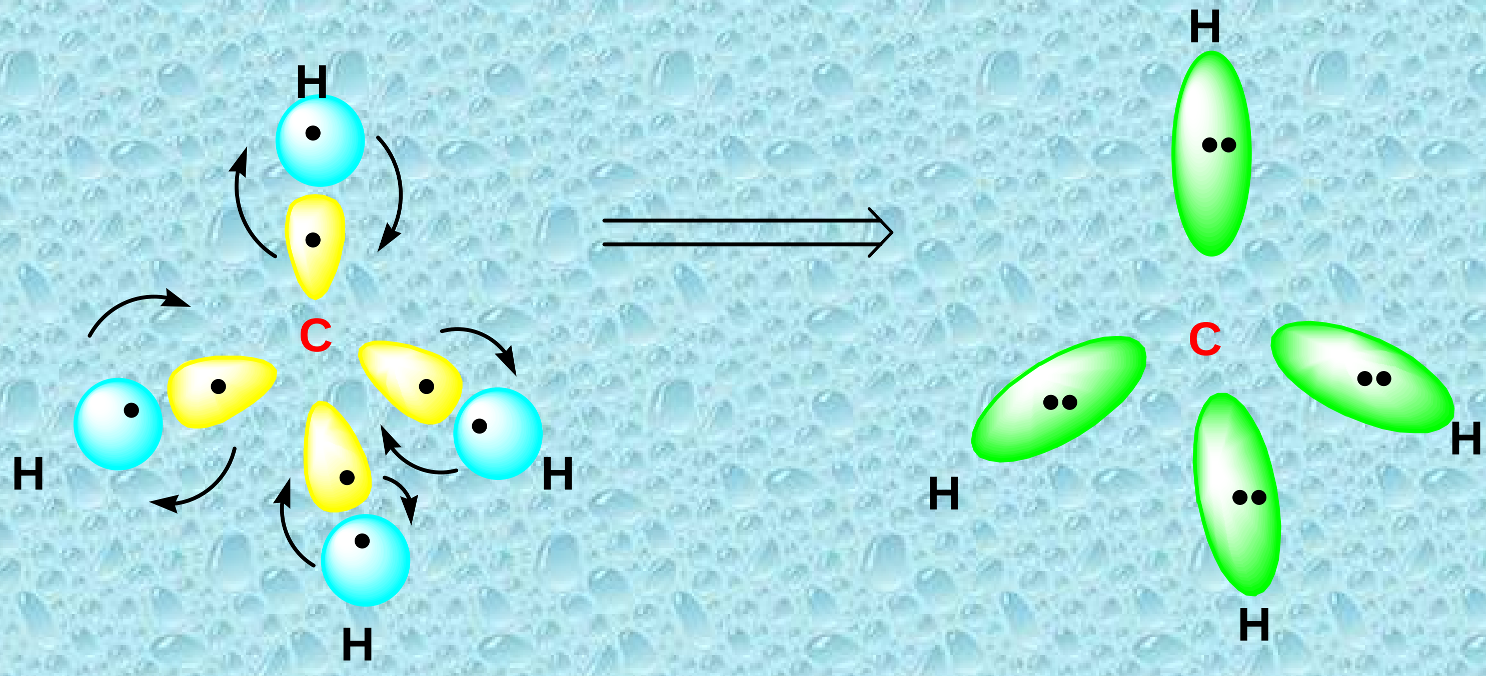
FORMATION OF CH_4:

- **Each hydrogen atom, $1s^1$, has one unshared electron in an s orbital.**
- **The half filled s orbital overlaps head-on with a half full hybrid sp^3 orbital**

of the carbon to form a sigma bond.

sp^3 P-7

sp^3 hybridized, TETRAHEDRAL, 109.5^o bond angles



NH_3 , H_2O [sp^3]
AMMONIA, WATER

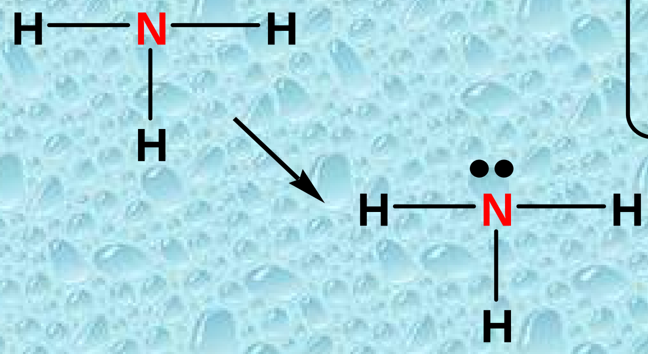
Unshared Pairs, Double or Triple Bonds

Unshared pairs occupy a hybridized orbital the same as bonded pairs:
See the example of NH_3 that follows.

Double and triple bonds are formed from electrons left behind and unused in p orbitals.
Since all multiple bonds are formed on top of sigma bonds, the
hybridization of the single (σ) bonds determine

the hybridization and shape of the molecule...

