

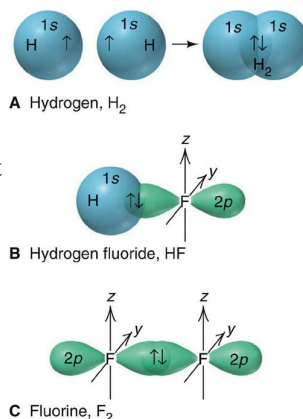
## Theories of Covalent Bonding

- Explain the observed shapes, polarities, magnetic and spectroscopic properties of molecules by using quantum mechanics – atomic and molecular orbitals
- The application of quantum mechanics to chemical bonding has led to two bonding theories

### 11.1 Valence Bond (VB) Theory

- A covalent bond results from the **overlap of valence atomic orbitals** on neighboring atoms occupied by unpaired electrons and the formation of an electron pair which has highest probability to be between the nuclei

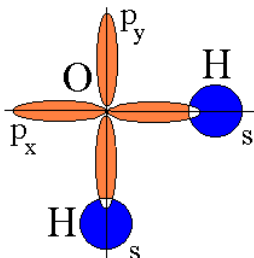
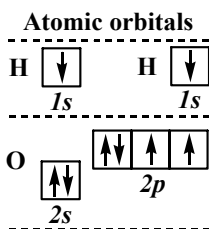
- The two electrons in the pair must have **opposite spins** – Pauli exclusion principle
- The overlapping orbitals are oriented in a way that provides **maximum overlap** between them
  - *s-s* orbital overlap is independent of orientation ( $H_2$ )
  - *s* and *p* orbitals overlap along the axis of the *p* orbital (HF)



### Hybridization of atomic orbitals

- Without modifications the VB theory predicts bond angles of  $90^\circ$  at the central atom of polyatomic molecules such as  $H_2O$ ,  $NH_3$  and  $CH_4$  which is inconsistent with the experiment

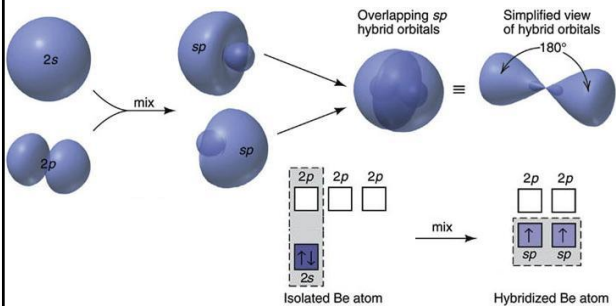
#### Example: $H_2O$



- The valence orbitals of the central atom must be modified in order to reproduce the experimentally observed bond angles
- **Hybridization** – mathematical mixing of two or more valence orbitals on the same atom
  - Result  $\rightarrow$  **hybrid orbitals**
  - The hybrid orbitals have shapes and orientations different than the original orbitals being mixed
  - The number of hybrid orbitals equals the number of original orbitals
  - The hybrid orbitals have equal energies (average of the energies of the original orbitals)

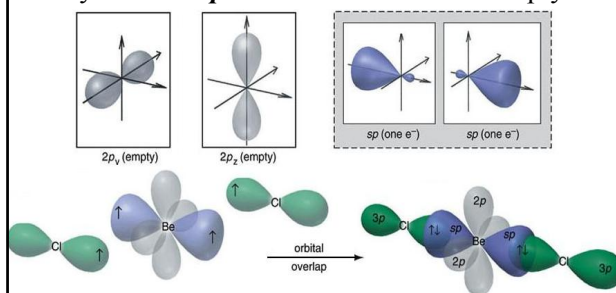
### *sp* Hybridization – a combination of one *s* and one *p* orbital

- The resulting two *sp* hybrid orbitals are identical and have linear orientation (used to describe the **linear electron group arrangement, bond angles  $180^\circ$** )

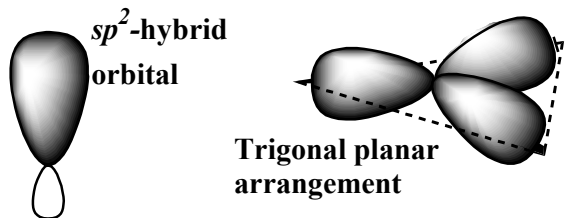


### Example: $BeCl_2$ (linear e-group arrangement)

- The *3p*-orbitals of two Cl atoms overlap with the two *sp*-hybrids of Be and form two bonds with linear arrangement (bond angle of  $180^\circ$ ); The two unhybridized *2p*-orbitals of Be remain empty



