Molecular Shapes & Structures

VSEPR Model

VSEPR: Valence-Shell Electron-Pair Repulsion method

Bond angle: angle between two atoms bonded to a central atom.

⇓

Regions of electron like to be
as far away as possible from the others.

Regions of electron density

Four regions of electron density around an atom:

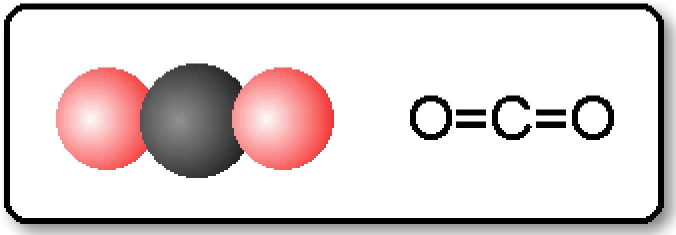
—

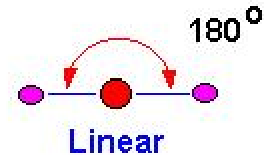
=

≡

•• Lone Pair

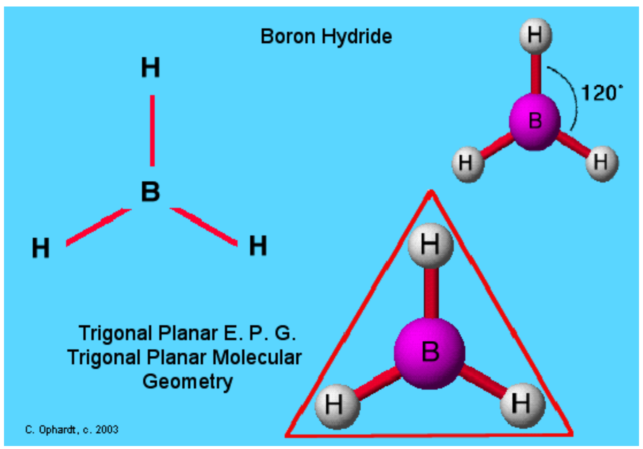
Bond Angles & Geometric Structures

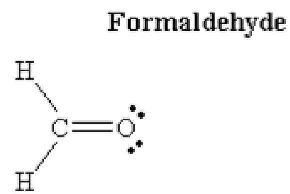


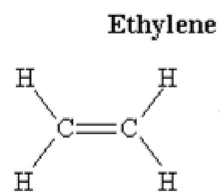


Linear molecules

2 regions

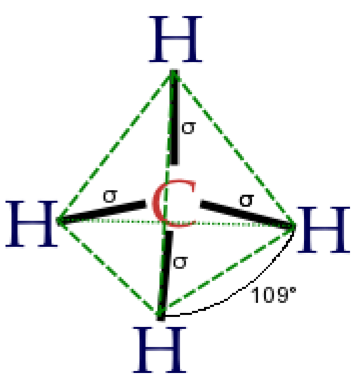


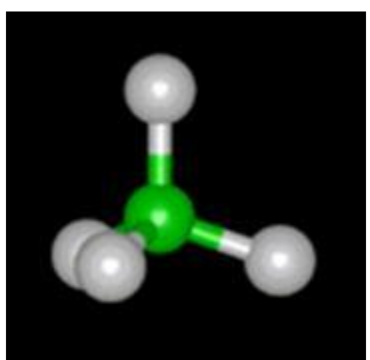




Trigonal planar molecules

3 regions



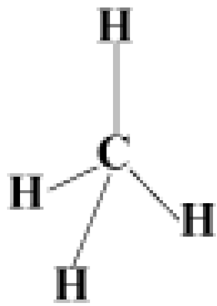


Tetrahedral arrangement

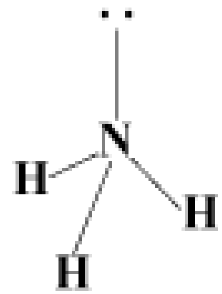
4 regions

Tetrahedral Electron Pair Geometry

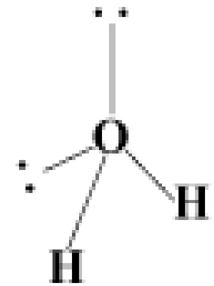
(Molecular Geometry-Shape)



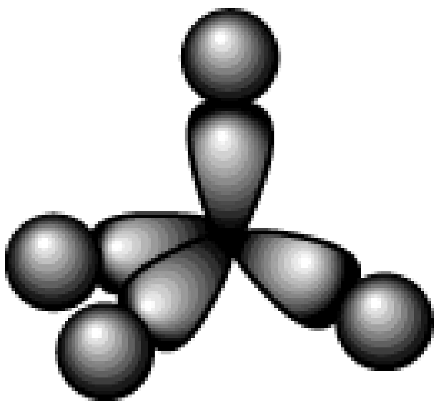
Methane (CH_4)



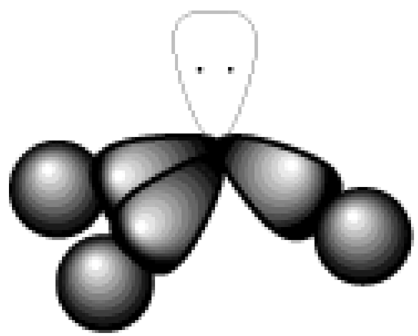
Ammonia (NH_3)



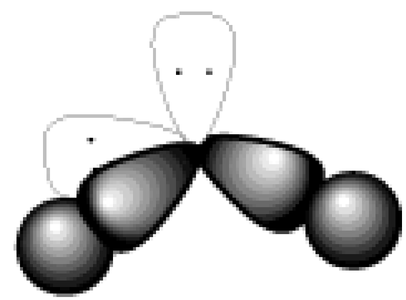
Water (H_2O)



Tetrahedral

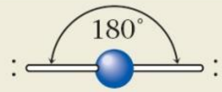
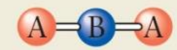
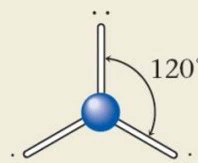
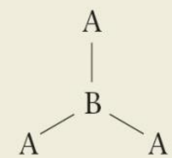
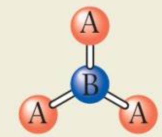
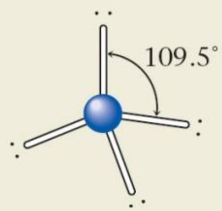
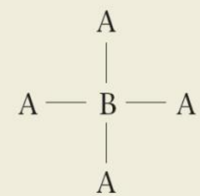
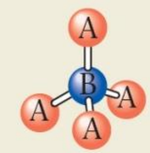
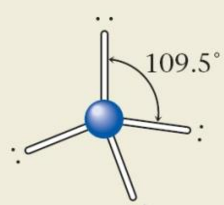
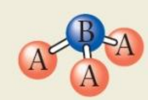
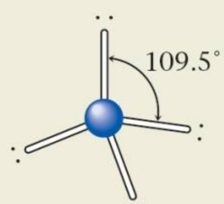
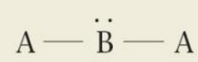
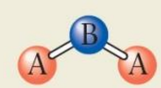


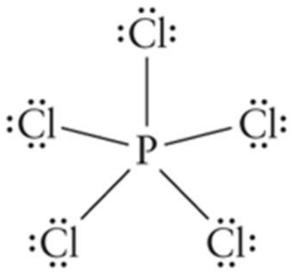
Trigonal Pyramidal



Bent (V-Shaped)

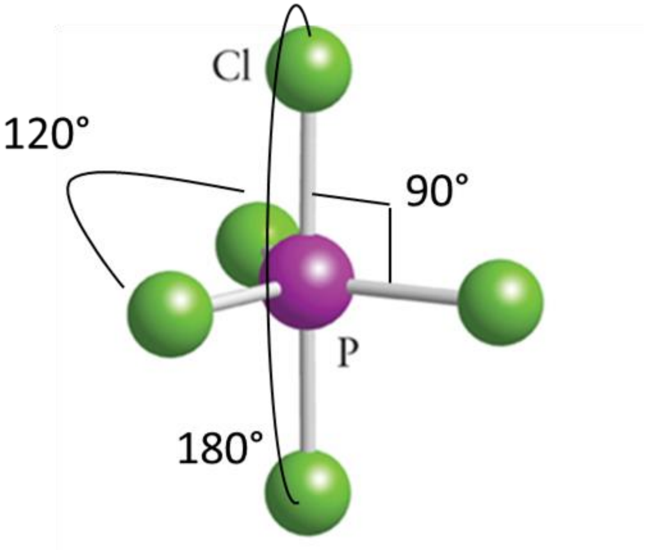
Table 12.4 Arrangements of Electron Pairs and the Resulting Molecular Structures for Two, Three, and Four Electron Pairs

Case	Number of Electron Pairs	Bonds	Electron Geometry (Arrangement)	Ball-and-Stick Model	Angle Between Pairs	Molecular Geometry (Shape)	Partial Lewis Structure	Ball-and-Stick Model	Example
1	2	2	Linear		180°	Linear	A—B—A		BeF_2
2	3	3	Trigonal planar (triangular)		120°	Trigonal planar (triangular)			BF_3
3	4	4	Tetrahedral		109.5°	Tetrahedral			CH_4
4	4	3	Tetrahedral		109.5°	Trigonal pyramid			NH_3
5	4	2	Tetrahedral		109.5°	Bent or V-shaped			H_2O

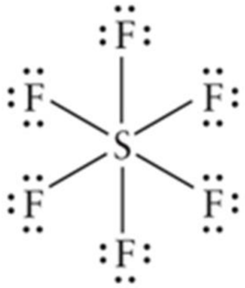


Phosphorus pentachloride, PCl_5

PF_5 has 5 electron regions, therefore it has a **Trigonal bipyramidal** shape of electron regions.

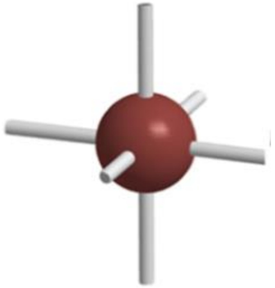


90° , 120°, 180°



Sulfur hexafluoride, SF_6

SF_6 has 6 electron regions, therefore it has a **Octahedral** shape of electron regions.



Octahedral

90°

Electron Pair Shapes (Geometry)

Linear

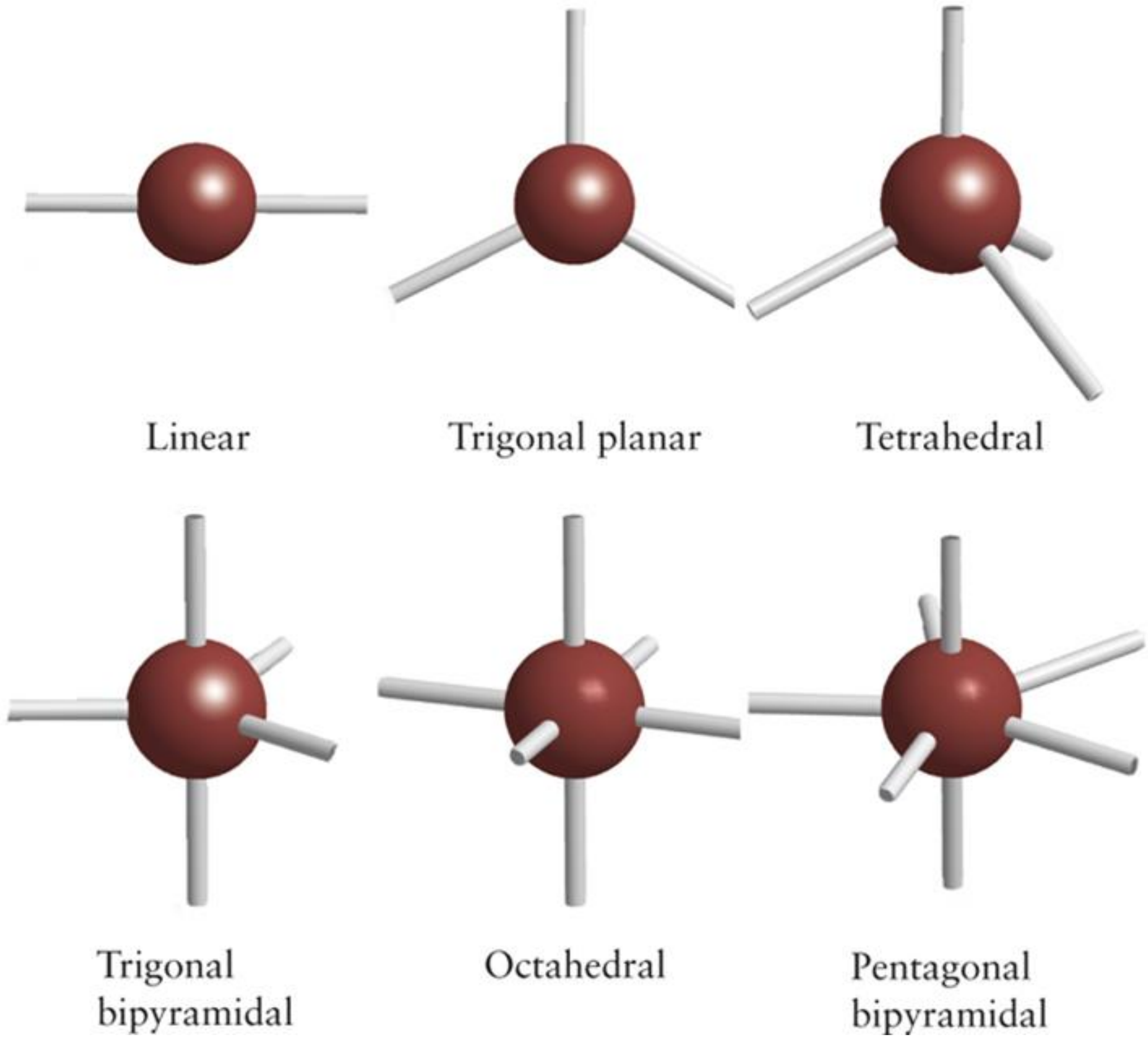
Trigonal bipyramidal

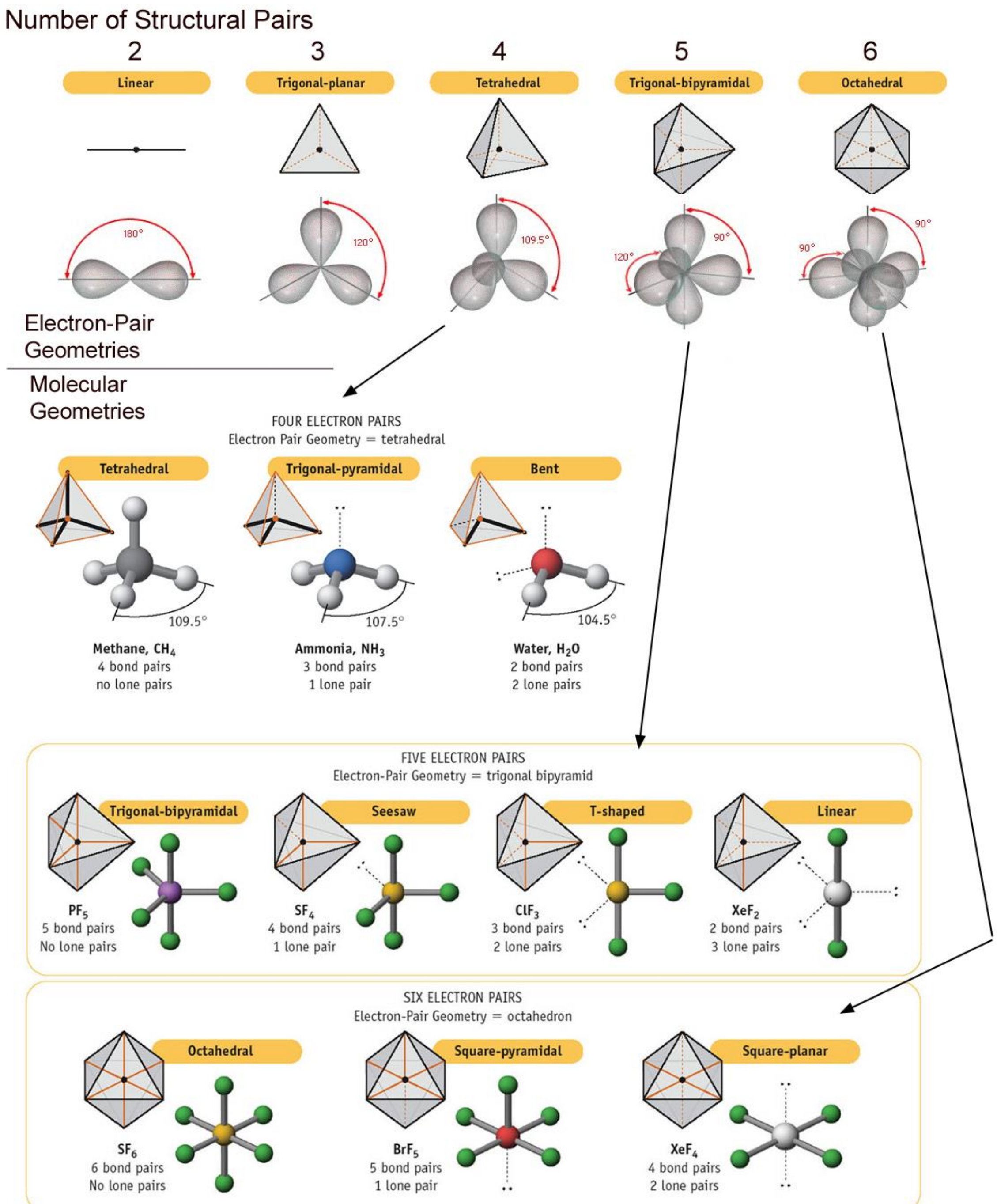
Trigonal planer

Octahedral

Tetrahedral

Electron Pair Shapes (Geometry)



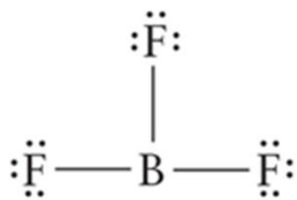

Number of Structural Pairs
2
3
4
5
6
Linear
Trigonal-planar
Tetrahedral
Trigonal-bipyramidal
Octahedral
180°
120°
109.5°
120°
90°
90°
90°
Electron-Pair Geometries
Molecular Geometries
FOUR ELECTRON PAIRS
Electron Pair Geometry = tetrahedral
Tetrahedral
Trigonal-pyramidal
Bent
109.5°
107.5°
104.5°
Methane, CH_4
4 bond pairs
no lone pairs
Ammonia, NH_3
3 bond pairs
1 lone pair
Water, H_2O
2 bond pairs
2 lone pairs
FIVE ELECTRON PAIRS
Electron-Pair Geometry = trigonal bipyramid
Trigonal-bipyramidal
Seesaw
T-shaped
Linear
PF_5
5 bond pairs
No lone pairs
SF_4
4 bond pairs
1 lone pair
ClF_3
3 bond pairs
2 lone pairs
XeF_2
2 bond pairs
3 lone pairs
SIX ELECTRON PAIRS
Electron-Pair Geometry = octahedron
Octahedral
Square-pyramidal
Square-planar
SF_6
6 bond pairs
No lone pairs
BrF_5
5 bond pairs
1 lone pair
XeF_4
4 bond pairs
2 lone pairs

Determine the (1) Lewis structure, (2) VSEPR electron arrangement name, (3), and (3) VSEPR molecular shape name.

