CHEMISTRY XL-14A

MOLECULAR SHAPE AND STRUCTURE

July 23, 2011

Robert Iafe

Valence shell electron pair repulsion theory (VSEPR)

- Lewis Theory
  - Connectivity, electron tracking
- VSEPR Theory
  - 3-D Structure around an atom
- Valence Bond Theory
- Molecular Orbital Theory

Valence shell electron pair repulsion theory (VSEPR)

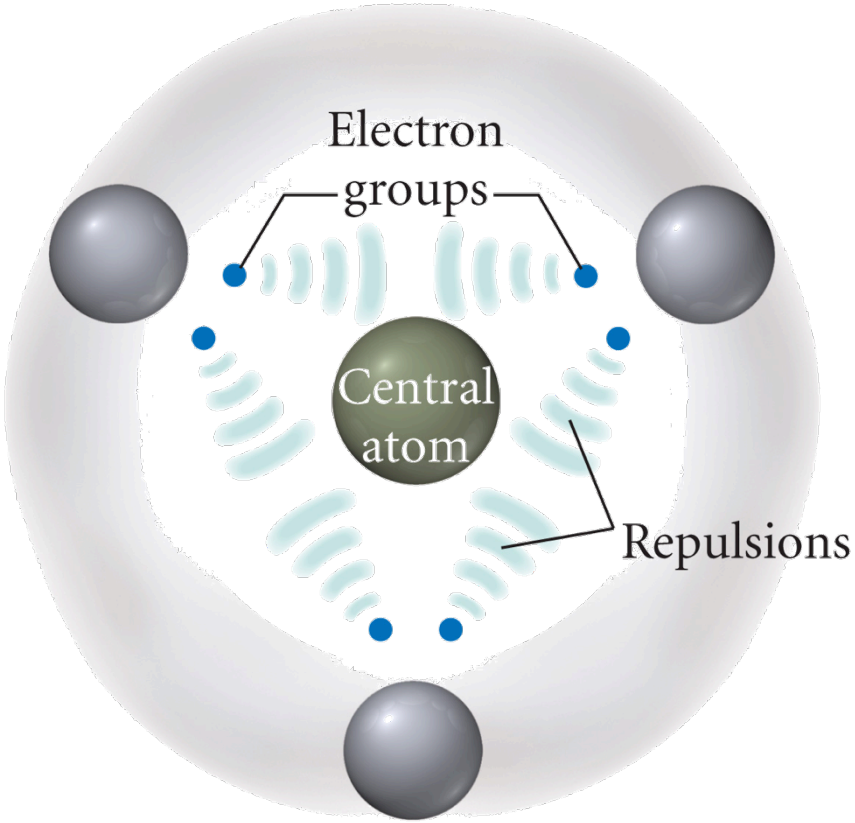
Valence-**S**hell **E**lectron-**P**air **R**epulsion **(VSEPR)**

- Accounts for 3D shapes of molecules
- Based on electron-electron repulsion
- Determine bond angles → shape

Rules are based on experimental observation:

1. Areas of electron concentration (bonds and lone pairs) around the central atom repel each other.
2. Bonds and lone pairs stay as far away from each other as possible (without changing distance)

Valence shell electron pair repulsion theory (VSEPR)



Valence shell electron pair repulsion theory (VSEPR)

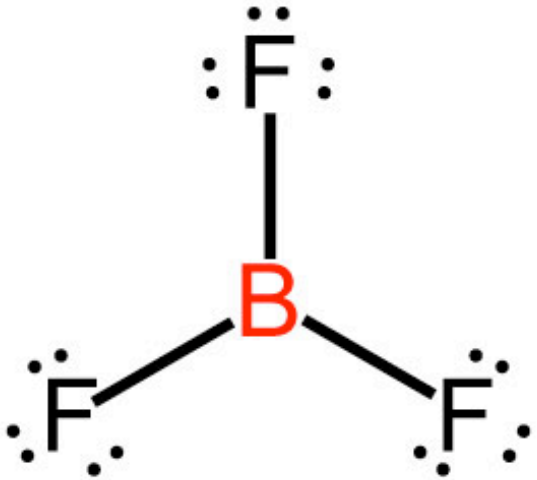
Valence-**S**hell **E**lectron-**P**air **R**epulsion **(VSEPR)** – Accounts for 3D shapes of molecules in terms of electron-electron repulsion

Rules are based on experimental observation:

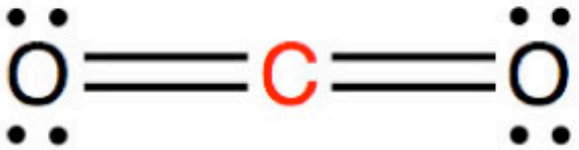
1. Regions of high electron concentration around the central atom (bonds and lone pairs) repel each other.
2. Single and Multiple bonds treated the same

Coordination Number

CN = # of atoms bonded

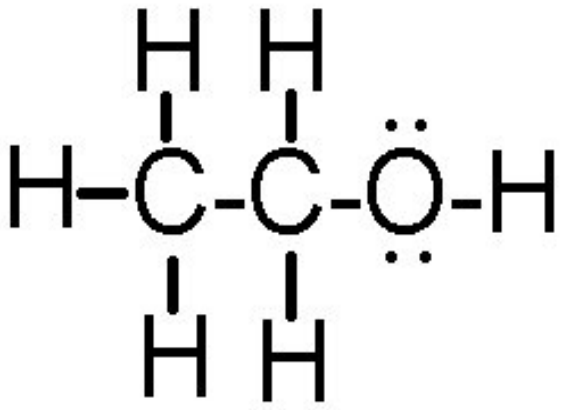


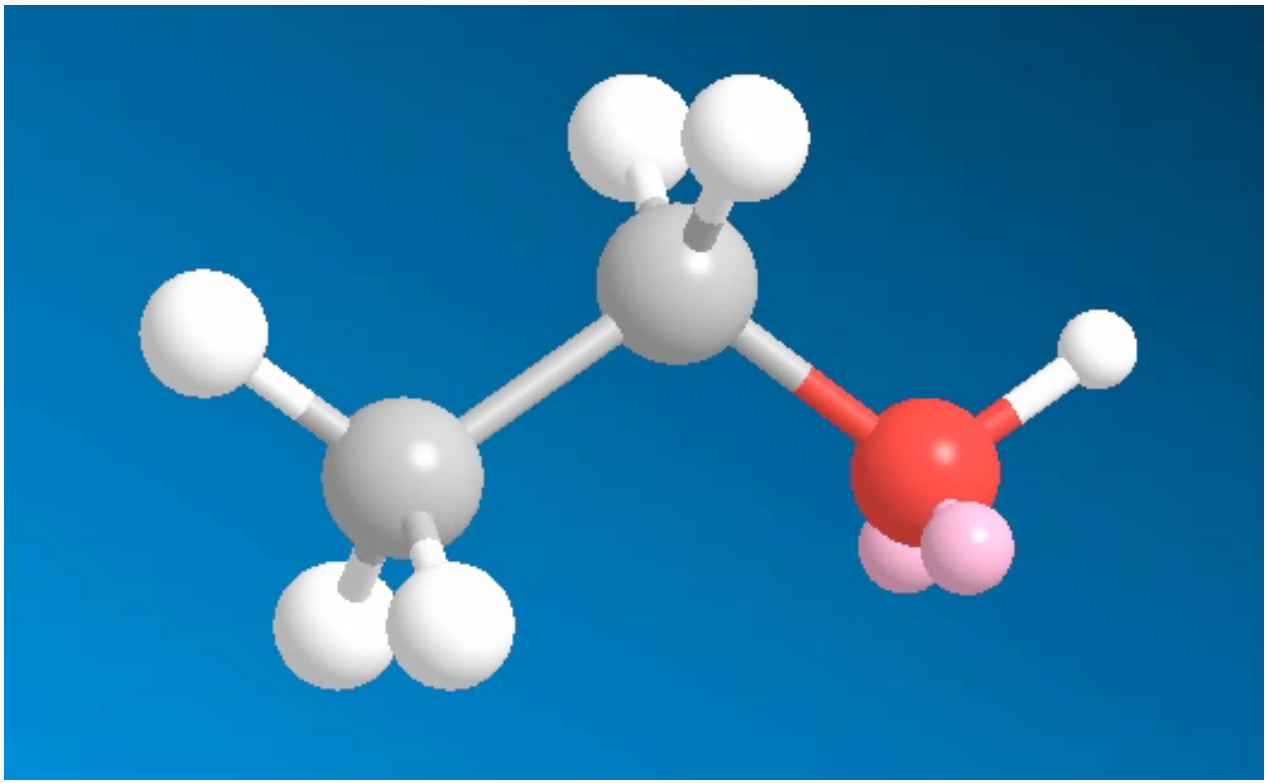
CN of B = 3
CN of F = 1



CN of C = 2
CN of O = 1

Ethanol





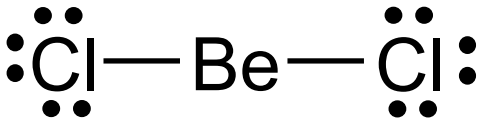
AXE Model

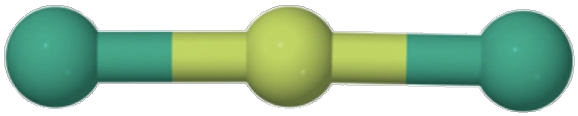
- A = Central Atom
- X = Atomic Substituents
- E = Lone Pairs (If none, not shown)

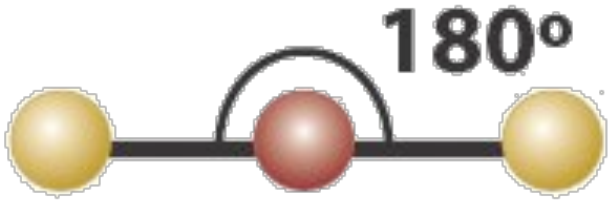
$$AX_nE_m$$

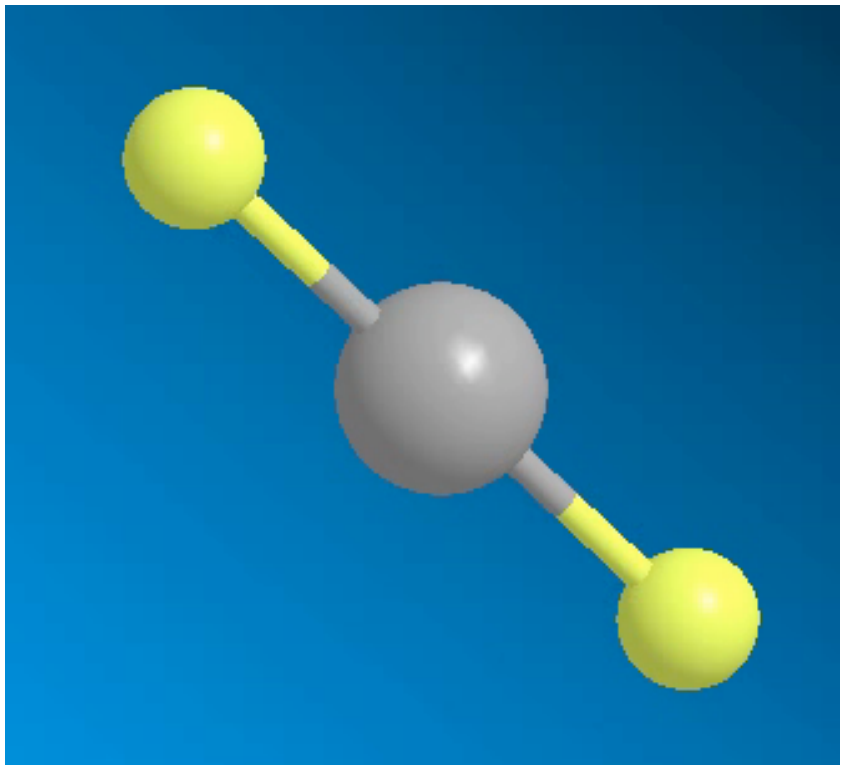
VESPR Base Shapes

- Linear: AX_2 – (2 e^- groups)



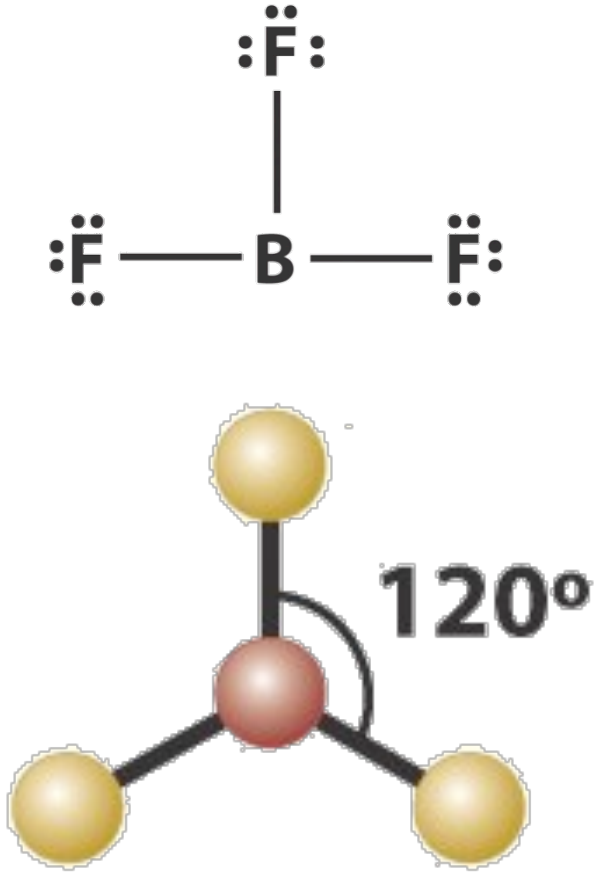


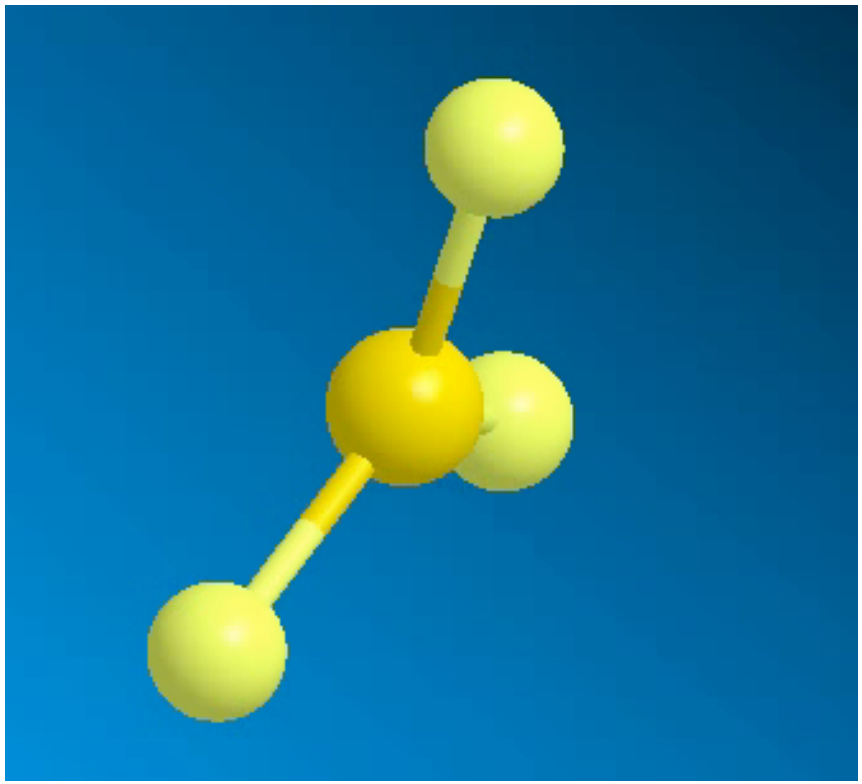




VESPR Base Shapes

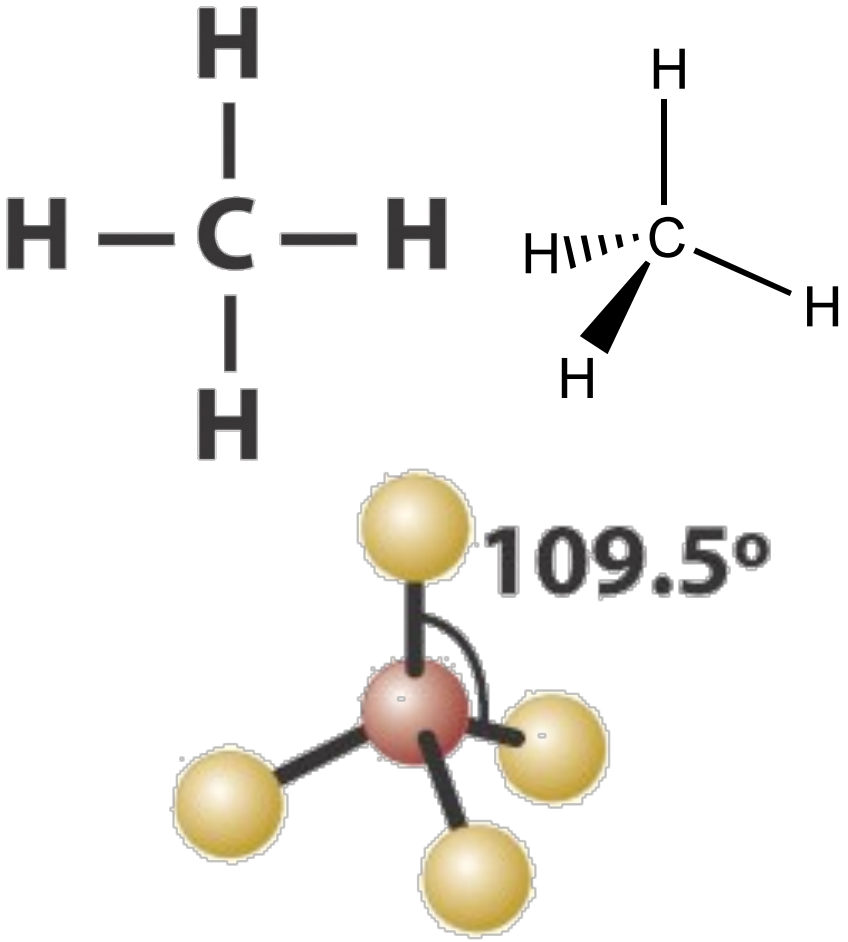
- Trigonal Planar: AX_3

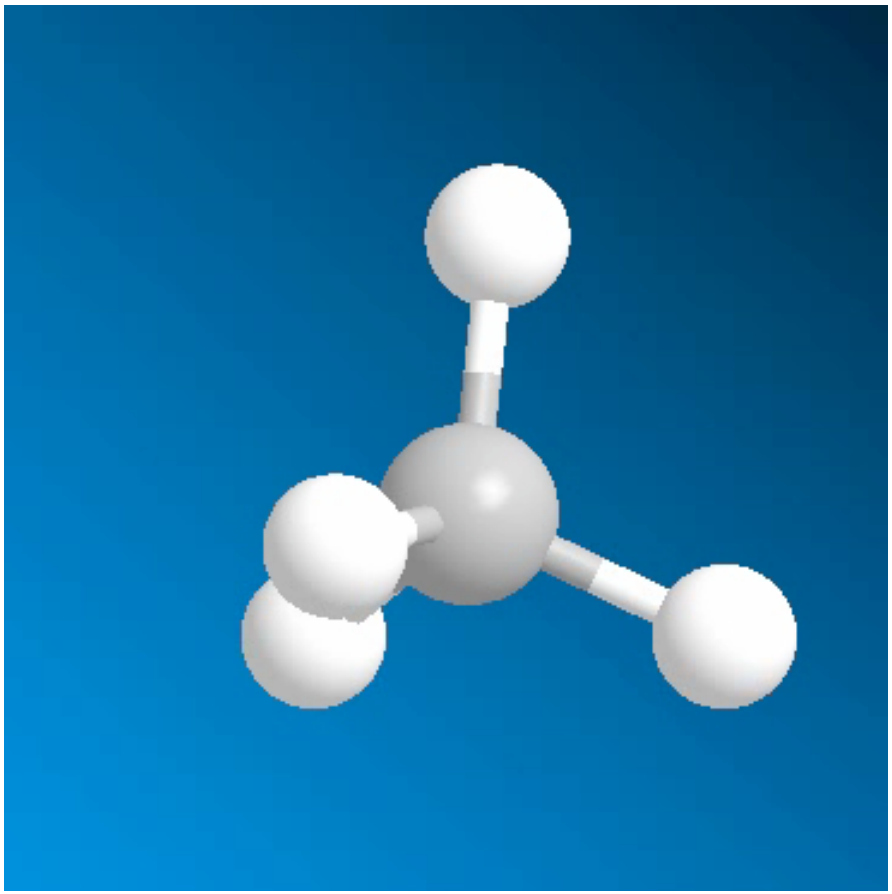




VESPR Base Shapes

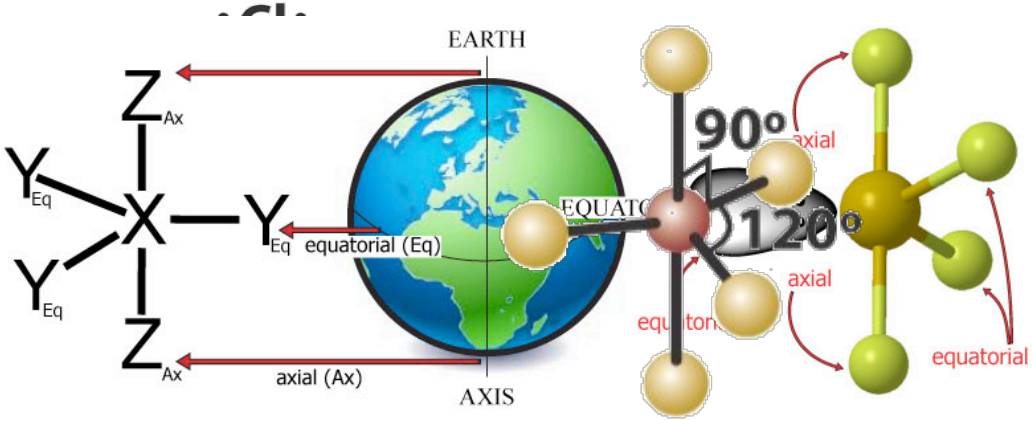
- Tetrahedral: AX_4

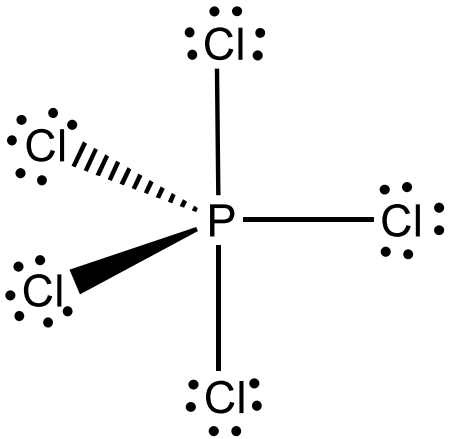


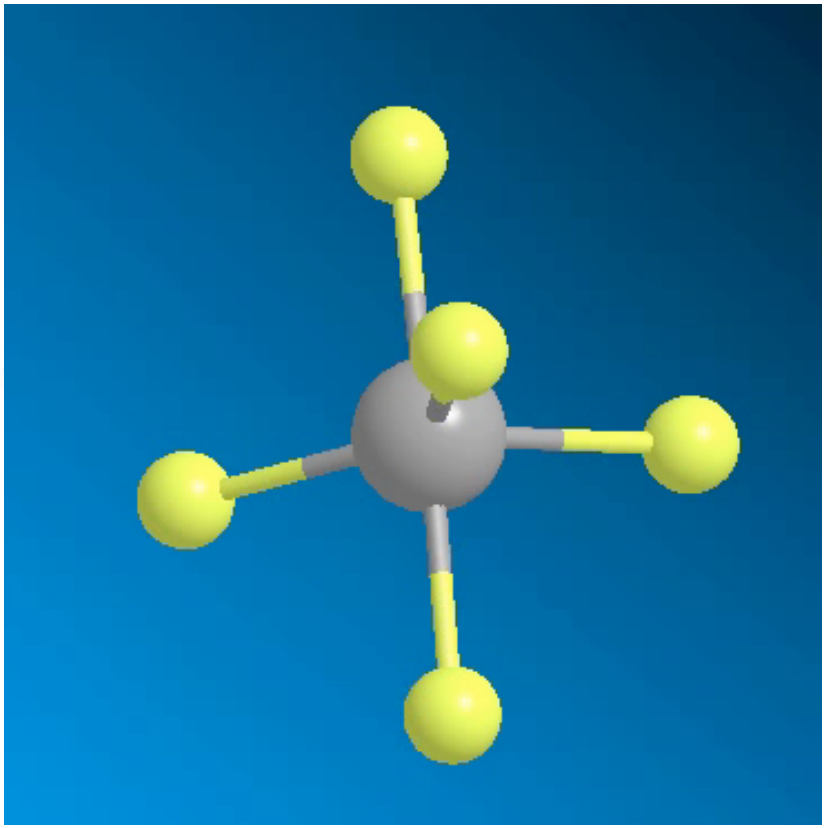


VESPR Base Shapes

- Trigonal Bipyramidal: AX_5

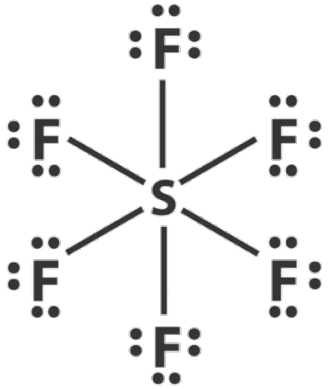


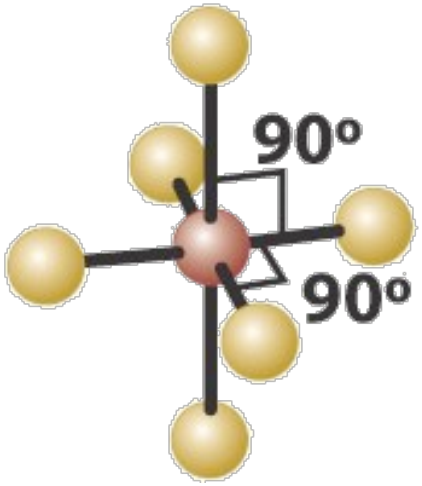


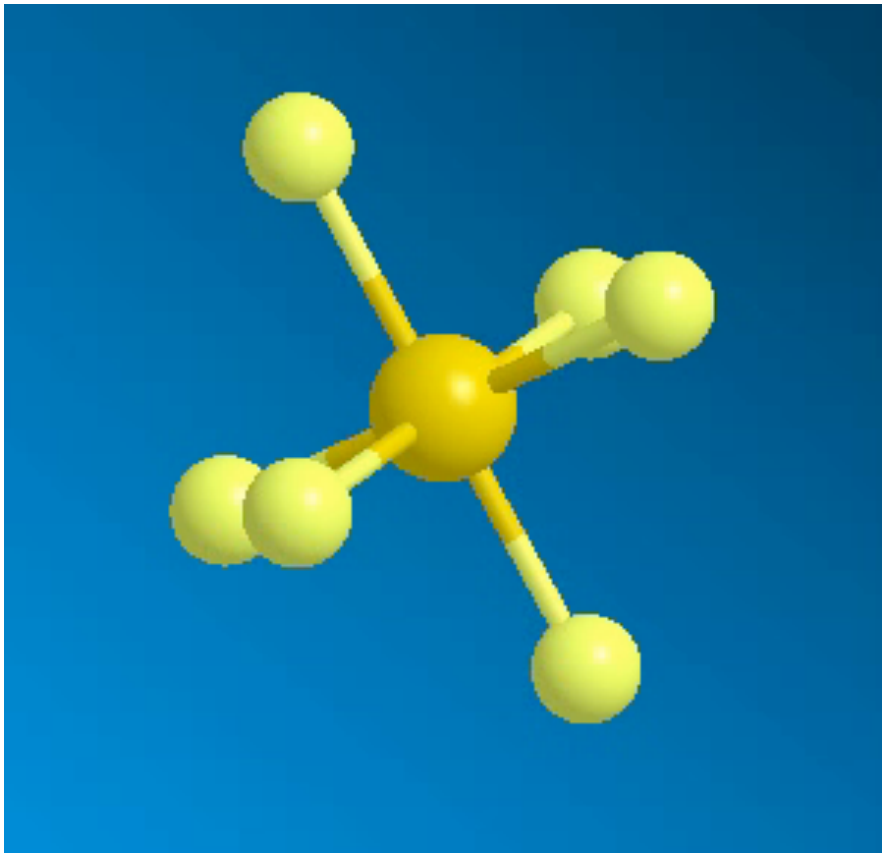


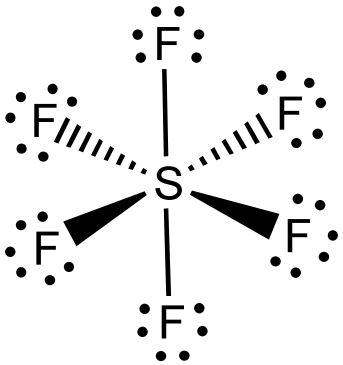
VESPR Base Shapes

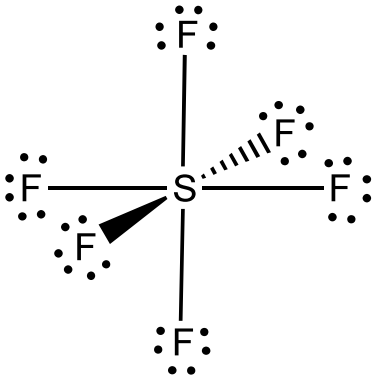
- Octahedral: AX_6







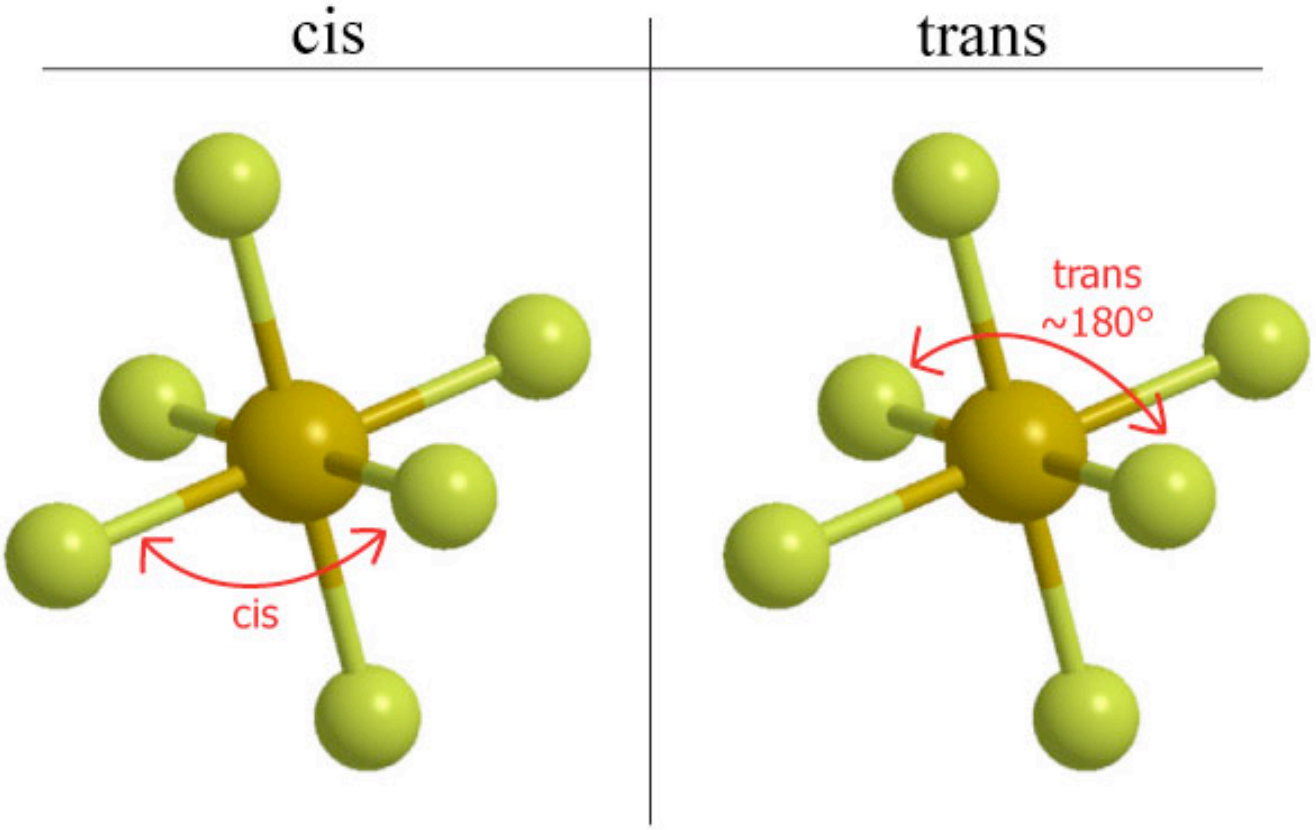




Octahedral – cis/trans

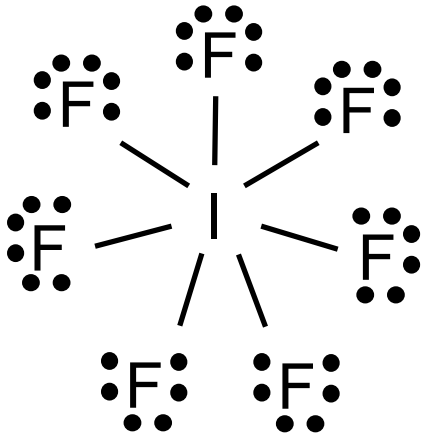
cis- : same side

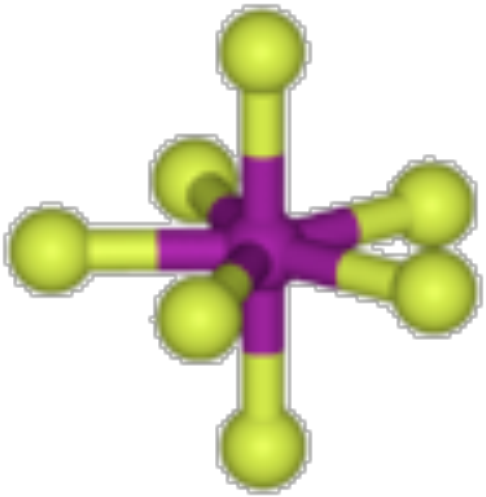
trans- : opposite side (across)

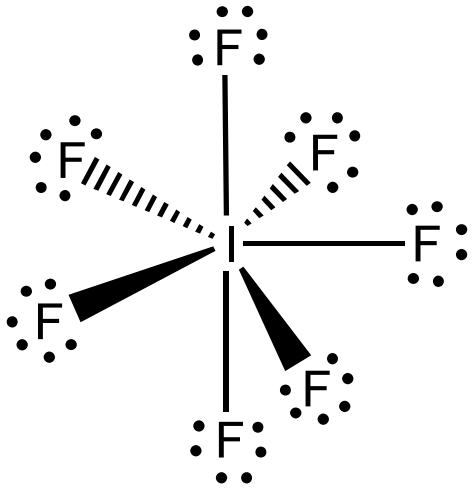


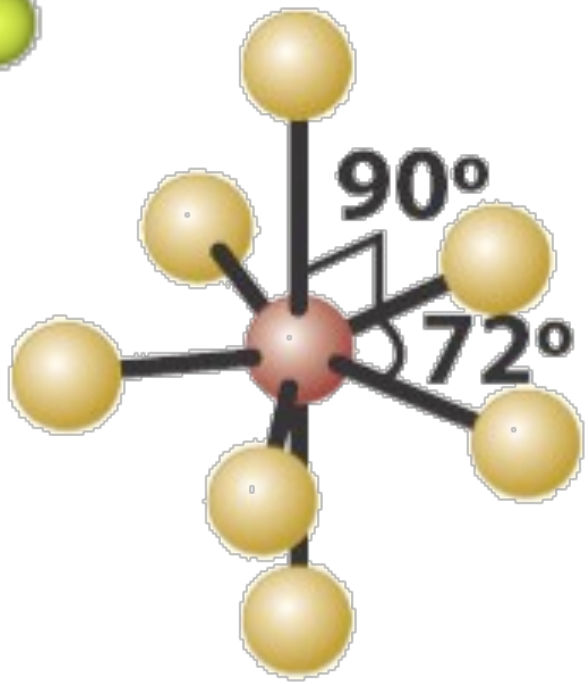
VESPR Base Shapes

- Pentagonal Bipyramidal: AX_7



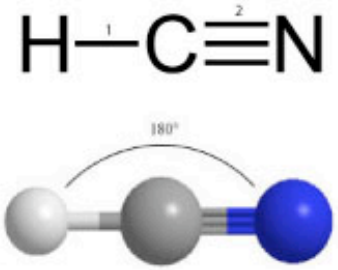


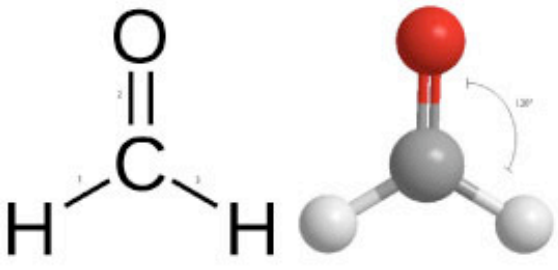




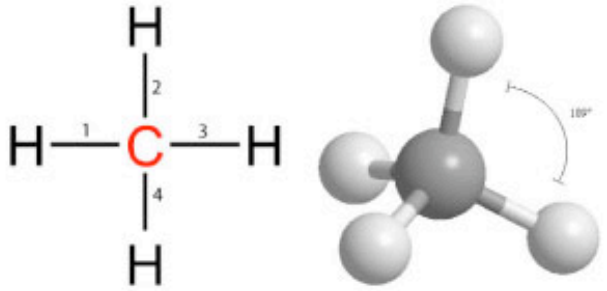
Bond Angles

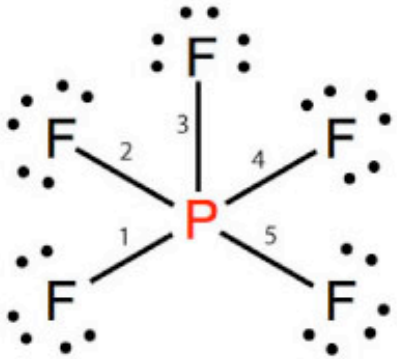
Bond angle is based on the number of electron groups.