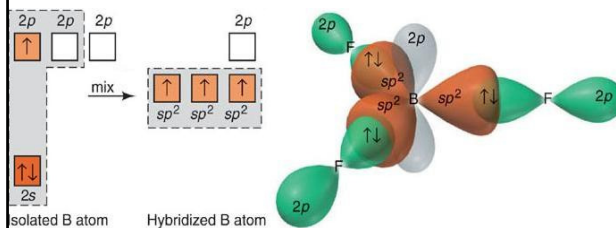
- **$sp^2$  Hybridization** – a combination of **one s** and **two p** orbitals
  - The resulting three  **$sp^2$  hybrid** orbitals are identical and point toward the corners of an equilateral triangle (used to describe the **trigonal planar e-group arrangement, bond angles  $120^\circ$** )



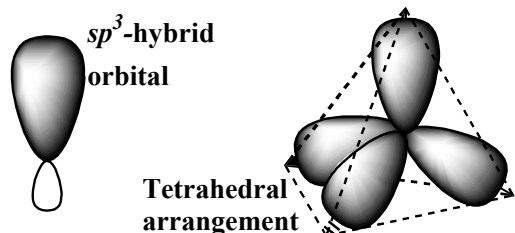
### Example:

**$BF_3$**  (trigonal planar e-group arrangement)

The  **$2p$** -orbitals of three **F** atoms overlap with the three  **$sp^2$** -hybrids of **B** and form three bonds with trigonal planar arrangement (bond angle of  $120^\circ$ ); The unhybridized  **$2p$** -orbital of **B** remains empty



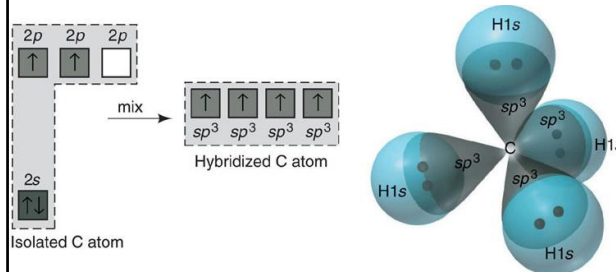
- **$sp^3$  Hybridization** – a combination of **one s** and **three p** orbitals
  - The resulting four  **$sp^3$  hybrid** orbitals are identical and point toward the corners of a tetrahedron (used to describe the **tetrahedral e-group arrangement, bond angles  $109.5^\circ$** )



### Example:

**$CH_4$**  (tetrahedral e-group arrangement)

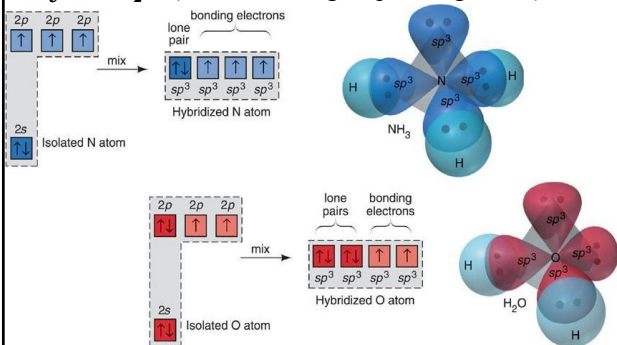
The  **$1s$** -orbitals of four **H** atoms overlap with the four  **$sp^3$** -hybrids of **C** and form four bonds with tetrahedral arrangement (bond angles of  $109.5^\circ$ )



- Hybrid orbitals can be used for bonding as well as for holding the lone pairs of the central atom

### Examples:

**$NH_3$**  and  **$H_2O$**  (tetrahedral e-group arrangement)

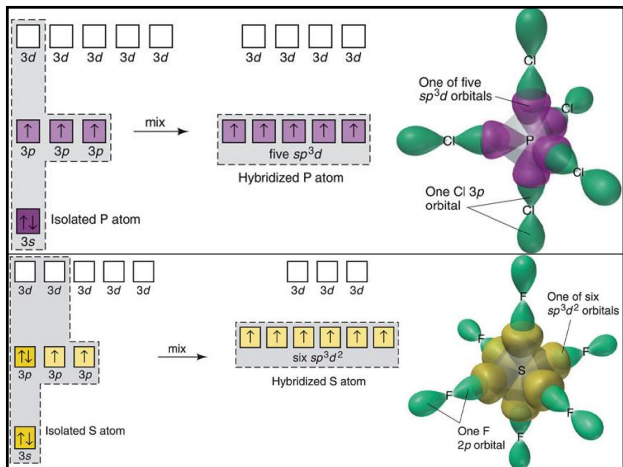


### • Hybrids involving d-Orbitals

- **$d$** -orbitals can be involved in the hybridization at central atoms from the third or later periods of the table which form expanded octets
- **$sp^3d$  Hybridization** – a combination of one **s**, **three p** and one **d** orbitals (used to describe the **trigonal bipyramidal e-group arrangement**)
- **$sp^3d^2$  Hybridization** – a combination of one **s**, **three p** and two **d** orbitals (used to describe the **octahedral e-group arrangement**)