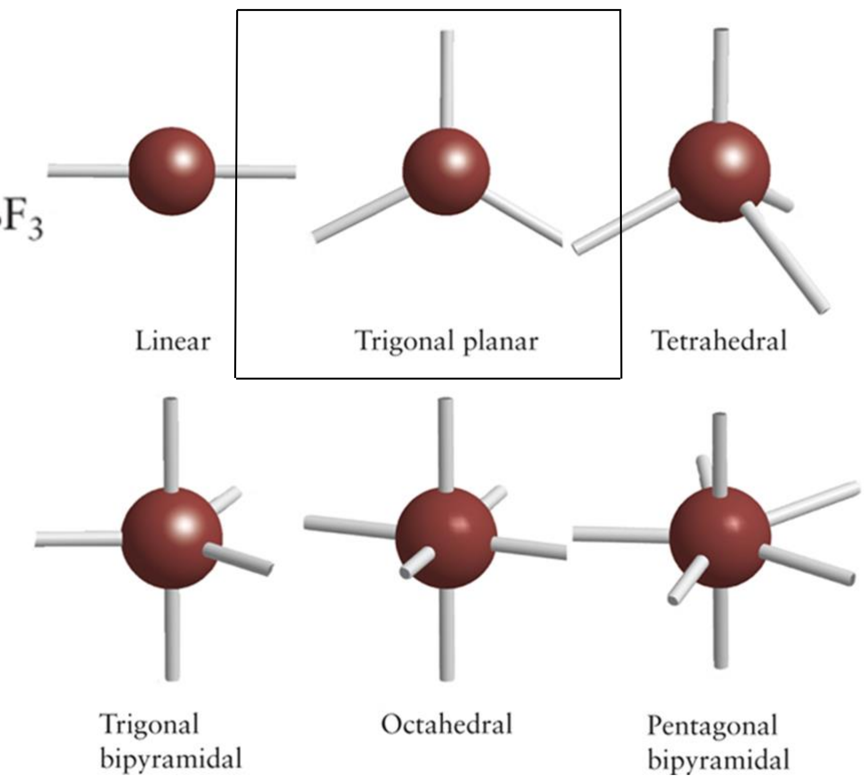
BF_3

3 electron regions

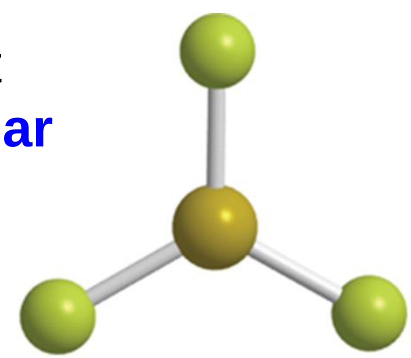
BF_3 Lewis structure



Boron trifluoride, BF_3



BF_3 has **3 electron regions**, therefore it has a **Trigonal planar** shape of electron regions.



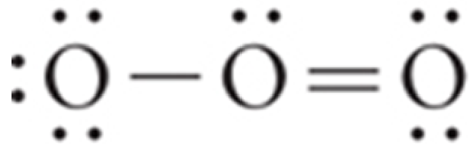
Boron trifluoride, BF_3

VSEPR 3D shape

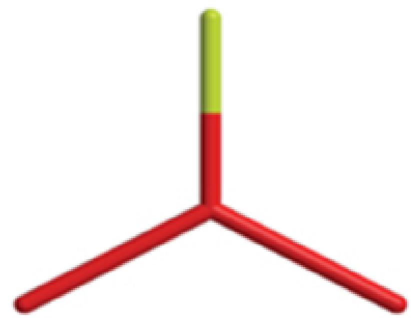
Determine the (1) Lewis structure, (2) VSEPR electron arrangement name, and (3) VSEPR molecular shape name.

O_3

Draw the Lewis structure.

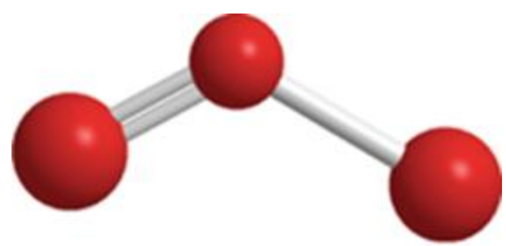


Count the bonds and lone pairs on the central atom. Draw the 3D shape. Assign the electron arrangement.



Trigonal planar

Identify the shape considering only atoms .

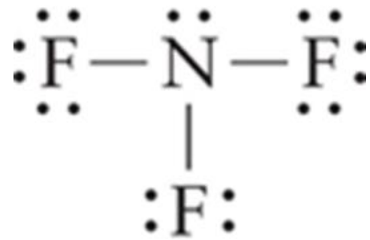


Angular or Bent

Determine the (1) Lewis structure, (2) VSEPR electron arrangement name, and (3) VSEPR molecular shape name.

NF_3

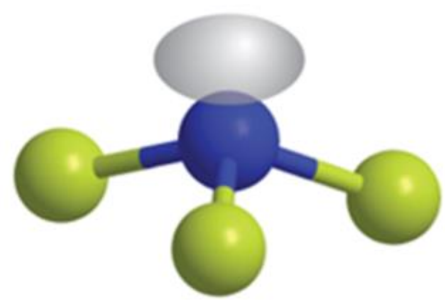
Draw the Lewis structure.



Count the bonds and lone pairs on the central atom. Draw the 3D shape. Assign the electron arrangement.

Tetrahedral

Identify the shape considering only atoms.

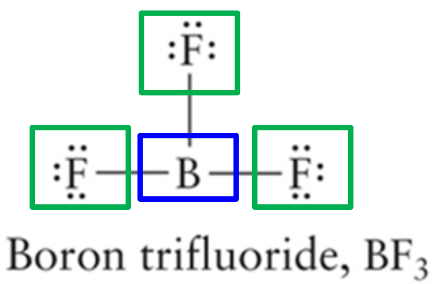


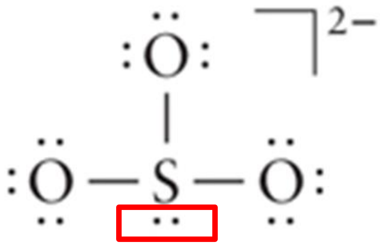
Trigonal pyramidal

VSEPR Formula

The generic VSEPR formula "$\mathbf{AX_nE_m}$" helps identify bonding pair, and lone pairs attachments to the central atom.

"**A**" represent a central atom, "**X**" an attached atom, and "**E**" a lone pair.





AX_3

AX_3E

BF_3 has three attached fluorine atoms and no lone pairs so is an example of an $\mathbf{AX_3}$ species.

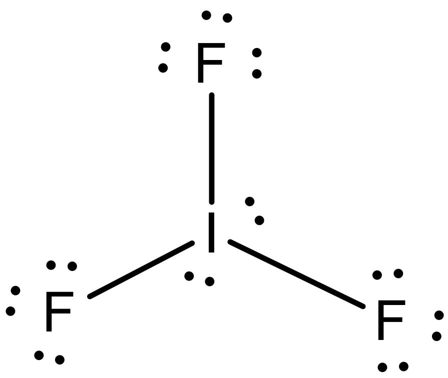
SO_3^{2-} has one lone pair so is an example of an $\mathbf{AX_3E}$ species.

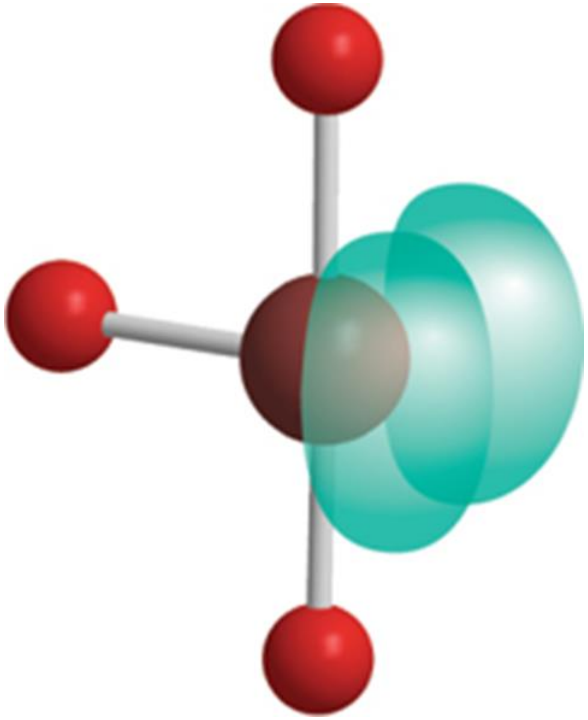
Determine the (1) Lewis structure, (2) VSEPR electron arrangement name, (3) VSEPR formula, and (4) VSEPR molecular shape name.

IF_3

"T" shaped

(1)





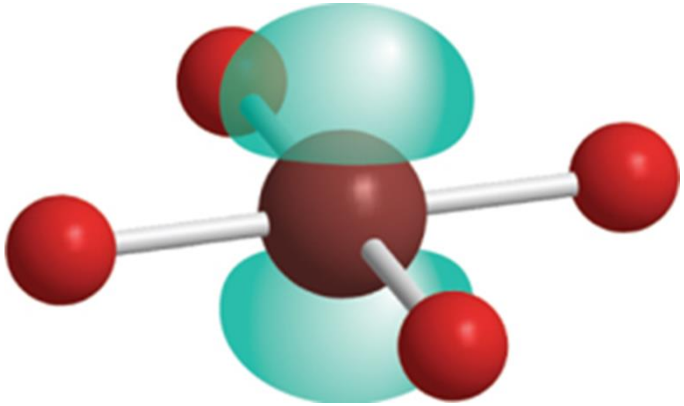
(2) 5 electron groups = trigonal bipyramidal

(3) AX_3E_2

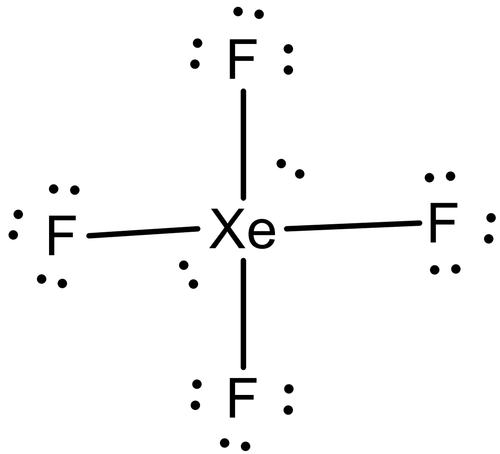
Determine the (1) Lewis structure, (2) VSEPR electron arrangement name, (3) VSEPR formula, and (4) VSEPR molecular shape name.

XeF_4

(4) Square planar



(1)

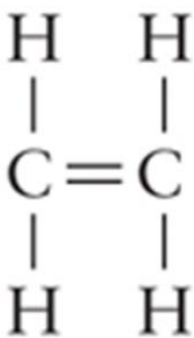


(2) 6 electron groups = octahedral

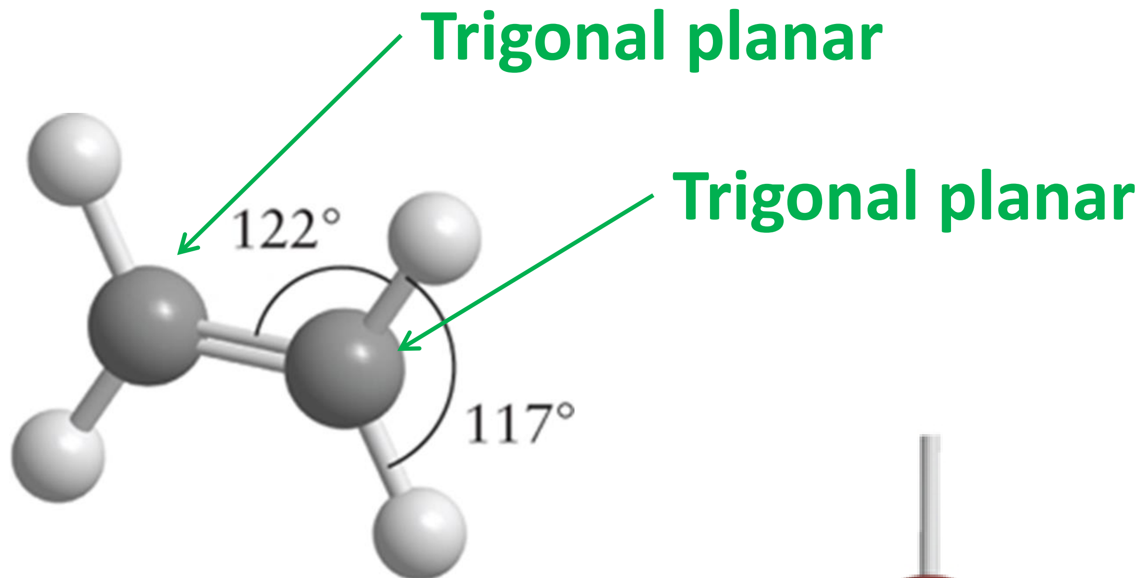
(3) AX_4E_2

The basic VSEPR model

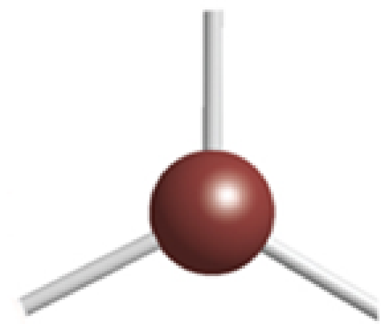
When there is more than one central atom, we consider the bonding about each atom independently.



Ethene, C_2H_4



Ethene, C_2H_4



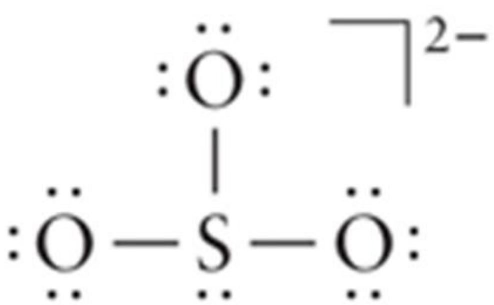
Trigonal planar

Lewis Diagram

VSEPR 3D shape

Molecules with Lone Pairs on the Central Atom

Identify the electron arrangement around the central atom and the generic VSEPR formula for sulfite.

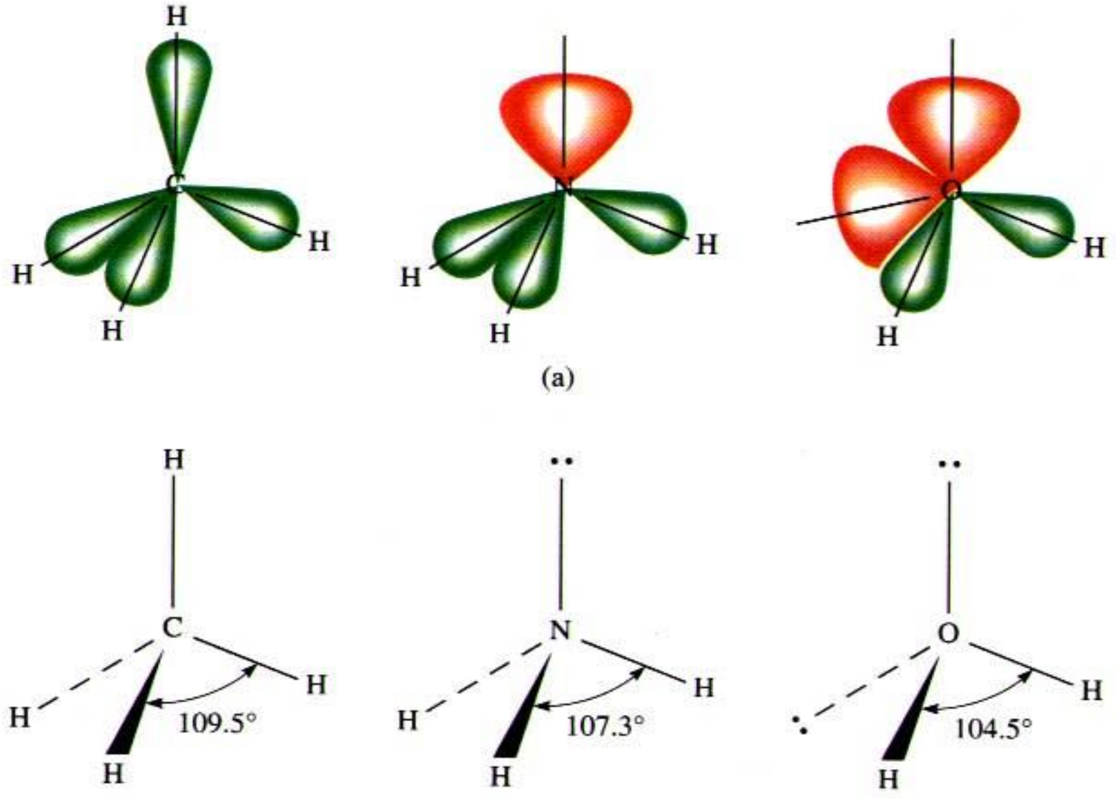


Tetrahedral

SO_3^{2-}, which has one lone pair, is an example of an **AX_3E** species.

Molecules with Lone Pairs on the Central Atom

Lone pairs cause **smaller bond angles than expected**. Lone pairs **push** bonding atoms closer together.

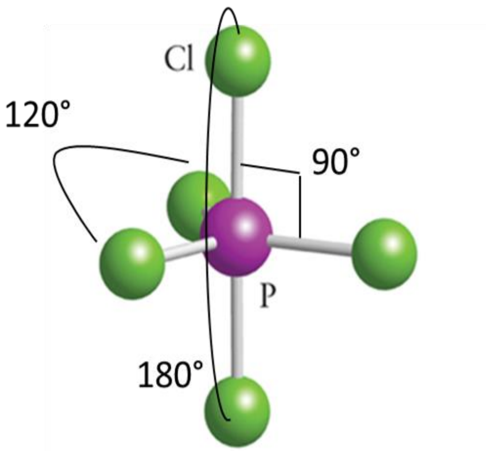


CH_4 NH_3 H_2O

Lone pairs are not localized so they spread over a **larger volume**.

lone pair repulsions energies follow as:

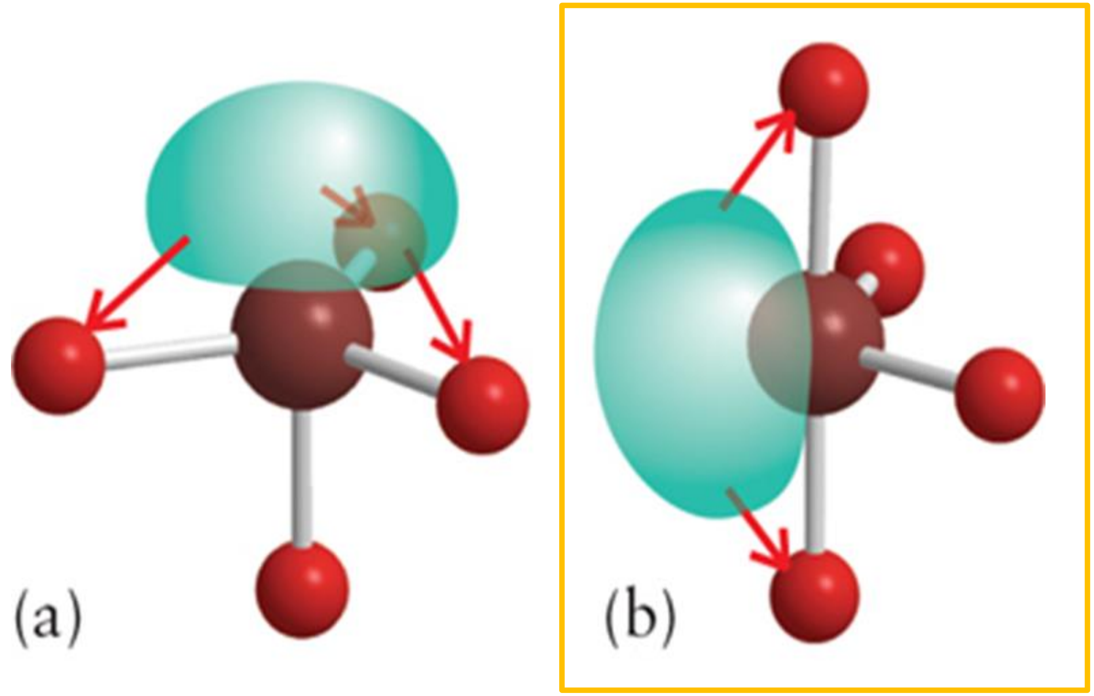
lone pair-lone pair > **lone pair-atom** > **atom-atom**



Trigonal bipyramidal

This lone pair has 3 neighbors at 90°

This lone pair has 2 neighbors at 90°

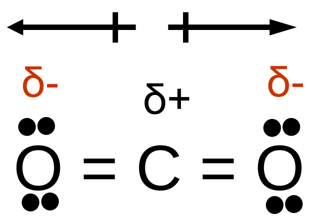


The one with the least amount of repulsion.

