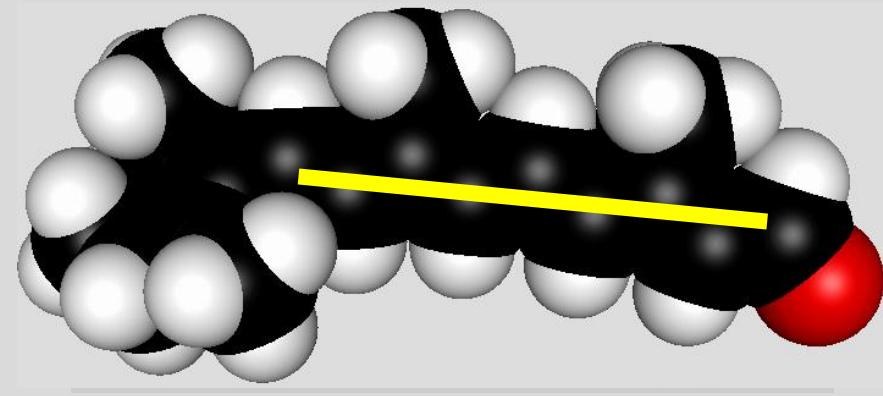
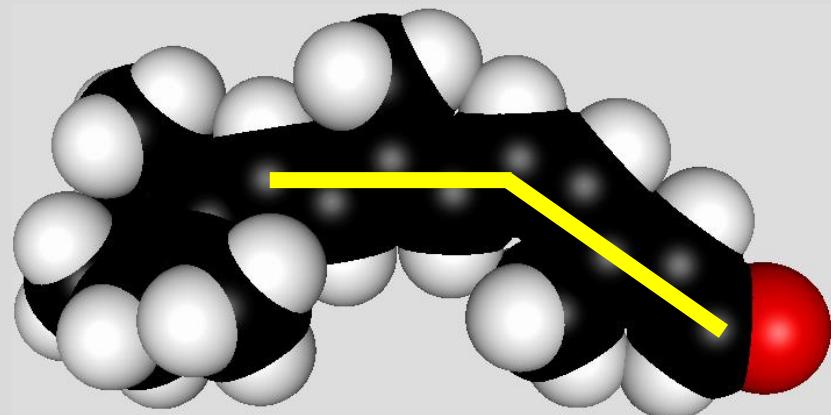


Lecture 4: Basic Concept of Chemical Bonding (Part II) & Molecular Geometry and Bonding Theories



The Chemistry of Our Vision:

Upon absorption of visible-light photons, the geometry of the retinal molecule will change.

This delicate geometrical change caused by the exposure to visible light is an important chemical process for stimulating our eyes.

Outline (Part II)

Basic Concept of Chemical Bonding

- Lewis Structures for Molecules
- Resonance Structures
- Exceptions to the Octet Rule
- Strength and Lengths of Bonds

Outline (Part II)

Basic Concept of Chemical Bonding

- Lewis Structures for Molecules
 - Brief Review
 - Drawing Procedure
 - Formal Charge
- Resonance Structures
- Exceptions to the Octet Rule
- Strength and Lengths of Bonds

Brief Review: Lewis Symbols for Elements

- The **Lewis symbol** for an “**element**” consists of *the element’s chemical symbol* plus *a dot for each valence electron*.
- The dots are placed on the four sides of the symbol—top, bottom, left, and right—and **each side can accommodate up to two electrons (all four sides are equivalent)**.

Table 8.1 Lewis Symbols

Group	Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
1A	Li	[He]2s ¹	Li·	Na	[Ne]3s ¹	Na·
2A	Be	[He]2s ²	·Be·	Mg	[Ne]3s ²	·Mg·
3A	B	[He]2s ² 2p ¹	·B·	Al	[Ne]3s ² 3p ¹	·Al·
4A	C	[He]2s ² 2p ²	·C·	Si	[Ne]3s ² 3p ²	·Si·
5A	N	[He]2s ² 2p ³	·N:	P	[Ne]3s ² 3p ³	·P:
6A	O	[He]2s ² 2p ⁴	·O:	S	[Ne]3s ² 3p ⁴	·S:
7A	F	[He]2s ² 2p ⁵	·F:	Cl	[Ne]3s ² 3p ⁵	·Cl:
8A	Ne	[He]2s ² 2p ⁶	·Ne:	Ar	[Ne]3s ² 3p ⁶	·Ar:

Brief Review: Octet Rule

Octet Rule

Fact: Noble gases (such as He, Ne, Ar) show *high ionization energies* and *low electron affinities (positive value)*, and they are chemically inert (i.e. very stable).

Group	Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol	
1A	Li	[He] $2s^1$	Li \cdot	Na	[Ne] $3s^1$	Na \cdot	→ <i>Low ionization energy</i>
			
7A	F	[He] $2s^2 2p^5$.F:	Cl	[Ne] $3s^2 3p^5$.Cl:	→ <i>High electron affinity (very negative value)</i>
8A	Ne	[He] $2s^2 2p^6$:Ne:	Ar	[Ne] $3s^2 3p^6$:Ar:	

Theory: The inertness of noble gases results from their stable electron configurations; each (except helium) has **EIGHT** electrons in its outermost shell.

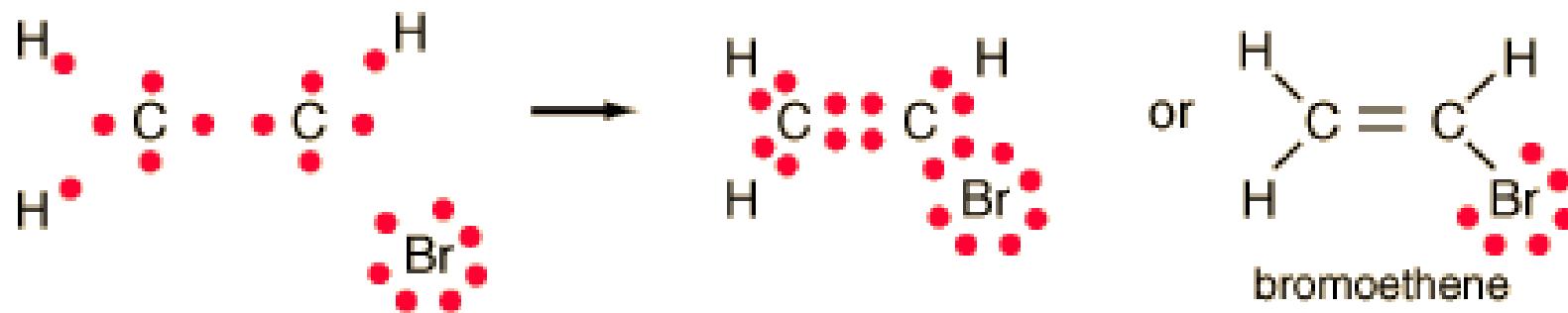
Deduction: Elements should become less reactive when they alter their electron structures to that of a noble gas.

Atoms tend to gain, lose, or share electrons until they acquire EIGHT electrons in their valence shells.

Lewis Structures for Molecules

How to draw Lewis structure of molecules based on Lewis symbols of elements & Octet rule?

Any rule?



A given molecule can be made up of heteroatoms connecting by single/double/triple bond (or lone pair on atom itself)



Drawing Procedure for Molecular Lewis Structures

1. Sum the valence electrons from all atoms of the given molecule.

Use the periodic table to determine the total number of valence electrons.

2. Write the symbols for the atoms and connect them with a **single bond**

A line costs two electrons (i.e. bonding electrons)

3. Complete the octets around all the atoms (not applicable to H/B/Be...).

Each dot represents a nonbonding electron!

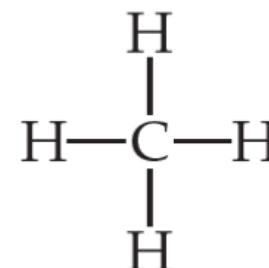
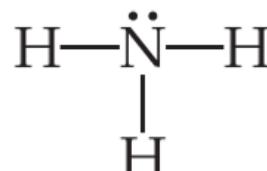
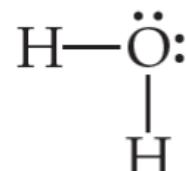
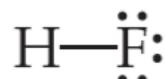
H can only have one pair of electrons on it!

4. If not enough electrons to give an atom an octet, try **multiple bonds.**

Use nonbonding electrons left on the atoms to form double/triple bonds.



Sum of valence electrons = 8 e⁻

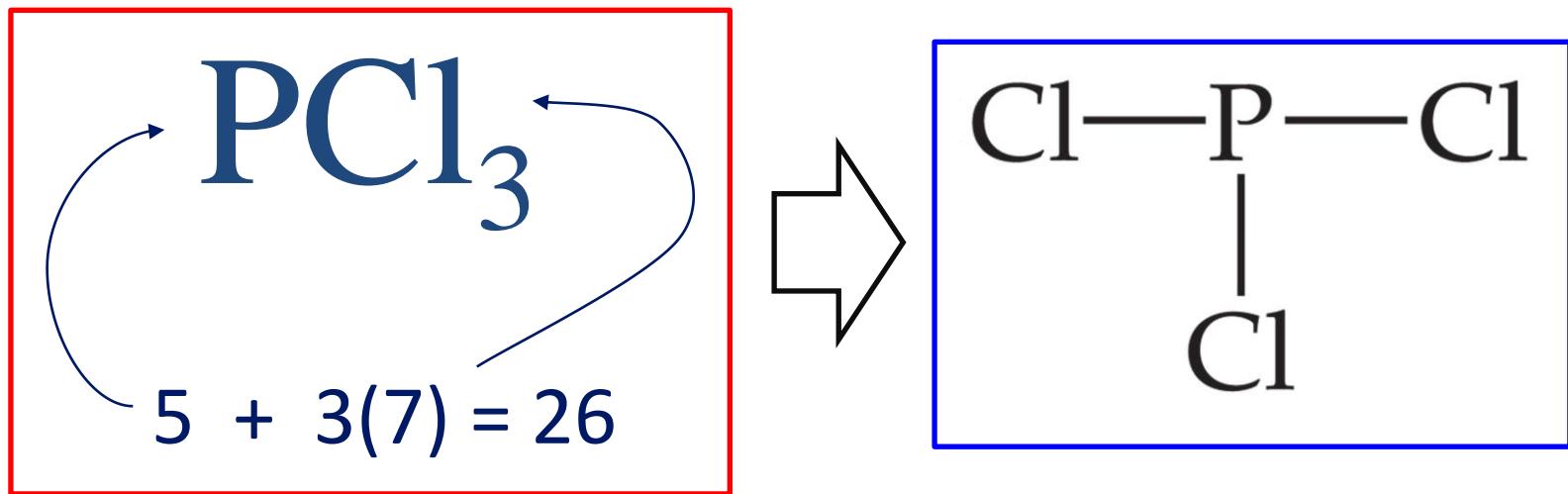


Drawing Lewis Structures

Example (single bond): Phosphorus Trichloride (PCl_3)

1. Sum the valence electrons from all atoms of the given molecule.

Use the periodic table to determine the total number of valence electrons.



2. Write the symbols for the atoms and connect them with a single bond

A line costs two bonding electrons

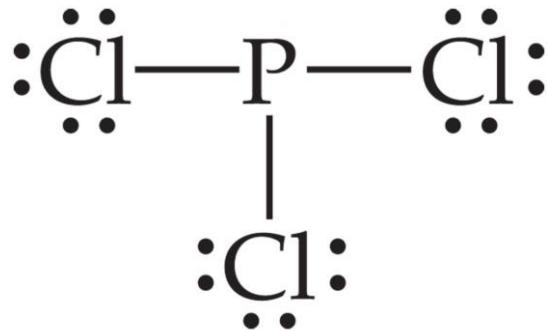
Keep track of the electrons: $26 - 6$ (three bonding pairs) = **20 left over**

Drawing Lewis Structures

Example (single bond): Phosphorus Trichloride (PCl_3)

3. Complete the octets around all the atoms.

Each dot left represent a nonbonding electron!

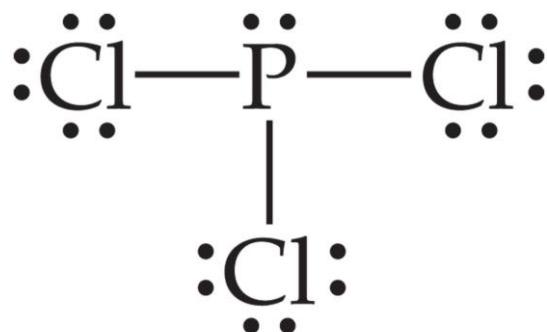


Complete the octets around the **outer Cl atoms**.

(20 left over from before):

Use these to complete the chlorine octets:

$20 - 18 = 2 \text{ left over}$



Complete the octet of the **central P atom** using the 2 remaining electrons.

(2 left over from before):

$2 - 2 = 0 \text{ left over (no step 4 needed)}$

Lewis Structure for Phosphorus Trichloride (PCl_3)!

