Chapter 9

Chemical Bonding II: Molecular Geometry and Bonding Theories

Topics

- Molecular Geometry
- Molecular Geometry and Polarity
- Valence Bond Theory
- Hybridization of Atomic Orbitals
- Hybridization in Molecules Containing Multiple Bonds
- Molecular Orbital Theory
- Bonding Theories and Descriptions of Molecules with Delocalized Bonding

9.1 Molecular Geometry

- **Lewis structures tell us how the atoms are connected to each other.**
- ***Valence Shell Electron Pair Repulsion (VSEPR)*** **Theory allows us to predict geometry and the shape of the molecules**

VSEPR

- Molecules take a ***shape that*** puts electron pairs in the valence shell of an atom as far away from each other as possible.
- The electron-pairs surrounding an atom (valence electrons) repel one another and are oriented as far apart as possible
- Structure around a given atom is determined principally by minimizing electron –pair repulsion

- To determine electron pairs Lewis structure should be drawn
- Find bonding and nonbonding lone pairs
- Lone pair take more space.
- Electron pairs are referred here as electron domains.
- Electron domain is a lone pair or a bond regardless of whether the bond is single, double or triple (Multiple bonds count as one pair).

VSEPR

- The number of electron domains determines
  - bond angles
  - primary structure
- The number of atoms determines
  - actual shape
- **Strategy to predict geometry:**

VSEPR Model: Valence-Shell Electron-Pair Repulsion Model

- Electron pairs move as far apart as possible to minimize repulsions.

Electron domain is a lone pair or a bond
(the bond may be single, double, or triple).

Strategy to predict geometry:

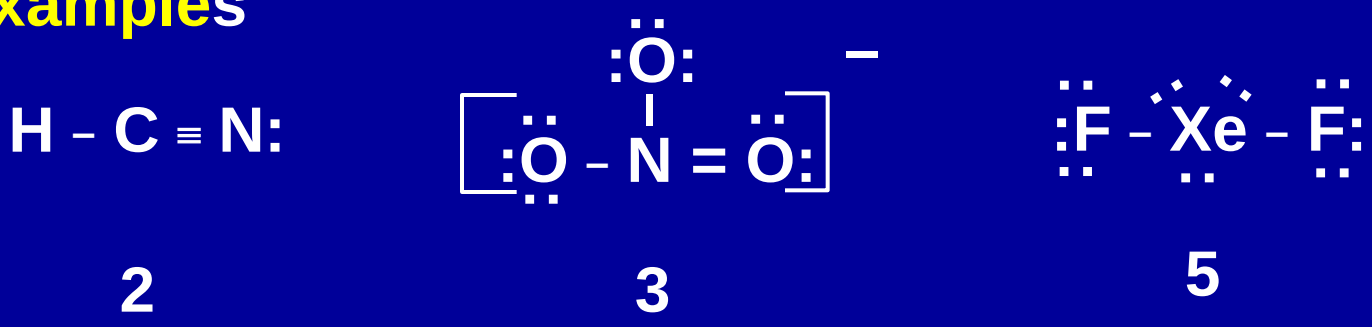
Electron-Domain Geometry and molecular geometry

Steps to determine Geometry

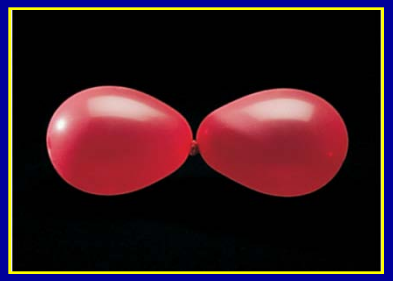
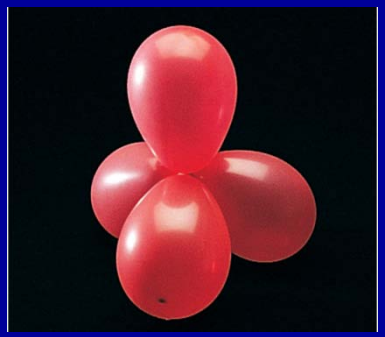
- **Step #1: Draw the molecule's Lewis structure.**
- **Step #2: Count the number of electron domains on**
- **the central atom.**
- **Step #3: Determine the *electron-domain geometry*.**

- **The electron-domain geometry is based on the number of electron domains around the central atom.**

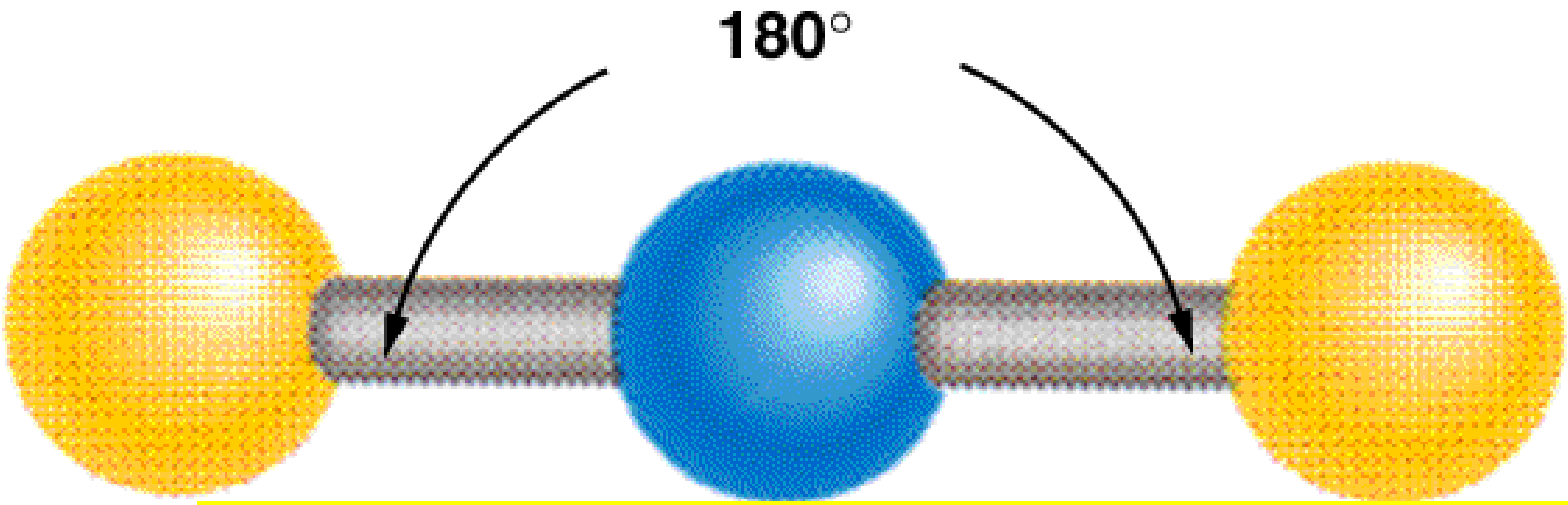
Examples



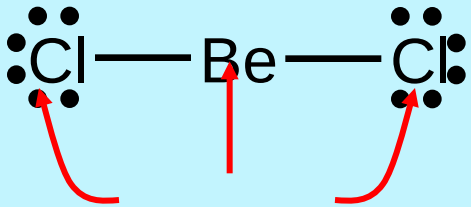
Electron domains and electron-domain- geometry

Number of *Electron* Domains	Electron-Domain Geometry	
2		Linear
3		Trigonal Planar
4		Tetrahedral

Beryllium Chloride

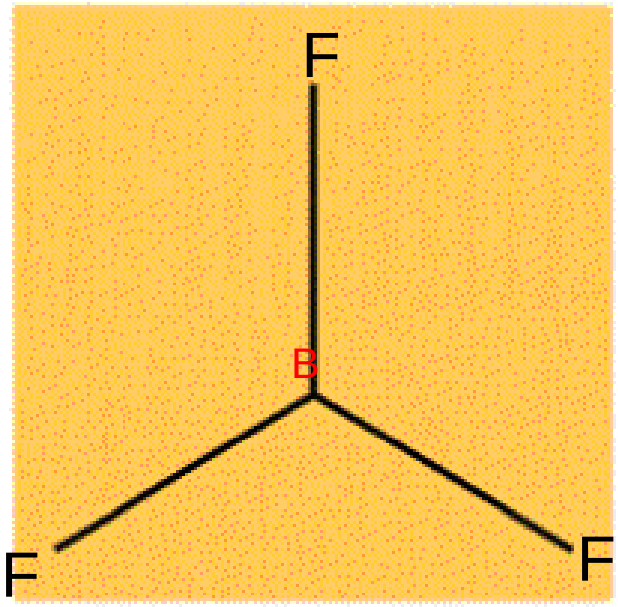


The best arrangement is to place the two electron domains of Be atom on opposite sides

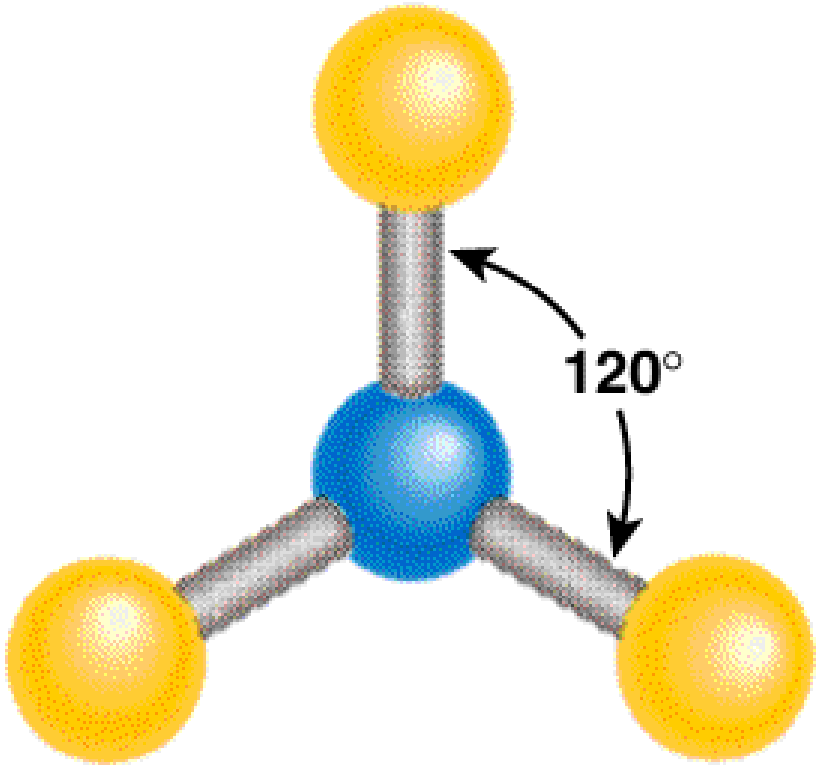


atoms bonded to central atom

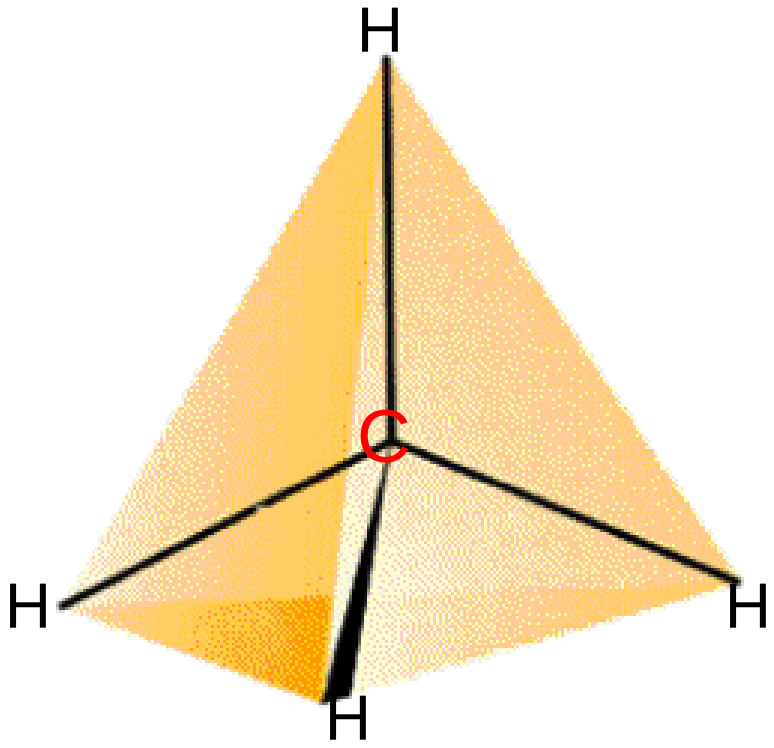
Boron Trifluoride



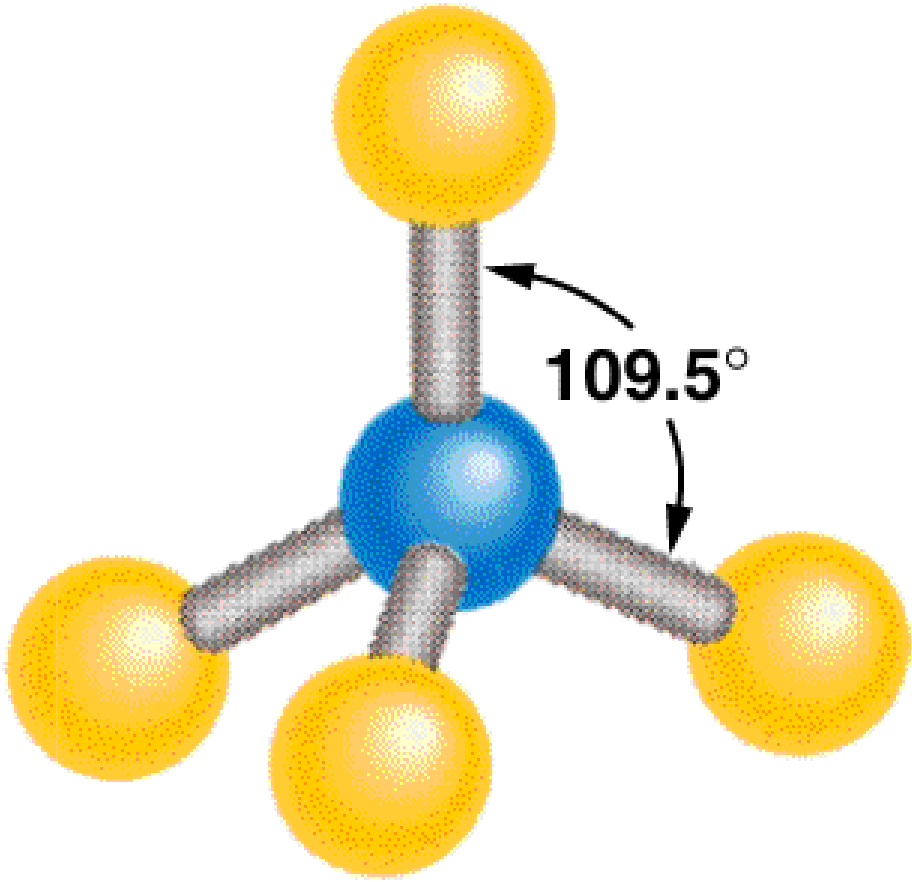
Planar



Methane

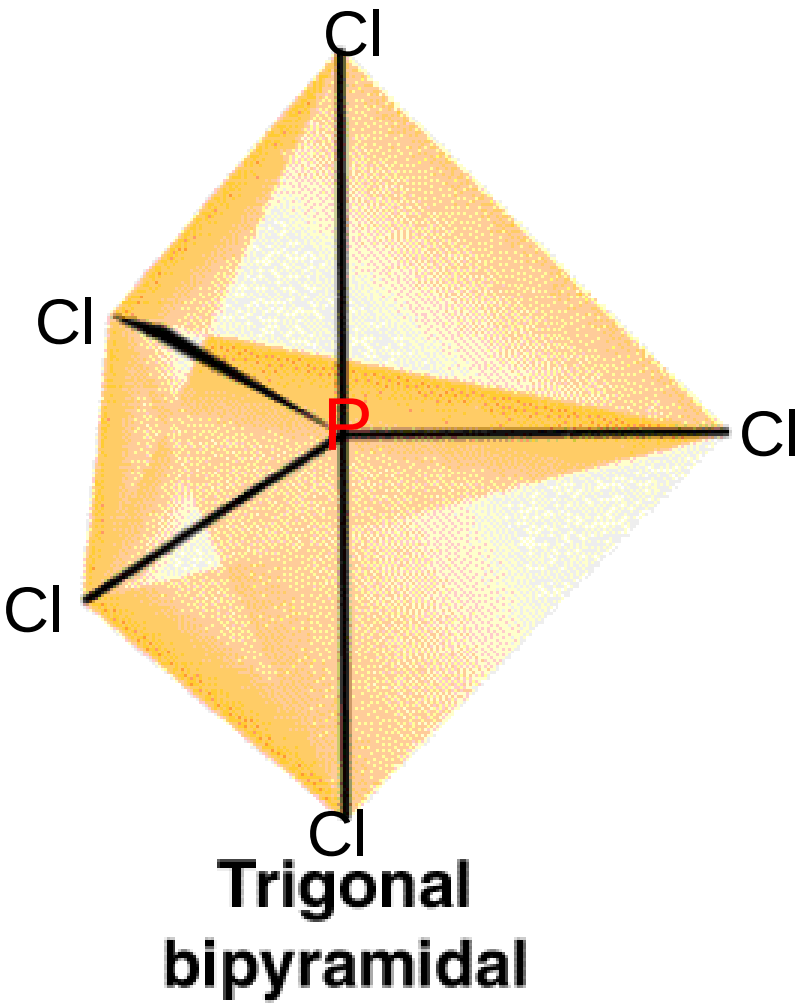


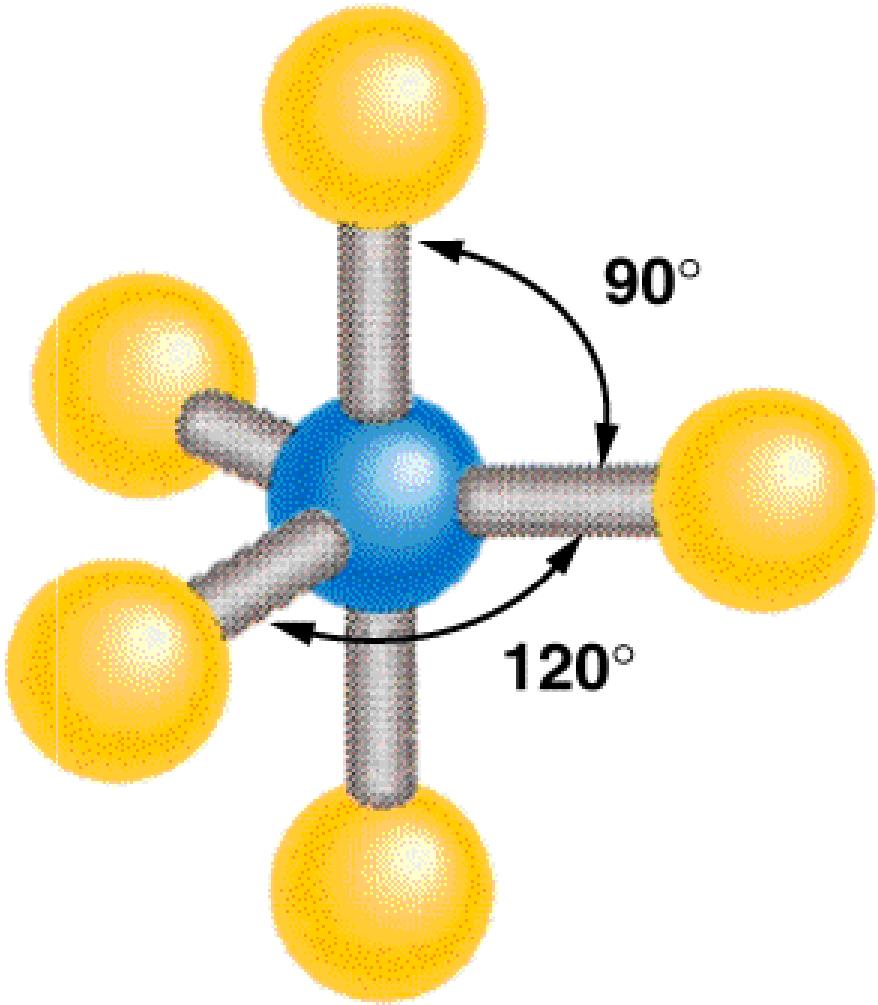
Tetrahedral



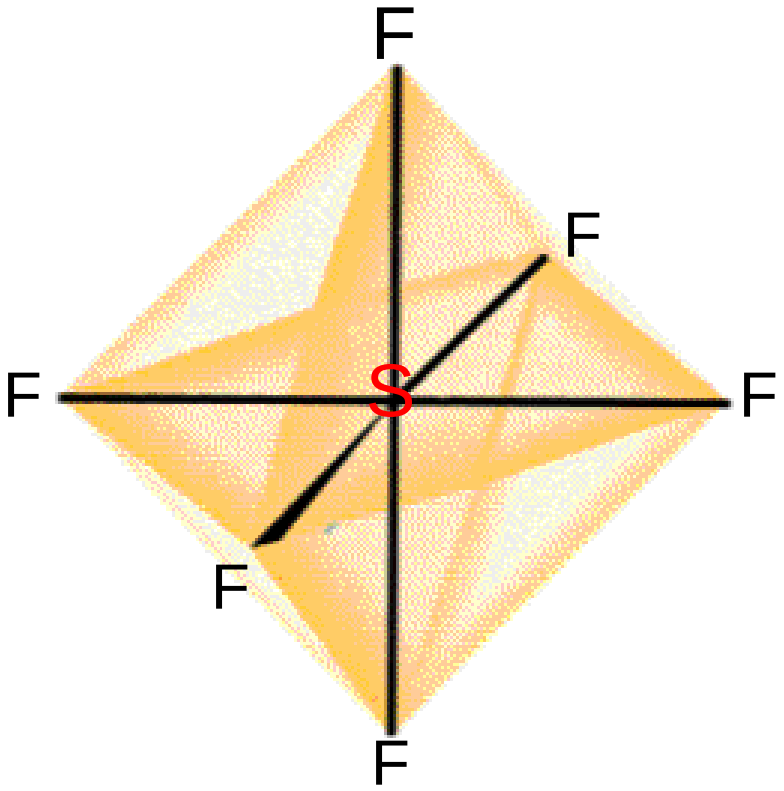
Number of *Electron* Domains		Electron-Domain Geometry
5		Trigonal bipyramidal
6		Octahedral

Phosphorus Pentachloride

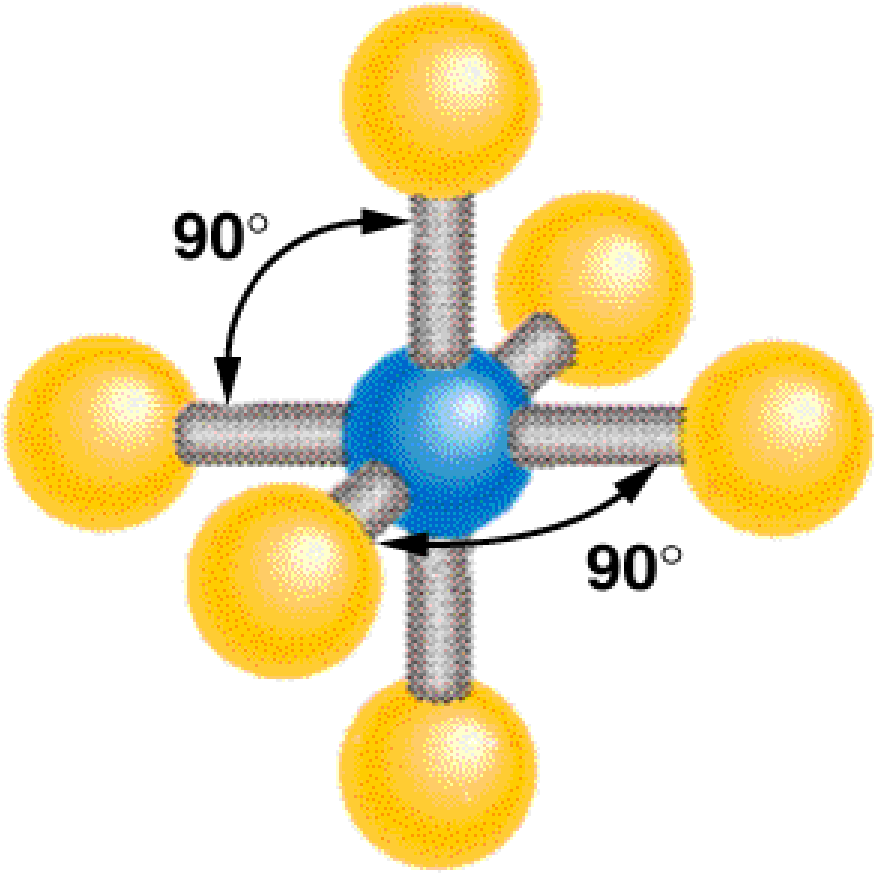




Sulfur Hexafluoride



Octahedral



VSEPR

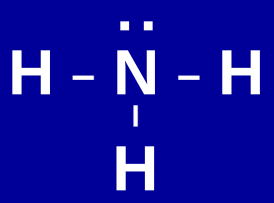
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_2	2	0	linear	linear
AB_3	3	0	Trigonal planar	Trigonal planar
AB_4	4	0	tetrahedral	tetrahedal
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AB_6	6	0	octahedral	octahedral

Step #4: Determine the molecular geometry

The *electron-domain geometry* *and* the number of bonded atoms determine the *molecular geometry*.