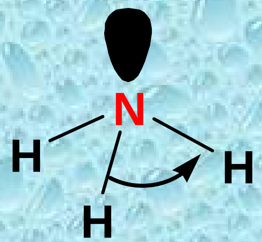
NH_3



N	5
3H	3

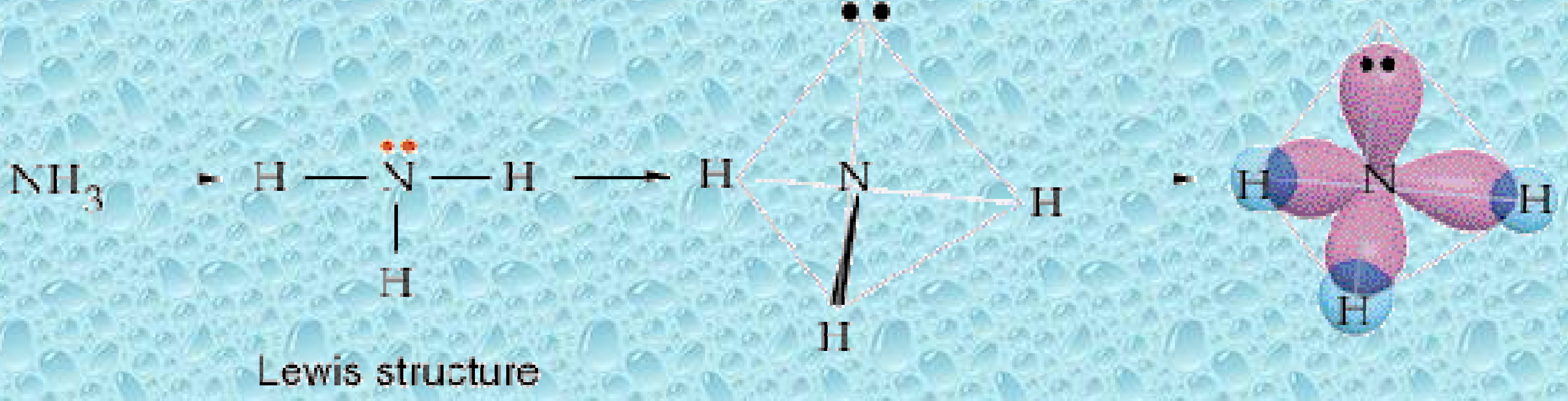
8e's/2=4 prs

Number of regions around CENTRAL ATOM: 4



shape : TETRAHEDRAL
bond angles: < 109.5^o

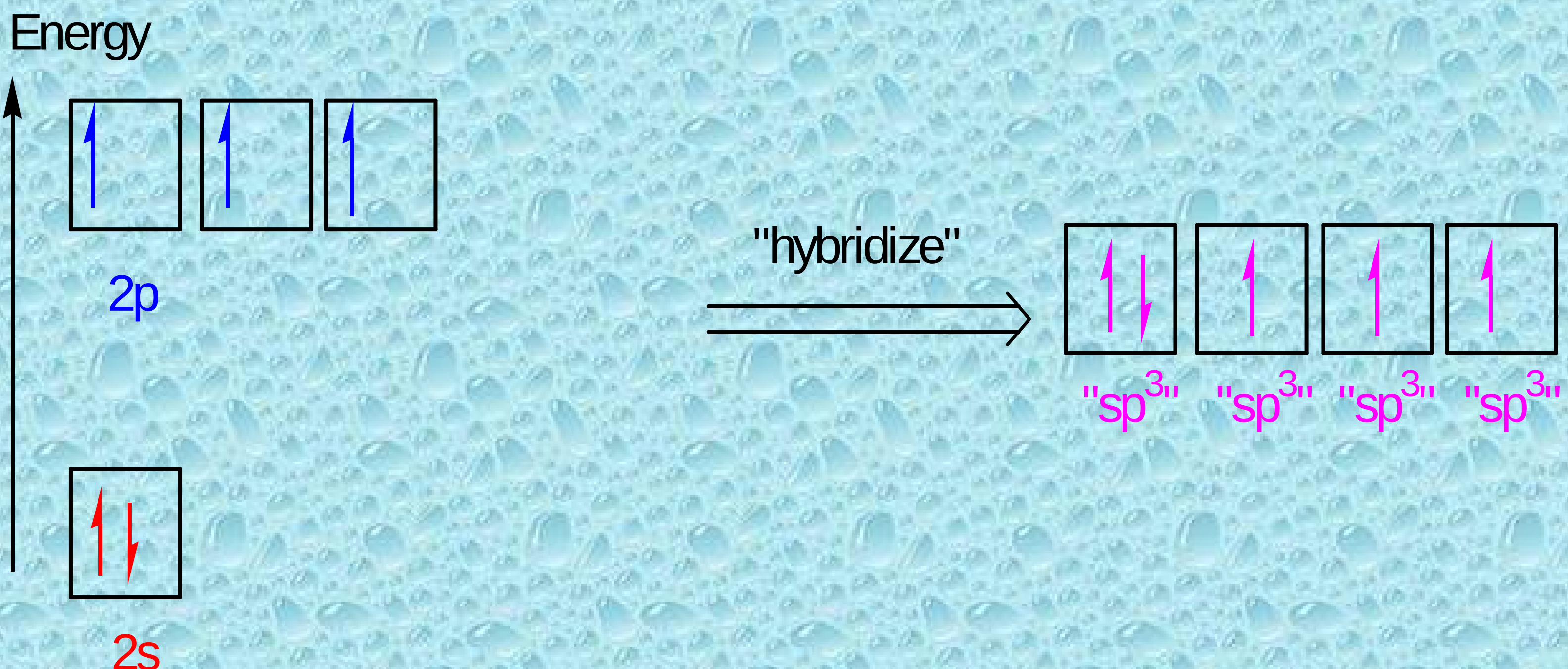
Hybrid orbitals can be used to explain bonding and molecular geometry



Hybridization of N in NH_3

Valence e's

Atomic N: $1s^2$ $2s^2$ $2p^3$



"arrange"

(VSEPR)

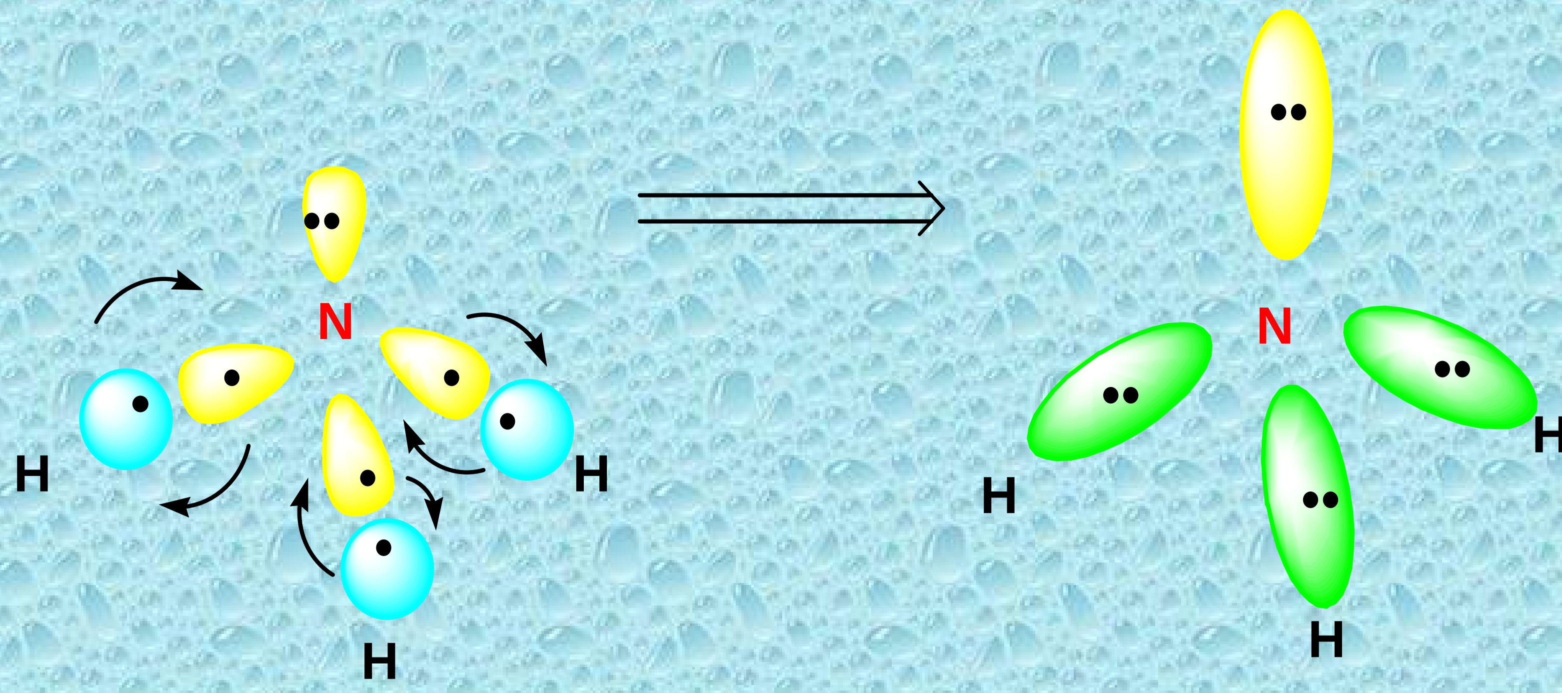
N is said to be "sp^3 hybridized"

FORMATION OF NH_3:

Each hydrogen atom, $1s^1$, has one unshared electron in an s orbital.