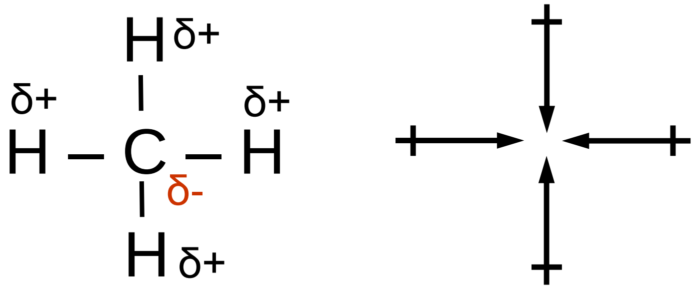
See-Saw

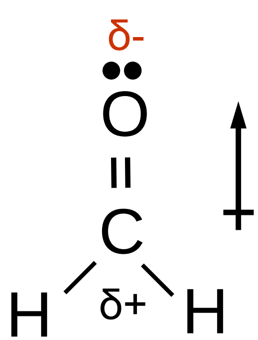
Polarity

1. It has polar bonds.
2. Centers of δ+ and δ- lie at different places (sides).

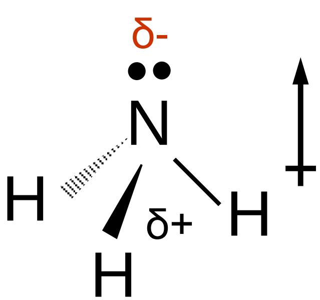


nonpolar molecule





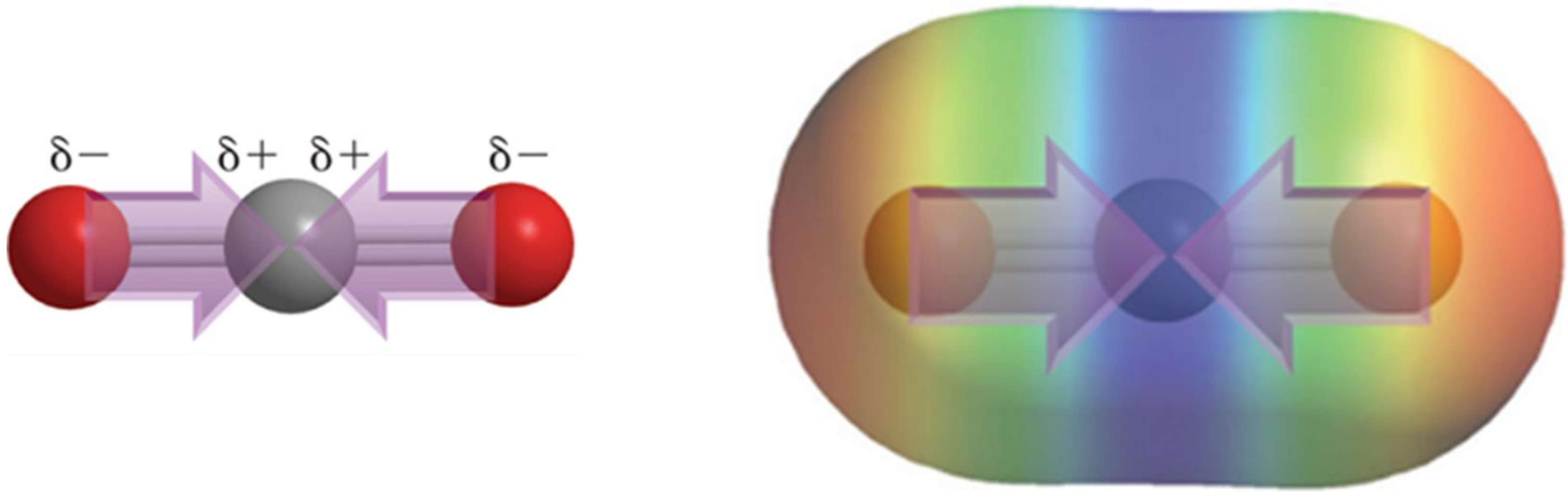
polar molecule



Some of the consequences of molecular shape

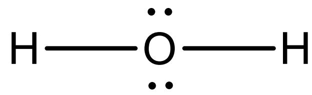
Electrostatic potential diagram (Elpot) for CO_2.

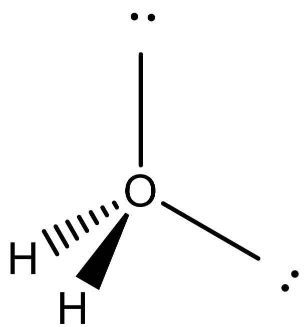
The negative charge converges on the positive center, so the molecule is nonpolar.

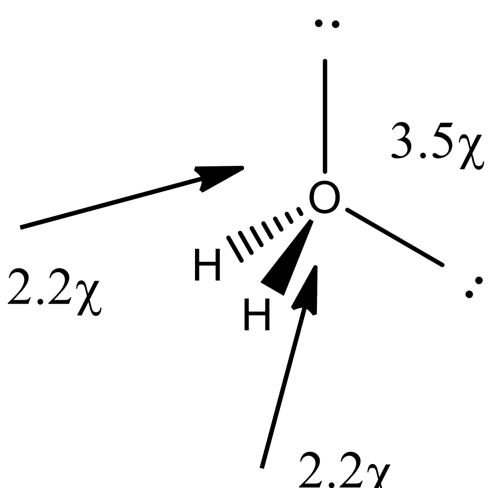


Carbon dioxide, CO_2

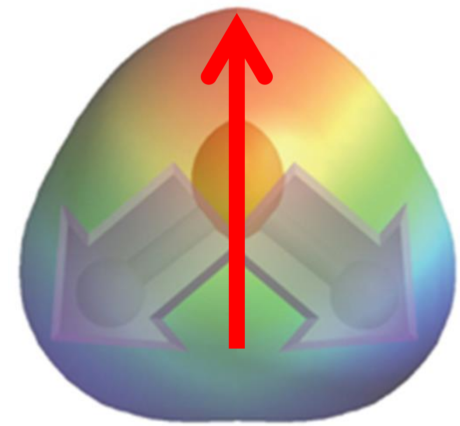
H_2O





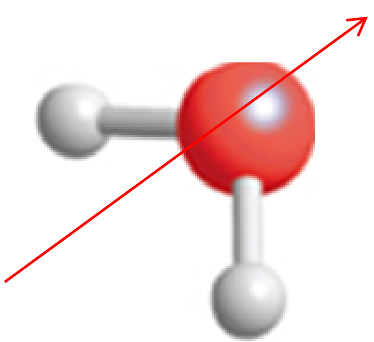


High electron density



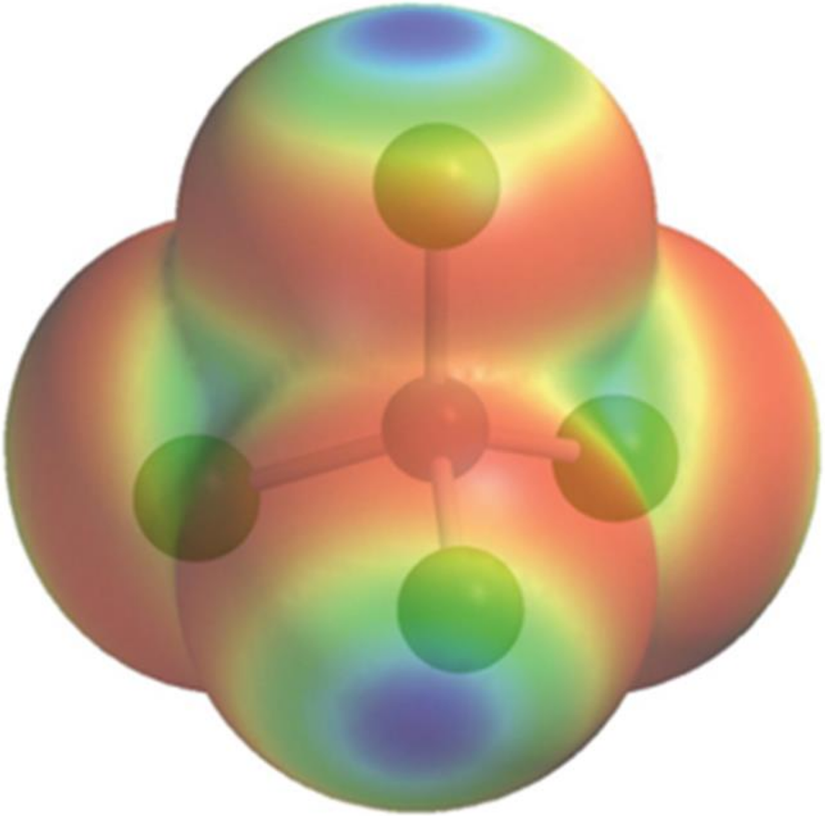
Low electron density

Water, H_2O



Some of the **consequences** of molecular shape

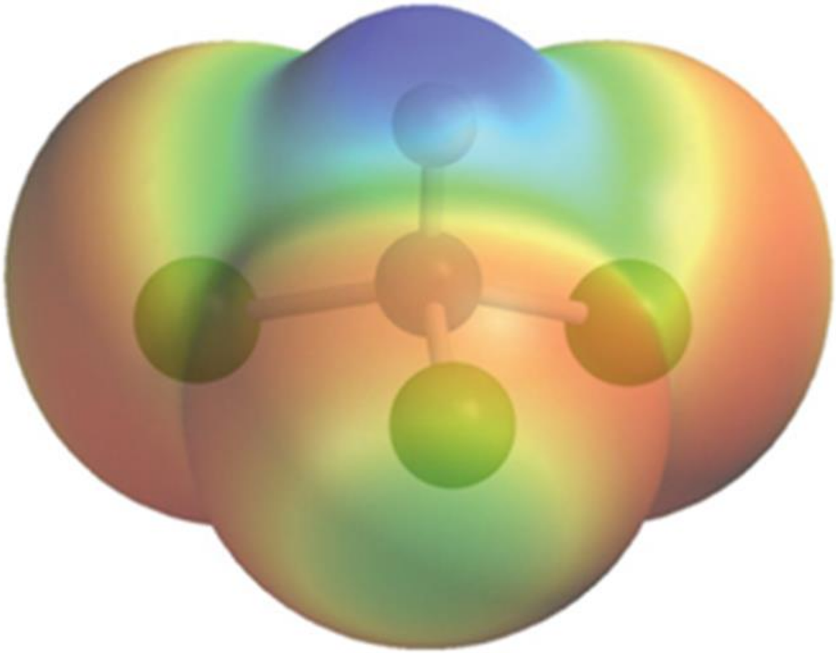
Changing one atom.



CCl_4

Symmetric dipole = Non-polar

Asymmetric dipole = Polar

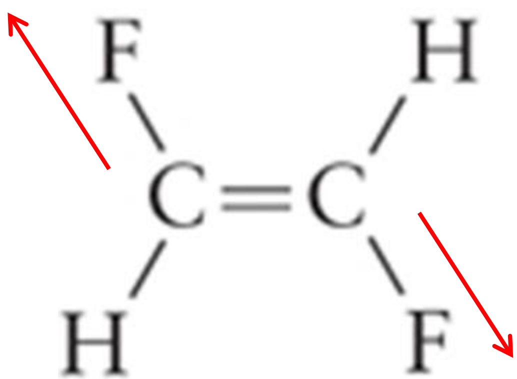


$CHCl_3$

Some of the **consequences** of molecular shape

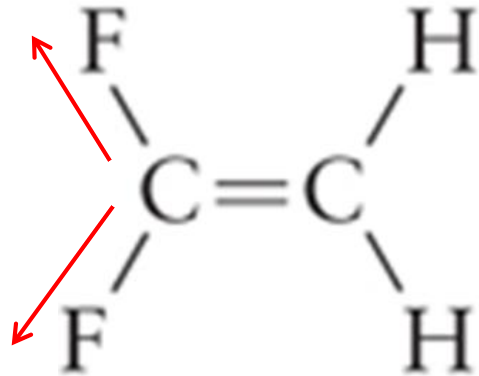
Double or triple bonds fix atoms into a position.

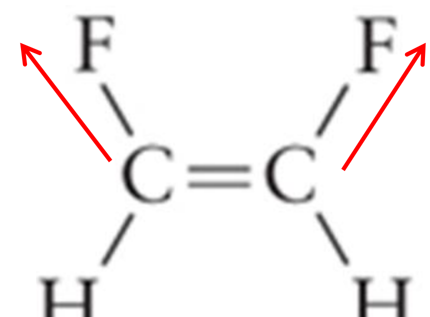
Opposing dipoles



Symmetric dipole = Non-polar

directional dipoles

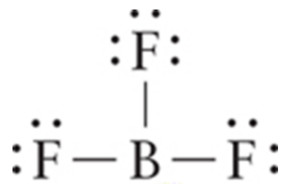


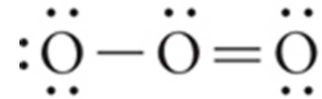


Asymmetric dipole = Polar

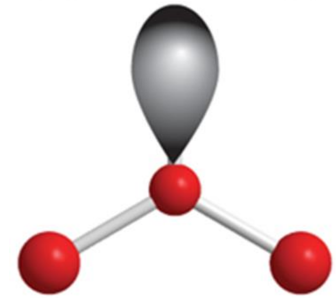
Predicting the polar character of a molecule for (a) a boron trifluoride molecule, BF_3, and (b) an ozone molecule O_3.

(1) Draw the Lewis structure.



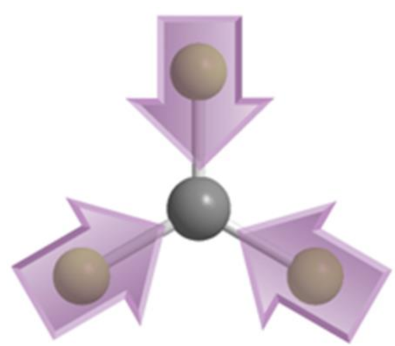


(2) Assign the electron arrangement.

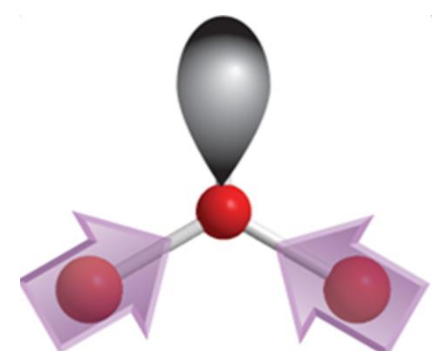


	(a)	(b)
	Trigonal planar	Trigonal planar
(3) Identify the VSEPR formula.	AX_3	AX_2E
(4) Name the molecular shape.	Trigonal planar	Angular or Bent

(5) Identify the polarity.



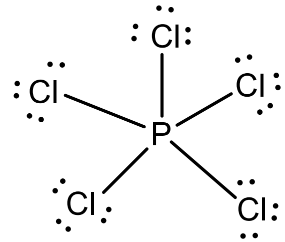
Symmetric dipole nonpolar

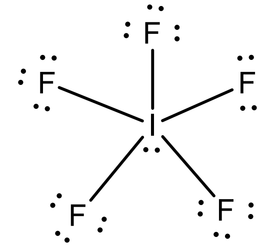


asymmetric dipole polar

Predict whether (a) PCl_5, (b) IF_5 is polar or nonpolar.

(1) Draw the Lewis structure.





(2) Assign the electron arrangement.

trigonal bipyramidal

octahedral

(3) Identify the VSEPR formula.

AX_5

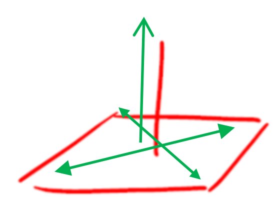
AX_5E

(4) Name the molecular shape.

trigonal bipyramidal

square pyramidal

(5) Identify the polarity.



Asymmetric dipole polar

Symmetric dipole nonpolar

Valence-Bond Theory (VB)

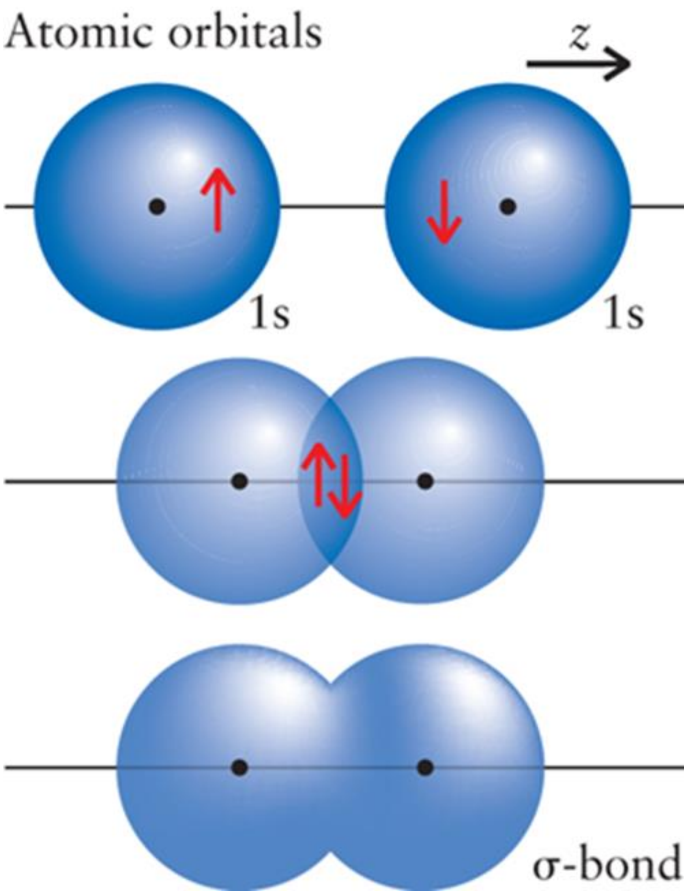
Types of bonds in Valence-Bond Theory

Sigma Bonds

The simplest molecule of all is H_2.

A “ground-state” hydrogen atoms has one electron in a 1s-orbital.

As two H atoms come together, their 1s-electrons pair (denoted ↑↓) begin to overlap.