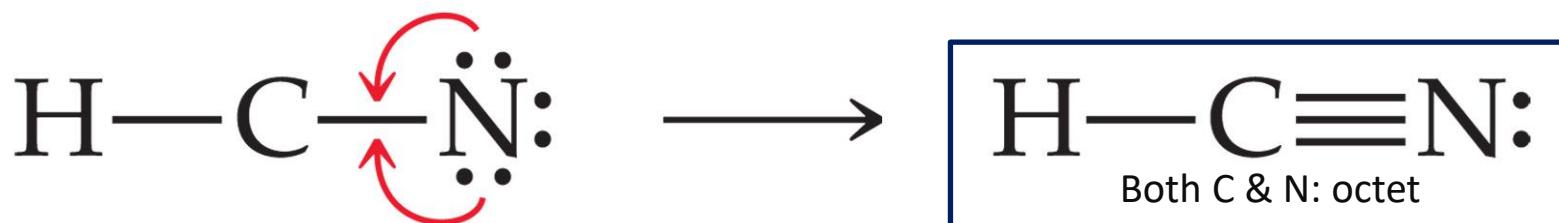
Drawing Lewis Structures

Example (multiple bond): Hydrogen Cyanide (**HCN**).

1. Sum the valence electrons from all atoms ($1 + 4 + 5 = 10 \text{ e}^-$)
 2. Write the atom symbols and connect them with a single bond (6 e^- left)
 3. Complete the octets around all the atoms.



- 4. If not enough electrons to give an atom an octet, try multiple bonds.**



Lewis Structure for Hydrogen cyanide (HCN)!

Lewis Structures: Formal Charges

- When a molecule has more than one possible Lewis structure..... e.g. CO_2 below
- Assigning **formal charges** to each atom in the molecule can help us to decide which structure is the most important (or more possible!).

Formal charge calculation for each atom (2 steps!)

- (1) The assigned electrons to atom: count all electrons of its lone pairs & half of the shared electrons with other atoms (i.e. **count 1 for each bond**).
- (2) Subtract that from the corresponding valence electrons and the difference is **its formal charge**.

$$\text{Formal charge} = \text{valence electrons} - \frac{1}{2}(\text{bonding electrons}) - \text{nonbonding electrons}$$

$\ddot{\text{O}}$	=	C	=	$\ddot{\text{O}}$
6	4	6		
6	4	6		

Valence electrons:
-(Electrons assigned to atom):

$\ddot{\text{O}}$	-	C	\equiv	O :
6	4	6		
7	4	5		

Formal charge:

Less charge! more important!

Lewis Structure for Carbon Dioxide (CO_2)!

Lewis Structures: Formal Charges

- In general, the best Lewis structure ...
 - ... is the one with the **(1) fewest formal charges**.
 - ... puts a **(2) “negative” formal charge on the most electronegative atom**.

Electronegativity: O (3.5) > N (3.0) > C (2.5) = S (2.5)

Example: Cyanate Ion (NCO^-). *Three possible Lewis structures*



Valence electrons

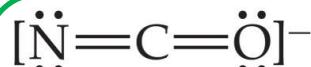
5 4 6

Electrons assigned

7 4 5

Formal charge

-2 0 +1



5 4 6

6 4 6

-1 0 0



5 4 6

5 4 7

0 0 -1

Lewis Structure for NCO^- !

Example: Thiocyanate Ion (NCS^-).



Formal charge

-2 0 +1



-1 0 0



0 0 -1

Lewis Structure for NCS^- !

Outline (Part II)

Basic Concept of Chemical Bonding

- Lewis Structures for Molecules
- Resonance Structures
- Exceptions to the Octet Rule
- Strength and Lengths of Bonds

Resonance Structures

- The best Lewis structure ...
 - (1) fewest formal charges.
 - (2) negative formal charge on the most electronegative atom.

Example: Ozone (O_3).

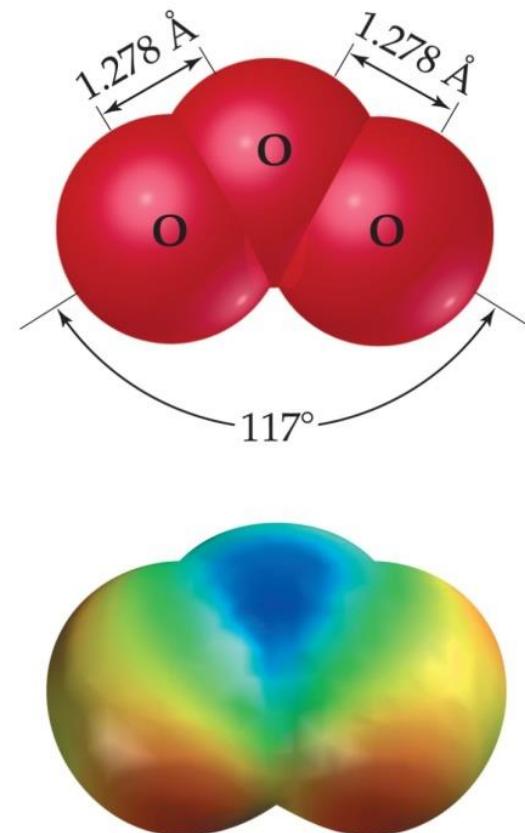


	Valence electrons	6	6	6	6	6	6
	Electrons assigned	7	5	6	6	5	7
	Formal charge	-1	+1	0	0	+1	-1

We call Lewis structures of this sort **resonance structures**.
(i.e. the delocalizing electron structure of the molecule.)



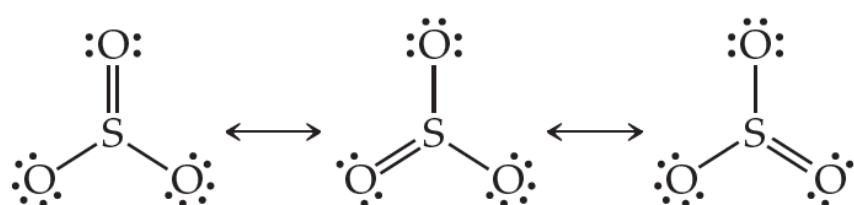
- As determined by experimental methods, O_3 looks like...
 - both O-O bonds have the same length (1.278 Å).
 - both outer oxygen atoms have a charge of -1/2.



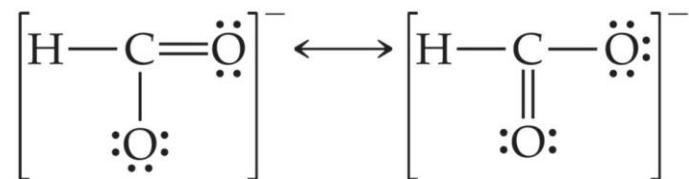
Resonance Structures

- The electrons associated with the **double bonds** in the following examples are also **not localized**. They are **delocalized**.

Sulfur Trioxide (SO_3):

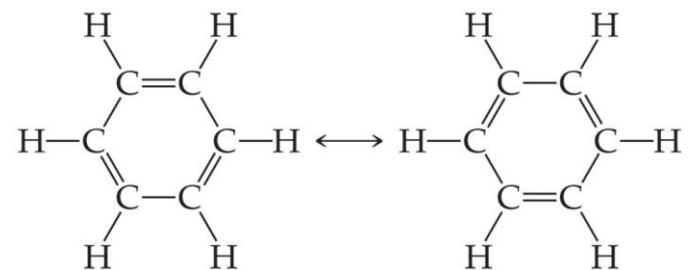
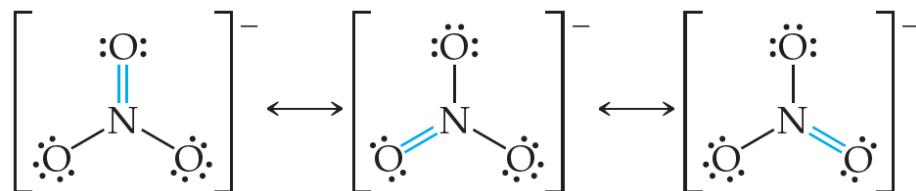


Formate anion (HCO_2^-):



Benzene (C_6H_6):

Nitrate anion (NO_3^-):



Basic Concept of Chemical Bonding

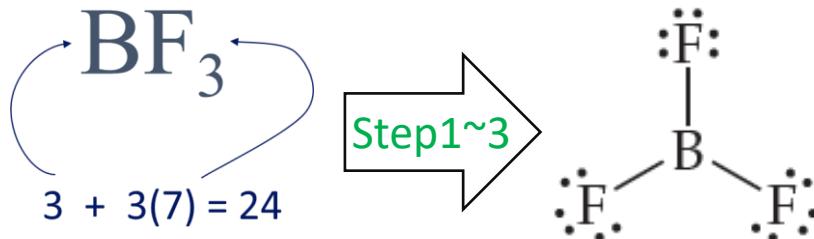
Outline (Part II)

- Lewis Structures for Molecules
- Resonance Structures
- Exceptions to the Octet Rule
- Strength and Lengths of Bonds

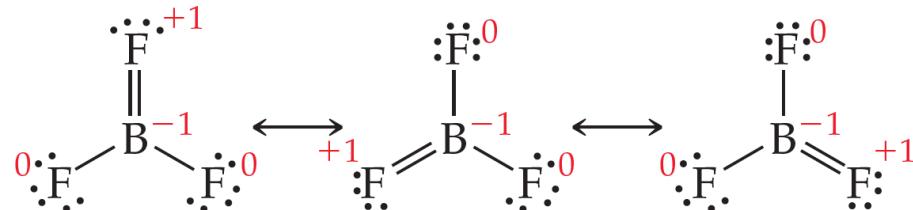
Exceptions to the Octet Rule

Molecules and Polyatomic Ions in which an Atom has...

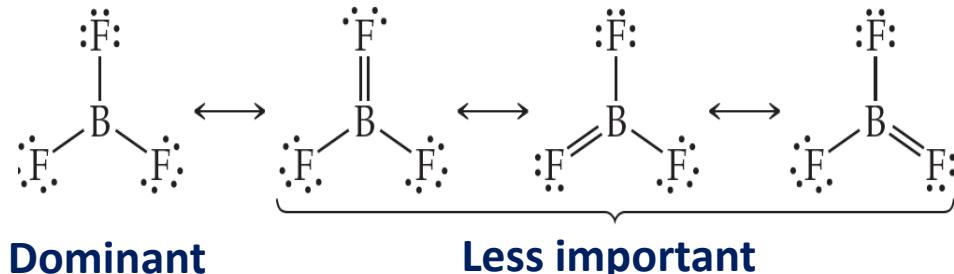
Fewer than an Octet of Valence Electrons (e.g. H/B/Be...)



Step 4 & Formal Charge & Resonance Analysis

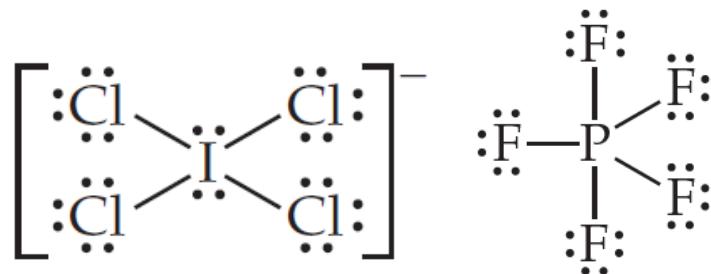


For the B=F double bond in each structure, the F atom has a formal charge of +1 while the less electronegative B atom has a formal charge of -1.....Less important!



More than an Octet of Valence Electrons

Hypervalent molecules are formed only for *central atoms from period 3 and below* in the periodic table (d orbitals).



Outline (Part II)

Basic Concept of Chemical Bonding

- Lewis Structures for Molecules
- Resonance Structures
- Exceptions to the Octet Rule
- Strength and Lengths of Bonds

Strength and Lengths of Bonds

In general, the bond enthalpy (i.e. strength of bond) increases with increasing number of bonds between two atoms!

Table 8.4 Average Bond Enthalpies (kJ/mol)

Single Bonds < 400 kJ/mole							
C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368	Bond Strength: Triple > Double > Single					
Si—Cl	464						

Multiple Bonds		Double: > 400 kJ/mole; Triple: > 800 KJ/mole			
C=C	614	N=N	418	O=O	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Strength and Lengths of Bonds

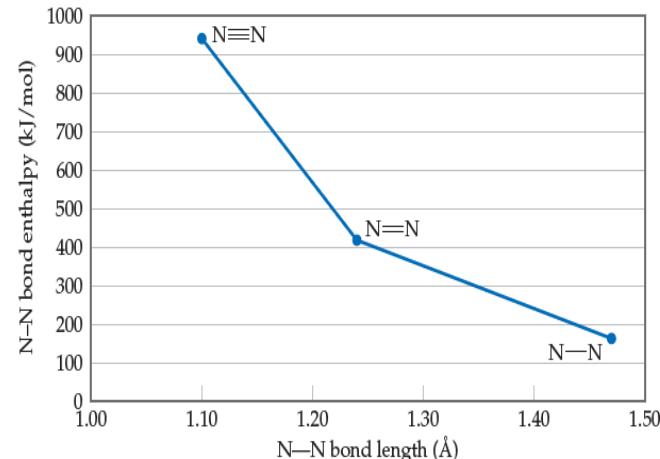
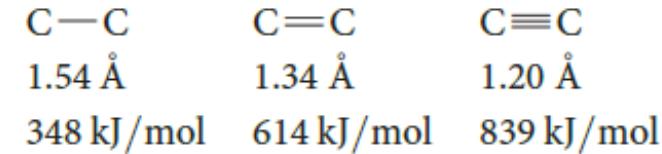
The stronger bond strength between two atoms the shorter bond distance

Bond Strength: Triple > Double > Single

Bond Length: Single > Double > Triple

Table 8.5 Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		



Molecular Geometry and Bonding Theories

Outline

- Shape of Molecules
- VSEPR Theory (*valence-shell electron-pair repulsion*)
- Hybridization Theory
- Valence-bond Theory

Molecular Geometry and Bonding Theories

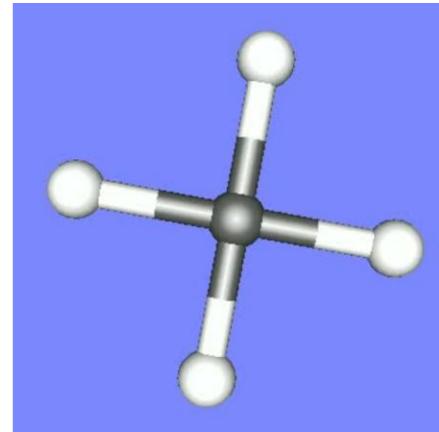
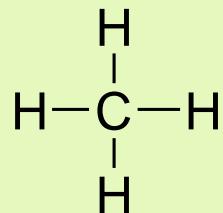
Outline

- Shape of Molecules
- VSEPR Theory
- Hybridization Theory
- Valence-bond Theory

Shape of Molecules

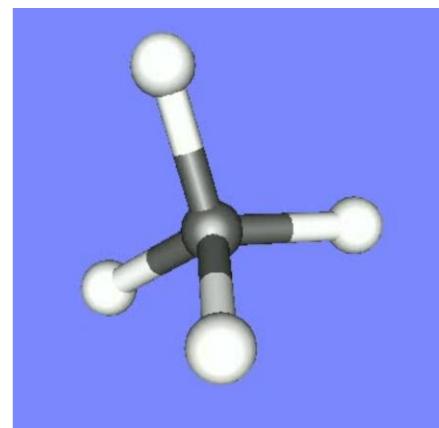
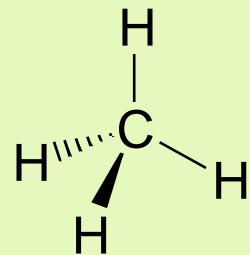
What is the real shape of methane molecule (CH_4)?!