### Examples:

**$PCl_5$**  (trigonal bipyramidal e-group arrangement)  
 **$SF_6$**  (octahedral e-group arrangement)



- Identification of the hybridization scheme
  - Draw the Lewis structure and identify the  $e^-$  group arrangement
  - Use the following correspondence

**Table 11.1 Composition and Orientation of Hybrid Orbitals**

	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one $s$ one $p$	one $s$ two $p$	one $s$ three $p$	one $s$ three $p$ one $d$	one $s$ three $p$ two $d$
Hybrid orbitals formed	two $sp$	three $sp^2$	four $sp^3$	five $sp^3d$	six $sp^3d^2$
Unhybridized orbitals remaining	two $p$	one $p$	none	four $d$	three $d$
Orientation					

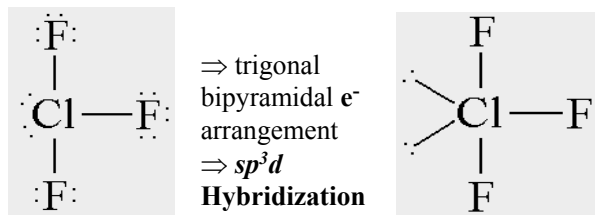
### Example:

What is the hybridization at the Cl atom in  $\text{ClF}_3$ ?

1. Lewis structure:  $n_{\text{tot}}=28$ ,  $n_{\text{rem}}=22$ ,  $n_{\text{need}}=20$

$n_{\text{need}} < n_{\text{rem}} \Rightarrow 2$  extra  $e^-$  (place at the central atom)

2. 2 lone pairs + 3 bonded atoms = 5

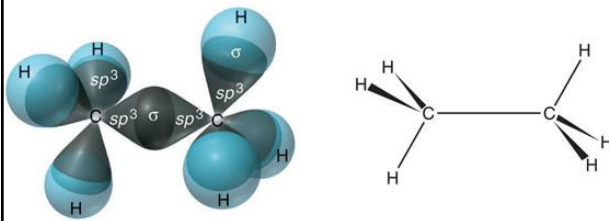


## 11.2 Types of Covalent Bonds

- The overlap (merging) of atomic orbitals can occur in two geometric configurations
  - **End-to-end overlap** along the internuclear axis ( $\sigma$ -bonding)
  - **Side-to-side overlap** on each side of the internuclear axis ( $\pi$ -bonding)
- Overlap between two  $s$  orbitals or between one  $s$  and one  $p$  orbital always leads to  $\sigma$ -bonds
- Overlap between two  $p$  orbitals leads to either  $\sigma$ -bonds or  $\pi$ -bonds
- Overlap involving **hybrids** always leads to  $\sigma$ -bonds

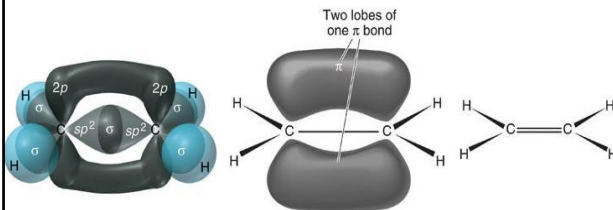
### Example: Ethane ( $\text{C}_2\text{H}_6$ )

- The two C atoms are in  $sp^3$  hybridization (tetrahedral)
- For each C, three of the  $sp^3$  hybrids overlap with the  $1s$  orbitals of the H atoms to form six  $\sigma$ -bonds
- The remaining  $sp^3$  hybrids of the C atoms overlap with each other along the internuclear axis to form a  $\sigma$ -bond
- The electron density increases in the overlapped regions between the nuclei along the internuclear axis