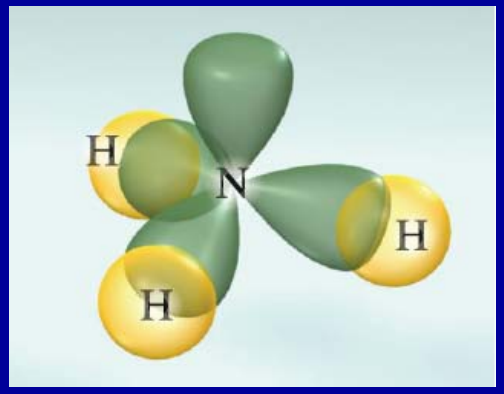
Example: Ammonia, NH_3

Step #1



Step #2 4 e^- domains

electron-domain geometry tetrahedral



Step #3

molecular geometry = trigonal pyramidal

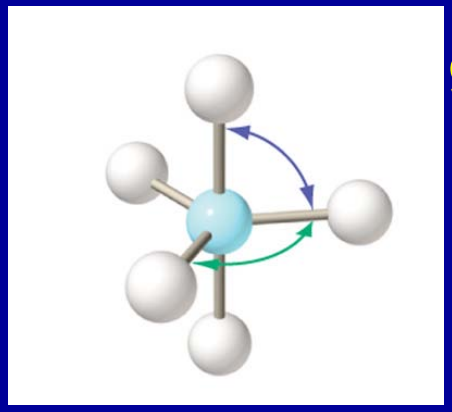
Effect of lone pairs on Geometry

Molecules with unshared (Lone) pairs of electrons

- Unshared pair of electrons (under the influence of one nucleus) spreads out over a volume larger than a bonding pair (under the influence of two nuclei).
- The electron pair geometry is approximately same as that observed when only single bonds are involved
- The bond angles are either equal to the ideal values or little less
- The molecular geometry is quite different when lone pairs are involved.
- Molecular geometry refers only to the positions of the bonded atoms

Axial and equatorial positions

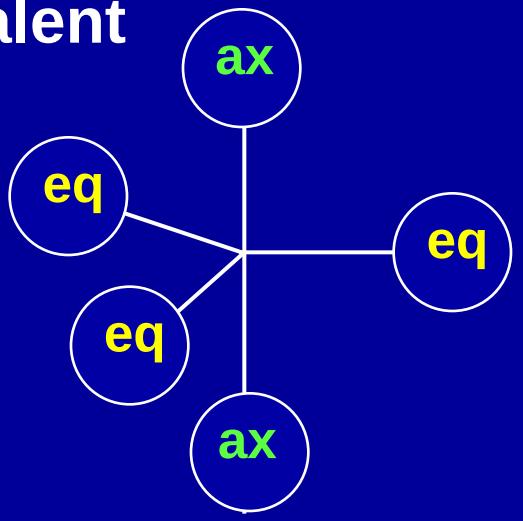
The 5 electron domains are not all equivalent



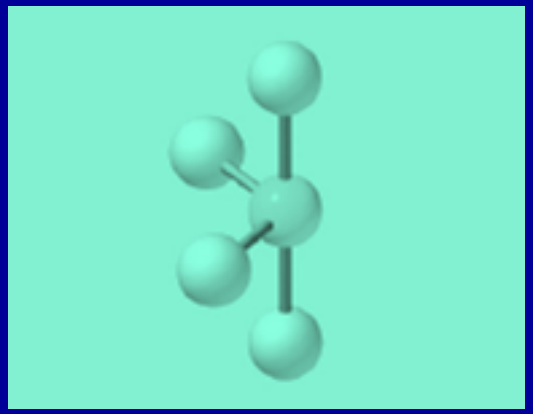
90°

120°

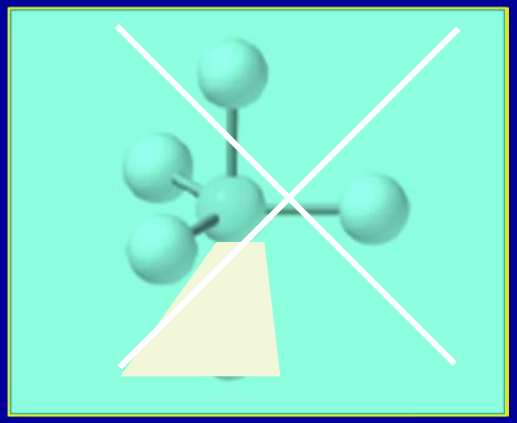
ax = axial
eq = equatorial



For SF_4, which geometry is correct?



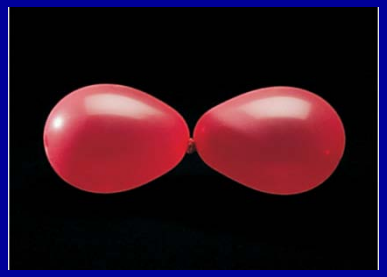
or



Why?

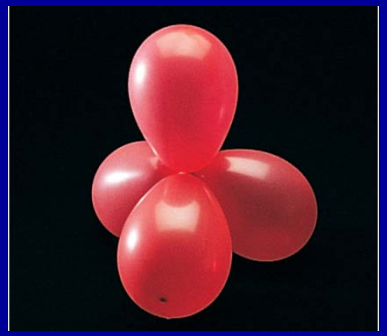
Fewest lone-pair – **bond-pair interactions** at angles of 90°

Note: The common molecular geometries are *all* derived from these 5 electron-domain geometries.



Linear

Bent
Trigonal planar



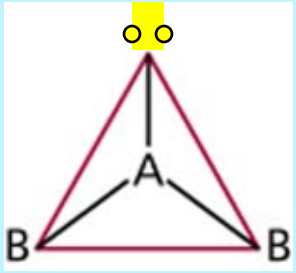
Bent
Trigonal pyramidal
Tetrahedral

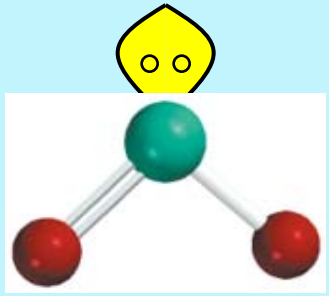
T-shaped
Seesaw
Trigonal bipyramidal

Linear
T-shaped
Square planar
Square pyramidal
Octahedral

Electron domain and molecular geometries of molecules with lone pairs on the central atom

Type of molecule	# of atoms bonded to central atom	# lone pairs on central atom	Electron domain geometry	Molecular *geometry*
AB_3	3	0	trigonal planar	trigonal planar
AB_2E	2	1	trigonal planar	Bent



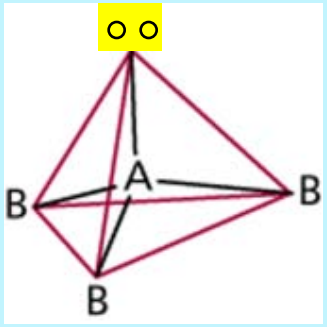


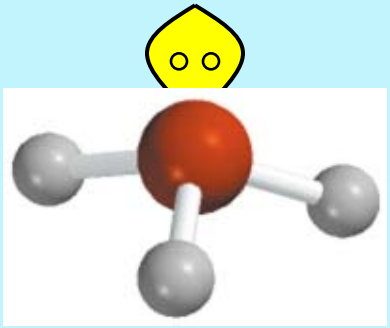
SO_2

< 120°

Type of molecule	# of atoms bonded to central atom	# lone pairs on central atom	Electron domain geometry	Molecular Geometry
AB_4	4	0	tetrahedral	tetrahedral
AB_3E	3	1	tetrahedral	trigonal pyramidal

NH_3

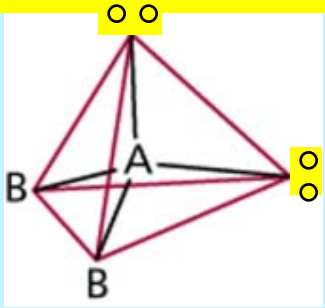


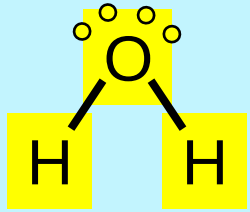


< 109.5°
107°

Type of molecule	# of atoms bonded to central atom	# lone pairs on central atom	Electron domain geometry	Molecular Geometry
AB_4	4	0	tetrahedral	tetrahedral
AB_3E	3	1	tetrahedral	trigonal pyramidal
AB_2E_2	2	2	tetrahedral	Bent
ABE_3	1	3	H-B	Linear

H_2O

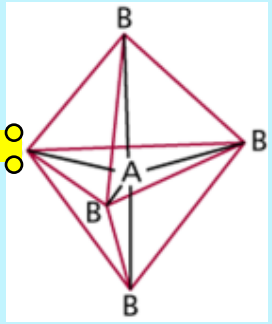


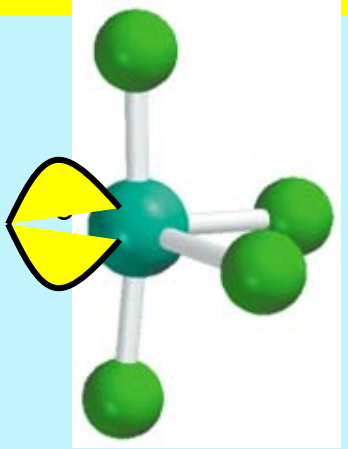


< 109.5º
104.5º

Type of molecule	# of atoms bonded to central atom	# lone pairs on central atom	Electron domain geometry	Molecular Geometry
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AB_4E	4	1	trigonal bipyramidal	distorted tetrahedron

SF_4



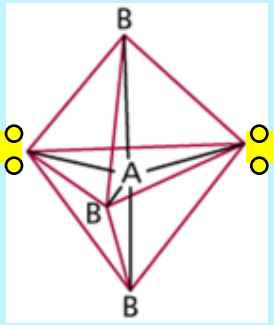


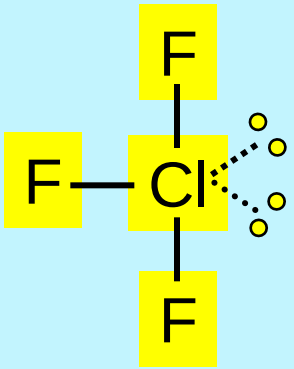
90^o, 120^o, 180^o

See-saw

Type of molecule	# of atoms bonded to central atom	# lone pairs on central atom	Electron domain geometry	Molecular Geometry
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AB_4E	4	1	trigonal bipyramidal	distorted tetrahedron
AB_3E_2	3	2	trigonal bipyramidal	T-shaped

ClF_3

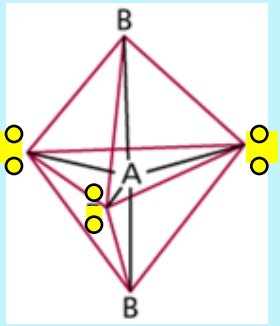


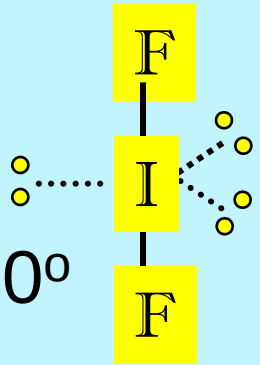


90°, 180°

Type of molecule	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AB_4E	4	1	trigonal bipyramidal	distorted tetrahedron
AB_3E_2	3	2	trigonal bipyramidal	T-shaped
AB_2E_3	2	3	trigonal bipyramidal	linear

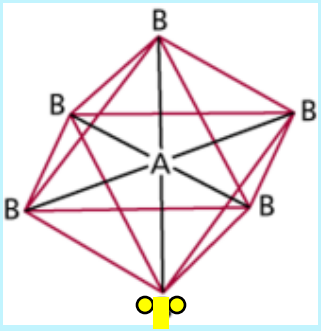
IF_2



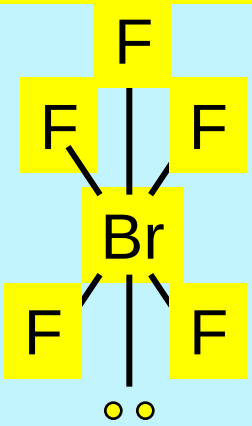


180°

Type of molecule	# of atoms bonded to central atom	# lone pairs on central atom	Electron domain geometry	Molecular Geometry
AB_6	6	0	octahedral	octahedral
AB_5E	5	1	octahedral	square pyramidal



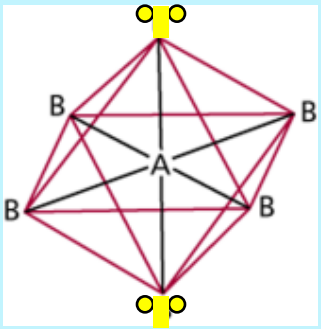
BrF_5

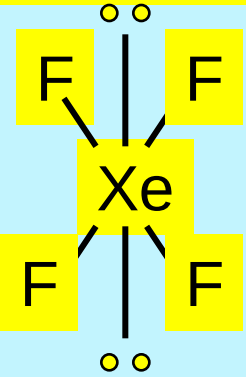


90^o, 180^o

Class	# of atoms bonded to central atom	# lone pairs on central atom	Electron domain geometry	Molecular Geometry
AB_6	6	0	octahedral	octahedral
AB_5E	5	1	octahedral	square pyramidal
AB_4E_2	4	2	octahedral	square planar

XeF_4

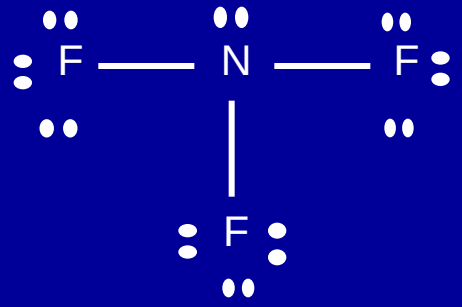




90°, 180°

NF_3

i)



ii) 4 electron domains on the central atom.

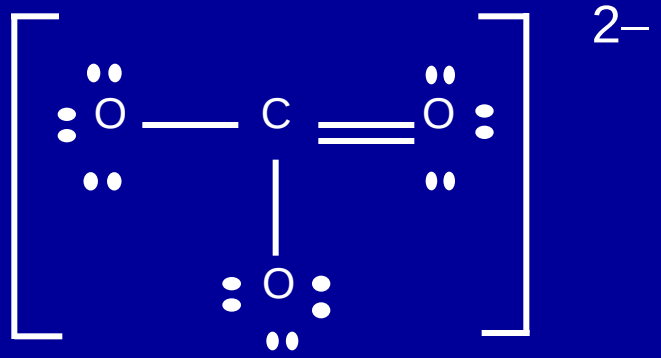
Electron-domain geometry: tetrahedral

iii) One lone pair on the central atom.

Molecular geometry: trigonal pyramidal

a) CO_3^{2-}

i)



ii) 3 electron domains on the central atom.

Electron-domain geometry: trigonal planar

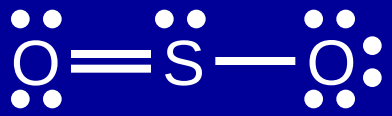
iii) No lone pairs on the central atom.

Molecular geometry: trigonal planar

Predicting Molecular Geometry

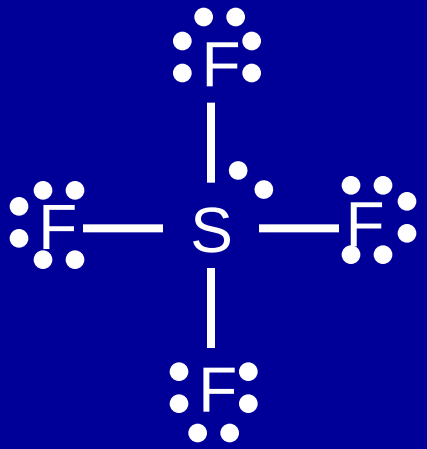
1. **Draw Lewis structure for molecule.**
2. **Count number of lone pairs on the central atom and number of atoms bonded to the central atom.**
3. **Use VSEPR to predict the geometry of the molecule.**

What are the molecular geometries of SO_2 and SF_4?



AB_2E

bent



AB_4E

distorted tetrahedron

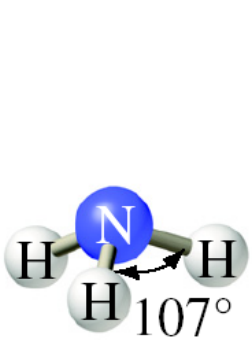
Deviations from ideal bond angles

- All electron domains repel each other.

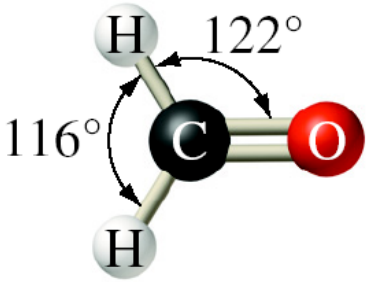
- The repulsion between domains depends on the types of domains involved.

single bond < double bond < triple bond < lone pair

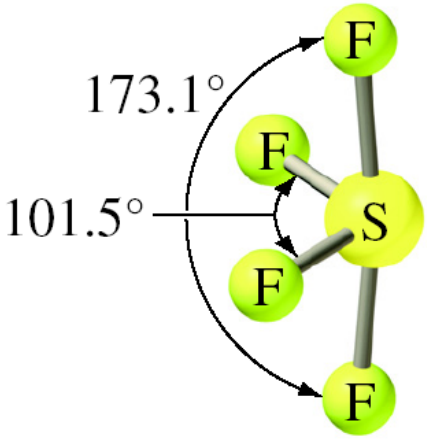
Increasingly repulsion



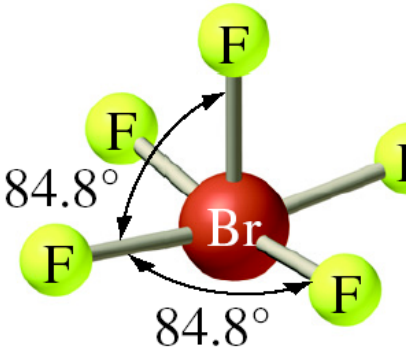
NH_3



CH_2O



SF_4



BrF_5

- **lone-pair - lone-pair repulsion is greater than lone-pair - bonding-pair repulsion is greater than bonding-pair - bonding-pair repulsion**

Geometry of molecules with more than one central atom

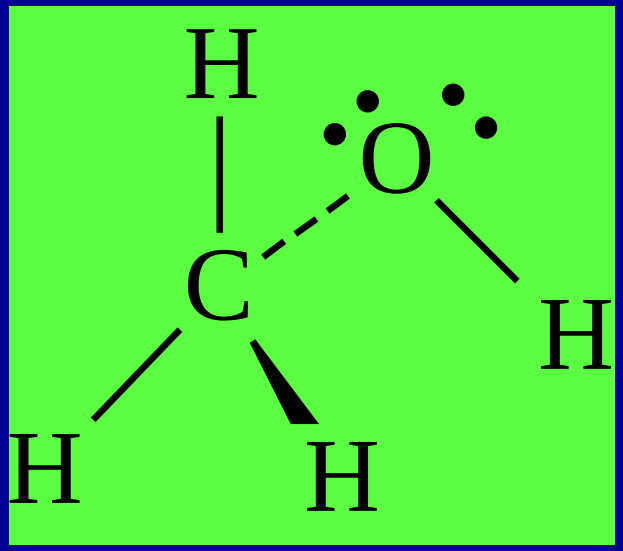
- The central atoms of the molecule should be labeled first.
- Geometry can be predicted by focusing on each central atom by counting the electron pairs around each central atom.

Geometry of molecules with more than one central atom

CH_3OH

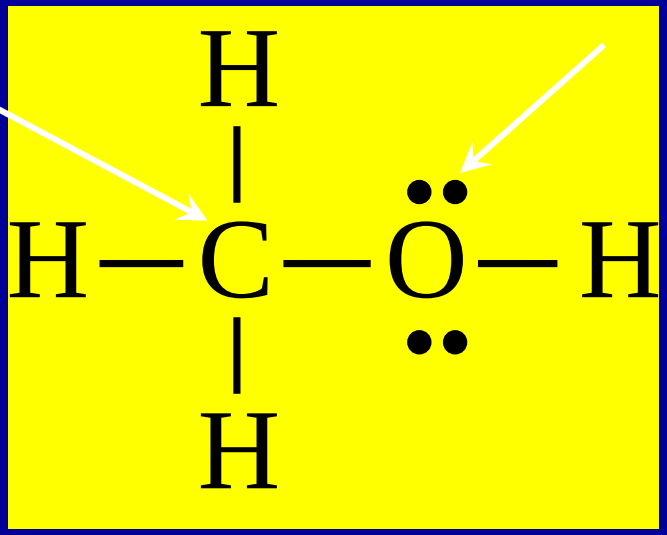
No lone pairs AX_4

tetrahedral



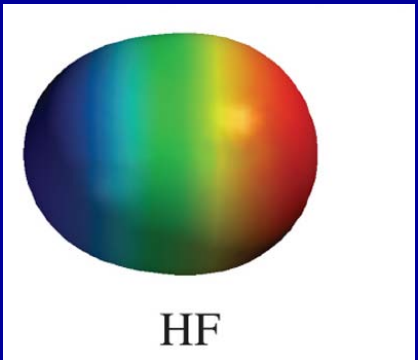
AX_4 2 lone pairs

bent



9.2 Molecular geometry and polarity

The HF bond is polar and HF has a *dipole moment* (μ).



$\delta+ \quad \delta-$

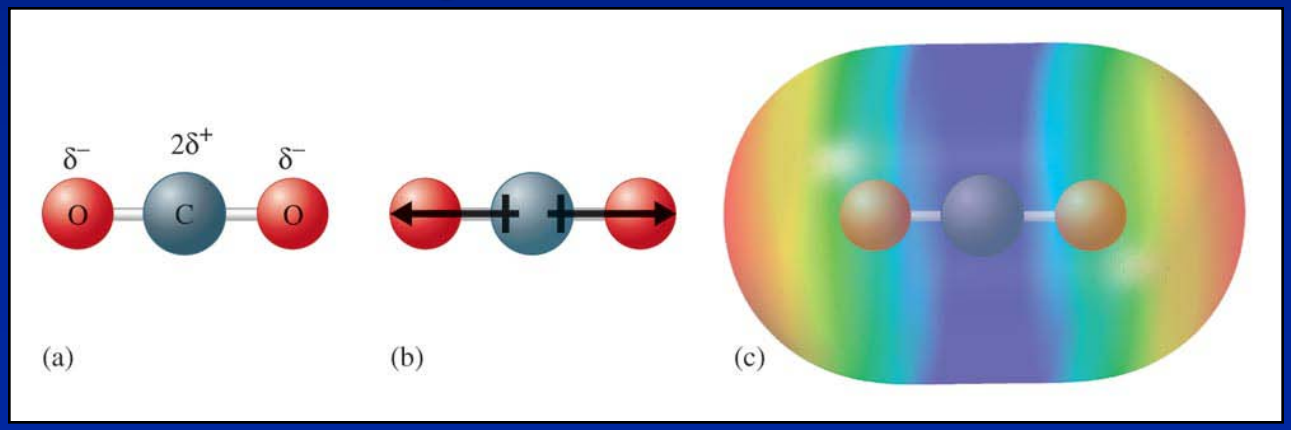
H – F

H – F

Diatomic molecules are Bond dipoles are polar if the *two atoms are different*

Polarity of polyatomic molecules

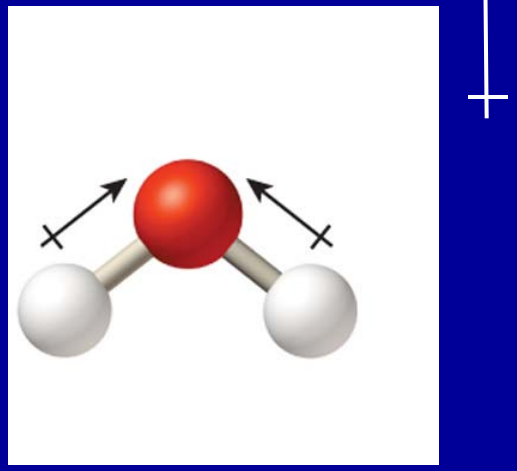
- **The effect of polar bonds on the polarity of the entire molecule depends on the molecule shape**
  - **carbon dioxide has two polar bonds, and is linear = *nonpolar molecule***
    - **Remember bond dipoles are additive since they are *vectors*.**



Molecules with more than two atoms

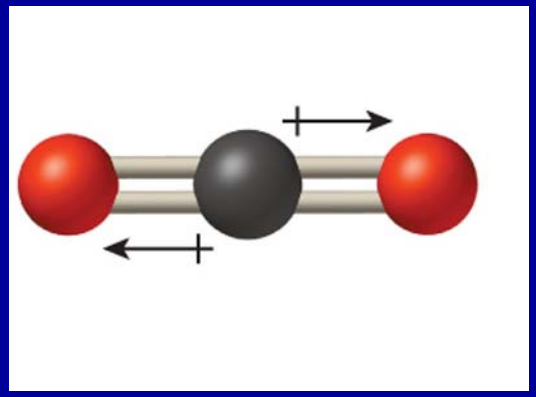
– Remember bond dipoles are additive since they are *vectors*.

H_2O



dipole moment > 0

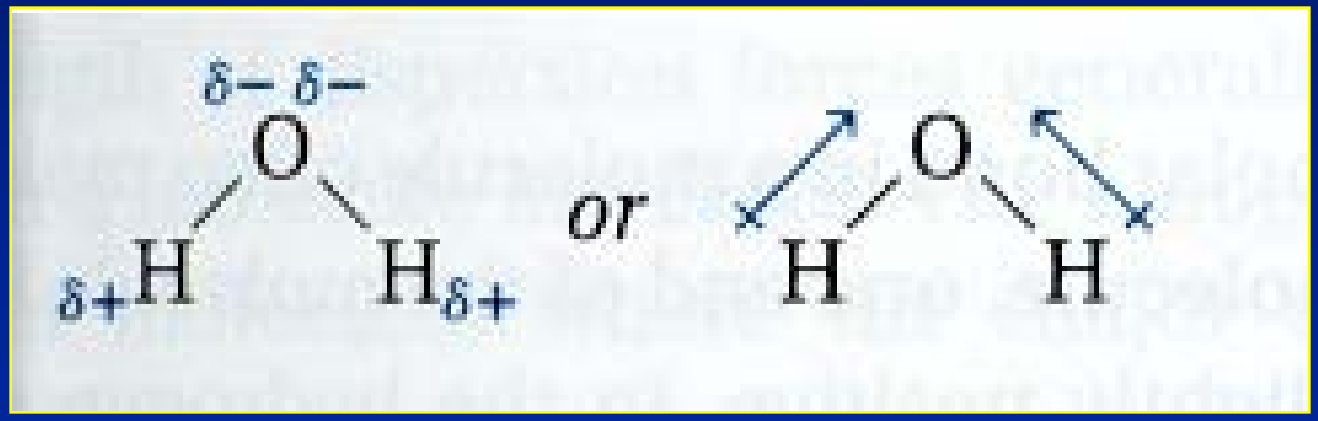
CO_2



dipole moment = 0

Polar molecules

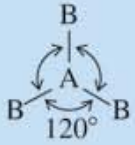
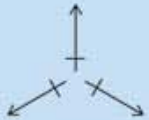
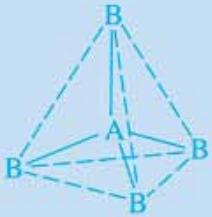
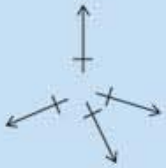
- The effect of polar bonds on the polarity of the molecule depends on the molecular shape
  - water has two polar bonds and a bent shape; the highly electronegative oxygen pulls the e^- away from H = very polar!



Thus, H_2O molecule has a dipole moment

Molecules with polar bonds but no resulting dipole moment

TABLE 8.2 Types of Molecules with Polar Bonds but No Resulting Dipole Moment

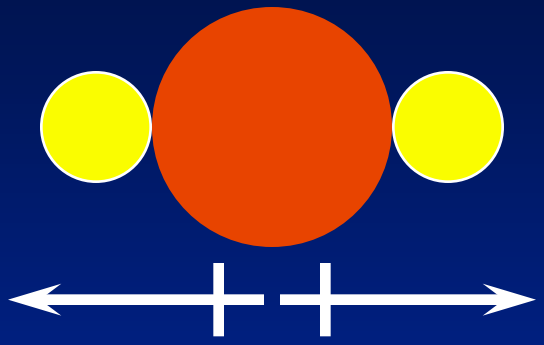
Type			Cancellation of Polar Bonds	Example	Ball-and-Stick Model
Linear molecules with two identical bonds	B—A—B	CO_2			
Planar molecules with three identical bonds 120 degrees apart				SO_3	
Tetrahedral molecules with four identical bonds 109.5 degrees apart				CCl_4	

How to decide for molecular polarity?