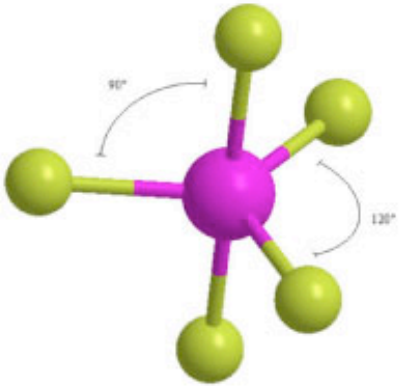


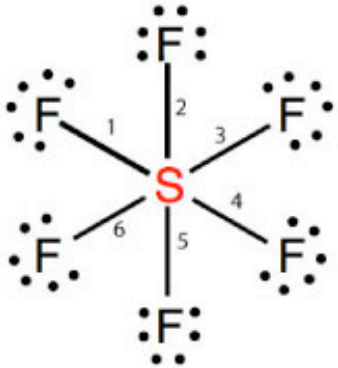


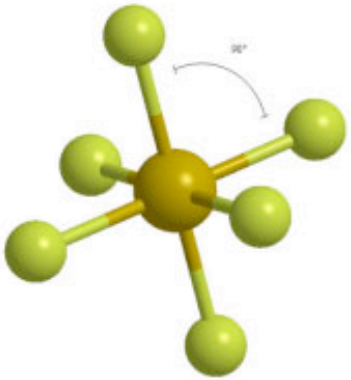
*Multiple bonds are **ONE** electron group.



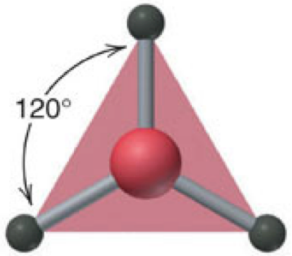


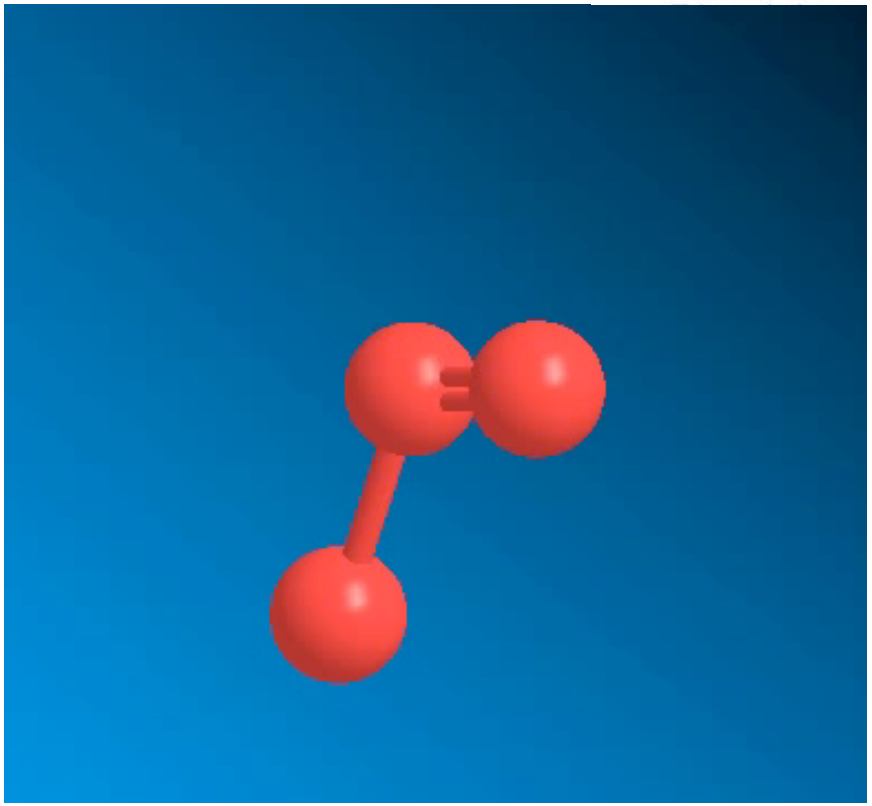


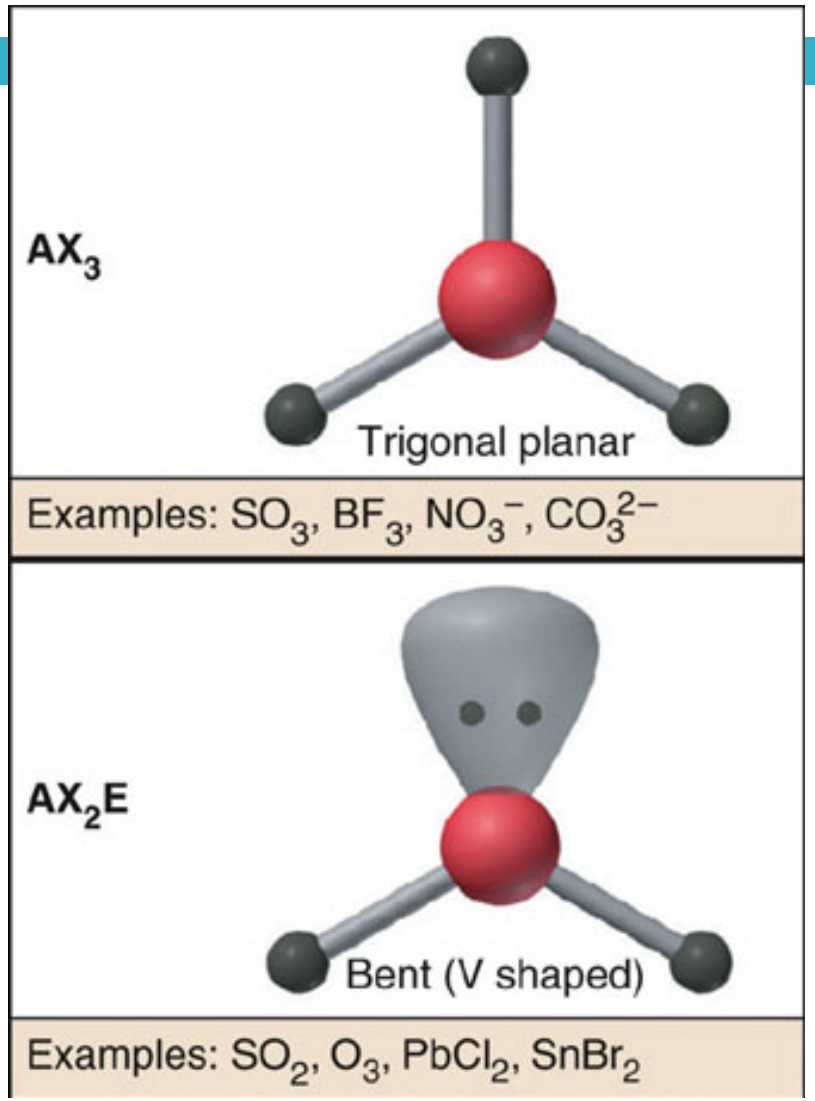




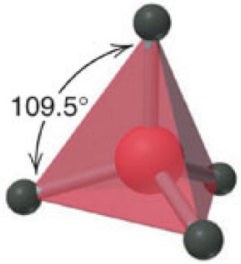
AX_3 Derivatives

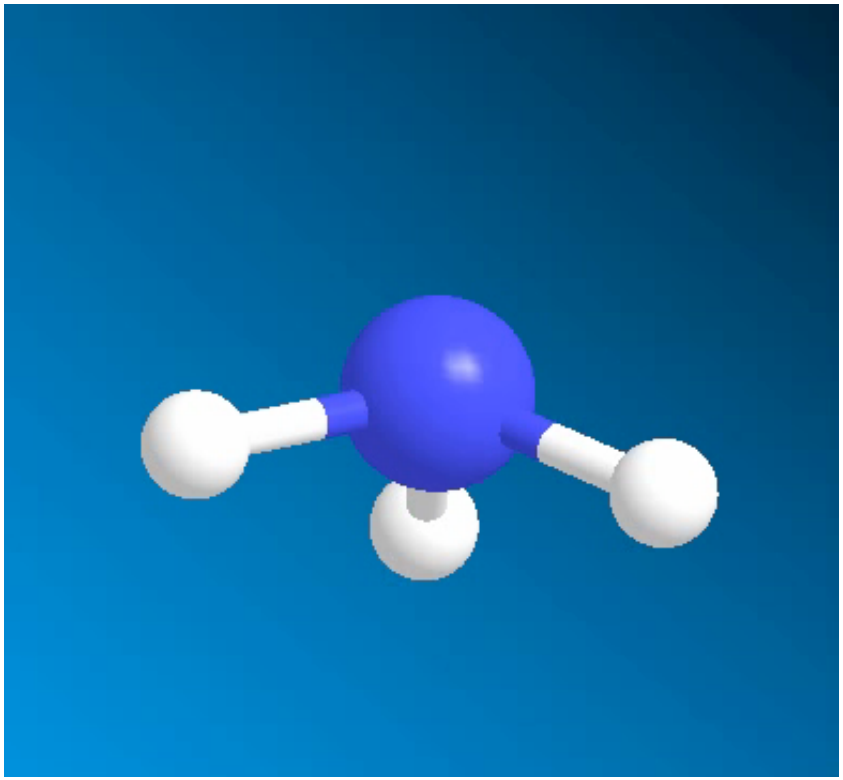


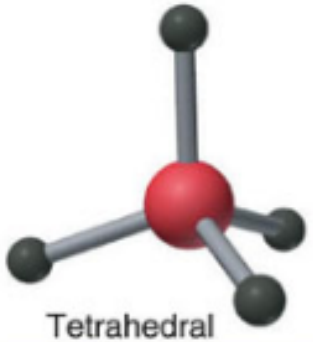
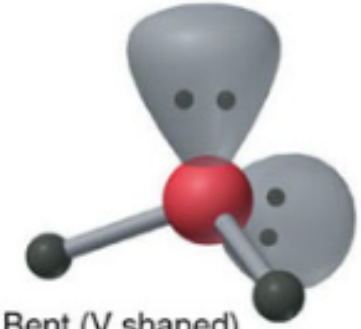




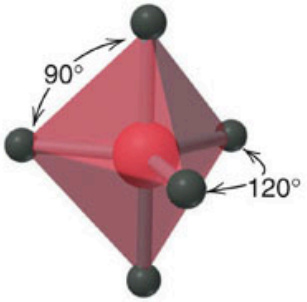
AX_4 Derivatives

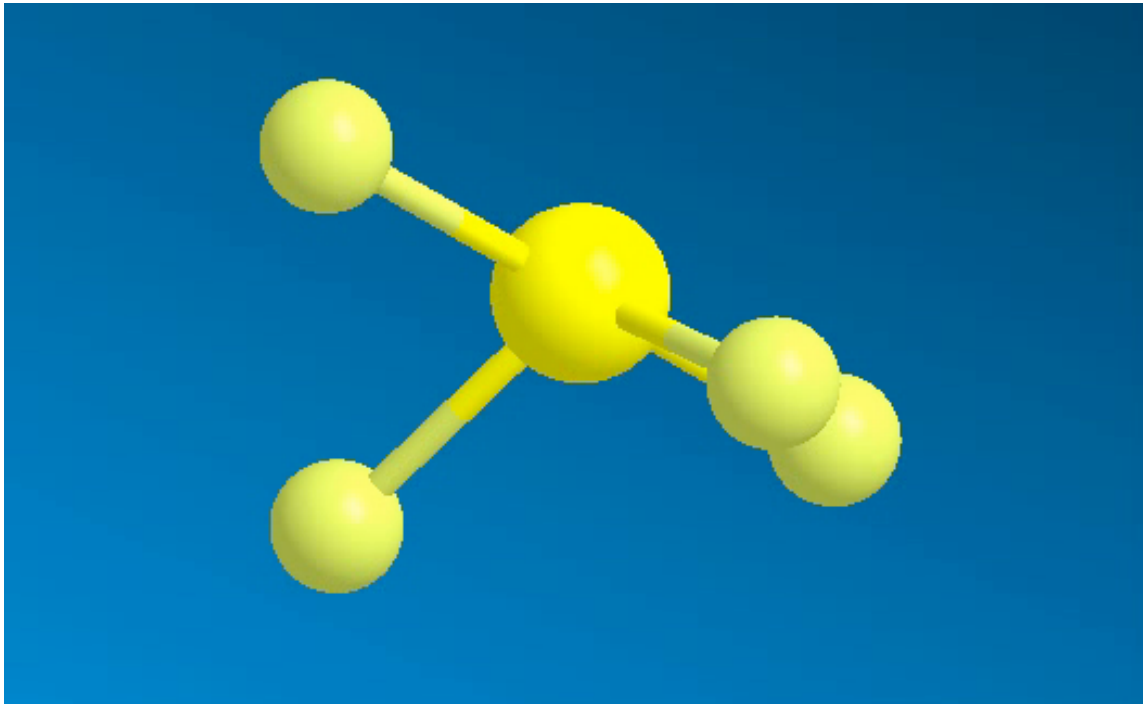


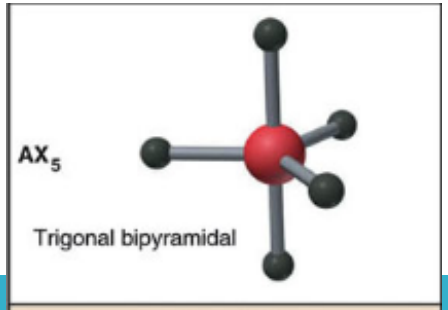


AX_4	 Tetrahedral
Examples: CH_4, $SiCl_4$, SO_4^{2-}, ClO_4^-	
AX_3E	 Trigonal pyramidal
Examples: NH_3, PF_3, ClO_3, H_3O^+	
AX_2E_2	 Bent (V shaped)
Examples: H_2O, OF_2, SCl_2	

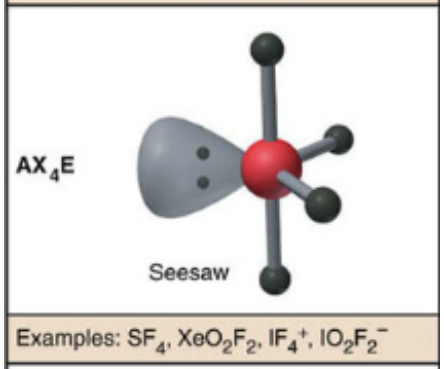
AX_5 Derivatives



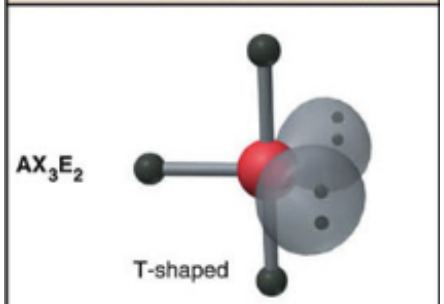




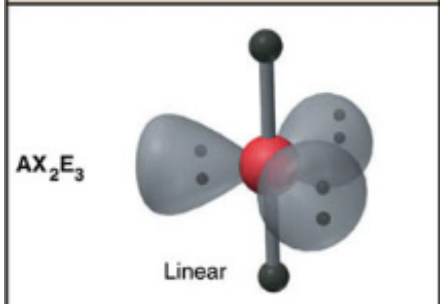
Examples: PF_5, AsF_5, SOF_4



Examples: SF_4, XeO_2F_2, IF_4^+, $IO_2F_2^-$

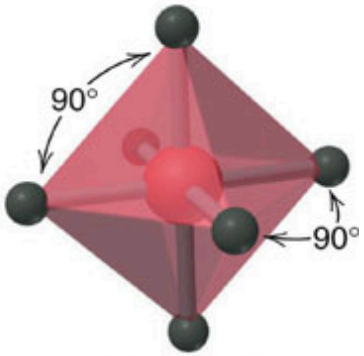


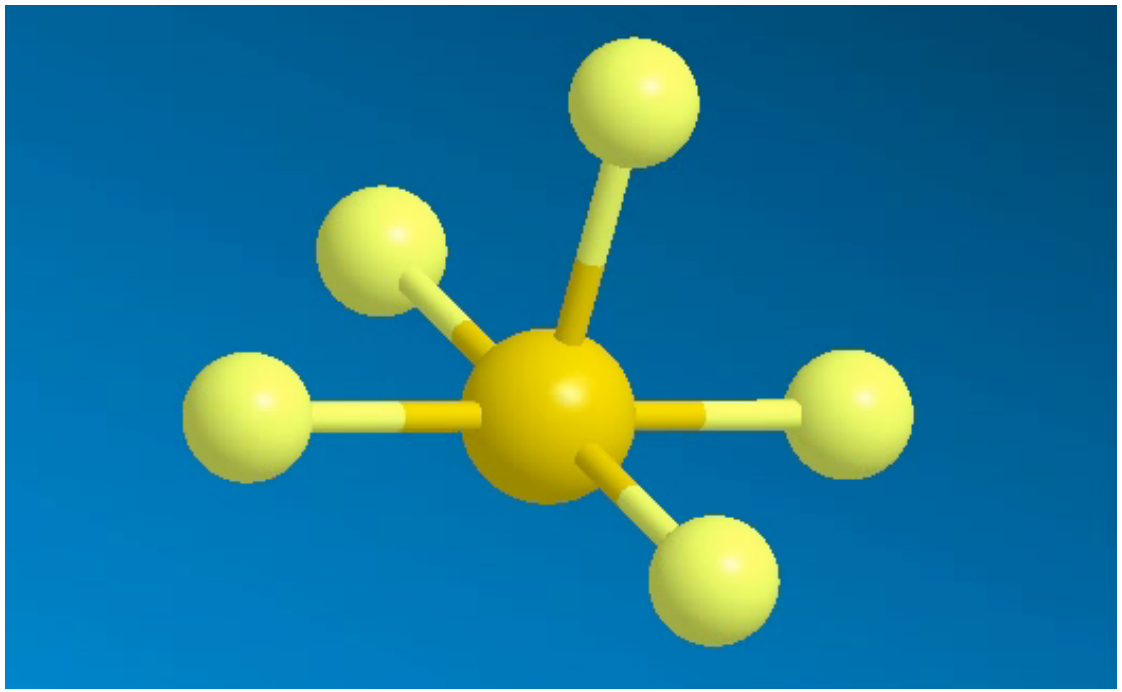
Examples: ClF_3, BrF_3

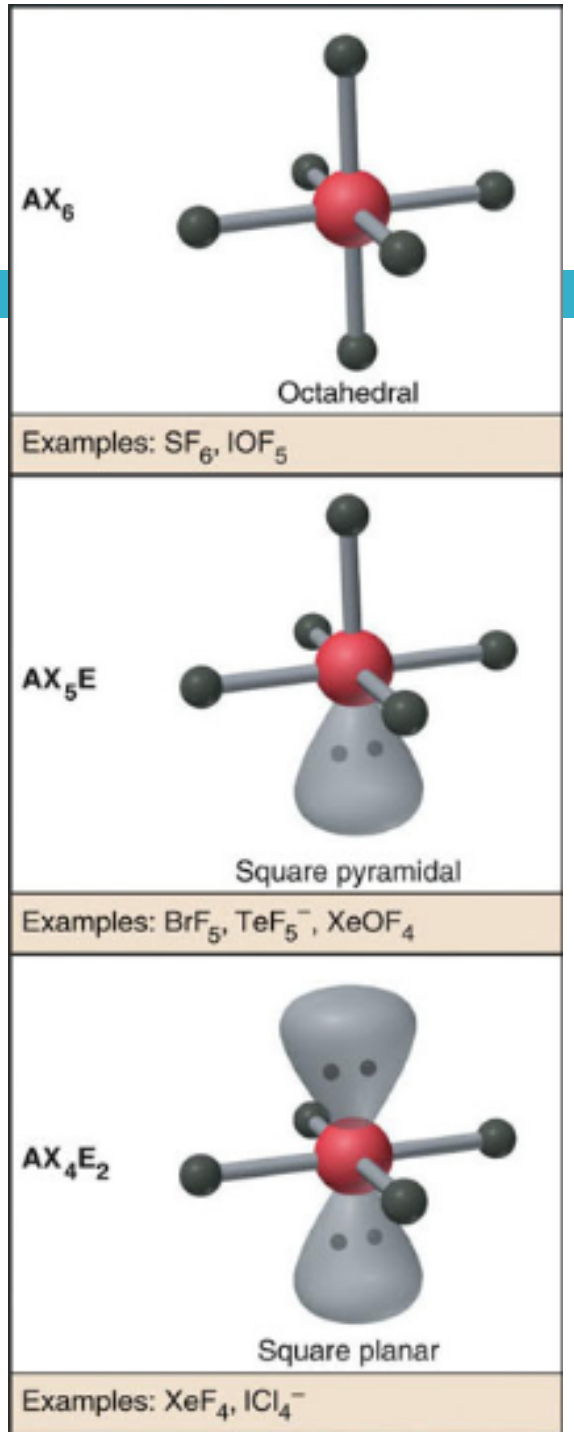


Examples: XeF_2, I_3^-, IF_2^-

AX_6 Derivatives







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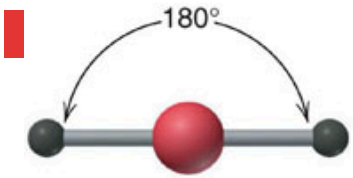
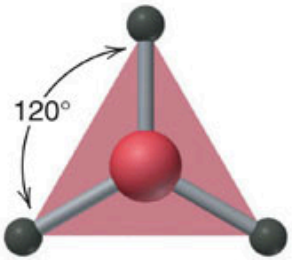
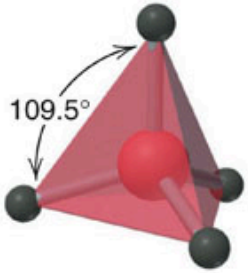
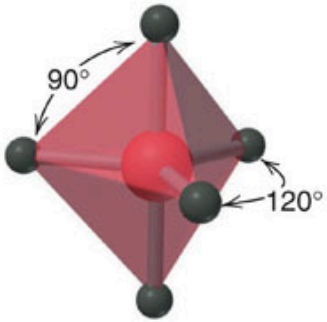
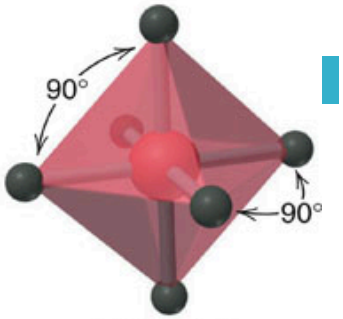
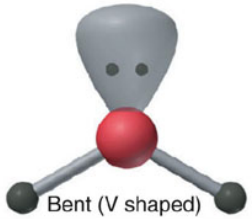
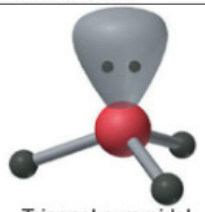
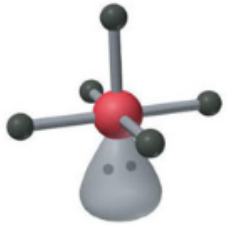
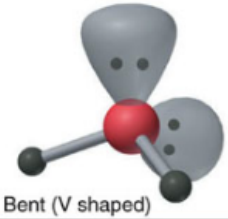
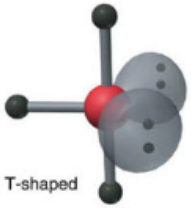
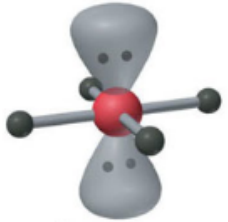
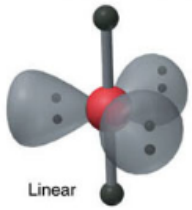
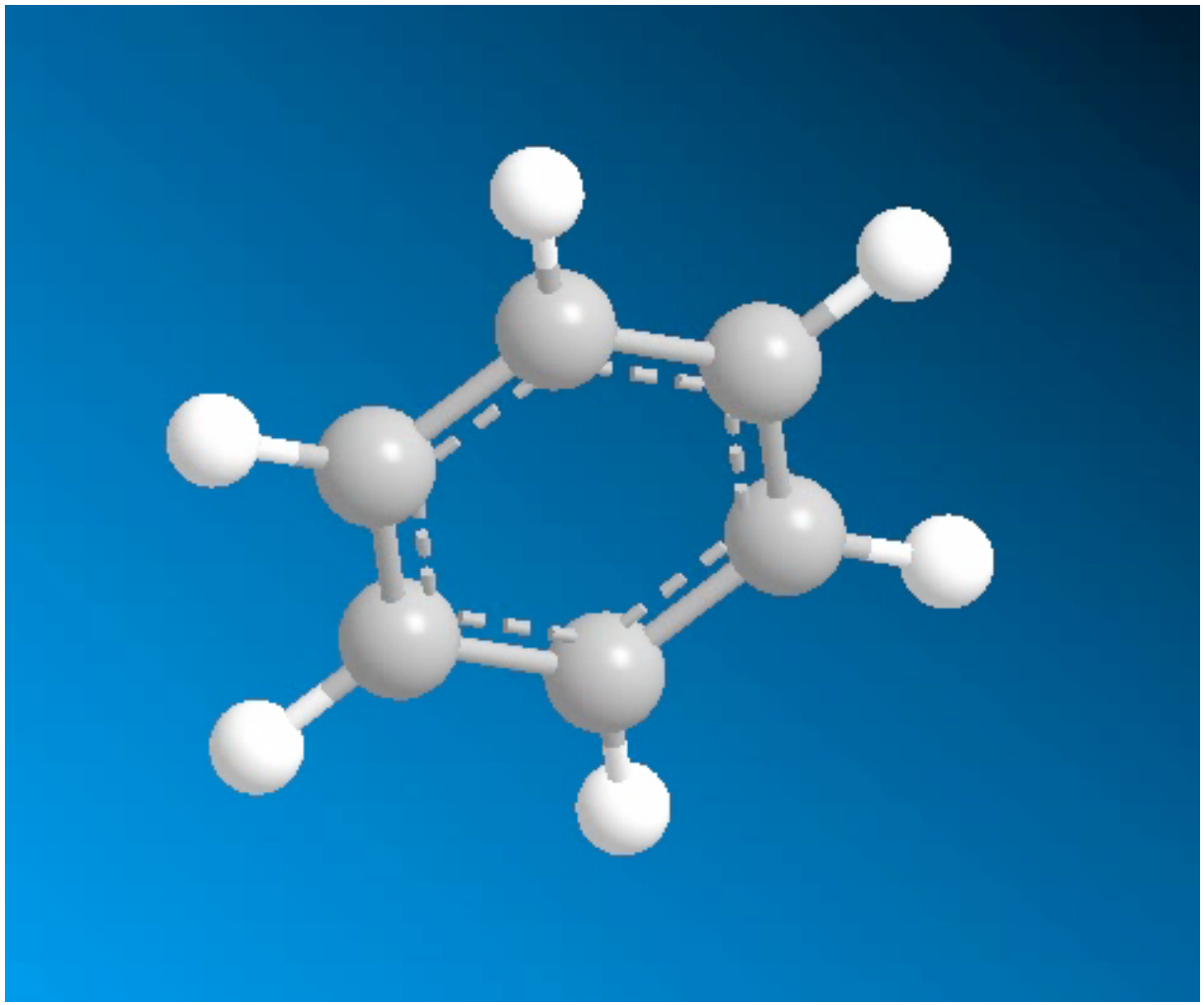
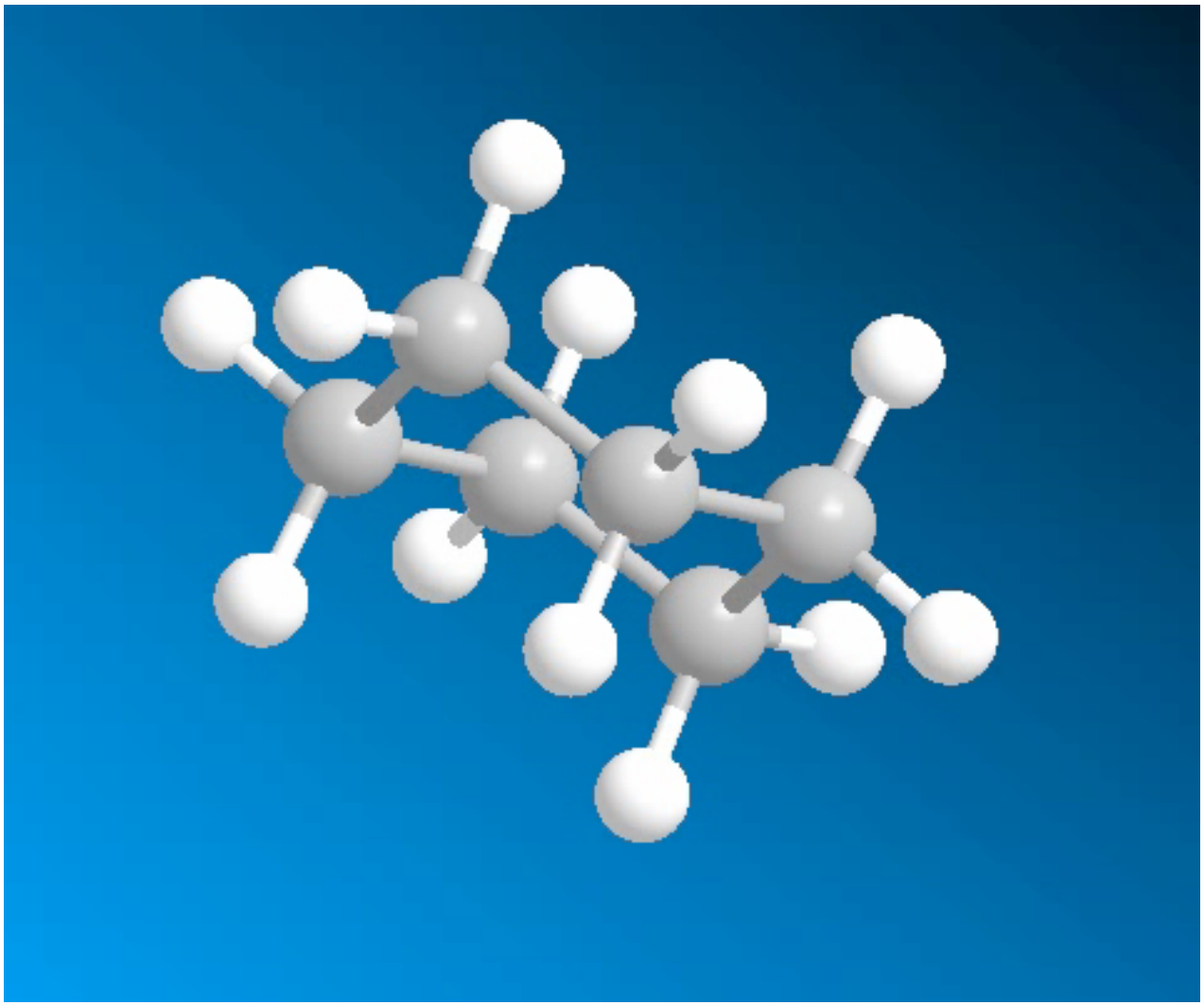
				
Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
	AX_2E  Bent (V shaped) Examples: SO_2, O_3, $PbCl_2$, $SnBr_2$	AX_3E  Trigonal pyramidal Examples: NH_3, PF_3, ClO_3, H_3O^+	AX_4E  Seesaw Examples: SF_4, XeO_2F_2, IF_4^+, $IO_2F_2^-$	AX_5E  Square pyramidal Examples: BrF_5, TeF_5^-, $XeOF_4$
		AX_2E_2  Bent (V shaped) Examples: H_2O, OF_2, SCl_2	AX_3E_2  T-shaped Examples: ClF_3, BrF_3	AX_4E_2  Square planar Examples: XeF_4, ICl_4^-
			AX_2E_3  Linear Examples: XeF_2, I_3^-, IF_2^-	

Benzene – C_6H_6

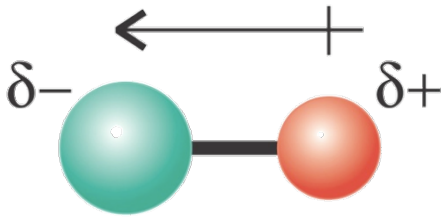


Cyclohexane – C_6H_{12}



Polar Molecules

A **polar covalent bond** has a non-zero dipole moment



Polar molecules – molecules with non-zero dipole moment: $\mu \neq 0$ D

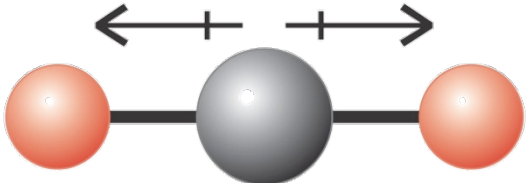
Examples: HCl HF HBr

A non-polar molecule has no dipole moment: $\mu = 0$ D

Examples: O_2 CH_4 SF_6

Polar Molecules

Polar bonds, Non-polar molecule?