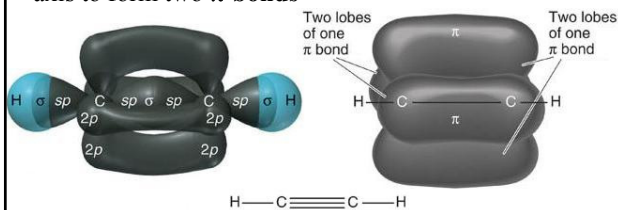
### Example: Ethylene ( $\text{C}_2\text{H}_4$ )

- The two C atoms are in  $sp^2$  hybridization (trig. planar)
- For each C, two of the  $sp^2$  hybrids overlap with the  $1s$  orbitals of the H atoms to form four  $\sigma$ -bonds
- The remaining  $sp^2$  hybrids of the C atoms overlap with each other along the internuclear axis to form a  $\sigma$ -bond
- The unhybridized  $p$  orbitals of the C atoms overlap with each other side-to-side above and below the internuclear axis to form a  $\pi$ -bond



### Example: Acetylene ( $C_2H_2$ )

- The two C atoms are in  $sp$  hybridization (linear)
- For each C, one of the  $sp$  hybrids overlaps with the  $1s$  orbitals of the H atoms to form two  $\sigma$ -bonds
- The remaining  $sp$  hybrids of the C atoms overlap with each other along the internuclear axis to form a  $\sigma$ -bond
- The unhybridized  $p$  orbitals of the C atoms overlap with each other side-to-side above and below the internuclear axis to form two  $\pi$ -bonds



➤ Single bonds are always  $\sigma$ -bonds

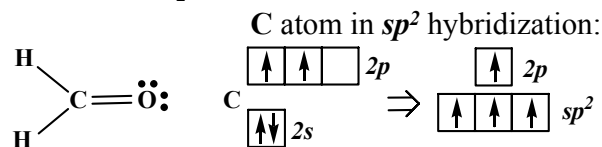
➤ Double bonds contain one  $\sigma$ -bond and one  $\pi$ -bond

➤ Triple bonds contain one  $\sigma$ -bond and two  $\pi$ -bonds

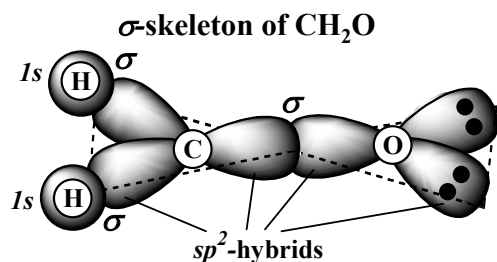
- $\pi$ -bonds are typically weaker than  $\sigma$ -bonds since side-to-side overlap is less extensive than end-to-end overlap

⇒ Double (or triple) bonds are less than twice (or three times) stronger than single bonds

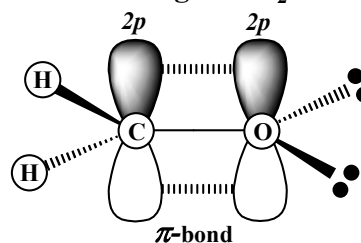
Example:  $CH_2O$  (trig. planar e-group arrangement)



- Two of the  $sp^2$ -hybrids of C are used to form  $\sigma$ -bonds with the H atoms and the third one with the O
- The O atom is also in  $sp^2$  hybridization; two of the  $sp^2$  hybrids are used to hold the lone pairs of O and one to form a  $\sigma$ -bond with C



### $\pi$ -bonding in $CH_2O$



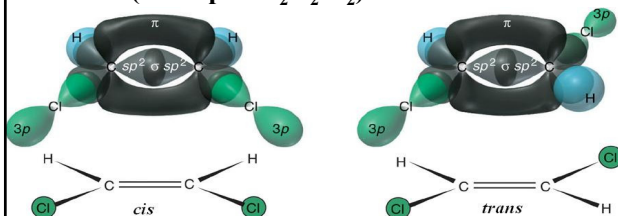
- The unhybridized  $p$ -orbitals of C and O are perpendicular to the  $\sigma$ -skeleton and overlap side-to-side to form a  $\pi$ -bond

⇒  $CH_2O$  has 3  $\sigma$ -bonds and 1  $\pi$ -bond

### • Internal rotation in molecules

- Allowed around single bonds (the overlap between the orbitals is preserved during rotation)
- Not allowed around double bonds (rotation disturbs the parallel alignment of the  $p$ -orbitals and reduces their overlap, the  $\pi$ -bond breaks)

⇒ Molecules with double bonds can have *cis-trans* isomers (Example:  $C_2H_2Cl_2$ )