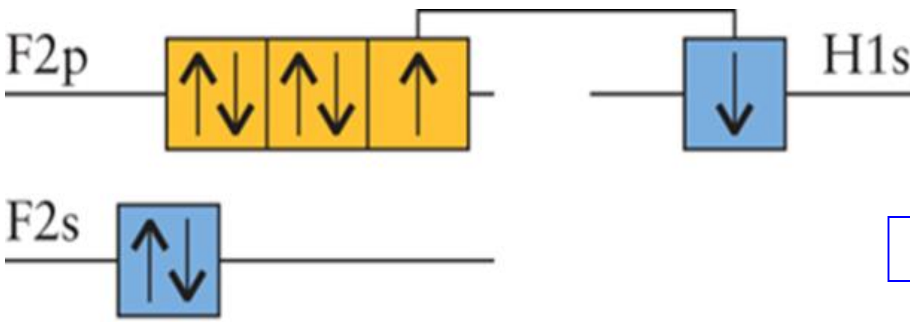


The resulting sausage-shaped distribution of electrons density is <u>between the nuclei</u>, and called a "σ-bond" (a sigma bond).

Types of bonds in Valence-Bond Theory

F has an unpaired electron atom in the $2p_z$-orbital. Hydrogen has an unpaired electron in the 1s-orbital.

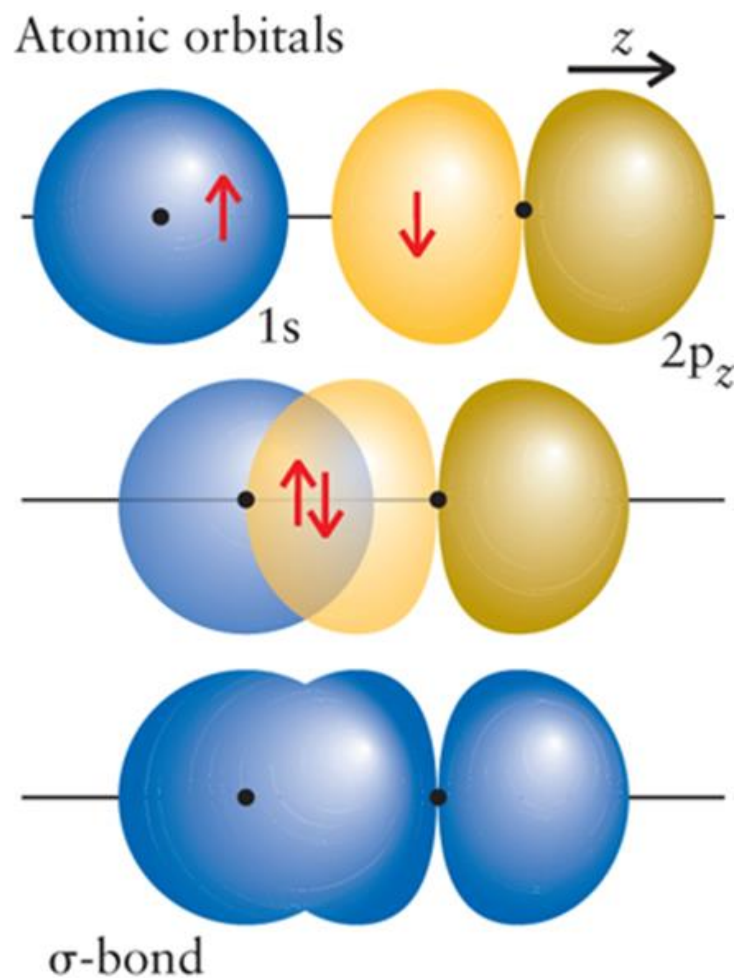
The orbitals overlap and merge into a cloud that spreads over both atoms



Hydrogen fluoride, HF

Sigma Bonds

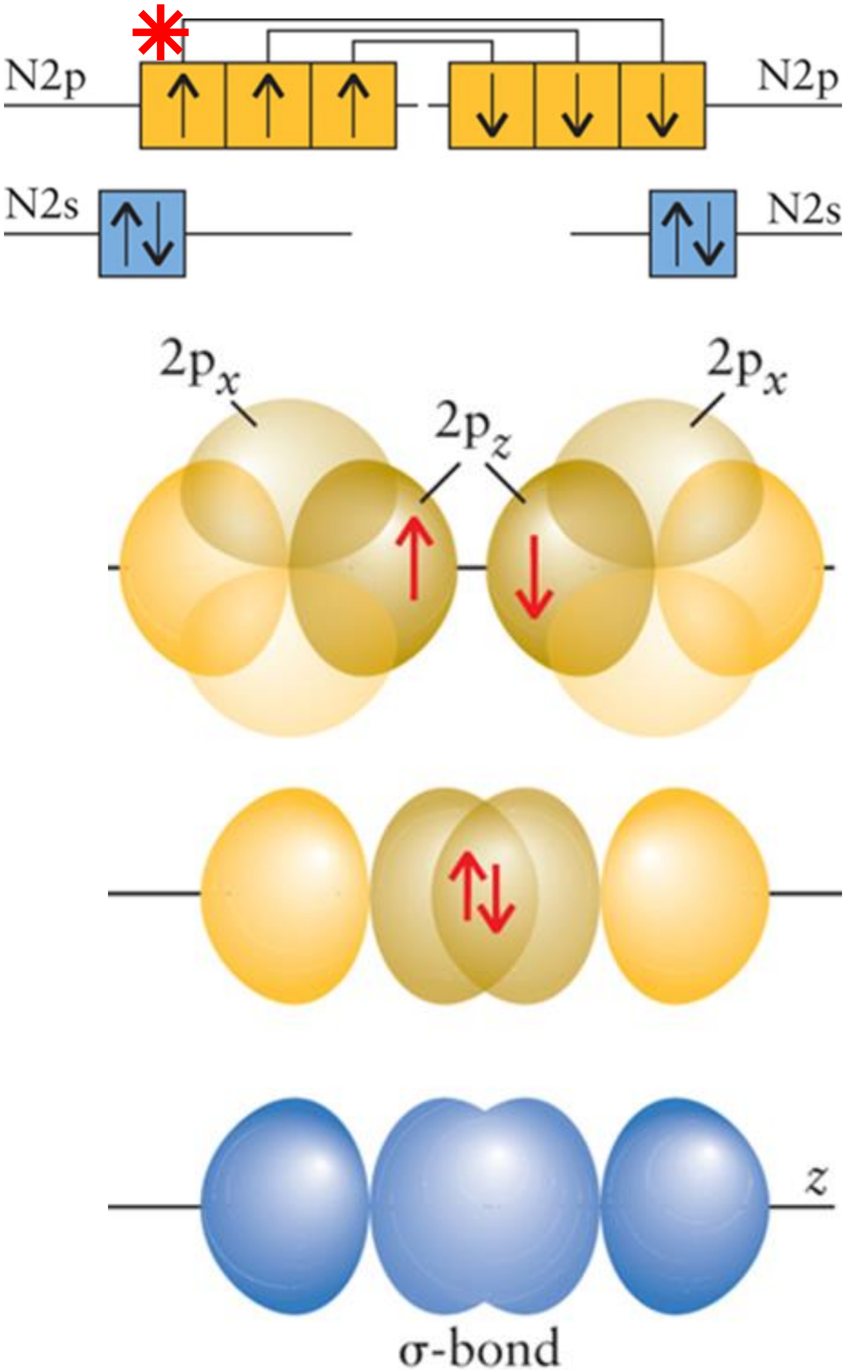
H F



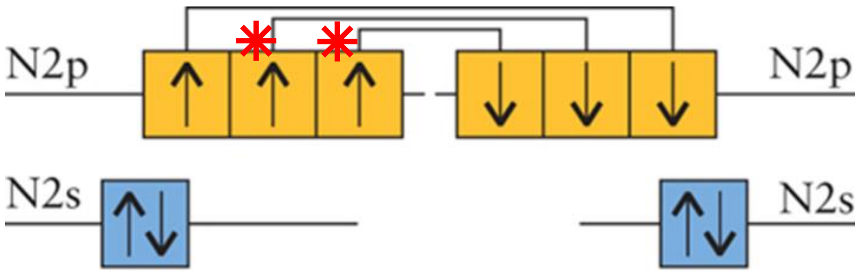
A different type of bond in a nitrogen molecule, N_2.

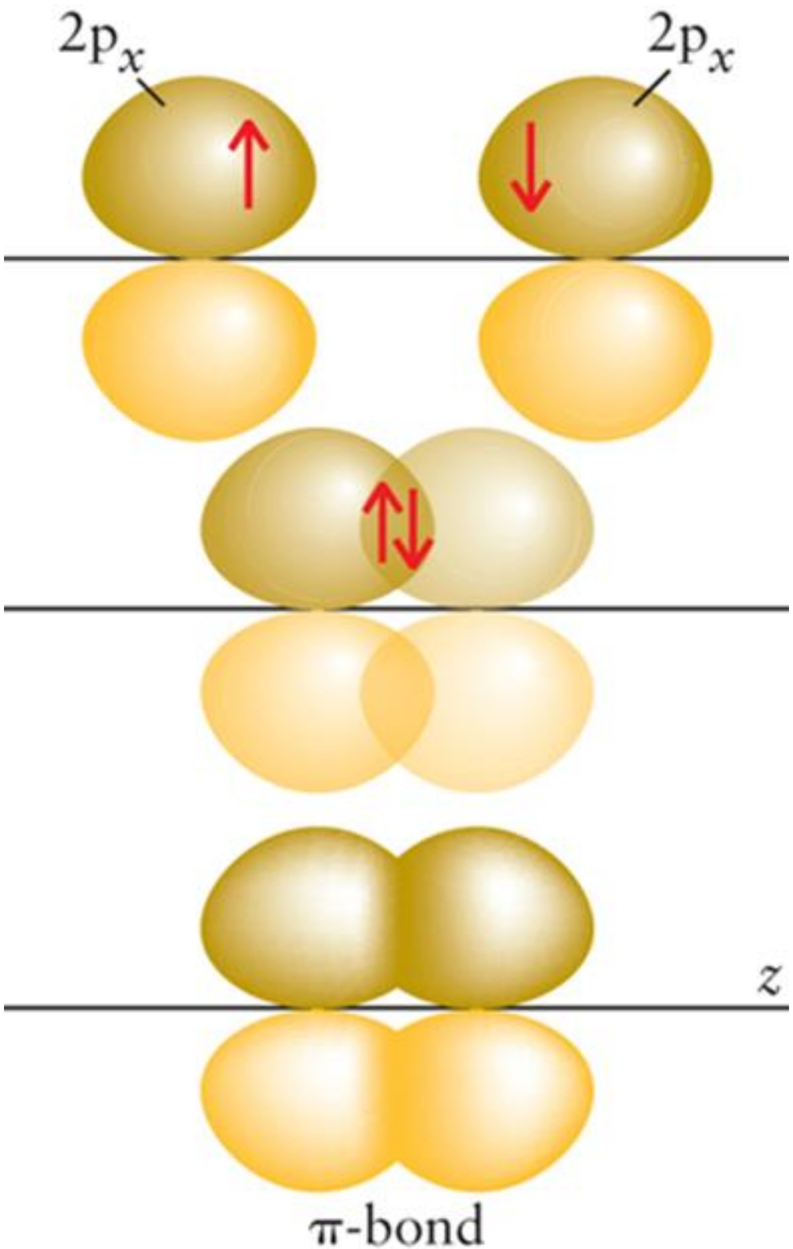
There is a single electron in each three 2p-orbitals.

*However, due to **bond angles**, only one of the three orbitals overlaps head-to-head to form a **σ-bond**



A different type of bond in a nitrogen molecule, N_2.

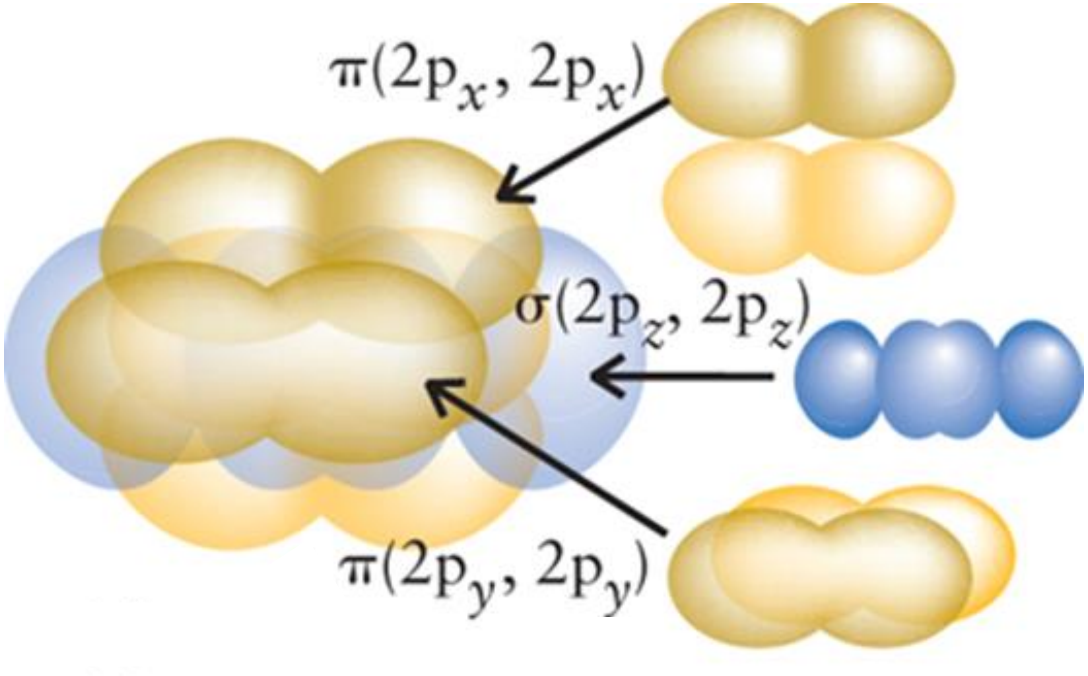




The other two 2p-orbitals ($2p_x$ and $2p_y$) are perpendicular to the internuclear axis.

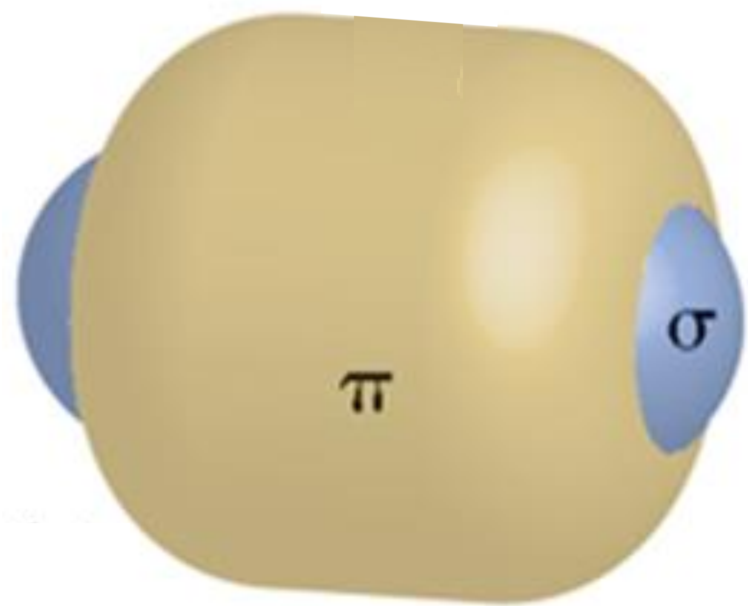
These p-orbitals can overlap only in a side-by-side arrangement.

This overlap results in a "**π-bond**."

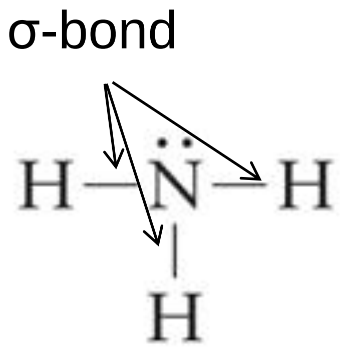


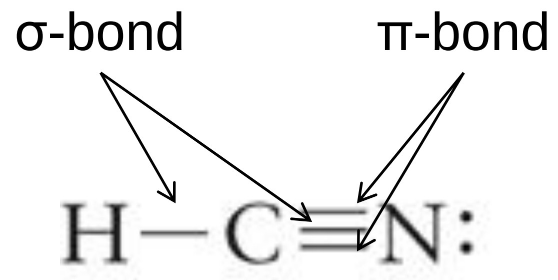
N2

Two π-bond merge forming a long doughnut-shaped cloud surrounding the σ-bond cloud, resembling a **cylindrical hot dog**.



How many σ-bonds and how many π-bonds are there in (a) NH_3 and (b) HCN?





3 @ σ-bond
1 lone pair

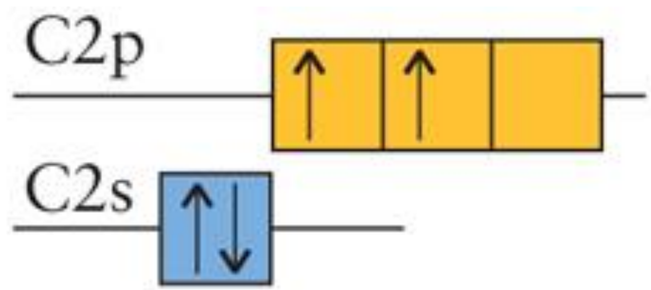
2 @ σ-bond
2 @ π-bond

Valence-bond theory:

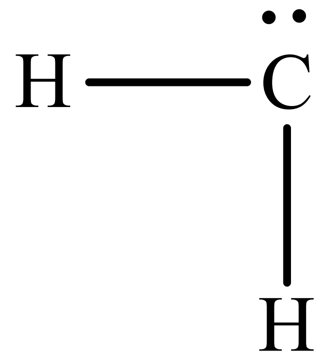
A single bond is a σ-bond.
A double bond is a σ-bond plus one π-bond.
A triple bond is a σ -bond plus two π -bonds.

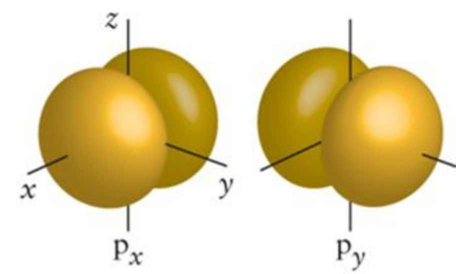
Difficulties with polyatomic molecules in VB theory.

A carbon atom has an electron configuration [He]$2s^2 2p_x^1 2p_y^1$ with four valence electrons.

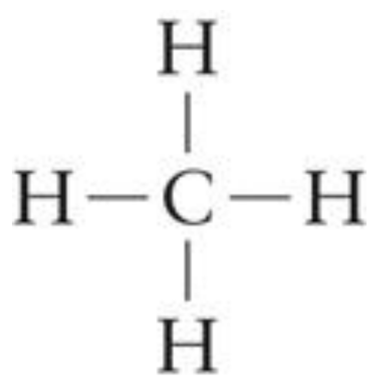


It looks as though a carbon atom should have a valence of 2 and form only two perpendicular bonds.





However, it always has a valence of 4 (it is commonly "tetravalent").