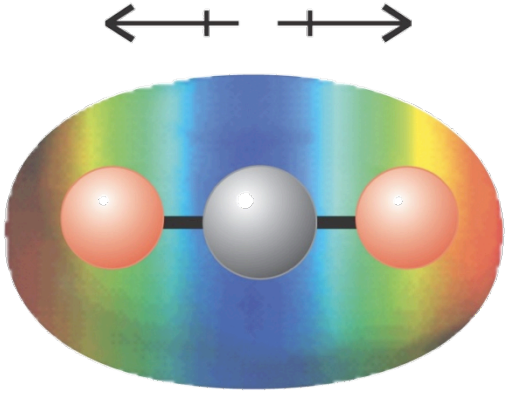


CO_2

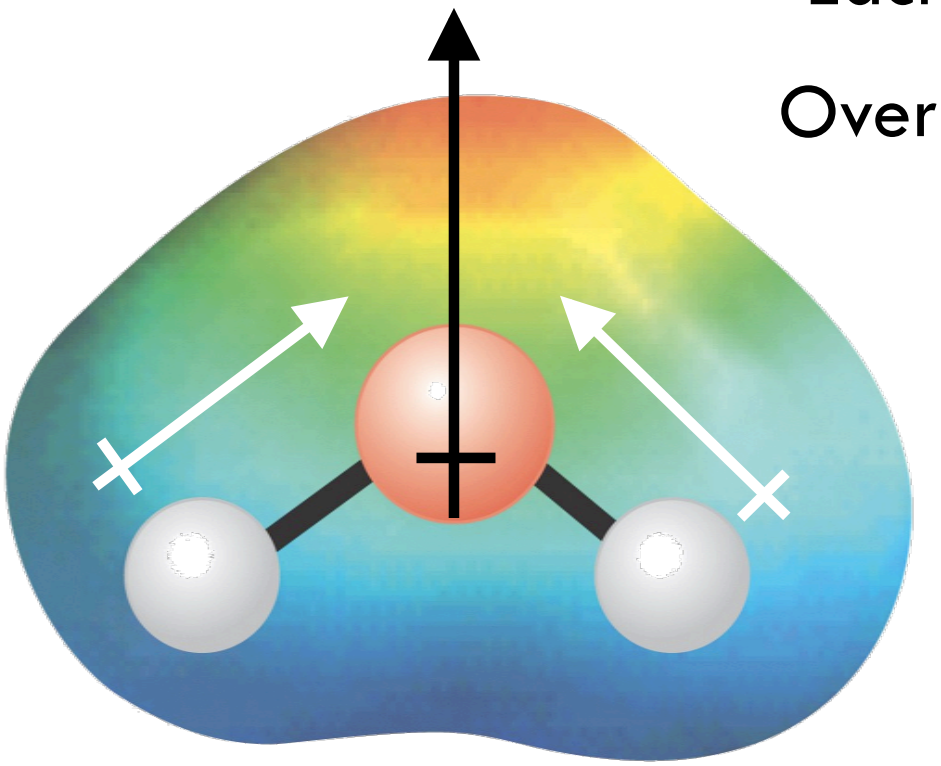
If the dipole moments cancel out (Vector sum = 0):

Each C-O bond is polar

Two equally polar bonds, with opposing dipole moments



Polar Molecules



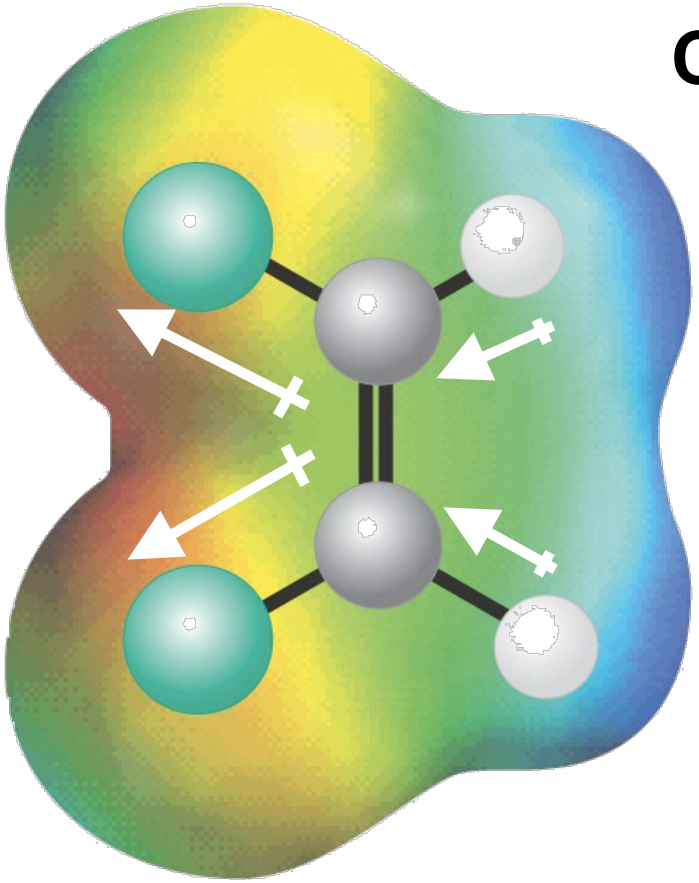
H_2O

Each O-H bond is polar

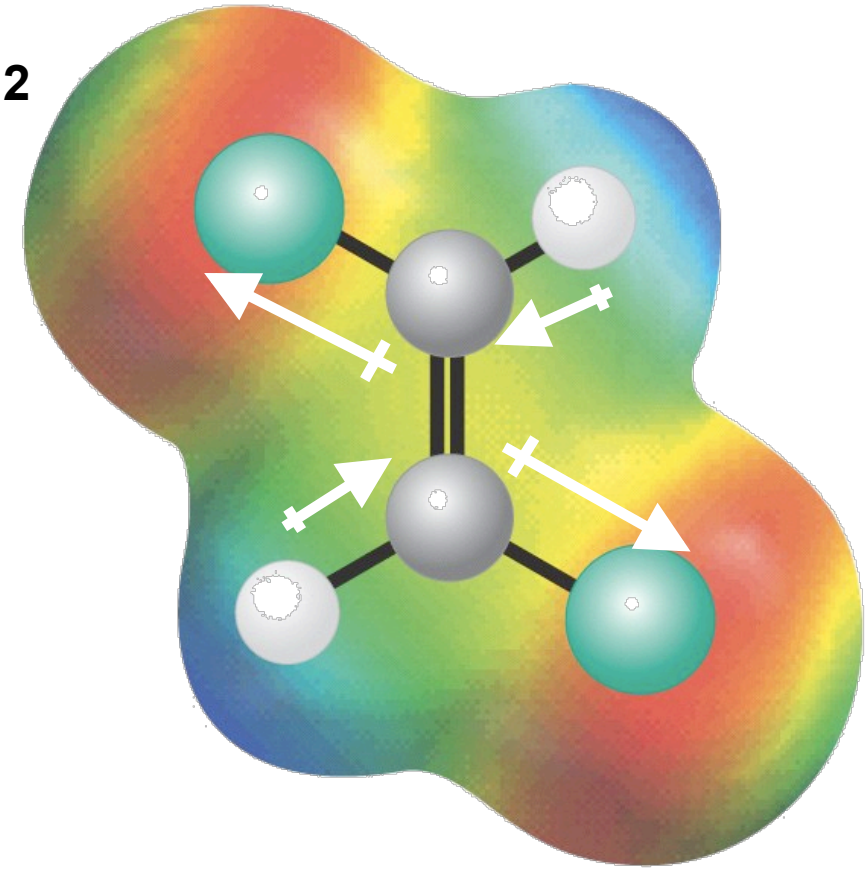
Overall molecule is ??????

Polar Molecules

$C_2H_2Cl_2$



cis-CH_2Cl_2

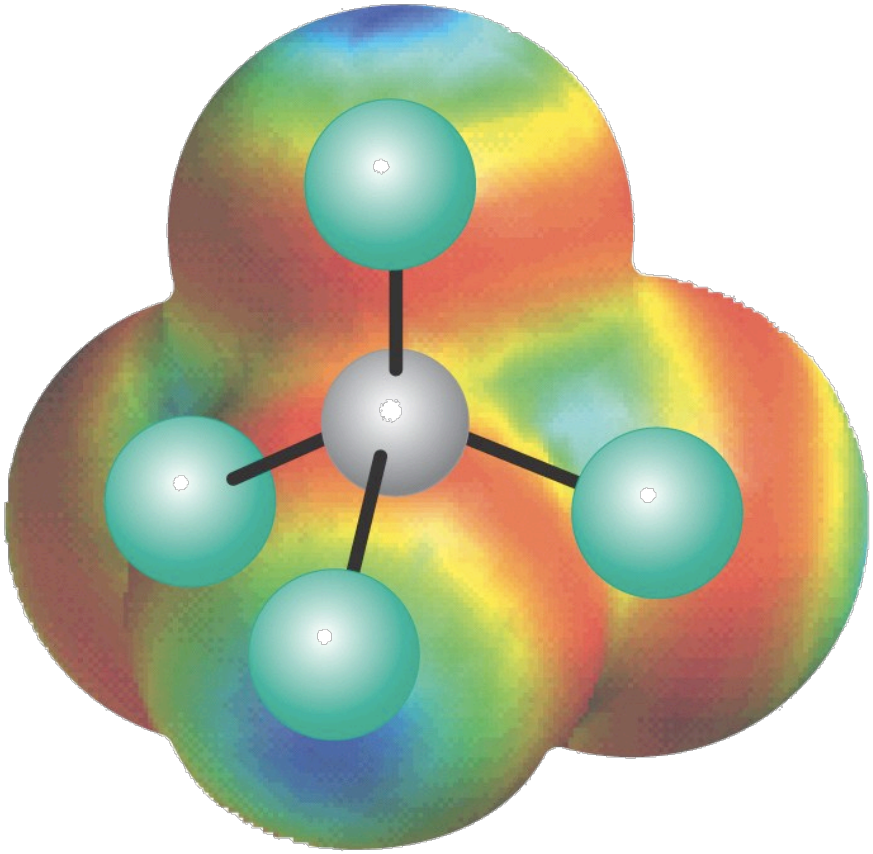


non-polar

trans-CH_2Cl_2

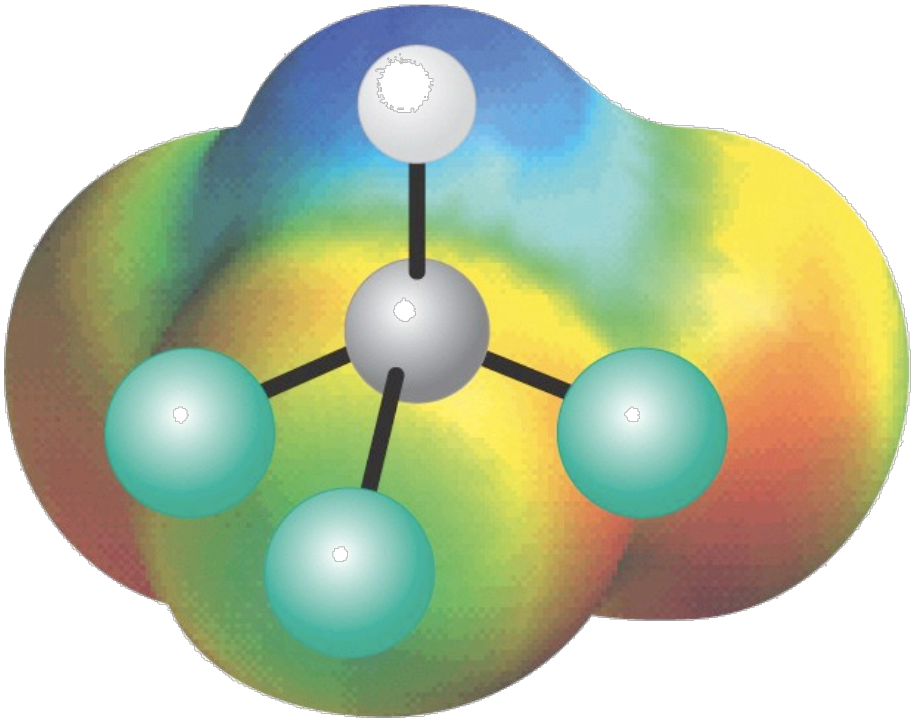
Polar Molecules

CCl_4



non-polar

$CHCl_3$

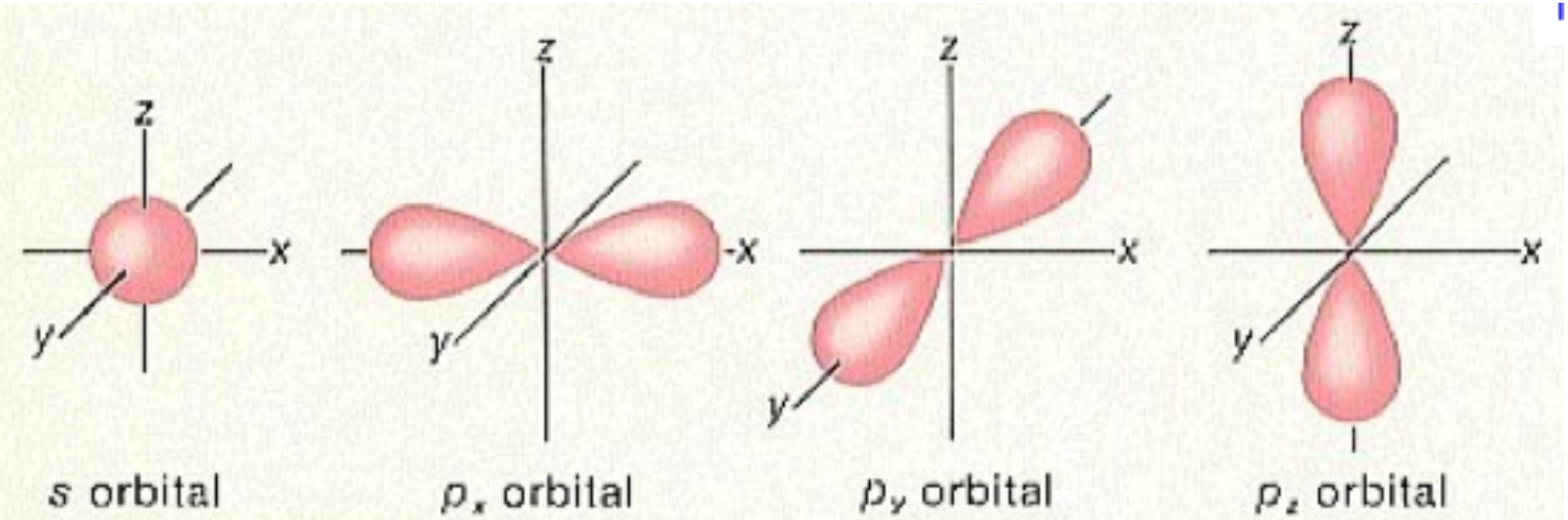


polar

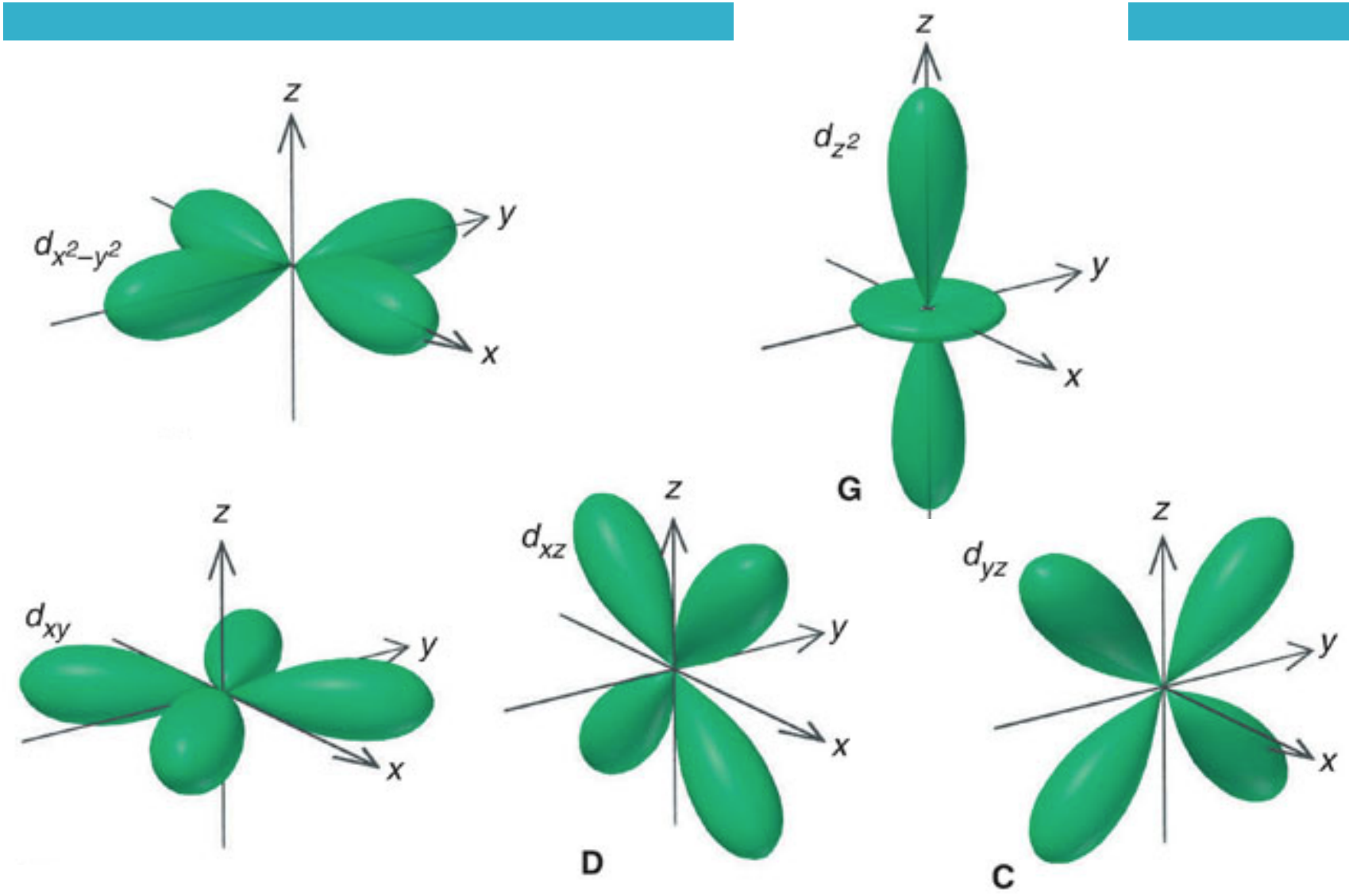
Valence Bond (VB) Theory

- Lewis Theory
  - Connectivity, electron tracking
- VSEPR Theory
  - 3-D Structure around an atom
- Valence Bond Theory
  - Extended 3-D Structure Information
  - Delocalization in Molecules
  - Illustrates Multiple Bonding
  - Prediction of Reactivity
- Molecular Orbital Theory

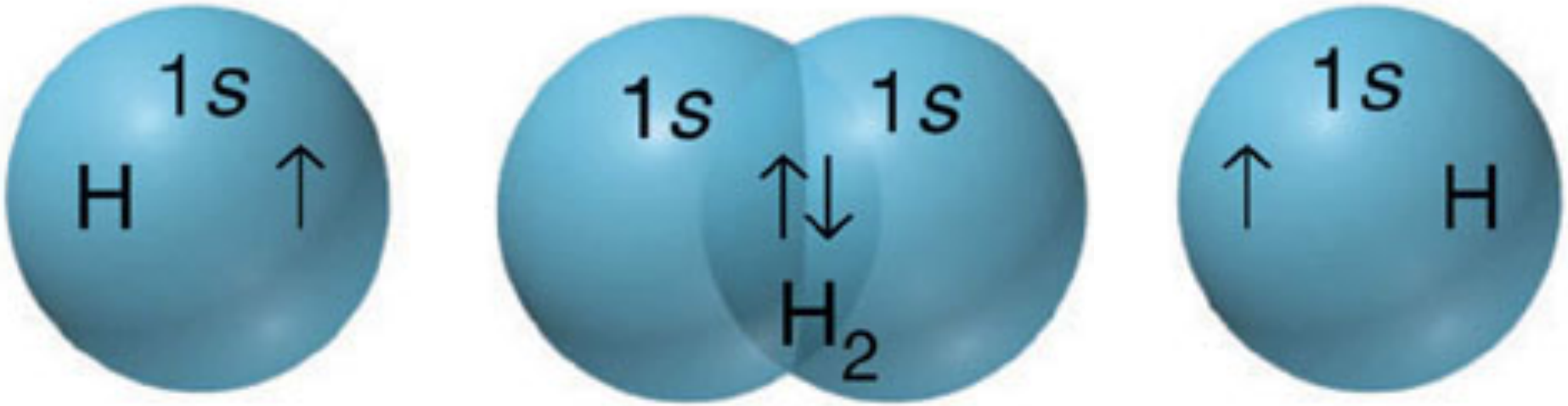
Answers to $H\Psi = E\Psi$



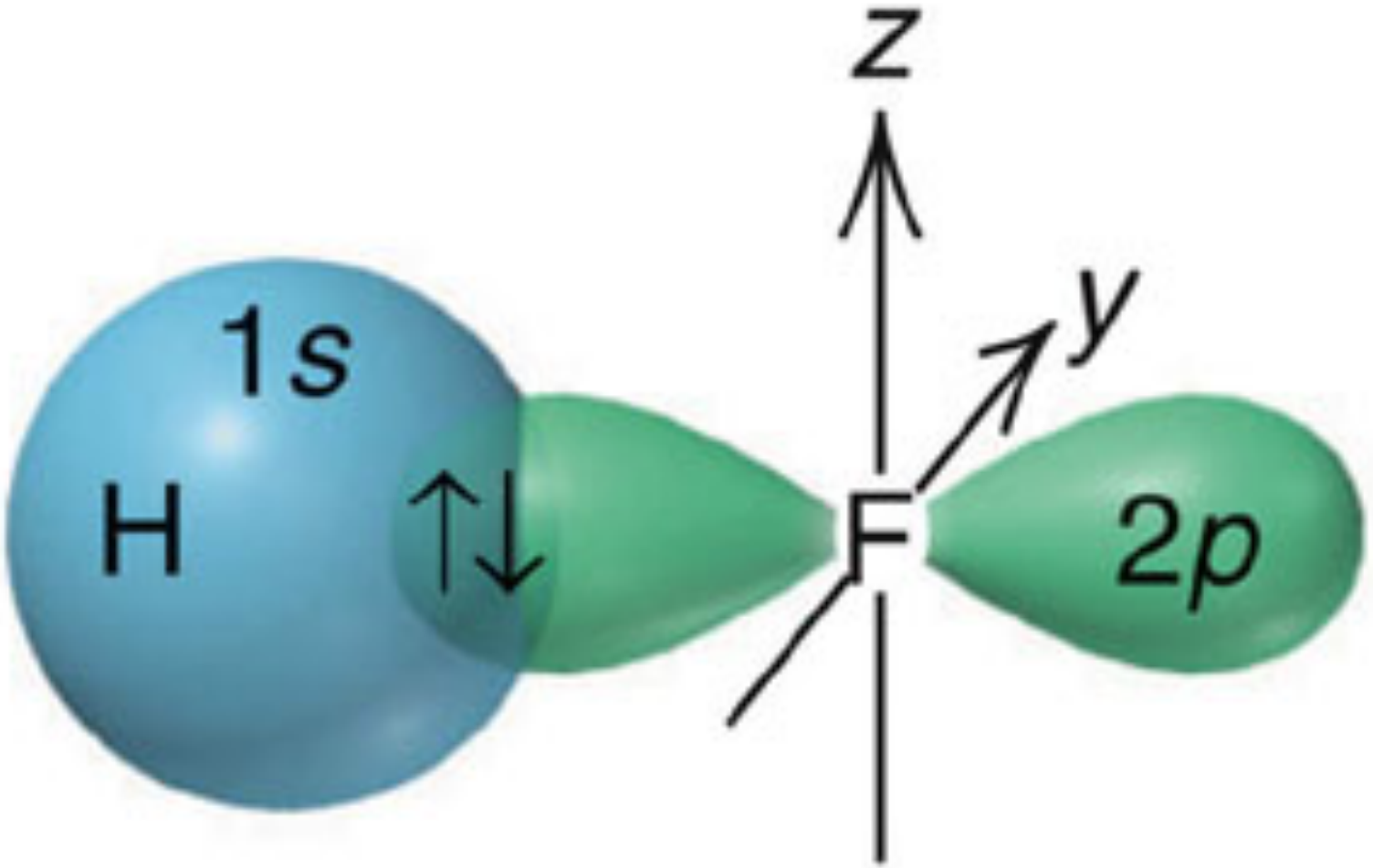
Answers to $H\Psi = E\Psi$



Bonding With Orbitals



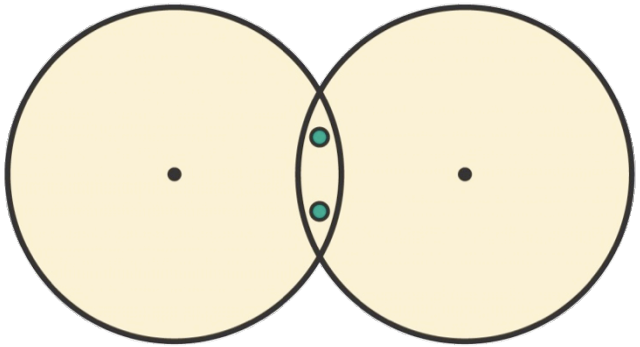
Bonding with Orbitals



Valence-Bond Theory

So far, we've been thinking of molecules using Lewis' Theory:

Bonding electrons are located in between bonded atoms – electrons are localized



But….

We learned in Ch. 1 that we learned to think of electrons as wavefunctions, which are described by atomic orbitals

Valence Bond Theory – quantum mechanical view of bonding

'Types' of Bonds – σ bond

Lets start with H_2, the simplest molecule:

Ground state H has one 1s electron

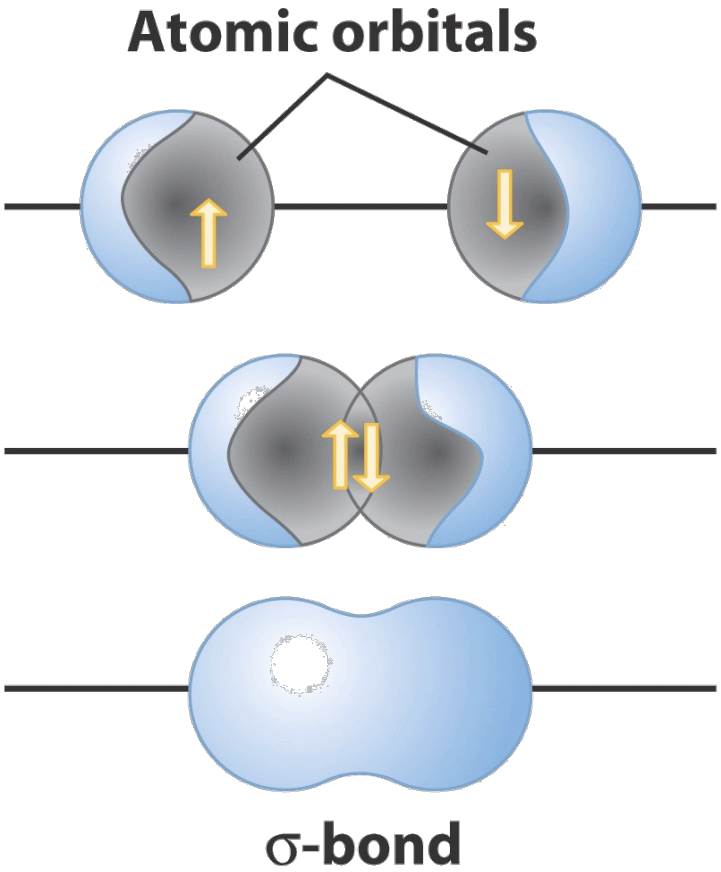
When the 2 H atoms bond, the atomic orbitals merge, forming a σ-bond

σ–bond (sigma bond) – along bond axis.

We say the atomic orbitals overlap

More overlap = Stronger bond

All single covalent bonds are σ-bonds



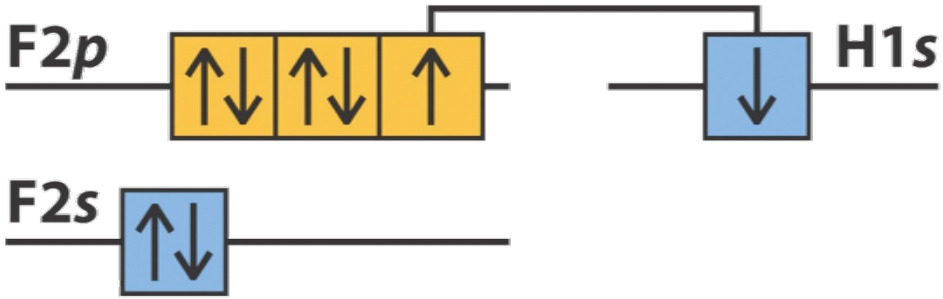
‘Types’ of Bonds – σ bond

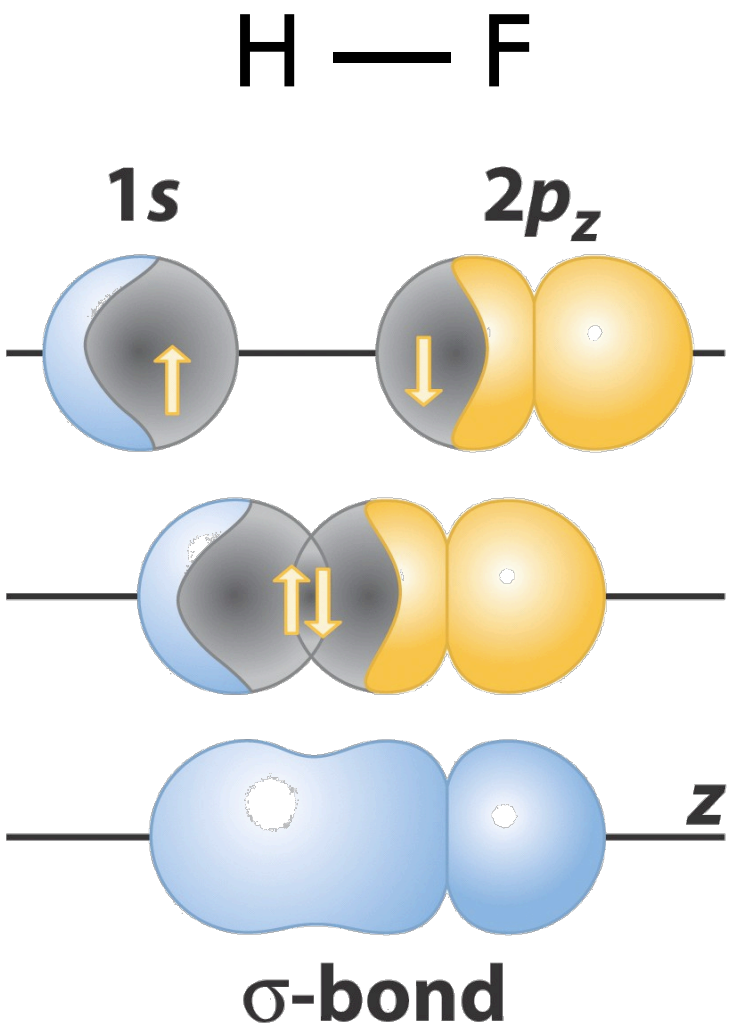
All single covalent bonds are s-bonds

Can have s-bonds between any types of orbitals:

- Two s orbitals
- Two p orbitals
- An s and a p orbital
- Etc….

Example: s-bond between 1s orbital of H and $2p_z$ orbital of F

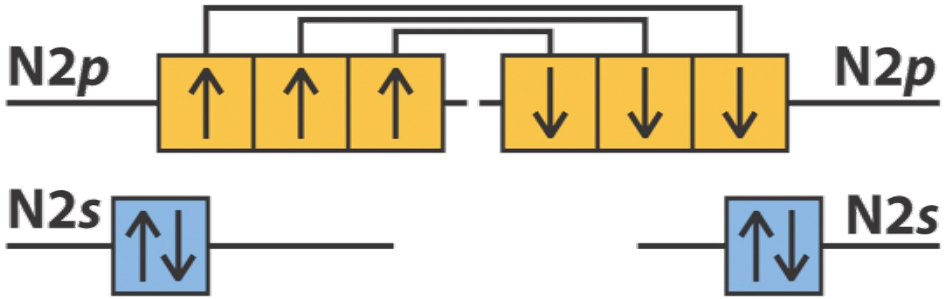




‘Types’ of Bonds – Multiple bonds

What happens in N_2?