The half filled s orbital of hydrogen overlaps head-on with a half full hybrid sp^3 orbital of the nitrogen to form a sigma bond.

sp^3 hybridized, TETRAHEDRAL,
~107° bond angles



H_2O Do Yourself…….

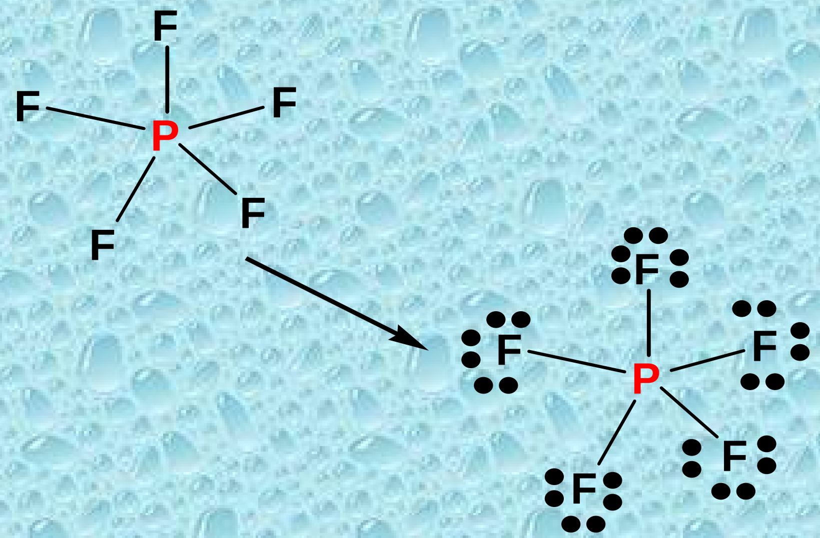
PCl_5 , PF_5, [***sp*^3^d**]

Phosphorus Pentachloride

Phosphorus Pentafloride

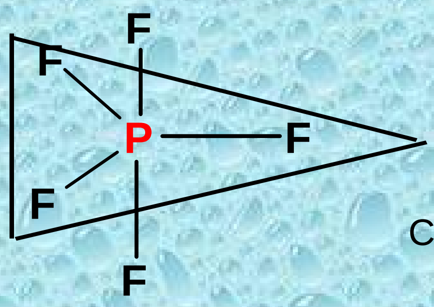
"sp^3d" Hybridization:

PF_5



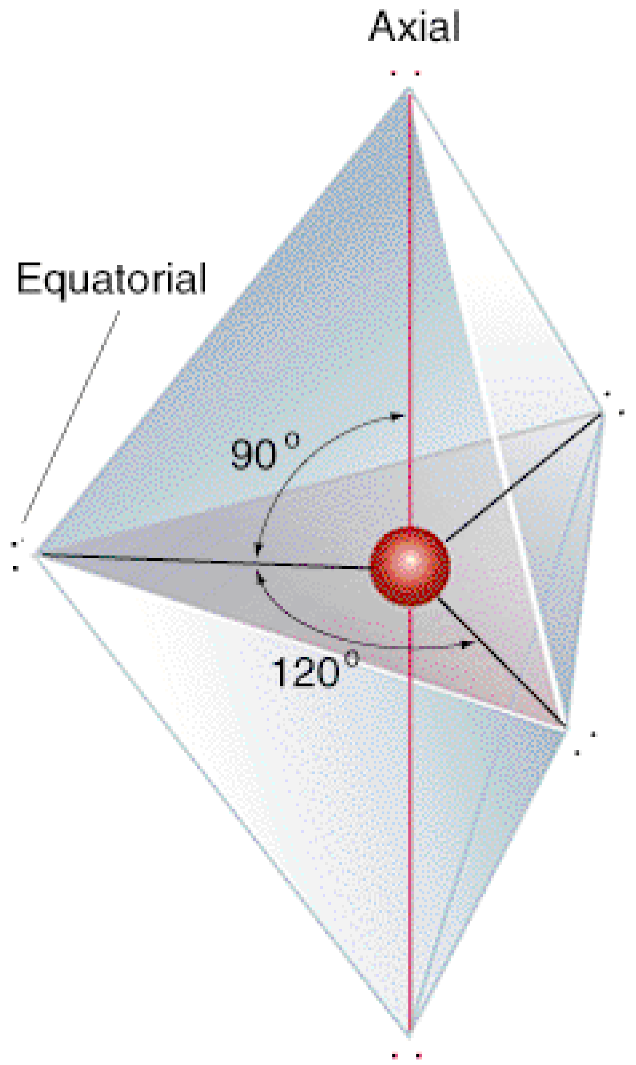
Trigonal Bipyramidal

Number of regions around CENTRAL ATOM: 5



shape : TRIGONAL BIPYRAMIDAL
bond angles: 90, 120, 180^o

Trigonal Bipyramidal



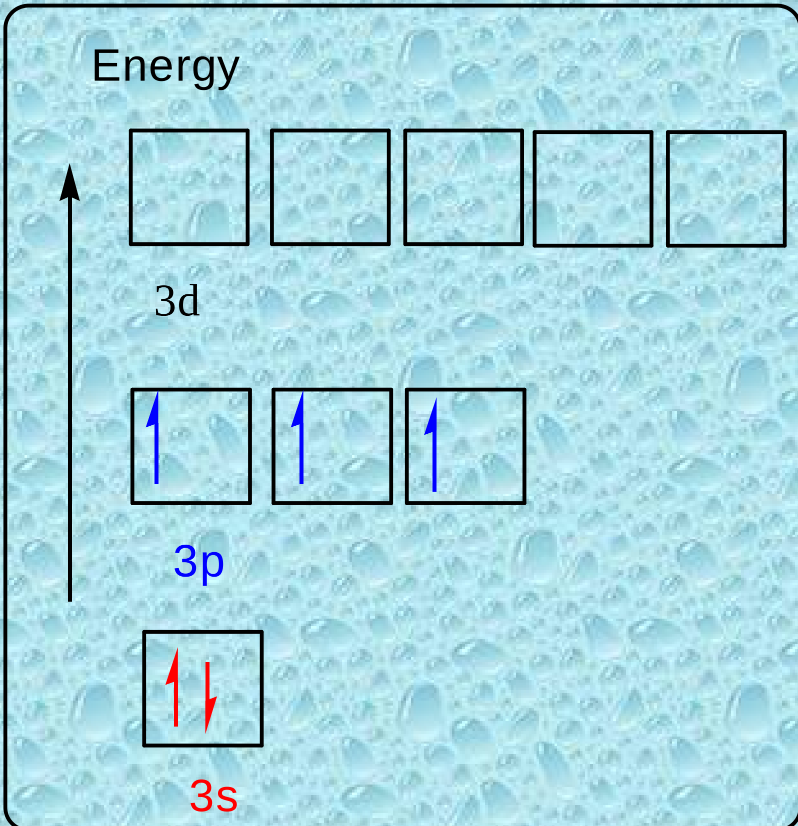
P^{15}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