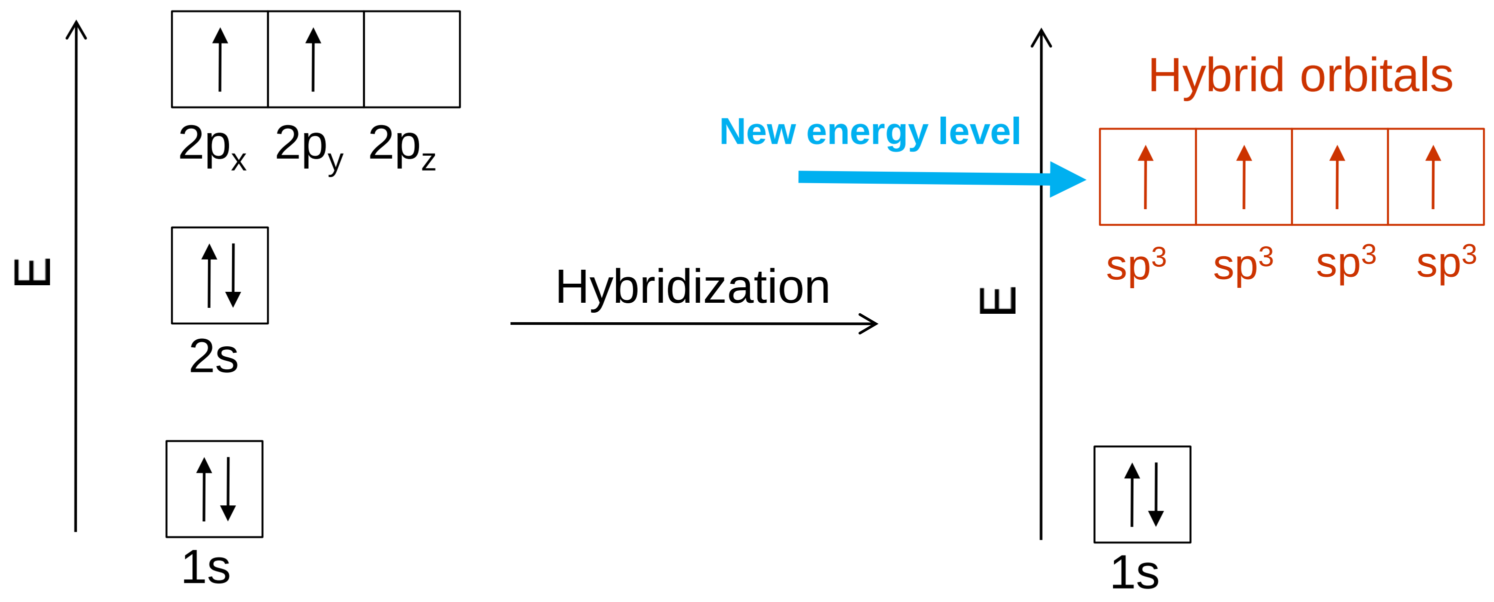
Hybridization - sp^3

CH_4

$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Four single bonds (δ bonds) - Tetrahedral (109.5º)

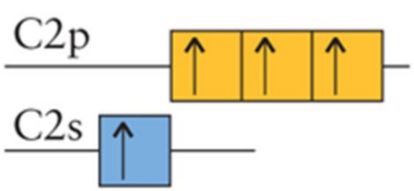
C (6)



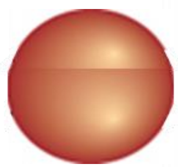
One electron is promoted (relocated) to a higher-energy orbital.

What about the bond angles?

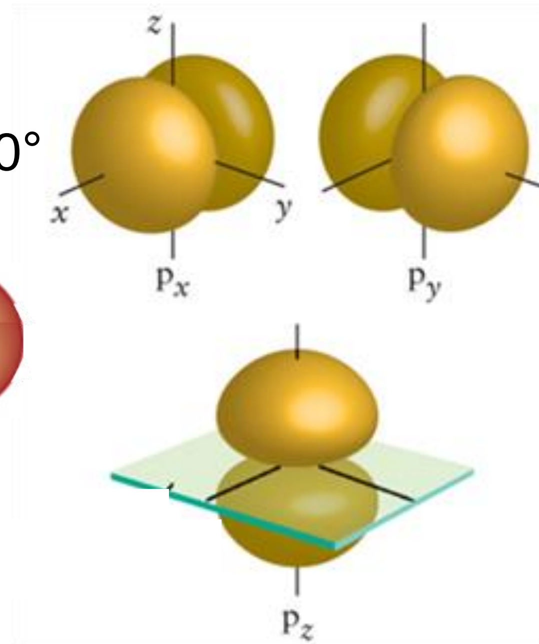
The 90° bond angles of our original orbitals do not match our observed 109.5° bond angles.



90°

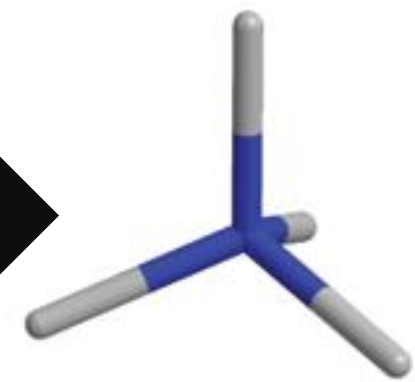


s



?

109.5°



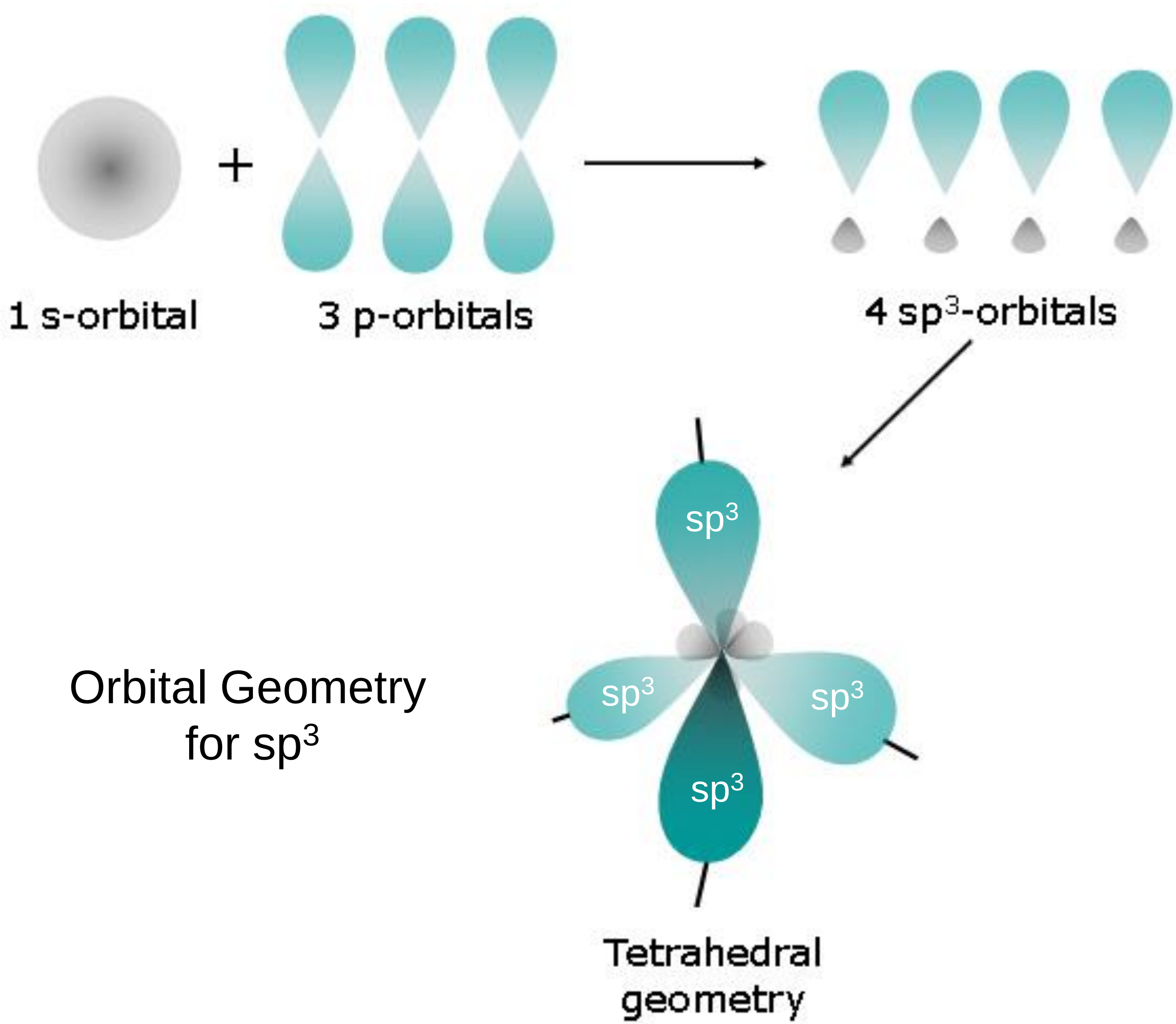
Correct number of orbital

Shape of the orbitals is wrong

Merging these two ideas together

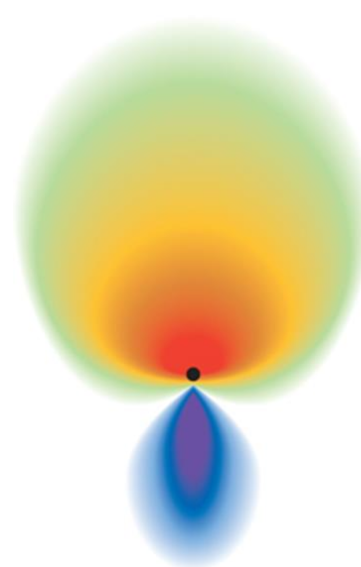
Correct view

Hybridization - sp^3



Orbital Geometry
for sp^3

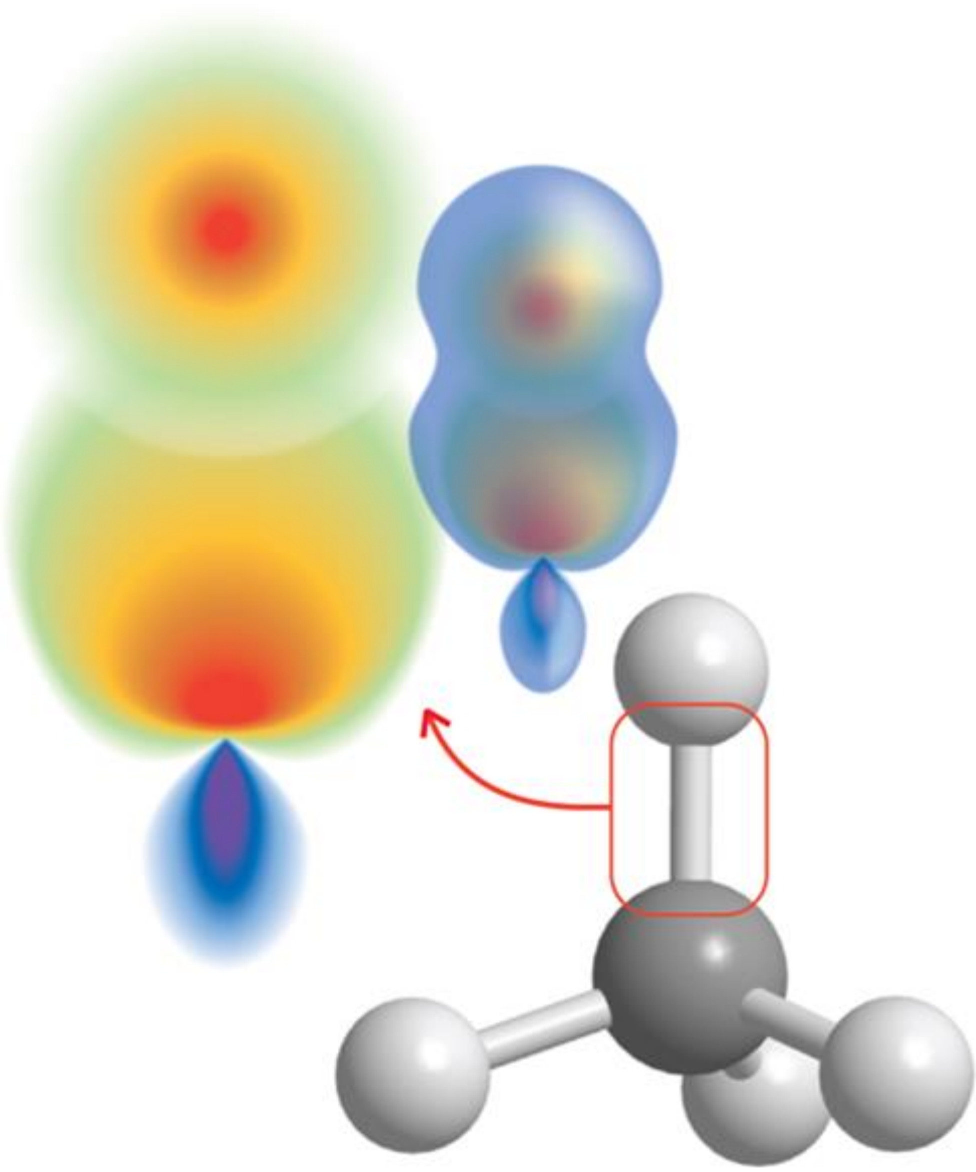
New Orbital



These new patterns are called **hybrid orbitals**.

The wavefunctions overlap (with either positive or negative amplitudes) and constructively reinforced each other.

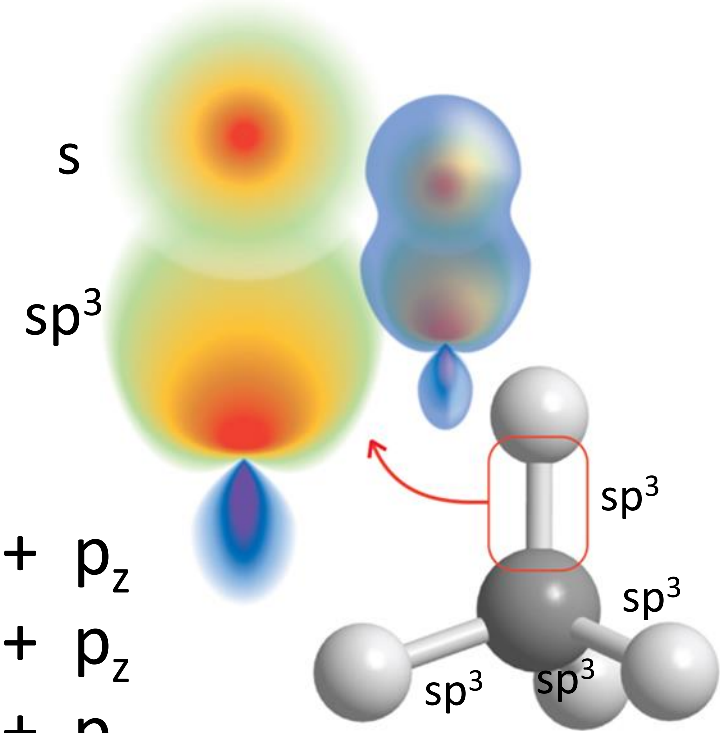
Wavefunctions have the opposite signs, the overall amplitude is reduced and might cancel.



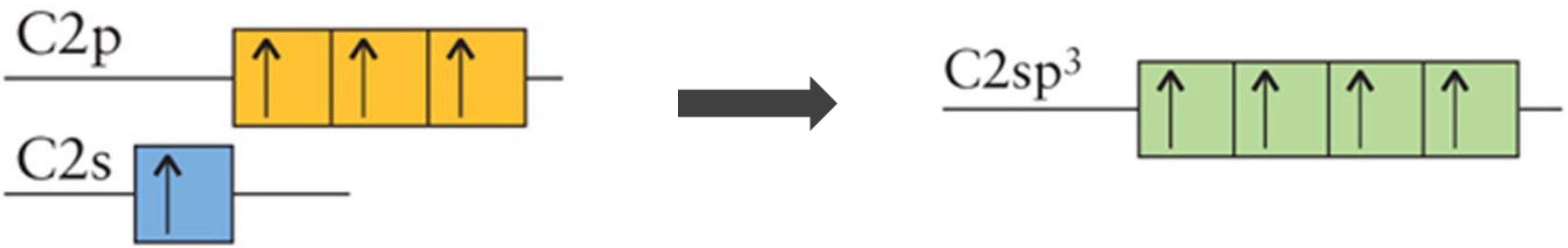
4 new hybrid orbitals

Hybrid orbital names

Each of the four hybrid orbitals, designated h_n. Each of the four hybrid orbital is formed from a linear **combinations** of the four original atomic orbitals:

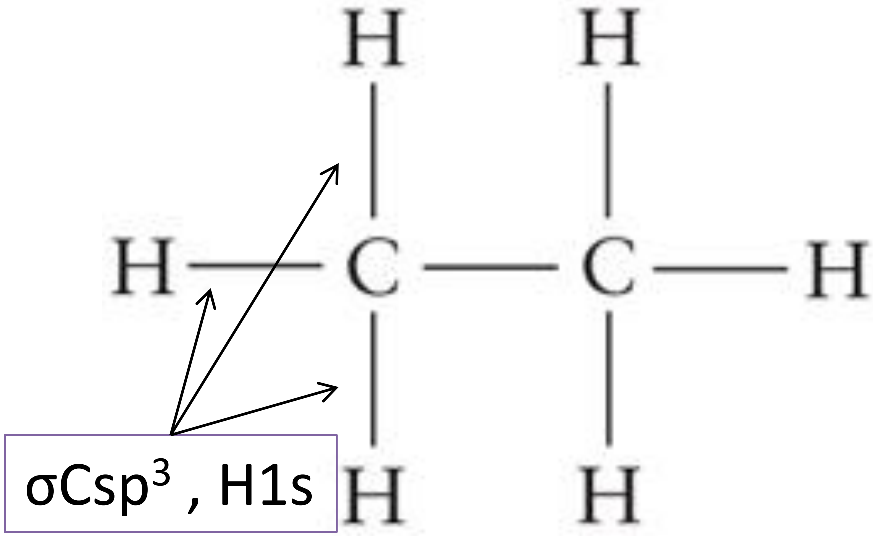


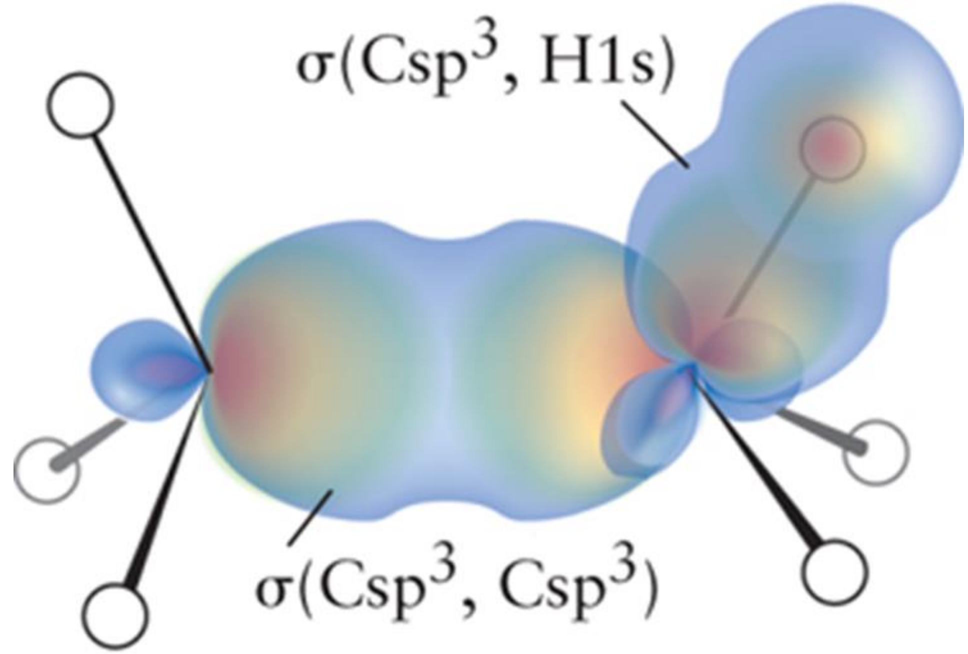
$$\begin{matrix} s \\ p_x \\ p_y \\ p_z \end{matrix} \quad \longrightarrow \quad \begin{aligned} h_1 &= s + p_x + p_y + p_z \\ h_2 &= s + p_x + p_y + p_z \\ h_3 &= s + p_x + p_y + p_z \\ h_4 &= s + p_x + p_y + p_z \end{aligned}$$



$s \quad p_x \quad p_y \quad p_z \longrightarrow sp^3 \quad sp^3 \quad sp^3 \quad sp^3$

Atomic orbitals — Hybrid orbitals

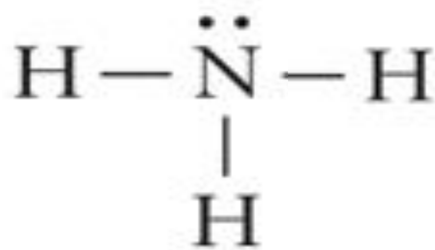




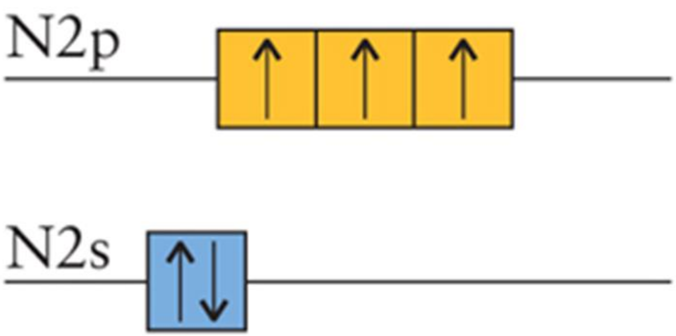
s p_x p_y p_z → sp^3 sp^3 sp^3 sp^3

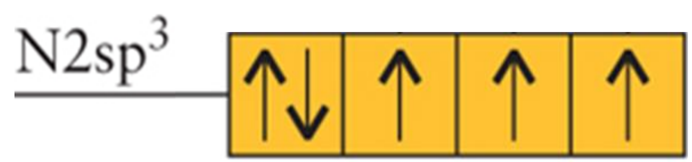
Atomic orbitals Hybrid orbitals

For every sigma bond we need a hybrid orbital.