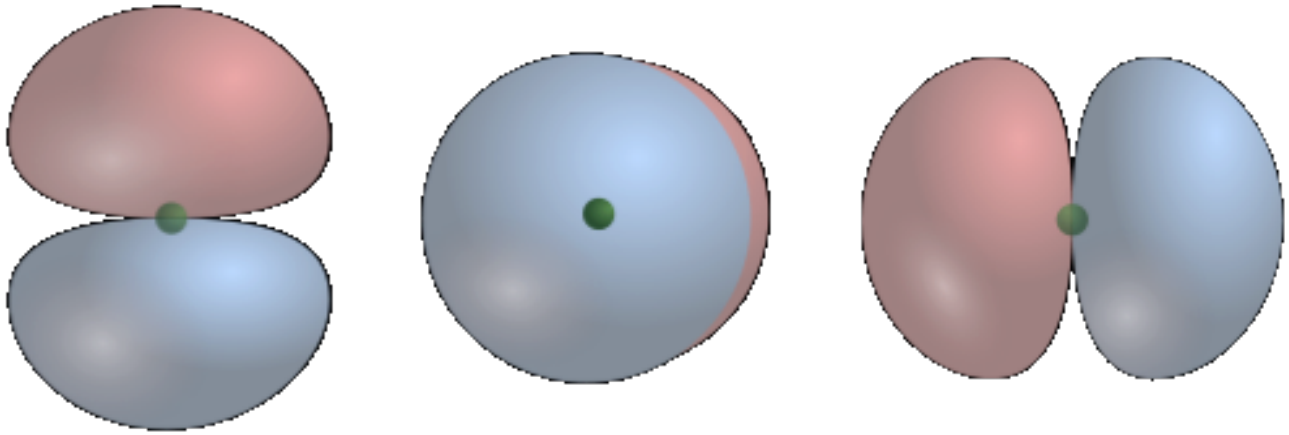
Remember the bond in N_2 is a triple bond…



Each N atom has 3 unpaired 2p electrons

Lets look at the atomic orbitals of N:

N — N

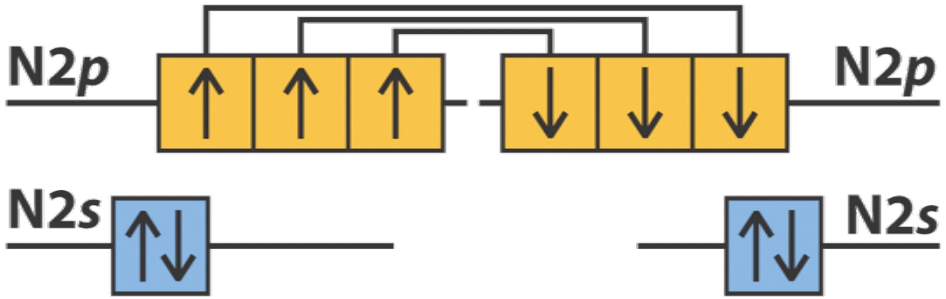


p_x p_y p_z

‘Types’ of Bonds – Multiple bonds

What happens in N_2?

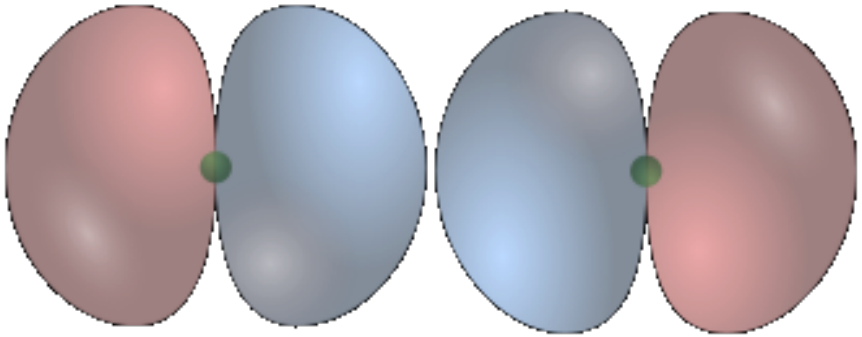
Remember the bond in N_2 is a triple bond…



Each N atom has 3 unpaired 2p electrons

How do the atomic orbitals bond?

N — N



p_z p_z

Between the $2p_z$ and $2p_z$ orbitals, we have bonding on the bond axis

This is a s-bond!

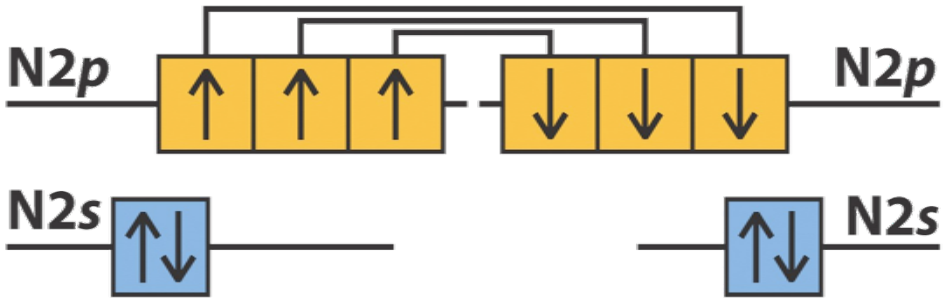
'Types' of Bonds – Multiple bonds

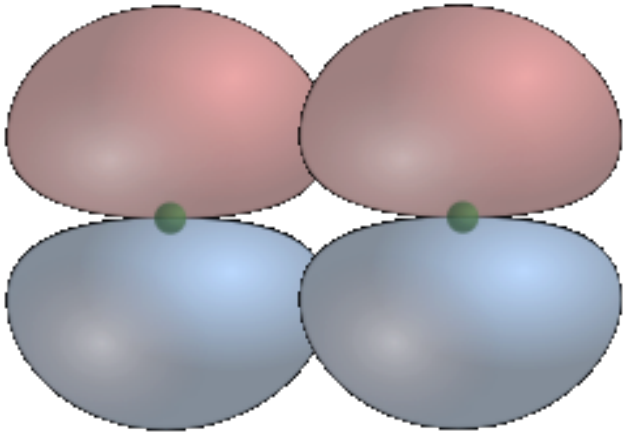
What happens in N_2?

Remember the bond in N_2 is a triple bond…

Each N atom has 3 unpaired 2p electrons

How do the atomic orbitals bond?





p_x p_x

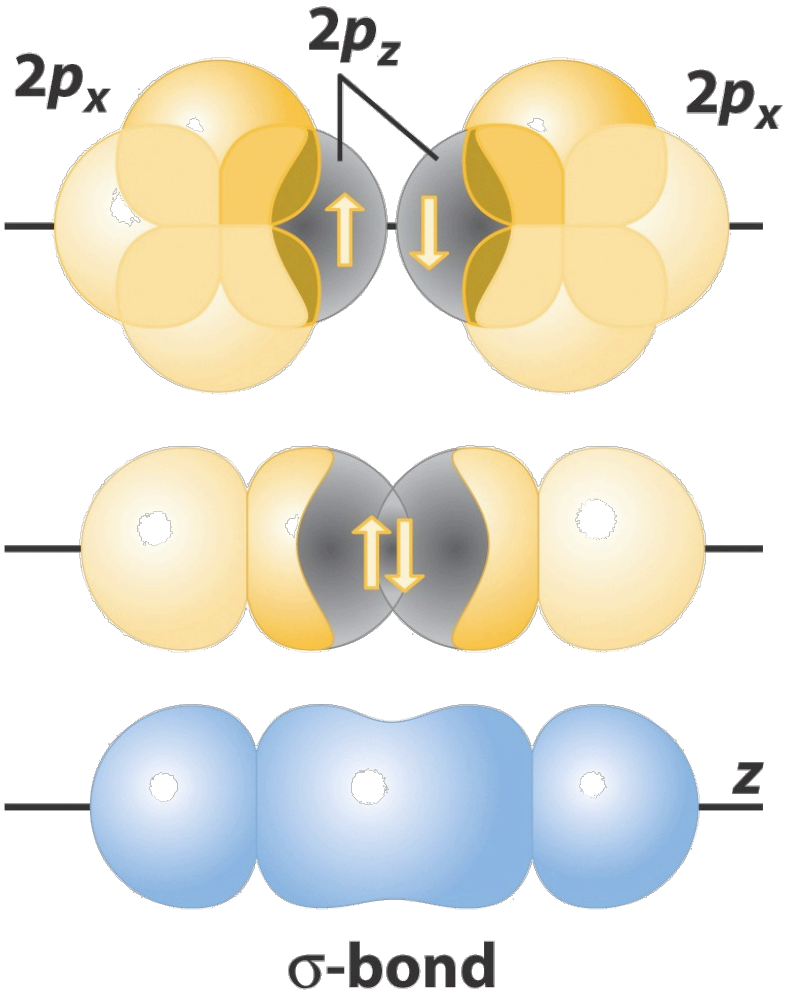
Between $2p_x$ and $2p_x$ orbitals, the bonding is not on the bond axis

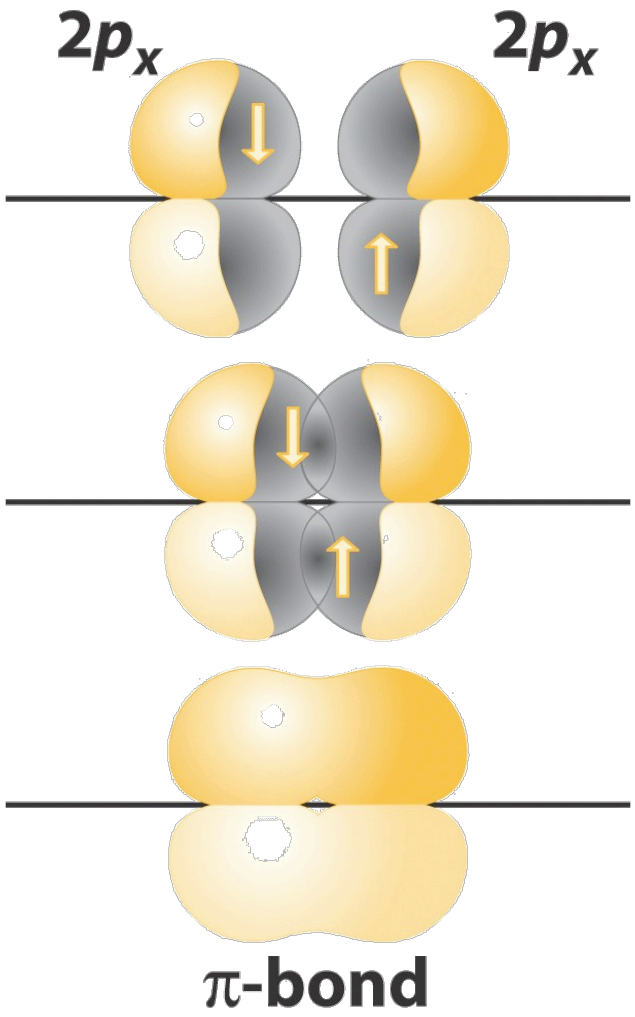
A different type of bond!

p-bond –nodal plane along bond axis

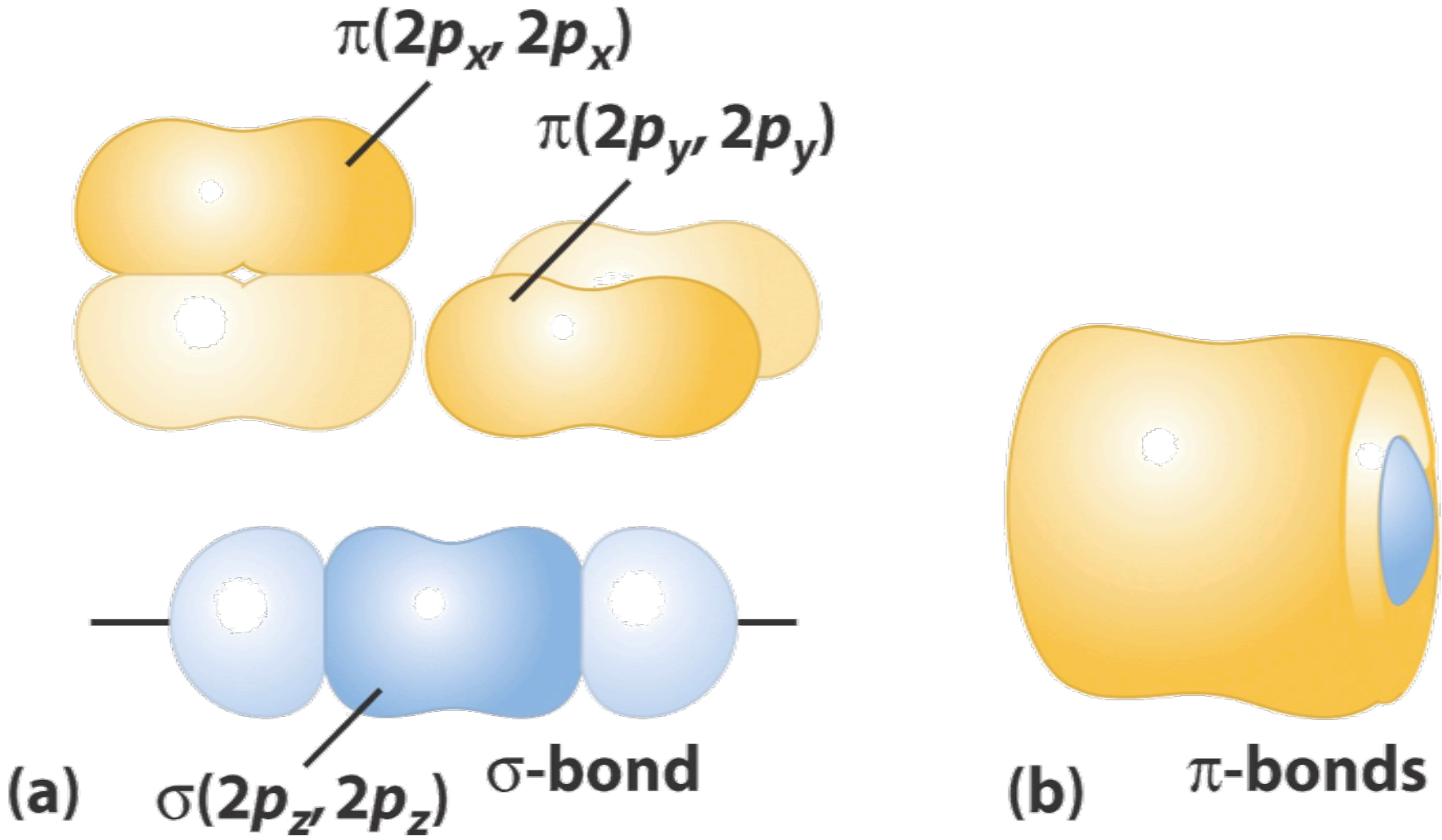
Bonding occurs above and below the bond axis

Bonding of N_2





Bonding of N_2

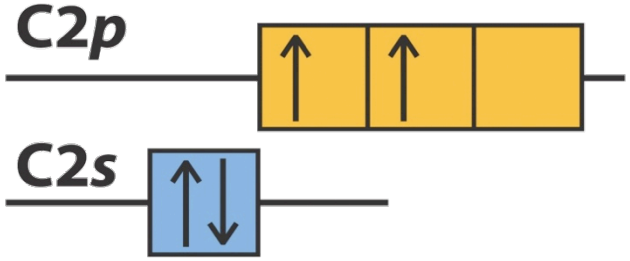


Hybridization of Orbitals

What about methane (CH_4)?

According to Valence Bond Theory:

C should only make 2 bonds!

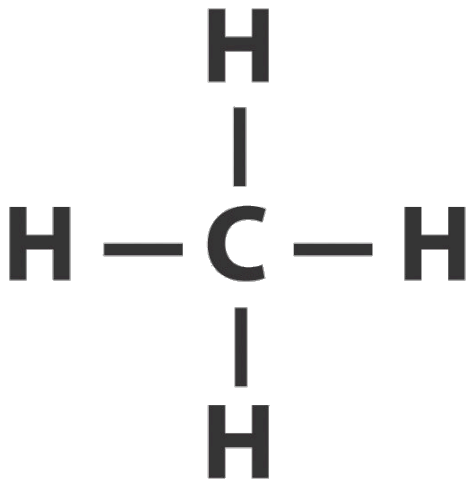


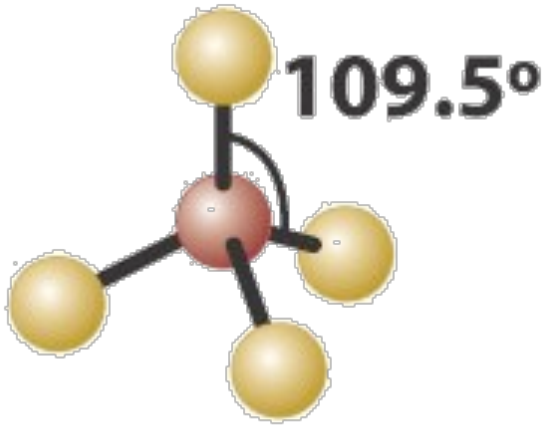
Carbon, $[He]2s^2 2p_x^1 2p_y^1$

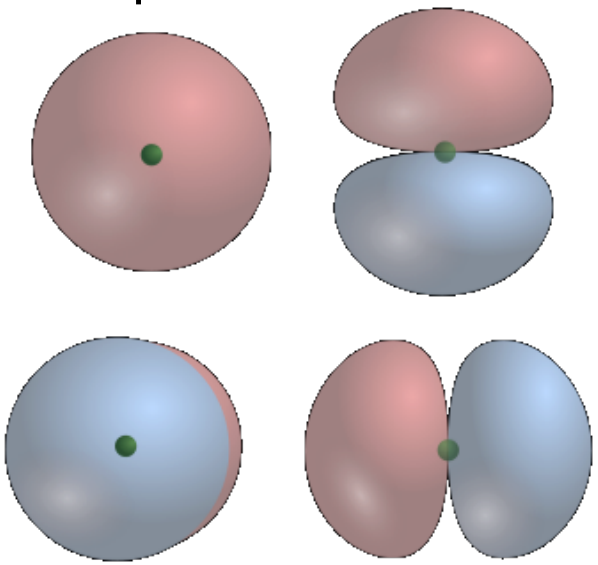
But we know that C can make 4 bonds

And CH_4 has a tetrahedral shape according to VSEPR:

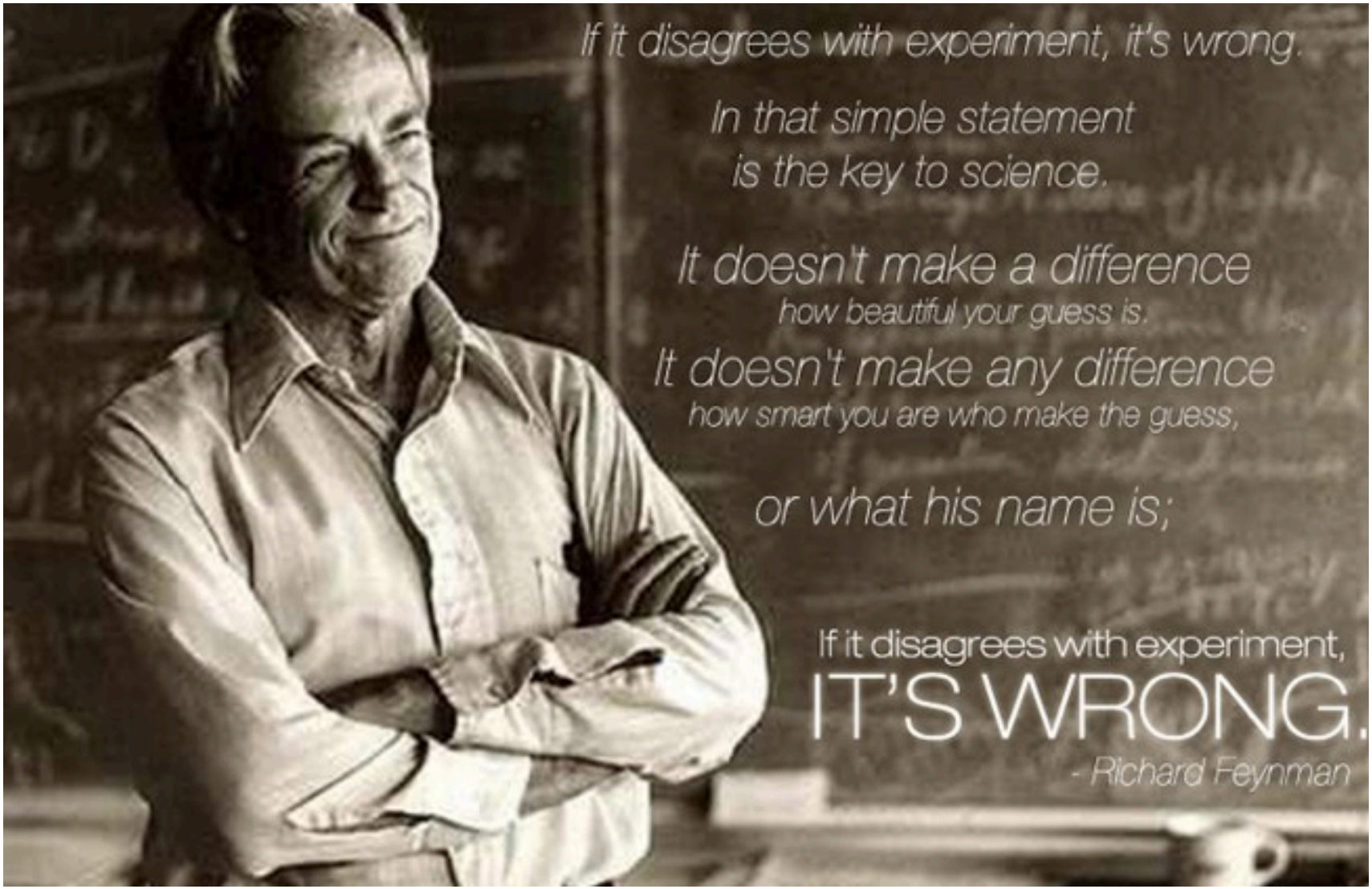
How do get a tetrahedral shape from the 2s and 2p orbitals?





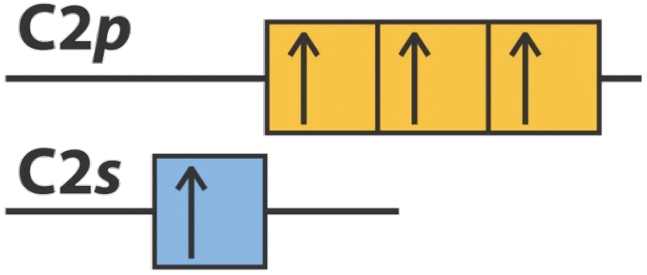


Experiments



Hybridization of Orbitals

We solve the 4 bond problem by promoting an electron:



Carbon, $[He]2s^1 2p_x^1 2p_y^1 2p_z^1$

It takes energy to promote an electron to a higher E orbital

But, overall the energy is lower if C can make 4 bonds instead of 2.

Ok, what about the geometry problem?

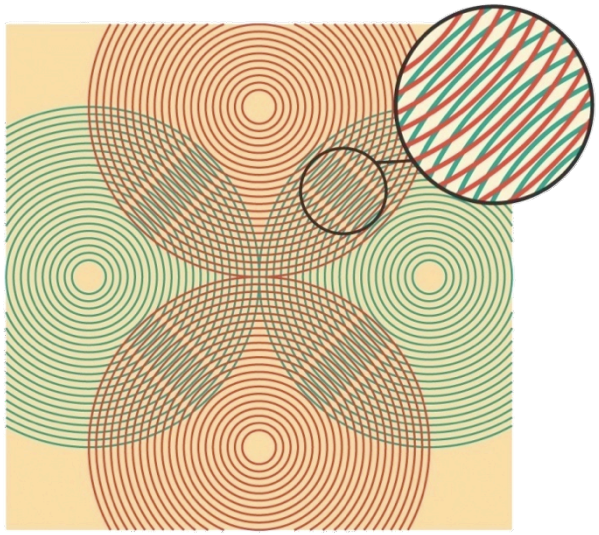
Hybridization of Orbitals

By promoting an electron, we can now make 4 bonds

But the geometry of the p_x, p_y, and p_z orbitals don't match the tetrahedral shape of CH_4

s and p orbitals are described by a wave-like model of the e

If we think of the orbitals as interfering with each other, we can define new hybrid orbitals:

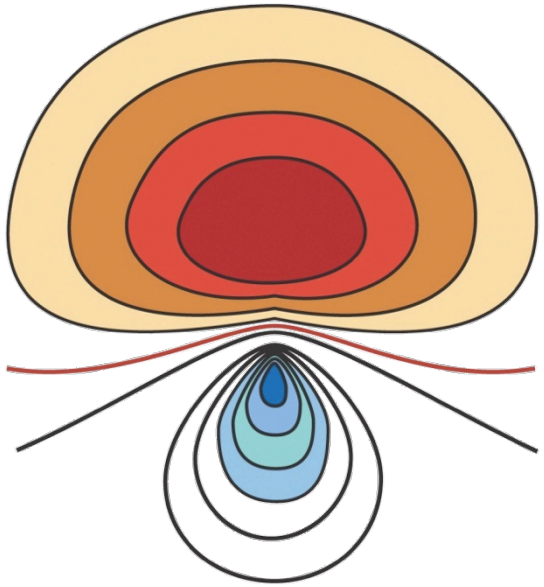


$$h_1 = s + p_x + p_y + p_z$$

$$h_2 = s - p_x - p_y + p_z$$

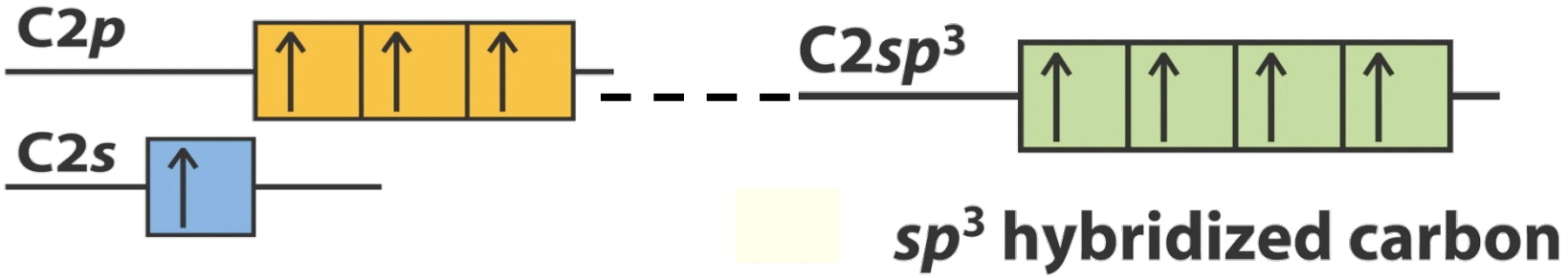
$$h_3 = s - p_x + p_y - p_z$$

$$h_4 = s + p_x - p_y - p_z$$



sp^3 Hybridization

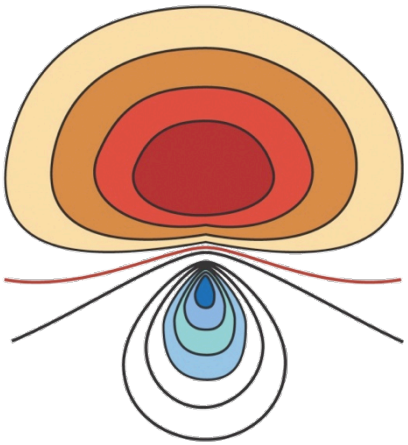
C in CH_4 uses 4 hybrid orbitals:



We took 1 s orbital and 3 p orbitals to make 4 sp^3 orbitals.

The sum of the atomic orbitals = the sum of the hybrid orbitals

The 4 sp^3 orbitals point in the 4 directions of the tetrahedral bonds

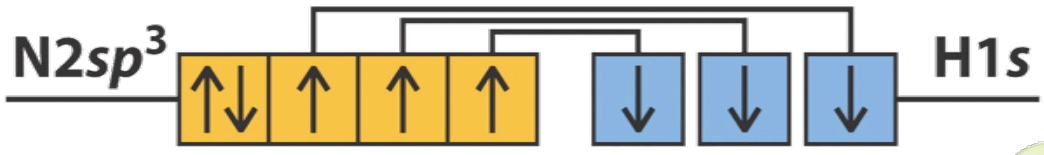


sp^3 Hybridization

Back to CH_4:

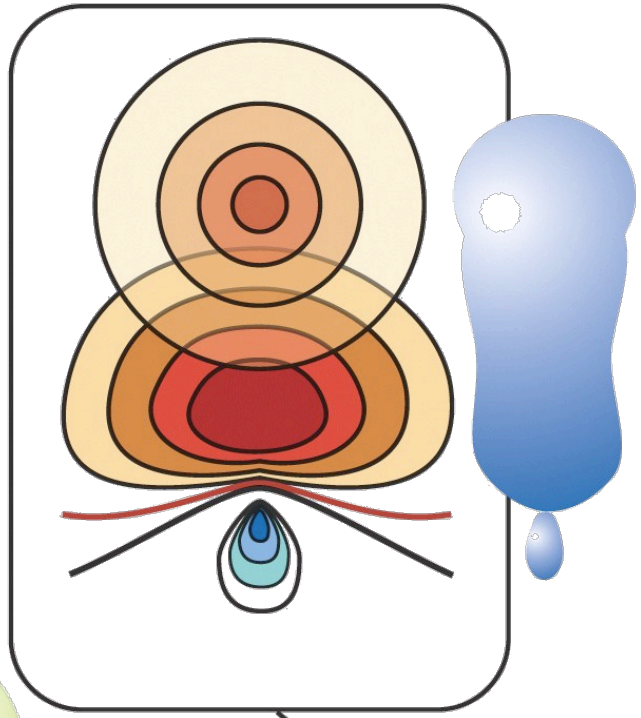
The 4 $2sp^3$ hybrid orbitals on carbon make s-bonds with the 1s orbitals of the 4 H atoms

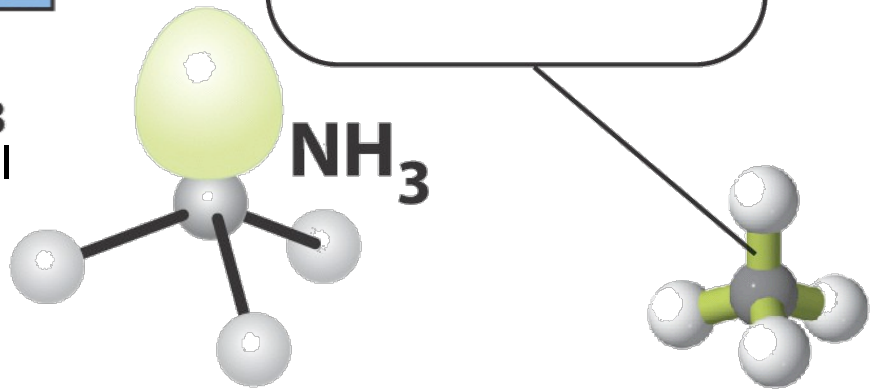
NH_3 also uses sp^3 hybrid orbitals:



Ammonia, NH_3

Whenever an atom has a tetrahedral structure, it is sp^3 hybridized

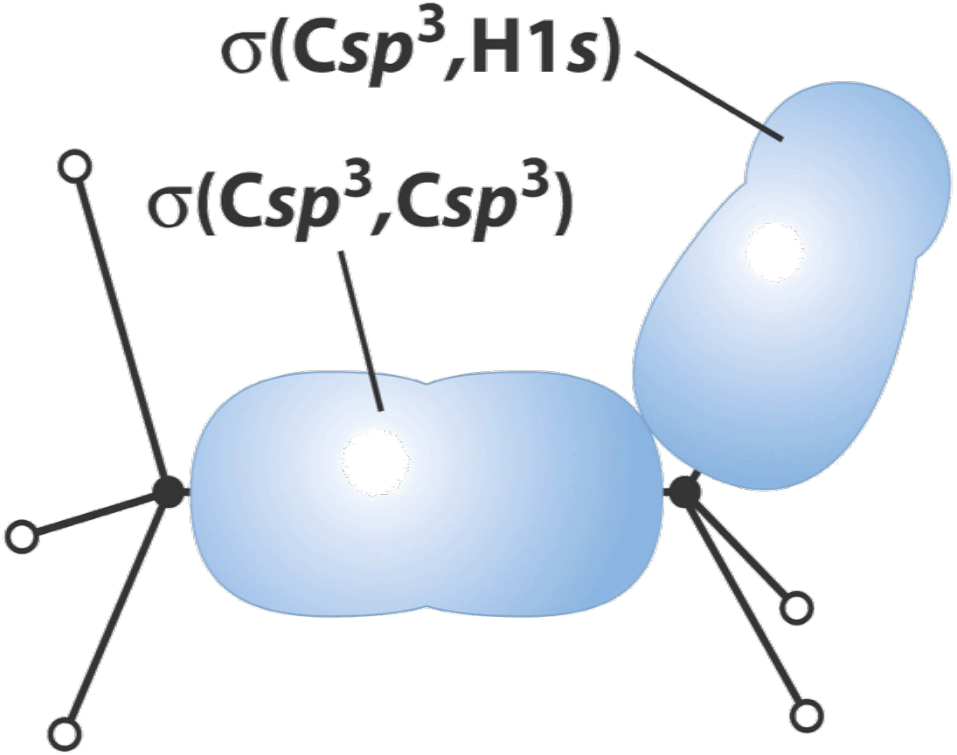




sp^3 Hybridization

Whenever an atom has a tetrahedral structure, we say it is sp^3 hybridized

This includes molecules with multiple central atoms:



Atomic Orbitals ➔ Hybrid Atomic Orbitals

sp^3 bonding works for tetrahedrally shaped molecules

What about the other VSEPR shapes?