Is it planar?



NO

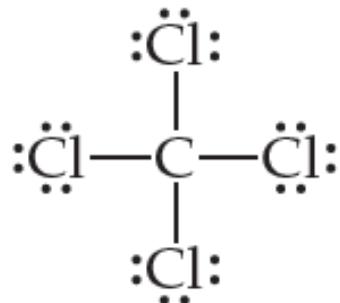
Is it tetrahedral?



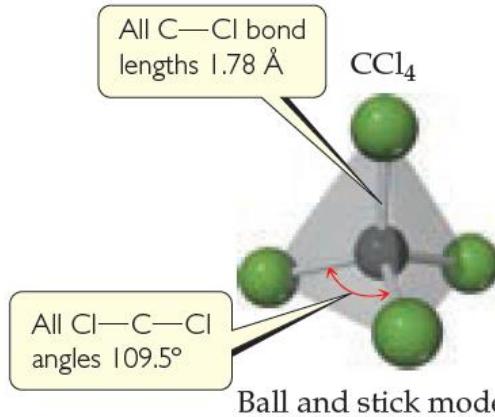
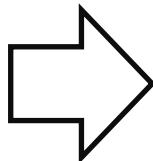
YES

Shape of Molecules

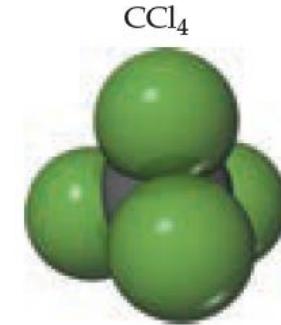
What is the shape of Carbon Tetrachloride (CCl_4)?!



Lewis structure

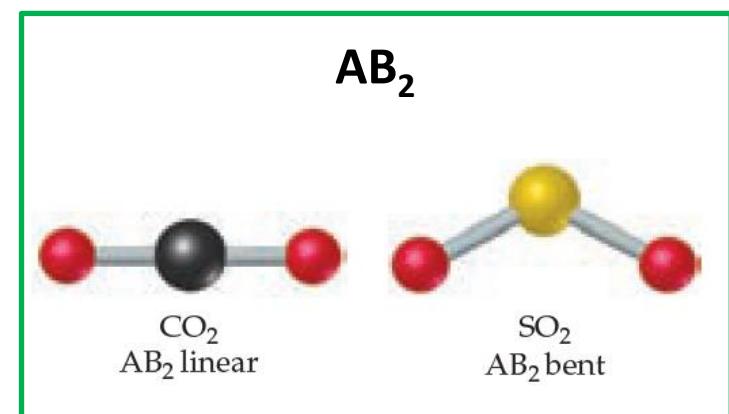
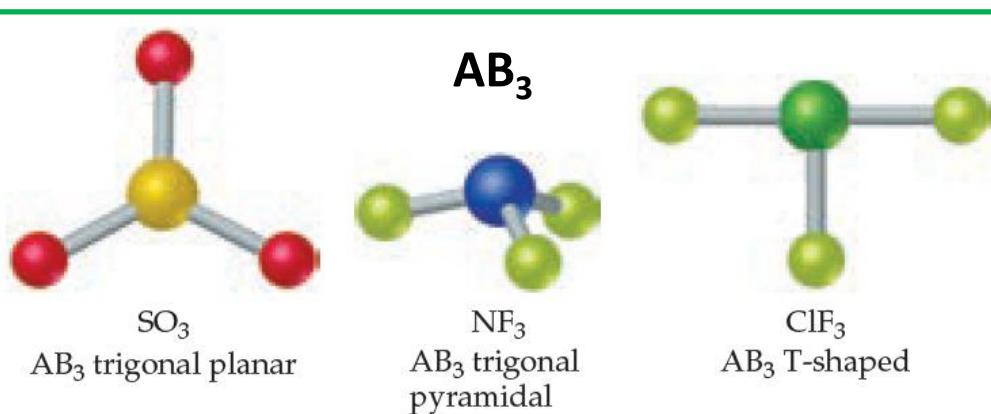


Ball and stick model



Space-filling model

General formula AB_n : the central atom A is bonded to n B atoms.



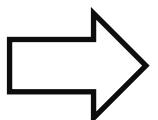
Molecular Geometry and Bonding Theories

Outline

- Shape of Molecules
- VSEPR Theory
 - Electron-domain Calculation
 - Electron-domain Geometry
 - Molecular Geometry
- Hybridization Theory
- Valence-bond Theory

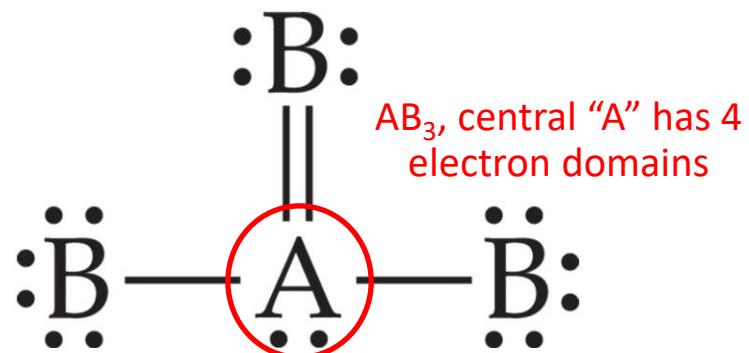
VSEPR Theory

Valence Shell Electron Pair Repulsion (VSEPR) Theory

 We can predict the three-dimensional structure of a molecule from its two-dimensional Lewis structure.

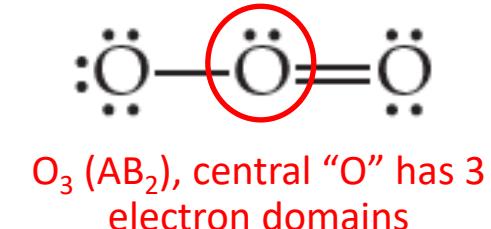
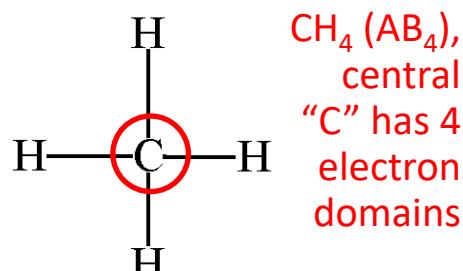
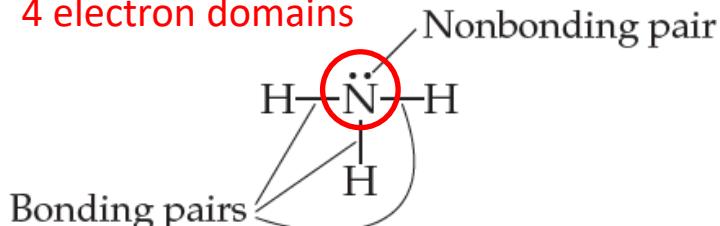
- The number of electron domains determines corresponding electron-domain geometry

each **nonbonding** electron pair, or
each **single bond**, or
each **double bond**, or
each **triple bond**, or
counts as **one** electron domain.



To determine the electron-domain geometry of AB_n molecule, we need to consider the number of electron domains of central A atom!

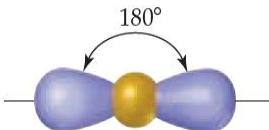
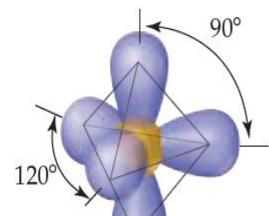
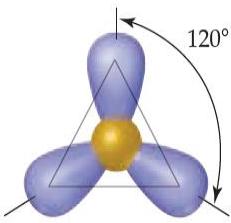
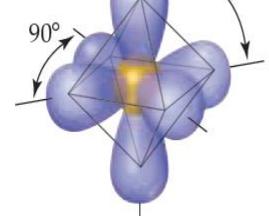
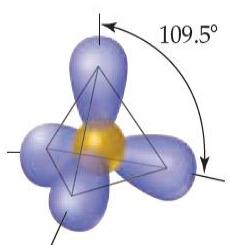
NH₃ (AB₃), central "N" has 4 electron domains



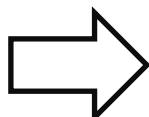
VSEPR Theory

Valence Shell Electron Pair Repulsion (VSEPR) Theory

Number of Electron Domains and corresponding Electron-Domain Geometries

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles	Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°	5		Trigonal bipyramidal	120° 90°
3		Trigonal planar	120°	6		Octahedral	90°
4		Tetrahedral	109.5°				

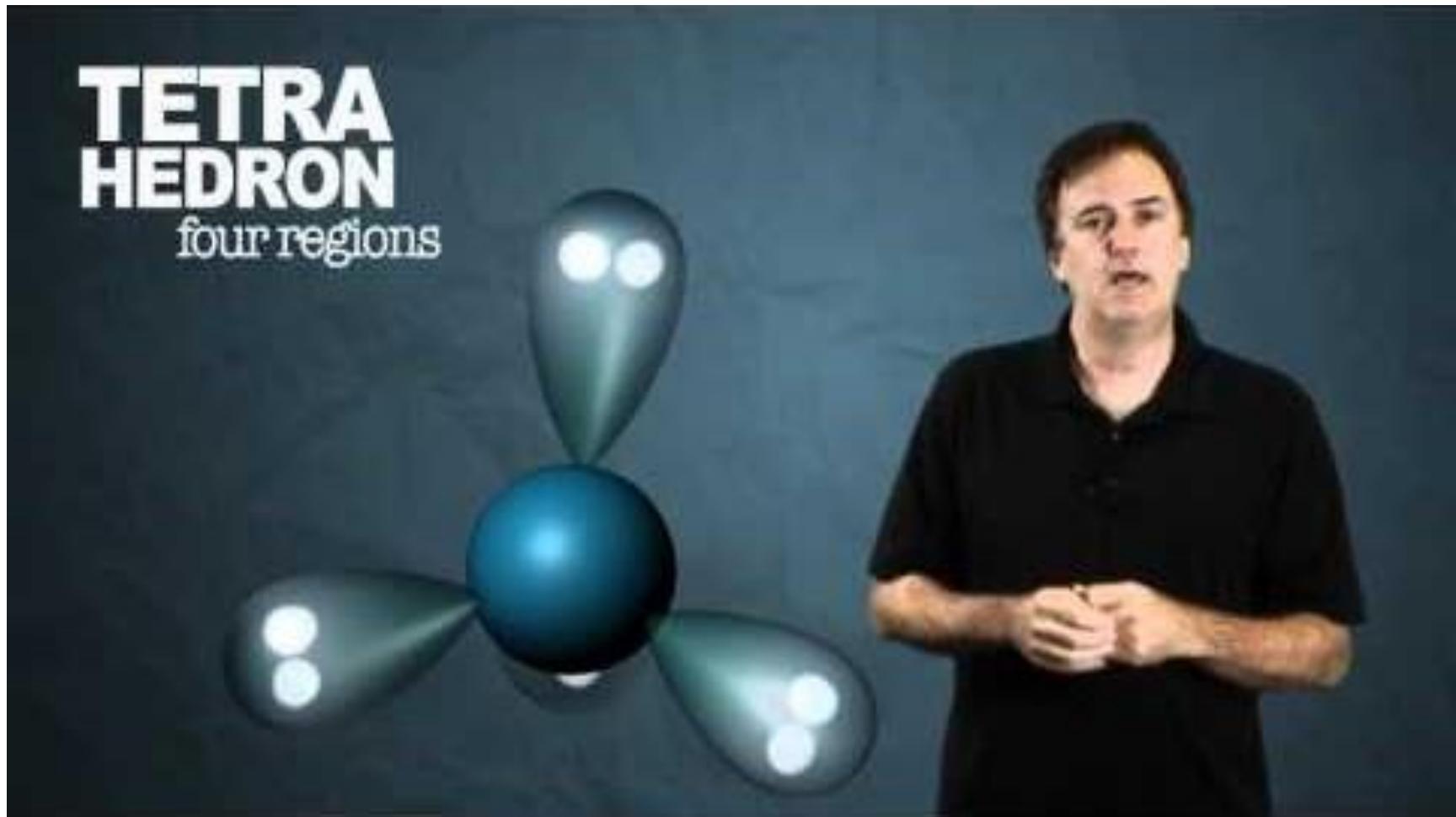
**YOU MUST REMEMBER THIS FIGURE!
(Especially electron domain 2 to 4)**



The key to convert 2D drawing of Lewis structure to 3D electron-domain geometry (& later Molecular geometry)

VSEPR Theory

VSEPR Theory: The *best spatial arrangement* of a given number of electron domains is the one that *minimizes repulsions* among them.