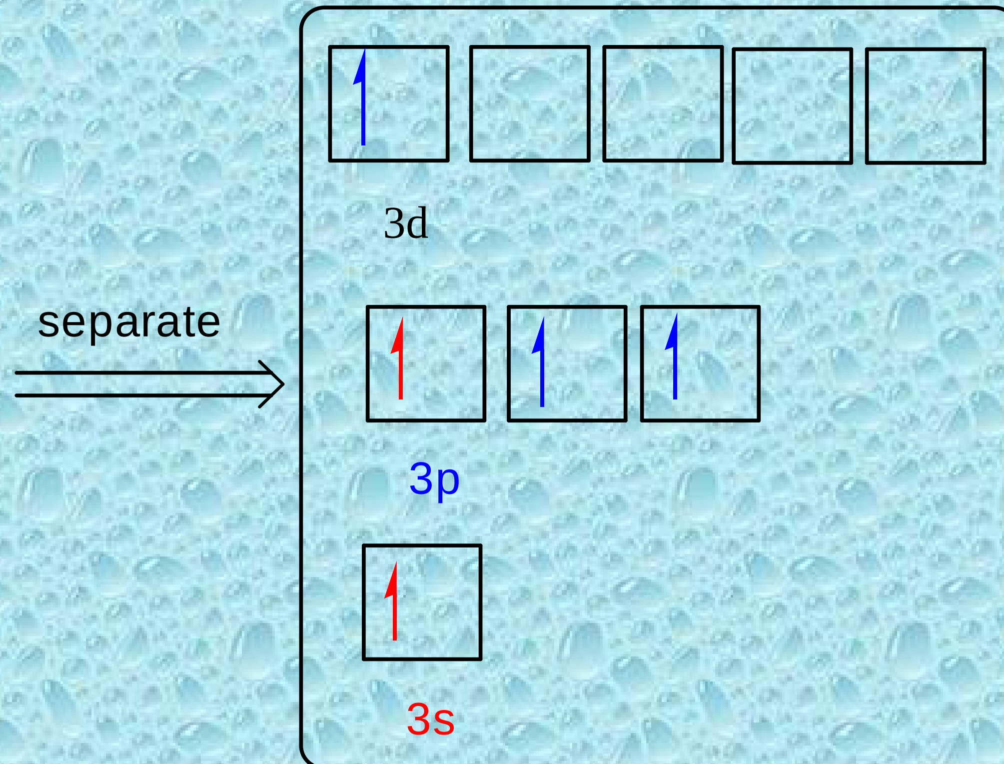
sp3d

P-10

P^{15} --- $1s^2, 2s^2, 2p^6$, $\mathbf{3s^1, 3p^3, 3d^1}$

Hybridization of P in PF_5

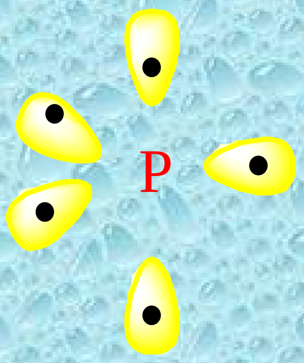




"arrange"

⟹

(VSEPR)



P is said to be "sp^3d hybridized"

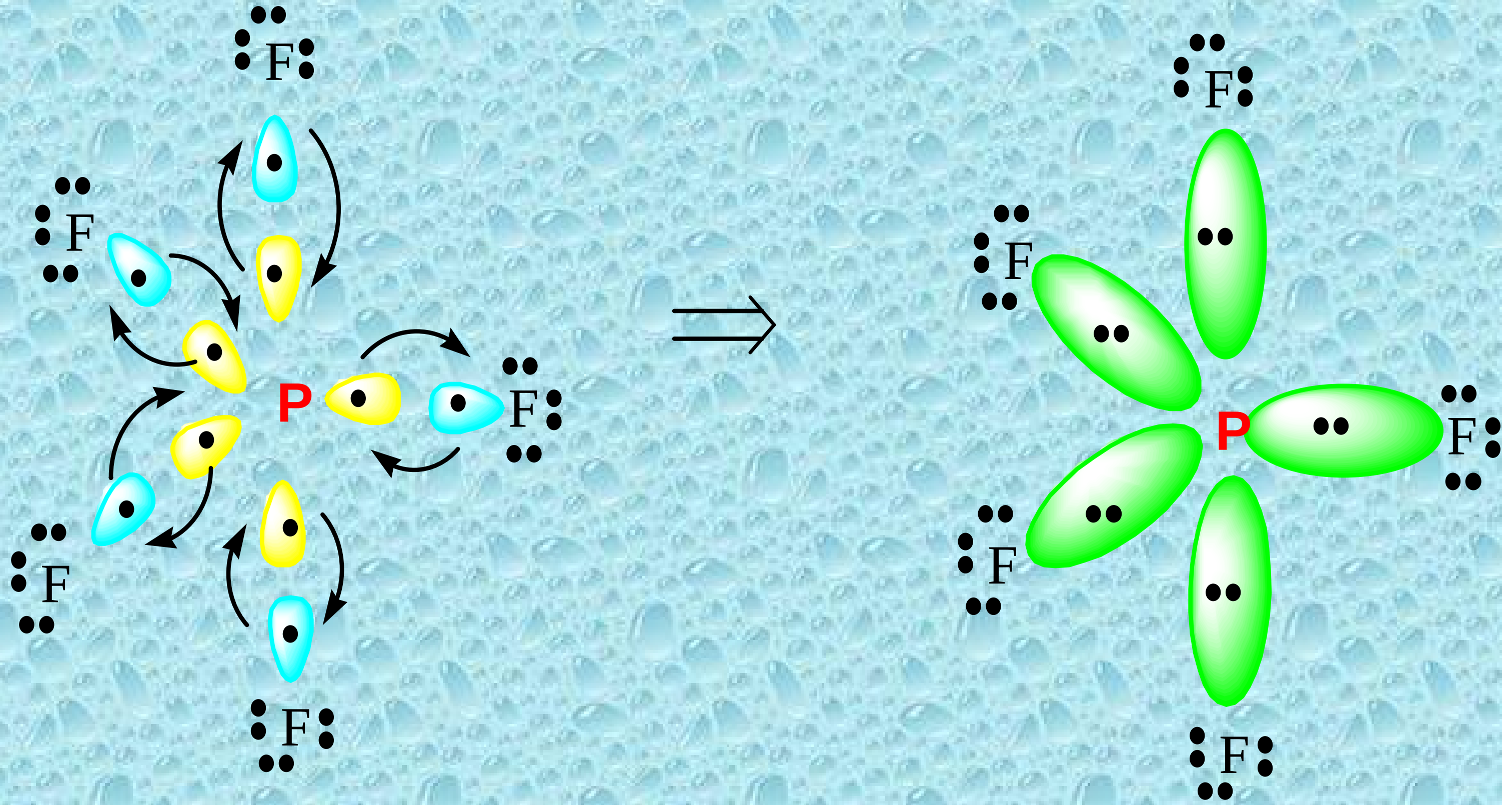
FORMATION OF PF_5:

Each fluorine atom, $1s^2 2s^2 2p^5$, has one unshared electron in a p orbital.