Linear bonding can be described by sp hybridization:

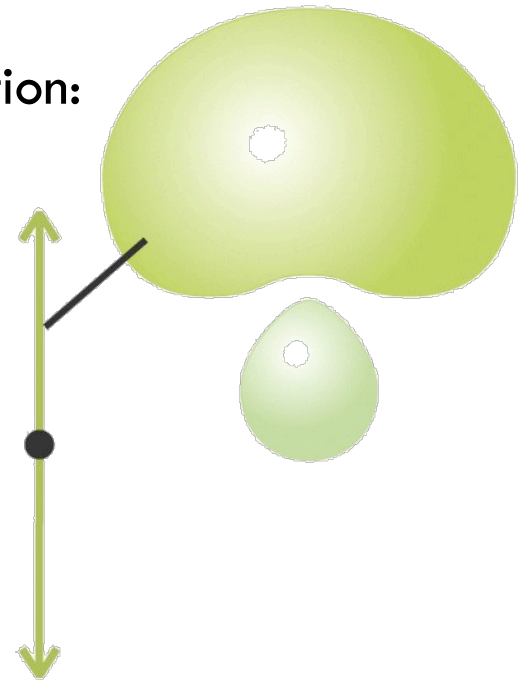
$$h_1 = s + p$$

$$h_2 = s - p$$

2 of the p orbitals remain as they were

Unused p orbitals are available

for p bonding



Other Types of Hybridization

sp^3 bonding works for tetrahedrally shaped molecules

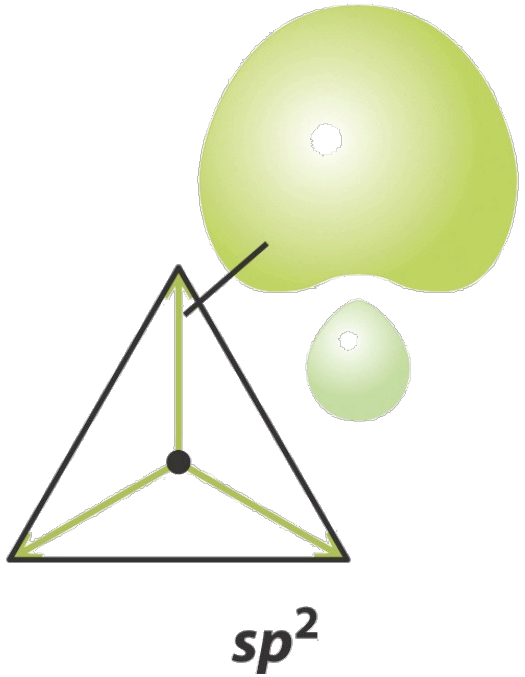
What about the other VSEPR shapes?

Trigonal planar can be described by **sp^2 hybridization**:

$$h_1 = s + \sqrt{2}p_y$$

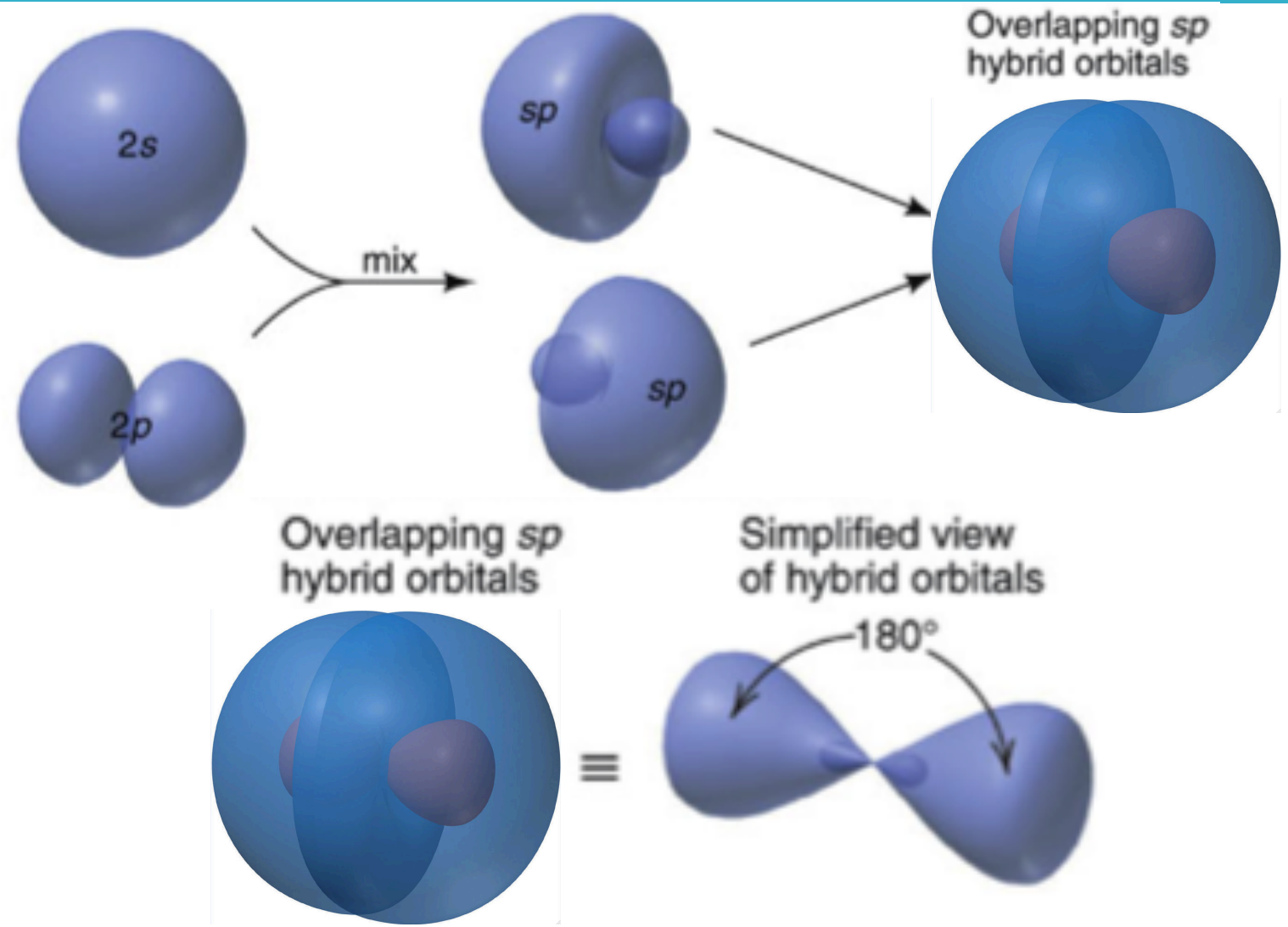
$$h_2 = s + \sqrt{\frac{3}{2}}p_x - \sqrt{\frac{1}{2}}p_y$$

$$h_3 = s - \sqrt{\frac{3}{2}}p_x - \sqrt{\frac{1}{2}}p_y$$

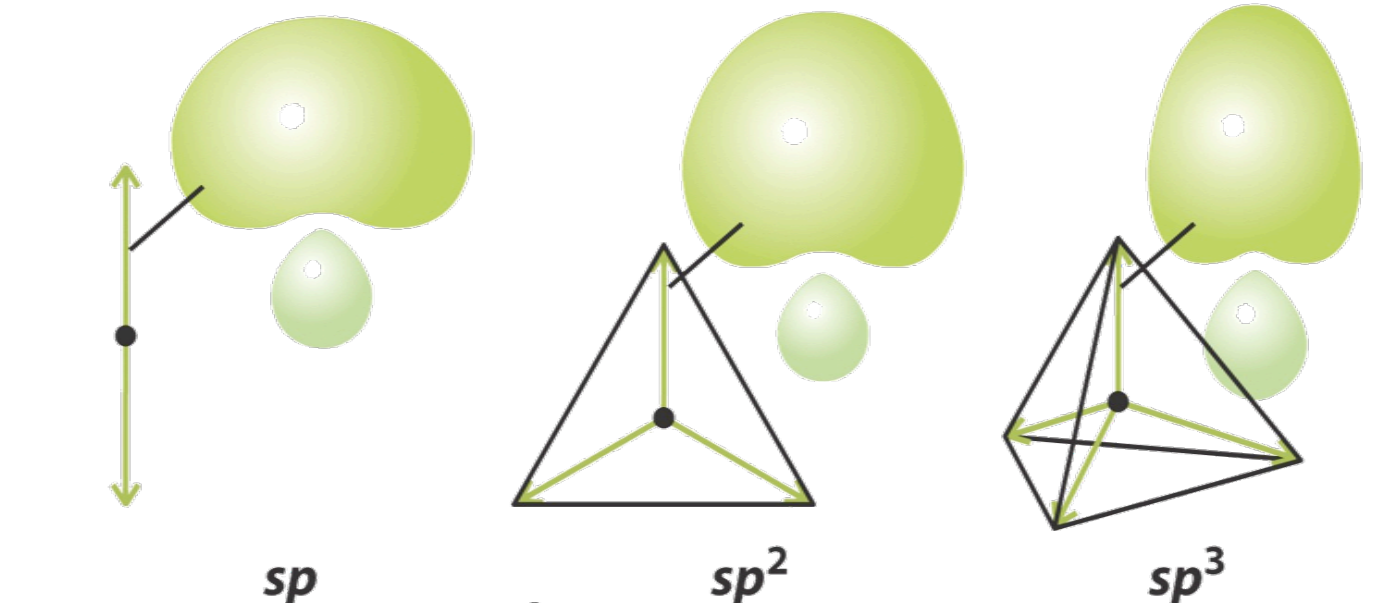


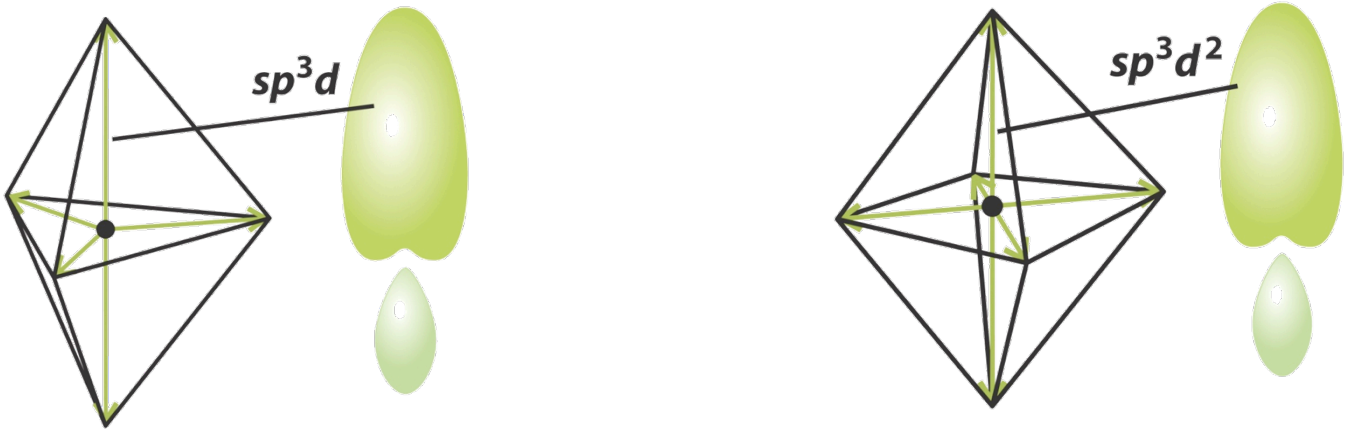
The p_z orbital is not used and remains as it was

Hybrid Orbitals

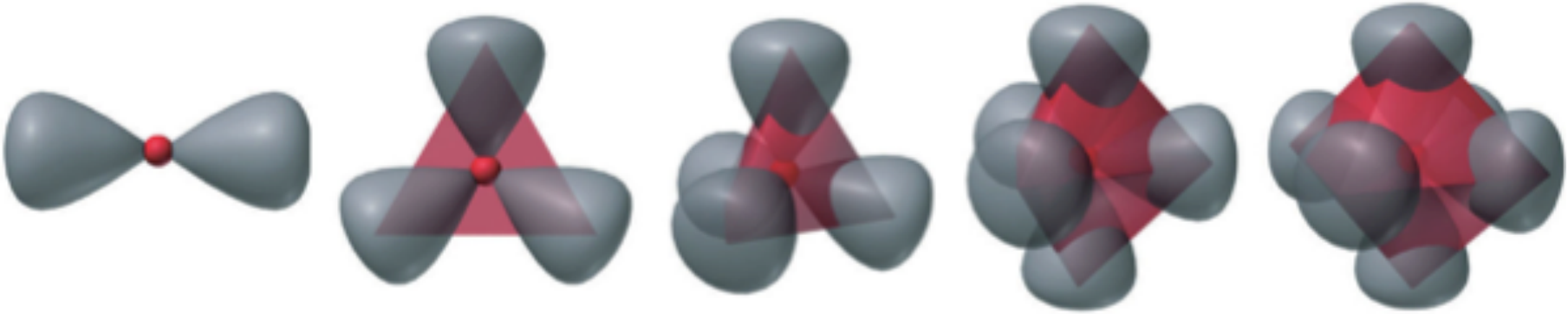


Hybrid Orbital Shapes

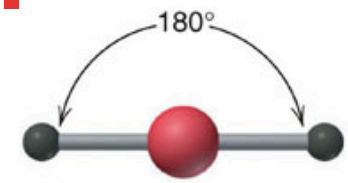




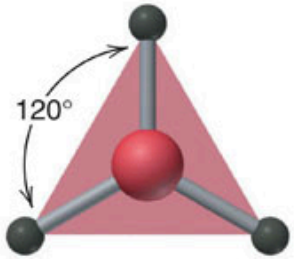
Look Familiar?



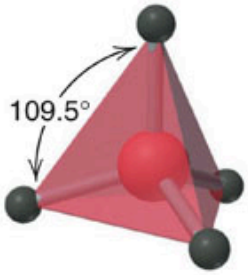
sp	sp^2	sp^3	sp^3d	sp^3d^2
2	3	4	5	6



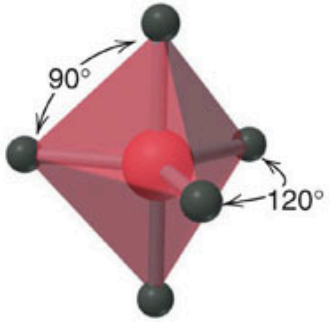
Linear



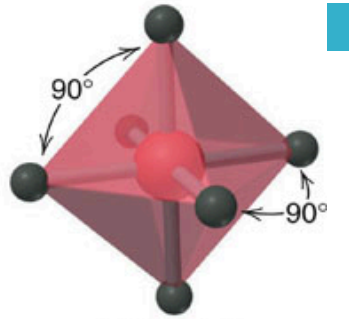
Trigonal planar



Tetrahedral

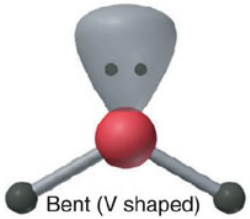


Trigonal bipyramidal



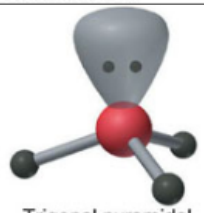
Octahedral

AX_2E



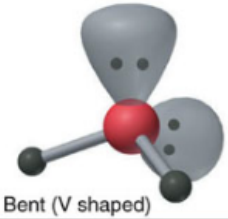
Examples: SO_2, O_3, $PbCl_2$, $SnBr_2$

AX_3E



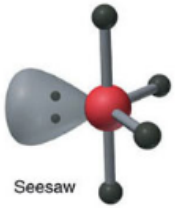
Examples: NH_3, PF_3, ClO_3^-, H_3O^+

AX_2E_2



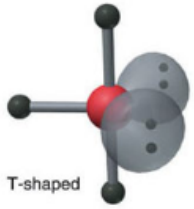
Examples: H_2O, OF_2, SCl_2

AX_4E



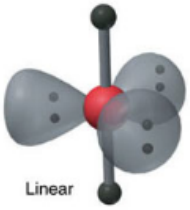
Examples: SF_4, XeO_2F_2, IF_4^+, $IO_2F_2^-$

AX_3E_2



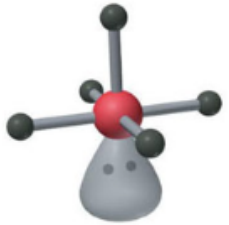
Examples: ClF_3, BrF_3

AX_2E_3



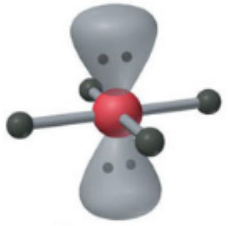
Examples: XeF_2, I_3^-, IF_2^-

AX_5E



Examples: BrF_5, TeF_5^-, $XeOF_4$

AX_4E_2



Examples: XeF_4, ICl_4^-

Other Types of Hybridization

N atomic orbitals always produce N hybrid orbitals

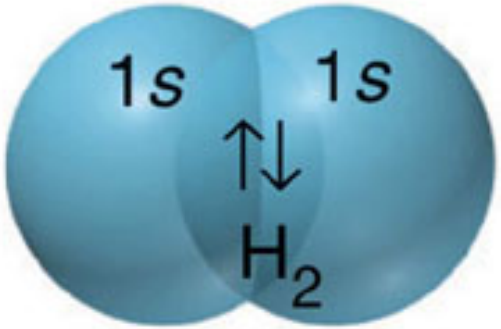
TABLE 3.2 Hybridization and Molecular Shape*

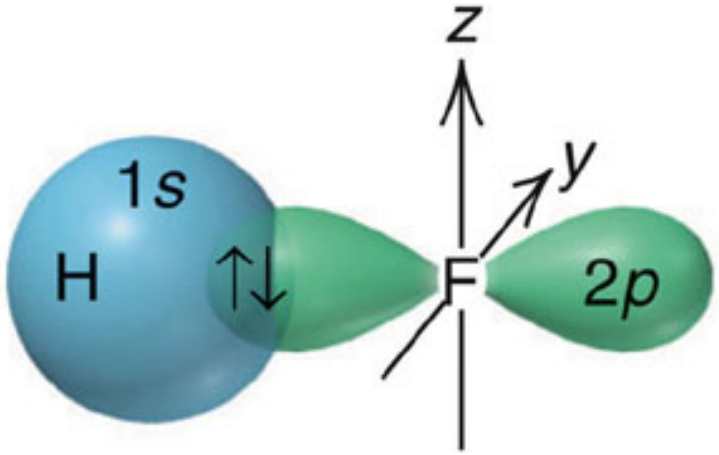
Electron arrangement	Number of atomic orbitals	Hybridization of the central atom	Number of hybrid orbitals
linear	2	sp	2
trigonal planar	3	sp^2	3
tetrahedral	4	sp^3	4
trigonal bipyramidal	5	sp^3d	5
octahedral	6	sp^3d^2	6

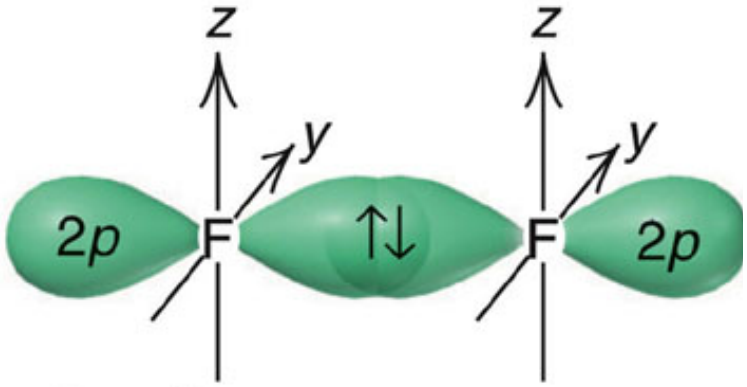
Spectroscopic data suggests terminal atoms use hybrid orbitals as well

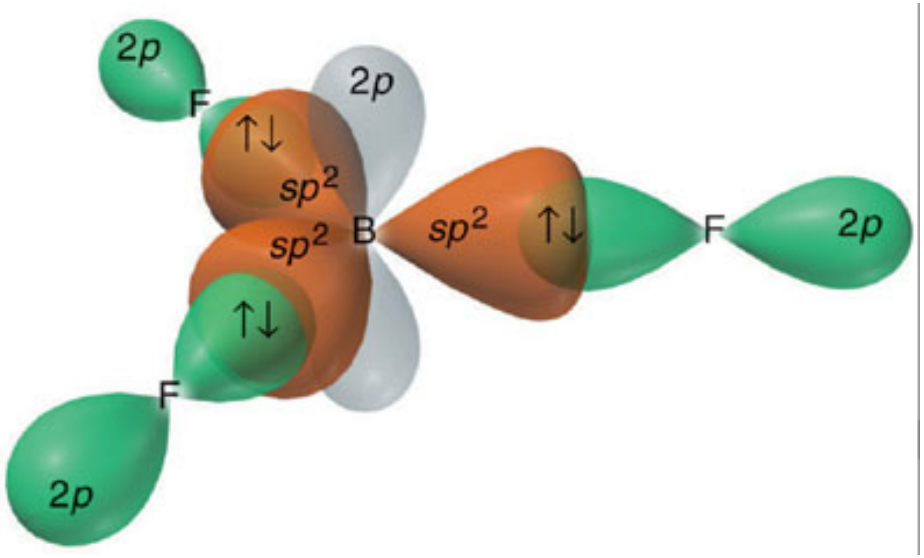
A terminal Cl uses sp^3 hybridization in the arrangement of its lone pairs?

Examples

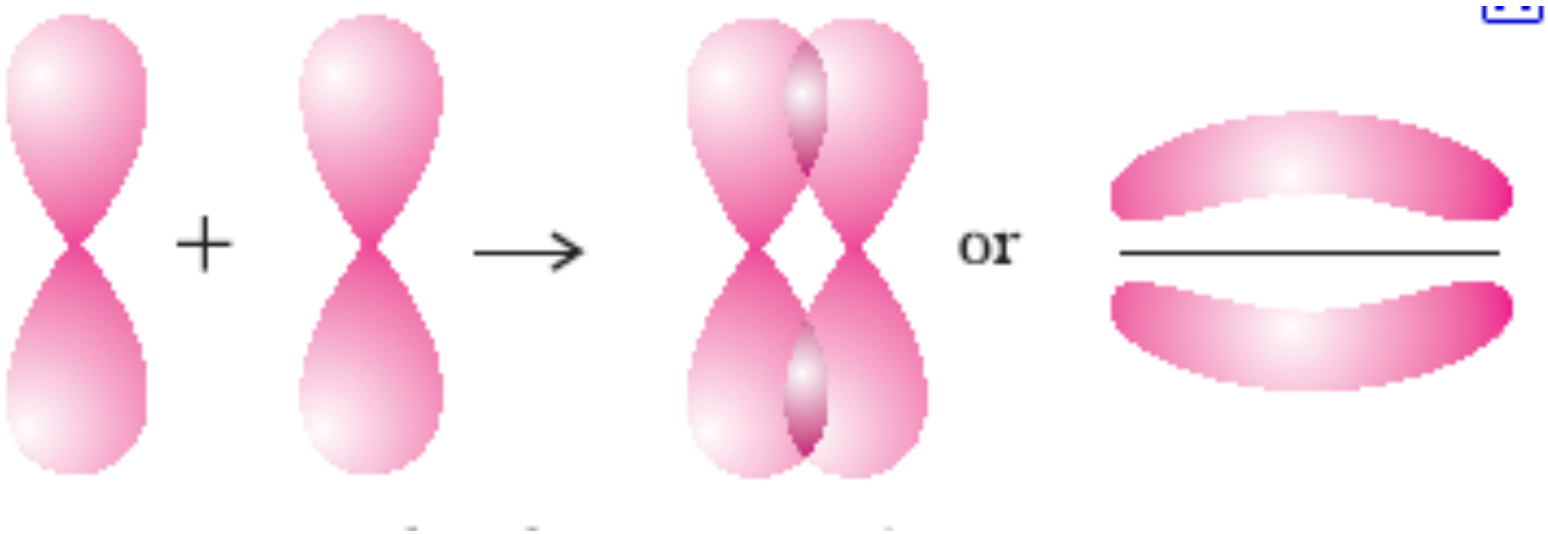




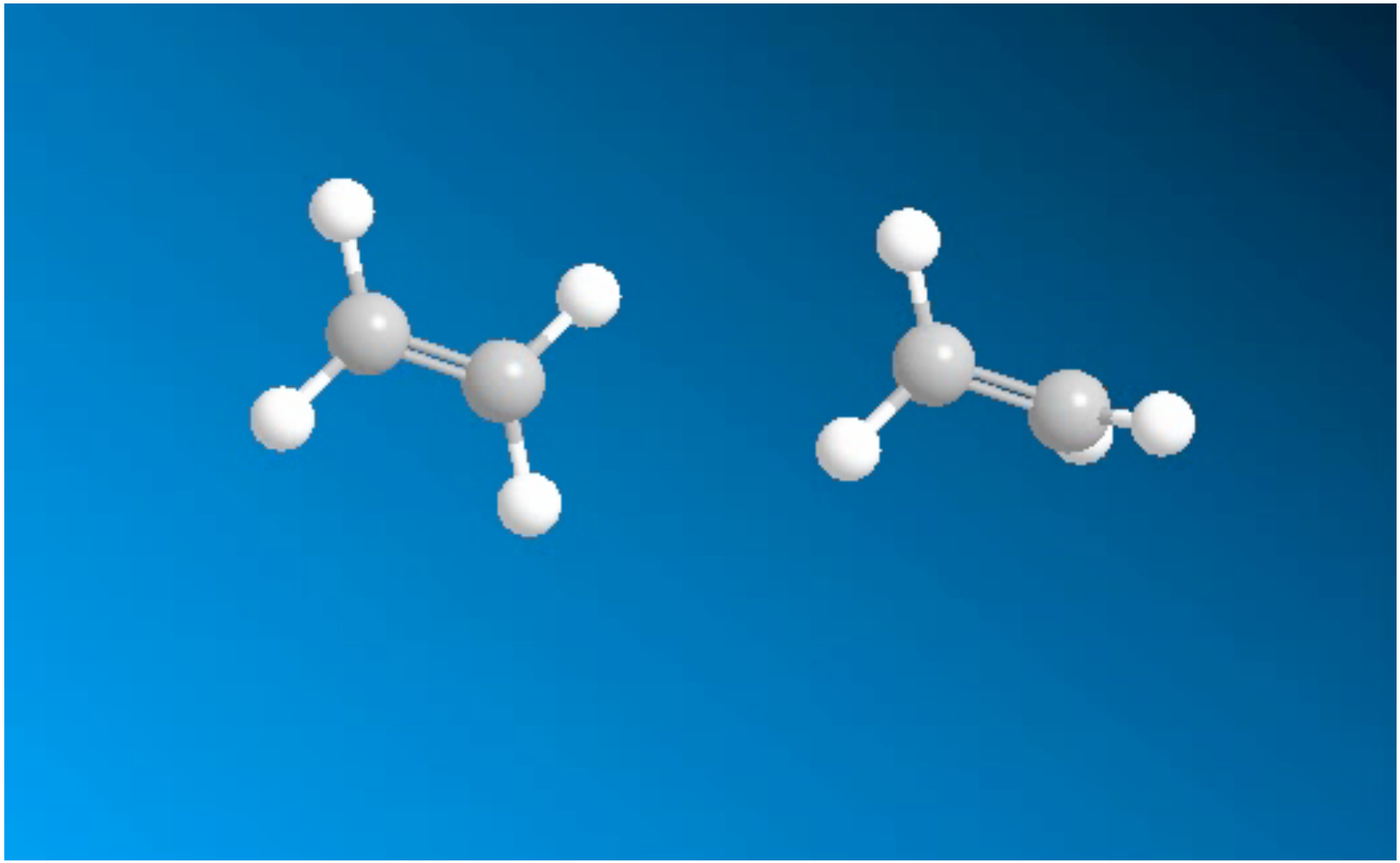




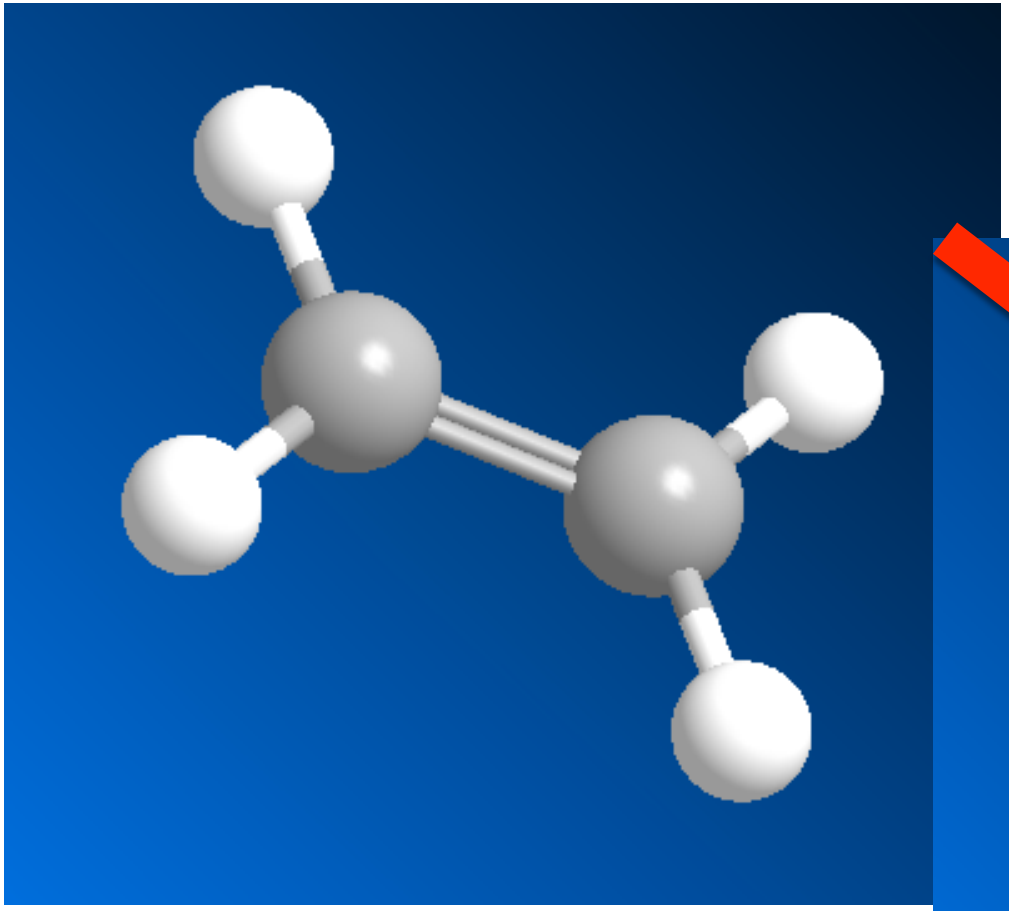
π Bond

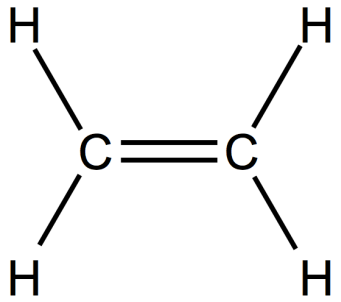


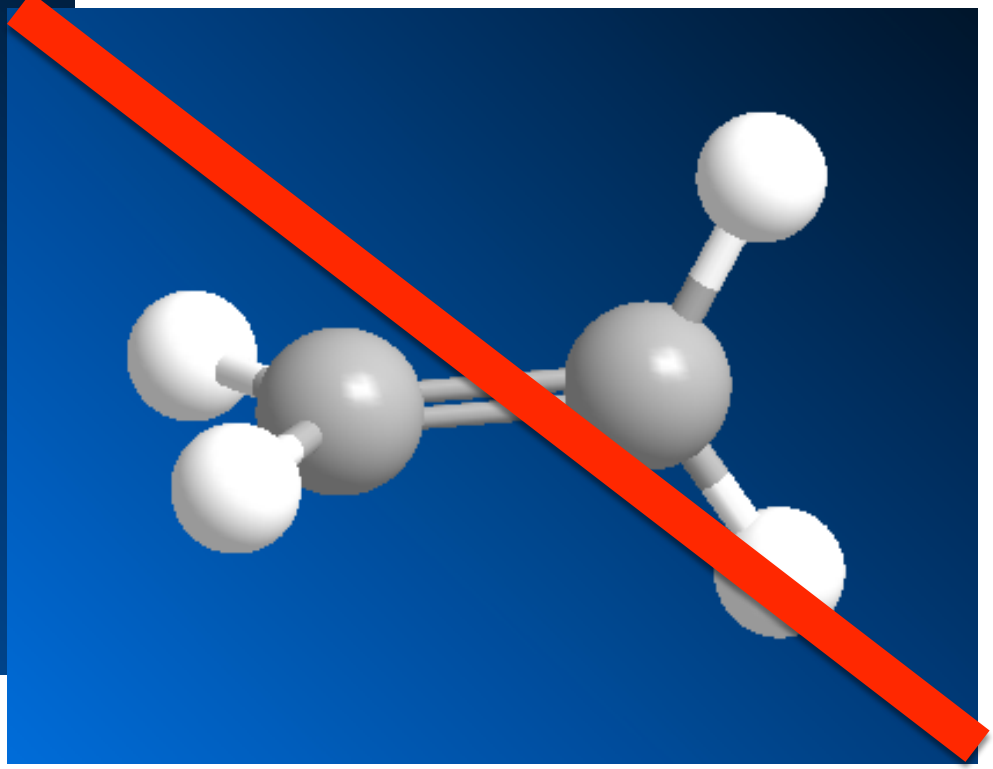
Ethylene



Ethylene







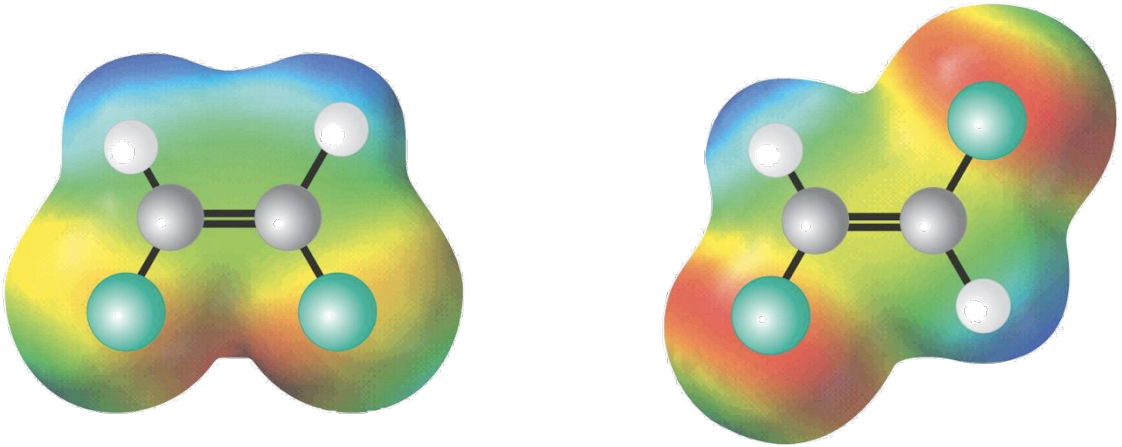
Characteristics of Multiple Bonds

double bond = 1 σ-bond + 1 π-bond

triple bond = 1 σ-bond + 2 π-bonds

- σ-bonds result from head-on overlap of orbitals
- π-bonds results from side-by-side overlap

Atoms in a single bond can rotate freely, whereas atoms in a double bond are much less likely to:



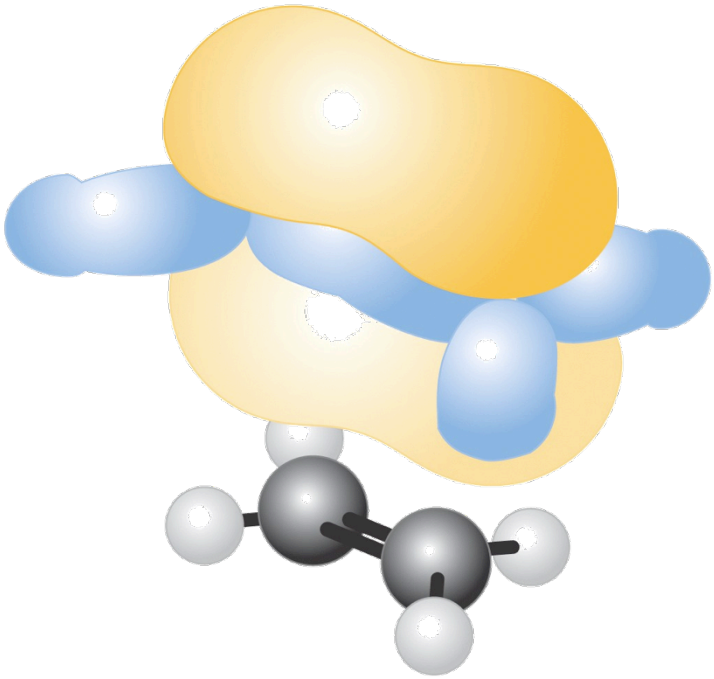
Characteristics of Multiple Bonds

The shape of ethylene (C_2H_4)

Experimental evidence:

All six atoms lie in the same plane with 120° bond angles

Suggests trigonal planar structure → sp^2 hybridization



Each C: sp^2 + p

s-bonds with the sp^2 orbitals

C — C

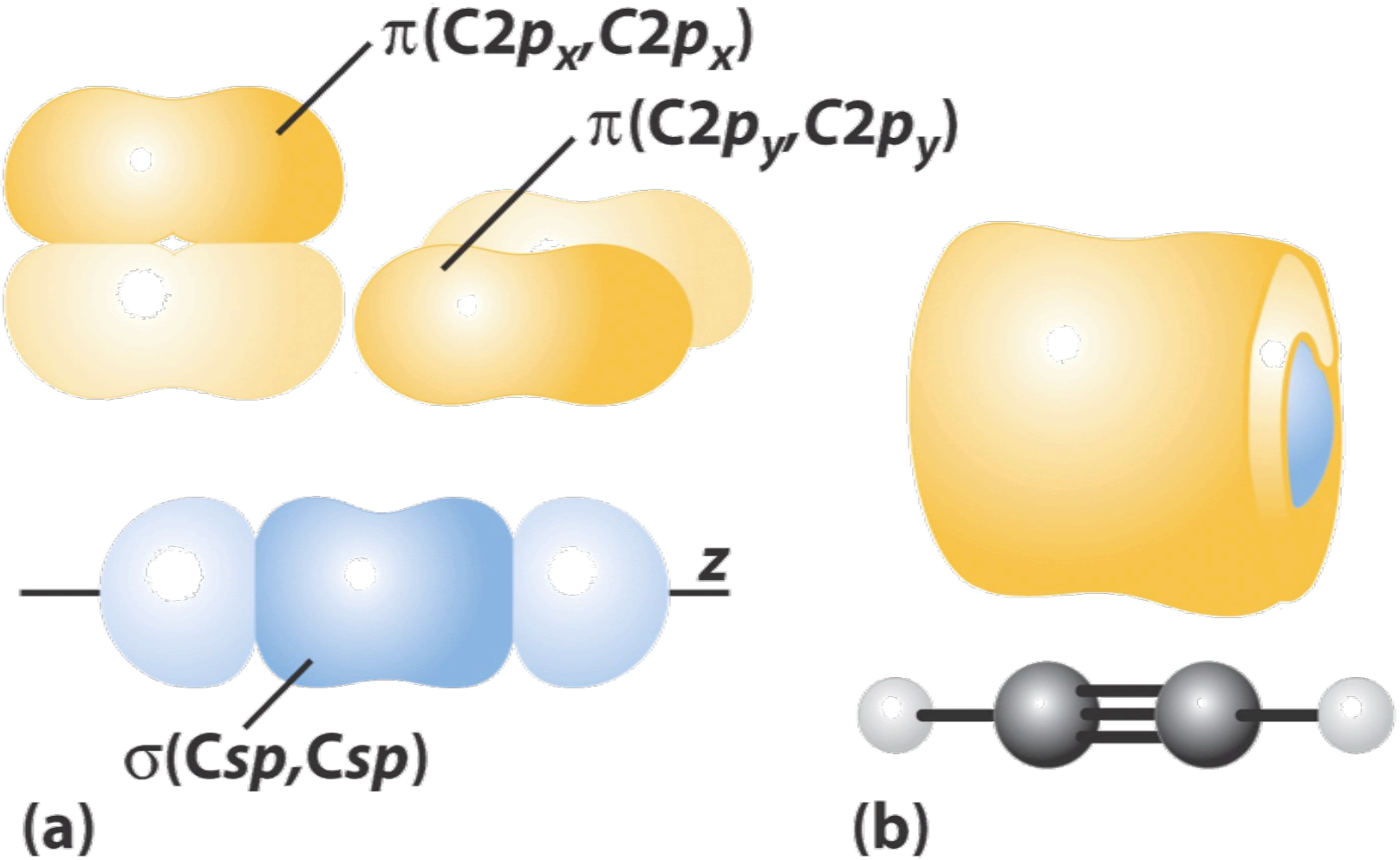
4 C — H

p-bond with the leftover p orbital

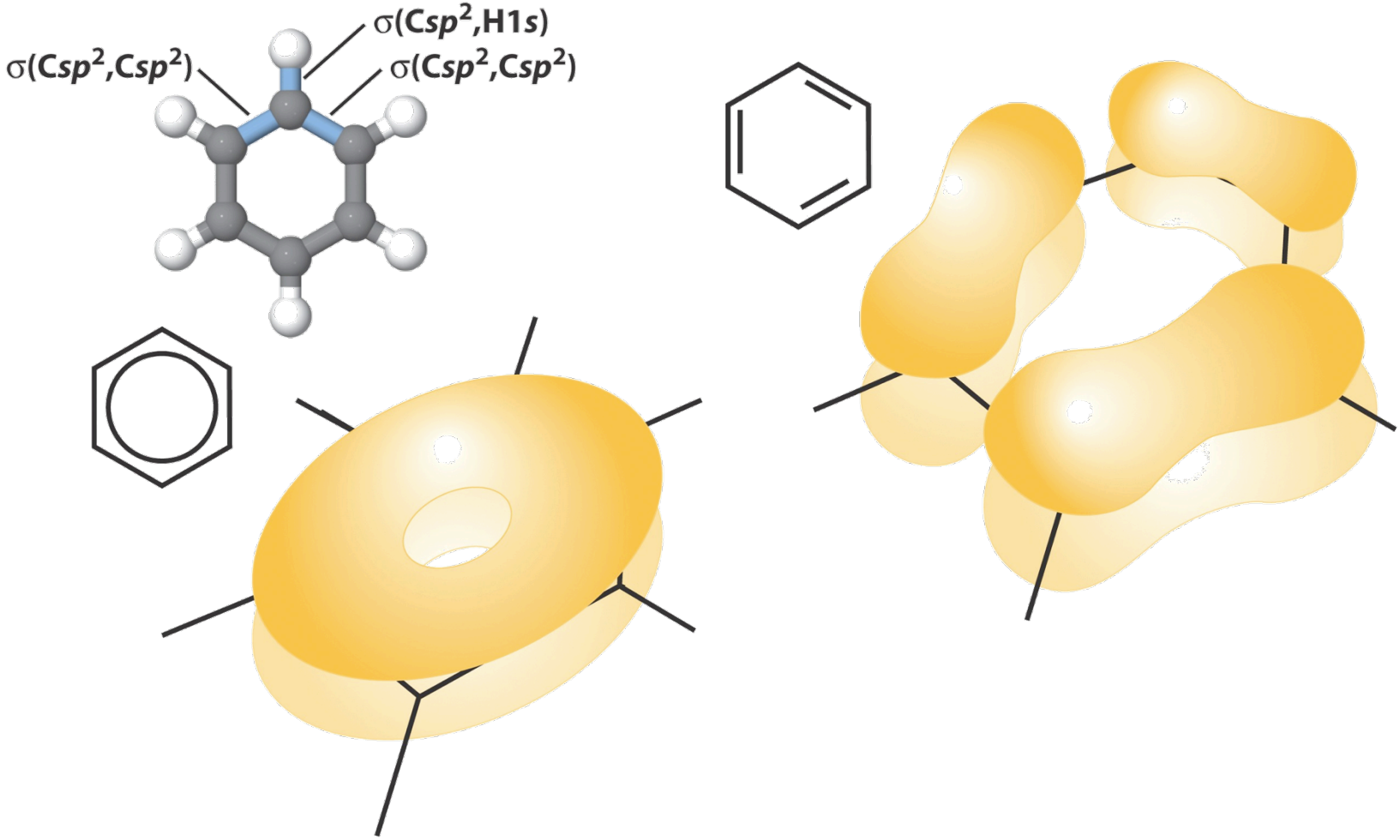
C — C

Characteristics of Multiple Bonds

The shape of acetylene (C_2H_2) is linear → sp hybridization



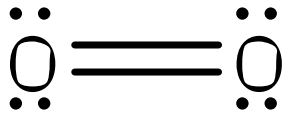
Hybridization and Benzene

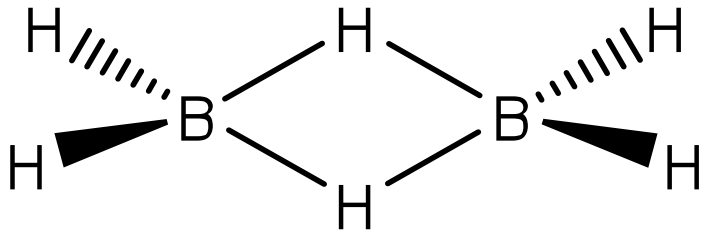


Molecular Orbital Theory

- Lewis Theory
  - Connectivity, electron tracking
- VSEPR Theory
  - 3-D Structure around an atom
- Valence Bond Theory
  - Extended 3-D Structure Information
  - Delocalization in Molecules (LIMITED)
  - Illustrates Multiple Bonding
  - Prediction of Reactivity
- Molecular Orbital Theory
  - Orbitals as a function of the whole molecule
  - Delocalization much more thorough
  - Anti-bonding and Non-bonding electrons
  - Behavior in a magnetic field
  - Spectral Data

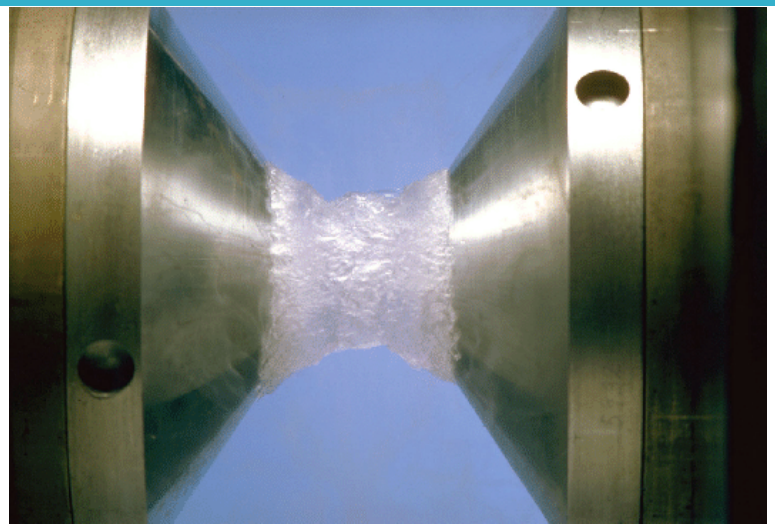
Why MO Theory?

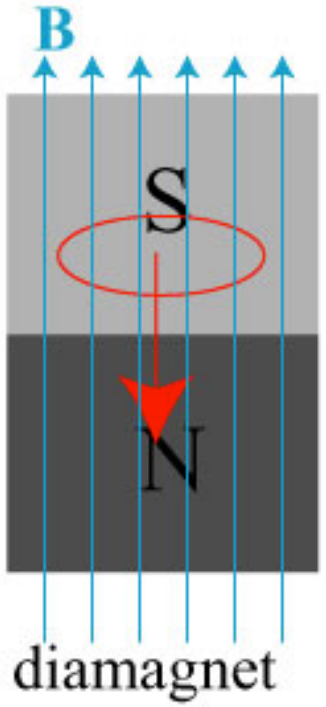


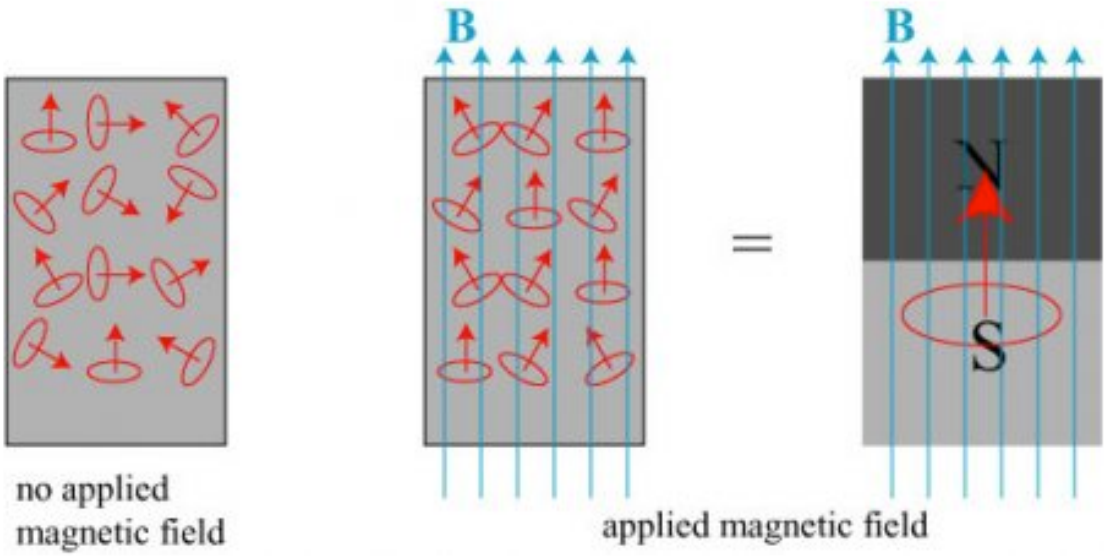


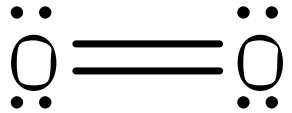
- O_2 Bond Dissociation Energy = 498 kJ/mol
- O_2^+ Bond Dissociation Energy = 623 kJ/mol

Paramagnetic / Diamagnetic

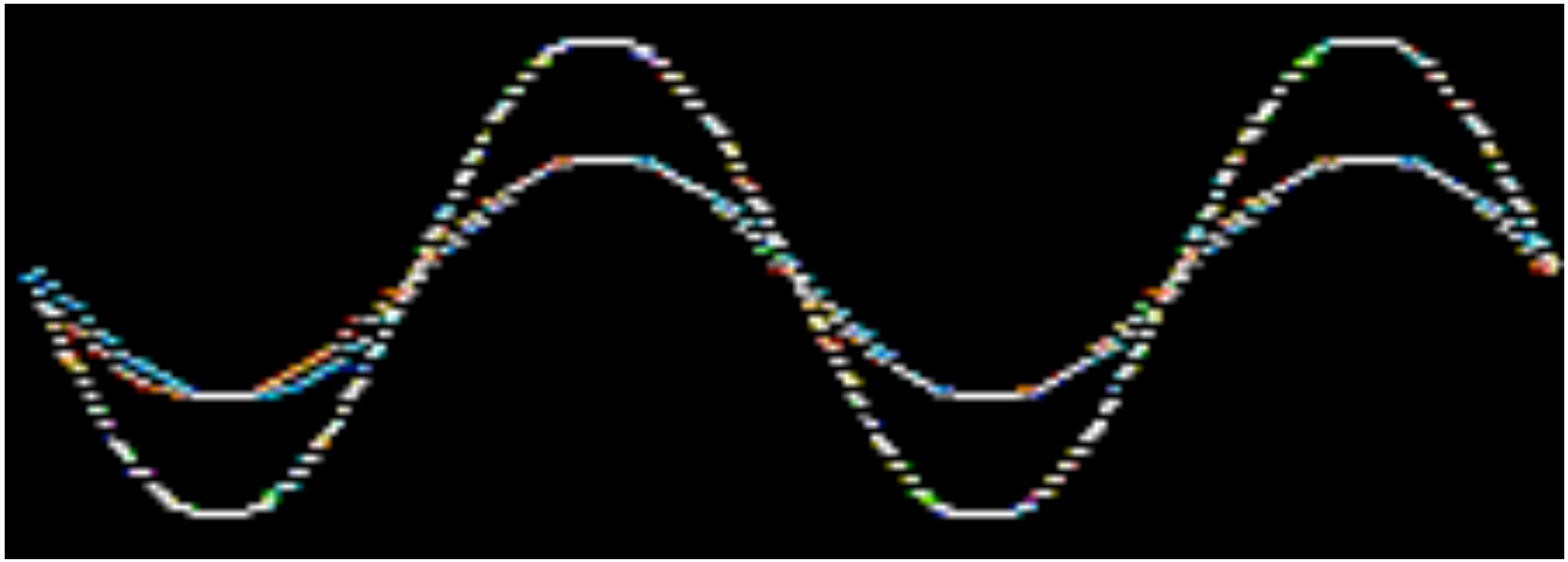








Constructive and Destructive Interference



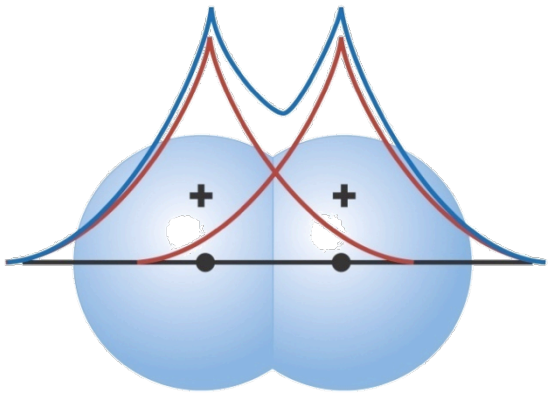
Molecular Orbitals

MO Theory – electrons occupy **molecular orbitals** spread over *entire* molecule

- All valence electrons are delocalized
- Molecular orbitals are built by adding together atomic orbitals
- Linear combination of atomic orbitals (LCAO)

H – H bond in H_2 with two 1s electrons:

$$\psi = \psi_{A1s} + \psi_{B1s}$$



- LCAO-MO shows constructive interference
- $E_{LCAO\text{-}MO} < E_{AO}$
- LCAO-MO are bigger than AO

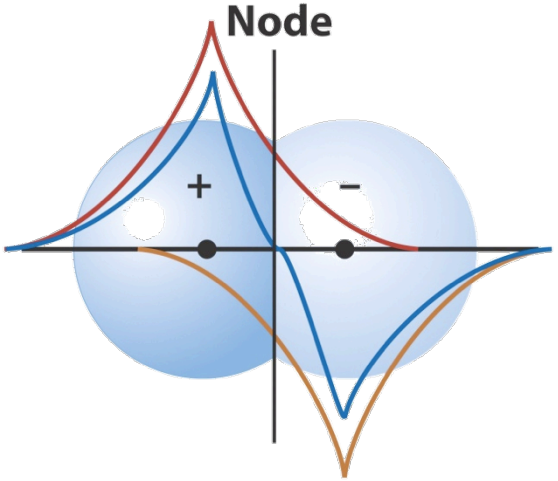
Molecular Orbitals

"Conservation of orbitals"

H_2 bonds with two 1s orbitals – it must have 2 LCAO-MOs

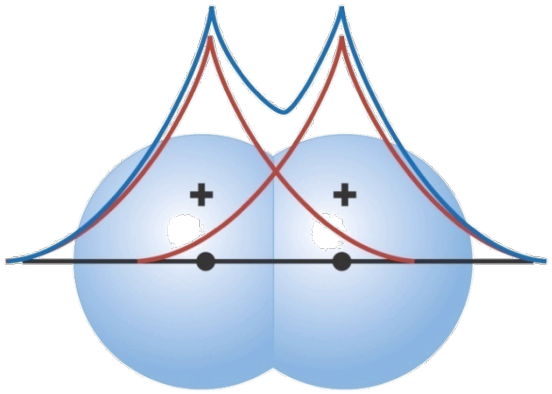
2nd LCAO-MO - destructive interference, higher PE than atomic orbitals

$\psi = \psi_{A1s} - \psi_{B1s}$



Nodal plane! – much less e- density "internuclearly"

This is an **antibonding orbital**

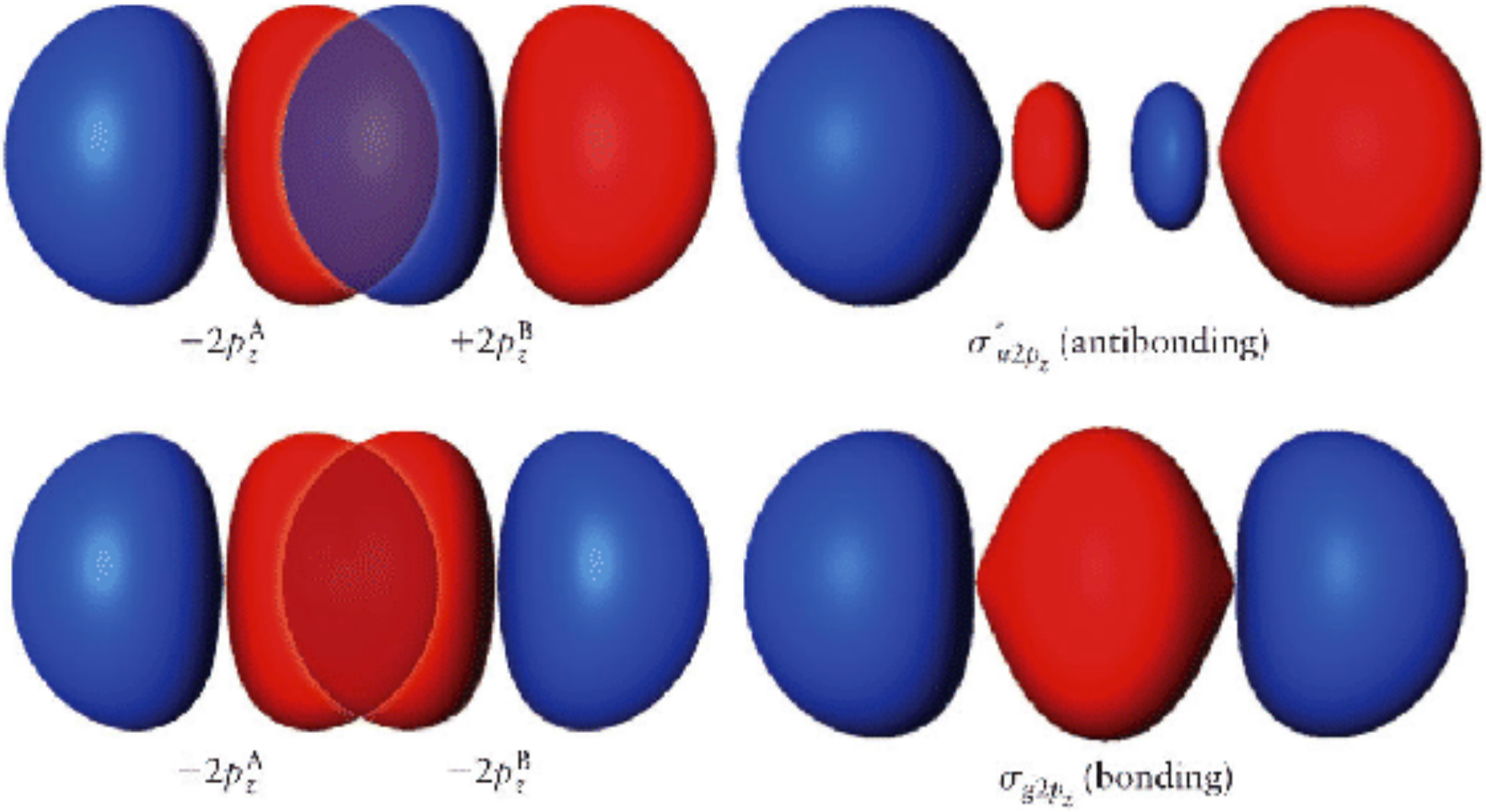


$\psi = \psi_{A1s} + \psi_{B1s}$

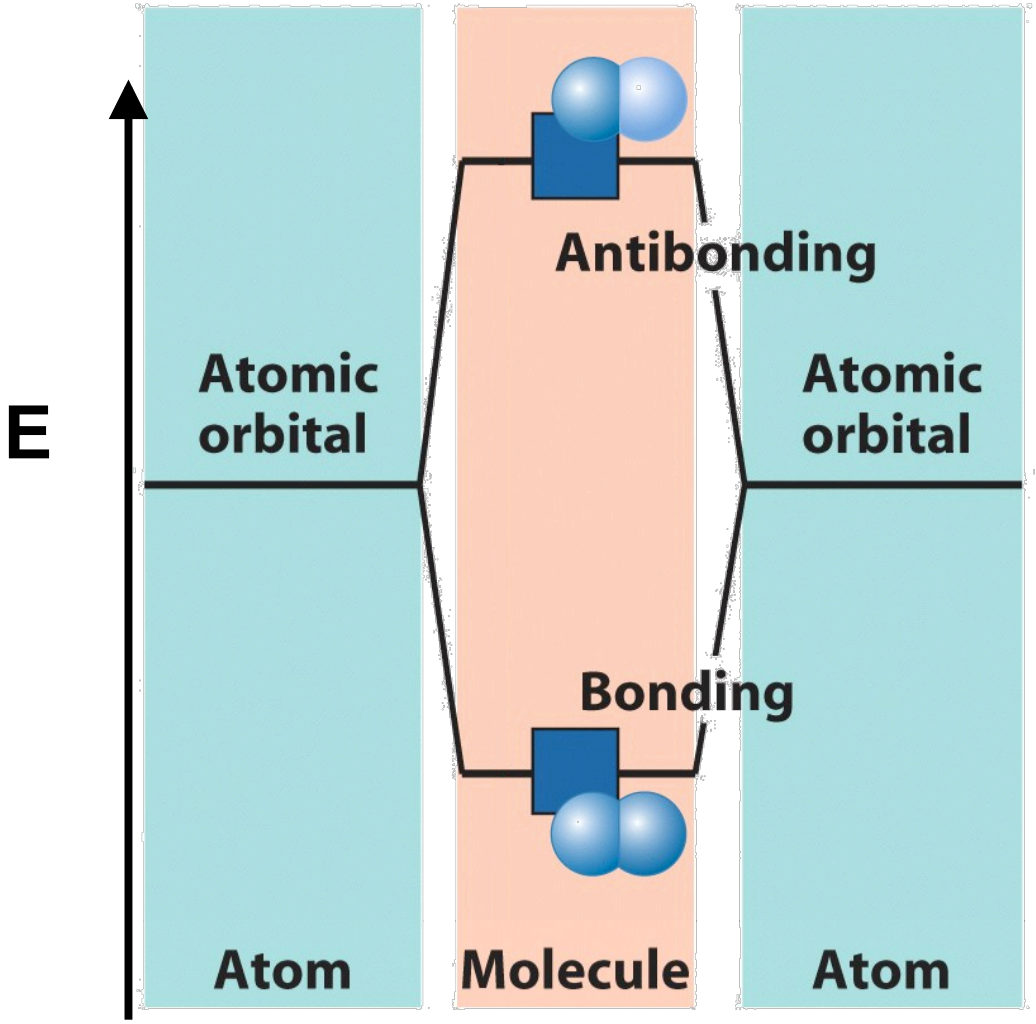
1st LCAO-MO is lower in energy than Atomic orbitals

This is called a **bonding orbital**

Sigma Bonds


$-2p_z^A$
$+2p_z^B$
$\sigma^*_{u2p_z}$ (antibonding)
$-2p_z^A$
$-2p_z^B$
σ_{g2p_z} (bonding)

Molecular Orbital Energy Diagram



Shows:

Relative Energies of

- Atomic Orbitals
- Bonding MOs
- Antibonding MOs

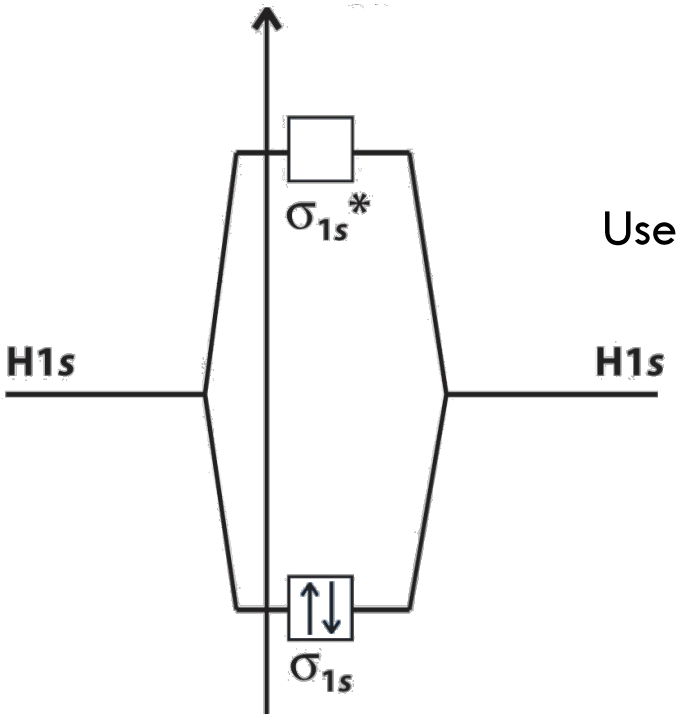
Shapes of LCAO-MOs

Type of MO – s or p

Molecular Electron Configuration

Electron Configurations of Diatomic Molecules

Shows ALL valence electrons using the Building-Up Principle:

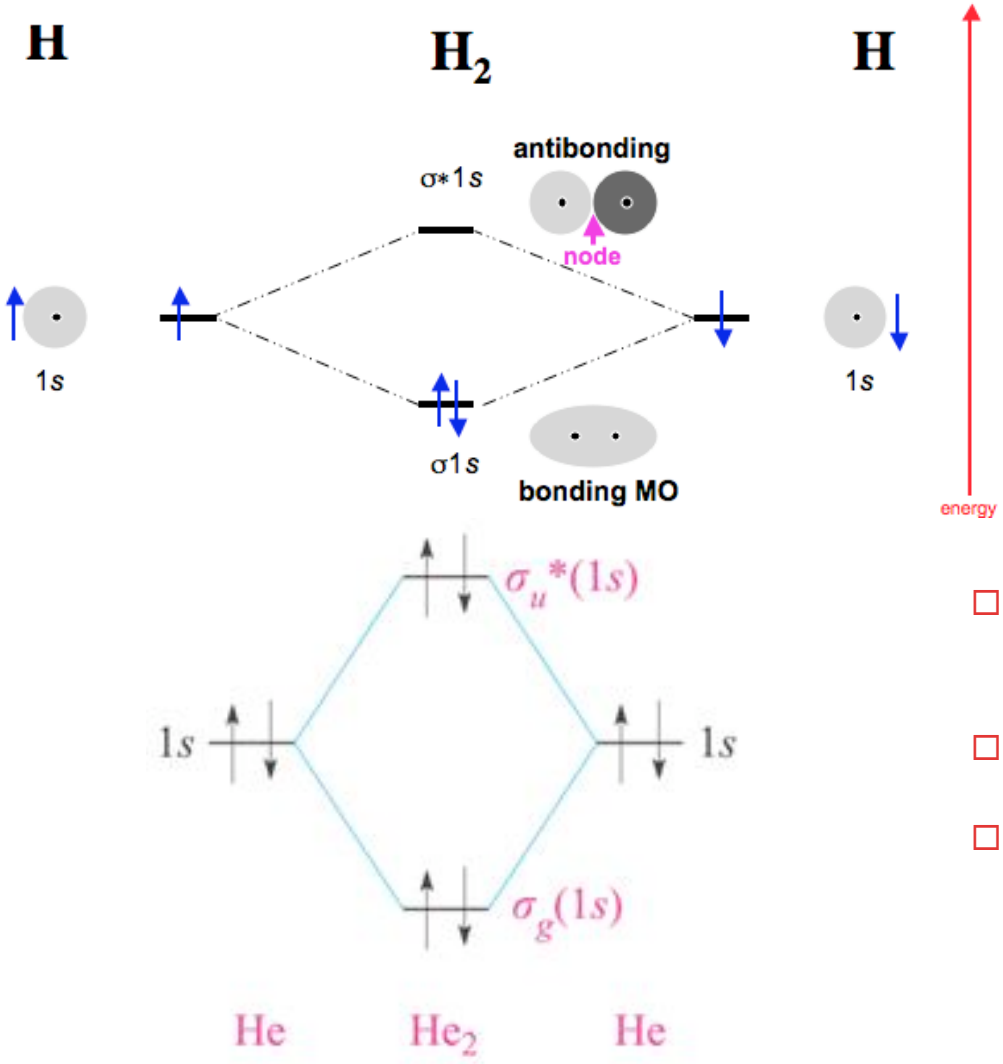


Use "Hund's Rule just like in atomic orbitals!

