

## Molecules Module – Lecture 6: Multiple Bonds and Introduce Molecular Orbital Theory

Learning Objective	Openstax 2e Chapter
Multiple Covalent Bonds	<a href="#"><u>8.3</u></a>
Molecular Orbital Theory	<a href="#"><u>8.4</u></a>

### Suggested Practice Problems

[Chapter 8 Exercises](#) – Questions: 23, 25, 27, 35, 37

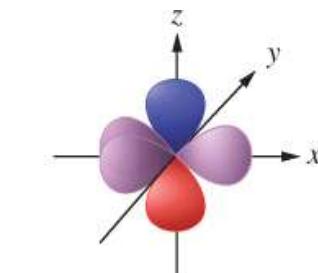
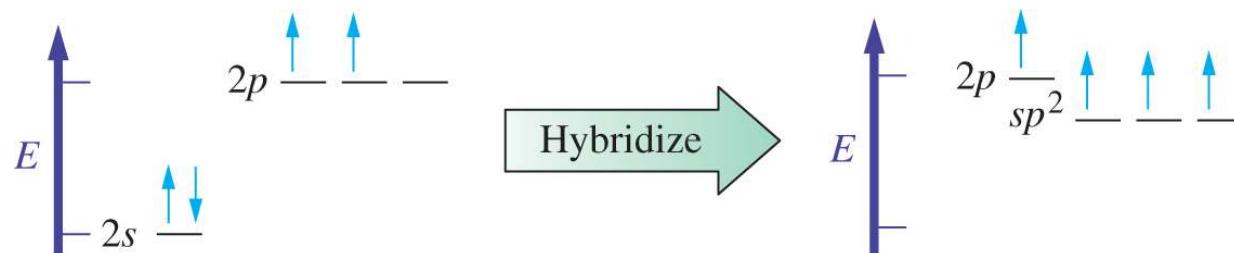
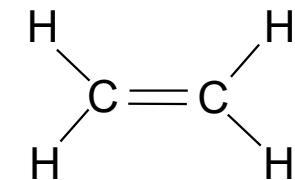
Answers can be found in the [Chapter 8 Answer Key](#)

# Multiple Covalent Bonds

Two different types of orbital overlap occur when multiple bonds are described by the VB method.

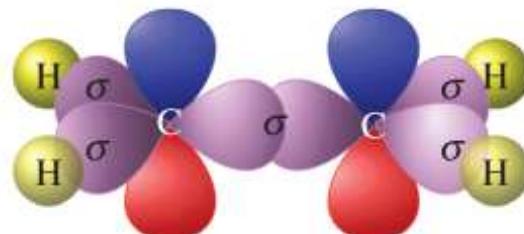
- **Example:**  $\text{C}_2\text{H}_4$

- Lewis theory tells us it has a double bond
- VSEPR theory tells us each carbon is trigonal planar