The half filled p orbital overlaps head-on with

a half full hybrid sp^3d orbital of the phosphorus to form a sigma bond.

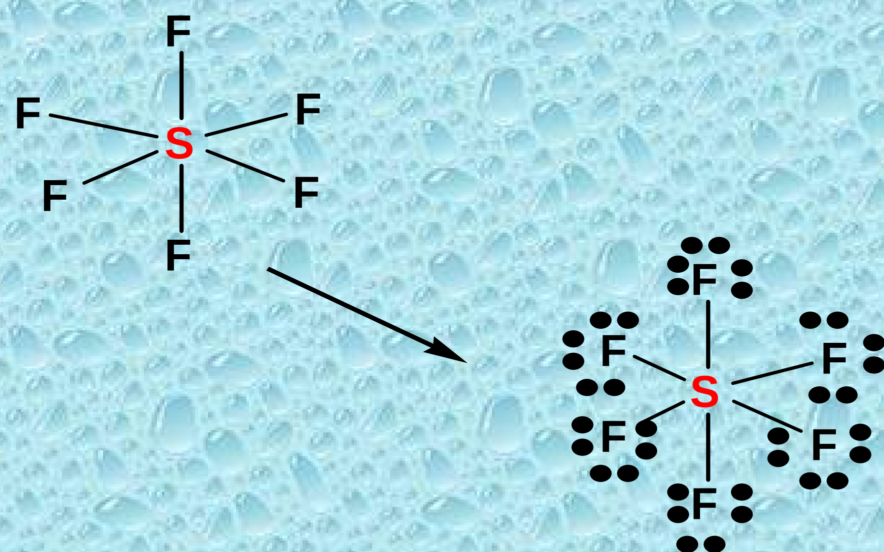
sp^3d hybridized, TRIGONAL BIPYRAMIDAL, 90, 120, 180^o bond angles

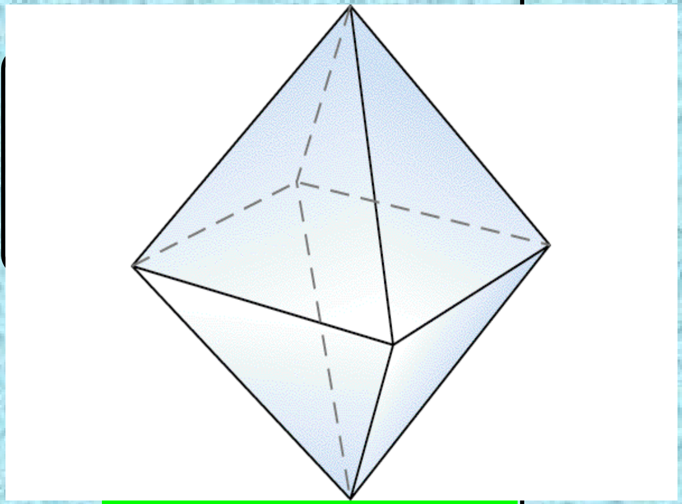


"sp^3d^2" Hybridization

SF_6 Sulphur Hexafloride

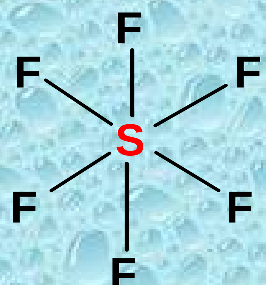
SF_6





OCTAHEDRAL

Number of regions around CENTRAL ATOM: 6



shape : OCTAHEDRAL
bond angles: 90, 180°

S^{16} -$1s^2$, $2s^2$, $2p^6$, **$3s^2$, $3p^4$**

$sp3d^2$

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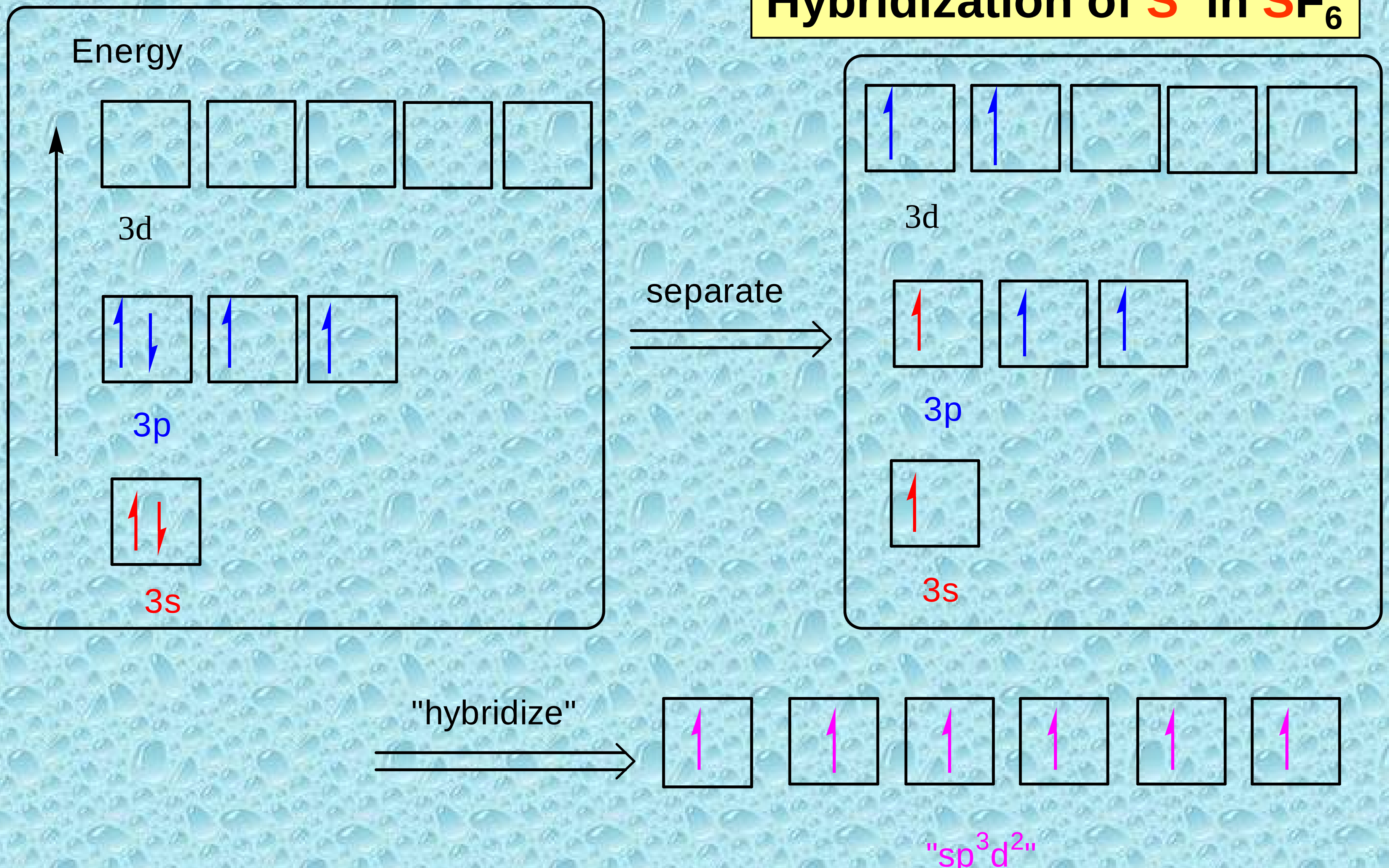
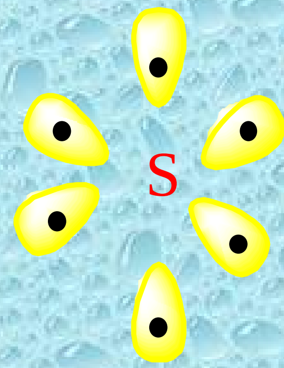
Hybridization of S in SF_6