## 11.3 Molecular Orbital (MO) Theory

- Limitations of the VSEPR model and the VB theory (based on localized bonding e-pairs) – fail in describing:
  - **Electron-deficient compounds** – have too few electrons ( $B_2H_6$ , Diborane – must have at least 7 bonds ( $14 e^-$ ) to bond the 8 atoms, but has only 12 valence  $e^-$ )
  - **Radicals** – odd electron species ( $NO$ , 11  $e^-$ s)
  - **Paramagnetism** – some molecules have paramagnetic properties without having unpaired  $e^-$ s in their Lewis structures ( $O_2$  is paramagnetic, but has no unpaired  $e^-$ s in its Lewis structure)

- The molecular orbital theory resolves these problems by introducing **molecular orbitals**
  - Similar to the atomic orbitals, but spread throughout the whole molecule
  - Can be occupied by no more than 2 electrons with opposite spins – Pauli exclusion principle (explains the significance of  $e^-$  pairs)
  - Can be occupied by single electrons (provides explanations of odd-electron species and paramagnetic properties)
- The **MOs** are solutions of the Schrödinger equation for the molecule as a whole (only approximate solutions are available)

### Formation of MOs in $H_2$

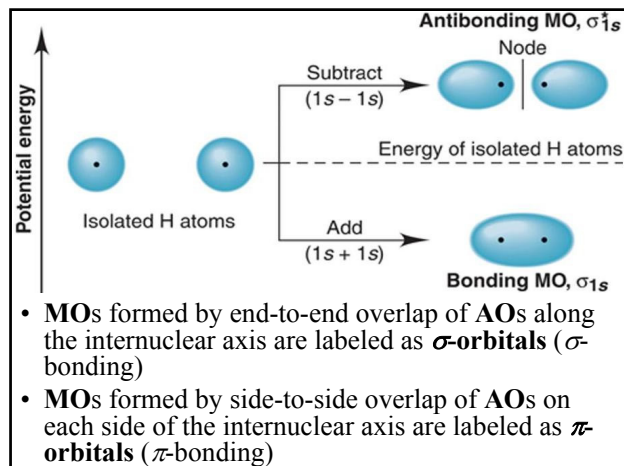
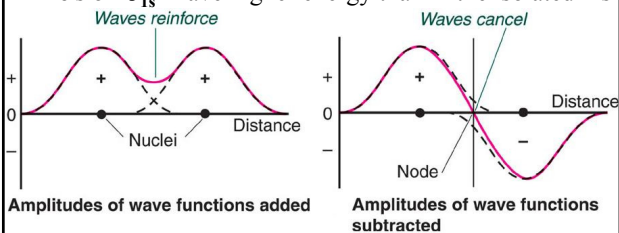
- As two **H** atoms (**A** and **B**) approach each other, their **1s** orbitals ( $1s_A$  and  $1s_B$ ) overlap and interfere with each other
- The interference yields two **MOs**
  - Constructive interference (the amplitudes of the wavefunctions add together) → **bonding MO** ( $\sigma_{1s}$ )

$$\sigma_{1s} = 1s_A + 1s_B$$

- Destructive interference (the amplitudes of the wavefunctions subtract from each other) → **antibonding MO** ( $\sigma_{1s}^*$ )

$$\sigma_{1s}^* = 1s_A - 1s_B$$

- The bonding **MO** (molecular orbital) is **enhanced** between the nuclei
  - Increased electron density between the nuclei
  - $e^-$ s on  $\sigma_{1s}$  have lower energy than in the isolated **Hs**
- The antibonding **MO** has a **node** between the nuclei
  - Reduced electron density between the nuclei
  - $e^-$ s on  $\sigma_{1s}^*$  have higher energy than in the isolated **Hs**



- MOs** formed by end-to-end overlap of **AOs** along the internuclear axis are labeled as  **$\sigma$ -orbitals** ( $\sigma$ -bonding)
- MOs** formed by side-to-side overlap of **AOs** on each side of the internuclear axis are labeled as  **$\pi$ -orbitals** ( $\pi$ -bonding)

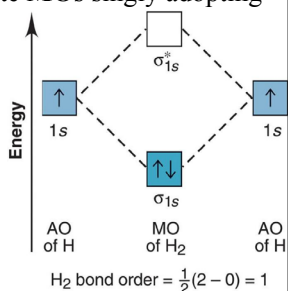
- MO energy level diagrams**
  - Electrons occupy first the lowest energy **MOs**
  - Each **MO** can accommodate up to two electrons with opposite spins (Pauli)
  - Electrons enter degenerate **MOs** singly adopting parallel spins (Hund)