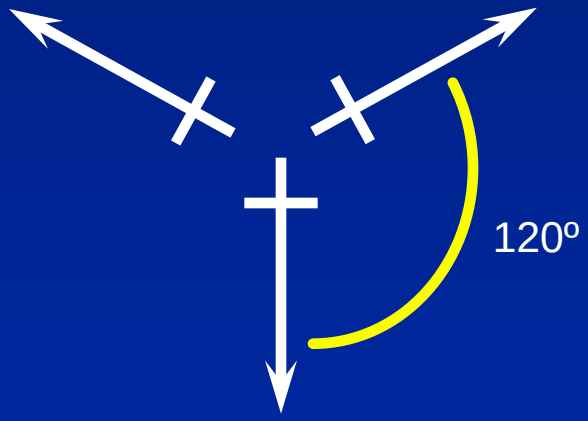
- Any diatomic molecule with a polar bond is a polar molecule
- For a three or more atoms molecule there are two considerations:
  - There must be a polar bond.
  - Geometry can't cancel it out.

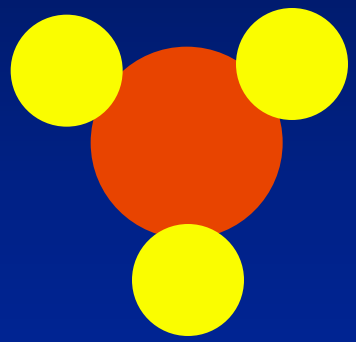
Geometry and polarity

- Three shapes will cancel them out.
- Linear

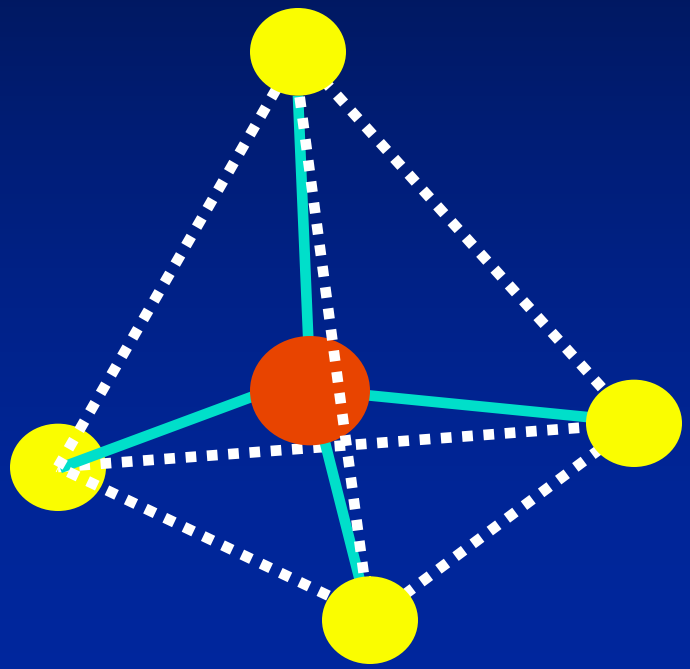


- Planar triangles

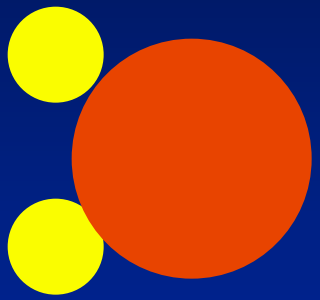


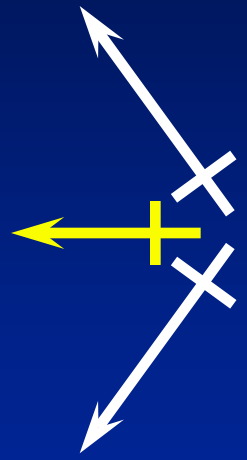


- Tetrahedral

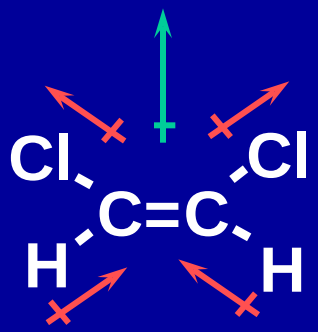


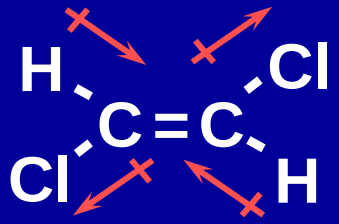
- Others don’t cancel, e.g.,
- Bent molecule

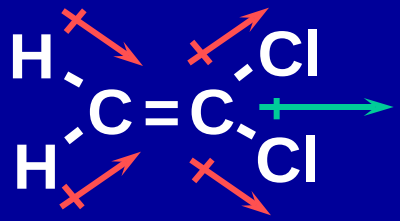




Example: Dichloroethene, $C_2H_2Cl_2$, exists as three isomers.







***cis*-1,2-dichloroethene** | ***trans*-1,2-dichloroethene** | **1,1-dichloroethene**

polar
μ = 1.90 D
bp = 60.3°C

nonpolar
μ = 0 D
bp = 47.5°C

polar
μ = 1.34 D
bp = 31.7°C

9.3 Valence Bond Theory

- Electrons in molecules occupy *atomic orbitals*.

- Covalent bonding results from the *overlap* of atomic orbitals.

- **Overlap**: two orbitals share a common region in space

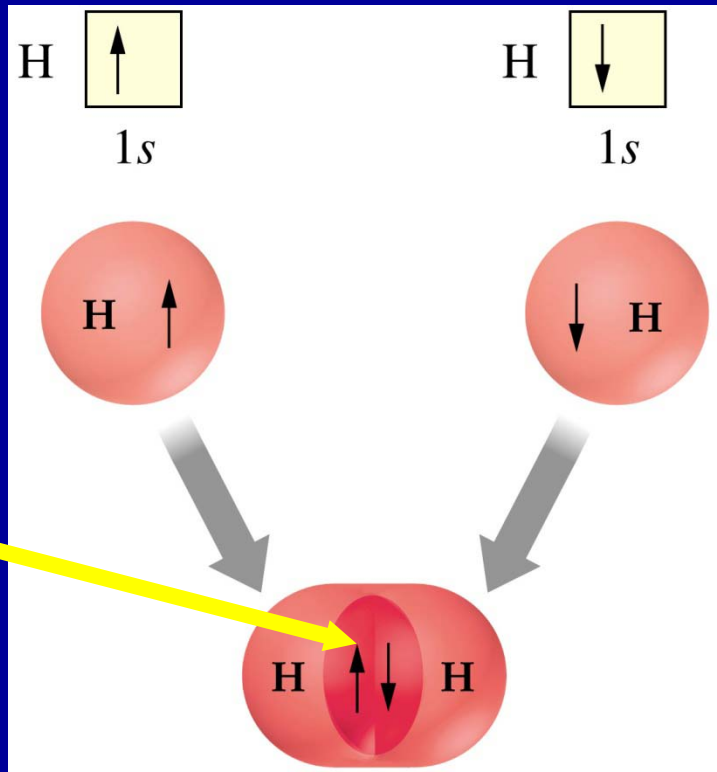
According to the model:

- **For an atom to form a covalent bond it must have an *unpaired electron***
- **Number of bonds formed by an atom should be determined by its number of unpaired electrons**

How do atoms share electrons between their valence shells?

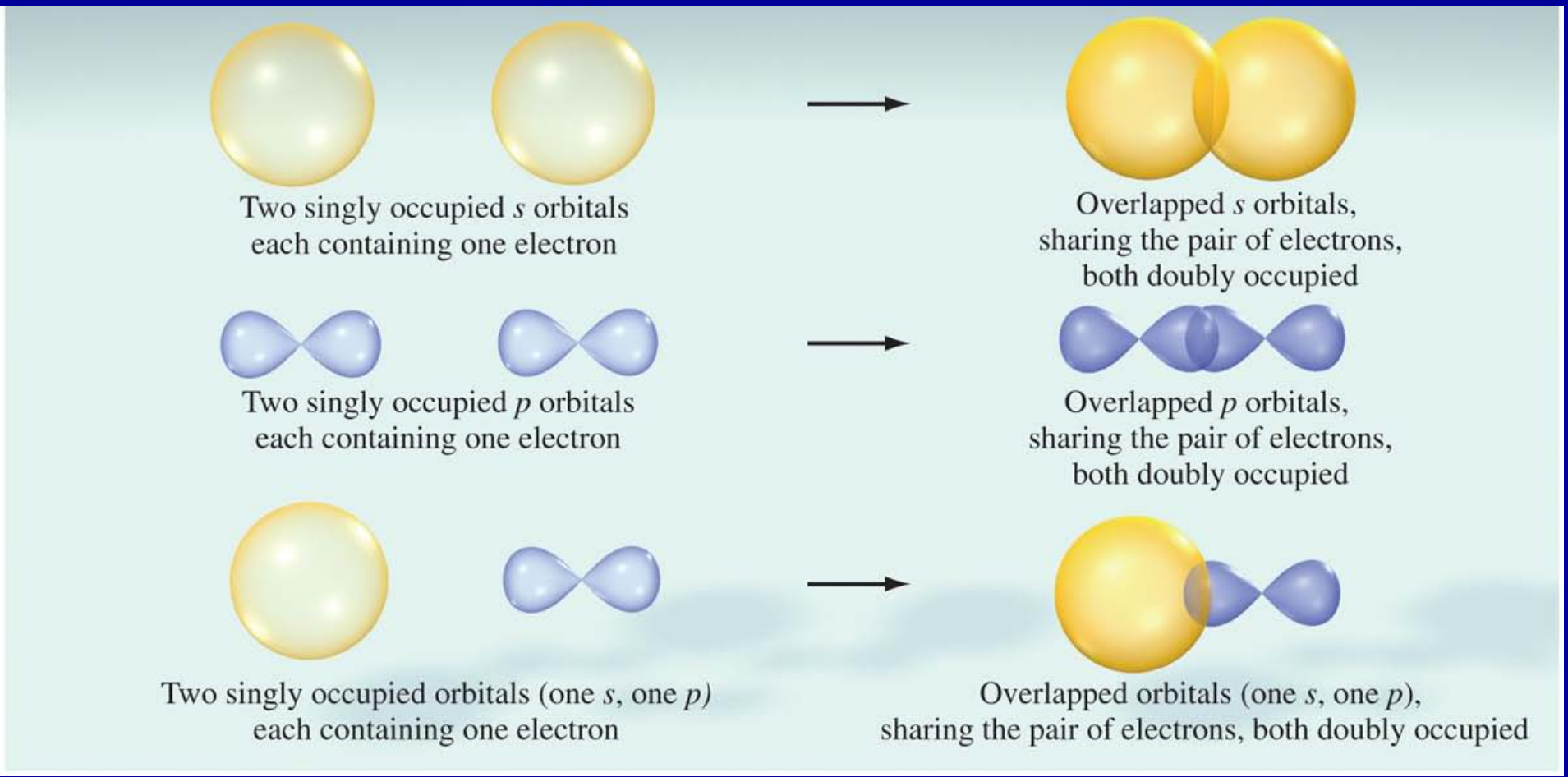
The localized electron bonding model

- A covalent bond is formed by the pairing of two electrons with opposing spins in the region of overlap of atomic orbitals between two atoms

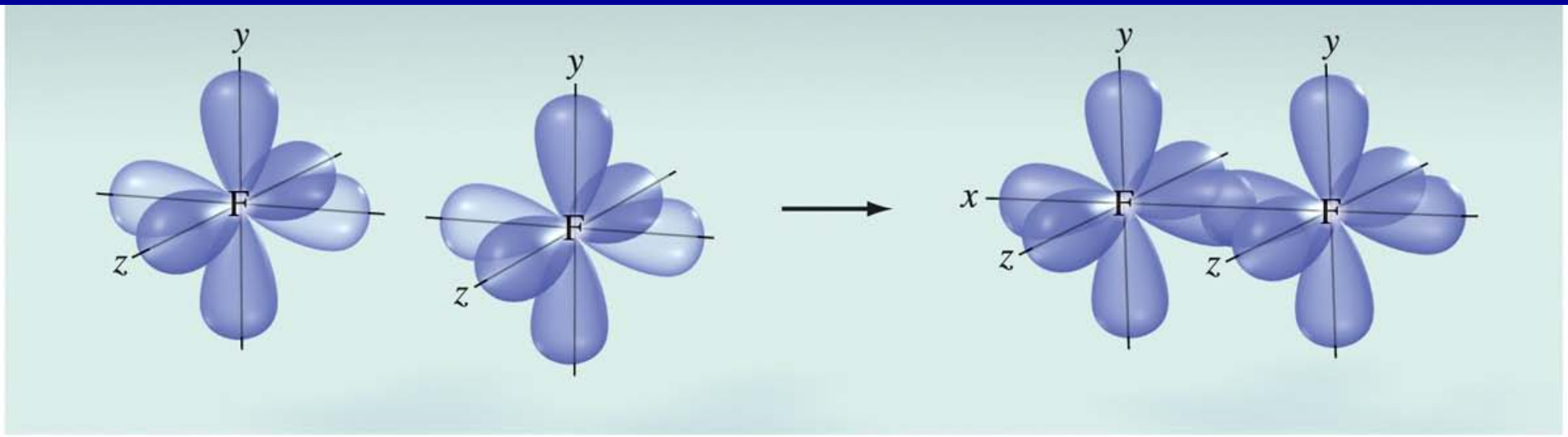


- This overlap region has high electron charge density
- The more extensive the overlap between two orbitals, the stronger is the bond between two atoms

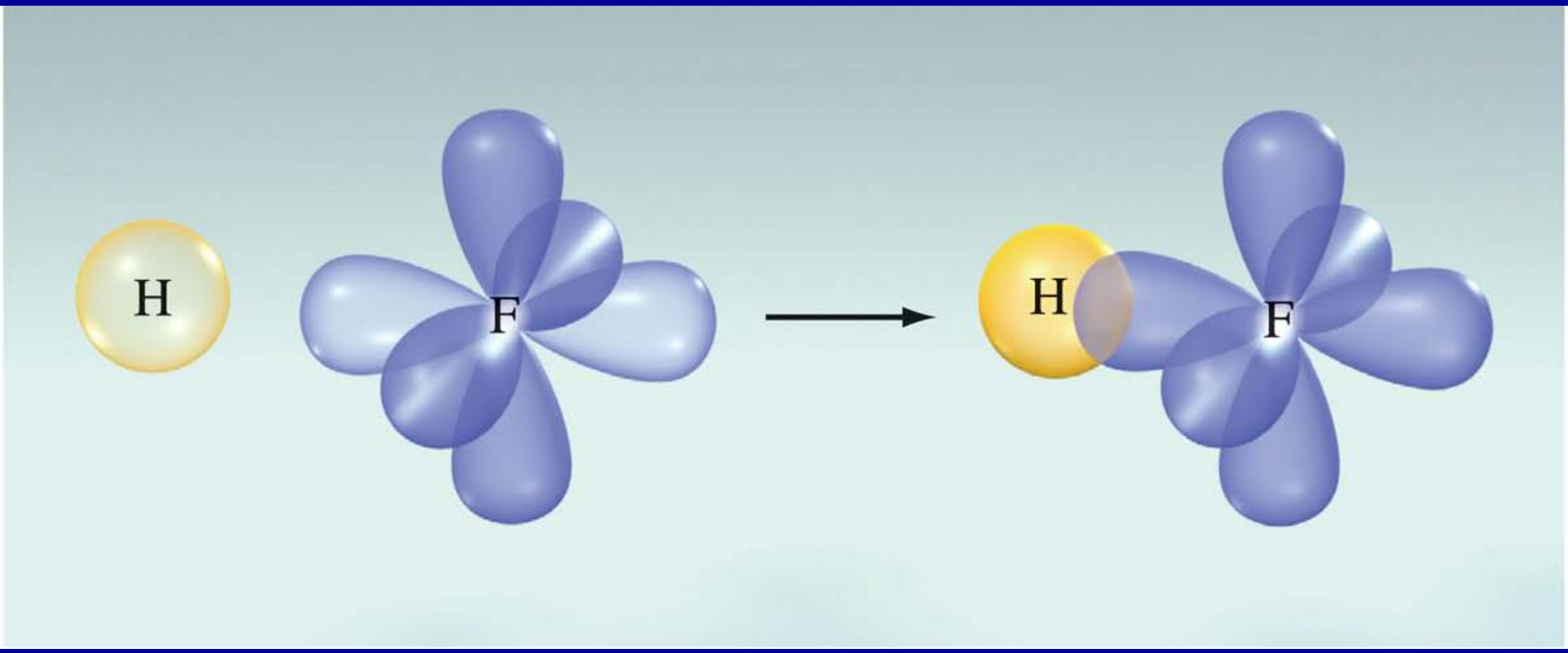
Representation of singly-occupied and doubly-occupied *s* and *p* atomic orbitals. Singly-occupied orbitals appear light; doubly-occupied orbitals appear darker.



Example: $F(1s^2 2s^2 2p^5) + F(1s^2 2s^2 2p^5) \rightarrow F_2$



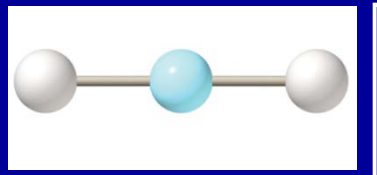
Example: $H(1s^1) + F(1s^2 2s^2 2p^5) \rightarrow HF$



9.4 Hybridization of Atomic Orbitals

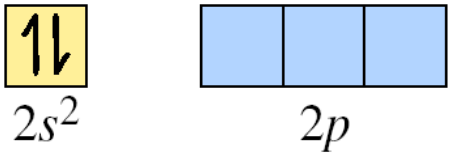
- Valence bond theory cannot account for many experimental observations.

Beryllium Chloride, $BeCl_2$

Cl–Be–Cl —VSEPR→ 

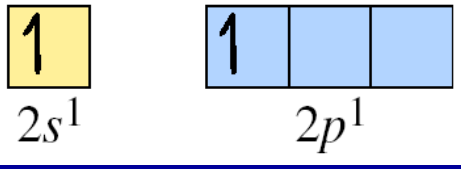
linear
both bonds equivalent

#1 Be

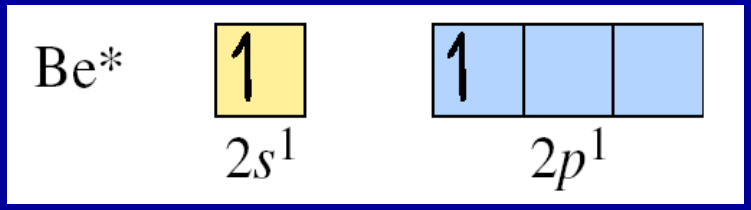


- No unpaired electrons

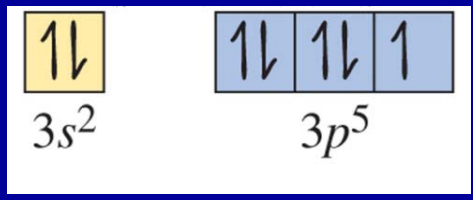
#2 Be*



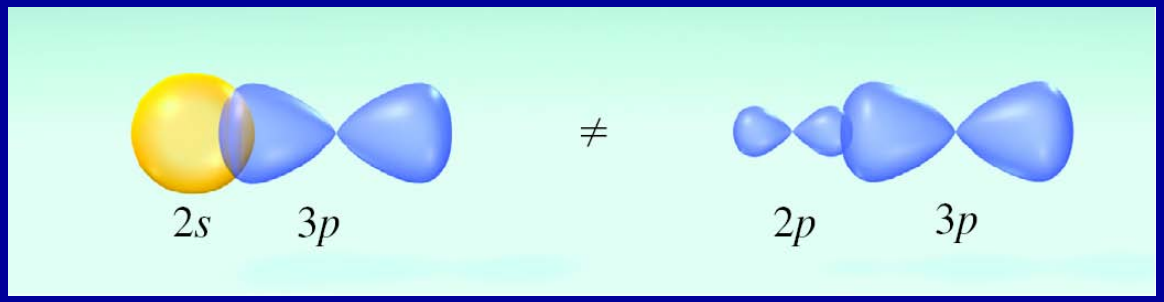
- 2 types of overlap with 2*s* and 2*p*



Cl



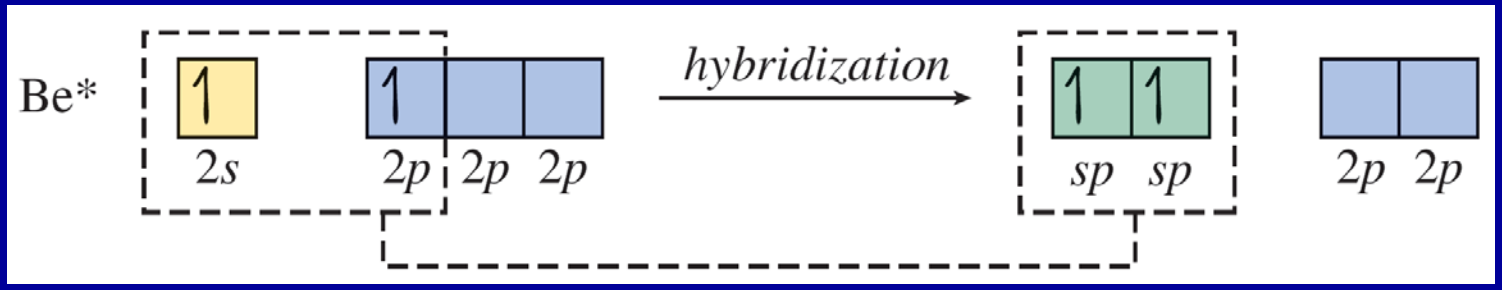
- The orbitals in which the two unpaired electrons reside are different from each other, 2s and 2p
- Thus, the bonds obtained as a result of the overlap with the 3p orbital of Cl are expected to be different



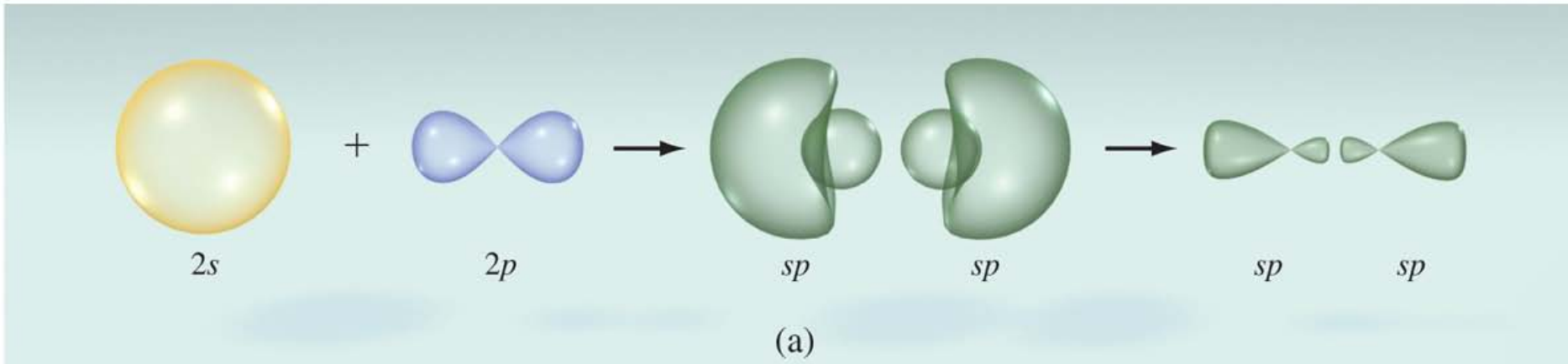
- However, experimentally, the bonds are identical in length and strength.

- The atomic orbitals on an atom mix to form hybrid orbitals.
- Hybridization of *s* and *p* orbitals
  - ***sp* hybridization**

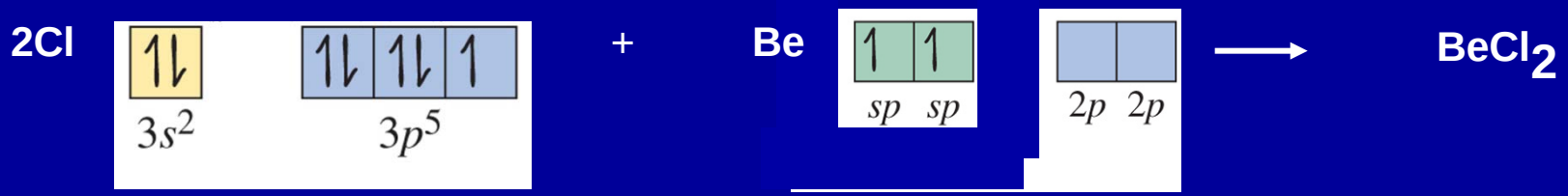
- **The two orbitals, 2s and 2p become mixed, or hybridized to form bonds**
- **The hybrid orbitals are designated 2sp or only sp**

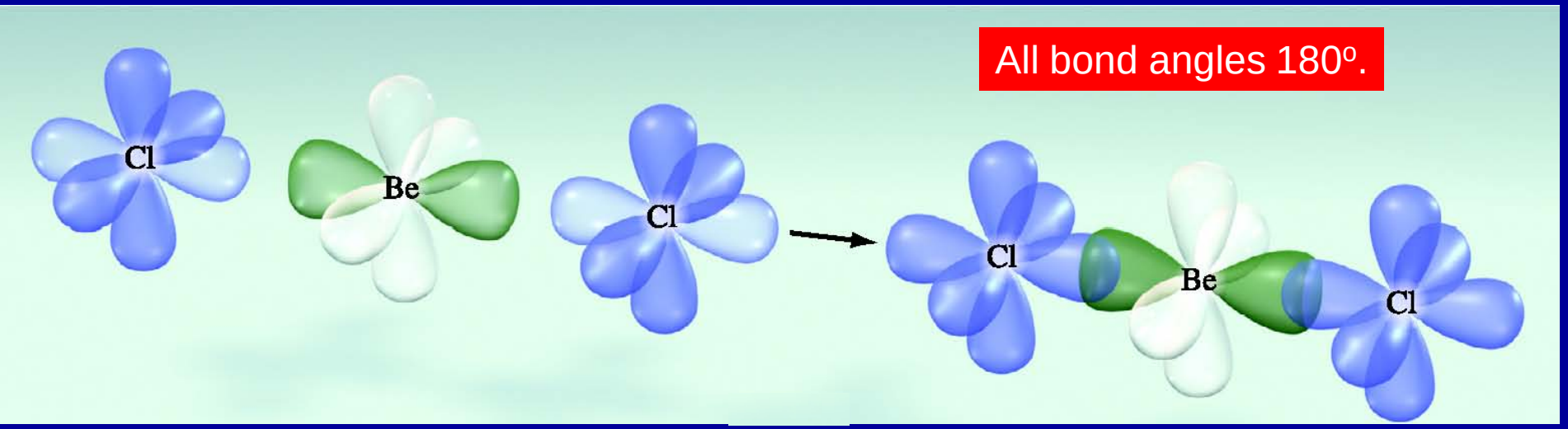


- **The two *sp* orbitals point in opposite directions inline with one another.**



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





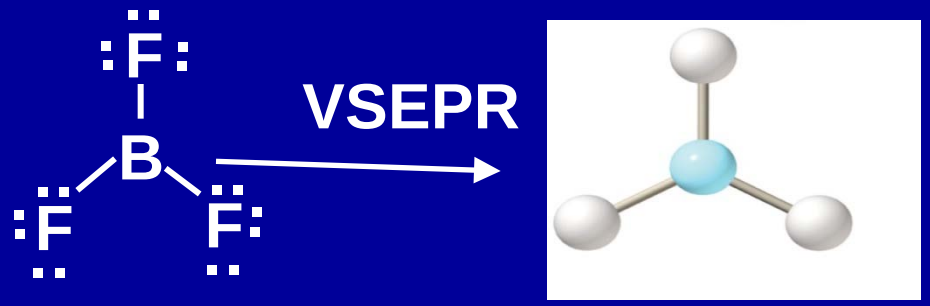
The total number of hybrid orbitals is equal to the number of atomic orbitals combined

Hybridization ?