3 @ $\sigma N sp^3$, H1s





s p_x p_y p_z

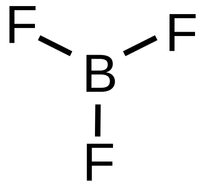
Atomic orbitals

sp^3 sp^3 sp^3 sp^3

Hybrid orbitals

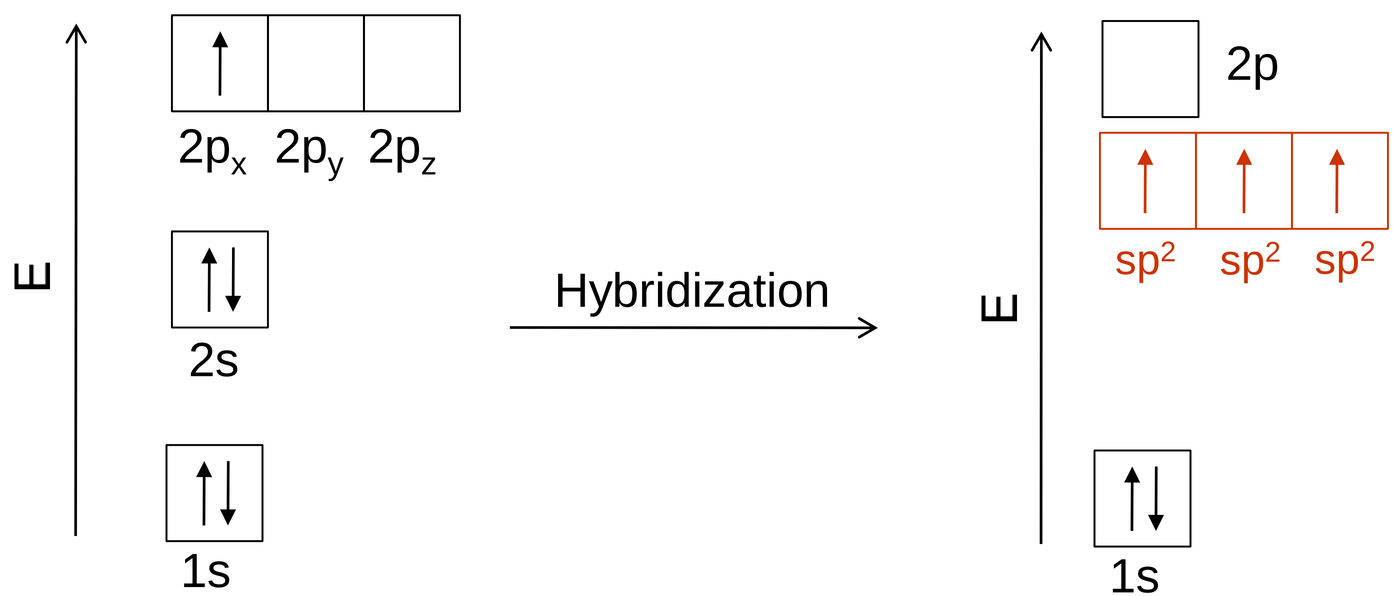
Hybridization - sp^2

BF_3



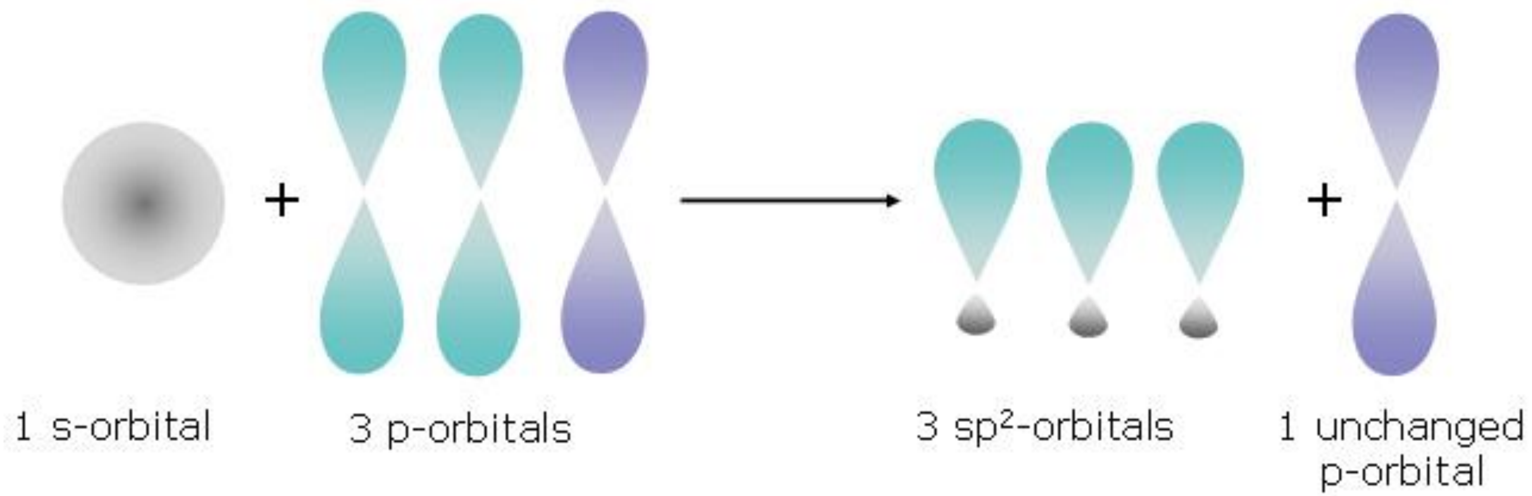
Three single bonds (δ bonds) - Trigonal Planar (120º)

B (5)



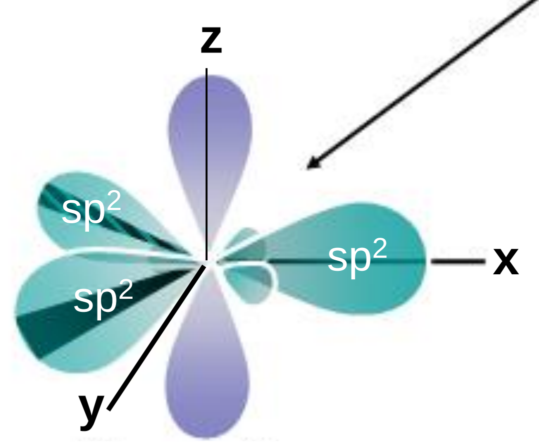
One electron is promoted (relocated) to a higher-energy orbital.

Hybridization - sp^2



not hybridized

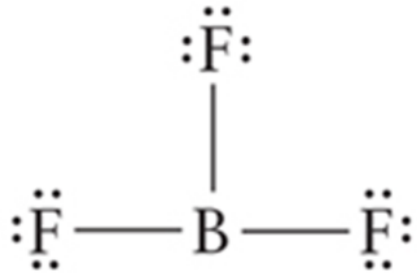
Orbital Geometry for sp^2



Trigonal Planar geometry

Hybridization - sp^2

sp^2 hybrid orbitals



only 3 sigma bonds form, one p-orbital is not hybridized.

$$h_1 = s + 2^{½} p_y$$

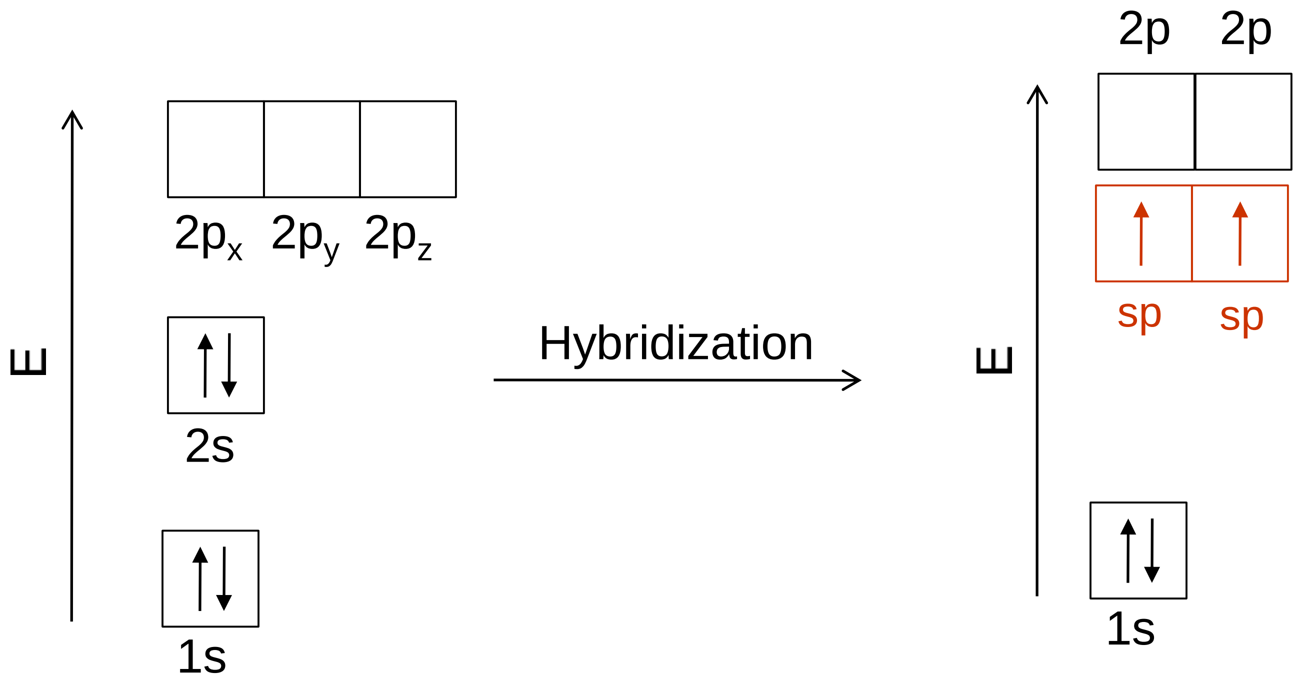
$$h_2 = s + \left(\frac{3}{2}\right)^{½} p_x - \left(\frac{1}{2}\right)^{½} p_y$$

$$h_3 = s + \left(\frac{3}{2}\right)^{½} p_x - \left(\frac{1}{2}\right)^{½} p_y$$

Hybridization - sp

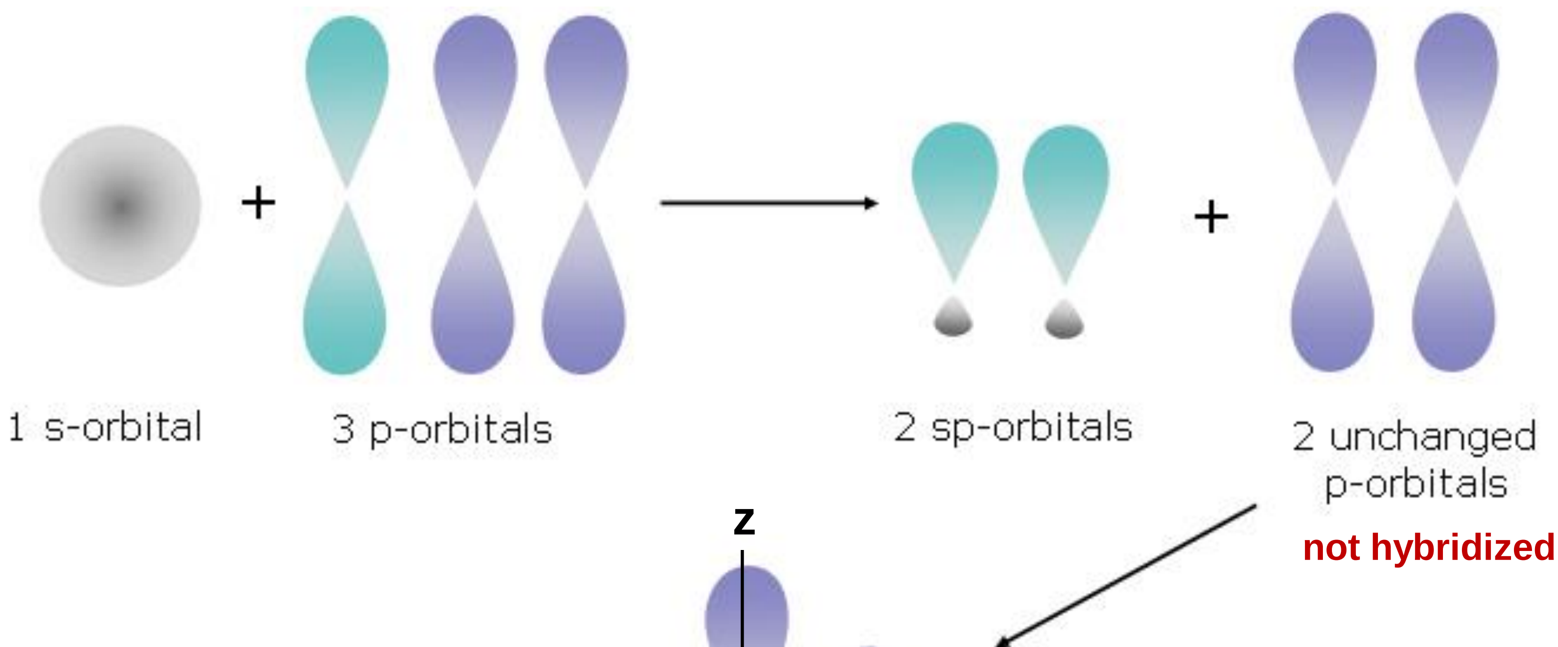
$BeCl_2$ Cl–Be–Cl Two single bonds (δ bonds) - Linear (180º)

Be (4)

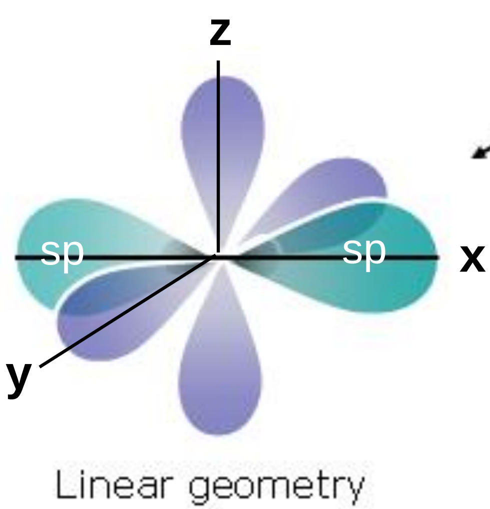


One electron is promoted (relocated) to a higher-energy orbital.

Hybridization - sp

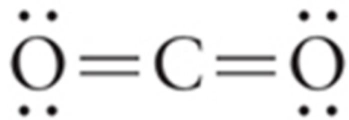


Orbital Geometry
for sp



Hybridization - sp

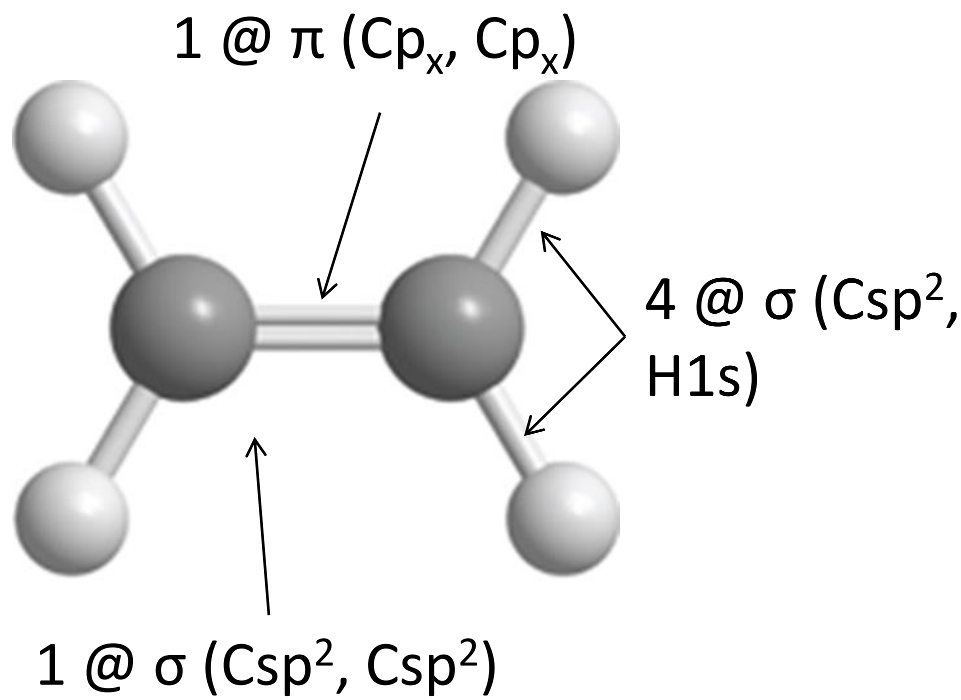
sp hybrid orbitals

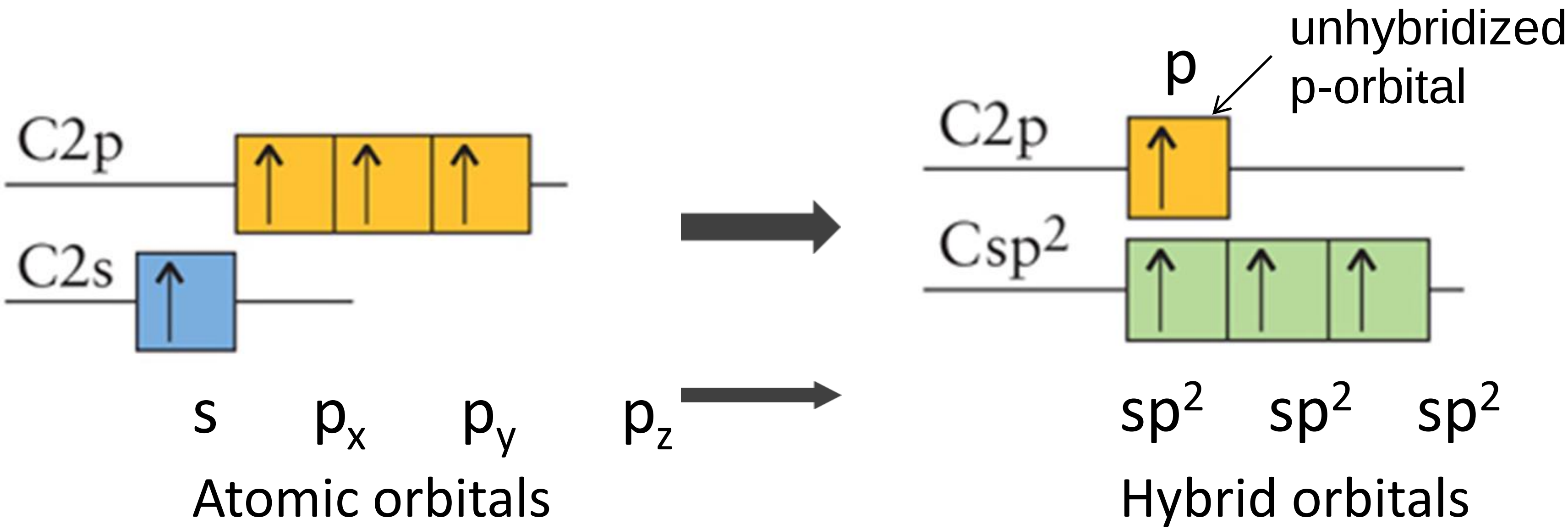


only 2 sigma bonds form, and two p-orbitals are not hybridized.