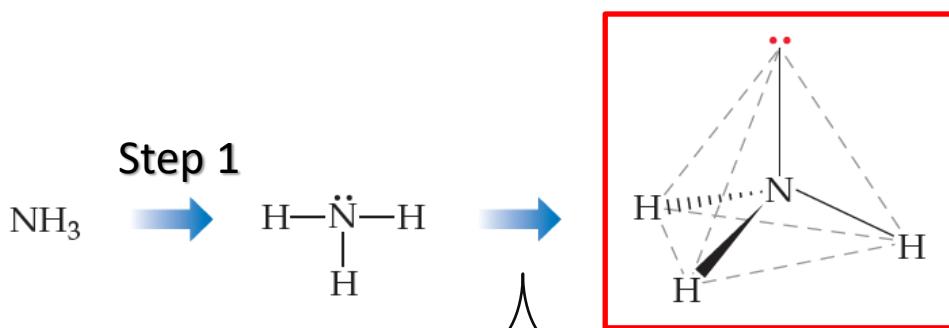


<https://www.youtube.com/watch?v=keHS-CASZfc>

VSEPR Theory

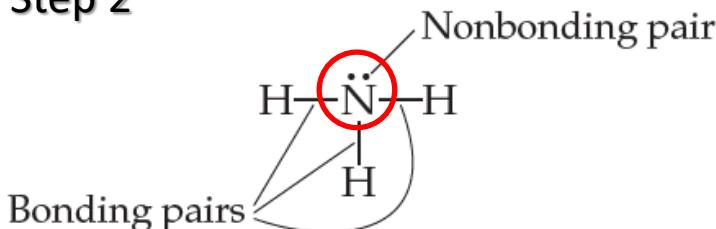
Steps for the drawing of Electron-Domain Geometries

1. Draw the **Lewis structure (2D)**
2. Count the total number of *electron domains of the “central atom”*.
3. Correlate to **Electron-domain geometry (3D)**



VSEPR Theory

Step 2

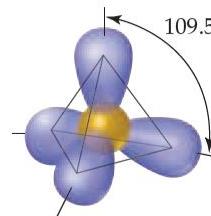


$\text{NH}_3 (\text{AB}_3)$, the central “N” has 4 electron domains

Step 3

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
----------------------------	---------------------------------	--------------------------	-----------------------

4

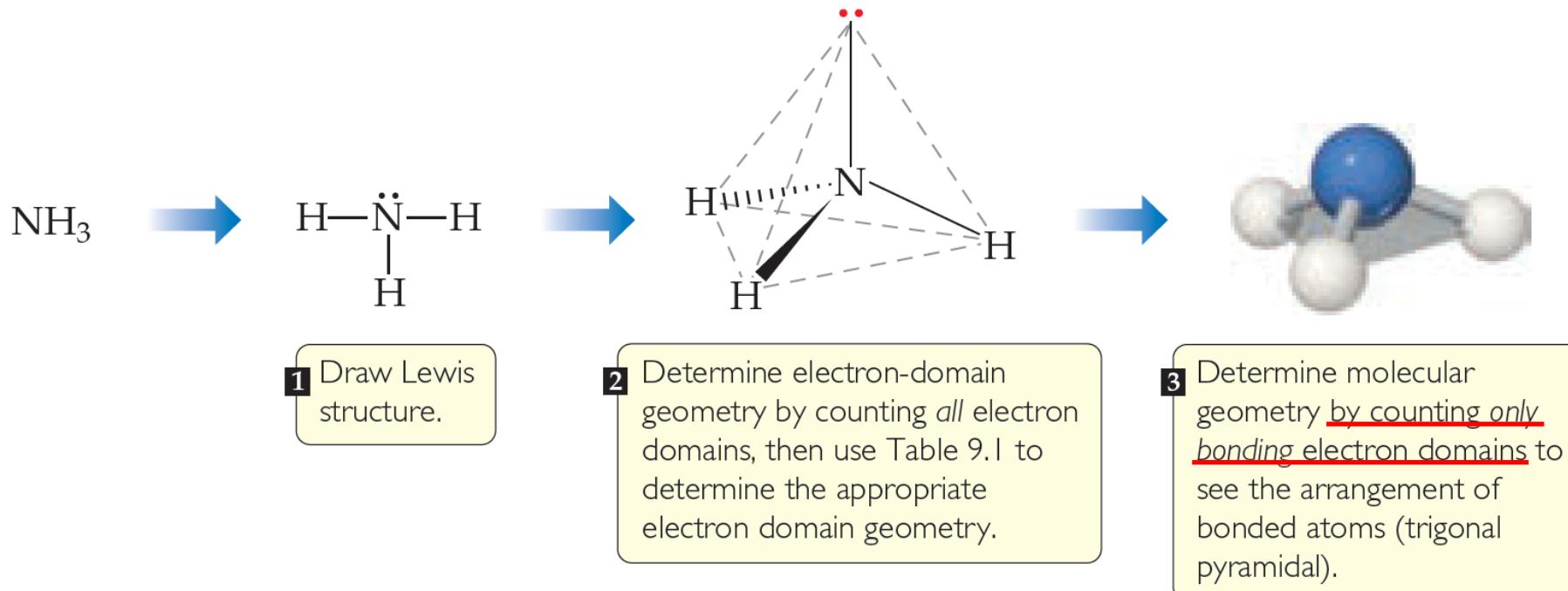


Tetrahedral 109.5°

VSEPR Theory

Derive “Molecular Geometry” from “Electron-Domain Geometry”

- **Electron-domain geometry** corresponds to the number of electron domains.
- **Molecular geometry (shape)** is defined by the positions of atoms in the molecules.
(lone pairs are not considered!)



VSEPR Theory

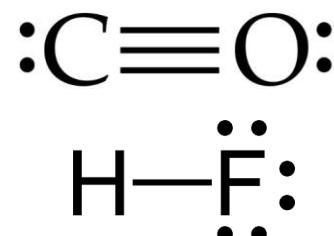
Electron-Domain Geometry vs. Molecular Geometry

Electron-Domain & Molecular Geometries for 2 Electron Domains around a Central Atom

Number of Electron Domains	Electron- Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2		2	0		$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$ (AB_2)

In this electron domain geometry, there is only one molecular geometry: linear.

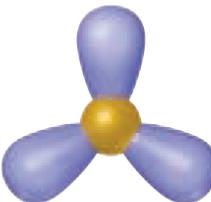
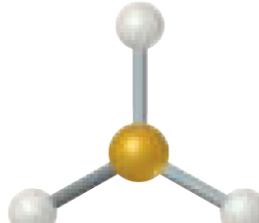
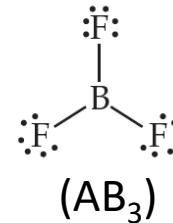
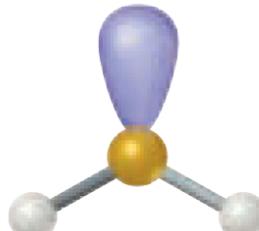
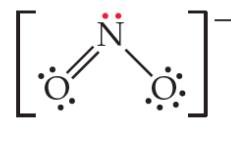
NOTE: If there are only **two atoms in the molecule** (AB , e.g. CO , HF ...), no matter how many electron domains of A or B, the “molecule geometry” must be linear.



VSEPR Theory

“Electron-Domain Geometry” and “Molecular Geometry” are not necessarily the same!

Electron-Domain & Molecular Geometries for 3 Electron Domains around a Central Atom

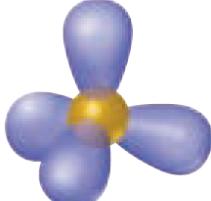
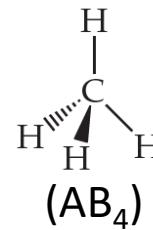
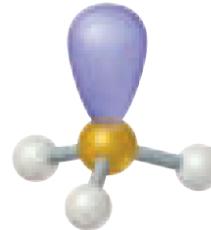
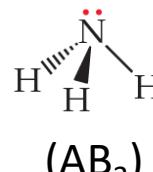
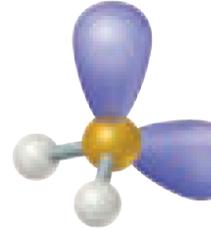
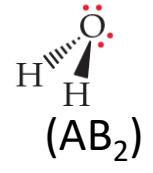
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
3	 Trigonal planar	3	0	 Trigonal planar	 (AB_3)
		2	1	 Bent	 (AB_2^-)

- There are two molecular geometries:
 - Trigonal planar, if there are no lone pairs
 - Bent, if there is a lone pair.

VSEPR Theory

“Electron-Domain Geometry” and “Molecular Geometry” are not necessarily the same!

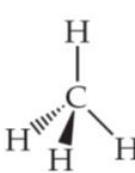
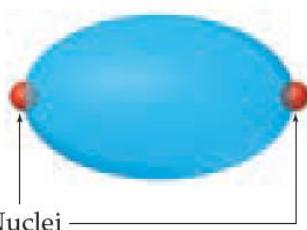
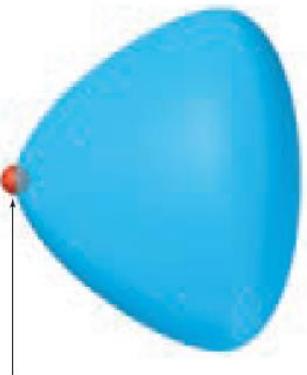
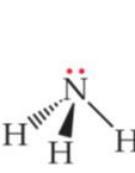
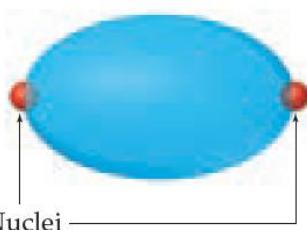
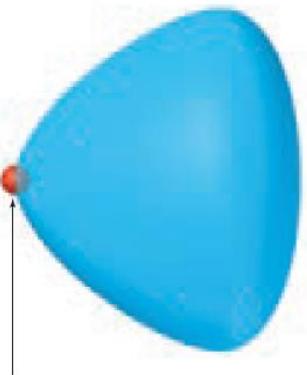
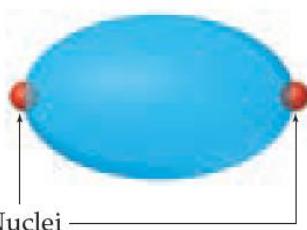
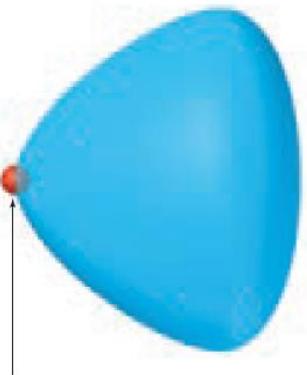
Electron-Domain & Molecular Geometries for 4 Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4		4	0	 Tetrahedral	 (AB_4)
		3	1	 Trigonal pyramidal	 (AB_3)
		2	2	 Bent	 (AB_2)

1*Electron-domain geometry
while 3*Molecular geometries!

VSEPR Theory

*The number of Lone Pairs also affects the Bond Angle of Molecular Geometry (slightly)

Molecular Geometry	Example		
Tetrahedral			
Trigonal pyramidal			
Bent			

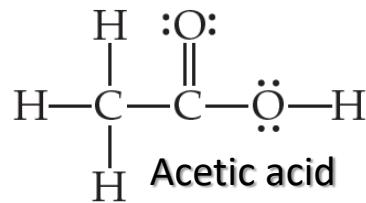
- Since nonbonding pair experience less nuclear attraction, it is spread out more in space (cf. bonding pair).
- As a result, electron domains for **nonbonding electron pairs** exert greater repulsive forces on adjacent electron domains and **tend to compress bond angles**.

VSEPR Theory

*How about the Geometries (Shapes) of Large Molecules?

In larger molecules, it makes more sense to consider the geometry of each central atom rather than the geometry of the molecule as a whole.