Electron configuration of H_2 → s_{1s}^2

Based on MO theory – a single electron can hold a bond together

Bond Order



Valence Bond Theory:

Bond order was # bonding pairs

MO Theory, bond order is:

- b = ½ (N – N*)

N = # e⁻s in bonding orbitals

- N* = # e⁻s in antibonding orbitals
- H_2 → b = 1
- He_2 → b = 0

2nd row Diatomic Molecules

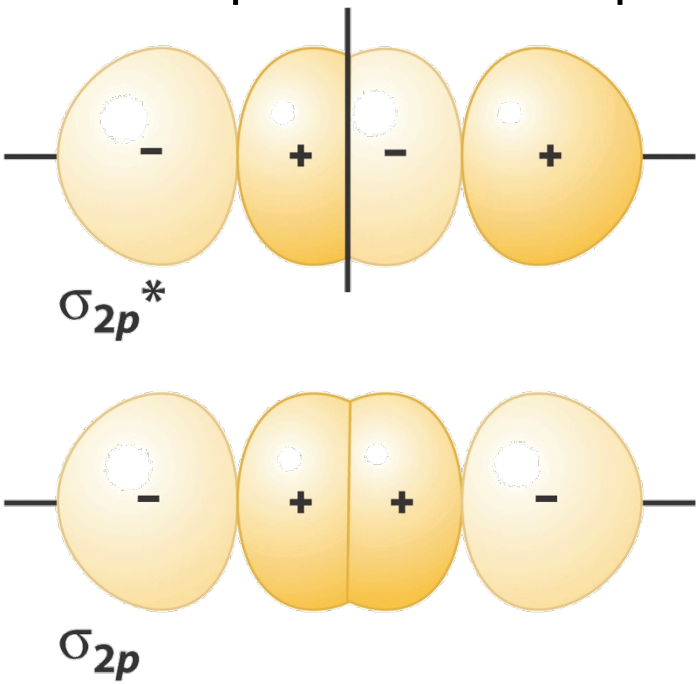
Must include both 2s and 2p orbitals in making our MOs

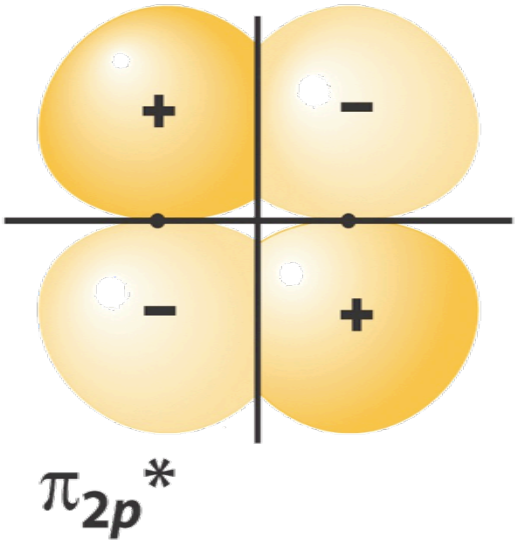
Only orbitals that are close in energy will form MOs

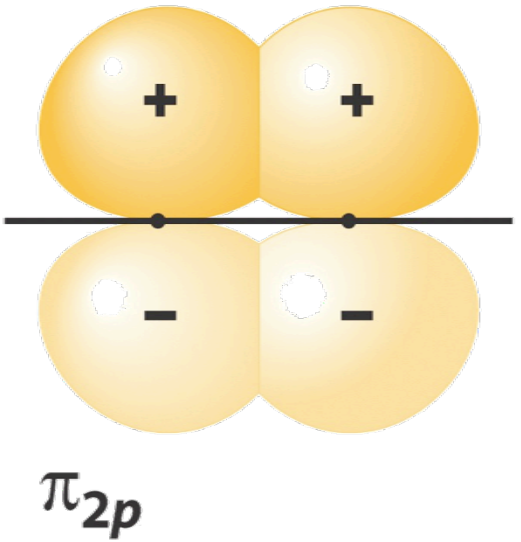
We have 2 (2s) orbitals and 6 (2p) orbitals → 8 atomic orbitals

2s orbitals overlap in the same way as the 1s orbitals of H_2

2p orbitals overlap in same orientations as in Valence bond theory:







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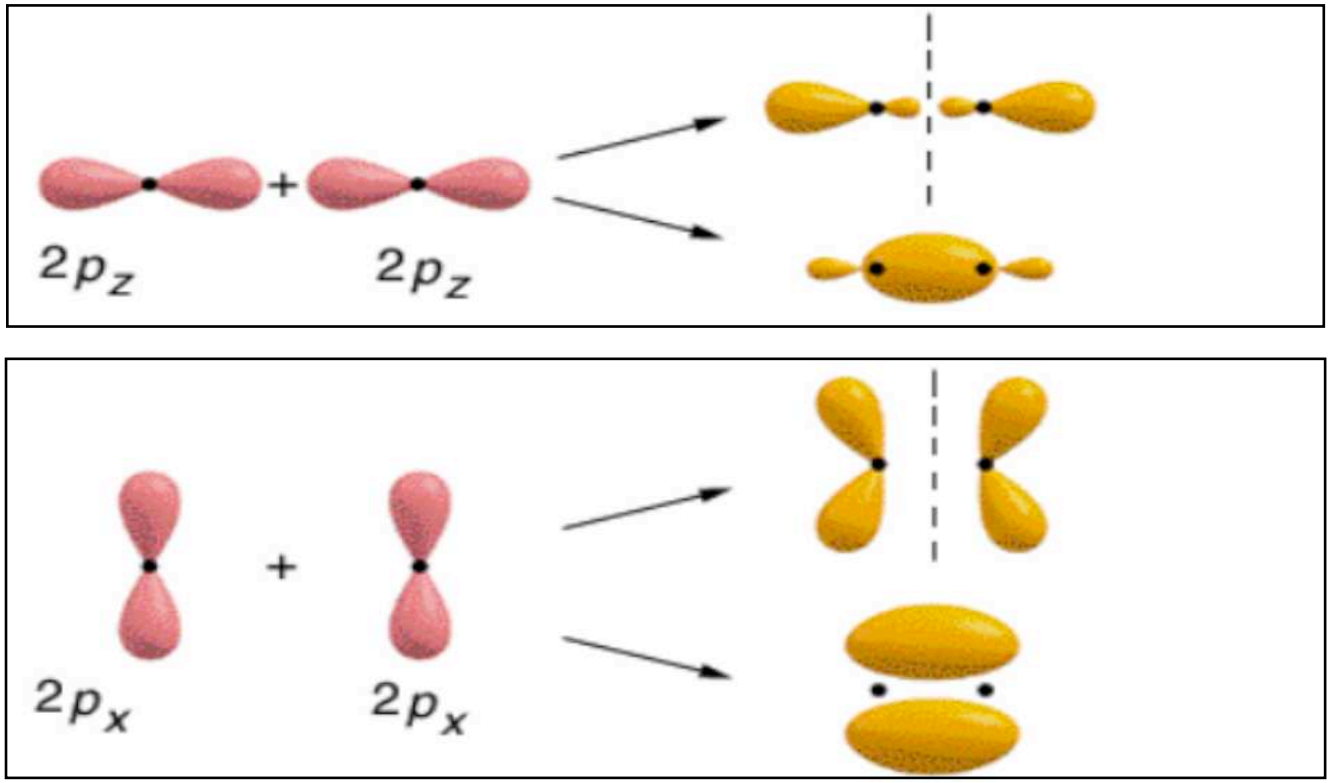
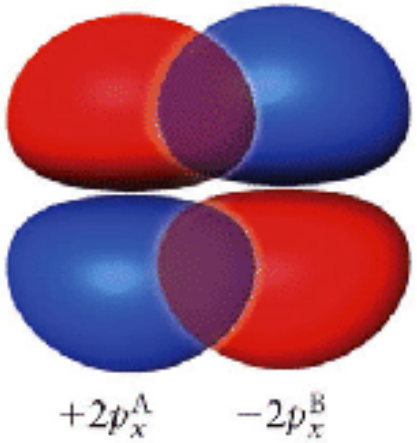
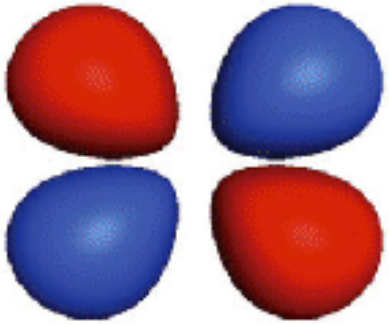


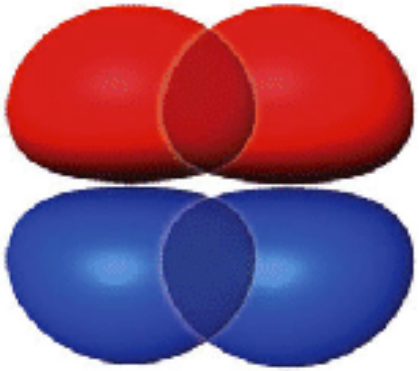
Pi Bonds



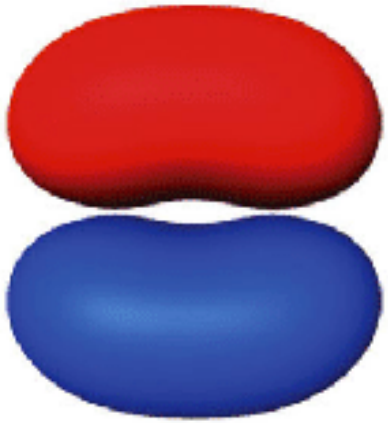
$+2p_x^A \quad -2p_x^B$



$\pi^*_{g2p_x}$ (antibonding)

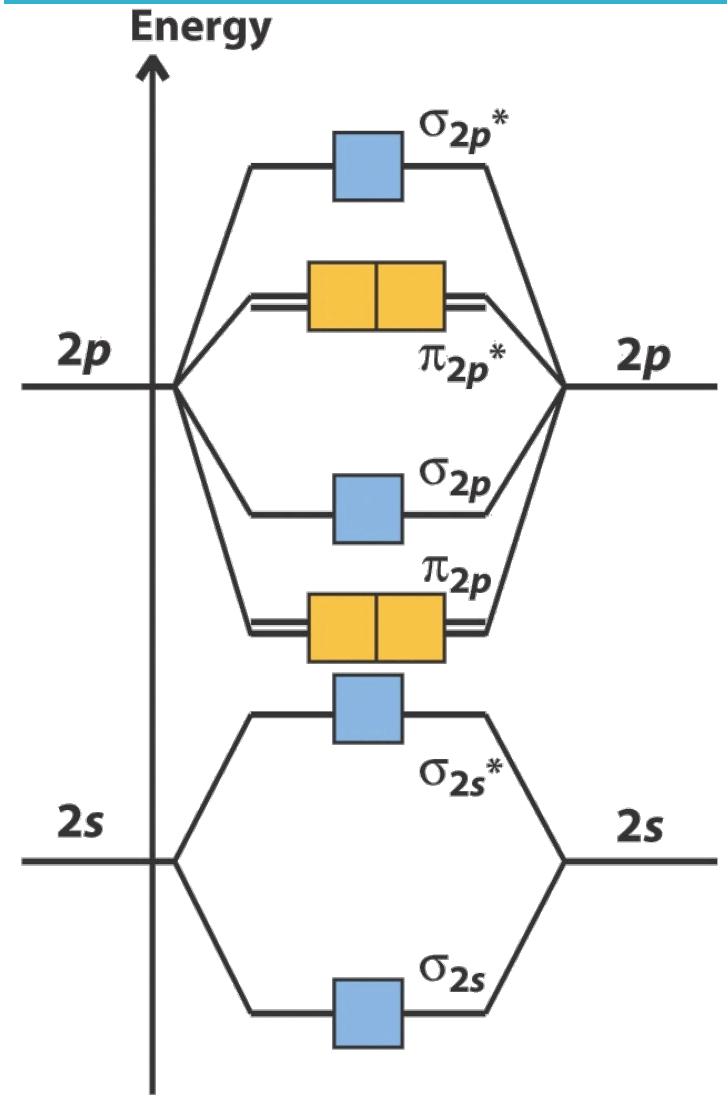


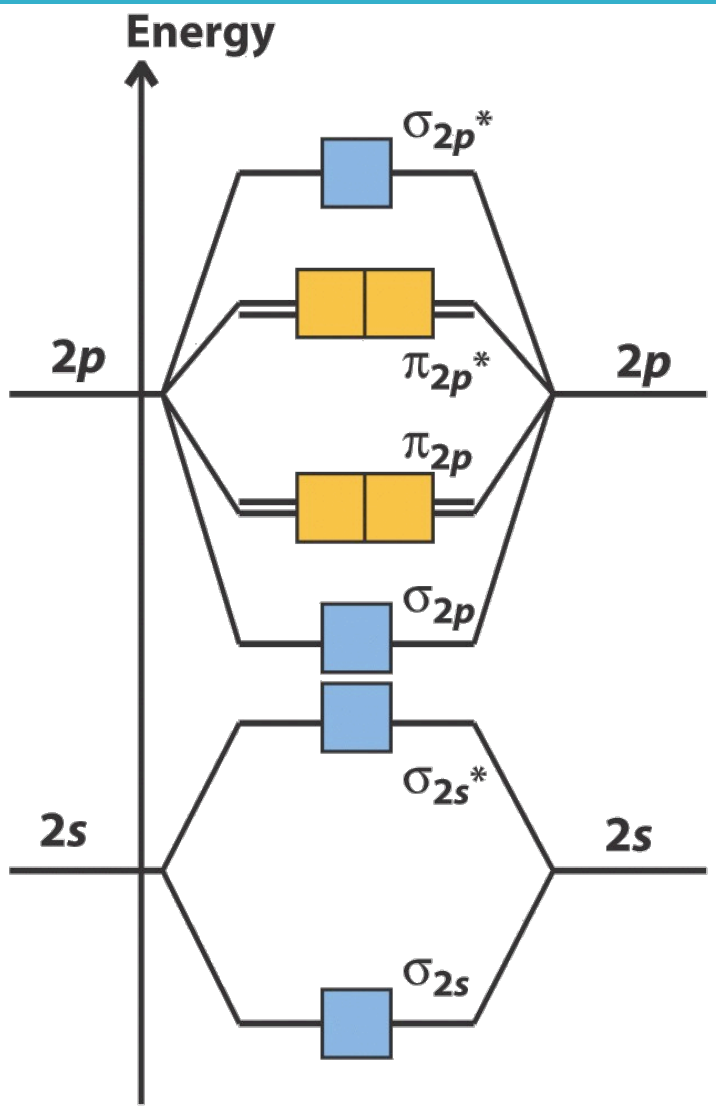
$+2p_x^A \quad +2p_x^B$



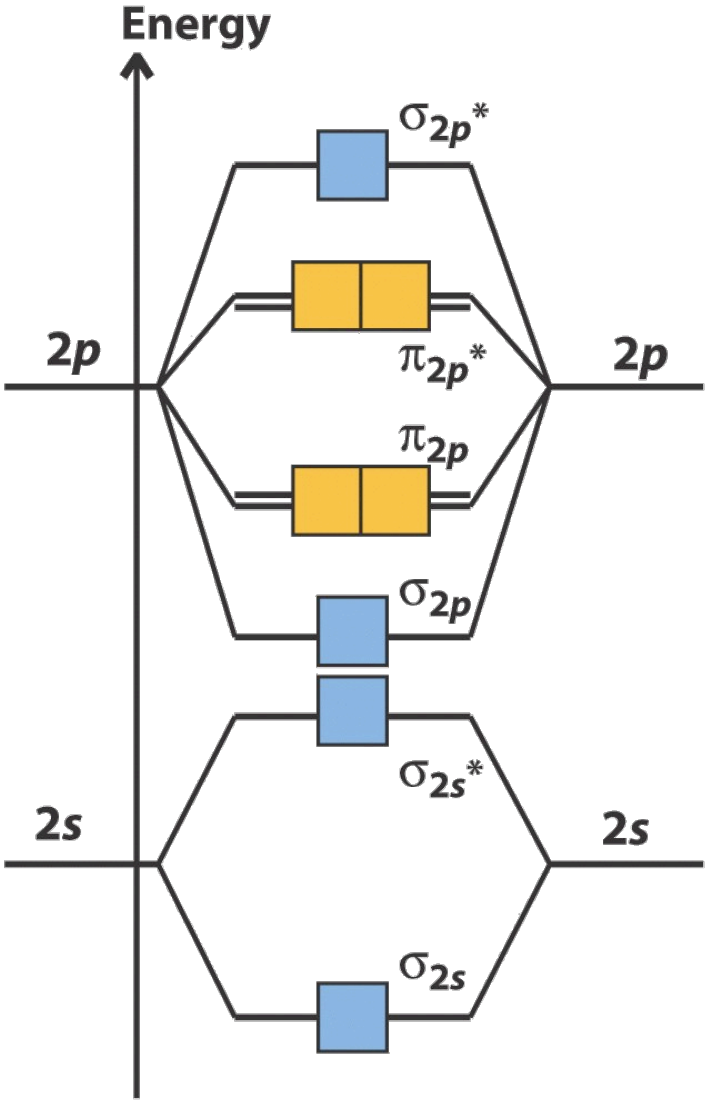
π_{u2p_x} (bonding)

2nd row Homonuclear Diatomic Molecules





2nd row Homonuclear Diatomic Molecules

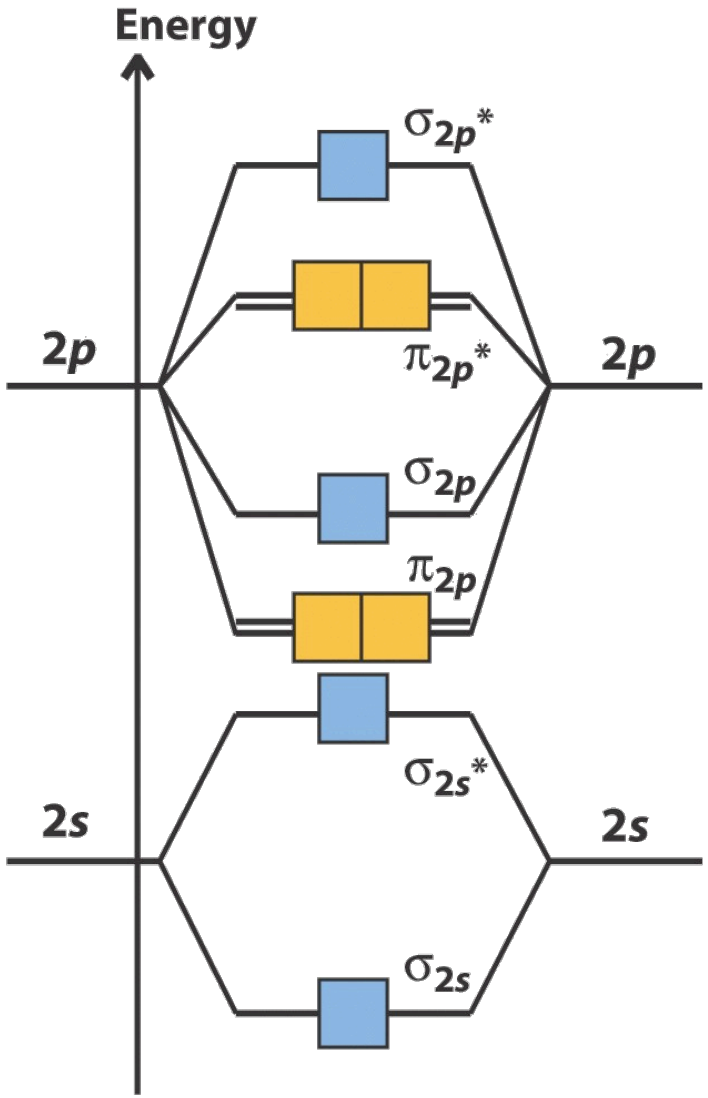


- Homonuclear Diatomic MO Energy diagram for all elements right of (and including) oxygen

O_2 F_2 'Ne_2'

And their combinations

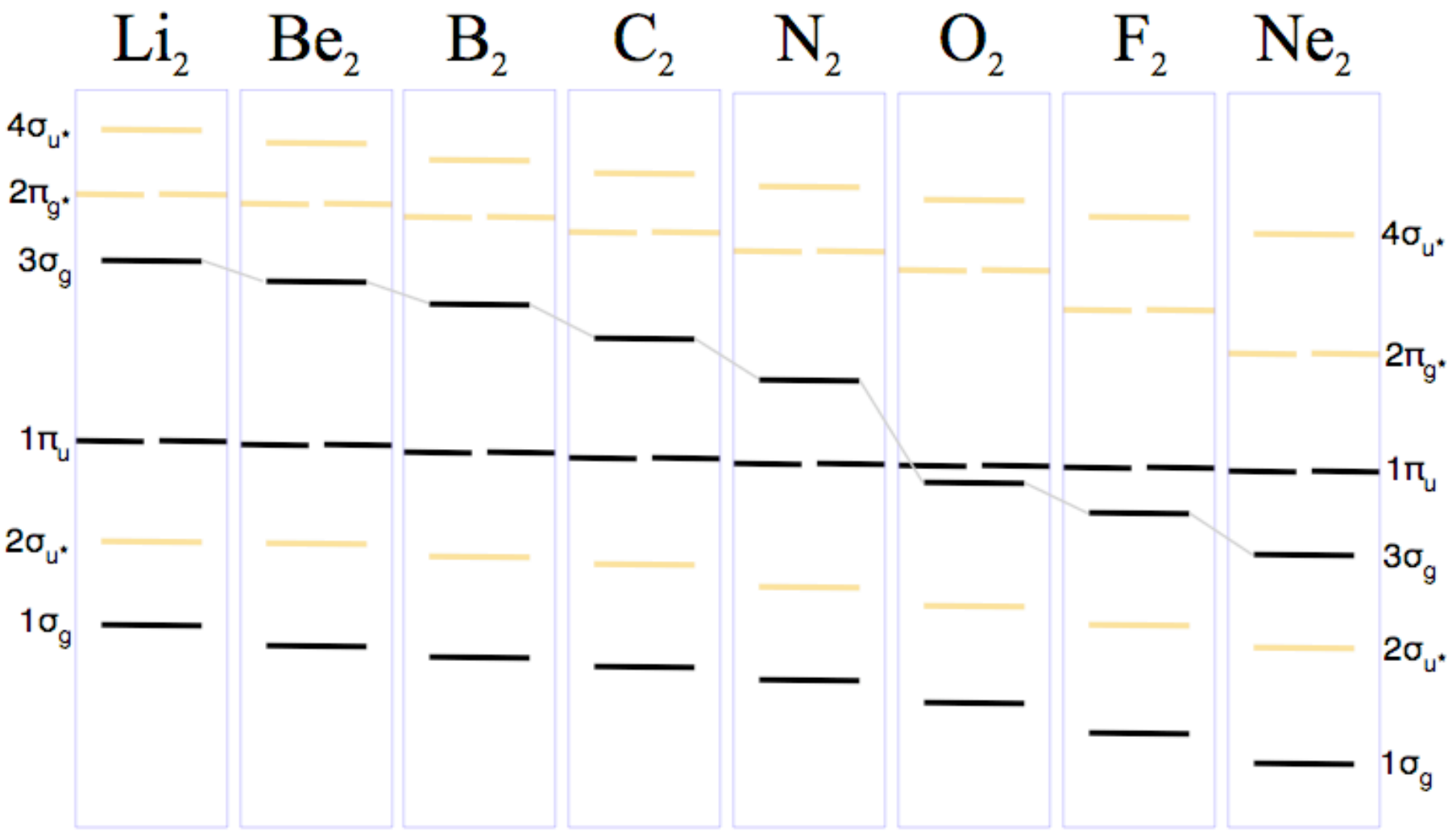
2nd row Homonuclear Diatomic Molecules



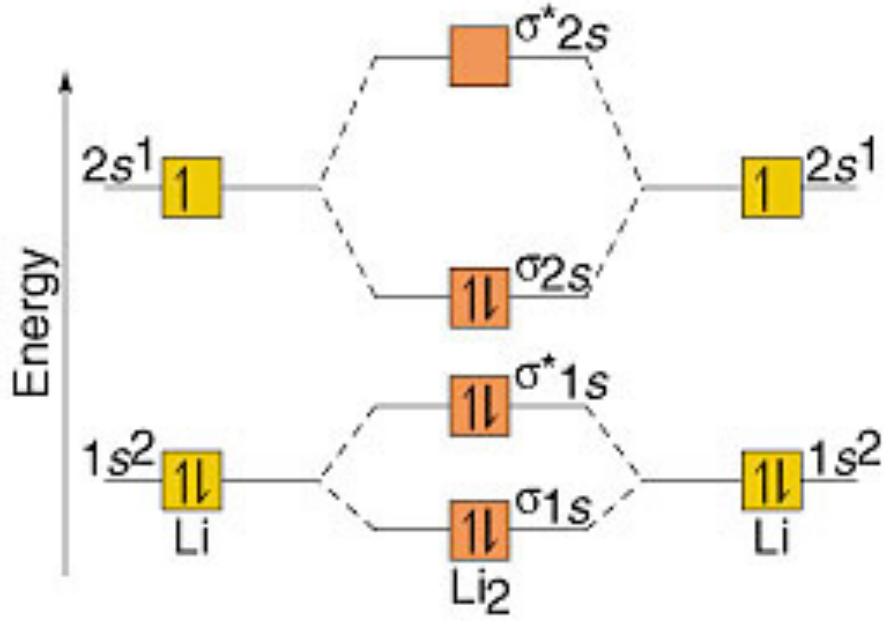
- Homonuclear Diatomic MO Energy diagram for all elements left of oxygen