"arrange"

⟹

(VSEPR)



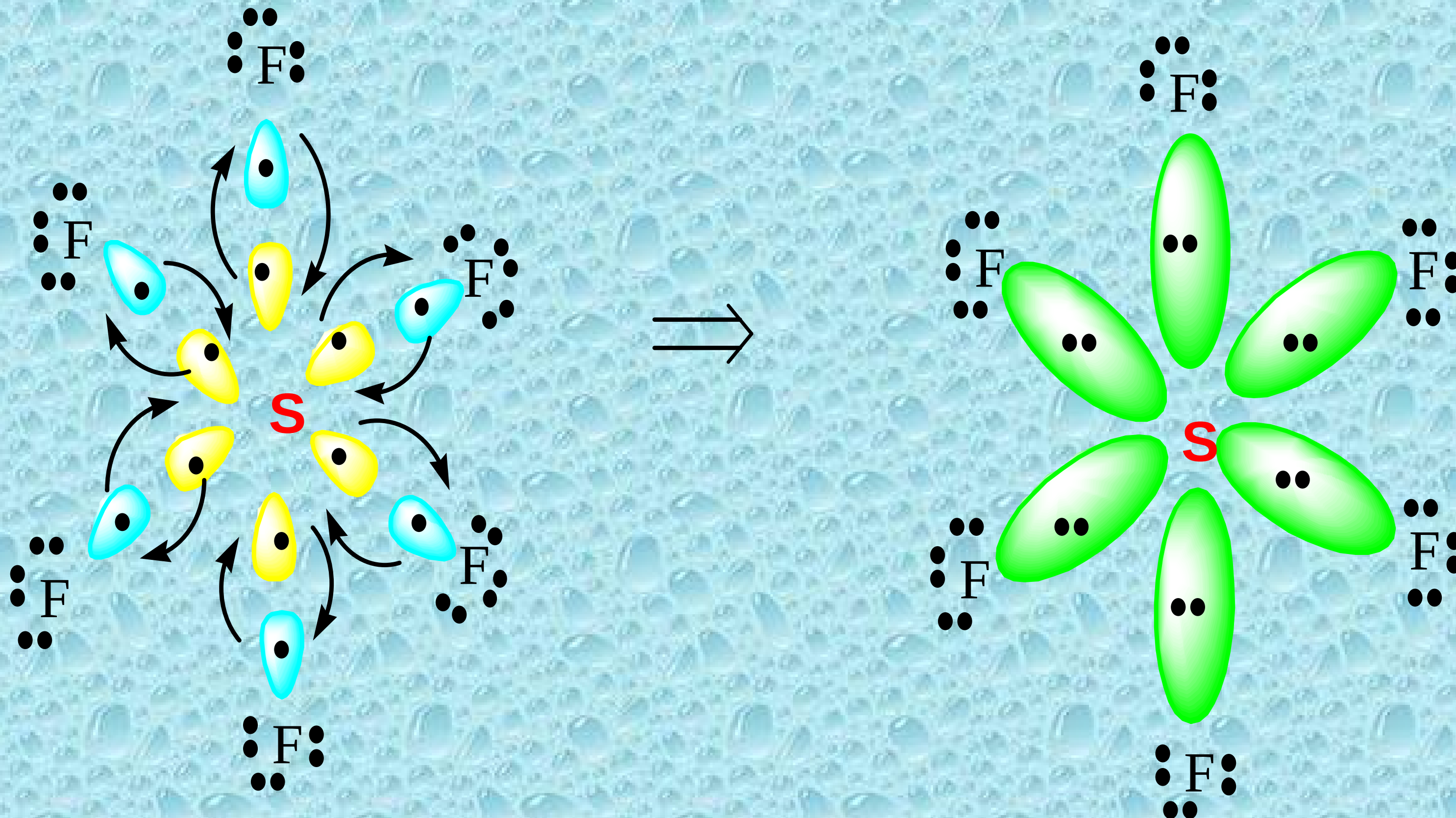
S is said to be "sp^3d^2 hybridized"

FORMATION OF SF_6:

Each fluorine atom, $1s^22s^22p^5$, has one unshared electron in a p orbital.

The half filled p orbital overlaps head-on with a half full hybrid sp^3d^2 orbital of the phosphorus to form a sigma bond.