### Bond order (BO)

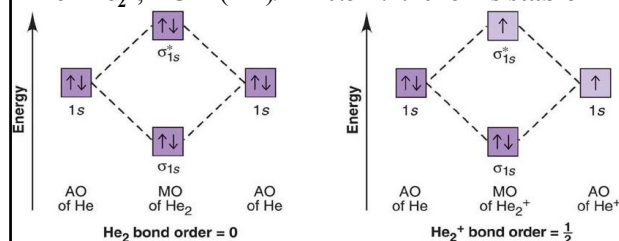
$$BO = (B - A)/2$$

**B** - #  $e^-$ s on bonding **MOs**  
**A** - #  $e^-$ s on antibonding **MOs**

➤ In general, the higher the **BO** the stronger the bond



- For  $H_2$ , the **two**  $e^-$ s enter  $\sigma_{1s}$  → **BO** =  $(2-0)/2 = 1$  (the energy of the molecule is lower than that of the free atoms) ⇒ the molecule is **stable**
- For  $He_2$ , the **four**  $e^-$ s fill both  $\sigma_{1s}$  and  $\sigma_{1s}^*$  → **BO** =  $(2-2)/2 = 0$  (the bonding effects of  $\sigma_{1s}$  and  $\sigma_{1s}^*$  cancel) ⇒ the molecule is **unstable**
- For  $He_2^+$ , **BO** =  $(2-1)/2 = 0.5$  ⇒ the ion is **stable**



• Electron configurations

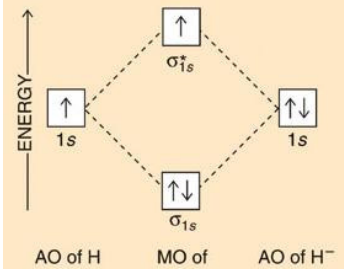
– For  $H_2 \rightarrow (\sigma_{1s})^2$ ; For  $He_2^+ \rightarrow (\sigma_{1s})^2 (\sigma_{1s}^*)^1$

**Example:** Is  $H_2^-$  a stable ion? Electr. Configuration?

Total # of valence e<sup>-</sup>s  $\rightarrow 1(H) + 1(H) + 1(\text{charge}) = 3$

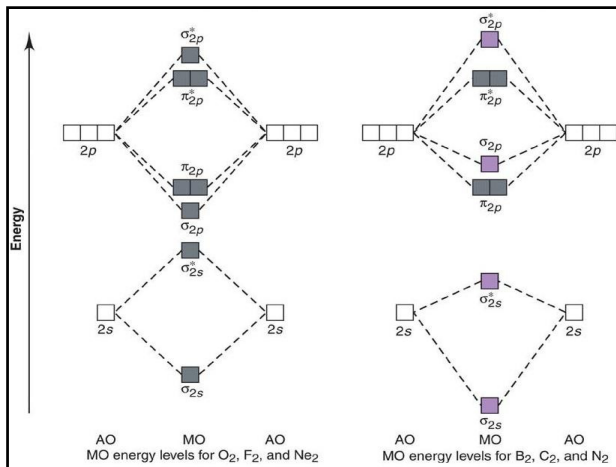
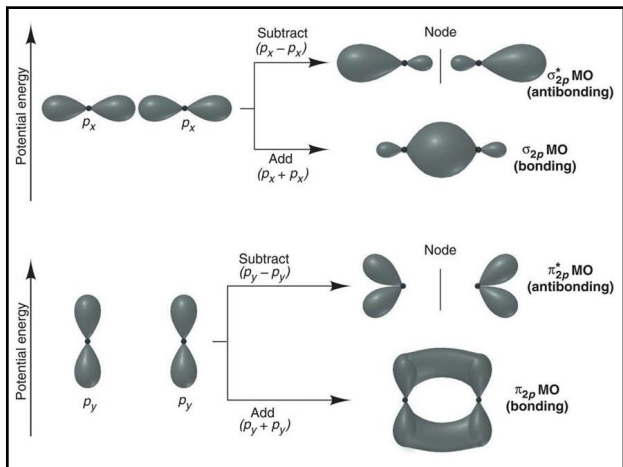
Electron configuration  
 $\Rightarrow (\sigma_{1s})^2 (\sigma_{1s}^*)^1$