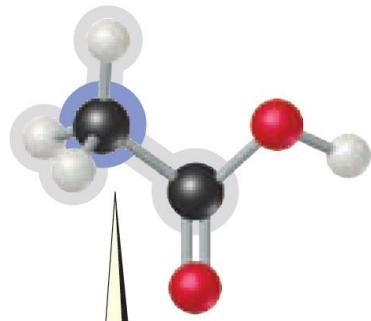
Lewis structure



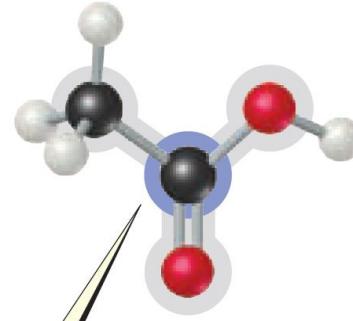
VSEPR
Analysis

	H	:O:	
	H—C		C—H
	H	..	O—H

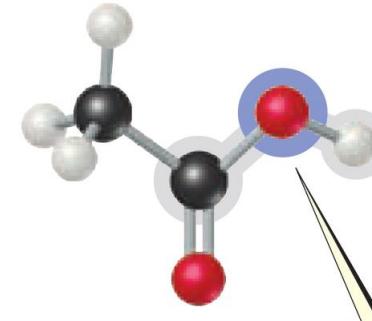
Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°



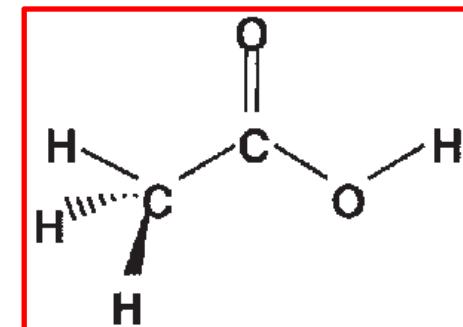
Electron-domain geometry tetrahedral,
molecular geometry tetrahedral



Electron-domain geometry trigonal planar,
molecular geometry trigonal planar



Electron-domain geometry tetrahedral,
molecular geometry bent



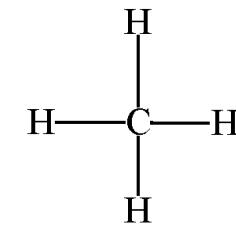
Molecular Geometry and Bonding Theories

Outline

- Shape of Molecules
- VSEPR Theory
- Hybridization Theory
 - Hybridization of Atomic Orbitals (s & p)
 - sp , sp^2 & sp^3 Hybrid Orbitals
- Valence-bond Theory

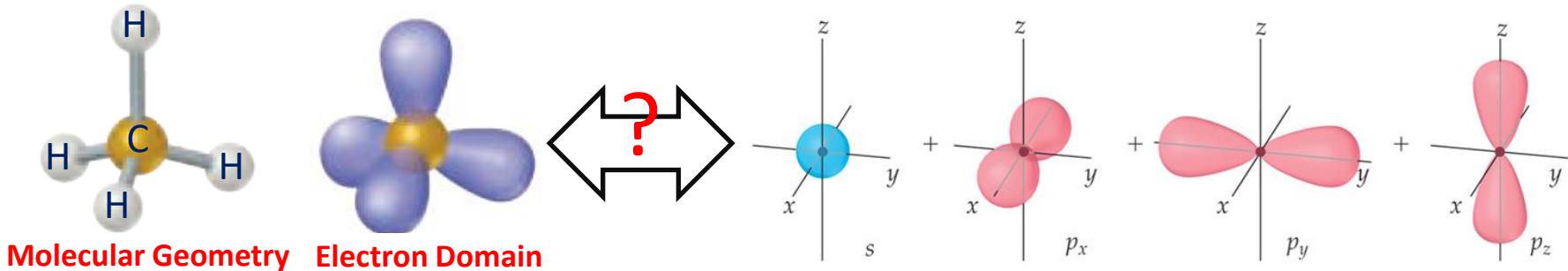
Hybridization Theory

Hybridization of Atomic Orbitals



VSEPR predicts the geometry of CH_4 is tetrahedral. However.....

The *s* and *p* orbitals of central carbon have very different shapes!.

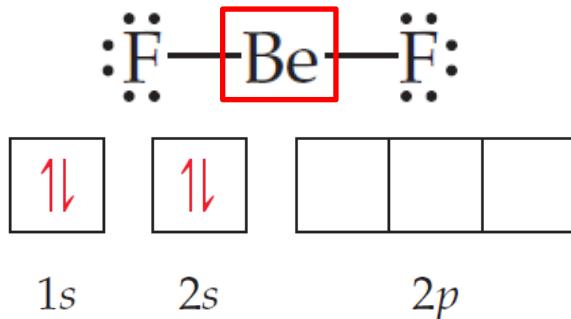


How to understand the electron domain of carbon (from CH_4) in terms of atomic orbitals of carbon (i.e. $2s$ & $2p$)?

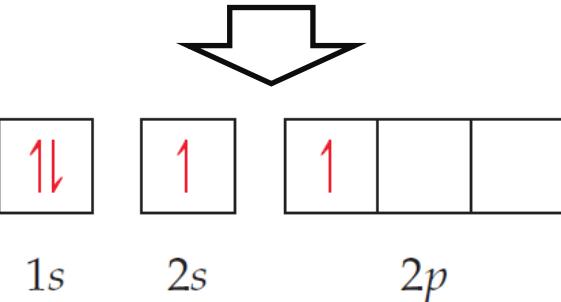
- This can be rationalized by the concept called *orbital hybridization*, which involves *mixing of atomic orbitals*.
- Mixing **X** number of atomic orbitals will give **X** number of hybrid orbitals.
- Hybrid orbitals have *different shapes and orientations* from the original atomic orbitals.

Hybridization Theory

sp Hybrid Orbitals (for central atom has two e-domains)

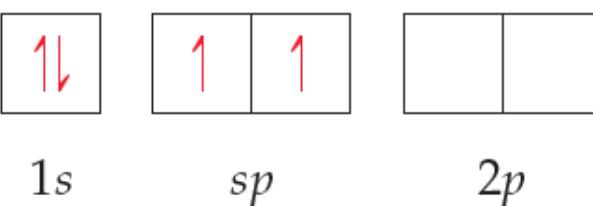


In beryllium (Be) ground electronic state, it would not be able to form bonds with fluorine (one for each) because it has no singly-occupied orbitals.



But if we promote an electron from the 2s to the 2p orbital, it can form two bonds with two fluorine atoms now.

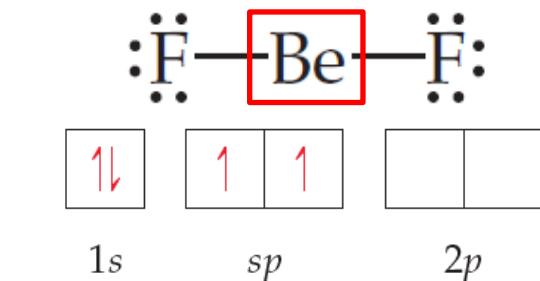
Although the promotion of an electron allows two Be-F bonds to form, we still have not explained the linear structure of BeF_2 .



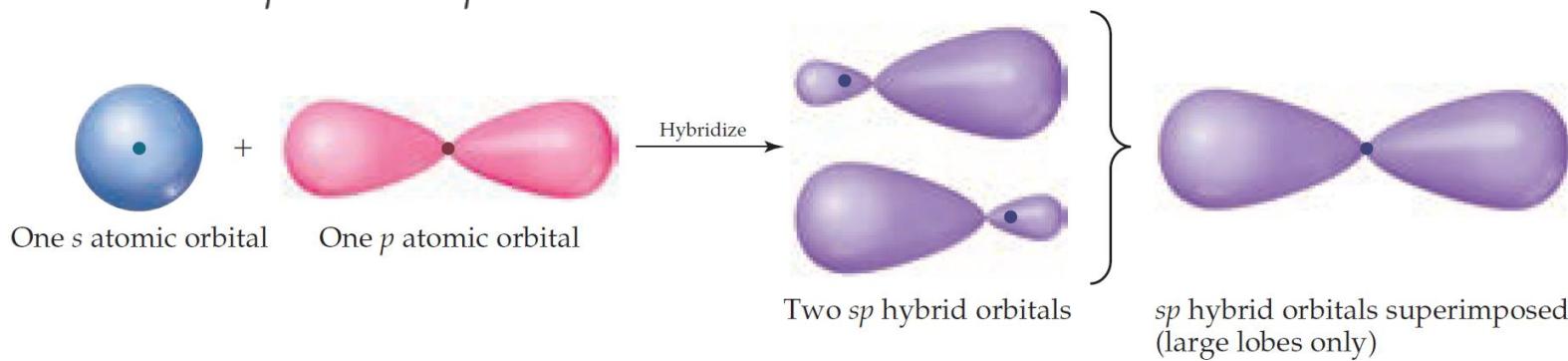
We can solve this dilemma by “mixing” one 2s orbital with one 2p orbital to generate two new “sp” orbitals.

Hybridization Theory

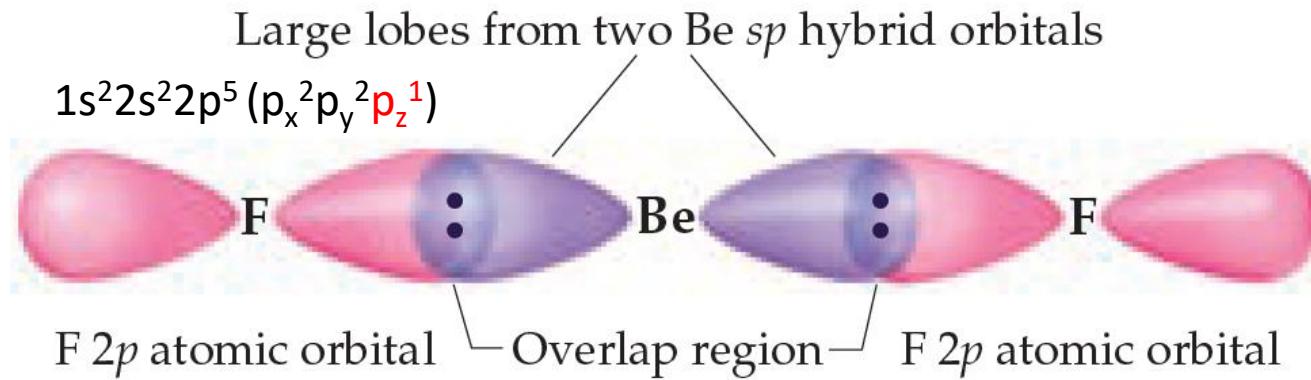
sp Hybrid Orbitals (for central atom has two e-domains)



We can solve this dilemma by “mixing” one 2s orbital with one 2p orbital to generate **two sp orbitals**.



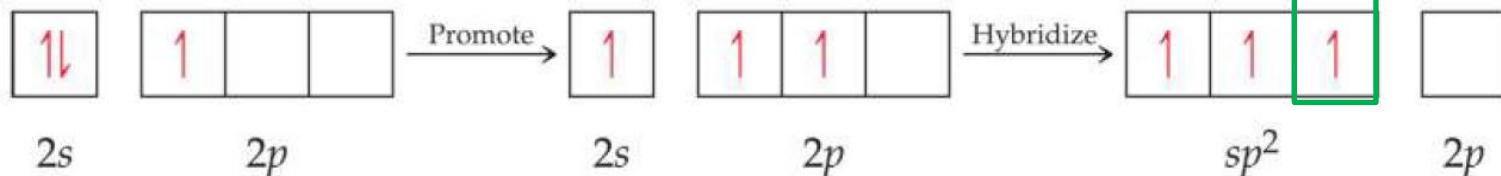
The two sp orbitals are **identical in shape & energy**, but their large lobes point in opposite directions. As **one s and one p orbital are hybridized**, we call each hybrid an **sp hybrid orbital**.