- Two or more atomic orbitals are mixed to produce a new set of orbitals (blended orbitals)
- Number of hybrid orbitals = number of atomic orbitals mixed

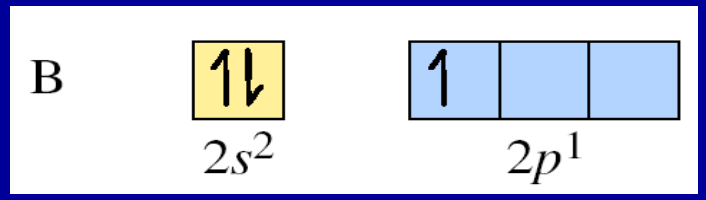
sp^2 hybridization

Example: Boron trifluoride, BF_3



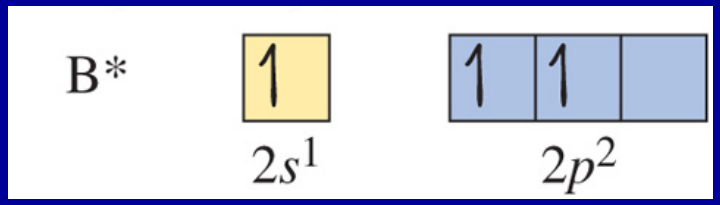
- trigonal planar
- all bonds equivalent

#1



- only 1 unpaired electron

#2

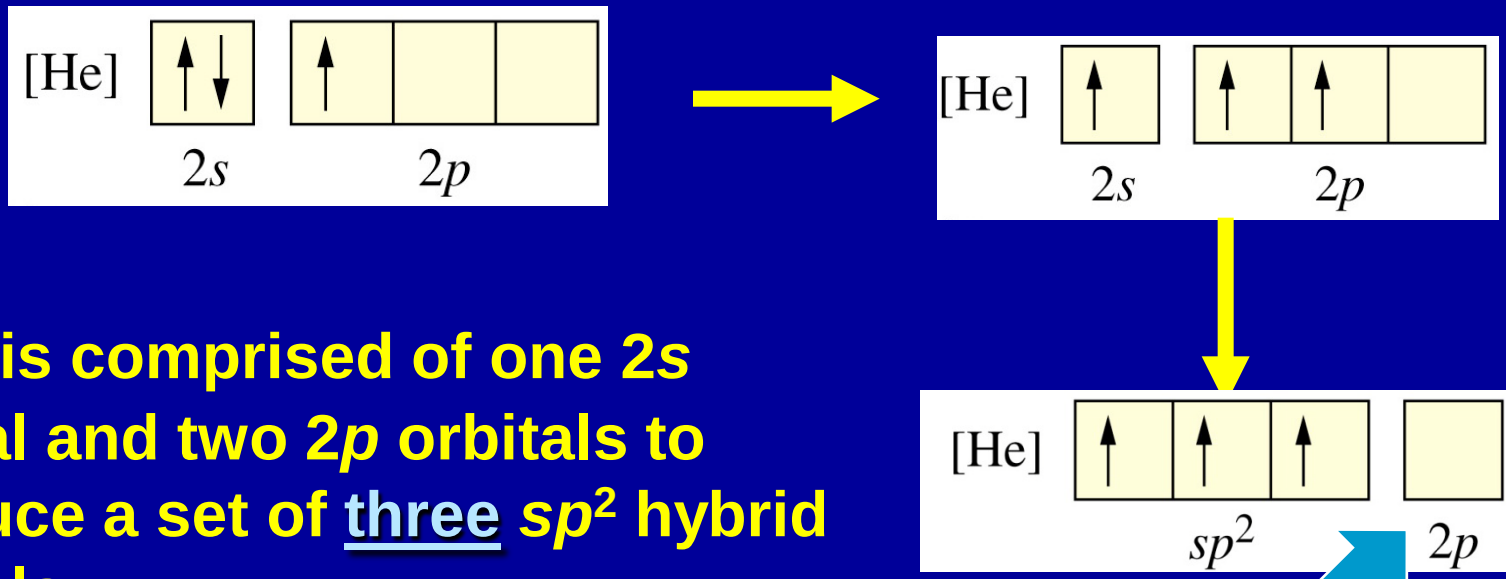


- 2 types of overlap with 2*s* and 2*p*

sp^2 Hybridization

Consider BF_3

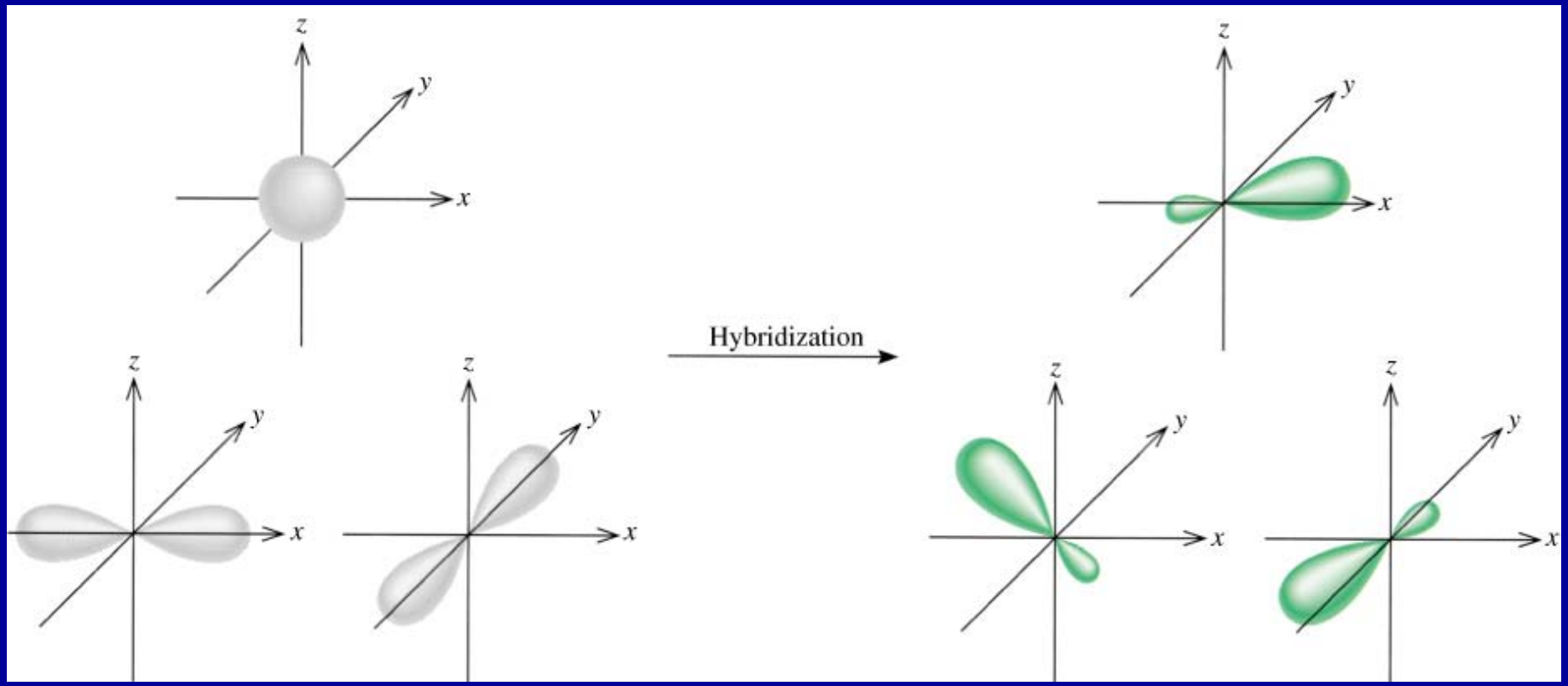
$_5B$



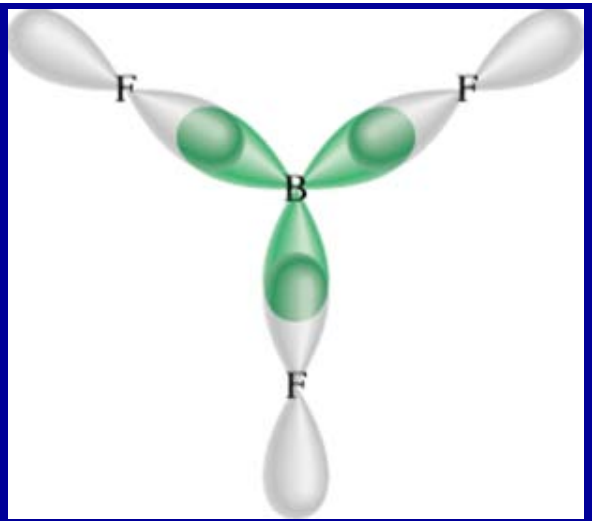
***sp*²** **is comprised of one 2*s* orbital and two 2*p* orbitals to produce a set of three *sp*² hybrid orbitals**

The empty 2*p* orbital remains unhybridized

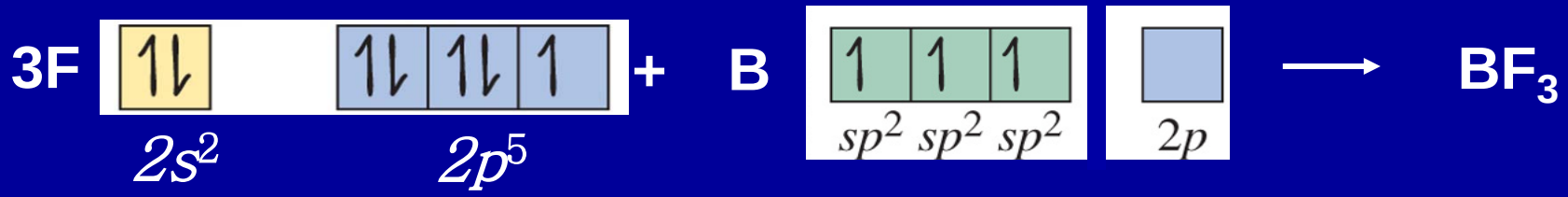
Formation of sp^2 Hybrid Orbitals

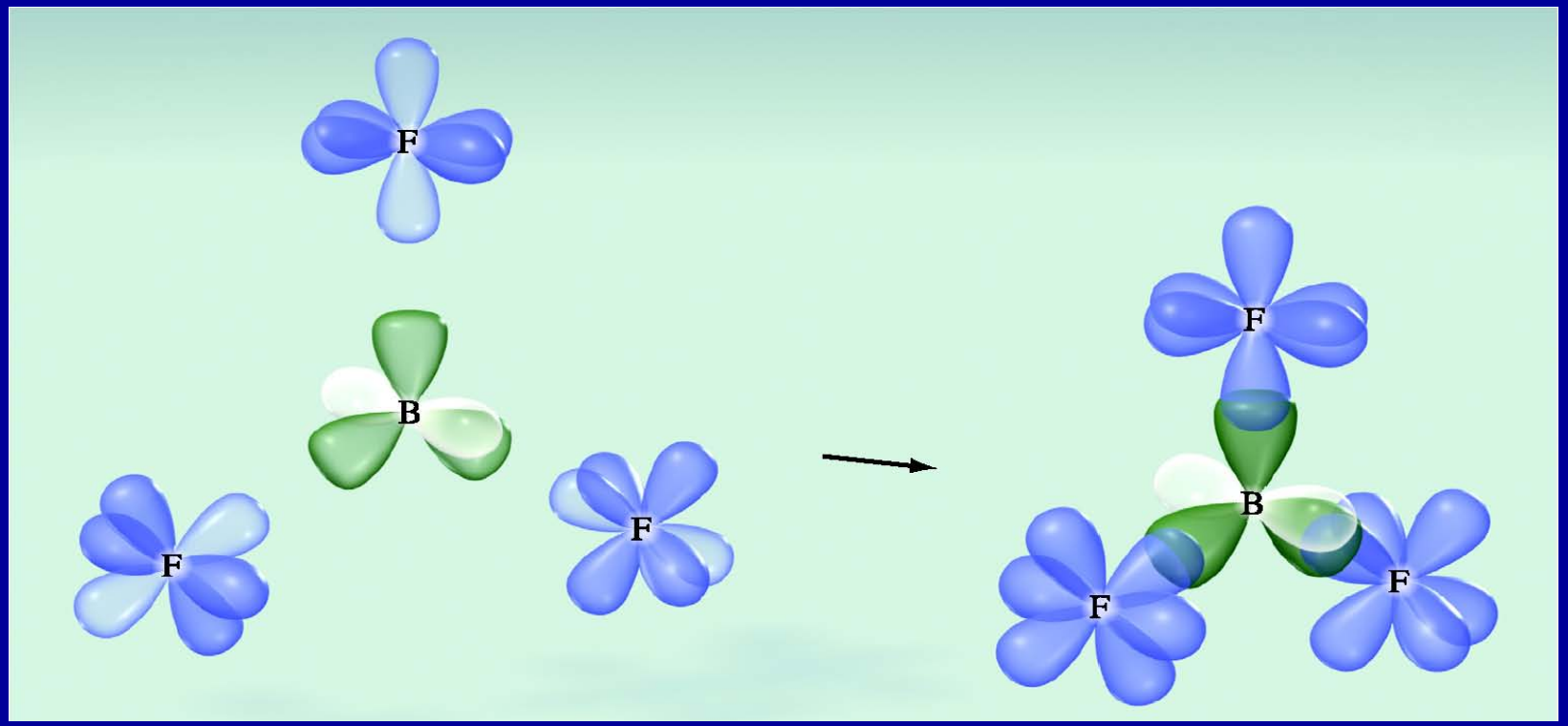


- The three sp^2 orbitals point to the corners of an equilateral triangle.



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

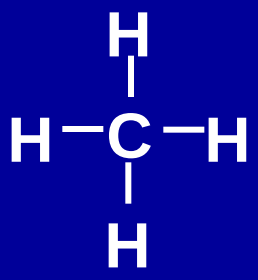




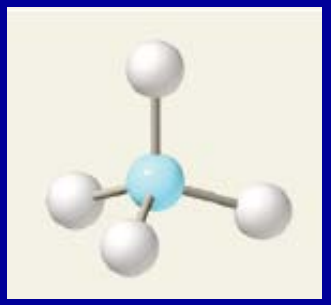
All bond angles 120°.

sp^3 hybridization

Example: Methane CH_4

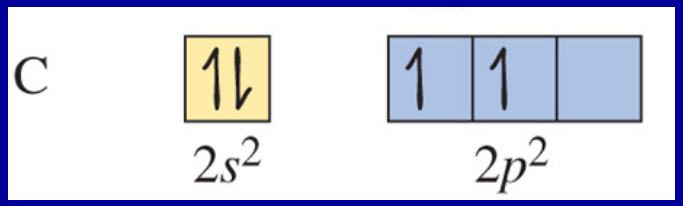


VSEPR →



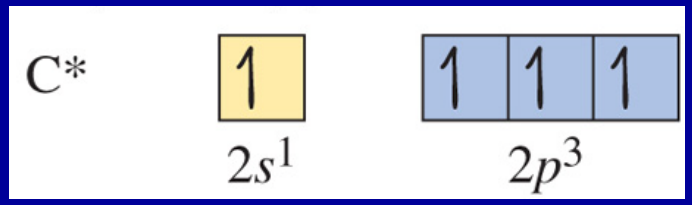
tetrahedral
all bonds equivalent

#1

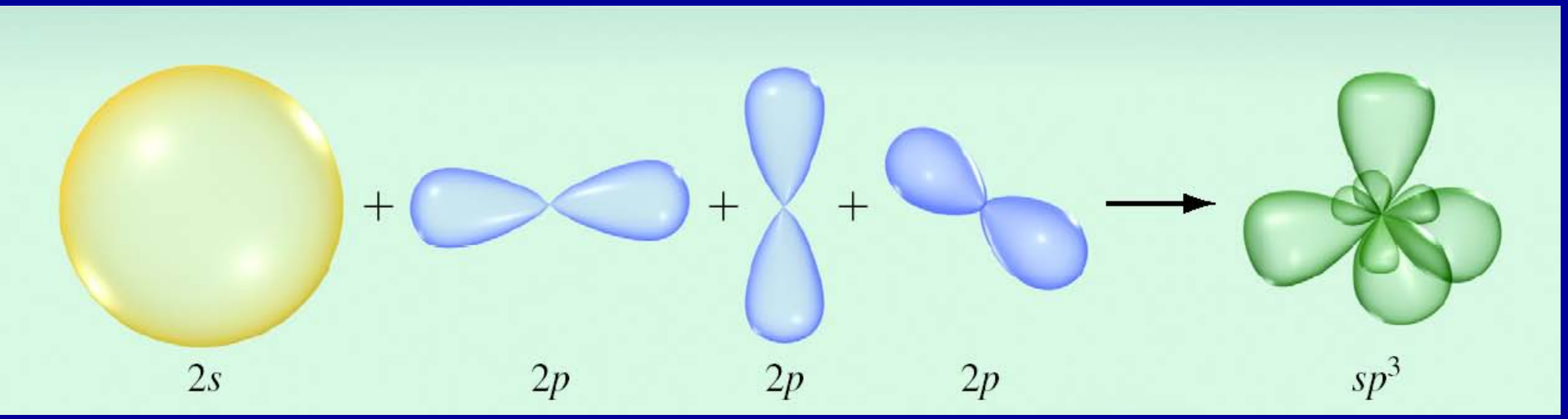


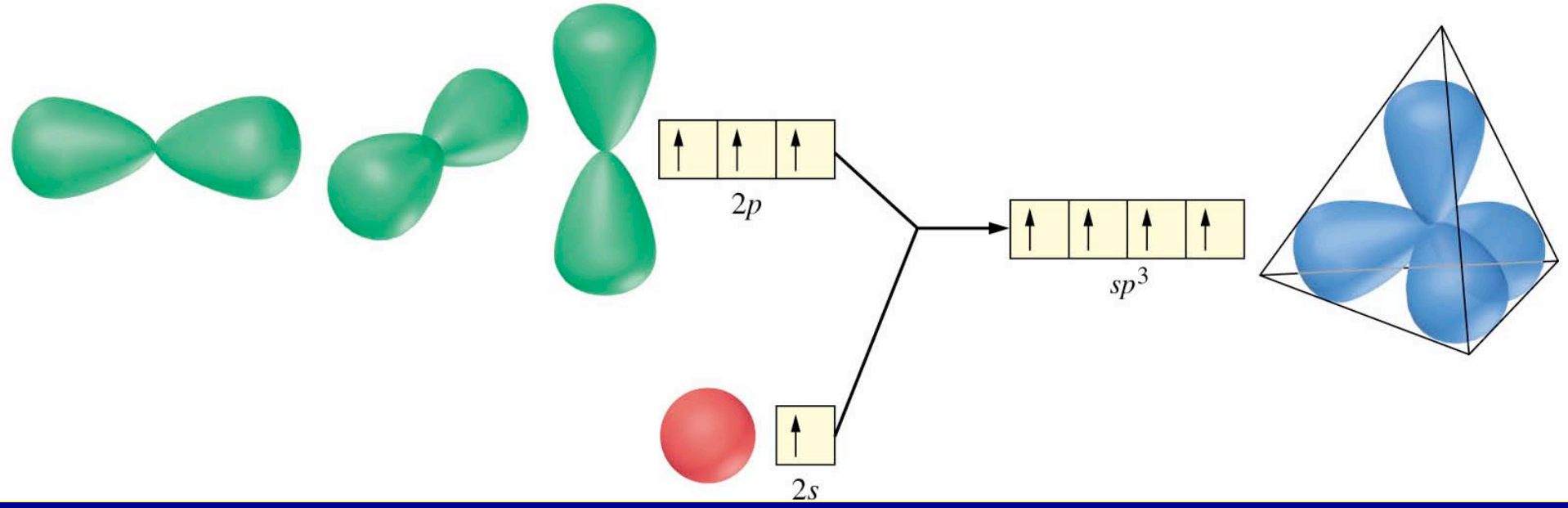
- **only 2 unpaired electrons**

#2

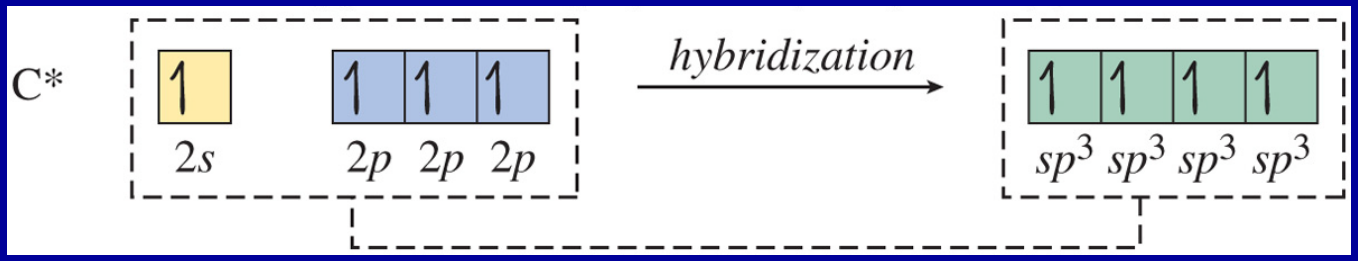


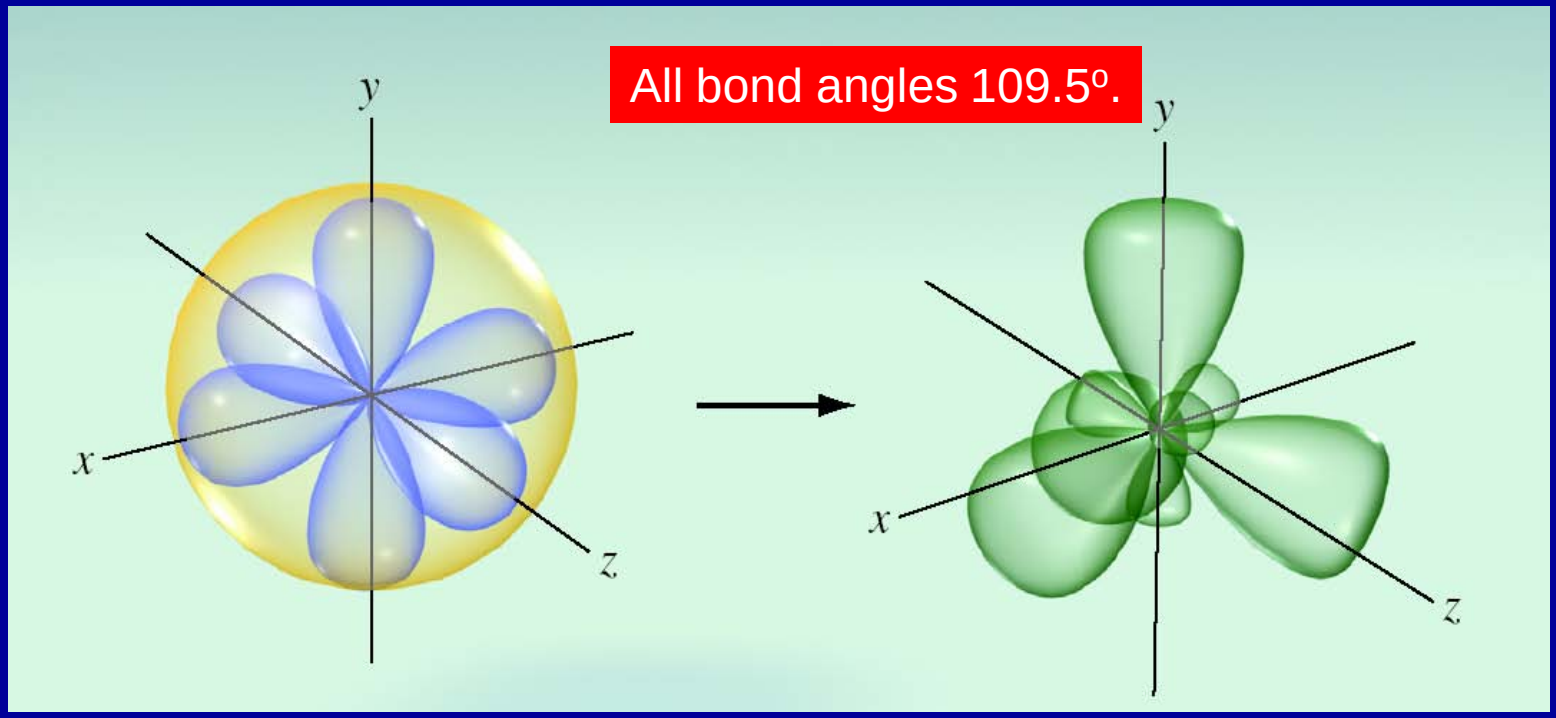
- **2 types of overlap with 2*s* and 2*p***


2s
2p
2p
2p
sp3

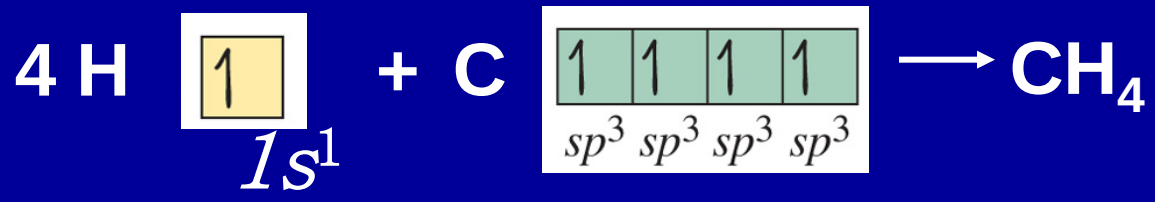

2p
sp3
2s

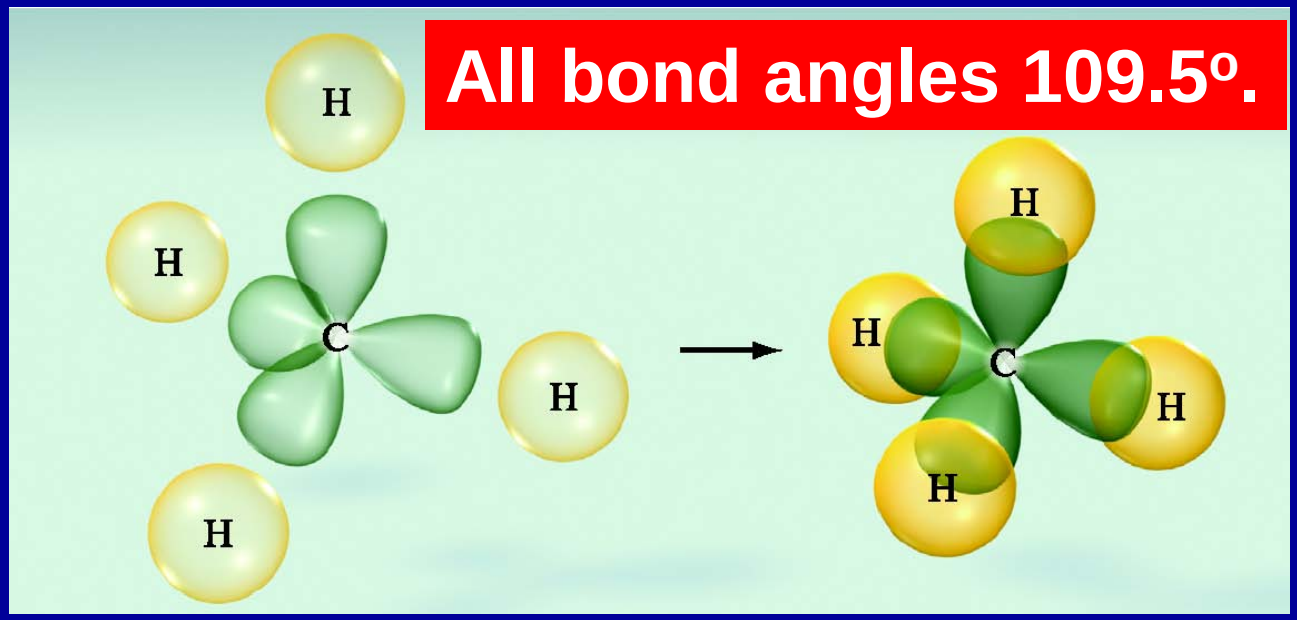
- **The sp^3 hybrid orbitals point to the corners of a tetrahedron.**





- Each C 2*sp*^{3} orbital overlaps a H 1*s* orbital to yield CH_4.