BO =  $(2-1)/2 = 0.5$   
 $\Rightarrow$  **the ion is stable**



**MOs for Period 2 Homonuclear Diatomic Molecules**

- Only the valence AOs are considered – **one 2s** orbital and **three 2p** orbitals for each atom
- When two atoms approach each other:
  - The **2s** orbitals overlap to form two  $\sigma$  MOs, bonding ( $\sigma_{2s}$ ) and antibonding ( $\sigma_{2s}^*$ ) (as in  $H_2$ )
  - The **2p** orbitals directed along the internuclear axis overlap to form **two**  $\sigma$  MOs, bonding ( $\sigma_{2p}$ ) and antibonding ( $\sigma_{2p}^*$ )
  - The **2p** orbitals perpendicular to the internuclear axis overlap to form **four**  $\pi$  MOs, **two** bonding ( $\pi_{2p}$ ) and **two** antibonding ( $\pi_{2p}^*$ )



**Example:  $N_2$**

Total # of valence e<sup>-</sup>s

$\rightarrow 5+5=10$

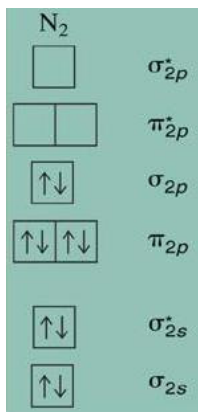
$\rightarrow$  place **10 e<sup>-</sup>s** on the lowest energy MOs

Electron configuration  $\rightarrow$

$N_2: (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2$

BO =  $(8 - 2)/2 = 3$

$\rightarrow$  Consistent with the Lewis structure ( $:N \equiv N:$ )



**Example:  $O_2$**

Total # of valence e<sup>-</sup>s  $\rightarrow 6+6=12$

$\rightarrow$  **12 e<sup>-</sup>s** on the lowest energy MOs

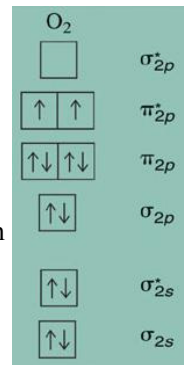
Electron configuration  $\rightarrow$

$O_2: (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^2$

BO =  $(8 - 4)/2 = 2$

$\rightarrow$  The electron configuration of  $O_2$  contains **two unpaired electrons** on the  $\pi_{2p}^*$  MOs (Hund's rule)  
 – Inconsistent with the Lewis structure ( $:\ddot{O}=\ddot{O}:$ )

$\rightarrow$  Explains the **paramagnetic**



### Example: Be<sub>2</sub>

Total # of valence e<sup>-</sup>s → 2+2=4

⇒ place 4 e<sup>-</sup>s on the lowest energy MOs

Electron configuration → (σ<sub>2s</sub>)<sup>2</sup>(σ<sub>2s</sub><sup>\*</sup>)<sup>2</sup>

BO = (2 - 2)/2 = 0 → (the molecule is unstable)

### Example: Ne<sub>2</sub>

Total # of valence e<sup>-</sup>s → 8+8=16

⇒ place 16 e<sup>-</sup>s on the lowest energy MOs

Electron configuration →

(σ<sub>2s</sub>)<sup>2</sup>(σ<sub>2s</sub><sup>\*</sup>)<sup>2</sup>(σ<sub>2p</sub>)<sup>2</sup>(π<sub>2p</sub>)<sup>4</sup>(π<sub>2p</sub><sup>\*</sup>)<sup>4</sup>(σ<sub>2p</sub><sup>\*</sup>)<sup>2</sup>

BO = (8 - 8)/2 = 0 → (the molecule is unstable)