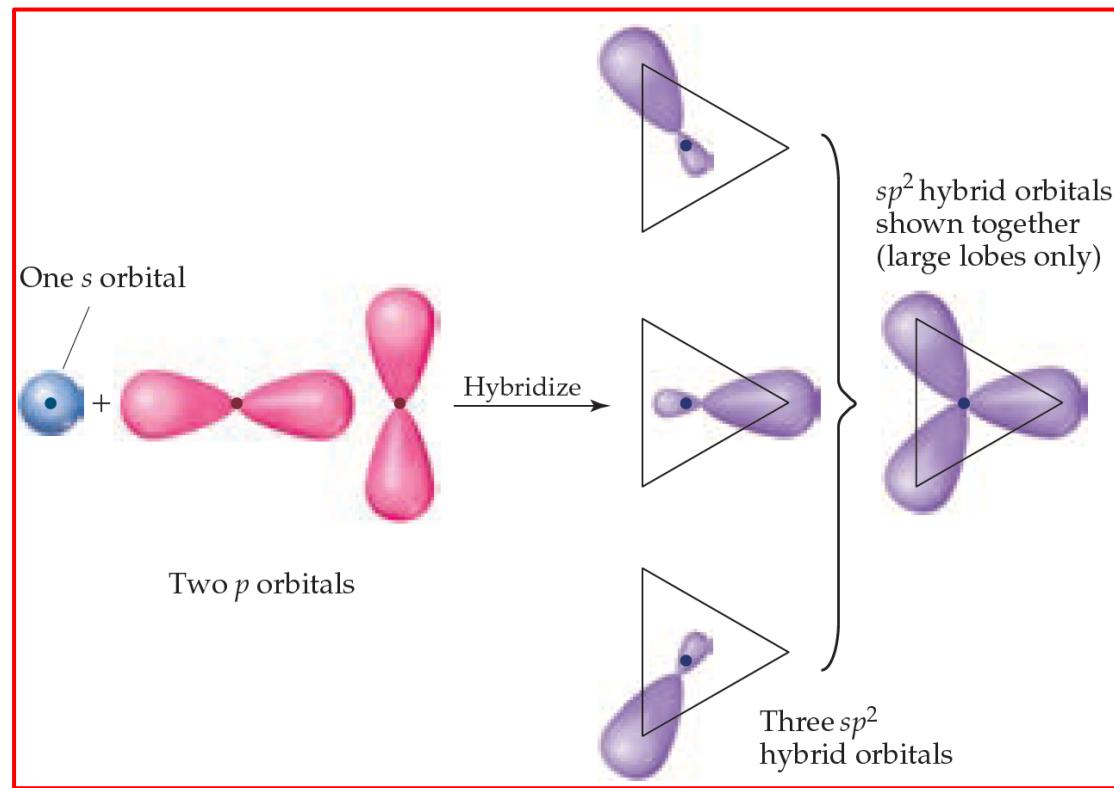
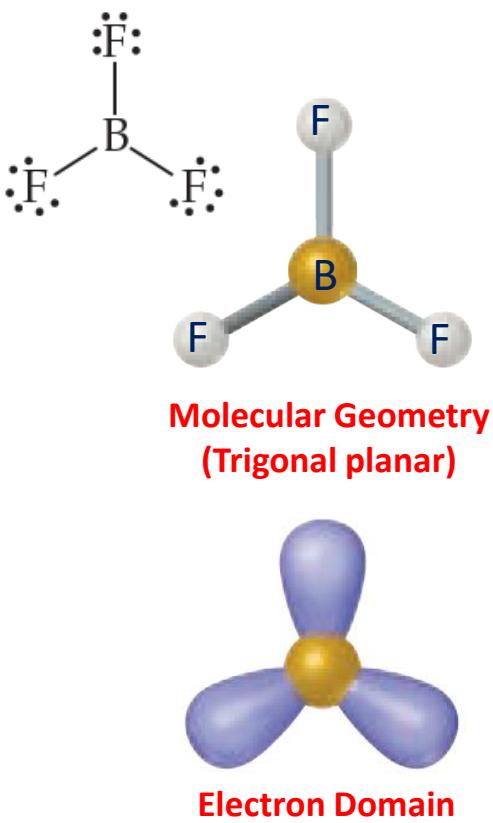
Hybridization Theory

sp² Hybrid Orbitals (for central atom has three e-domains)

For BF_3 , we can use similar method for central boron...



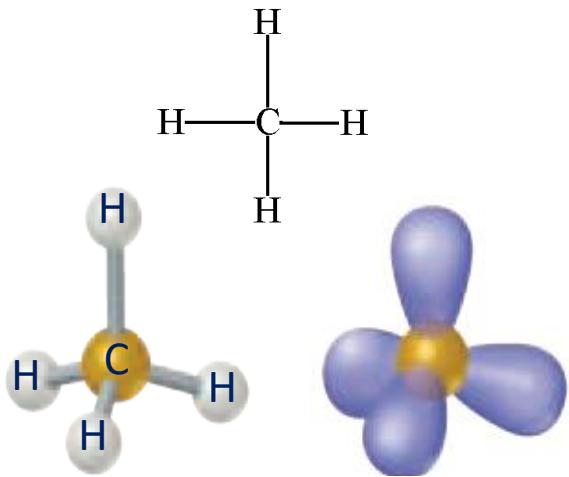
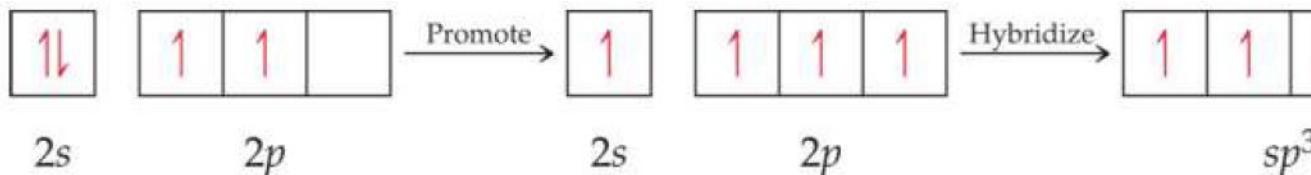
"mixing" one $2s$ orbital with two $2p$ orbitals to generate **three sp² new orbitals** (same energy but different orientation)!



Hybridization Theory

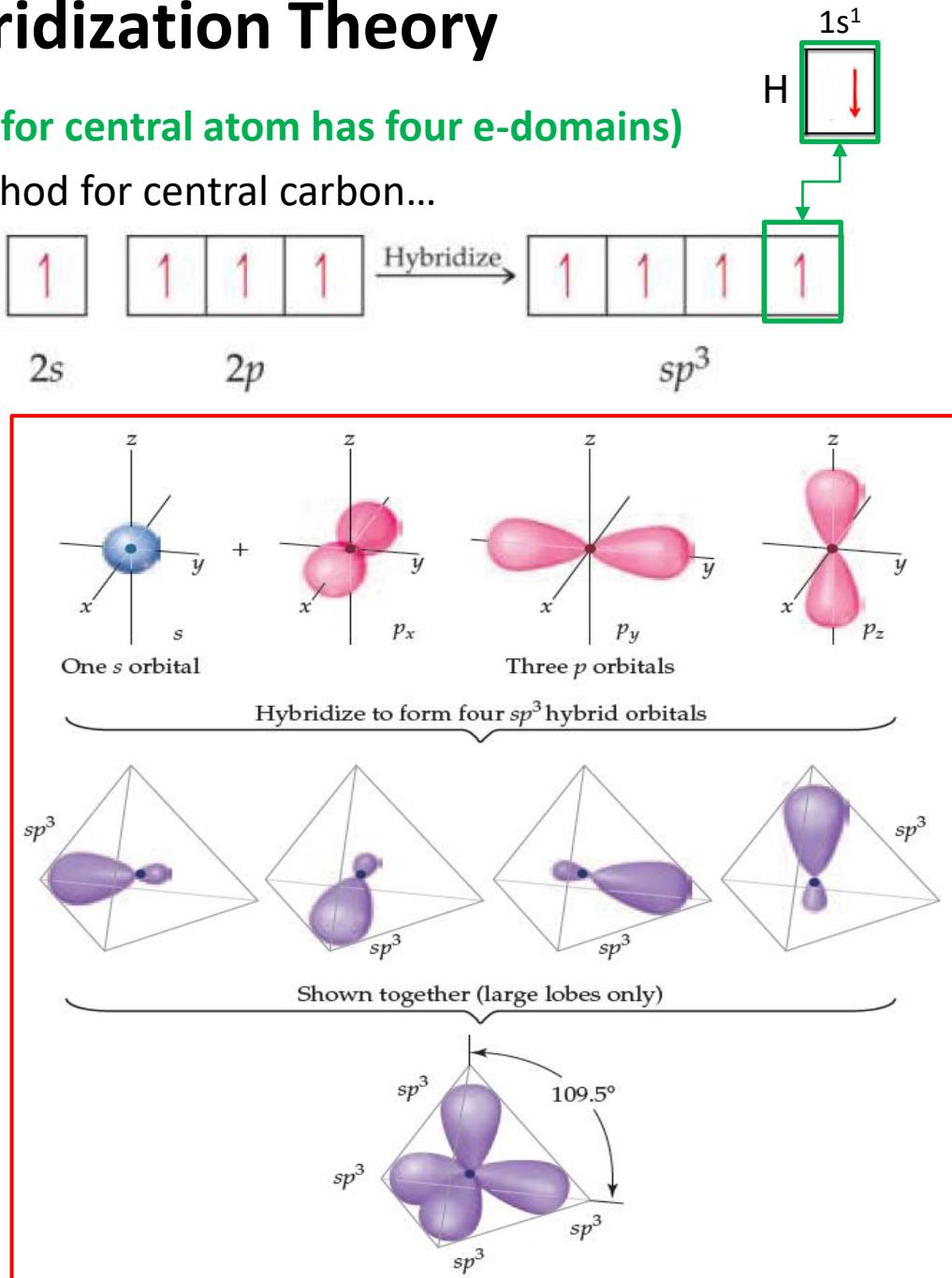
sp³ Hybrid Orbitals (for central atom has four e-domains)

For CH₄, we can use similar method for central carbon...



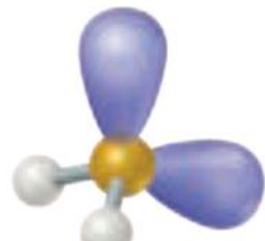
Molecular Geometry **Electron Domain (Tetrahedral)**

“Mixing” two 2s orbital with two 2p orbital to generate **four sp⁴ new orbitals** (sample energy but different orientation)!



Hybridization Theory

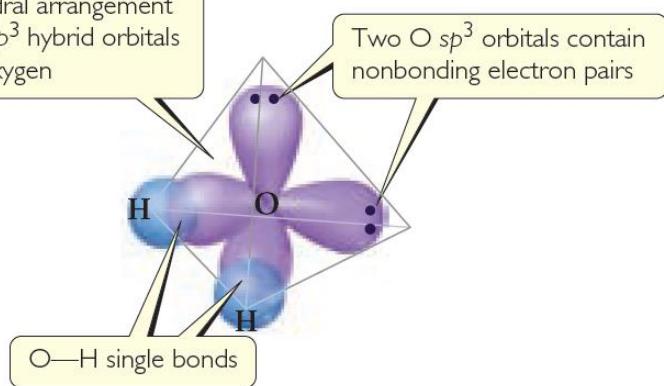
Hybrid Orbital Summary



Bent



Tetrahedral arrangement
of four sp^3 hybrid orbitals
about oxygen



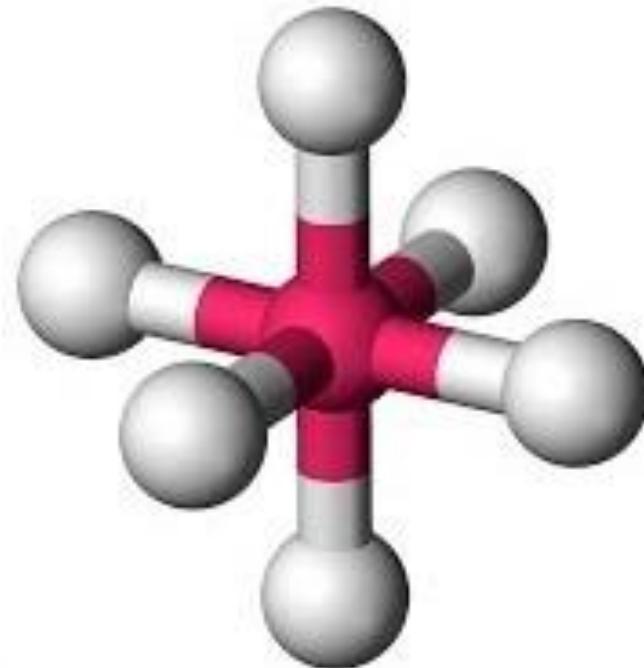
Atomic Orbital Set	Hybrid Orbital Set	electron-domain Geometry	Examples
s,p	Two sp	180° Linear	$\text{BeF}_2, \text{HgCl}_2$
s,p,p	Three sp^2	120° Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	109.5° Tetrahedral	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$

Three steps allow us to decide the hybrid orbitals used by an atom in bonding:

1. Draw *Lewis structure* for the molecule or ion.
2. Use the *VSEPR model* to determine the **electron-domain geometry** of the central atom.
3. Specify the *hybrid orbitals* needed to accommodate the electron pairs based on their geometric arrangement.

Hybridization Theory

Summary of VSEPR + Hybridization Theory



<https://www.youtube.com/watch?v=Q9-JjyAEqnU>

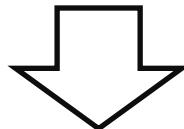
Molecular Geometry and Bonding Theories

Outline

- Shape of Molecules
- VSEPR Theory
- Hybridization Theory
- Valence-bond Theory
 - Sigma Bond
 - Pi Bond
 - Resonance Structure

Valence-bond Theory

VSEPR + Hybridization theory can rationalize the shape of a molecule and orbitals used for connecting each atom.



How to describe the formation of covalent bonds in terms of the atomic or hybrid orbitals?

Valence-bond theory can provide a more fundamental view of chemical bonding:

- Bonding is due to overlap of an atomic (or hybrid) orbital from one atom with an atomic (or hybrid) orbital from another atom.
- This leads to an accumulation of electron density in the region between the nuclei (i.e. the formation of chemical bond).

Valence-bond Theory

Sigma Bond (σ bond)

Characteristics of σ bonds :

- Head-to-head overlap of atomic (or hybrid) orbitals (any of them!).
- Electron density concentrated *on the internuclear axis*.