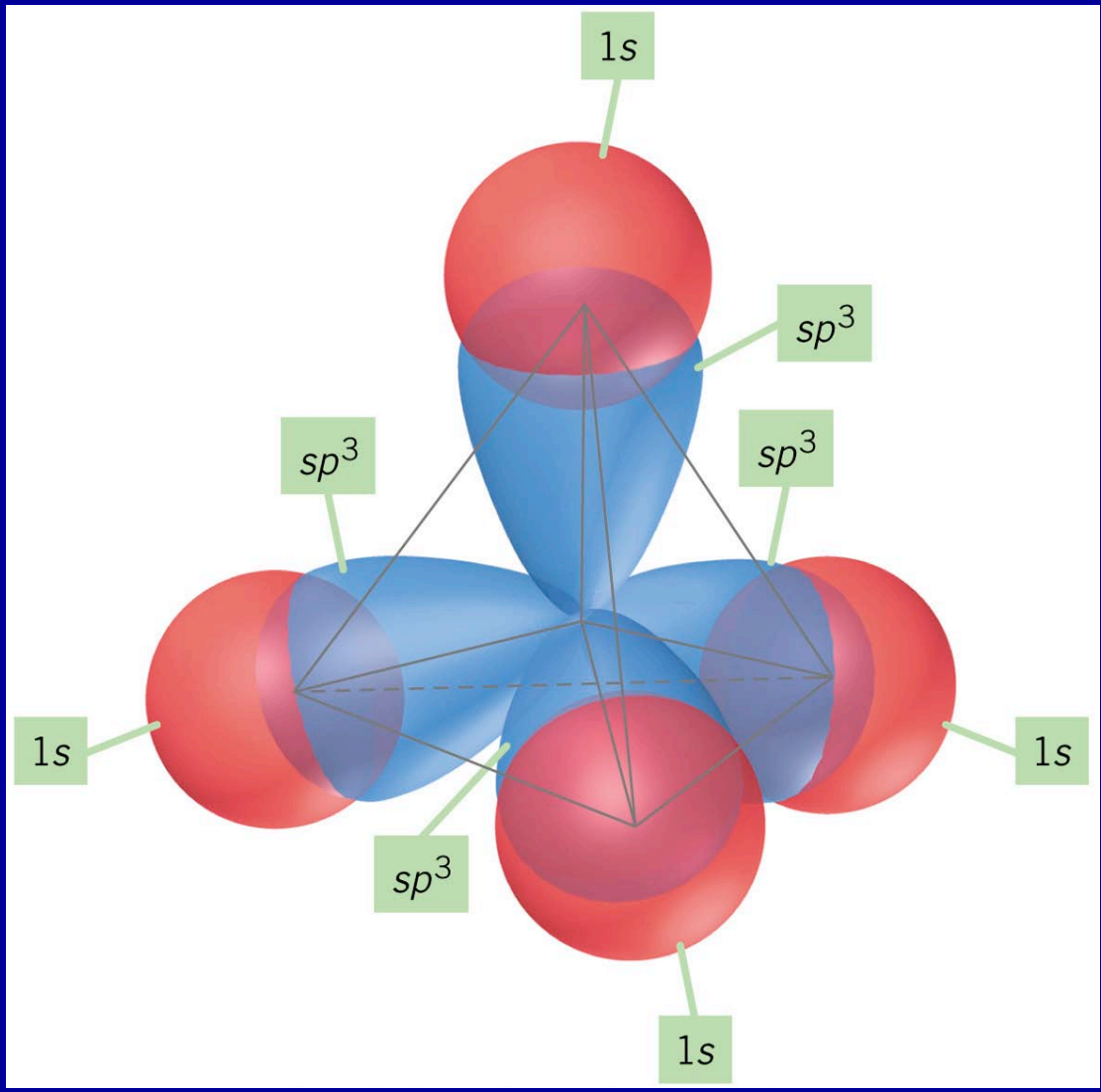


  - sp^3 hybridization has tetrahedral geometry.

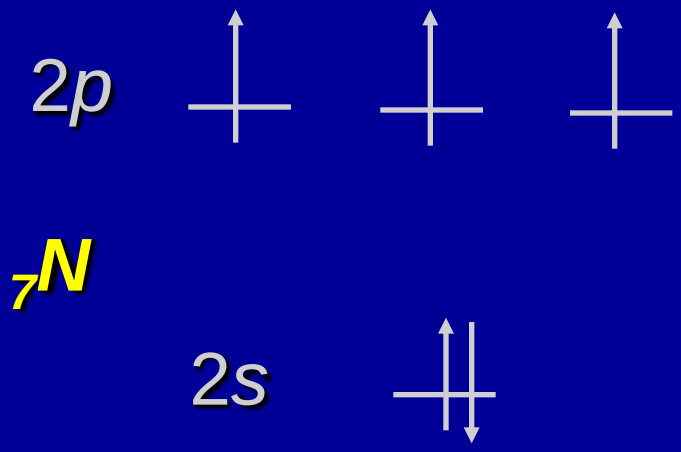
sp^3 Hybridization in CH_4

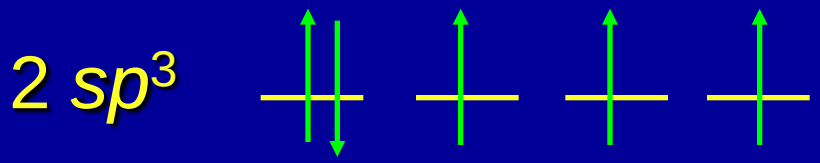
The carbon atom in methane (CH_4) has bonds that are sp^3 hybrids

Note that in this molecule carbon has all single bonds



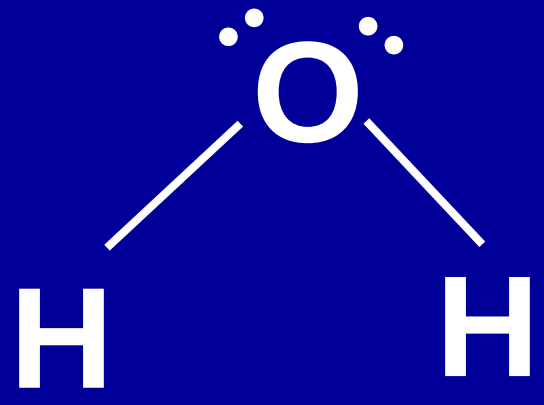
sp^3 *Orbital Hybridization in* NH_3

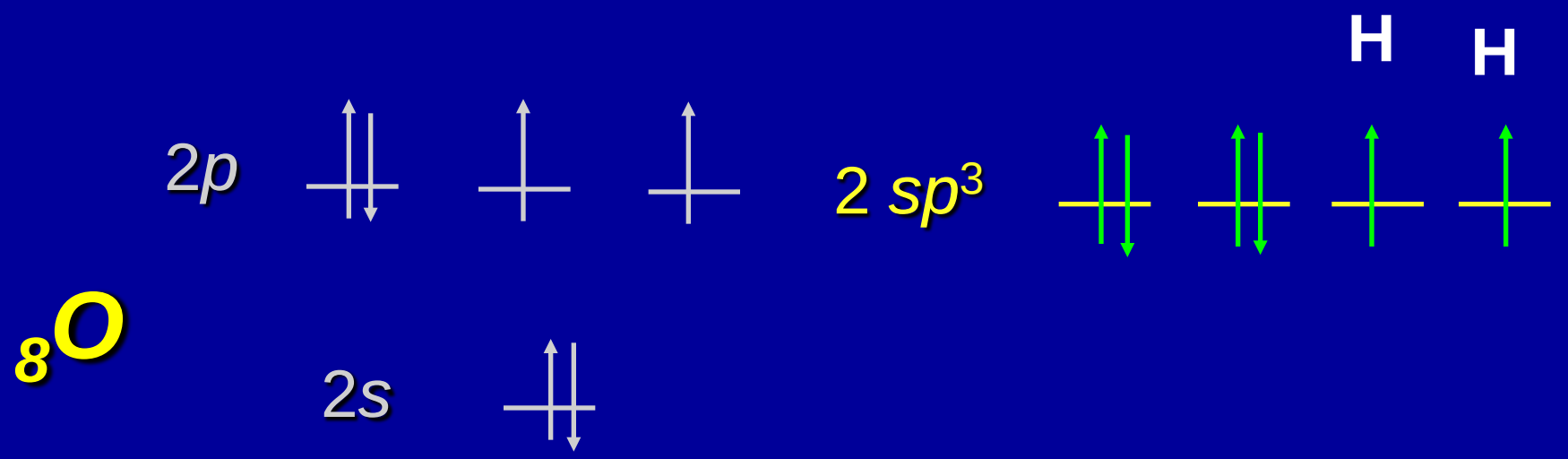




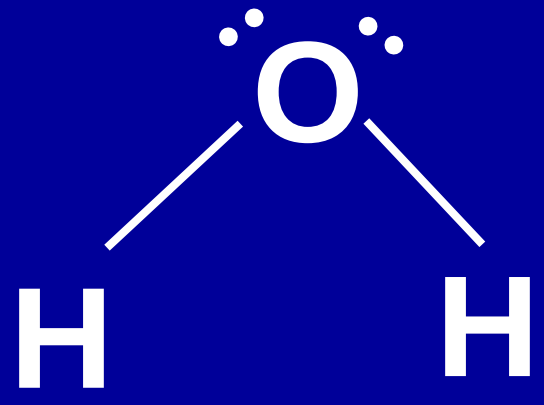
3 Equivalent half-filled orbitals are used to form bonds with 3H atoms. The 4^{th} sp^3 holds the lone pair

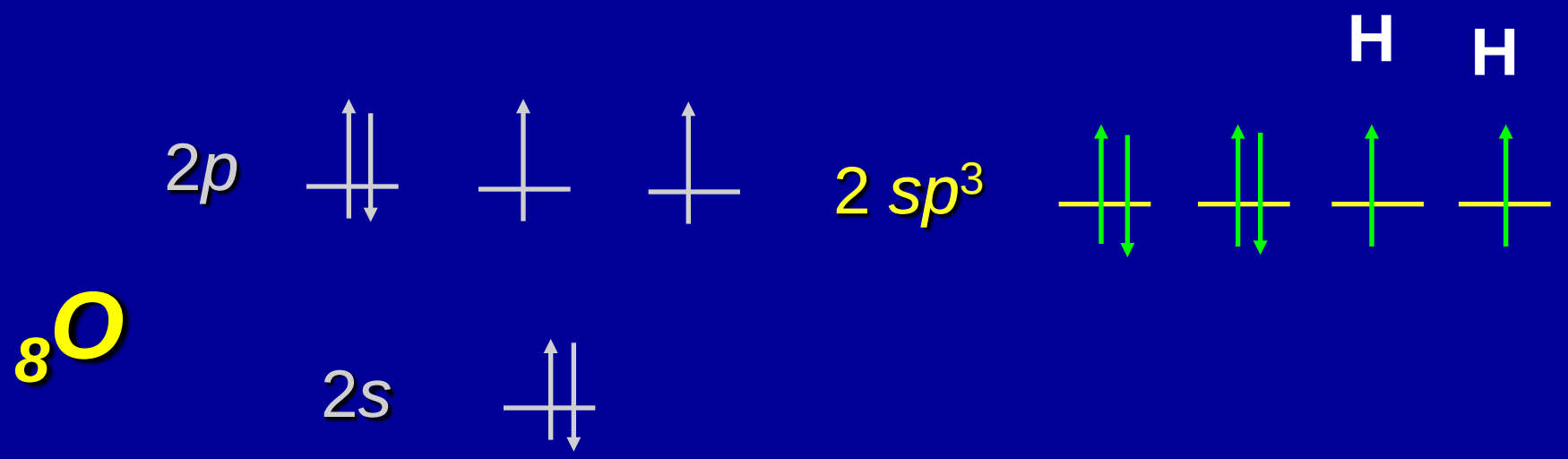
How about hybridization in H_2O?





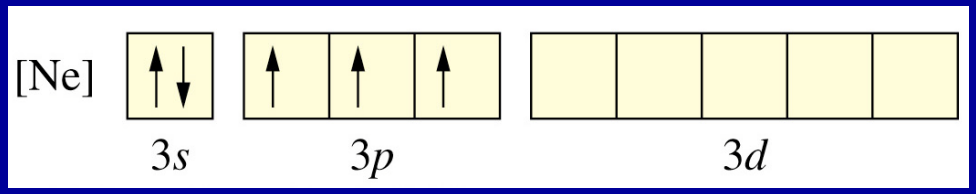
How about hybridization in H_2O?



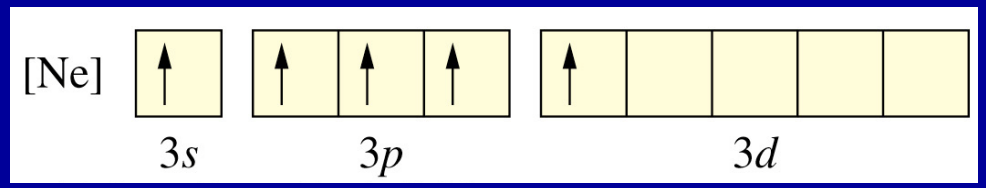


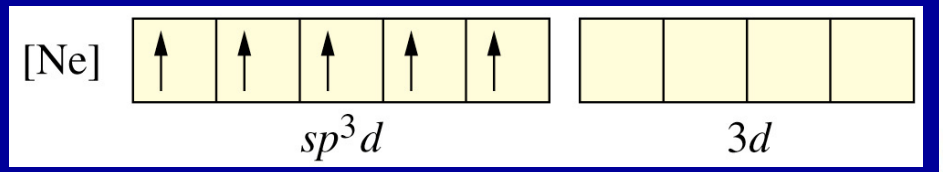
dsp^3/sp^3d Hybridization

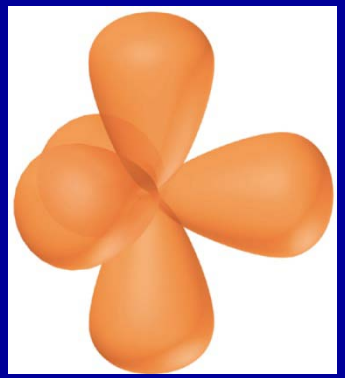
This hybridization allows for expanded valence shell compounds – typical for group 5A elements, e.g., $_{15}P$



A 3*s* electron can be promoted to a 3*d* subshell, which gives rise to a set of five sp^3d hybrid orbitals



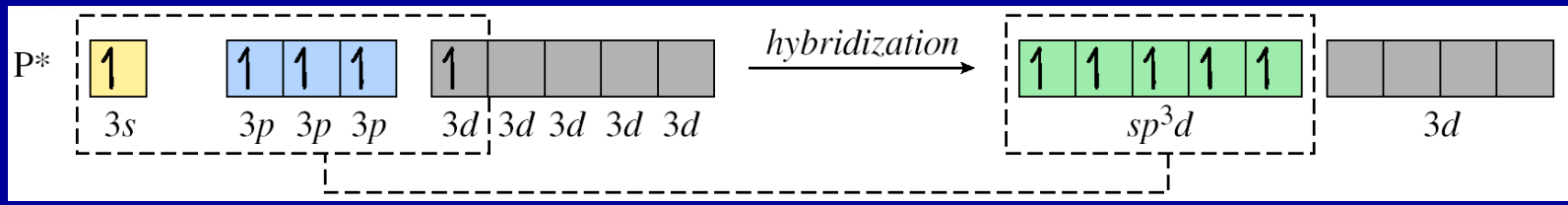


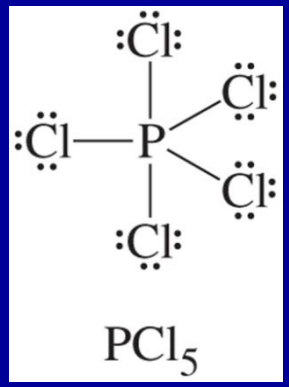


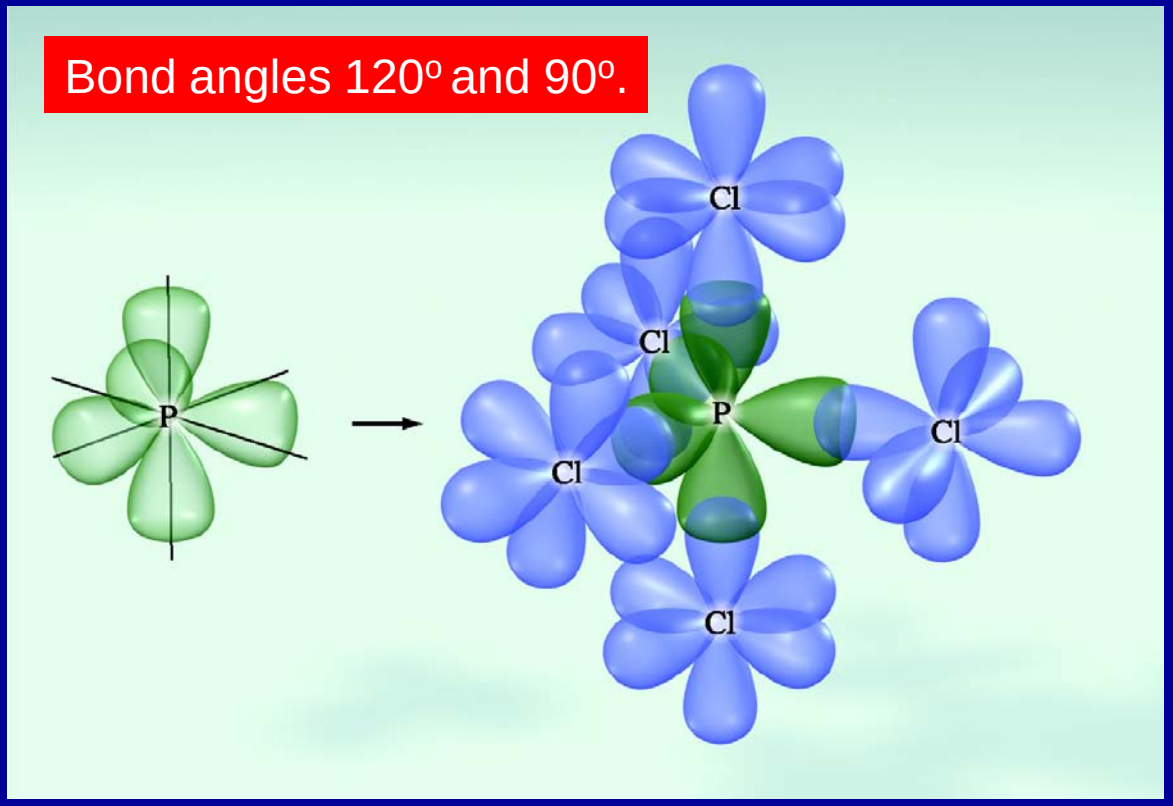
Central atoms without d-orbitals, N, O, F, do not form expanded octet

Hybridization of *s*, *p* and *d* orbitals

- **Expanded octets**



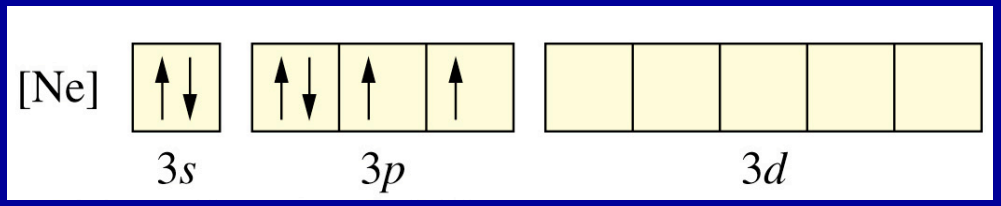


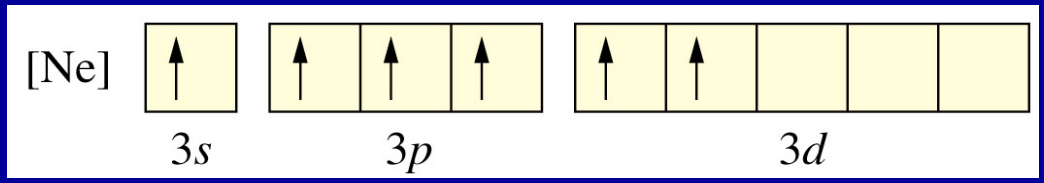


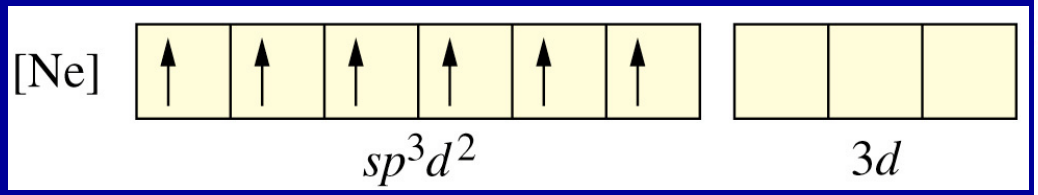
d $^2sp^3/sp^3d^2$ hybridization

This hybridization allows for expanded valence shell compounds – typically group 6A elements, e.g., S

A 3*s* and a 3*p* electron can be promoted to the 3*d* subshell, which gives rise to a set of six sp^3d^2 hybrid orbitals







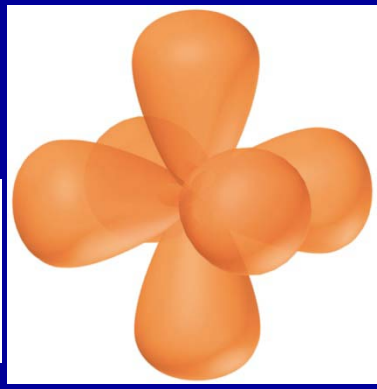
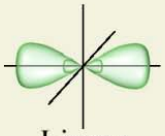
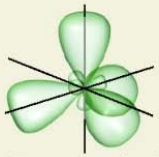
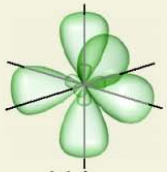
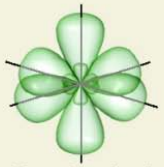


TABLE 9.4 Number of Electron Domains and Hybrid Orbitals on Central Atom

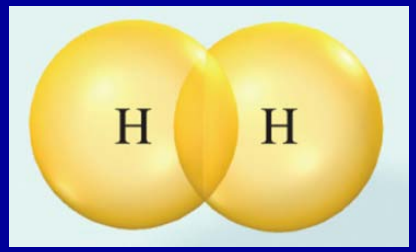
Number of Electron Domains on Central Atom	Hybrid Orbitals	Geometry
2	sp	 Linear
3	sp^2	 Trigonal planar
4	sp^3	 Tetrahedral
5	sp^3d	 Trigonal bipyramidal
6	sp^3d^2	 Octahedral

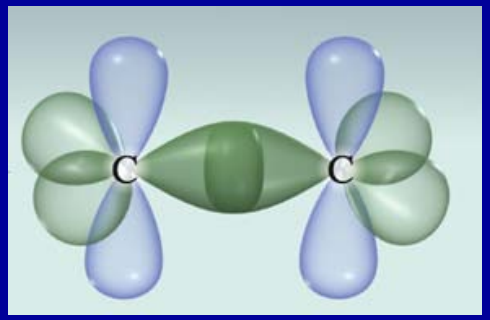
Lewis structure → Number of electron domains → Type of hybridization

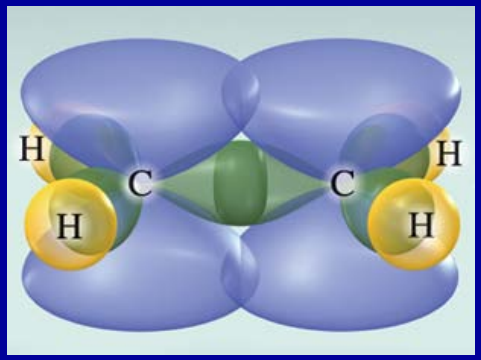
9.5 Hybridization in Molecules Containing Multiple Bonds

Sigma σ and pi π bonds

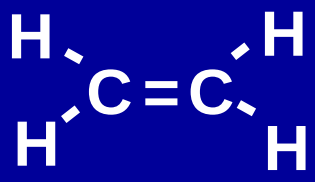
- **Sigma bond** is formed when two orbitals each with a single electron overlap (**End-to-end overlap**). Electron density is concentrated in the **region directly between** the two bonded atoms
- **Pi-bond** is formed when ***two parallel*** p-orbitals overlap **side-to-side (sideways)**
  - The orbital consists of two lopes one above the bond axis and the other below it.
  - Electron density is concentrated in the lopes
  - Electron density is zero along the line joining the two bonded atoms