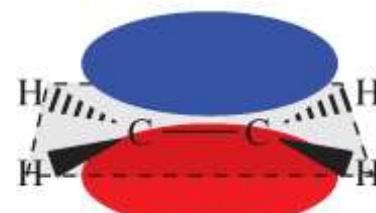


The set of orbitals  $sp^2 + p$

**Sigma ( $\sigma$ ) bond – direct orbital overlap**



**Pi ( $\pi$ ) bond – indirect orbital overlap**

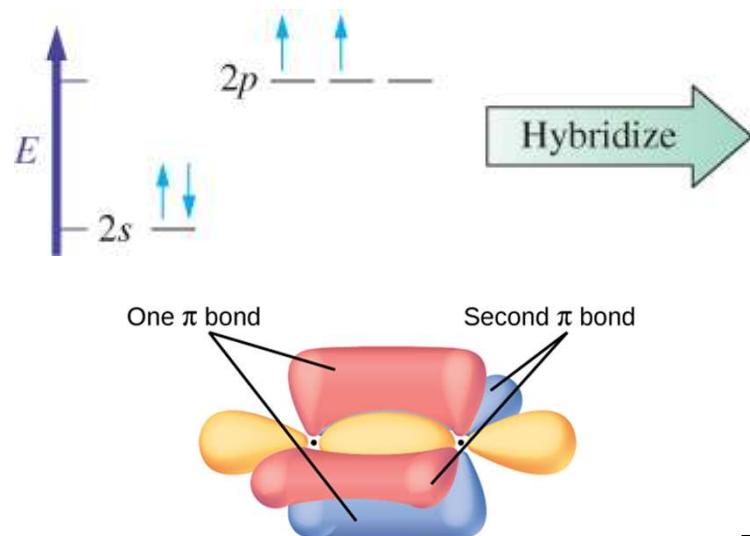


# Multiple Covalent Bonds

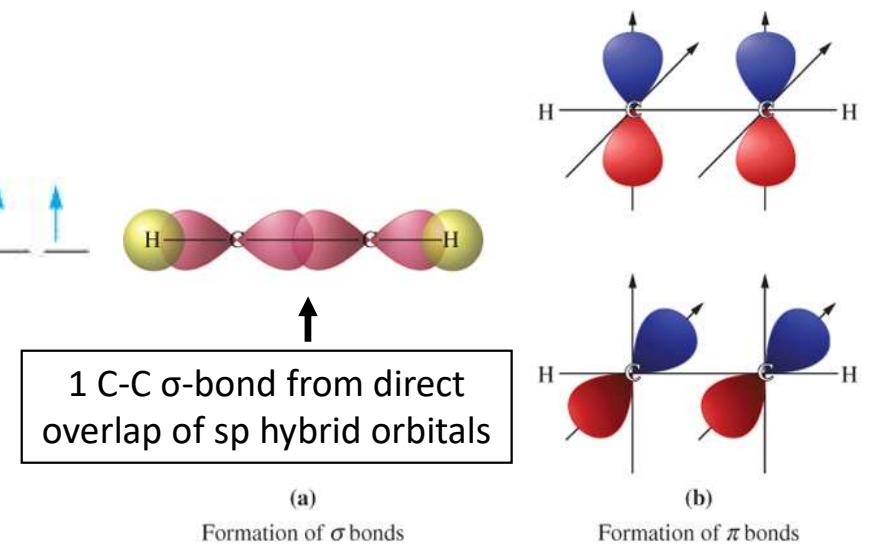
Two different types of orbital overlap occur when multiple bonds are described by the VB method.

- **Example: C<sub>2</sub>H<sub>2</sub>**

- Lewis theory tells us it has a triple bond
- VSEPR theory tells us each carbon is linear



Alternate picture showing  $\pi$ -bonds with calculated shape. Wire frame shows  $\pi$ -bond in x-y plane.  $\sigma$ -bond is hidden below.

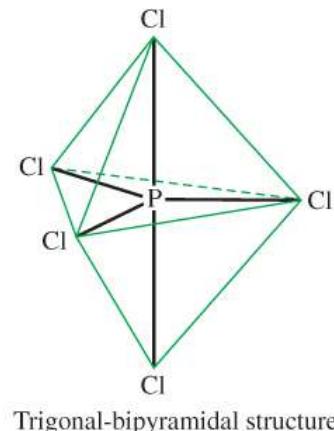
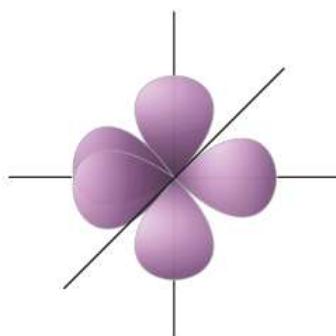
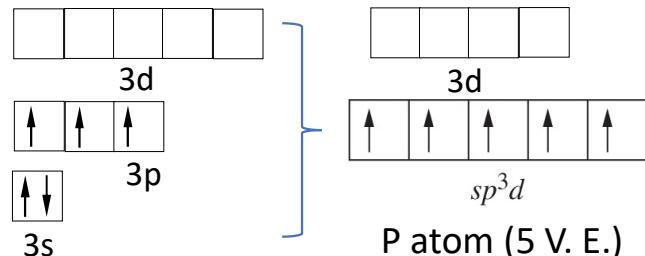


2 C-C  $\pi$ -bonds from indirect overlap of unhybridized p orbitals

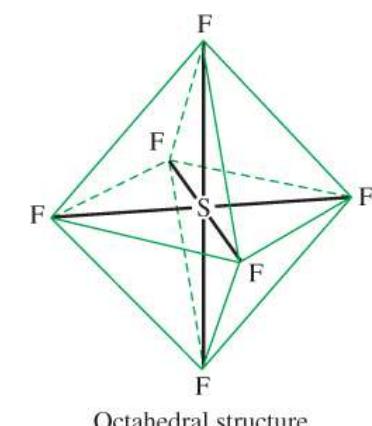
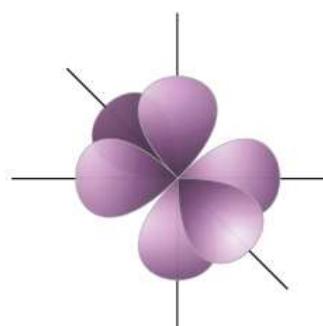
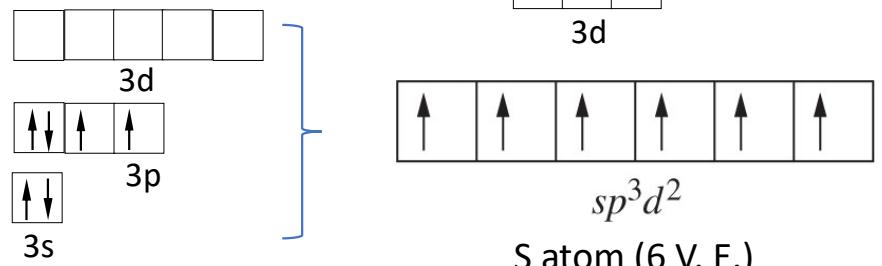
## What about trigonal bipyramidal and octahedral structures?