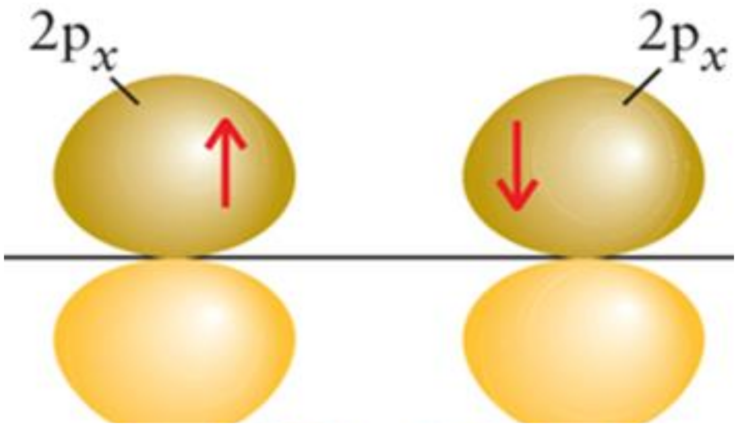
$$h_1 = s + p_x$$
$$h_2 = s - p_x$$

Suggest a structure in terms of hybrid orbitals for each carbon atom in ethyne, C_2H_2 .

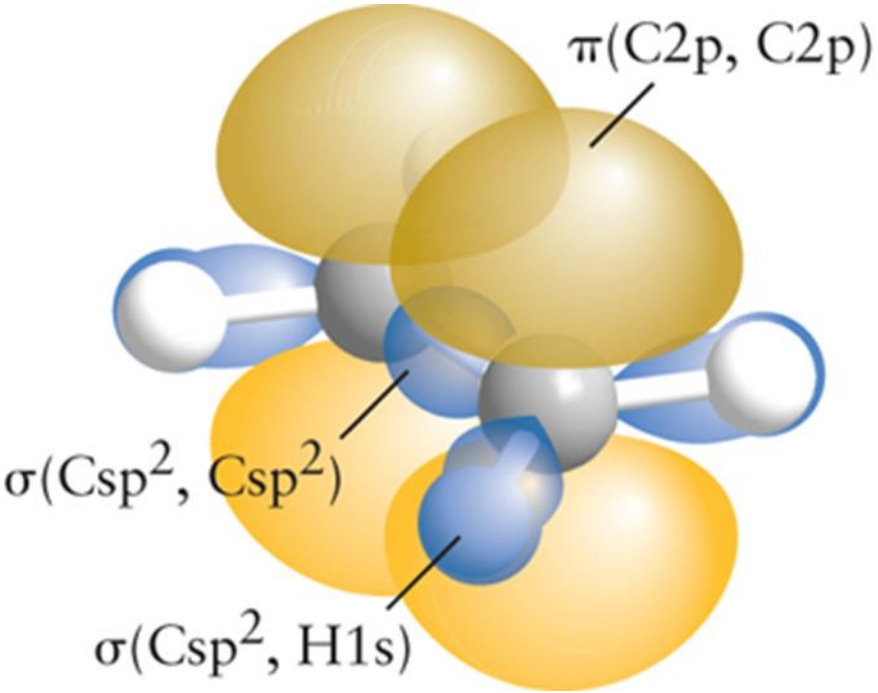


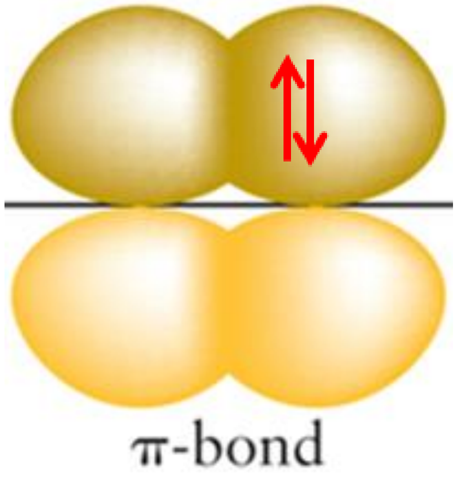


The unhybridized 2p-orbital, is perpendicular to the C-C plane.



The electrons in the two unhybridized 2p-orbitals form a π-bond through side-by-side overlap.





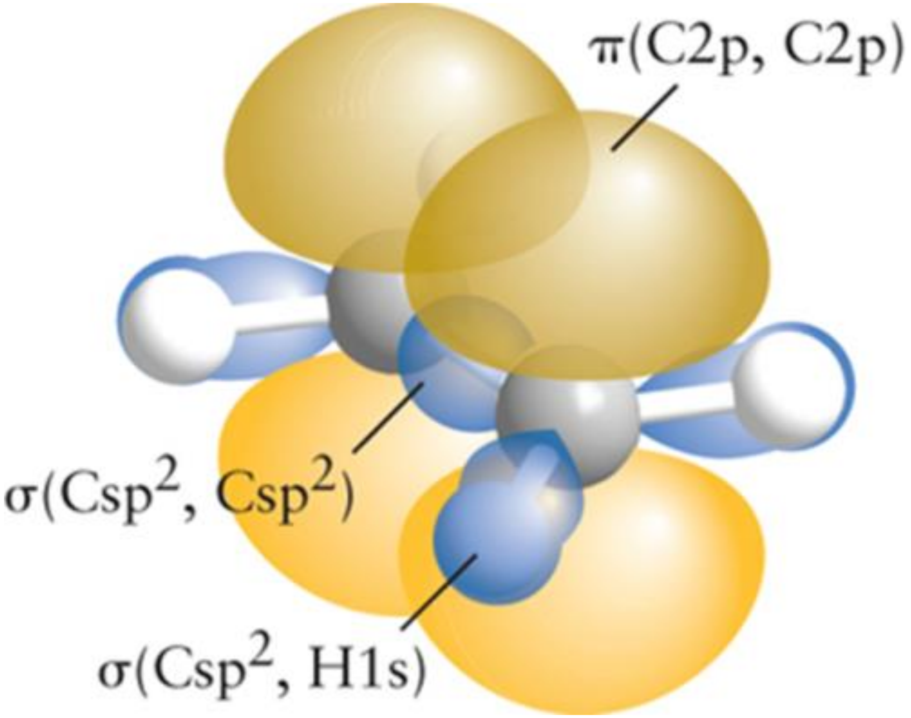
π-bond spin-pairing

Double bond properties

Double bond prevents one part of a molecule from rotating around another.

The **π-bonds** of ethene, hold the entire molecule flat.

Rotation around the C-C bond is prohibited.



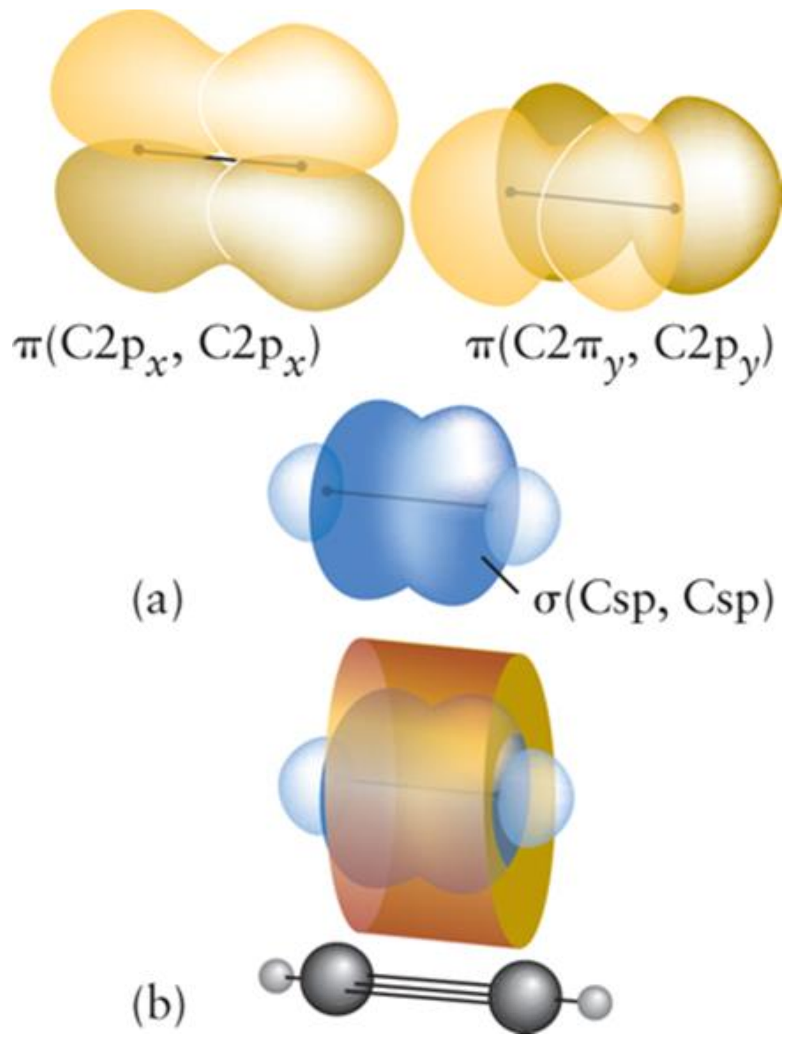
Triple bond properties

Ethyne HC-CH (acetylene) has sp hybridized carbon.

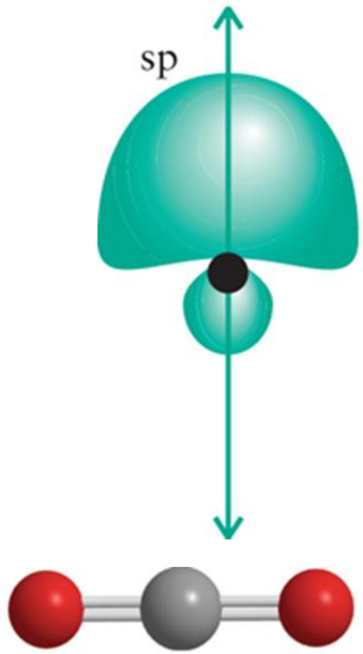
Each carbon has two remaining p-orbitals, each forms two π-bonds.

The two π orbitals built from p-orbitals, form a cylindrical symmetry.

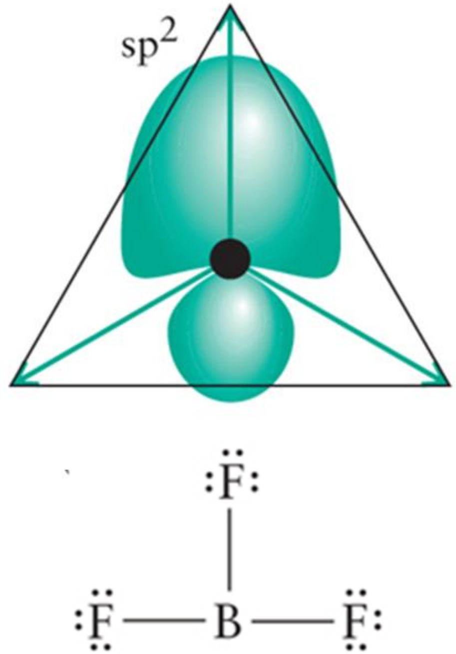
The triple bond is weaker than the sum of three carbon–carbon single bonds.



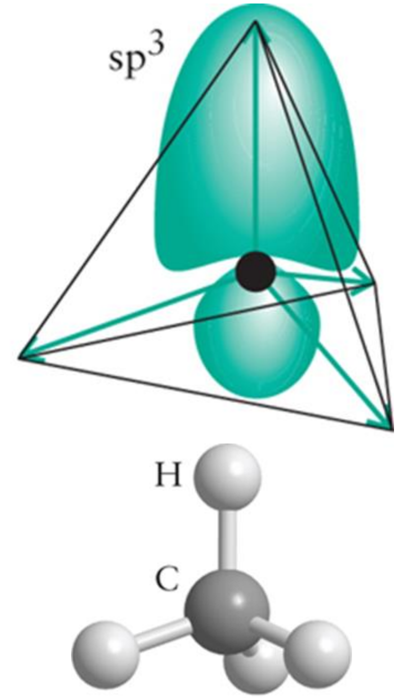
hybridization orbitals showing the amplitude of a single wavefunction.



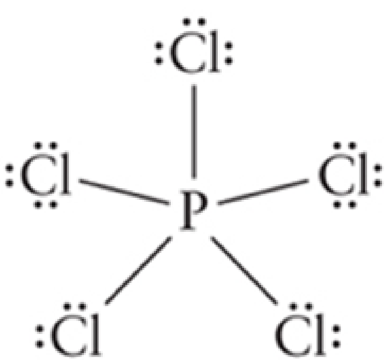
2 σ-bonds
linear



3 σ-bonds
trigonal planar

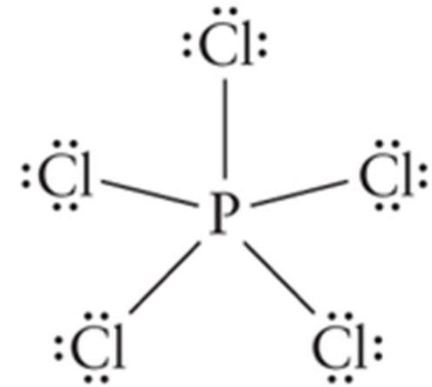


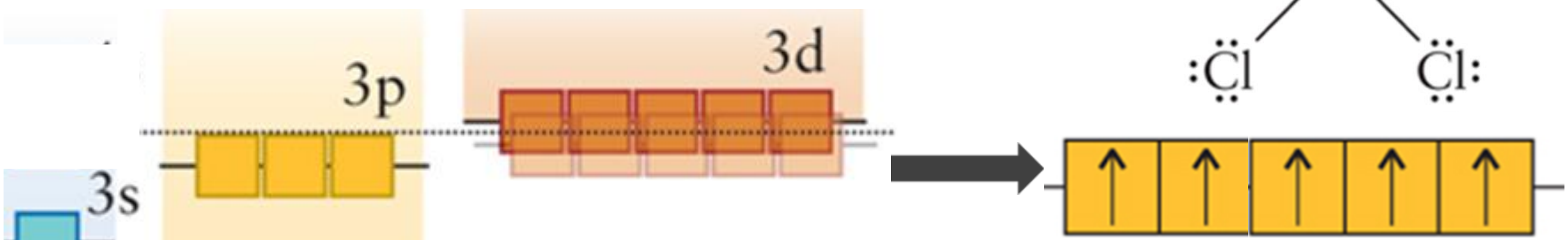
4 σ-bonds
tetrahedral



How do we account of 5 σ-bonds in trigonal bipyramidal or 6 σ-bonds in octahedral compounds?

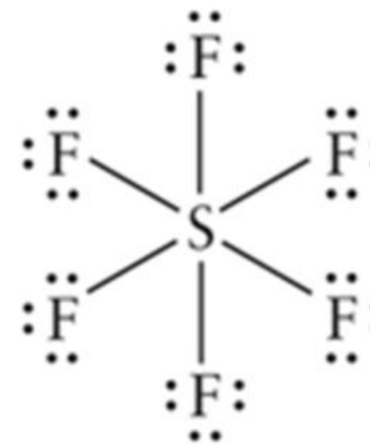
Trigonal bipyramidal have five electron pairs, so one d-orbital along with the valence s- and p-orbitals of the atom.

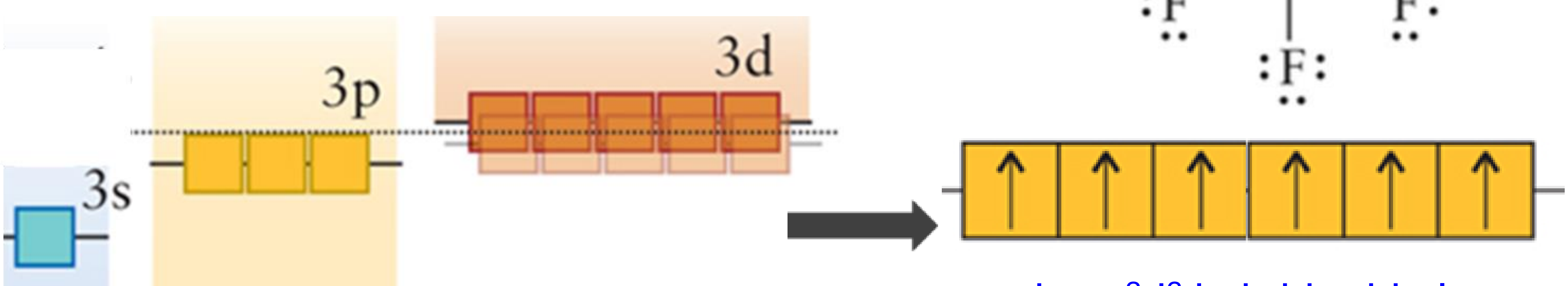




five sp^3d hybrid orbitals

six electron pairs, in an octahedral, use two d-orbitals in addition to the valence s- and p-orbitals to form.