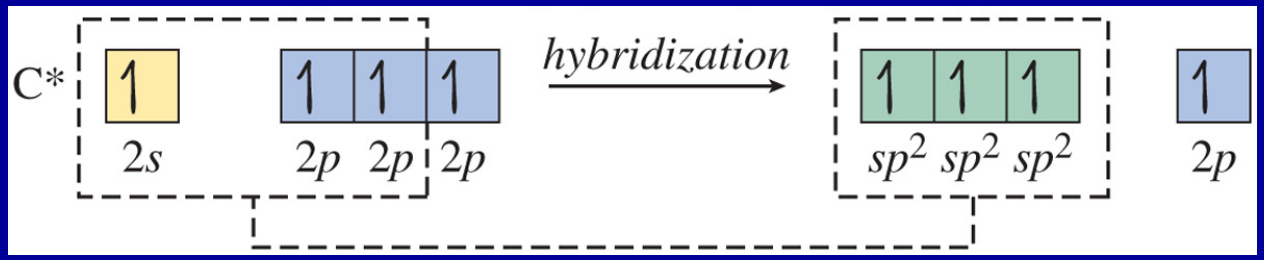


Example: Ethylene, C_2H_4



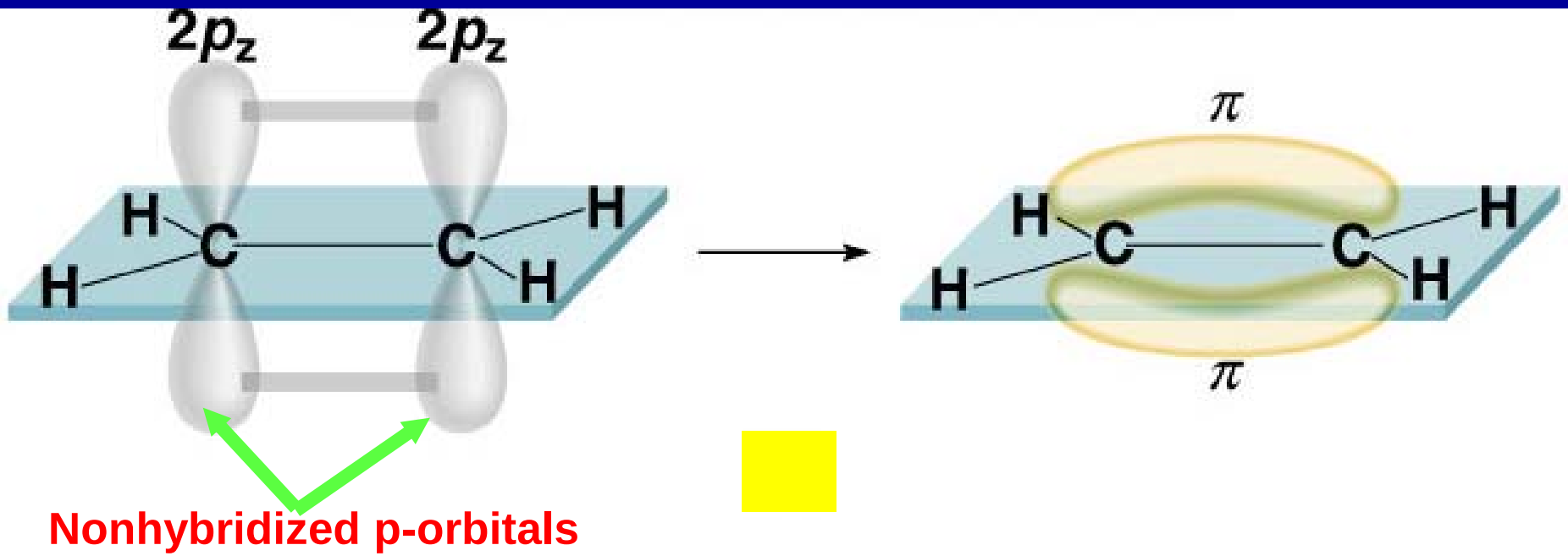
number of electron domains = 3

hybridization = sp^2

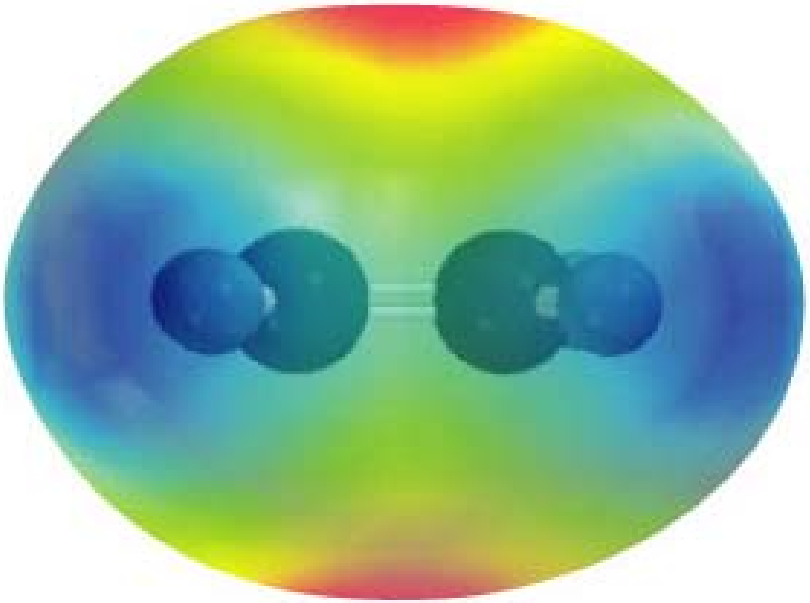


Non-hybridized orbital

Double bond = 1 σ bond + 1 π bond



Nonhybridized p-orbitals

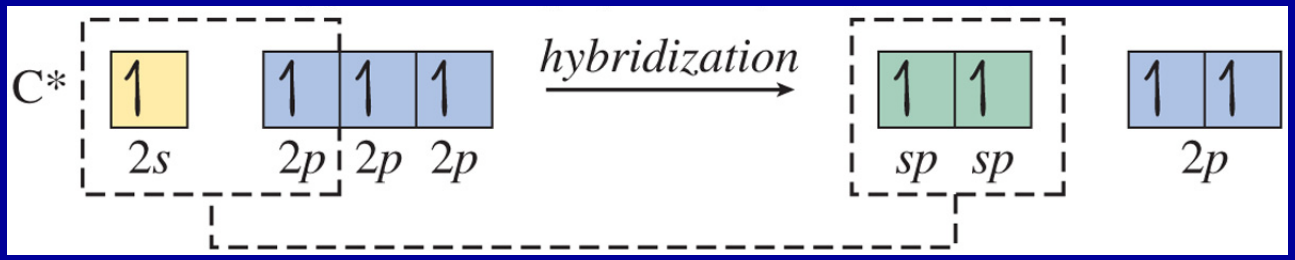


Acetylene, C_2H_2 Example:

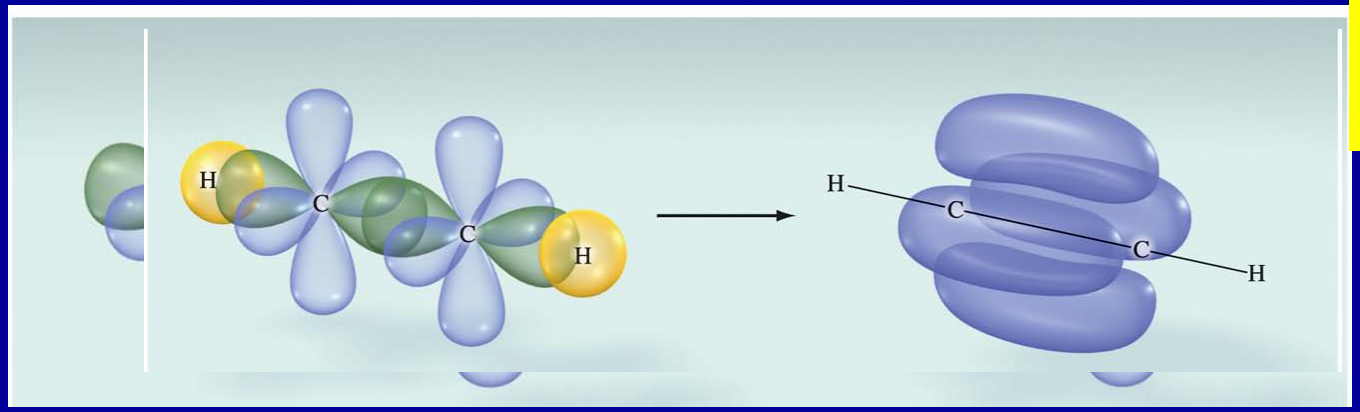
$H - C \equiv C - H$

number of electron domains = 2

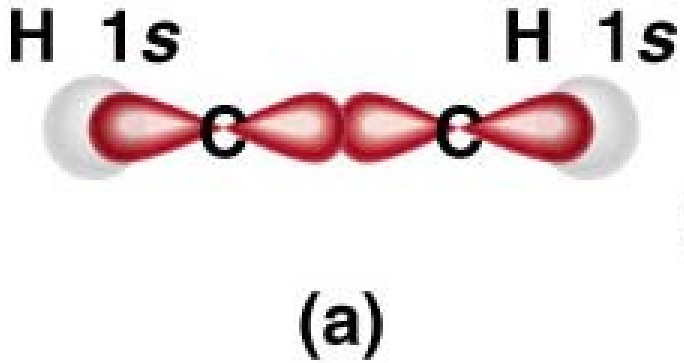
hybridization = *sp*



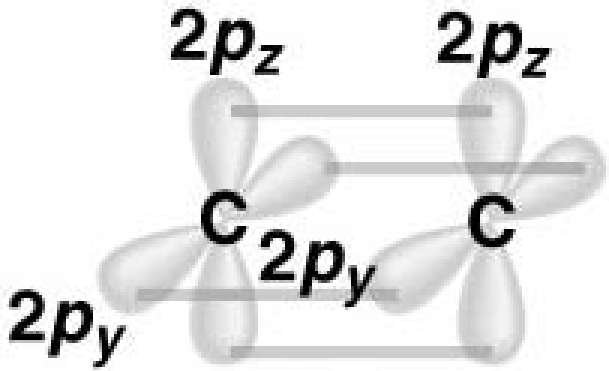
Unhybridized orbitals



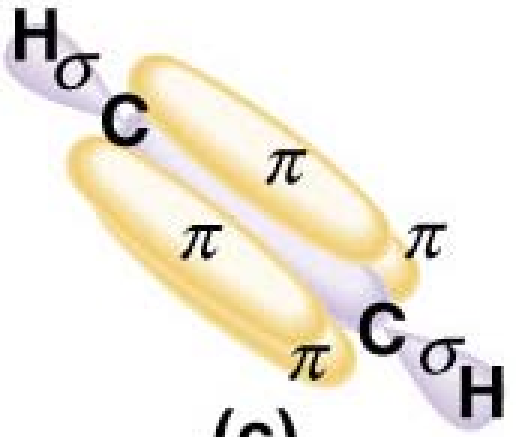
Triple bond = 1 σ bond + 2 π bonds



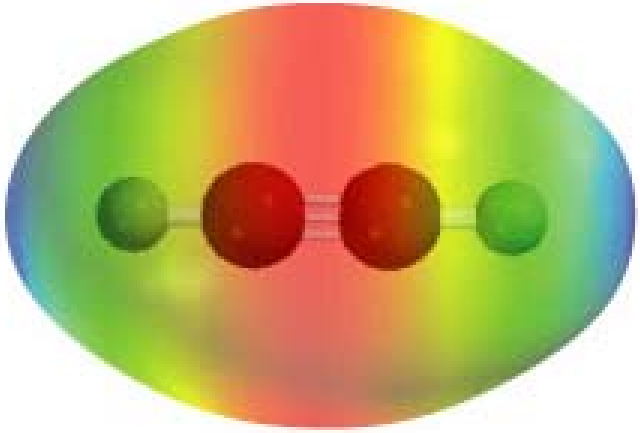
(a)



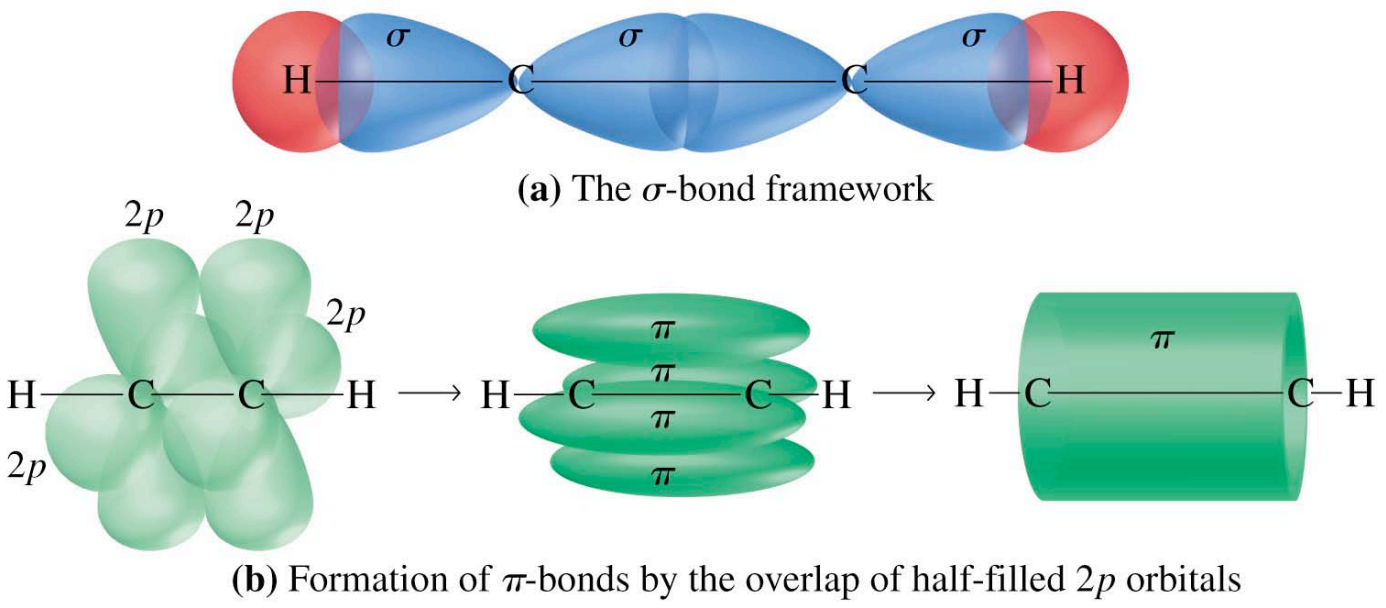
(b)



(c)

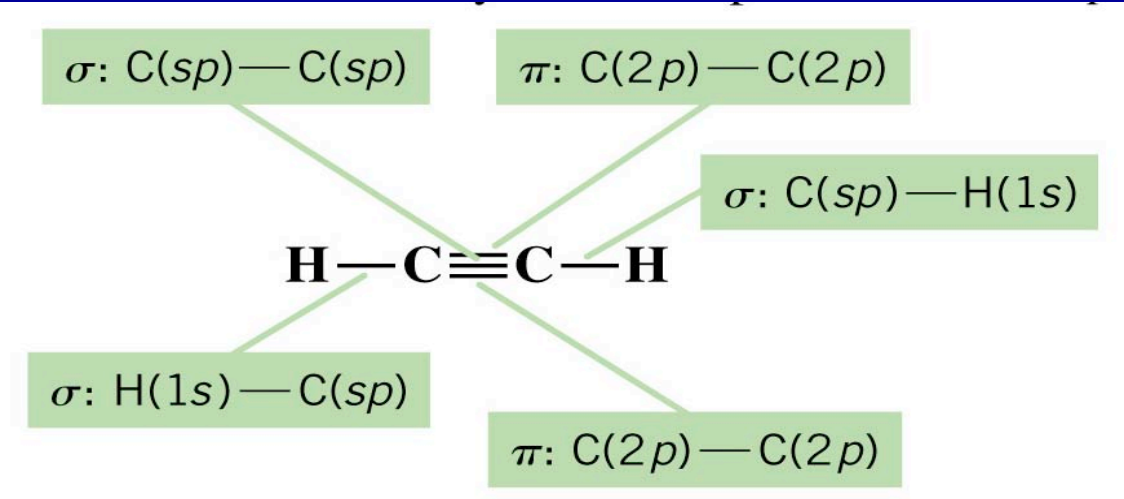


Carbon–Carbon Triple Bonds



(a) The σ-bond framework

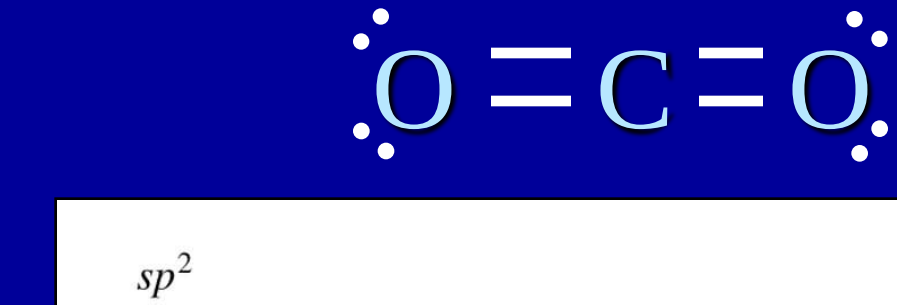
(b) Formation of π-bonds by the overlap of half-filled $2p$ orbitals

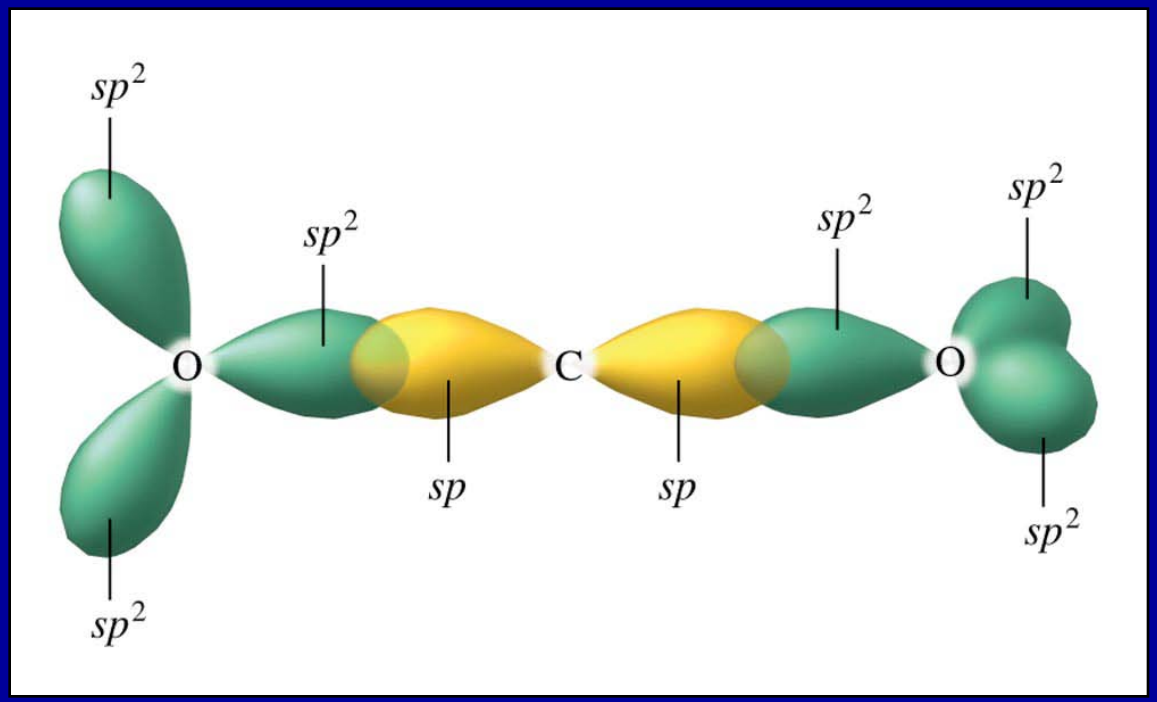


Hybridization in molecules containing multiple bonds

- The extra electron pairs in double or triple bonds ***have no effect upon the geometry*** of molecules
- **Extra electron pairs** in multiple bonds are not located in hybrid orbitals
- Geometry of a molecule is fixed by the electron pairs in hybrid orbitals around the central atom
  - All unshared electron pairs
  - Electron pairs forming single bonds
  - One (only one) electron pair in a multiple bond

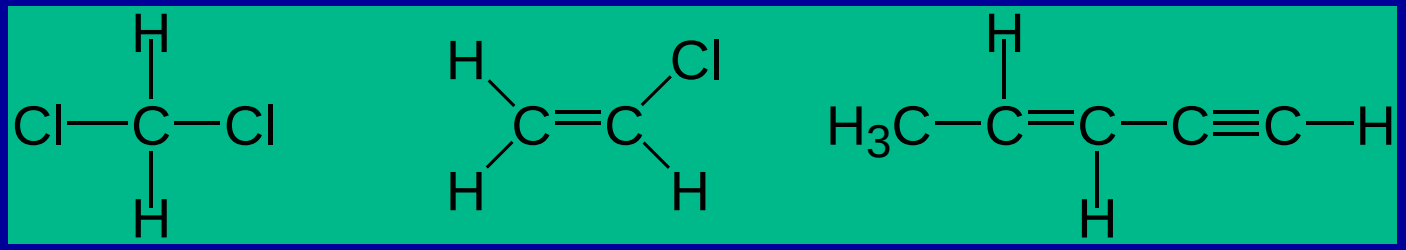
CO_2





- **C can make two σ and two π**
- **O can make one σ and one π**

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



(a) **(b)** **(c)**

(a) 4 sigma bonds

(b) 5 sigma bonds, 1 pi bond

(c) 10 sigma bonds, 3 pi bonds

Success of the localized electron model

- Overlap of atomic orbitals explained the stability of covalent bond
- Hybridization was used to explain the molecular geometry predicted by the localized electron model
- When lewis structure was inadequate, the concept of resonance was introduced to explain the observed properties

Weakness of the localized electron model

- It incorrectly assumed that electrons are localized and so the concept of resonance was added
- Inability to predict the magnetic properties of molecules like O_2 (molecules containing unpaired electrons)
- No direct information about bond energies

9.6 Molecular Orbital Theory

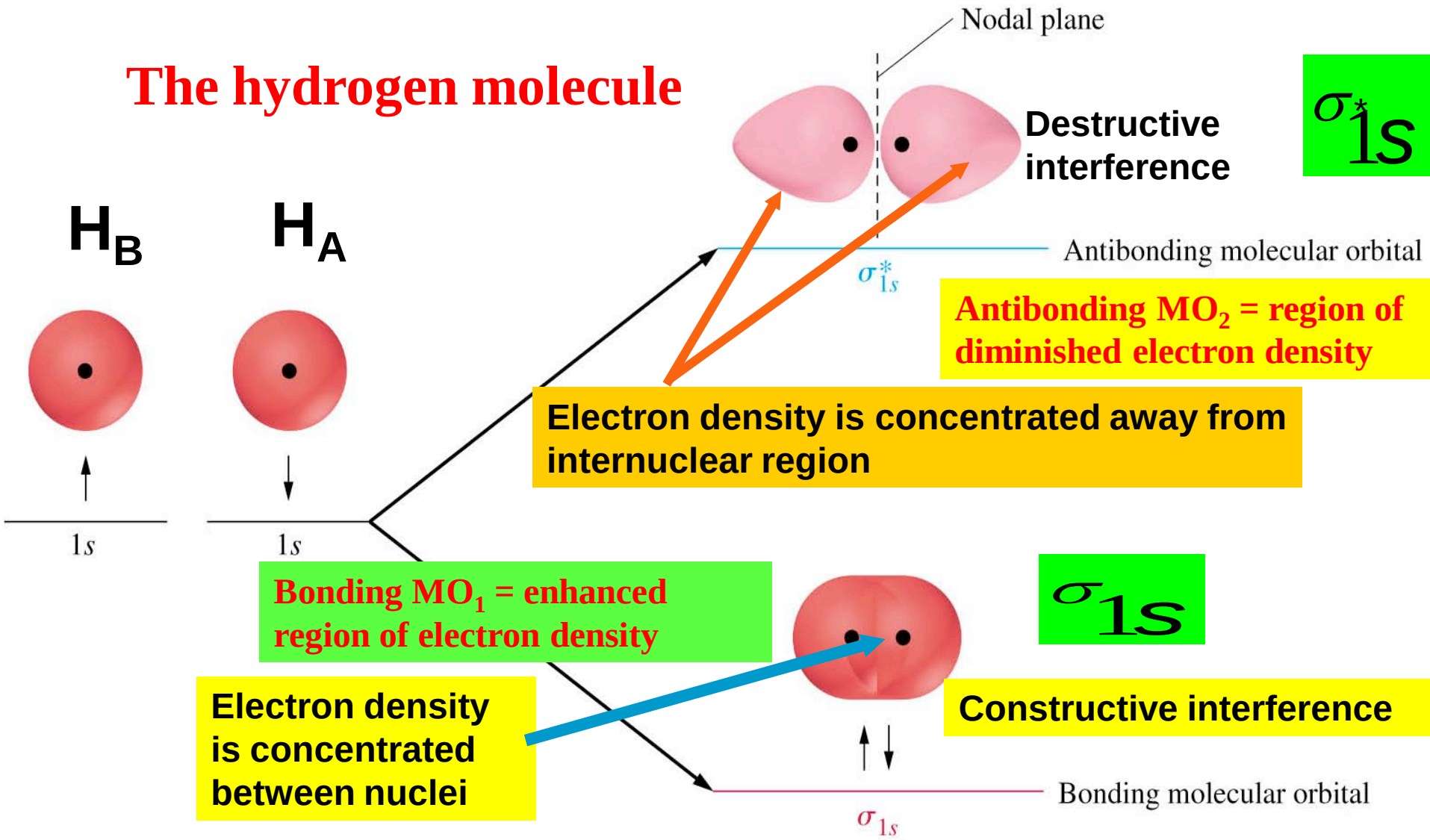
- **Molecular orbitals (MOs) are *mathematical equations* that describe the regions in a molecule where there is a high probability of finding electrons**
- ***Atomic orbitals of atoms are combined to give a new set of molecular orbitals characteristic of the molecule as a whole***
- **The molecular orbitals are spread out over the entire molecule. Electrons are now in *orbitals that belong to the molecule as a whole*.**
  - **The number of atomic orbitals combined *equals* the number of molecular orbitals formed.**
  - **(Two s-orbitals ⟶ Two molecular orbitals)**

Molecular orbitals

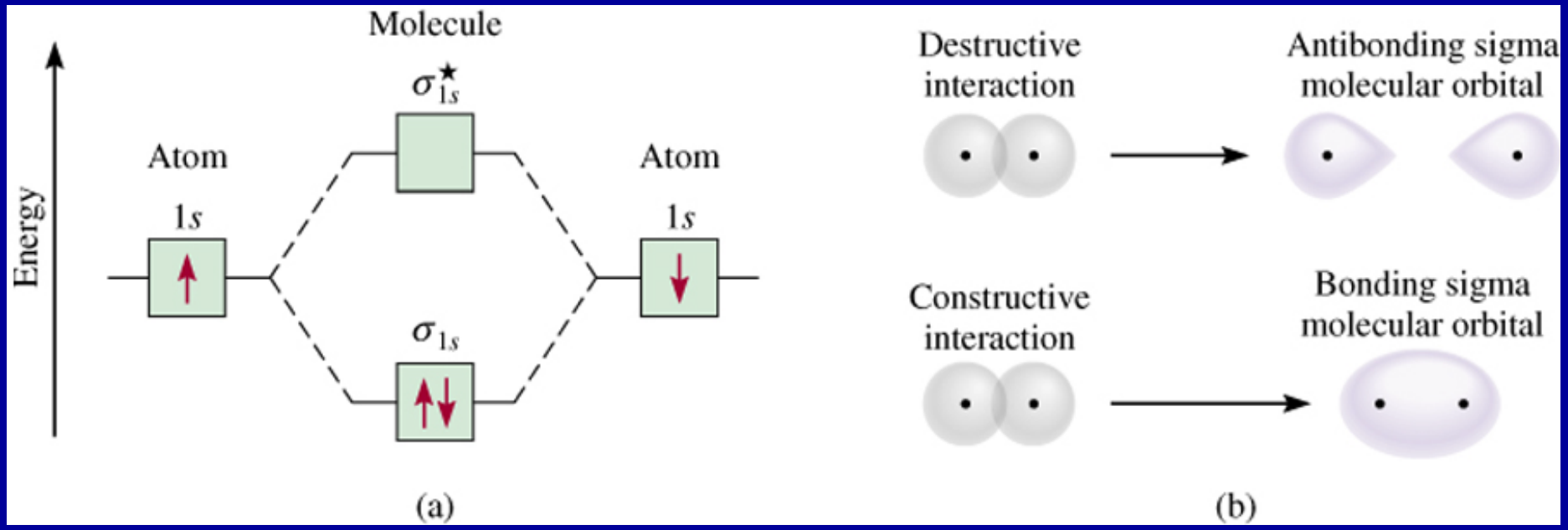
- Two atomic orbitals combine to form a bonding molecular orbital and an anti-bonding MO*.
  - **Electrons in bonding MO's stabilize a molecule**
  - **Electrons in anti-bonding MO's destabilize a molecule**
- **For the orbitals to combine, they must be of comparable energies. e.g., 1s(H) with 2s(Li) is not allowed**
- **The molecular orbitals are arranged in order of increasing energy.**
- **The electronic structure of a molecule is derived by feeding electrons to the molecular orbitals according to same rule applied for atomic orbitals**

Formation of molecular orbitals by combination of 1s orbitals

The hydrogen molecule



Energy level diagram in hydrogen (H_2).



Bonding molecular orbital has lower energy and greater stability than the atomic orbitals from which it was formed.

antibonding molecular orbital has higher energy and lower stability than the atomic orbitals from which it was formed.

Molecular orbitals diagram

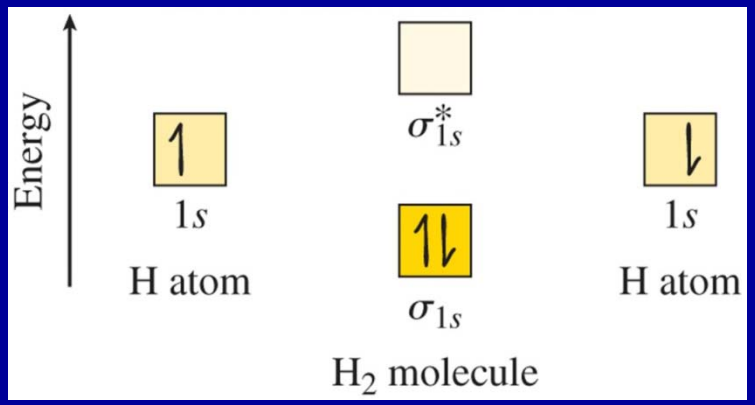
- Each molecular orbital can hold a maximum of two electrons with opposite spins
- Electrons go into the lowest energy molecular orbital available
- Hund's rule is obeyed

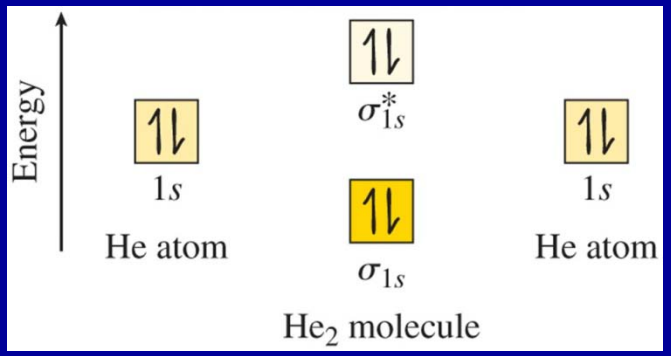
Molecular orbital model will be applied only to the diatomic molecules of the elements of the first two periods of the Periodic Table

Bond order.

$$\text{bond order} = \frac{\text{number of electrons in bonding molecular orbitals} - \text{number of electrons in antibonding molecular orbitals}}{2}$$

- Higher bond order = stronger (more stable) bond
- Zero bond order, the molecule will not exist

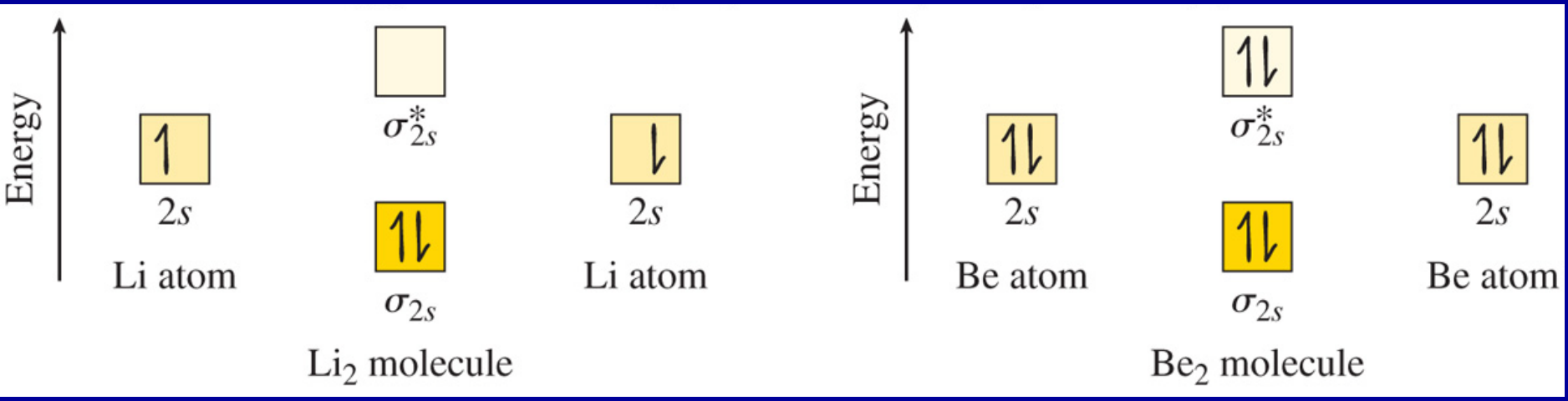




bond order = 1/2 (2 – 0) = 1
single bond

bond order = 1/2 (2 – 2) = 0
no bond

Examples Using Antibonding Orbitals



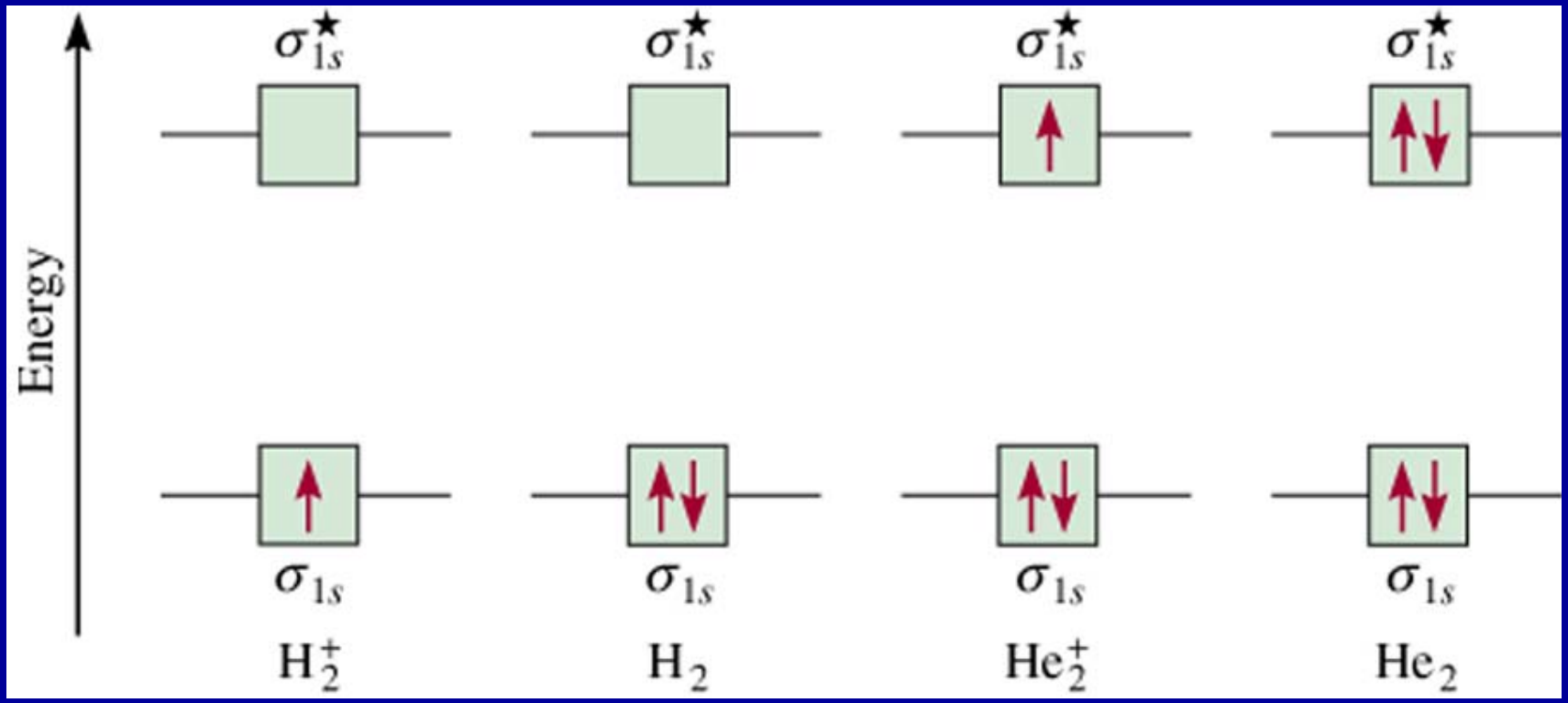
bond order = 1/2 (2 – 0) = 1
single bond

bond order = 1/2 (2 – 2) = 0
no bond

The molecule exist

The molecule does not exist

$$\textbf{bond order} = \frac{1}{2}\left(\begin{array}{l}\text{Number of electrons in bonding MOs}\end{array} - \begin{array}{l}\text{Number of electrons in antibonding MOs}\end{array}\right)$$



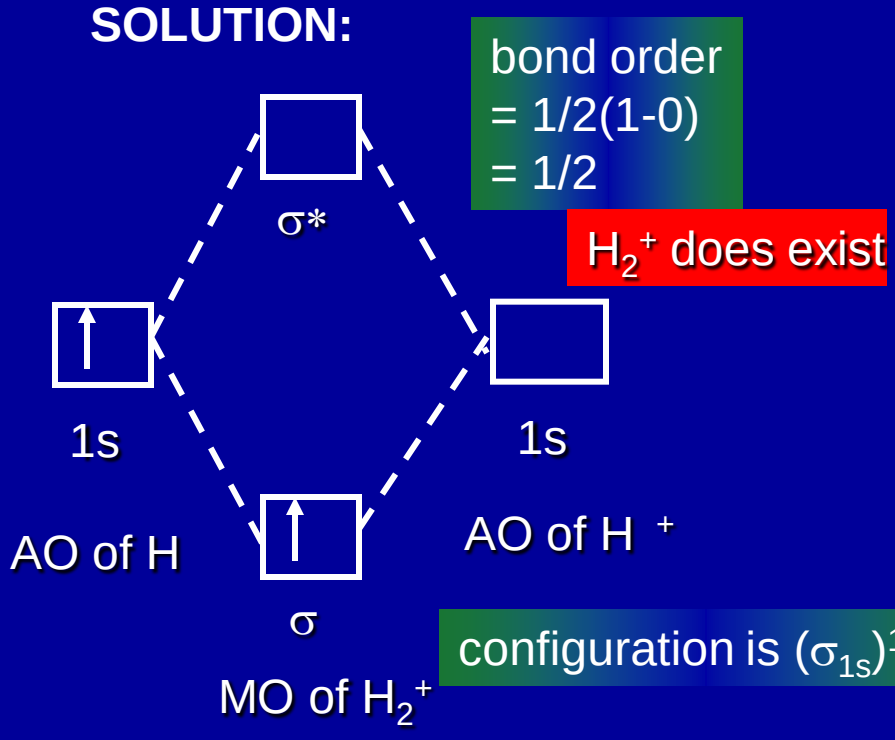
bond order	½	1	½	0

Predicting Species Stability Using MO Diagrams

PROBLEM: Use MO diagrams to predict whether H_2^+ and H_2^- exist. Determine their bond orders and electron configurations.

PLAN: Use H_2 as a model and accommodate the number of electrons in bonding and antibonding orbitals. Find the bond order.

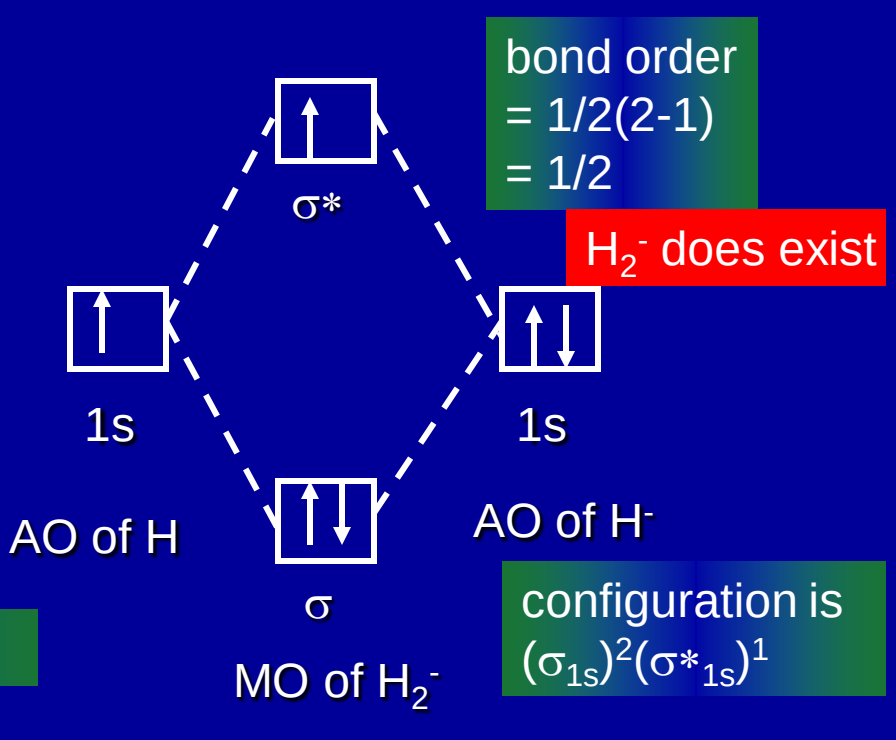
SOLUTION:



bond order
= 1/2(1-0)
= 1/2

H_2^+ does exist

configuration is $(\sigma_{1s})^1$



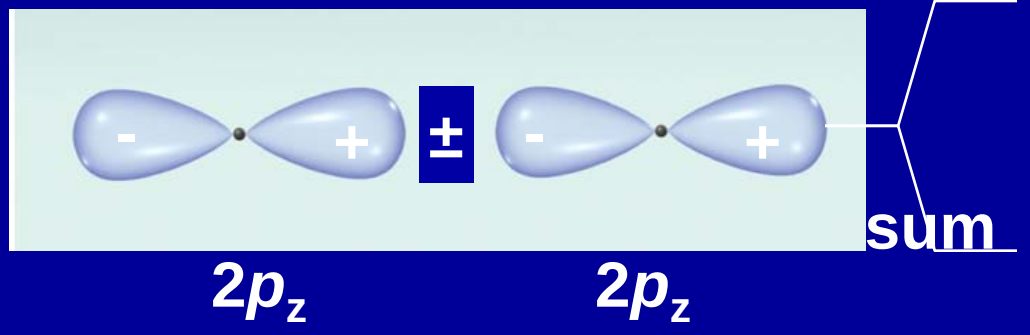
bond order
= 1/2(2-1)
= 1/2

H_2^- does exist

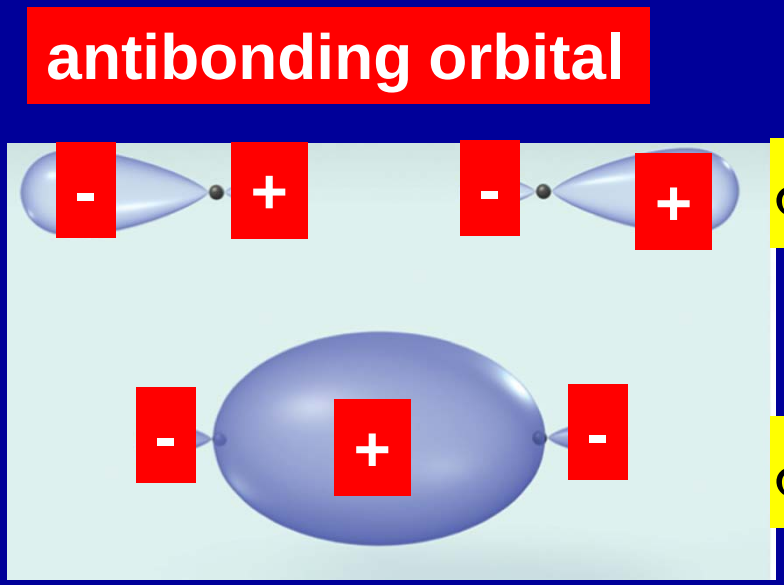
configuration is $(\sigma_{1s})^2(\sigma^*_{1s})^1$

Pi (π) molecular orbitals

- Wave functions representing *p* orbitals combine in two different ways yielding either σ orbitals or π orbitals.
- End-to-end combination yields sigma (σ) orbitals

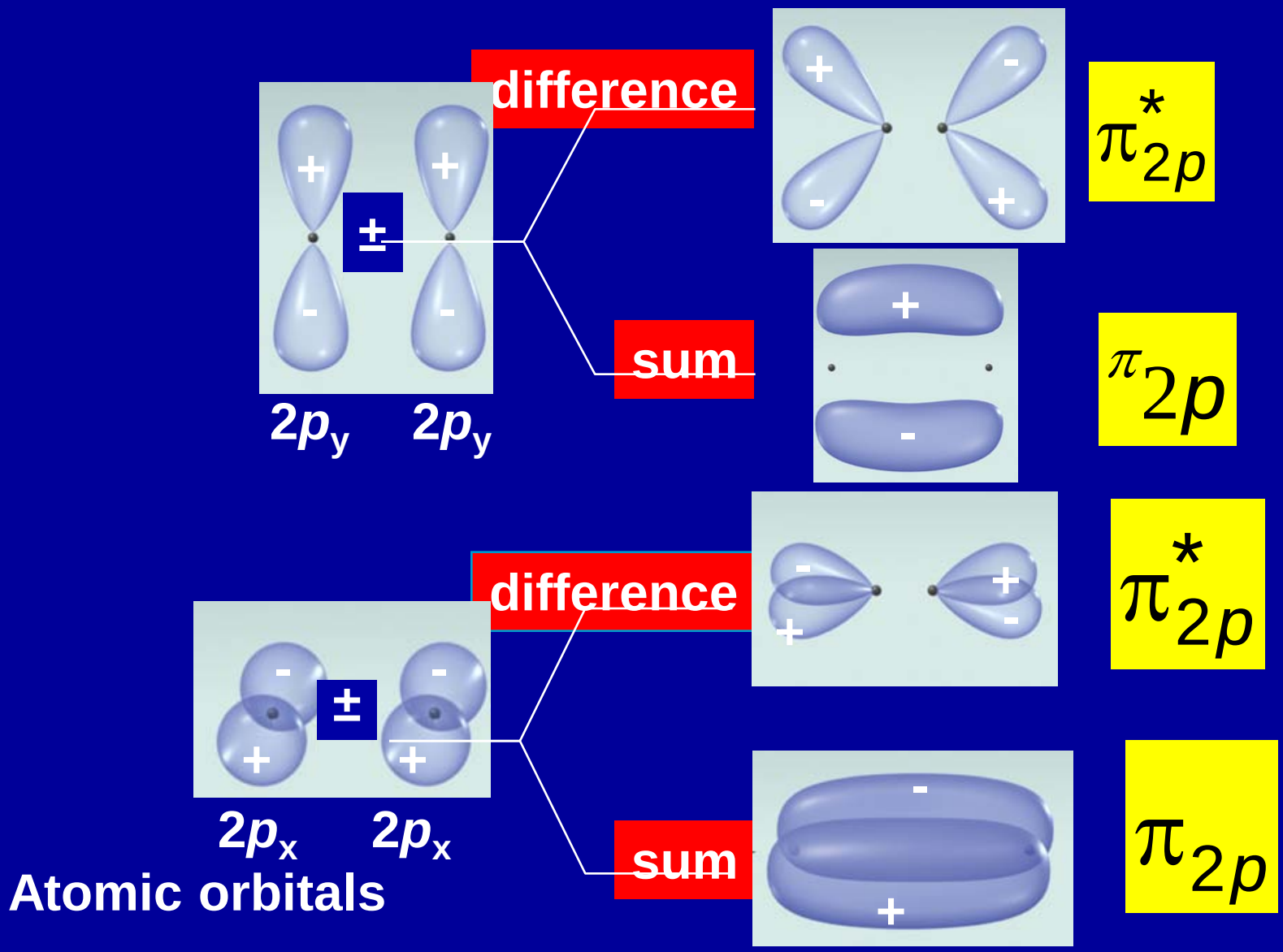


Atomic orbitals

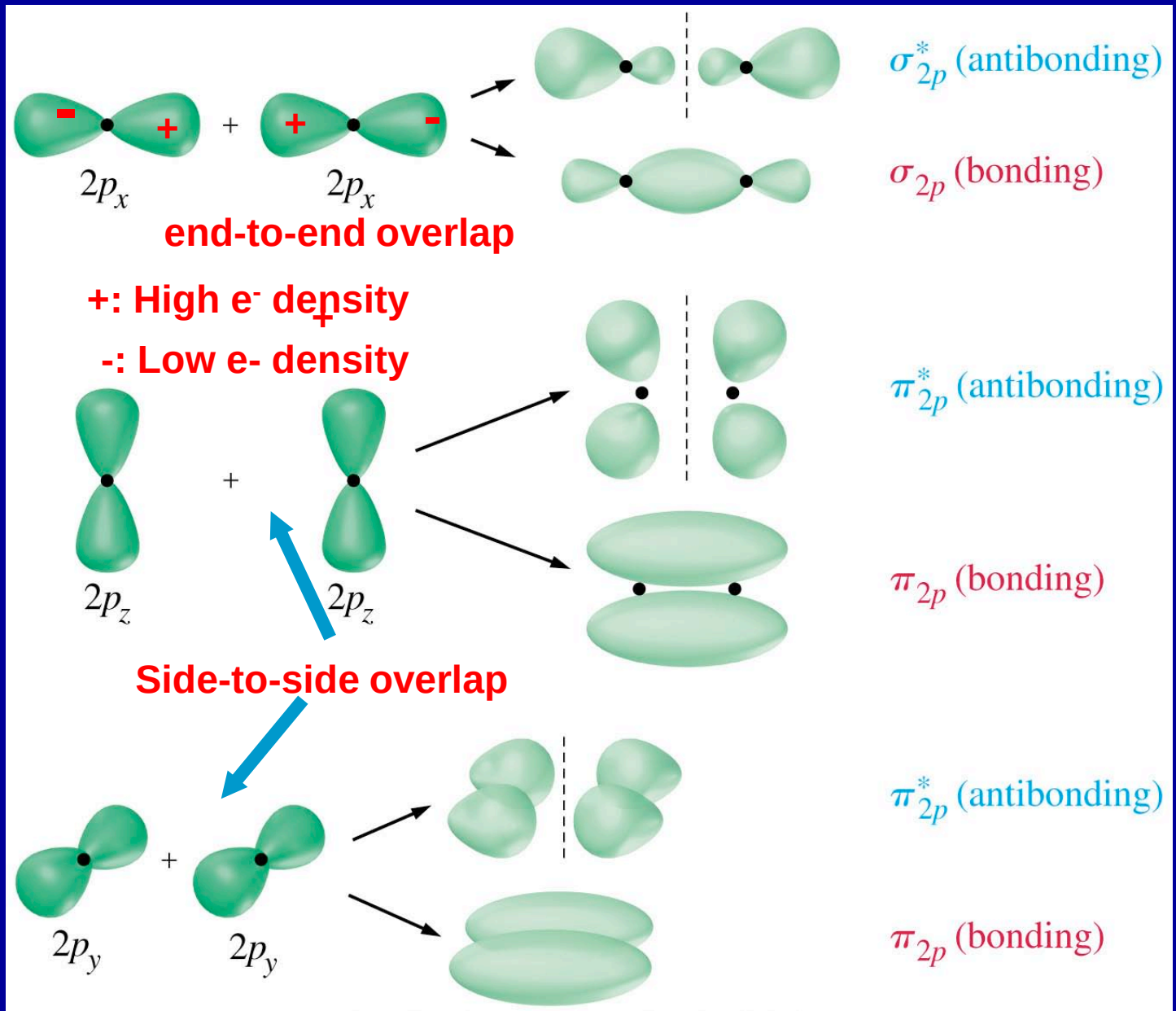


Molecular orbitals

Sideways combination yields pi (π) orbitals



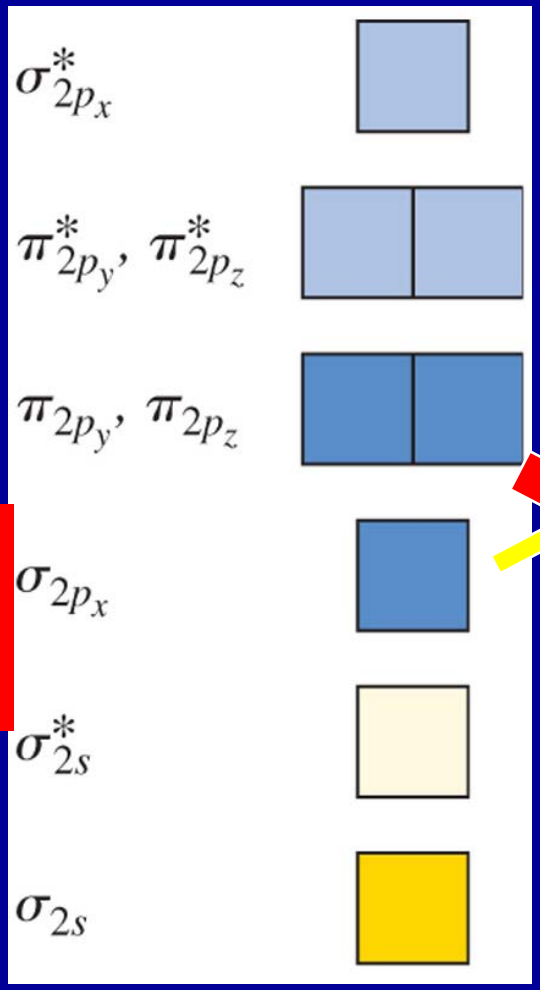
Possible interactions between two equivalent *p* orbitals and the corresponding molecular orbitals



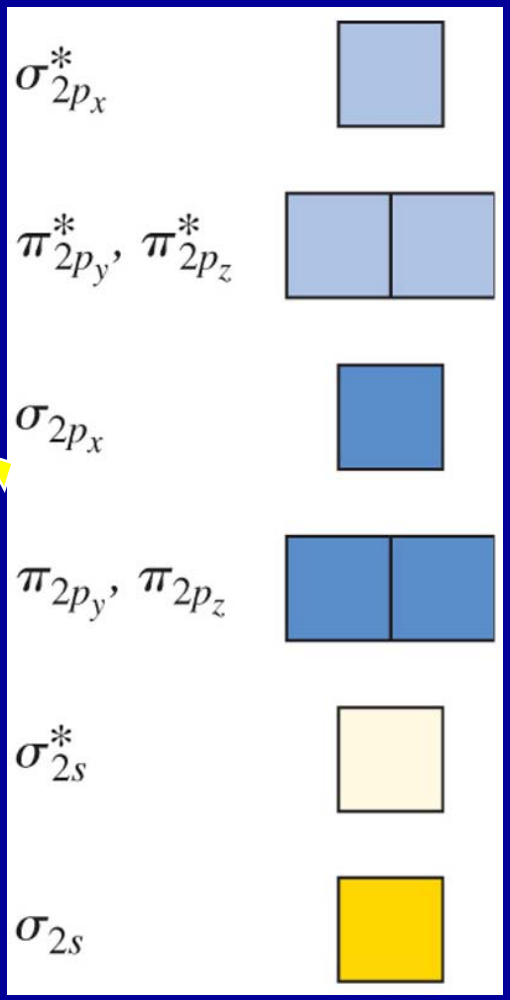
Energy order of the π_{2p} and σ_{2p} orbitals changes across the period.