Li_2 Be_2 B_2 C_2 N_2

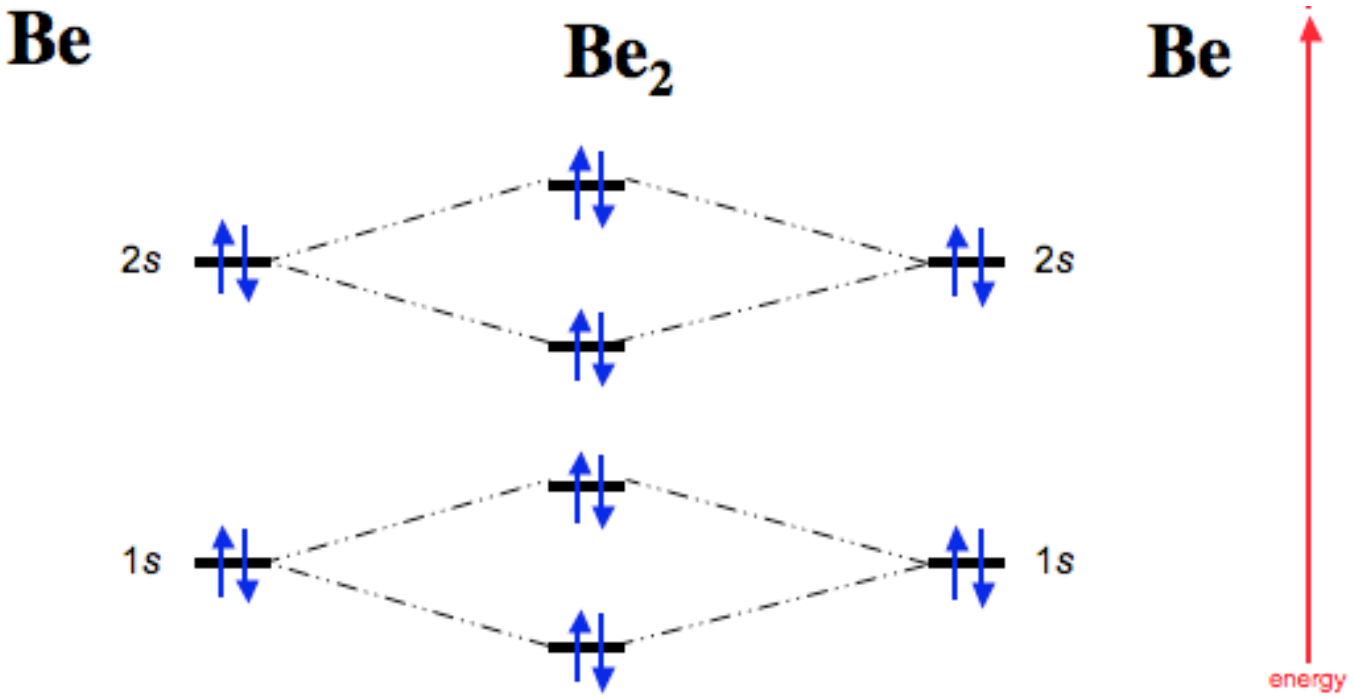
Relative MO Energy Levels



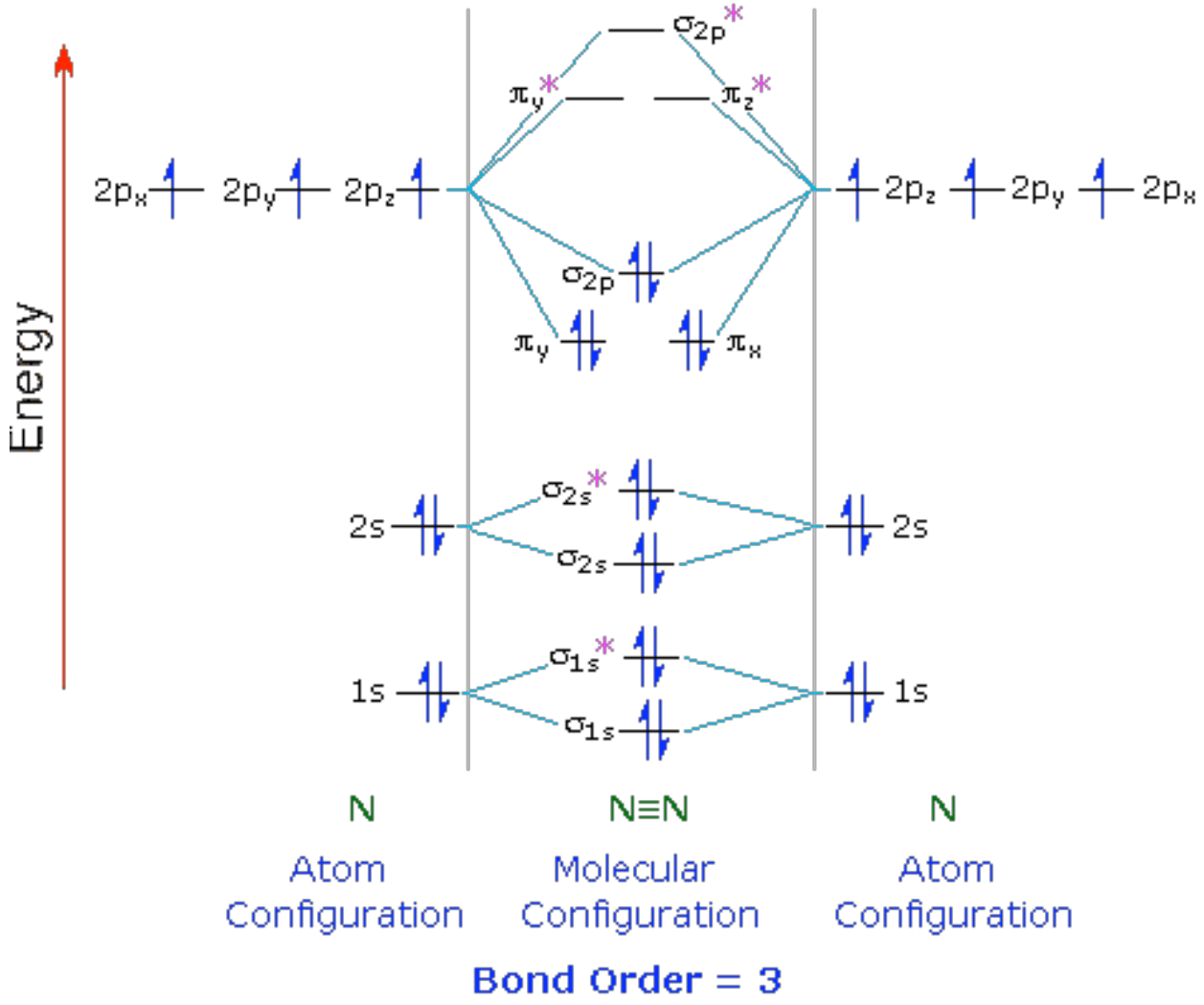
MO Diagram for Li_2



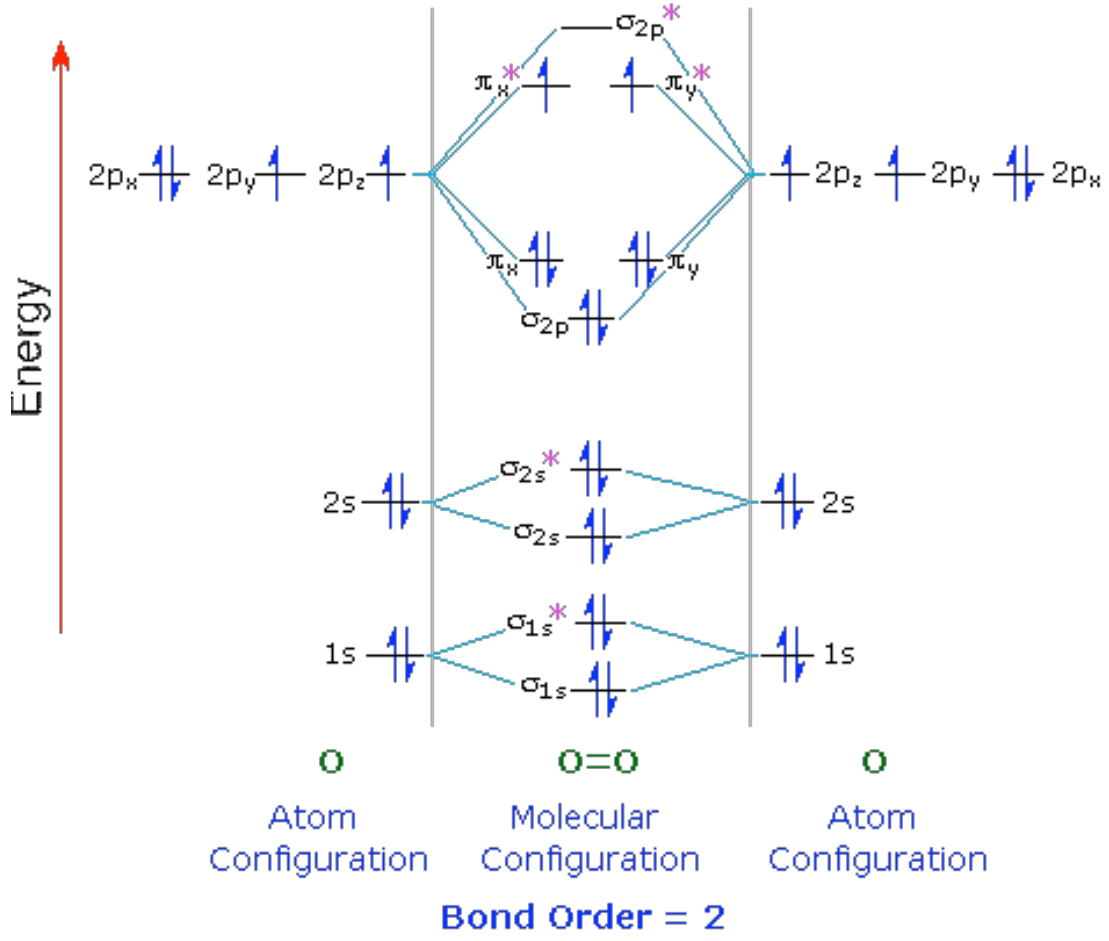
MO Diagram for Be_2



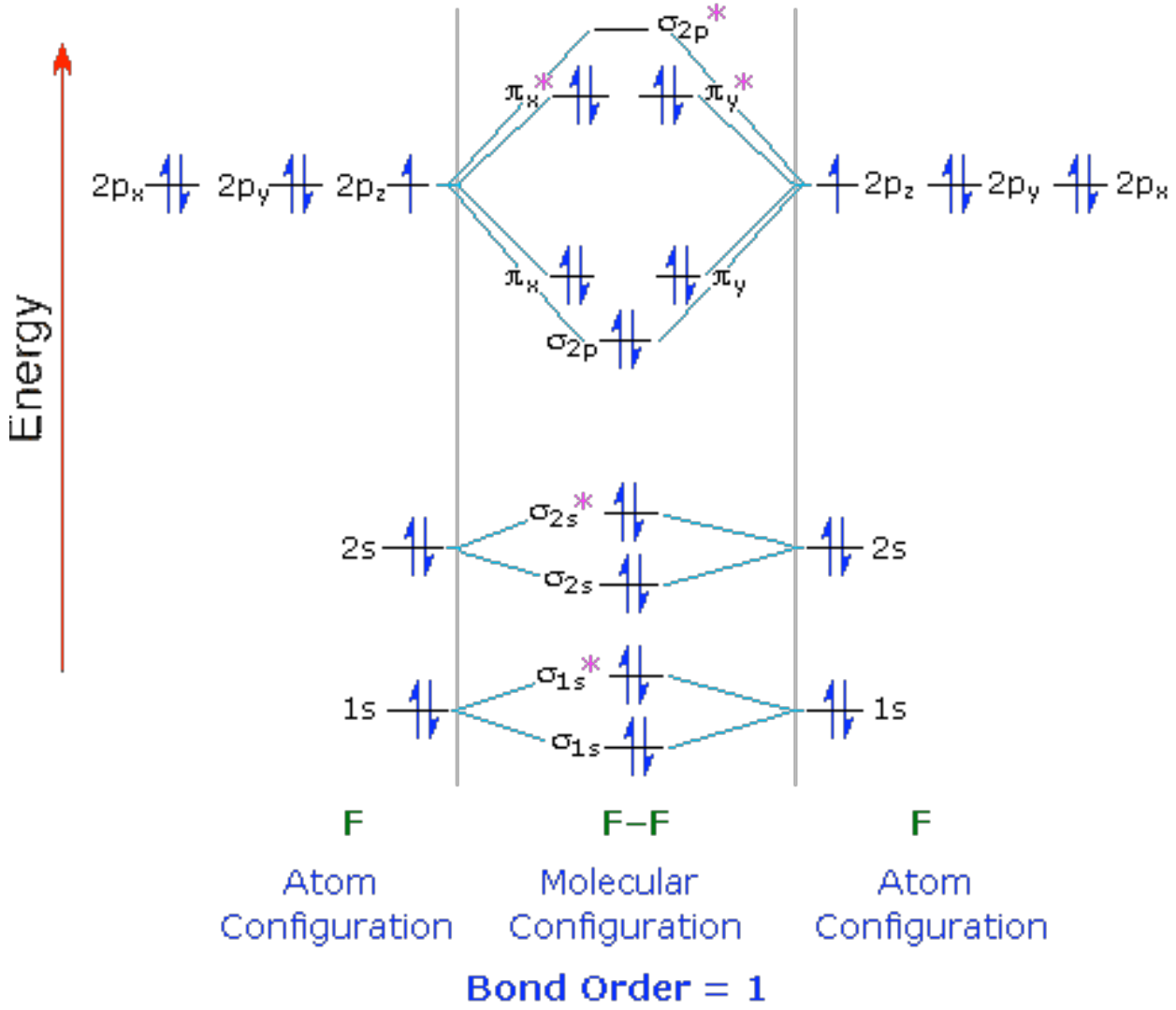
MO Diagram for N_2

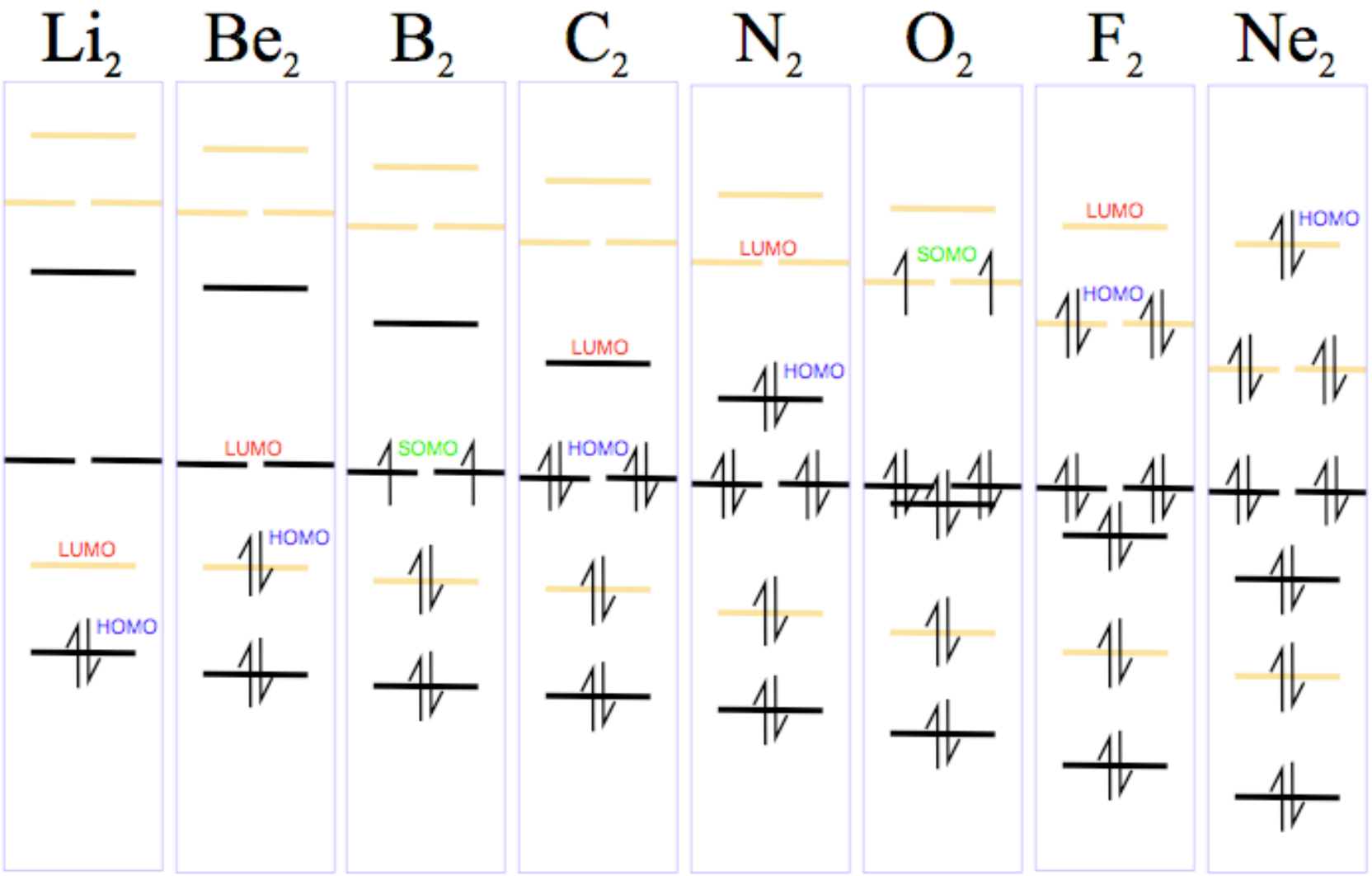


MO Diagram for O_2



MO Diagram for F_2

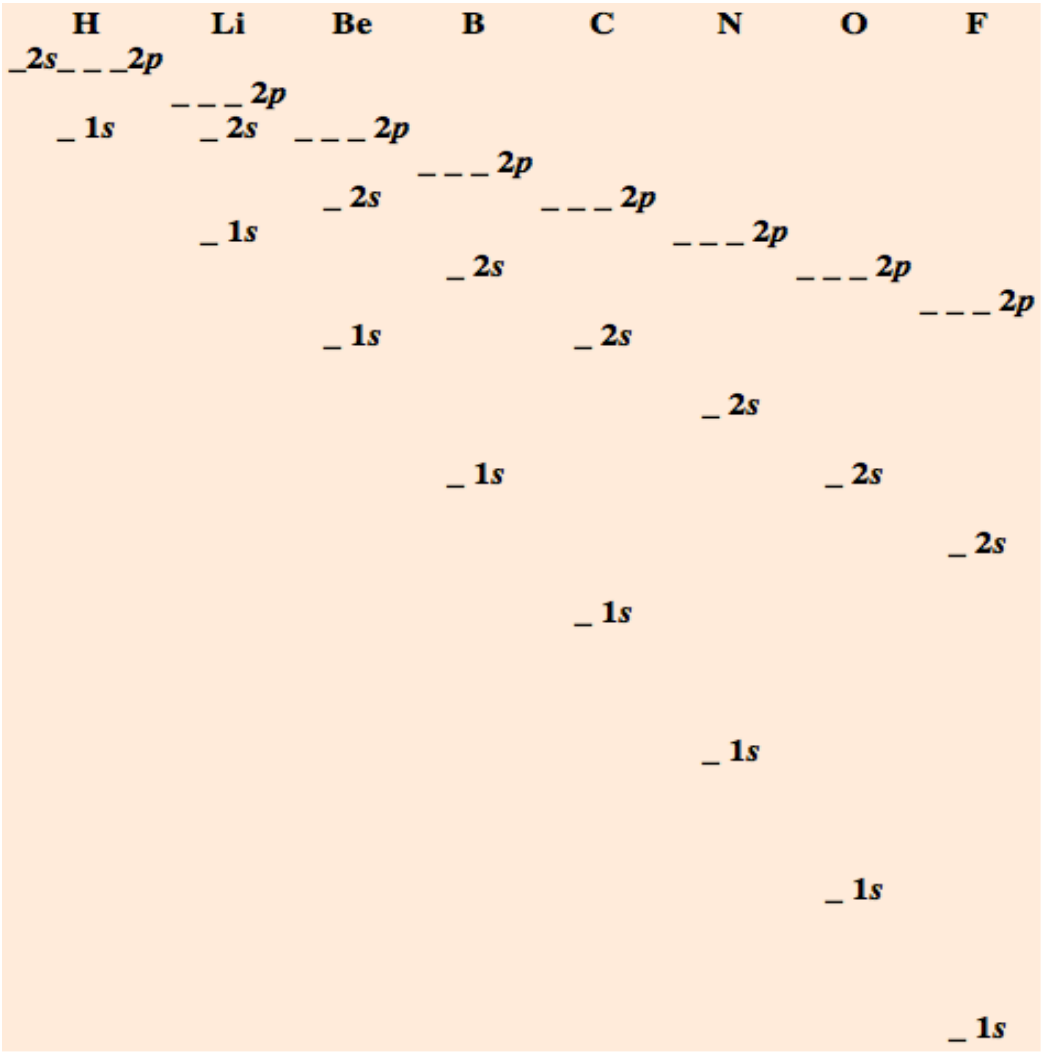




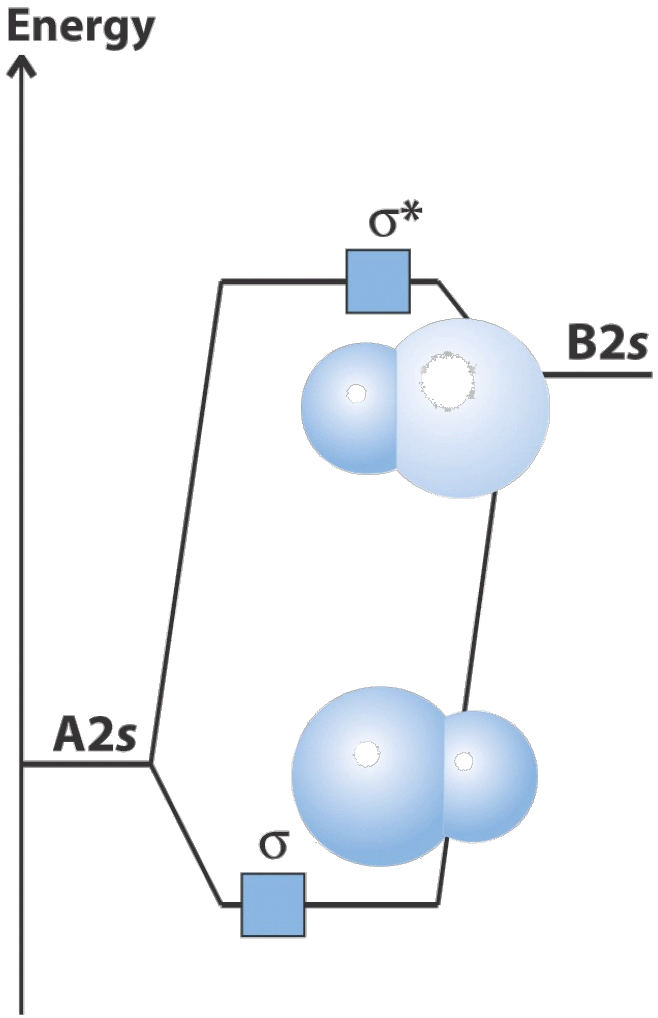
bond order = (electrons in bonding MOs – electrons in antibonding MOs) / 2

1	0	1	2	3	2	1	0
Li–Li	Be Be	B–B	C=C	N≡N	O=O	F–F	Ne Ne
known in the gas phase	dimer unknown	known in the gas phase paramagnetic diradical	known in the gas phase at high temp.	stable gas	stable gas paramagnetic diradical. Singlet & triplet states	stable gas	dimer unknown

Relative AO Energy Levels



Heteronuclear Diatomic Molecules

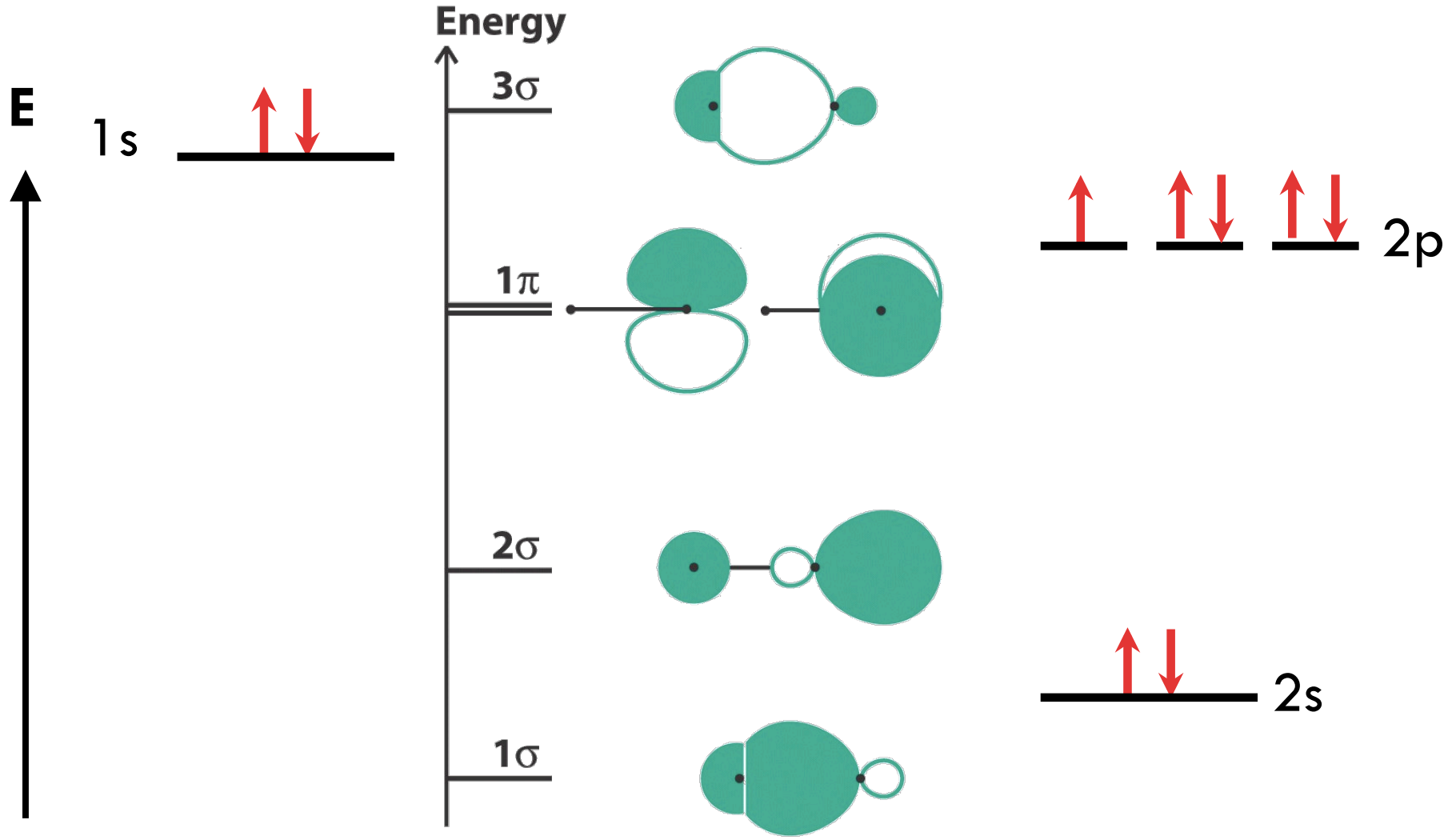


Account for ΔEN between AO's

More electronegative atoms will have lower energy atomic orbitals

Contributions are dependent on energy level

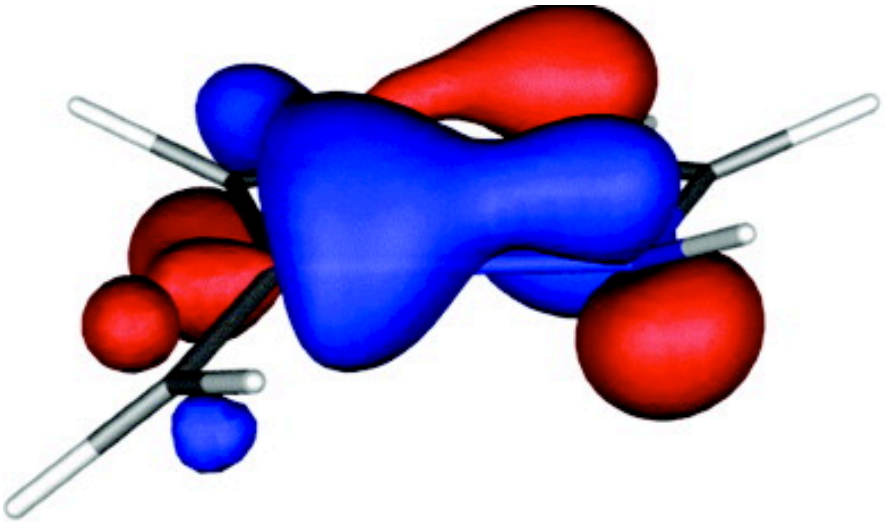
MO diagram for HF

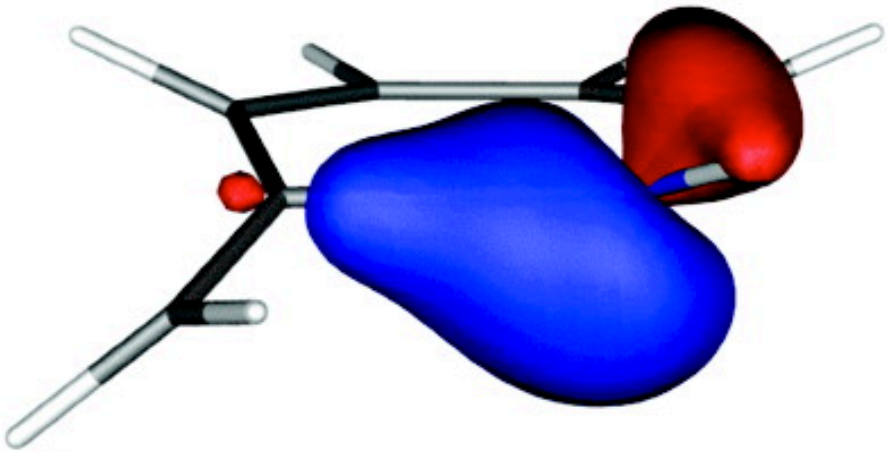


Orbitals in Polyatomic Molecules

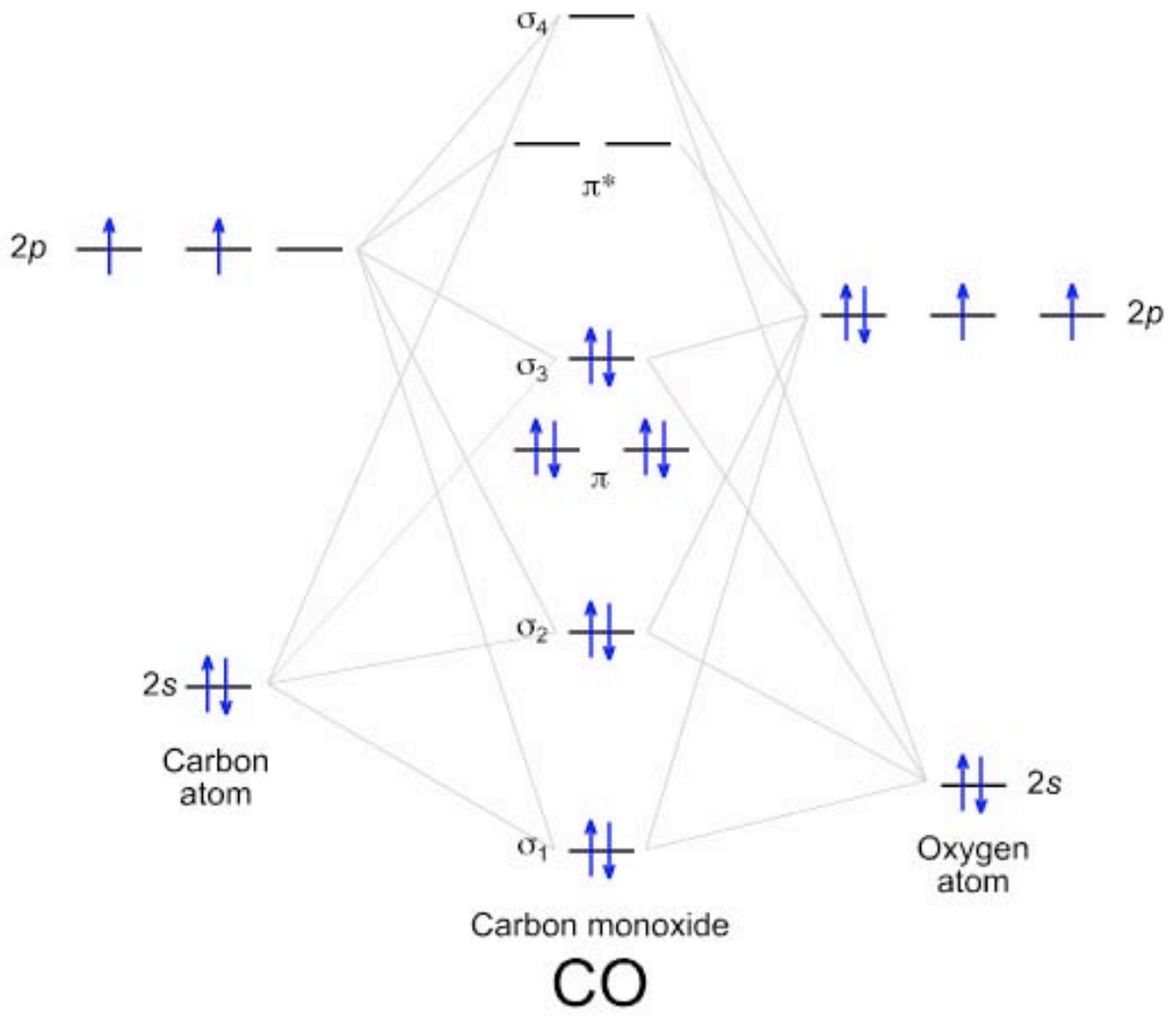
An electron pair in a bonding orbital helps to bind together the whole molecule – can become very complex

Occasionally some MOs are neither bonding nor antibonding –these are called nonbonding orbitals





MO Diagram for Carbon Monoxide



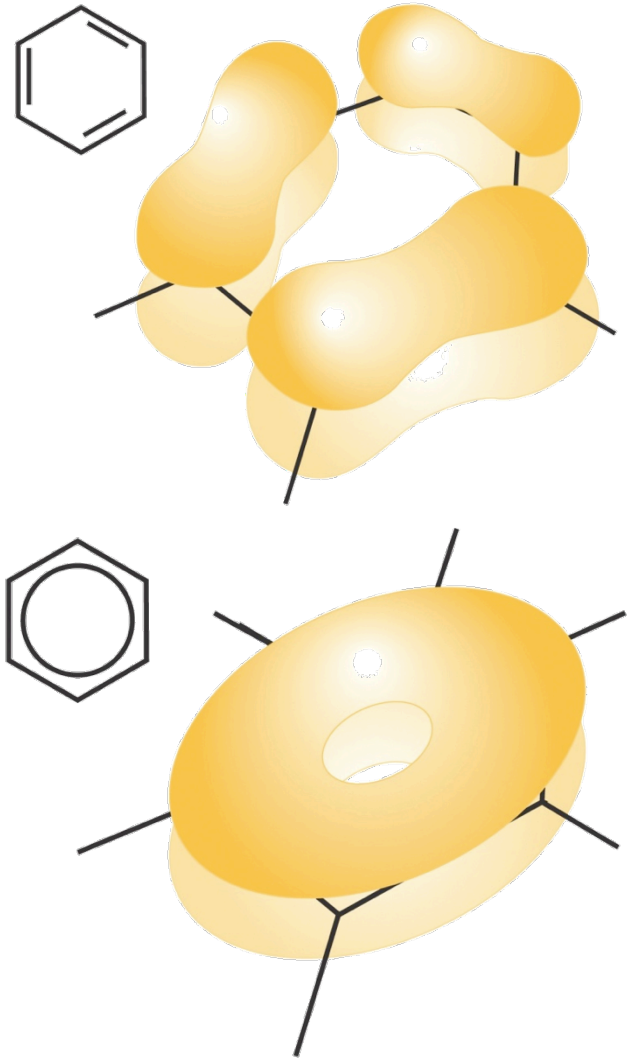
Organic Molecules

Chemists commonly mix VB and MO theories when discussing organic molecules:

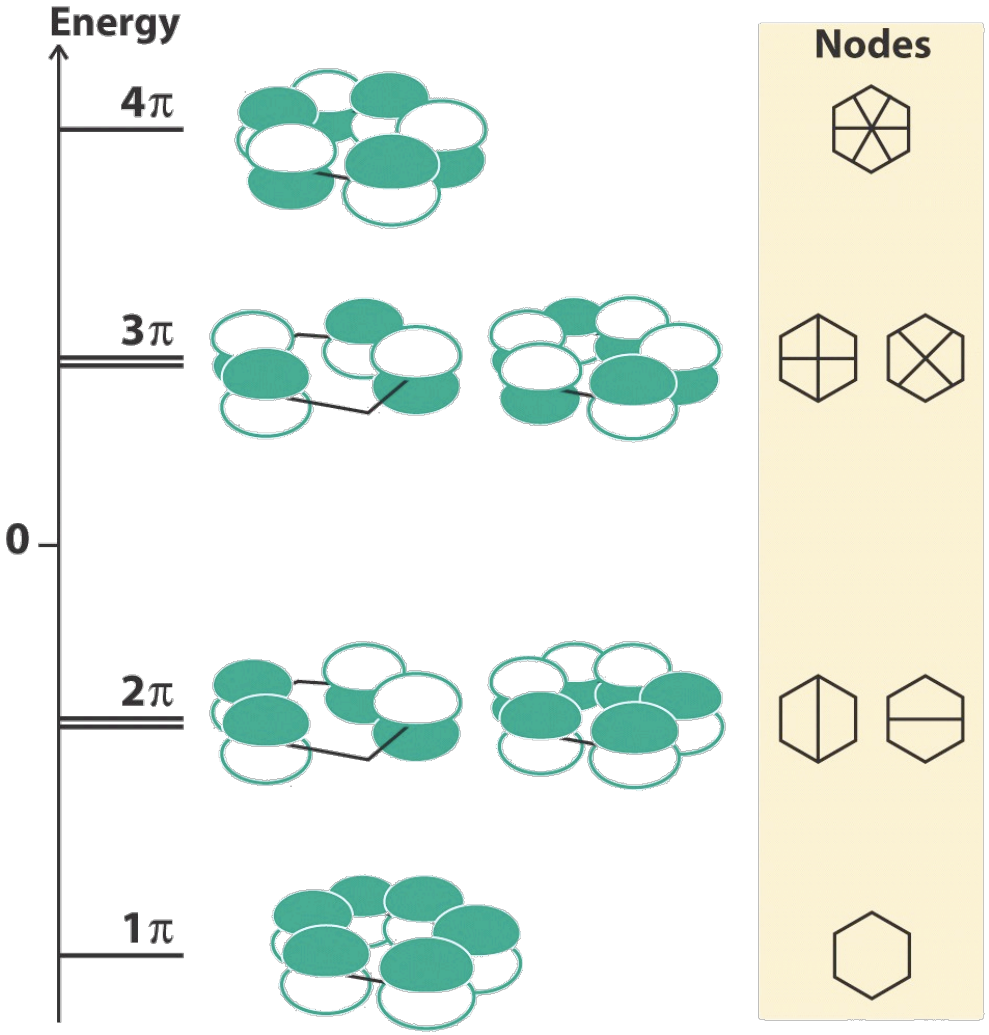
- VB theory is good for talking about σ bonds
- MO theory is better for considering π bonds

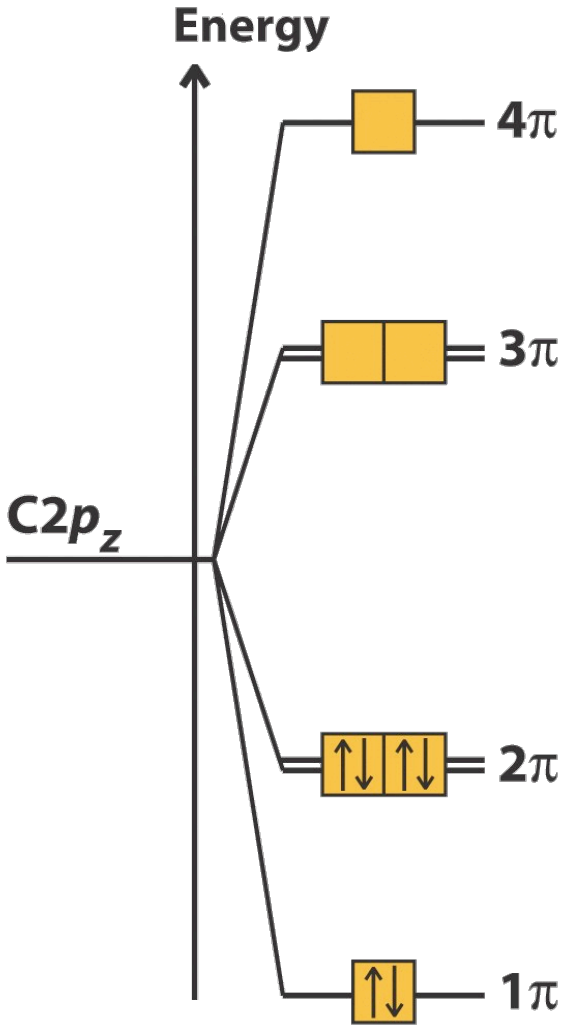
Consider Benzene (C_6H_6):

- VB perspective – each C is sp^2 hybridized
  - σ framework is overlap of sp^2 orbitals
- MO perspective – conjugation of π bonds extremely important
  - π MOs account for delocalization of electrons

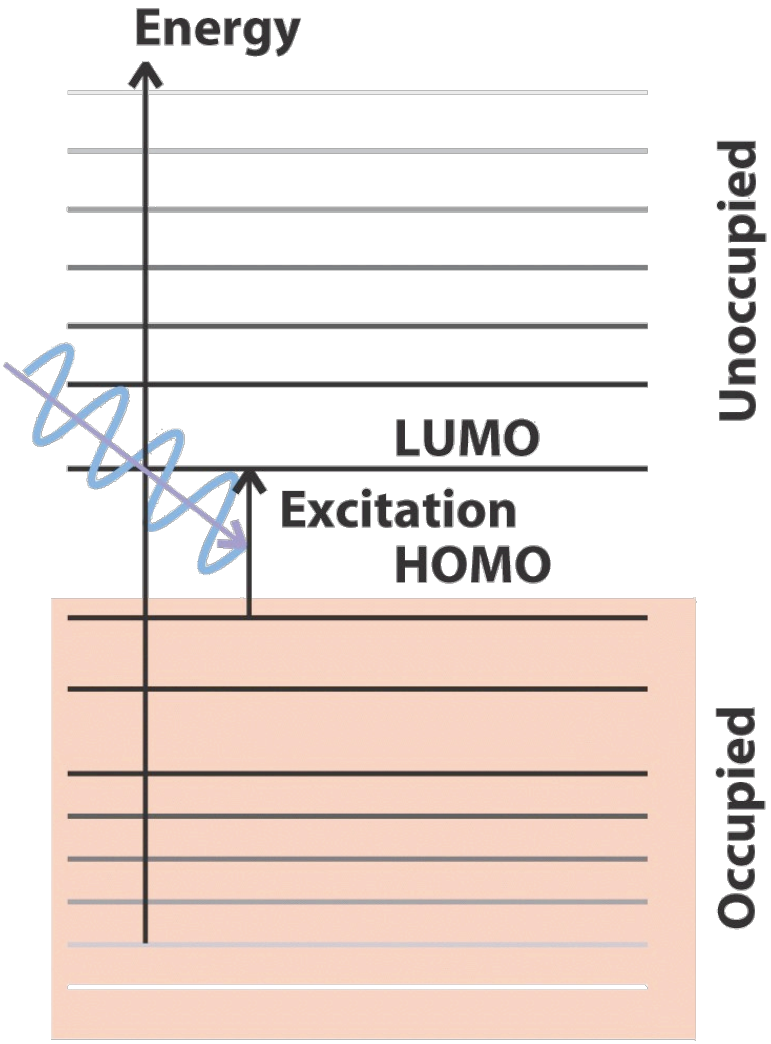


π Orbitals of Benzene





HOMO←→LUMO Transitions



HOMO – highest occupied MO

LUMO – lowest unoccupied MO