- For 3<sup>rd</sup> and 4<sup>th</sup> period elements, atomic *d* orbitals can be involved in hybridization.
- This is related to molecules with expanded valence shells.

**Example:** PCl<sub>5</sub>



**Example:** SF<sub>6</sub>



## Hybrid Orbitals and Valence-Shell Electron-Pair Repulsion (VSEPR) Theory

Steps in the determination of hybrid orbitals from a molecular formula.

- (1) Write a plausible Lewis structure.
- (2) Use VSEPR to predict electron-group geometry.
- (3) Select the corresponding hybridization scheme from Table 11.1.

**TABLE 11.1 Some Hybrid Orbitals and Their Geometric Orientations**

% s-character	Hybrid Orbitals	Geometric Orientation (Electron group geometry)	Example
1/2=50%	$sp$	Linear	$\text{BeCl}_2$
1/3=33%	$sp^2$	Trigonal-planar	$\text{BF}_3$
1/4=25%	$sp^3$	Tetrahedral	$\text{CH}_4$
1/5=20%	$sp^3d$	Trigonal-bipyramidal	$\text{PCl}_5$
1/6=17%	$sp^3d^2$	Octahedral	$\text{SF}_6$

## Example 1

What is the hybridization at the central oxygen atom in O<sub>3</sub>?

(1) Write Lewis structure



(2) Use VSEPR to predict electron-group geometry.

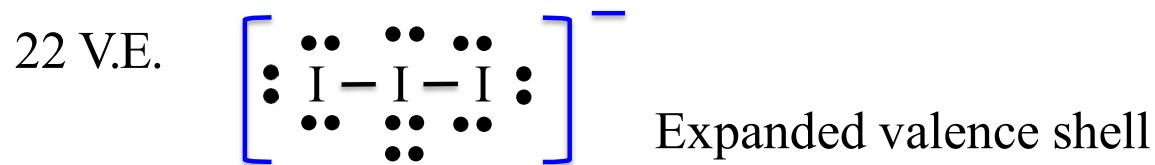
At the central O atom, it is AX<sub>2</sub>E, thus should be trigonal planar for the electron group geometry and bent for the molecular geometry.

(3) Select the corresponding hybridization scheme.

For a trigonal planar electron group geometry, the hybridization is sp<sup>2</sup>.

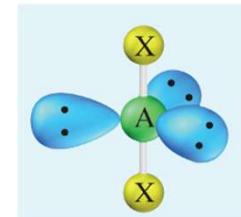
## Example 2 What is the hybridization at the central iodine atom in $I_3^-$ ?

(1) Write Lewis structure



(2) Use VSEPR to predict electron-group geometry.

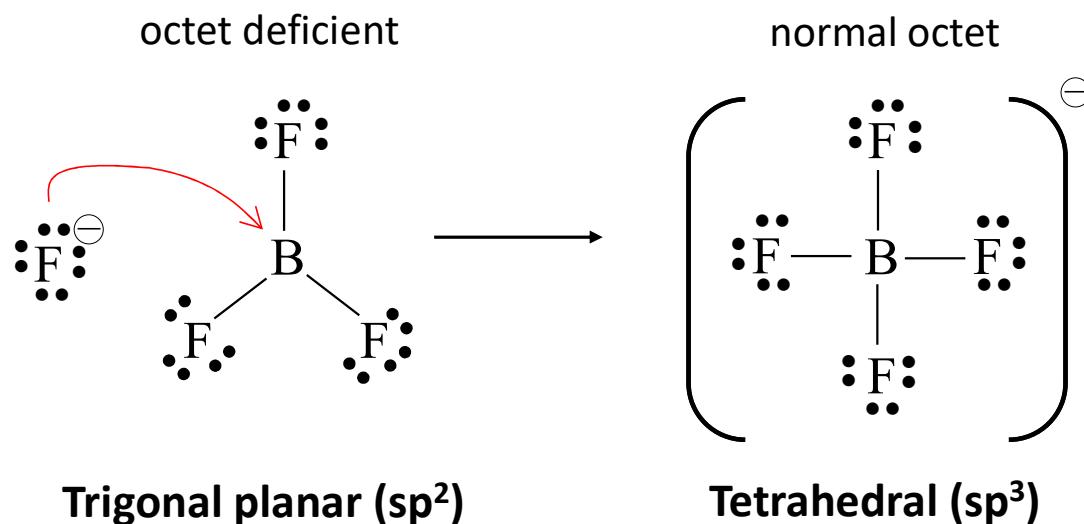
- At the central I atom, it is  $AX_2E_3$ , thus should be trigonal bipyramidal (electron group geometry). Molecular geometry is linear.



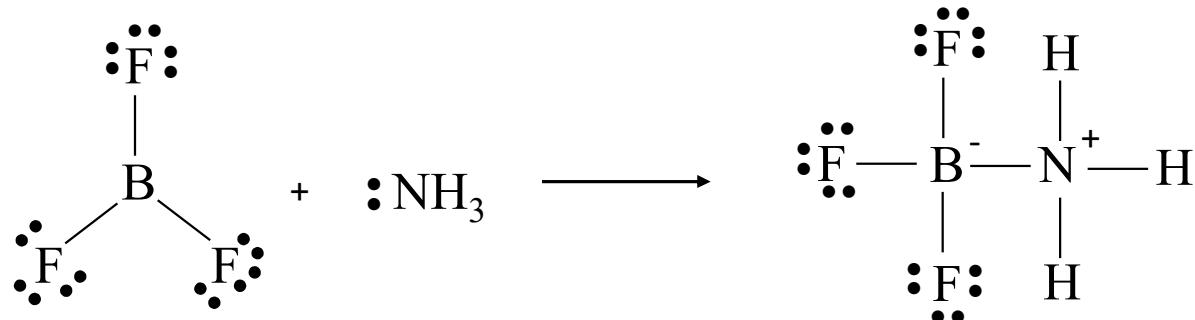
(3) Select the corresponding hybridization scheme.

- For trigonal bipyramidal, it is  $sp^3d$  hybridization.
- Recall that  $O_3$  is bent, but azide  $N_3^-$  is linear.

## Hybridization scheme can change in a reaction

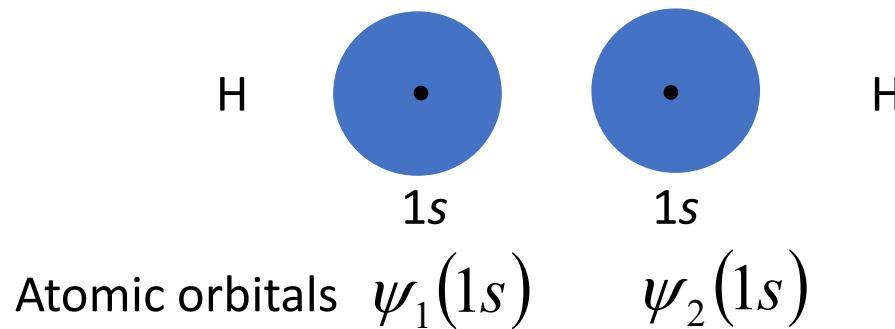


Similarly,  $\text{BF}_3$  can readily react with  $\text{NH}_3$



# Molecular Orbital (MO) Theory

- We have learned that atomic orbitals (AOs) are localized on atoms.
- In molecular orbital (MO) theory, we combine atomic orbitals to create new molecular orbitals that are localized differently.
- **Example:**  $\text{H}_2$

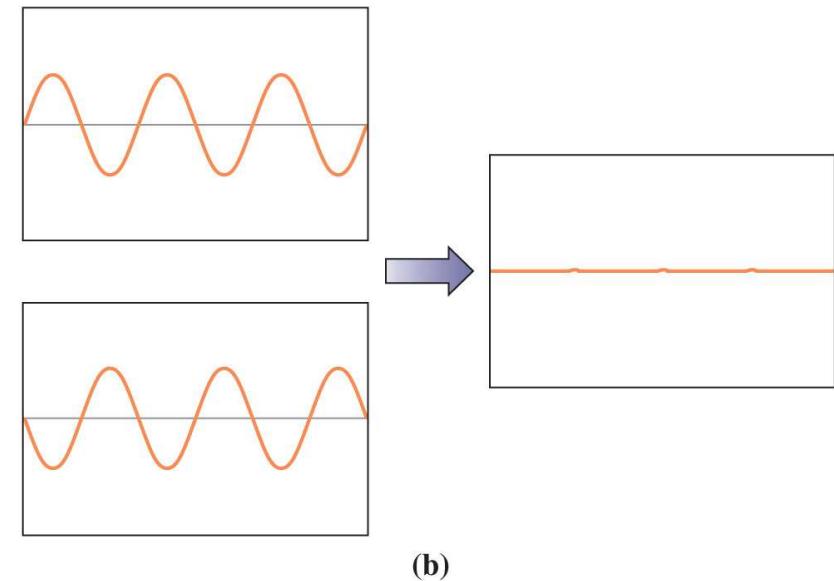
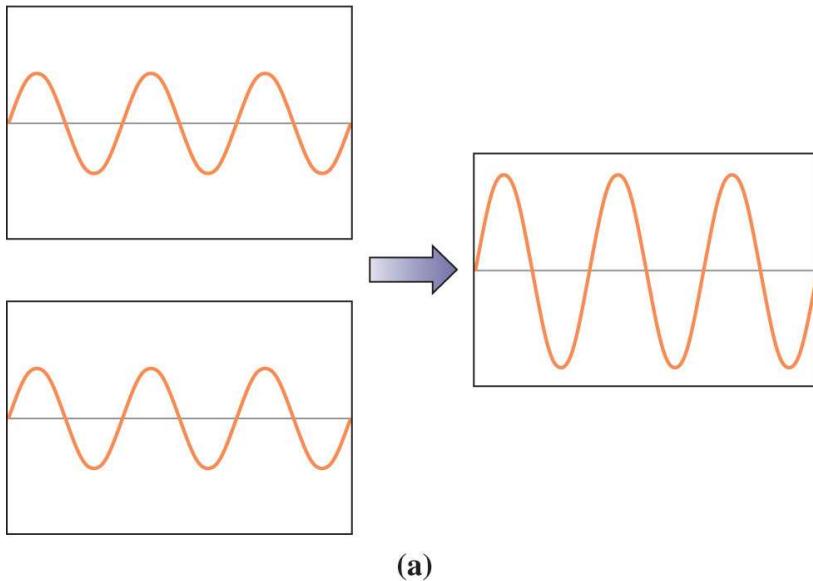


We can define two molecular orbitals (MO) for  $\text{H}_2$  as:

$$\psi_{Mol} = \psi_1 + \psi_2$$
$$\psi_{Mol} = \psi_1 - \psi_2$$

- This is known as the **linear combination of atomic orbitals (LCAO)** approximation. So, the LCAO-MO theory.

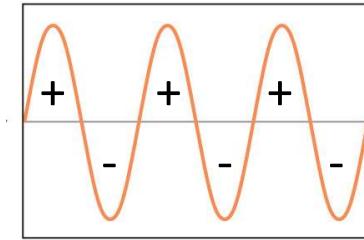
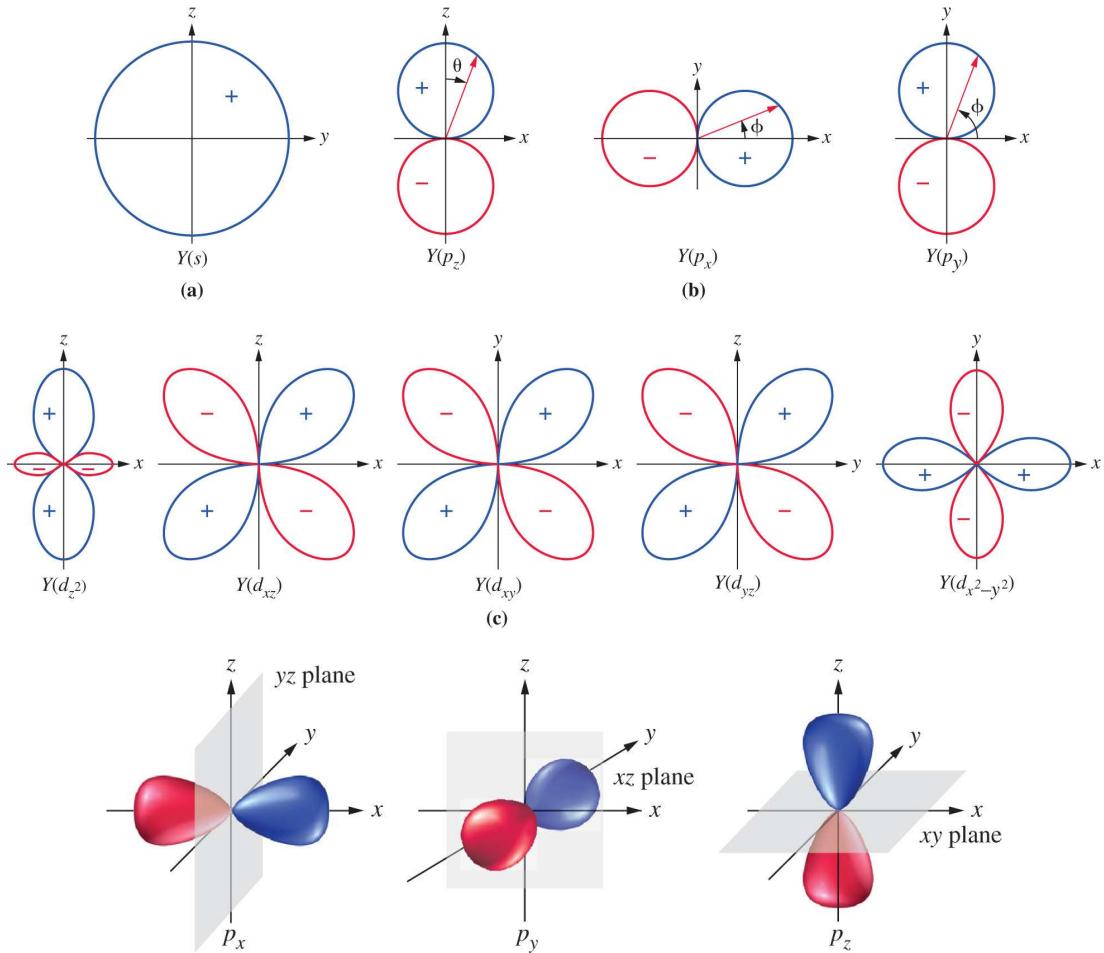
## Review: Constructive & Destructive Interference of Waves



**Constructive interference** occurs when the troughs and crests are in phase, leading to addition of the two waves.

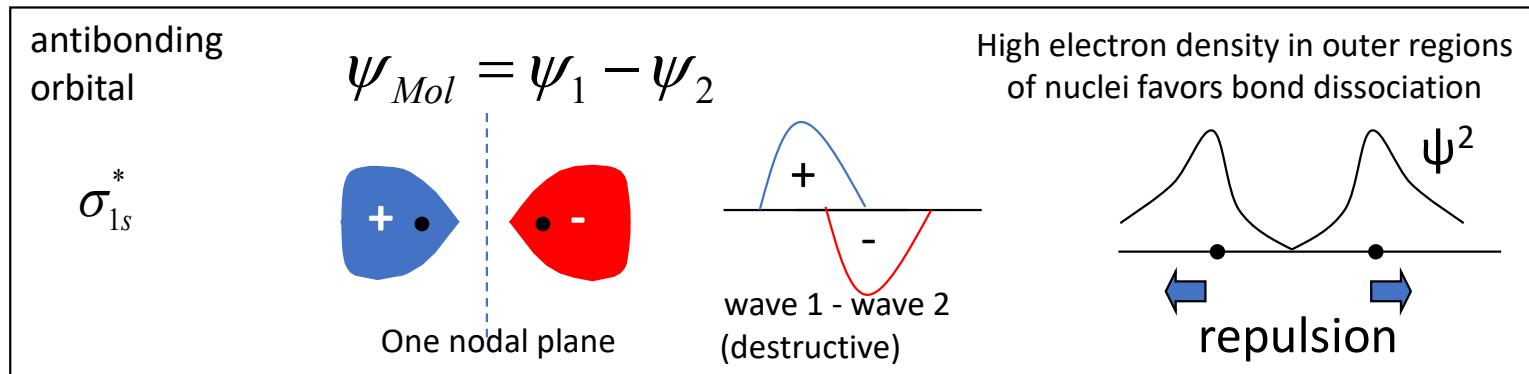
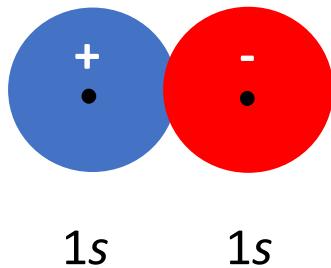
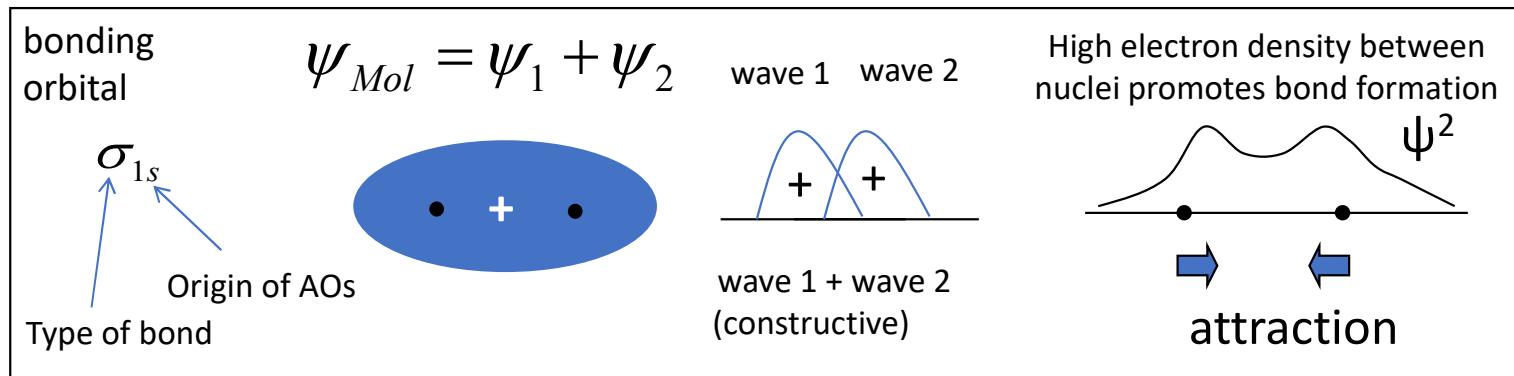
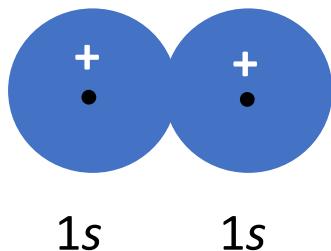
**Destructive interference** occurs when the troughs and crests are out of phase, leading to cancellation of the two waves.

## Wavefunctions can also be “in phase” or “out of phase”

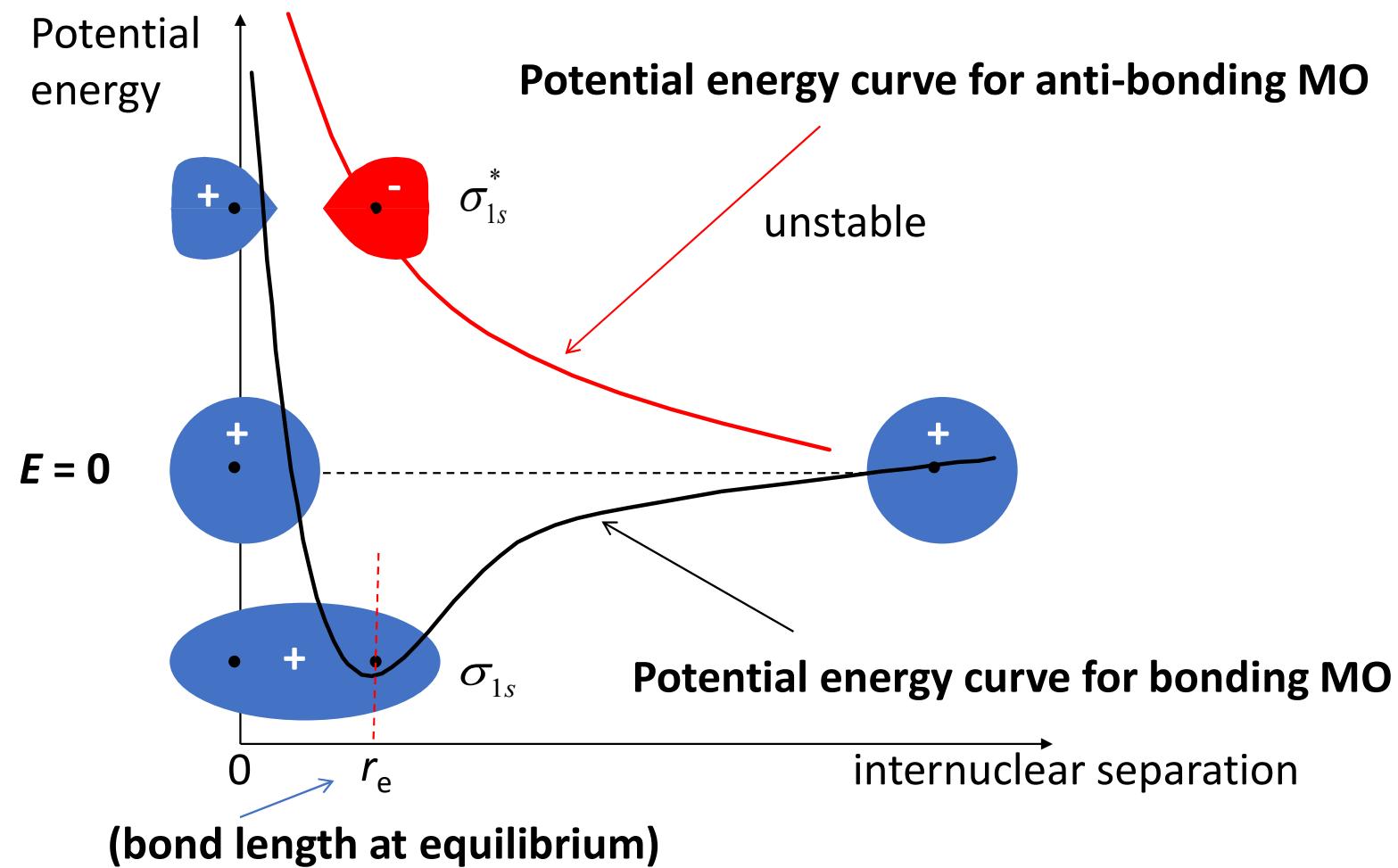


- The “signs” of AOs (atomic wavefunctions) have nothing to do with electron spin and charge.
- They reflect the “phase” relationship between different regions of the “standing wave”.

# Construct and Label MOs of H<sub>2</sub>



# MO and Potential Energy

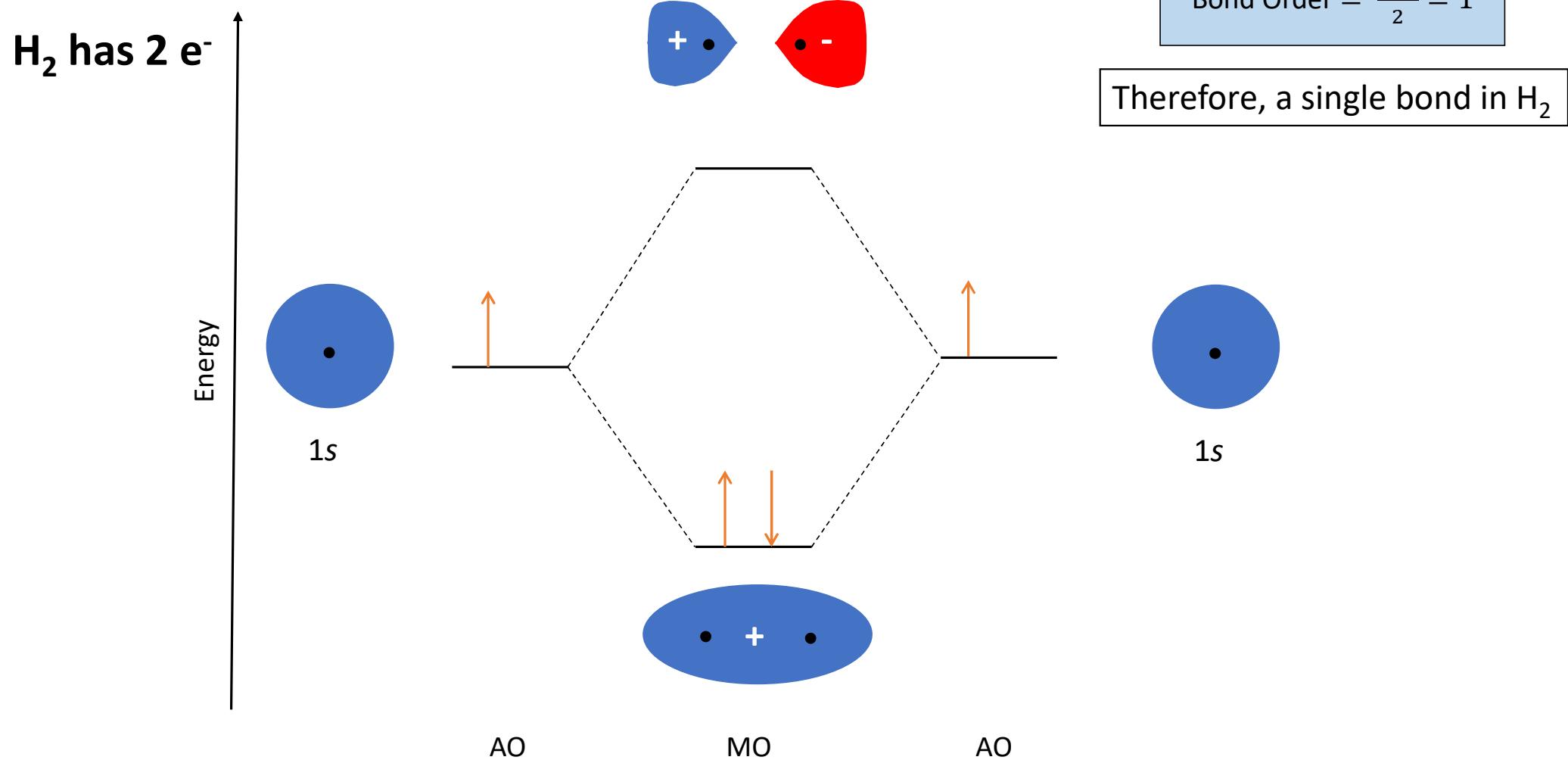


## Basic Rules in MO Theory

- Each MO can be represented mathematically as a linear combination of AOs
- The total number of MOs is equal to the total number of AOs
- MOs can be classified as bonding, antibonding, or nonbonding
- The electron configuration for the molecule is obtained by placing electrons into the MOs according to their energies (from low to high) following similar Hund's rules.
- Stable species have more electrons in bonding MOs than antibonding MOs.

$$\text{Bond Order} = \frac{\# \text{ of } e^- \text{ in bonding MOs} - \# \text{ of } e^- \text{ in antibonding MOs}}{2}$$

# Diatomc Molecules in the 1<sup>st</sup> Period



# Diatom Molecules in the 1<sup>st</sup> Period

$$\text{Bond Order} = \frac{2-2}{2} = 0$$