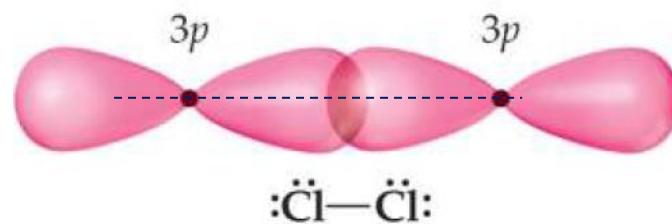
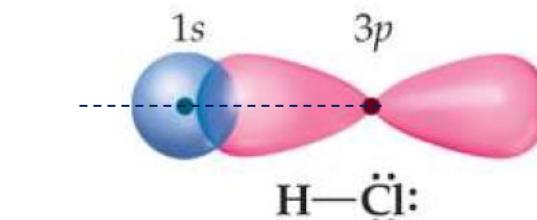
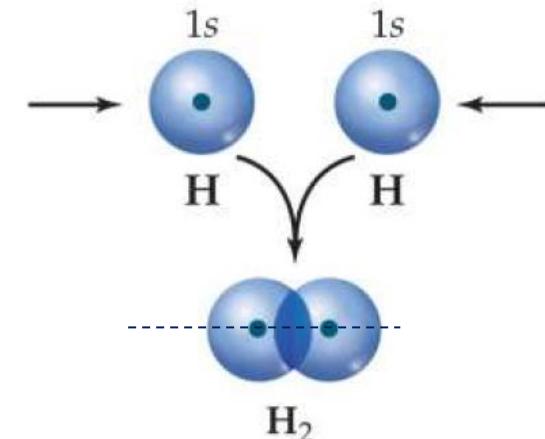
A **hydrogen molecule (H_2)** is formed by overlapping the **1s orbital** of one hydrogen atom with the **1s orbital** of another hydrogen atom, forming a H–H σ bond.

The bond in **hydrogen chloride (HCl)**:

1s of H head-to-head overlap with 3p of Cl, forming a H–Cl σ bond.

The bond in **chlorine molecule (Cl_2)**:

3p of Cl head-to-head overlap with each other, forming a Cl–Cl σ bond.



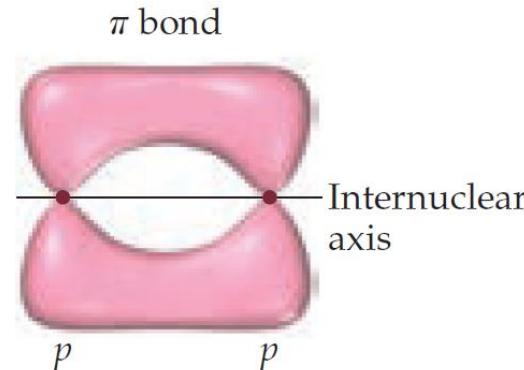
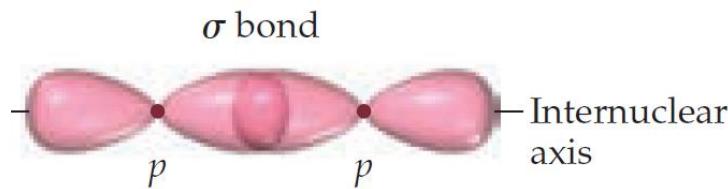
Valence-bond Theory

Pi Bond (π bond)

Characteristics of π bonds :

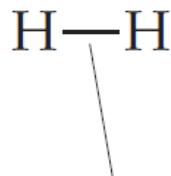
- **Side-to-side** overlap of p orbitals (only between p orbitals!).
- Electron density concentrated **above and below the internuclear axis**.
- Orbital are less overlapped and hence **weaker than σ bonds**.

Comparison of σ and π bonds

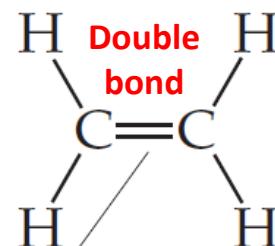


In general, there is only one σ bond allowed between two atoms while not for π bonds

Single bond

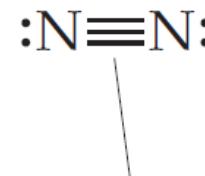


One σ bond



One σ bond plus
one π bond

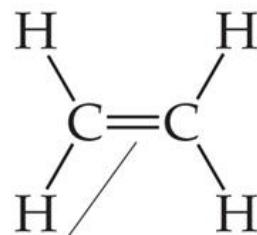
Triple bond



One σ bond plus
two π bonds

Valence-bond Theory

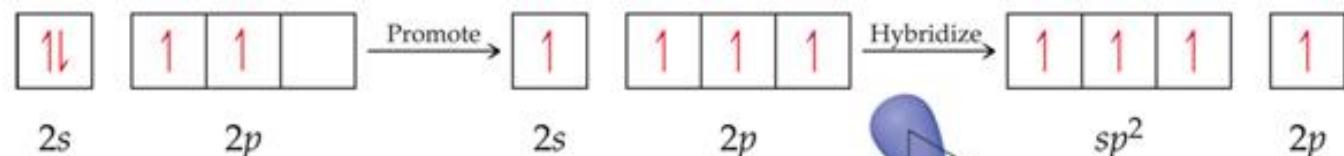
Case 1_Ethene



One σ bond plus one π bond

VSEPR + Hybridization + Valence-bond Theory

three e-domains!



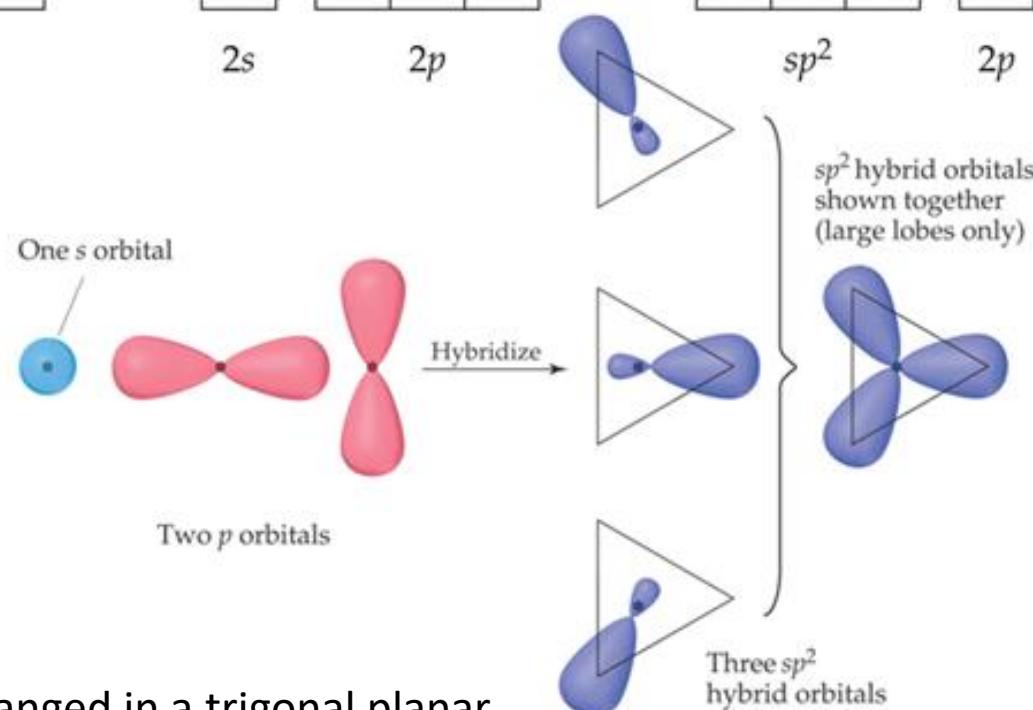
For each carbon...three e-domains!

1. One 2s electron is promoted to the empty 2p orbital.

2. Mixing **ONE s orbital** and **TWO p orbitals** to form **THREE sp² hybrid orbitals** (**ONE p orbital** is remaining unchanged).

3. The three sp² hybrid orbitals are arranged in a trigonal planar geometry to minimize repulsion between them (VSEPR theory).

4. Each sp² hybrid orbital and the remaining p orbital contains one electron.



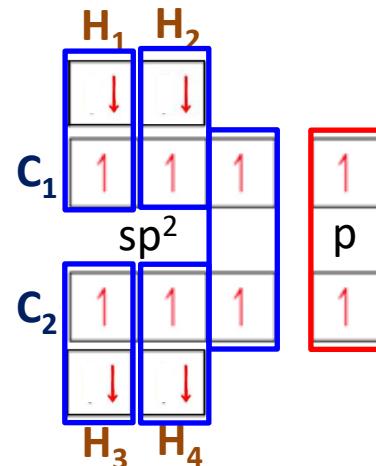
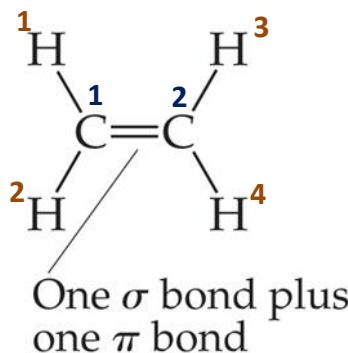
Valence-bond Theory

Case 1_Ethene

For ethene, the C=C double bond:

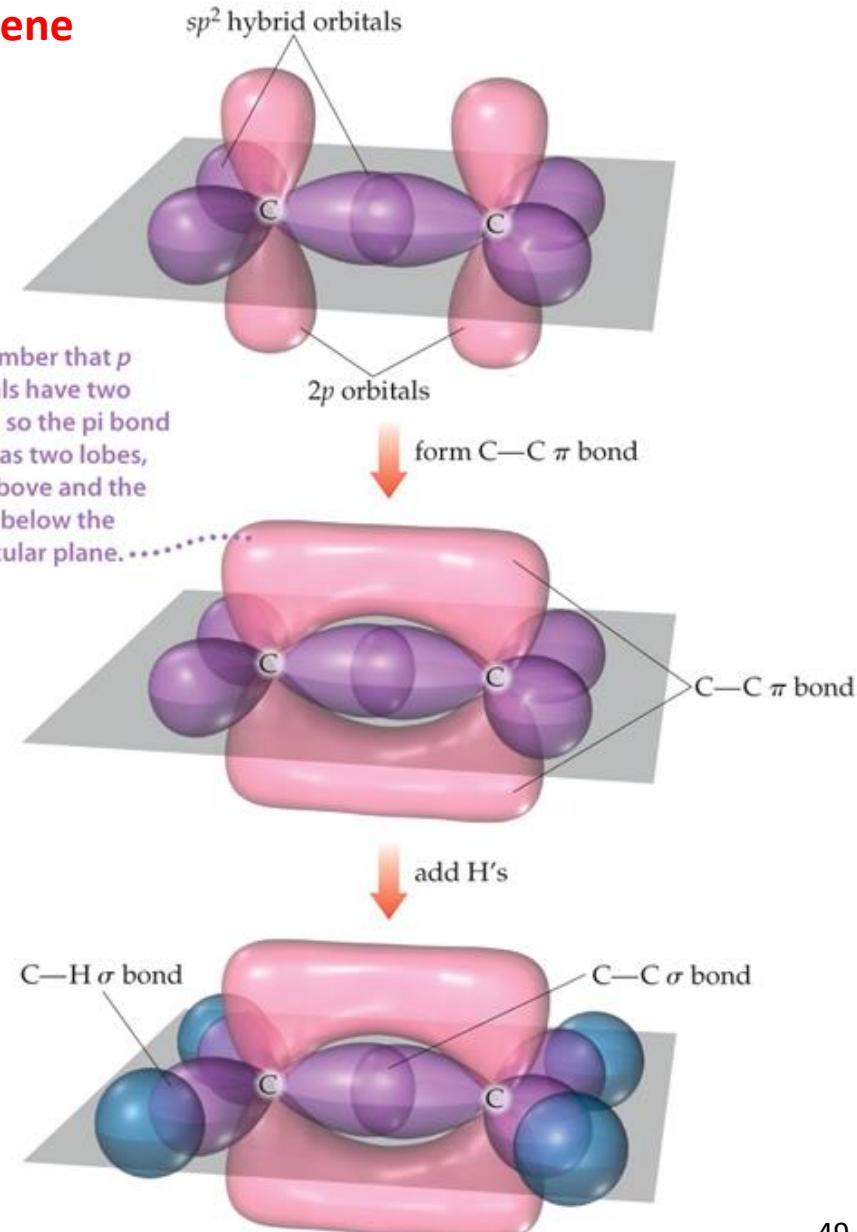
one **σ bond** formed by overlapping an *sp*² hybrid orbital from each C atom.

one **π bond** formed by overlapping the unhybridized *p* orbital from each C atom.



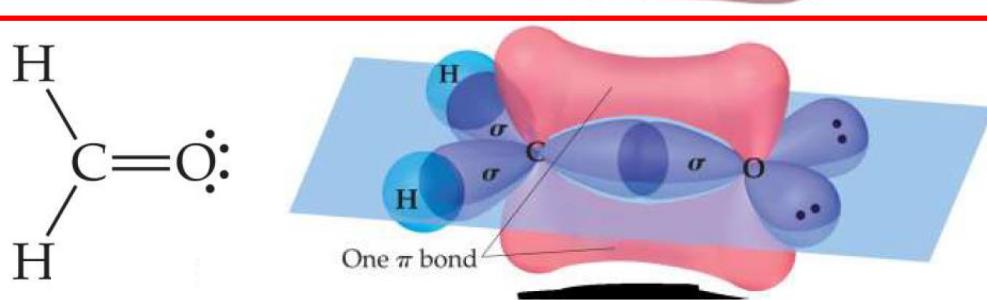
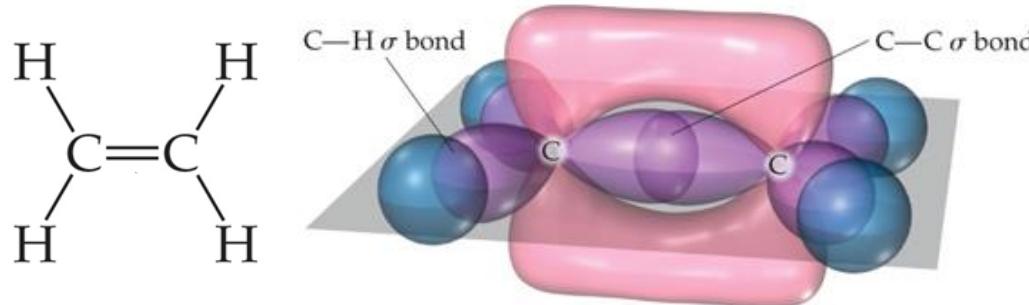
For the C–H single bonds:

The remaining **two sp^2 orbitals** of each C atom overlap with the **1s orbital** of the four H atoms to form four **σ bonds**.