sp3d² hybridized, TRIGONAL BIPYRAMIDAL, 90, 120, 180° bond angles



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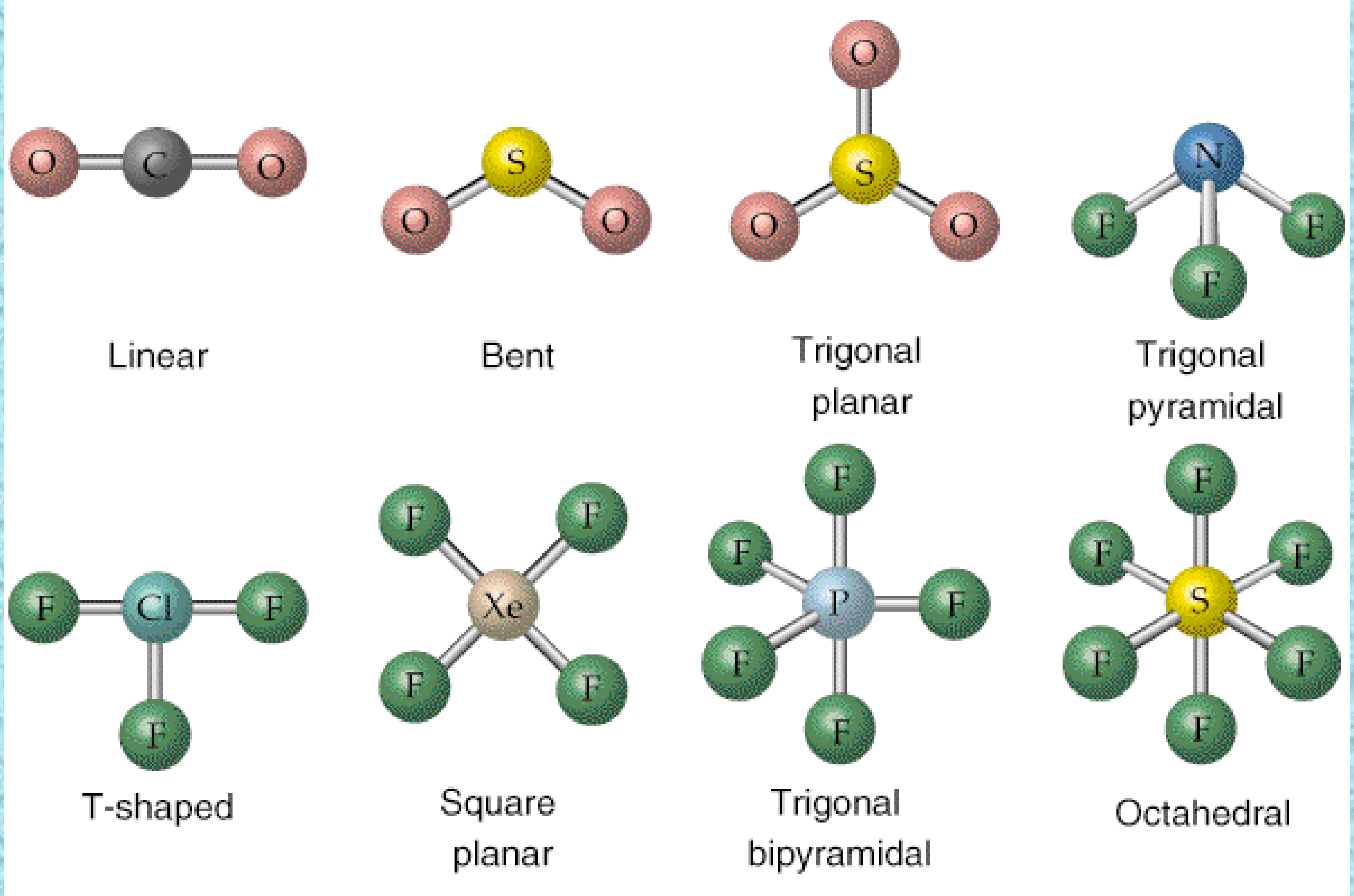
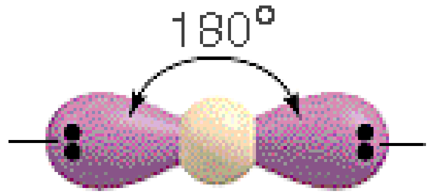
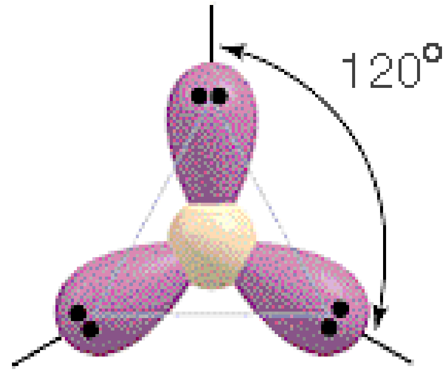
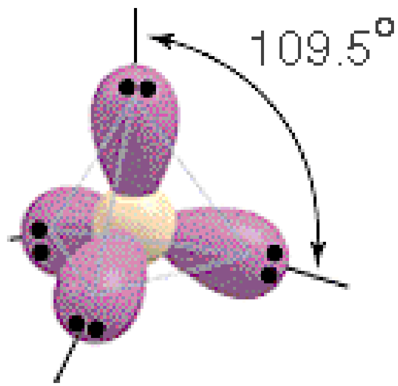
Summary: Regions, Shapes and Hybridization

#, regions	shape	hybridization
2	linear	sp
3	trigonal planar	sp^2
4	tetrahedral	sp^3
5	trigonal bipyramidal	sp^3d
6	octahedral	sp^3d^2


O
C
O
S
O
O
O
S
O
O
N
F
F
F
Linear
Bent
Trigonal planar
Trigonal pyramidal
F
Cl
F
F
F
F
Xe
F
F
F
F
P
F
F
F
F
F
F
S
F
F
F
F
T-shaped
Square planar
Trigonal bipyramidal
Octahedral

ELECTRON-PAIR GEOMETRIES AS A FUNCTION OF THE NUMBER OF ELECTRON PAIRS

	Number of Electron Pairs	Arrangement of Electron Pairs	Electron-Pair Geometry	Predicted Bond Angles
sp	2		Linear	180°
sp^2	3		Trigonal planar	120°
sp^3	4		Tetrahedral	109.5°

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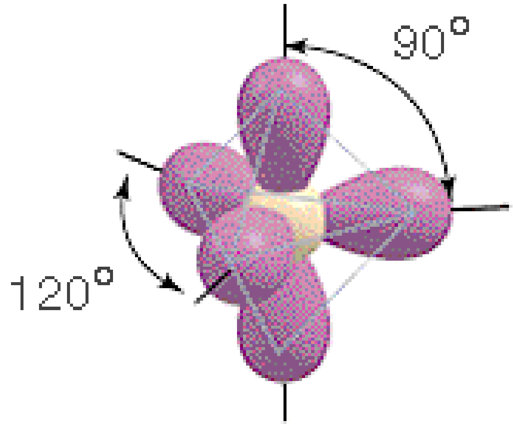
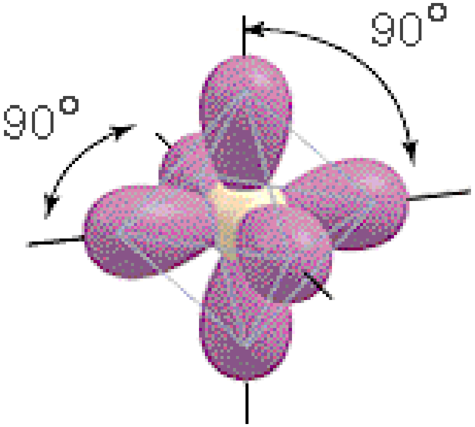
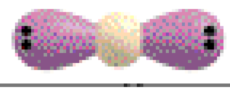
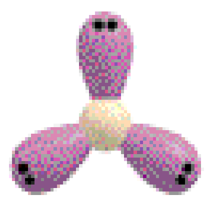
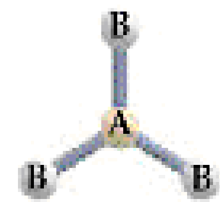
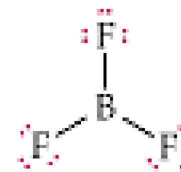
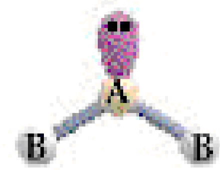
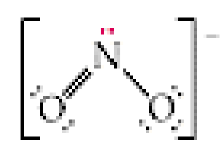
ELECTRON-PAIR GEOMETRIES AS A FUNCTION OF THE NUMBER OF ELECTRON PAIRS

Number of Electron Pairs	Arrangement of Electron Pairs	Electron-Pair Geometry	Predicted Bond Angles
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90° 180°