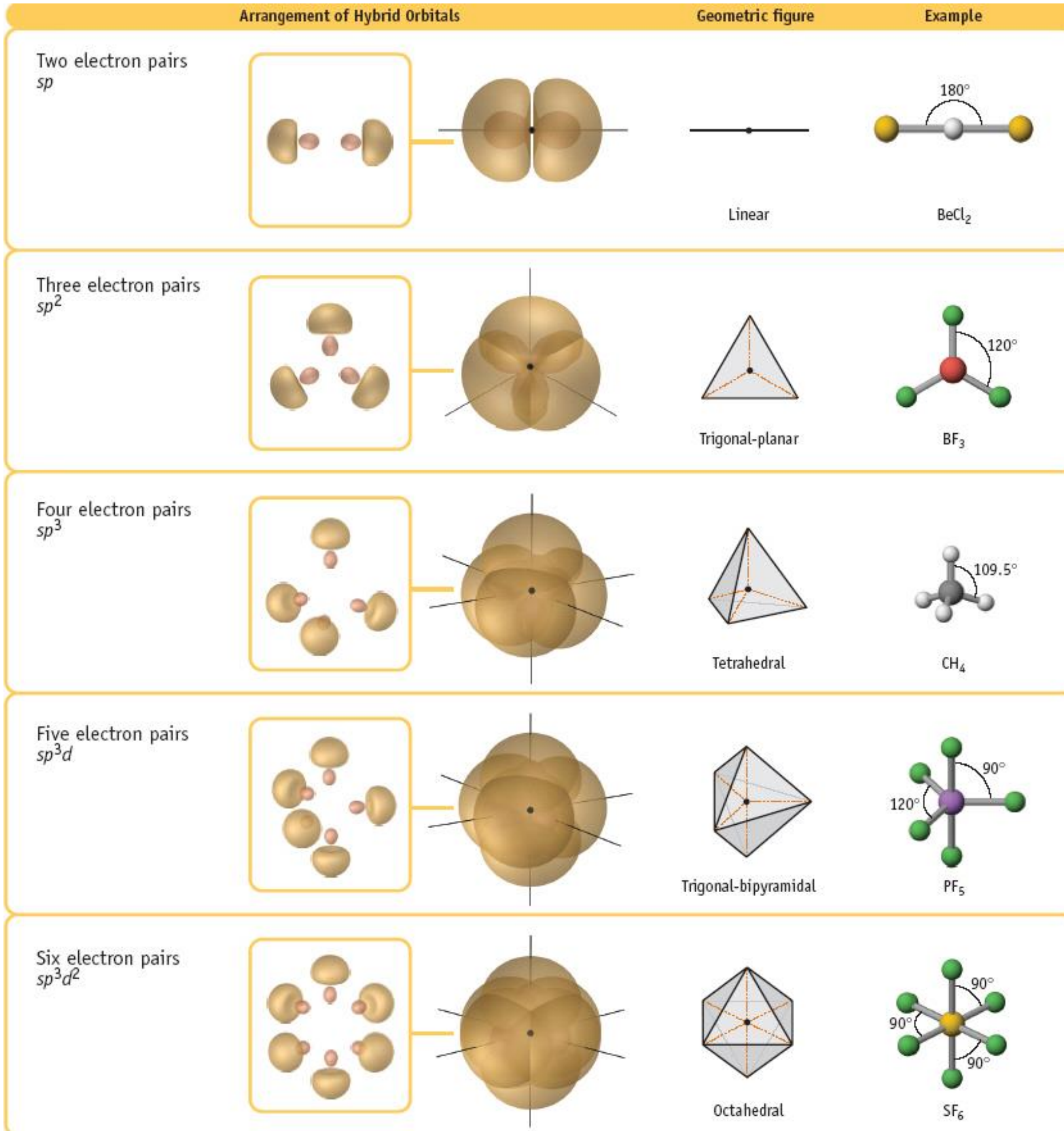
six sp^3d^2 hybrid orbitals

Summery

Number of electron regions = Number of hybrid orbitals

Molecular Geometry	Number of electron regions	Hybridization of central atom	Number of hybrid orbitals
Linear	2	sp	2
Trigonal Planar	3	sp^2	3
Tetrahedral	4	sp^3	4
Trigonal Bipyramidal	5	sp^3d	5
Octahedral	6	sp^3d^2	6

Summery


Arrangement of Hybrid Orbitals
Geometric figure
Example
Two electron pairs
sp
180°
Linear
$BeCl_2$
Three electron pairs
sp^2
120°
Trigonal-planar
BF_3
Four electron pairs
sp^3
109.5°
Tetrahedral
CH_4
Five electron pairs
sp^3d
90°
120°
Trigonal-bipyramidal
PF_5
Six electron pairs
sp^3d^2
90°
90°
90°
Octahedral
SF_6

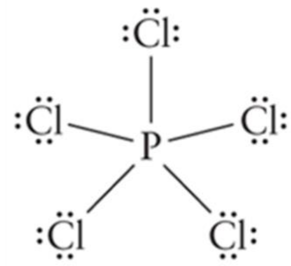
Summery

To Find the hybridization of the central atom:

1. Draw the Lowis structure.
2. Determine the electron regions around the central atom.
3. Identify the molecular shape (molecular geometry)
4. # of electron regions = # of hybrid orbitals
5. Construct the hybrid orbitals, starting with s-orbital, and proceeding to the p- and d-orbitals.

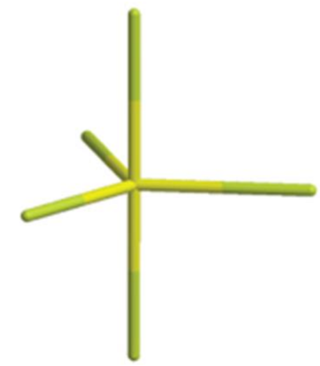
Sample exercise: Assigning a hybridization scheme for phosphorous in PCl_5?

1. Draw the Lewis structure.



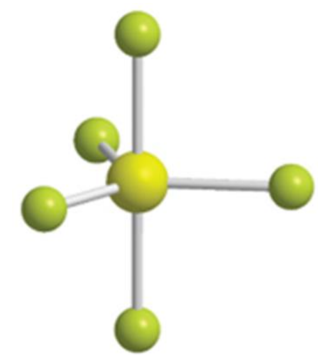
2. Determine the electron regions around the central atom.

Trigonal bipyramidal



3. Identify the molecular shape.

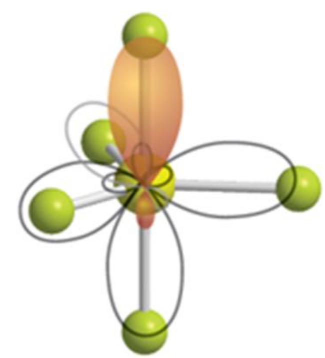
Trigonal bipyramidal



4. Select the same number of atomic orbitals as there are hybrid orbitals.

5

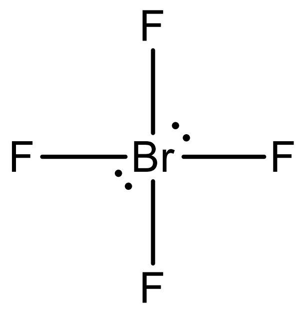
5. Construct the hybrid orbitals, starting with the s-orbital, then p- and d-orbitals.

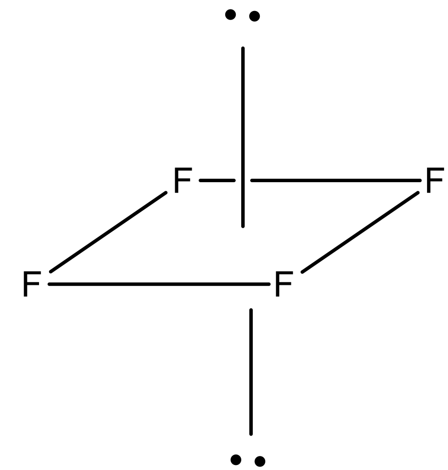


five sp^3d hybrid orbitals

Sample exercise: Assigning a hybridization scheme for bromine in BrF_4^- ?

1. Draw the Lewis structure.



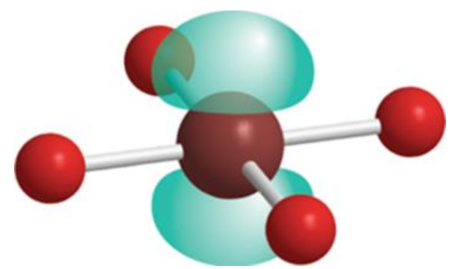


2. Determine the electron regions around the central atom.

octahedral

3. Identify the molecular shape.

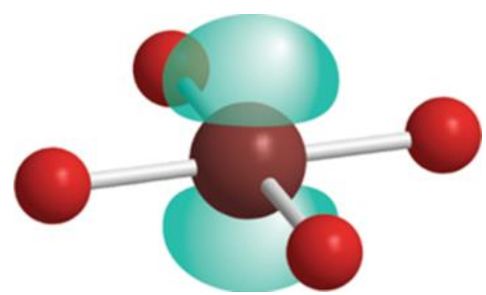
Square planar



4. Select the same number of atomic orbitals as there are hybrid orbitals.

6

5. Construct the hybrid orbitals, starting with the s-orbital, then p- and d-orbitals.



6 sp^3d^2 hybrid orbitals

Characteristics of Multiple Bonds

Atoms of the Period 2 elements C, N, and O readily form double bonds (especially oxygen).

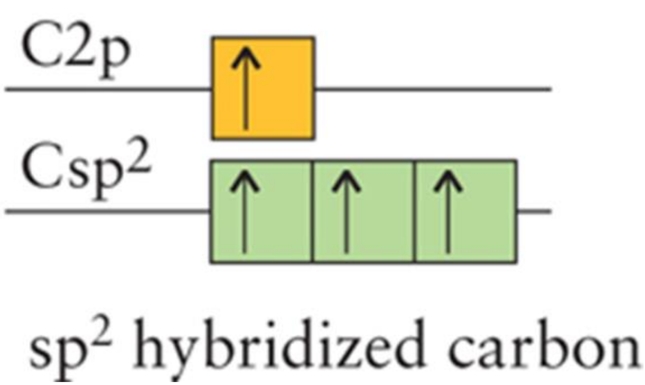
However, double bonds are rarely found between atoms of elements in Period 3 and later periods, because the atoms are so *large* and *bond lengths consequently are so great* that it is difficult for their p-orbitals to take part in effective side-by-side overlap.

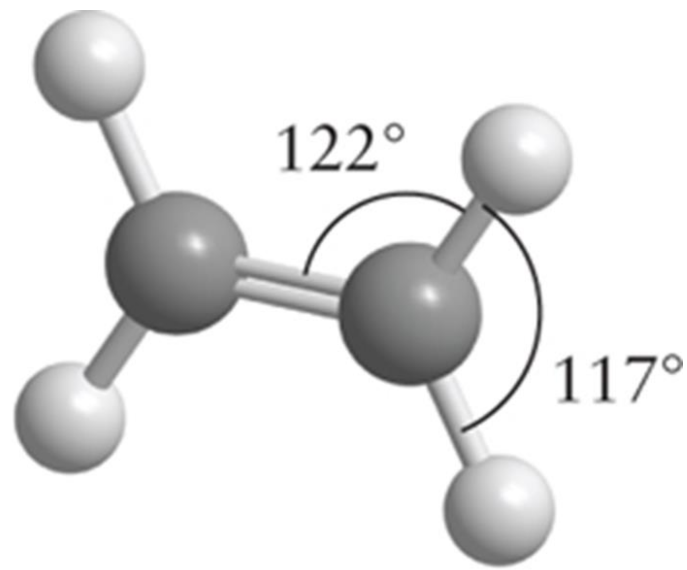
Characteristics of Multiple Bonds

Ethene, $CH_2{=}CH_2$ has a double bond.

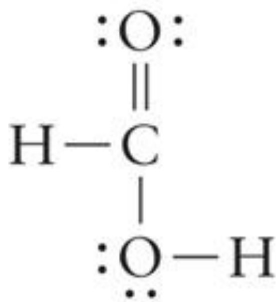
All six atoms in ethene lie in the same plane, with a bond angles near 120°.

This angle suggests a trigonal planar electron arrangement and sp^2 hybridization for each C atom.





Account for the structure of a formic acid molecule, HCOOH, in terms of hybrid orbitals, bond angles, and σ- and π-bonds.

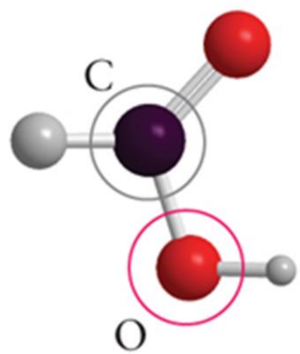


O has 4 groups or sp^3

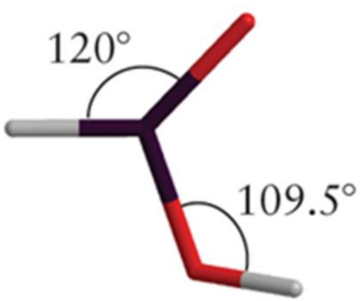
C has 3 groups or sp^2

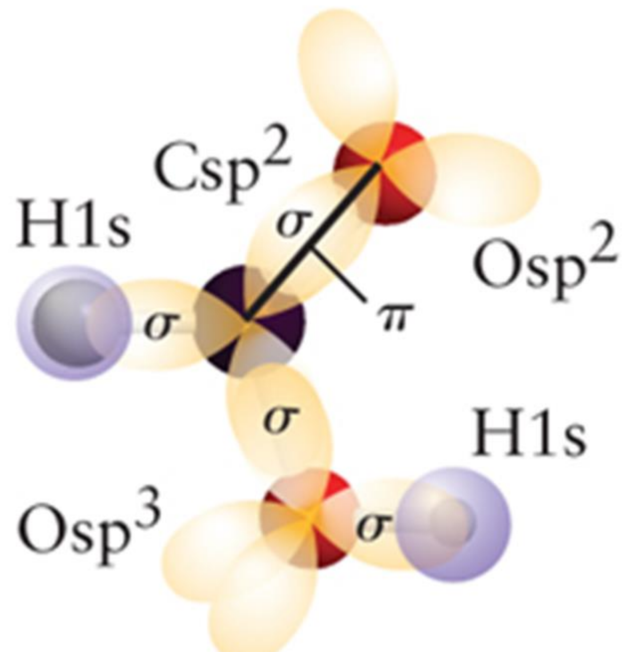
Draw the Lewis structure.

Use the VSEPR model to identify the electron arrangements around the central C and O atoms.



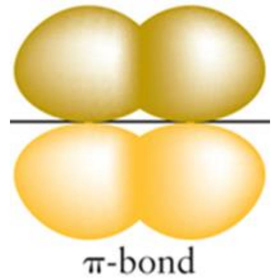
Identify the hybridization and bond angles.

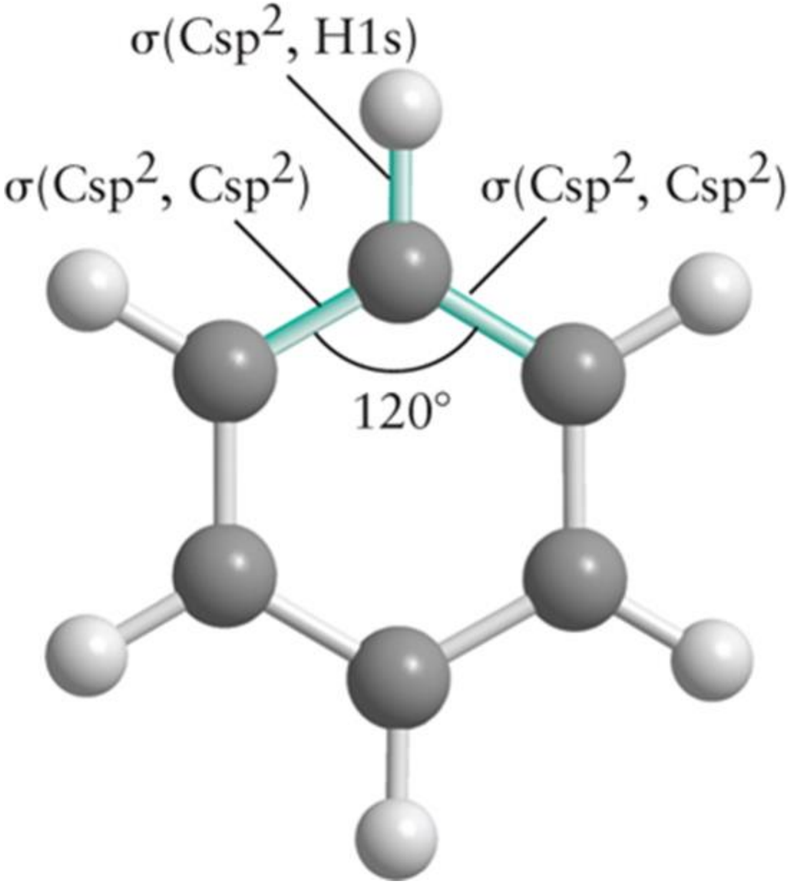


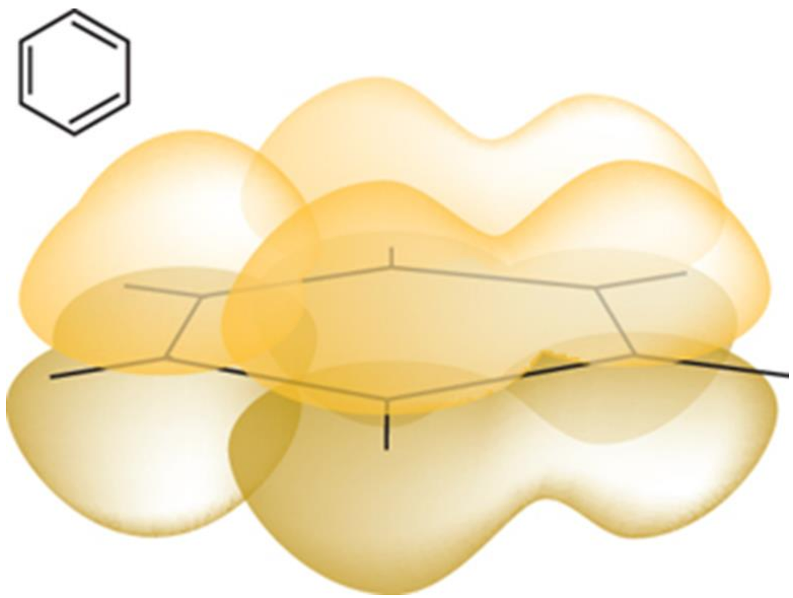


Form the bonds.

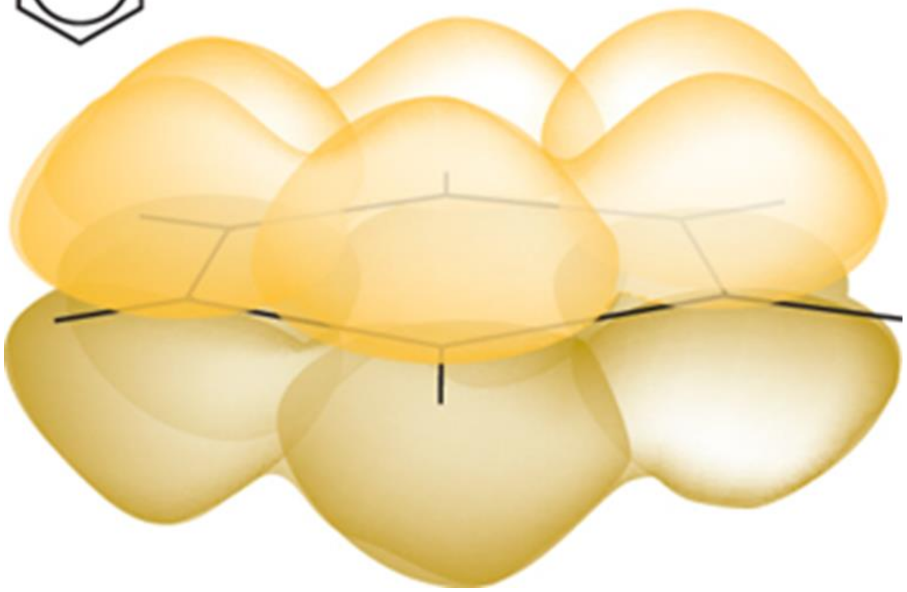
In benzene, the C and H atoms all lie in the same plane, and carbons join forming a ring.







The Kekulé structures of benzene show 6 hybridized sp^2 carbon atoms.



Since every carbon neighbor has a π-bond, there are two or **resonance hybrid** structures.

The electrons are **spread around the entire ring** through the **π-bonds** .