Valence-bond Theory

Case 2_Formaldehyde



Ethene has four C-H single bonds:

σ bond: sp²-s between C & H atom.

Formaldehyde has two C-H single bonds

σ bond: sp²-s between C & H atom.

Two lone pairs on two sp² orbital of O!

Three e-domains for both C atoms!

The C=C double bond:

1***σ bond:** sp²-sp² between C atoms.

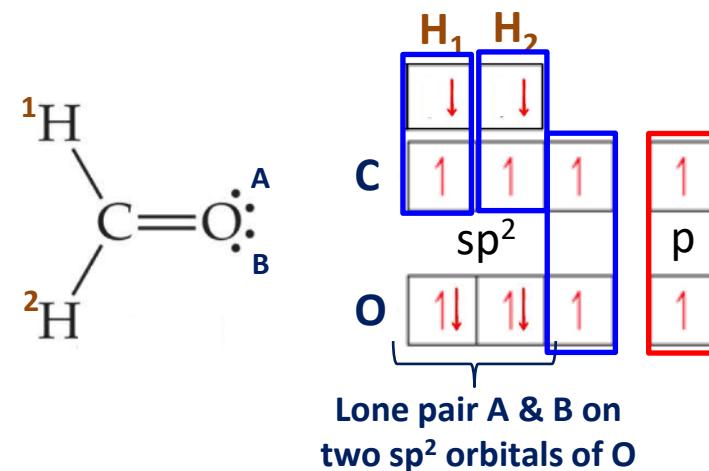
1***π bond:** p-p between C atoms.

Three e-domains for C & O atoms!

The C=O double bond:

1***σ bond:** sp²-sp² between C&O atom.

1***π bond:** p-p between C&O atom.

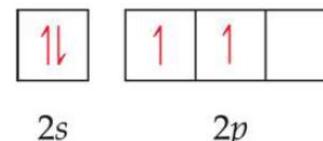


Valence-bond Theory

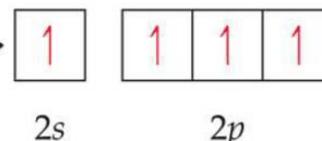
Case 3_Acetylene



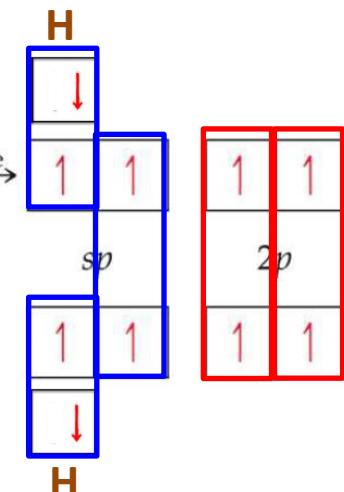
$1^*\sigma$ bond & $2^*\pi$ bonds



Promote



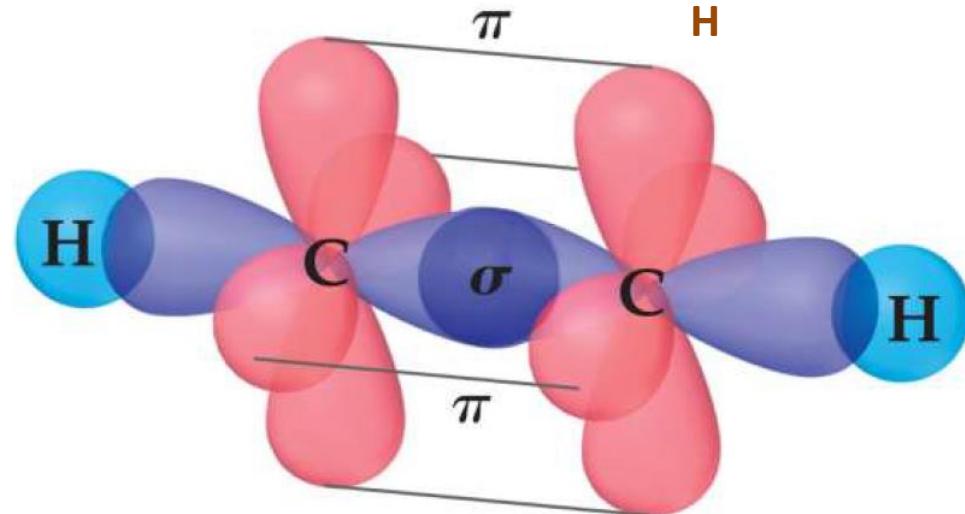
Hybridize



For each carbon...two e-domains (*sp*)

One 2s electron is promoted to the empty 2p orbital.

TWO *sp* hybrid orbitals are formed by mixing ONE s orbital and ONE p orbitals (TWO p orbital is remaining unchanged).



The C≡C triple double bond:

$1^*\sigma$ bond: *sp-sp* between C atoms.

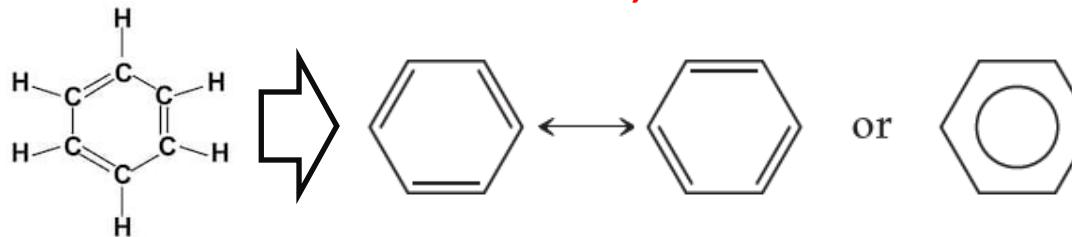
$2^*\pi$ bond: *p-p* between C atoms.

The C–H single bonds:

The remaining one *sp* orbitals of each C atom overlap with the *1s* orbital of the two H atoms to form two σ bonds.

Valence-bond Theory

Resonance Structure, Delocalization and π Bonding_Benzene (C_6H_6)



Resonance structures can be more fundamentally viewed with the valence-bond theory.

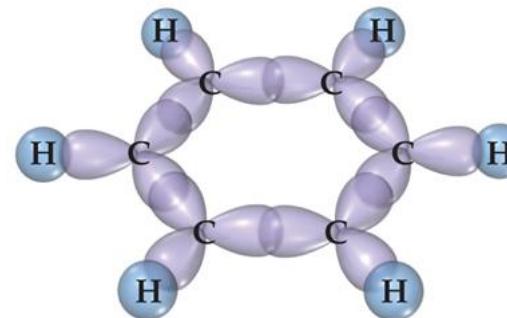
Three e-domain for each C atoms (sp^2)!

The C=C double bond:

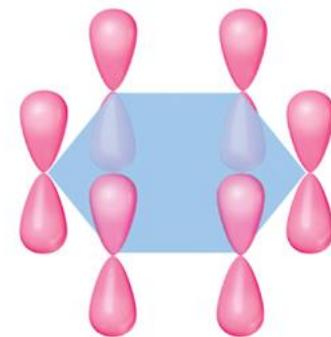
1* σ bond: sp^2-sp^2 between C atoms.

1* π bond: p-p between C atoms.

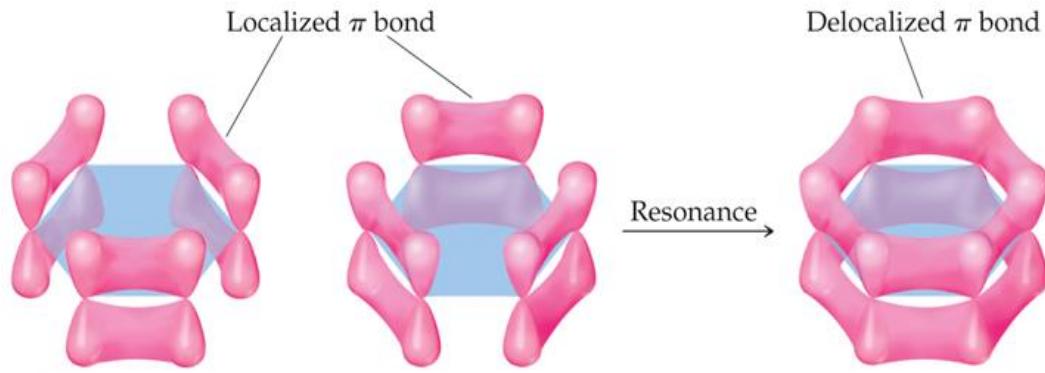
- A benzene molecule has **six C-C/C-H σ bonds** and one unhybridized p orbital on each C atom.
- The **π electrons** in benzene are not localized, they **are delocalized**.
- The even distribution of the π electrons in benzene makes the molecule very stable.



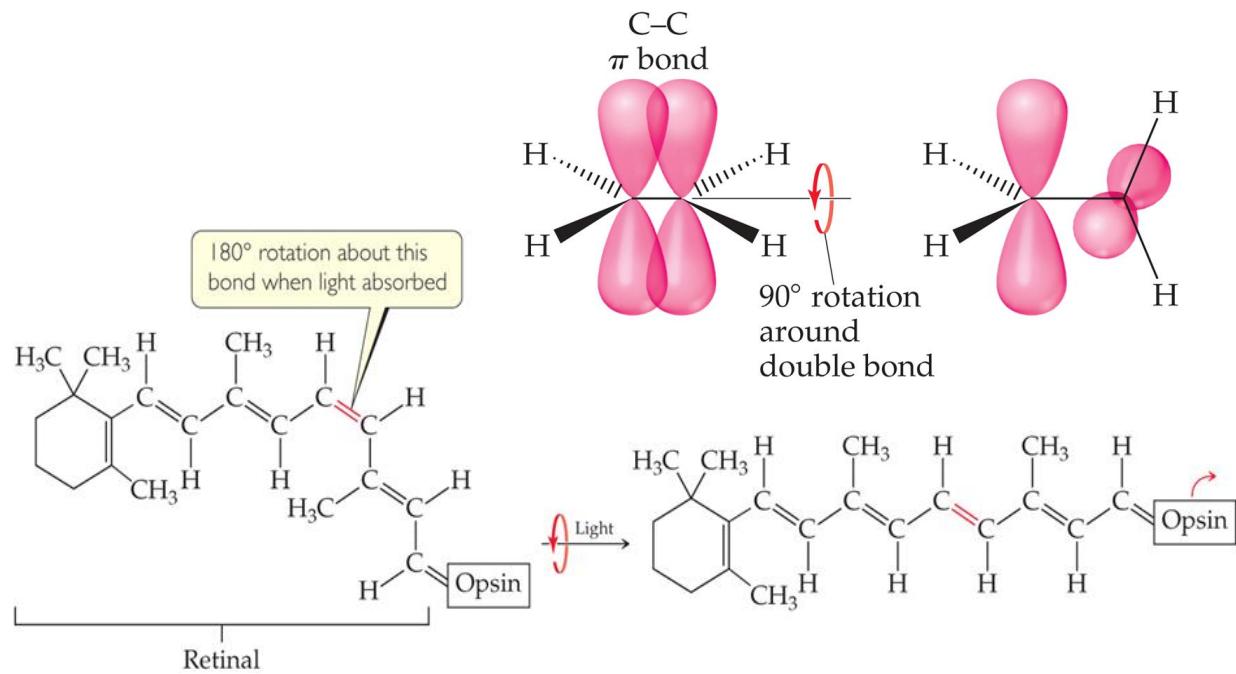
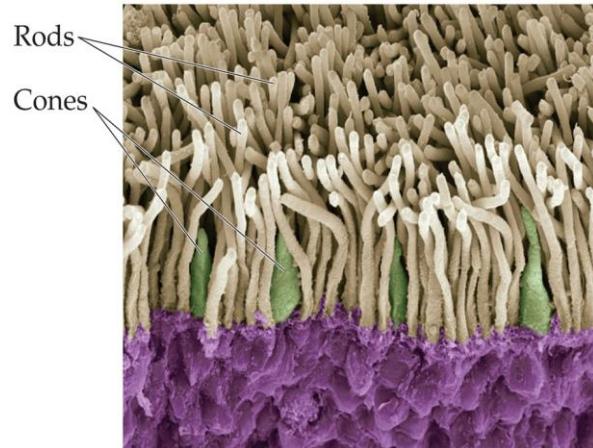
(a) σ bonds



(b) 2p atomic orbitals



The Chemistry of Vision



The retinal molecule!

- A rhodopsin molecule, at the tops of the rod and cone cells, consists of an opsin (a protein) which bonded to retinal (a reddish purple pigment).
- A visible-light photon provides energy to break a C–C π bond of retinal, followed by a 180° rotation about that C–C σ bond, leading to a change in molecular geometry.
- This geometric change causes separation of retinal from opsin, triggering reactions that produce a nerve impulse.

**The End
&
Thanks For Your Attention !**