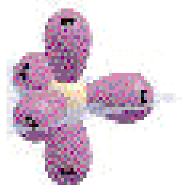
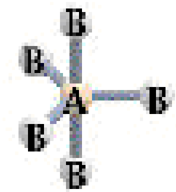
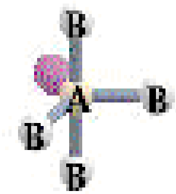
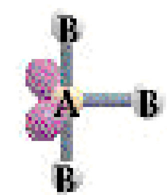
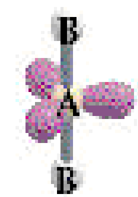
sp^3d

sp^3d^2

ELECTRON-PAIR GEOMETRIES AND MOLECULAR SHAPES FOR MOLECULES WITH TWO, THREE, AND FOUR ELECTRON PAIRS ABOUT THE CENTRAL ATOM

Total Electron Pairs	Electron-Pair Geometry	Bonding Pairs	Nonbonding Pairs	Molecular Geometry	Example
2 pairs **sp**	 Linear	2	0	 Linear	$\ddot{O}=C=\ddot{O}$
3 pairs **sp^2**	 Trigonal planar	3	0		
		2	1	 Bent	

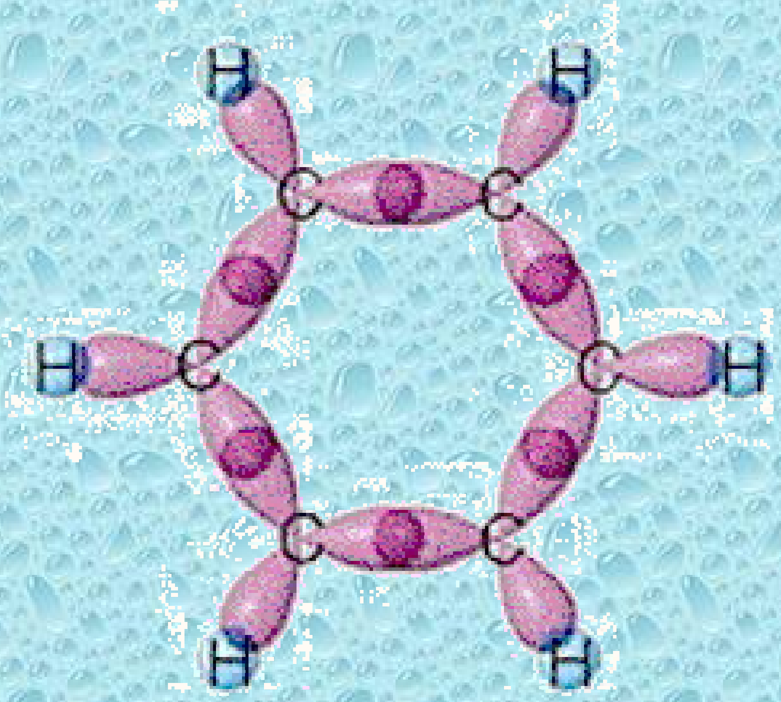
ELECTRON-PAIR GEOMETRIES AND MOLECULAR SHAPES FOR MOLECULES WITH FIVE AND SIX ELECTRON PAIRS ABOUT THE CENTRAL ATOM

Number of Electron Pairs	Electron-Pair Geometry	Bonding Pairs	Nonbonding Pairs	Molecular Geometry	Example
5 pairs	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	$PC1_5$
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	$C1F_3$
		2	3	 Linear	XeF_2

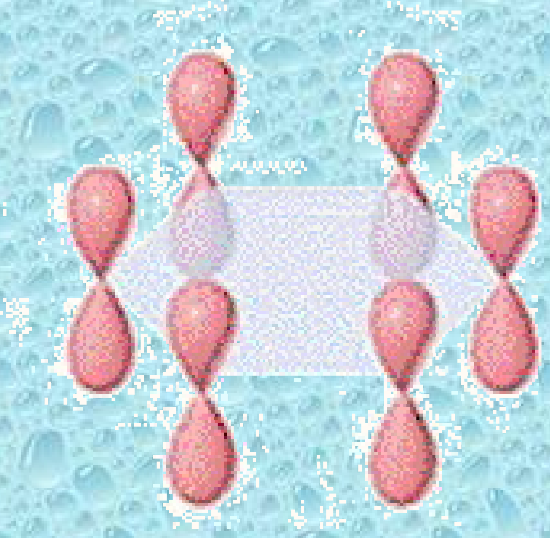
sp^3d

Delocalized π bonds

When a molecule has two or more resonance structures, the pi electrons can be delocalized over all the atoms that have pi bond overlap.



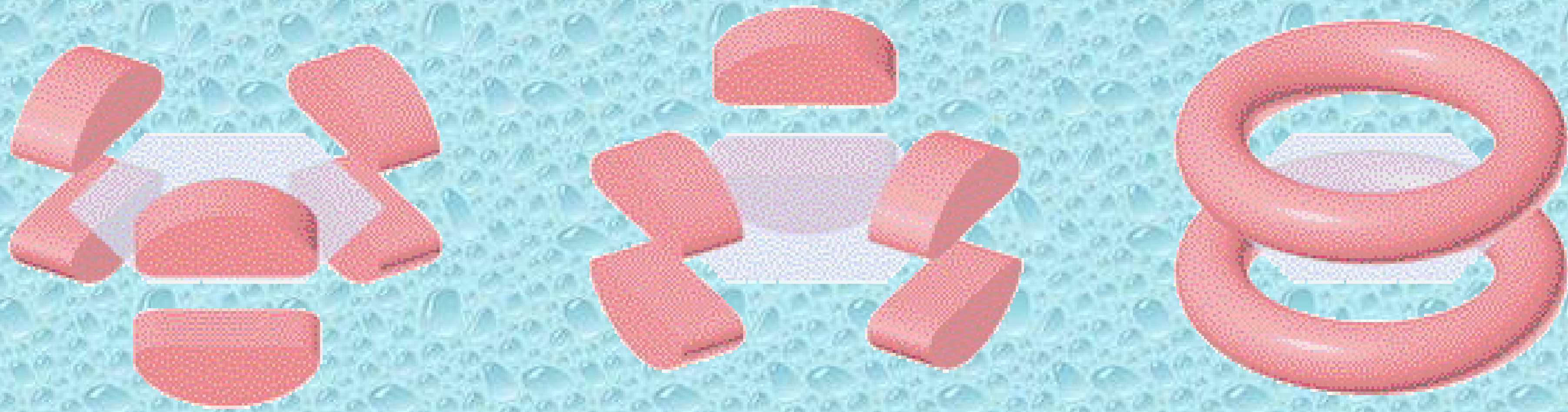
(a) σ bonds



(b) 2p atomic orbitals

Example: C_6H_6 benzene

Benzene is an excellent example. For benzene the π orbitals all overlap leading to a very delocalized electron system



(a) Localized π bonds (b) Localized π bonds (c) Delocalized π bonds

In general delocalized π bonding is present in all molecules where we can draw resonance structures with the multiple bonds located in different places.