Due to lower nuclear charge of B, C & N there is no s-p orbitals interaction

Due to high nuclear charge of O, F& Ne there is an s-p orbitals interaction



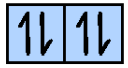
B_2, C_2, N_2



O_2, F_2, Ne_2

Magnetism

- *Diamagnetic substance*
  - A substance whose electrons are all paired.
  - ↑↓
  - Weakly repelled by magnetic fields.
- *Paramagnetic substance*
  - A substance with one or more unpaired electrons.
  - ↑
  - Attracted by magnetic fields.

	Li_2	B_2	C_2	N_2	O_2	F_2	Ne_2	
$\sigma^*_{2p_x}$								$\sigma^*_{2p_x}$
$\pi^*_{2p_y}$, $\pi^*_{2p_z}$								$\pi^*_{2p_y}$, $\pi^*_{2p_z}$
σ_{2p_x}								π_{2p_y}, π_{2p_z}
π_{2p_y}, π_{2p_z}								σ_{2p_x}
σ^*_{2s}								σ^*_{2s}
σ_{2s}								σ_{2s}
Bond order	1	1	2	3	2	1	0	
Bond length (pm)	267	159	131	110	121	142	–	
Bond enthalpy (kJ/mol)	104.6	288.7	627.6	941.4	498.7	156.9	–	
Magnetic properties	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	–	

For simplicity the σ_{1s} and σ^*_{1s} orbitals are omitted. These two orbitals hold a total of four electrons.
Remember that for O_2 and F_2, σ_{2p_x} is lower in energy than π_{2p_y}, and π_{2p_z}.

Patterns

- As bond order increases, bond energy increases.
- As bond order increases, bond length decreases.
- Direct correlation of bond order to bond energy is not always there
- O_2 is known to be paramagnetic.

SAMPLE PROBLEM Using MO Theory to Explain Bond Properties

PROBLEM: As the following data show, removing an electron from N_2 forms an ion with a weaker, longer bond than in the parent molecules, whereas the ion formed from O_2 has a stronger, shorter bond:

	N_2	N_2^+	O_2	O_2^+
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

Explain these facts with diagrams that show the sequence and occupancy of MOs.

PLAN: Find the number of valence electrons for each species, draw the MO diagrams, calculate bond orders, and then compare the results.

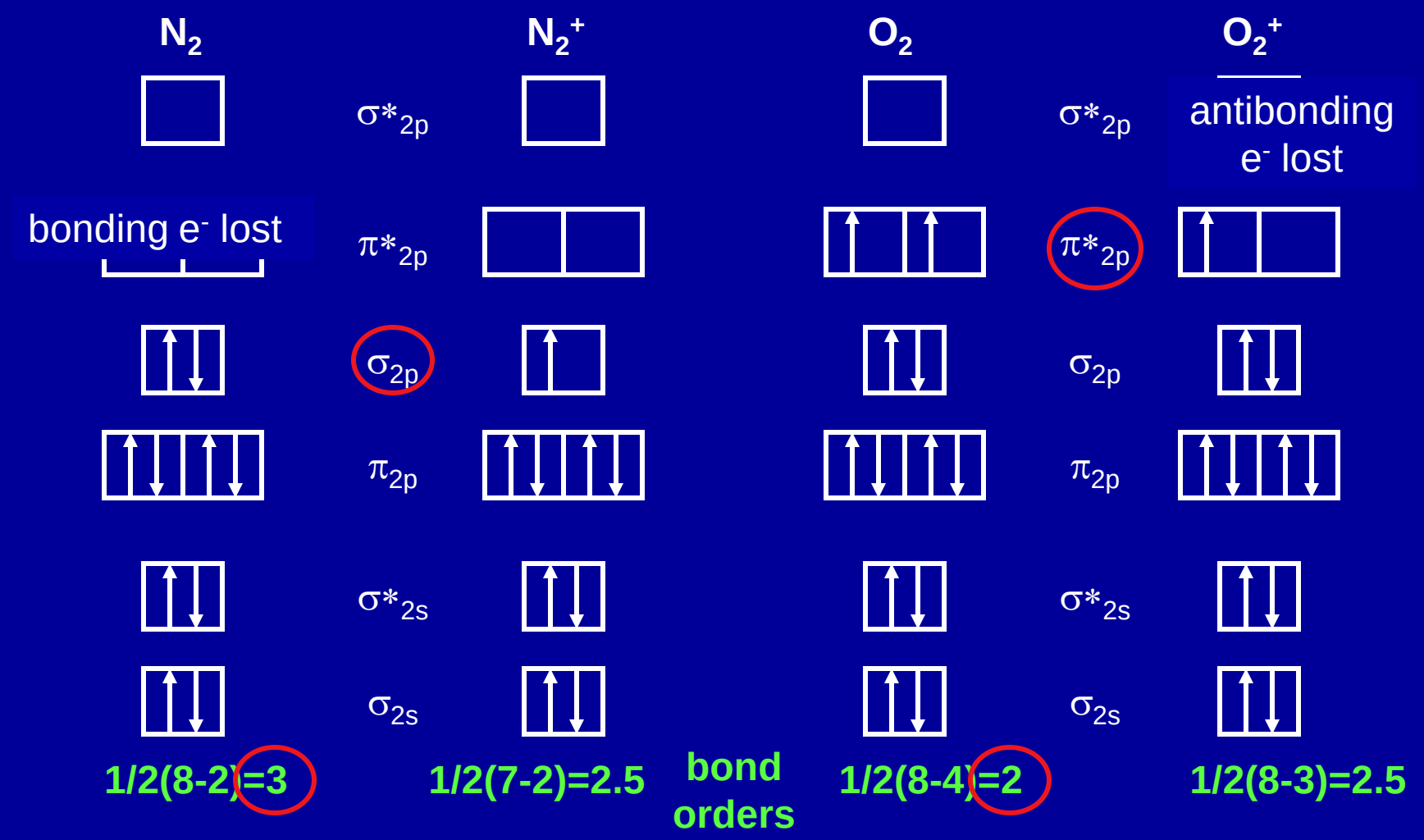
SOLUTION:

N_2 has 10 valence electrons, so N_2^+ has 9.

O_2 has 12 valence electrons, so O_2^+ has 11.

SAMPLE PROBLEM Using MO Theory to Explain Bond Properties

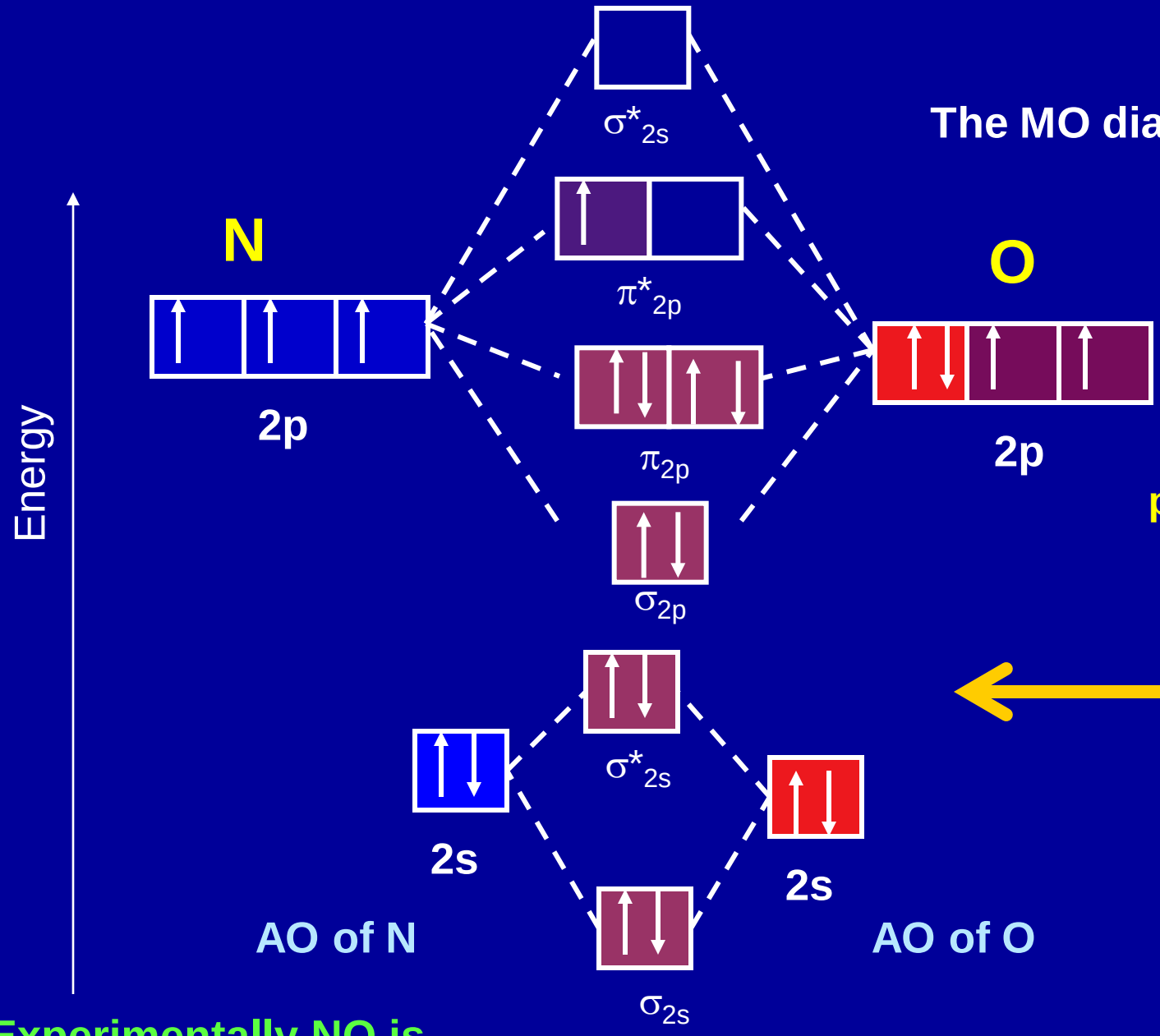
continued



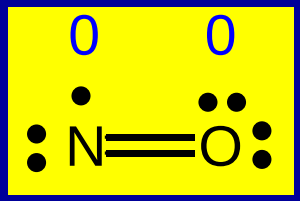
Bonding in heteronuclear diatomic molecules

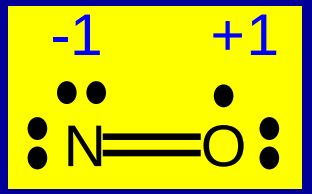
- Only molecules of atoms adjacent to each other in the Periodic Table
- Use same energy level used for homonuclear molecules

The MO diagram for NO



possible Lewis structures





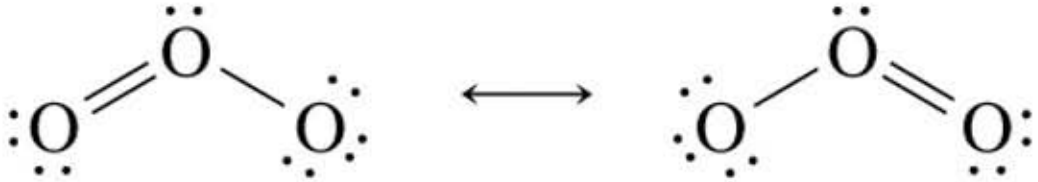
Experimentally NO is paramagnetic

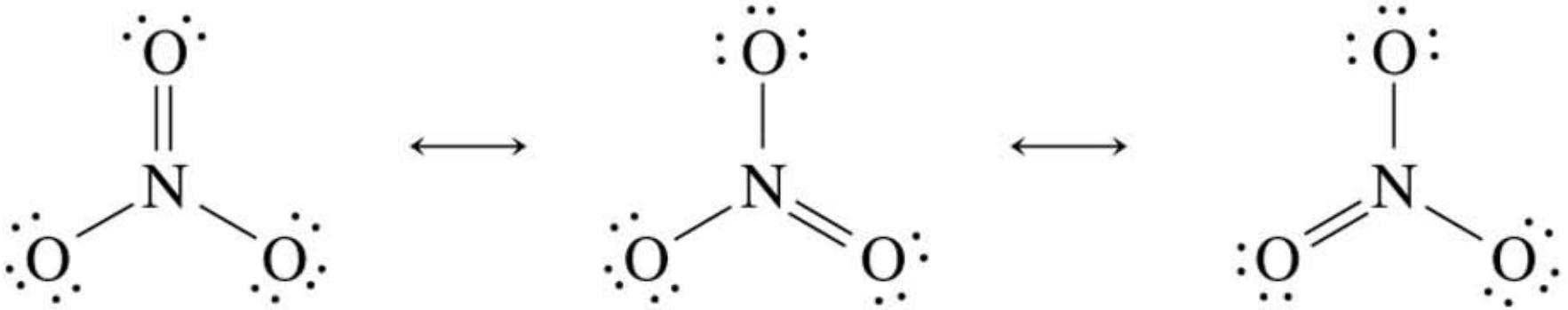
Bond order= $\frac{8-3}{2} = 2.5$

9.7 Bonding Theories and Descriptions of Molecules with Delocalized Bonding

- In *localized bonds* the σ and π bonding electrons are associated with only two atoms.
- *Resonance* requires *delocalized bonds* when applying valence bond theory.

The resonance structures for O_3 and NO_3^-

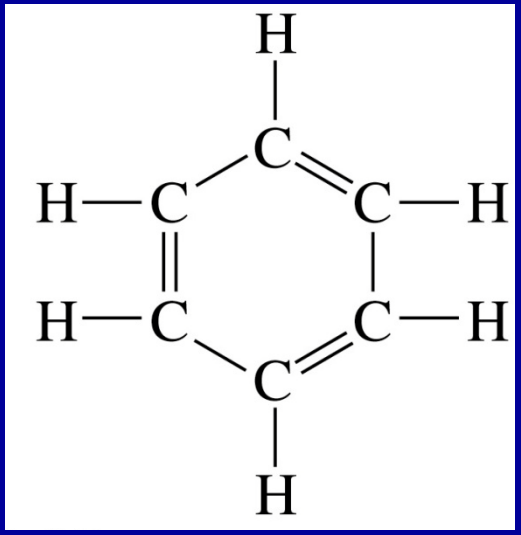




- The two extra electrons in the double bond are found in the delocalized π-orbital associated with the whole molecule
- Also, there are 3 σ-bonds localized between S and O atoms
- Thus bond distances are the same

Bonding in Benzene

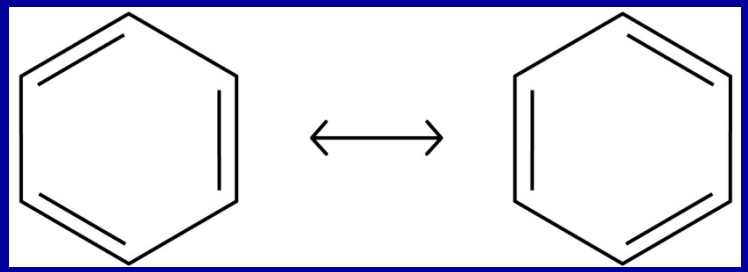
The structure of benzene, C_6H_6, discovered by Michael Faraday in 1825, was not figured out until 1865 by F. A. Kekulé

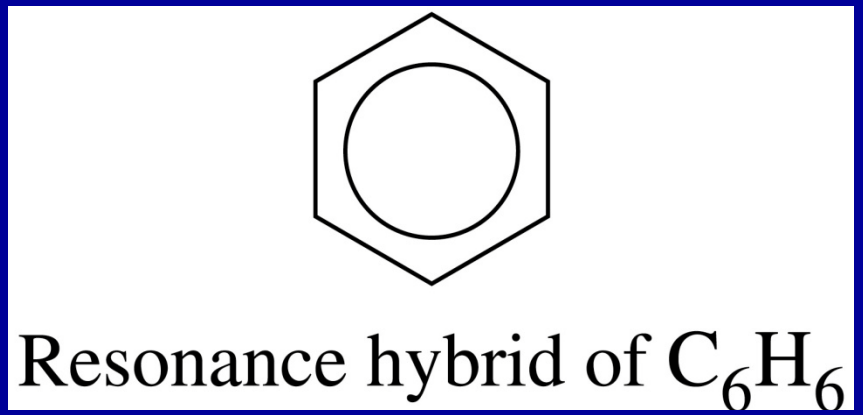


Kekulé discovered that benzene has a cyclic structure and he proposed that a hydrogen atom was attached to each carbon atom and that alternating single and double bonds joined the carbon atoms together

Benzene

This kind of structure gives rise to two important resonance hybrids and leads to the idea that all three double bonds are delocalized across all six carbon atoms



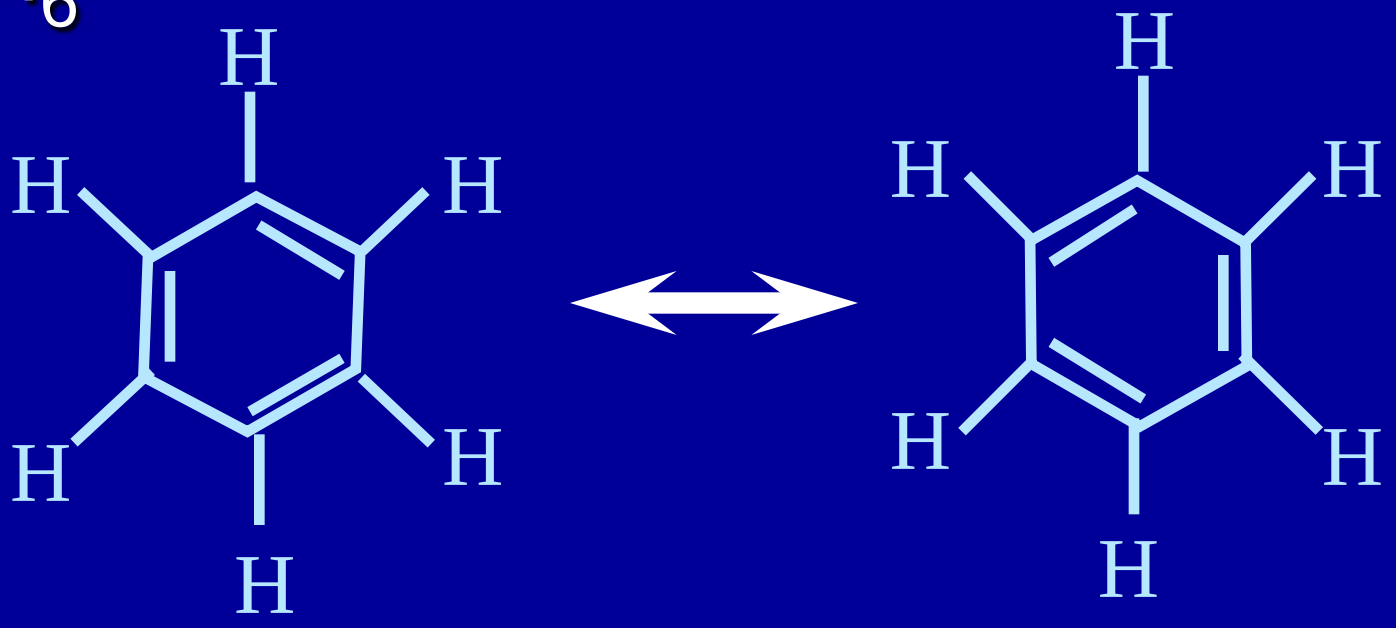


Benzene

- A **better description of bonding in benzene results when a combination of the two models is used for interpretation**
- **Six p-orbitals can be used to π-molecular orbitals**
- **The electrons in the resulting π-molecular orbitals are delocalized above and below the plane of the ring.**
- **Thus, C-C bonds are equivalent as obtained from experiment**

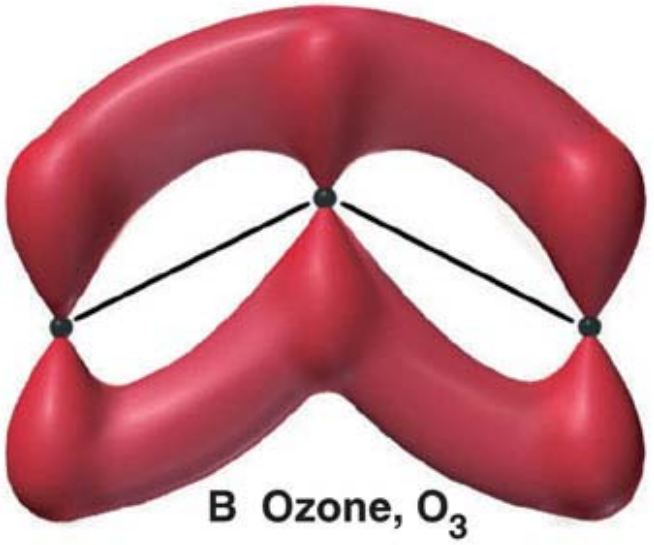
π delocalized bonding

- C_6H_6



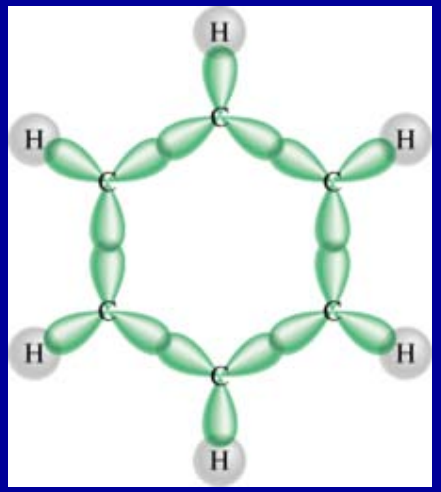
The lowest energy π-bonding MOs in benzene and ozone.

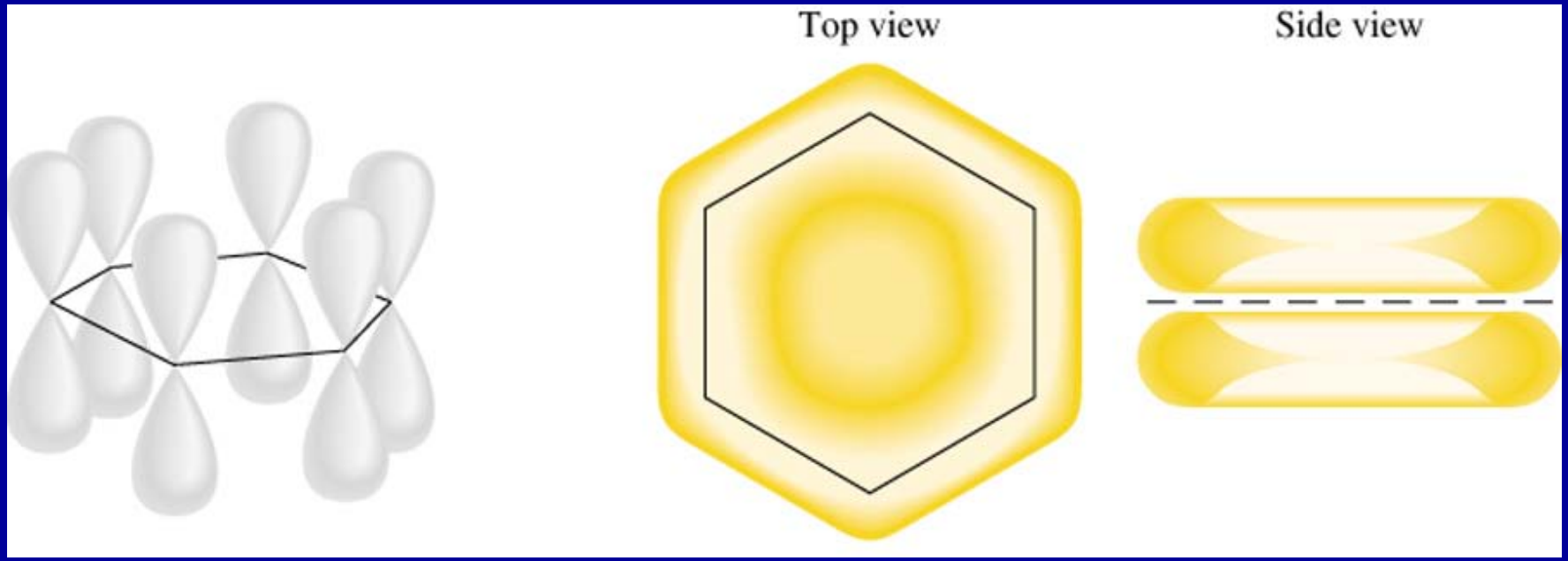
A Benzene, C_6H_6



B Ozone, O_3

Delocalized molecular orbitals **are not confined between two adjacent bonding atoms, but actually extend over three or more atoms.**





Key Points

- Molecular geometry
  - VSEPR model
- Molecular geometry and polarity
- Valence bond theory
- Hybridization of atomic orbitals
  - *s* and *p*
  - *s*, *p*, and *d*
- Hybridization involving multiple bonds

Key Points

- Molecular orbital theory
  - Bonding and antibonding orbitals
  - Sigma (σ) molecular orbitals
  - Pi (π) molecular orbitals
  - MO diagrams