	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	
σ <sub>2p</sub> <sup>*</sup>	□	□	□	□	□	σ <sub>2p</sub> <sup>*</sup>
π <sub>2p</sub> <sup>*</sup>	□□	□□	□□	↑↑	↑↓↑↓	π <sub>2p</sub> <sup>*</sup>
σ <sub>2p</sub>	□	□	↑↓	↑↓↑↓	↑↓↑↓	σ <sub>2p</sub>
π <sub>2p</sub>	↑↑	↑↓↑↓	↑↓↑↓	↑↓	↑↓	π <sub>2p</sub>
σ <sub>2s</sub> <sup>*</sup>	↑↓	↑↓	↑↓	↑↓	↑↓	σ <sub>2s</sub> <sup>*</sup>
σ <sub>2s</sub>	↑↓	↑↓	↑↓	↑↓	↑↓	σ <sub>2s</sub>
Bond order	1	2	3	2	1	
Magnetic properties	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	
Valence electron configuration	(σ <sub>2s</sub> ) <sup>2</sup> (σ <sub>2s</sub> <sup>*</sup> ) <sup>2</sup> (π <sub>2p</sub> ) <sup>2</sup>	(σ <sub>2s</sub> ) <sup>2</sup> (σ <sub>2s</sub> <sup>*</sup> ) <sup>2</sup> (π <sub>2p</sub> ) <sup>4</sup>	(σ <sub>2s</sub> ) <sup>2</sup> (σ <sub>2s</sub> <sup>*</sup> ) <sup>2</sup> (π <sub>2p</sub> ) <sup>4</sup> (σ <sub>2p</sub> ) <sup>2</sup>	(σ <sub>2s</sub> ) <sup>2</sup> (σ <sub>2s</sub> <sup>*</sup> ) <sup>2</sup> (σ <sub>2p</sub> ) <sup>2</sup> (π <sub>2p</sub> ) <sup>4</sup> (π <sub>2p</sub> <sup>*</sup> ) <sup>2</sup>	(σ <sub>2s</sub> ) <sup>2</sup> (σ <sub>2s</sub> <sup>*</sup> ) <sup>2</sup> (σ <sub>2p</sub> ) <sup>2</sup> (π <sub>2p</sub> ) <sup>4</sup> (π <sub>2p</sub> <sup>*</sup> ) <sup>4</sup>	

### Example:

Predict the electron configuration, BO and bond strength of the N<sub>2</sub><sup>-</sup> ion

Total # of valence e<sup>-</sup>s → 5+5+1=11

⇒ place 11 e<sup>-</sup>s on the lowest energy MOs

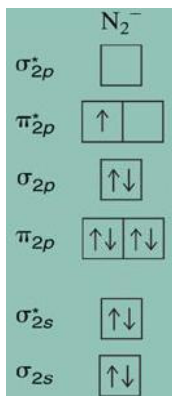
Electron configuration →

(σ<sub>2s</sub>)<sup>2</sup>(σ<sub>2s</sub><sup>\*</sup>)<sup>2</sup>(π<sub>2p</sub>)<sup>4</sup>(σ<sub>2p</sub>)<sup>2</sup>(π<sub>2p</sub><sup>\*</sup>)<sup>1</sup>

BO = (8 - 3)/2 = 2.5

→The ion exists (BO > 0)

→The bond is weaker than that in N<sub>2</sub> (lower bond order 2.5 < 3)



### MOs for Heteronuclear Diatomic Molecules

- Diagrams are asymmetric since the AOs of the two atoms have different energies

#### Example: NO

Total # of valence e<sup>-</sup>s → 5+6=11

⇒ place 11 e<sup>-</sup>s on the lowest energy MOs

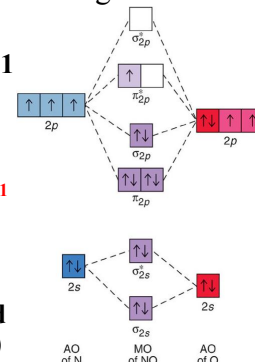
Electron configuration →

(σ<sub>2s</sub>)<sup>2</sup>(σ<sub>2s</sub><sup>\*</sup>)<sup>2</sup>(π<sub>2p</sub>)<sup>4</sup>(σ<sub>2p</sub>)<sup>2</sup>(π<sub>2p</sub><sup>\*</sup>)<sup>1</sup>

BO = (8 - 3)/2 = 2.5

→Contains **one unpaired e<sup>-</sup>**

→Explains the existence of **odd electron molecules (radicals)**

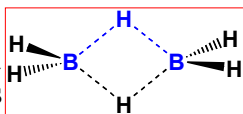


### MOs in Polyatomic Species

- The general approach is similar
- The MOs are built by more than two AOs  
– Linear Combinations of Atomic Orbitals (LCAO)
- The MOs are spread over the entire molecule  
– **Delocalization** of electrons  
– Explains the existence of **electron deficient molecules** (on average less than two electrons may be binding two atoms → multi-center bonds)

#### Example: B<sub>2</sub>H<sub>6</sub>

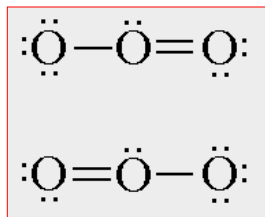
The H-bridges are based on a three-center MO holding 2e<sup>-</sup>s



- Delocalization** and **multi-center bonds** eliminate the need of resonance structures used by the Lewis's and VB models

#### Example: O<sub>3</sub>

Resonance structures:



Lowest energy π-MO:

