

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

Learning Objective	Openstax 2e Chapter
Multiple Covalent Bonds	<u>8.3</u>
Molecular Orbital Theory	<u>8.4</u>

Suggested Practice Problems

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

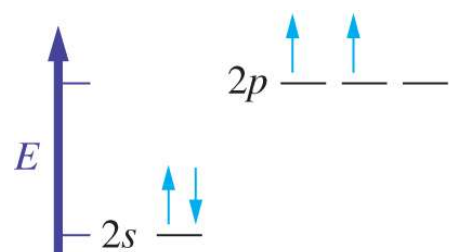
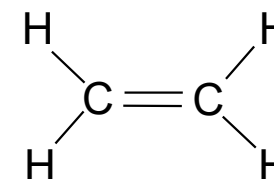
Answers can be found in the [Chapter 8 Answer Key](#)

Multiple Covalent Bonds

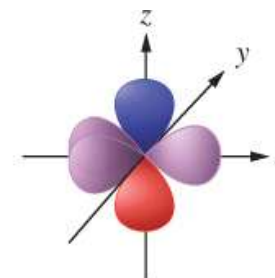
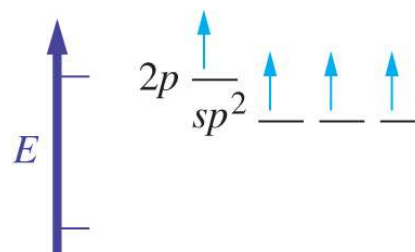
Two different types of orbital overlap occur when multiple bonds are described by the VB method.

- **Example:** C_2H_4

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

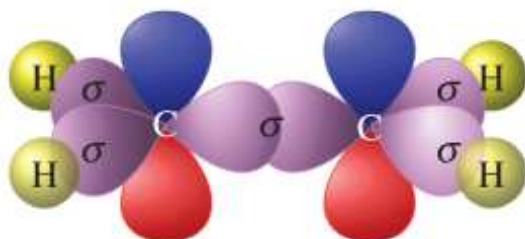


Hybridize

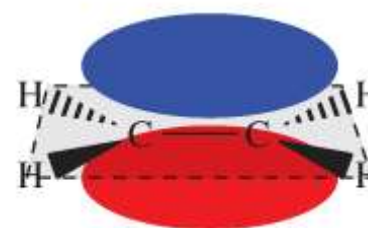


The set of orbitals $sp^2 + p$

Sigma (σ) bond – direct orbital overlap



Pi (π) bond – indirect orbital overlap

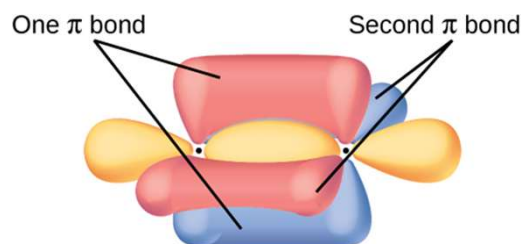
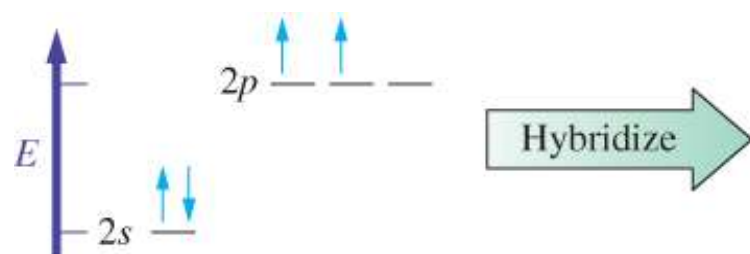


Multiple Covalent Bonds

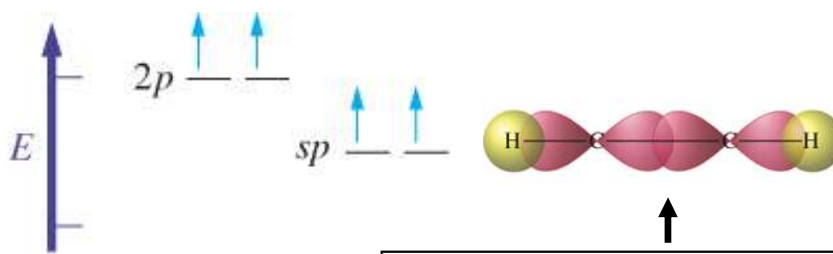
Two different types of orbital overlap occur when multiple bonds are described by the VB method.

• Example: C_2H_2

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

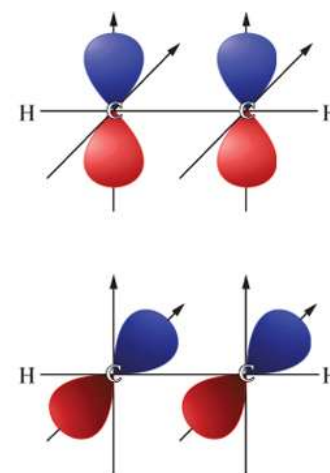


Picture showing two π -bonds cut away to show σ -bond on x-axis



1 C-C σ -bond from direct overlap of sp hybrid orbitals

(a)
Formation of σ bonds



(b)
Formation of π bonds

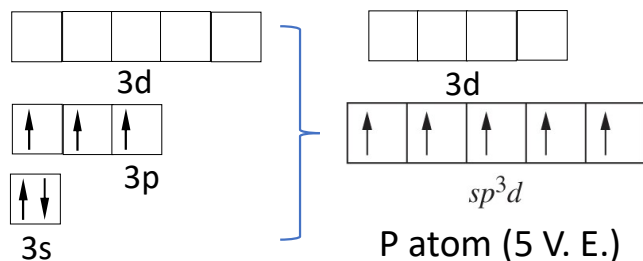
2 C-C π -bonds from indirect overlap of unhybridized p orbitals

Alternate picture showing π -bonds with calculated shape. Wire frame shows π -bond in x-y plane. σ -bond is hidden below.

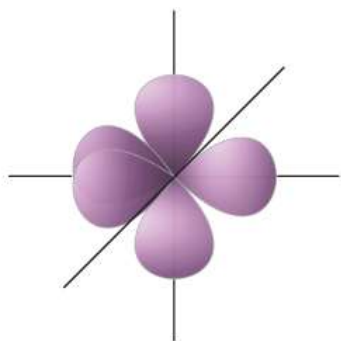
What about trigonal bipyramidal and octahedral structures?

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

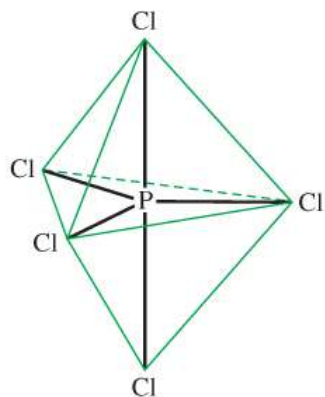
Example: PCl₅



P atom (5 V. E.)

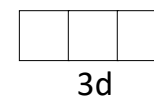
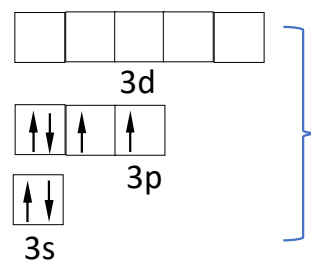


(a) sp^3d orbitals

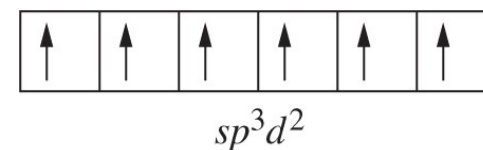


Trigonal-bipyramidal structure

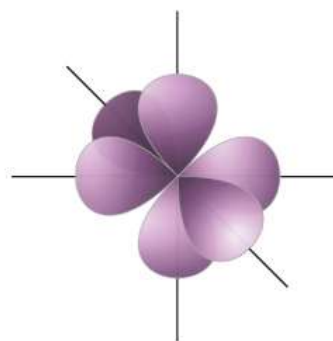
Example: SF₆



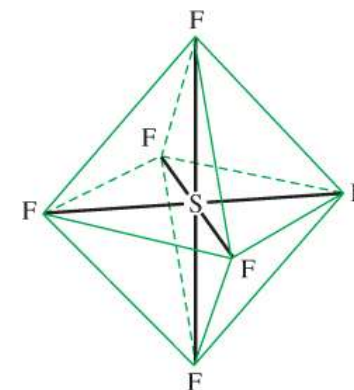
3d



S atom (6 V. E.)



(b) sp^3d^2 orbitals



Octahedral structure

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.

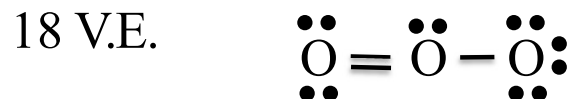
TABLE 11.1 Some Hybrid Orbitals and Their Geometric Orientations

% s-character	Hybrid Orbitals	Geometric Orientation (Electron group geometry)	Example
$1/2=50\%$	sp	Linear	BeCl_2
$1/3=33\%$	sp^2	Trigonal-planar	BF_3
$1/4=25\%$	sp^3	Tetrahedral	CH_4
$1/5=20\%$	sp^3d	Trigonal-bipyramidal	PCl_5
$1/6=17\%$	sp^3d^2	Octahedral	SF_6

Example 1

What is the hybridization at the central oxygen atom in O_3 ?

(1) Write Lewis structure



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

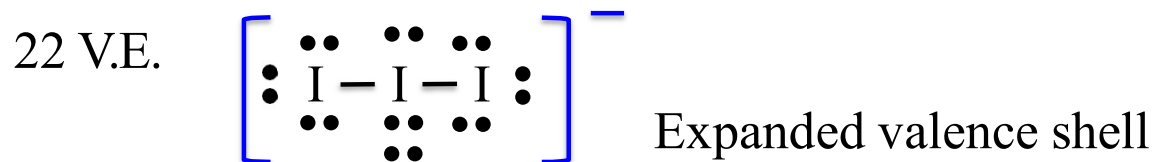
At the central O atom, it is AX_2E , thus should be trigonal planar for the electron group geometry and bent for the molecular geometry.

(3) Select the corresponding hybridization scheme.

For a trigonal planar electron group geometry, the hybridization is sp^2 .

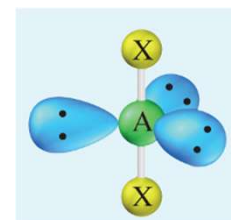
Example 2 What is the hybridization at the central iodine atom in I_3^- ?

(1) Write Lewis structure



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

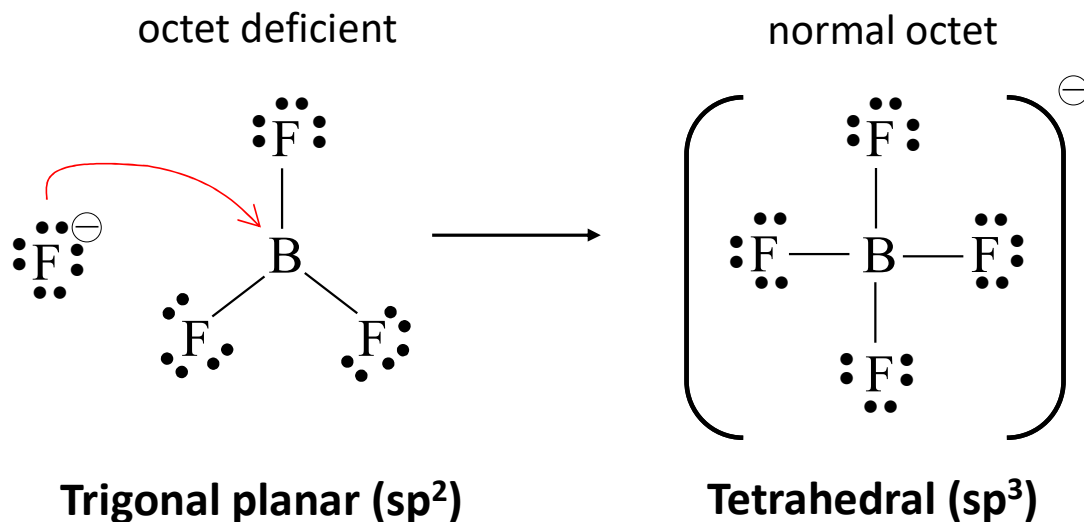
- At the central I atom, it is AX_2E_3 , thus should be trigonal bipyramidal (electron group geometry). Molecular geometry is linear.



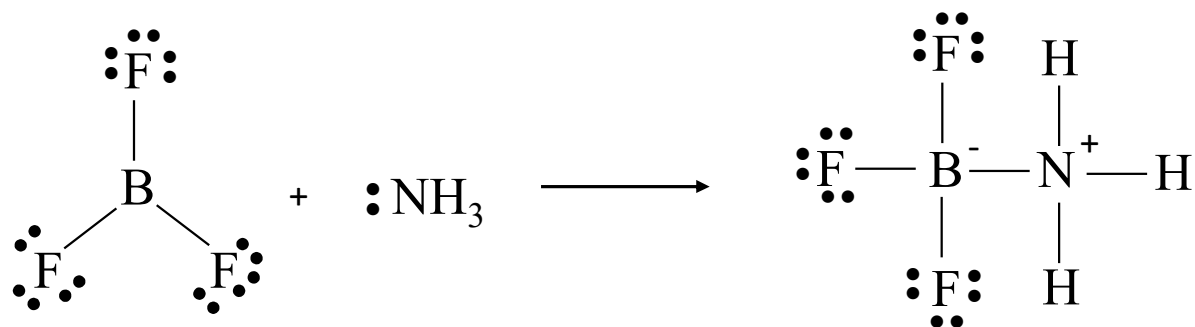
(3) Select the corresponding hybridization scheme.

- 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

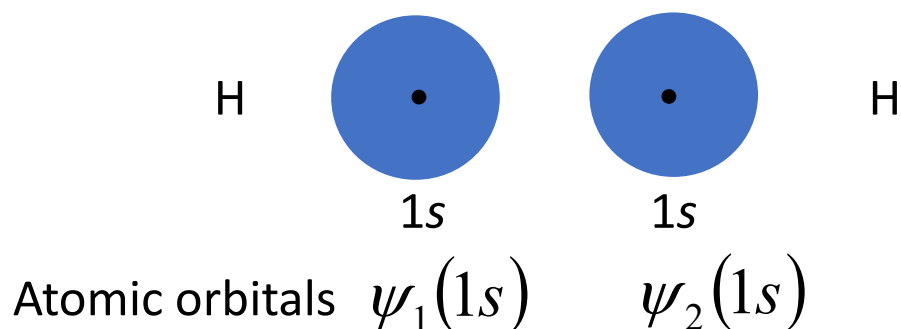


Similarly, BF_3 can
readily react
with NH_3



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:** H_2



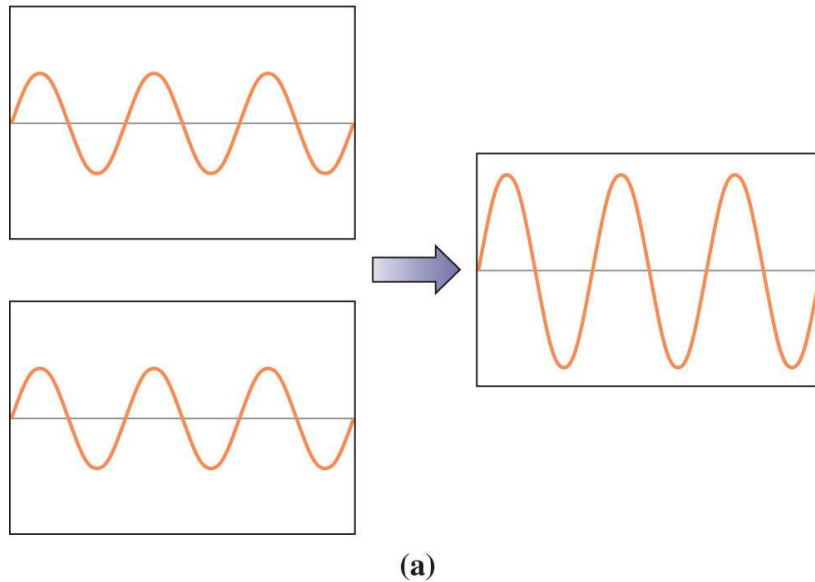
We can define **two** molecular orbitals (MO) for H_2 as:

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

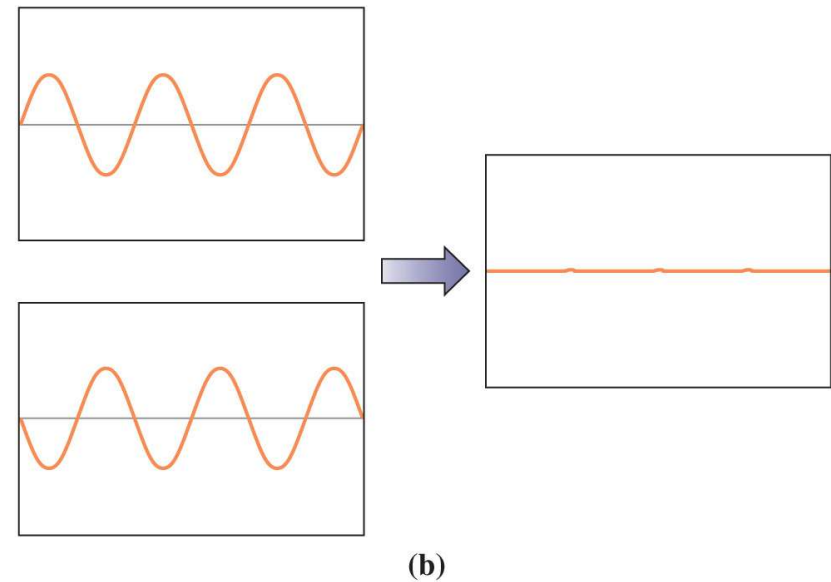
$$\psi_{Mol} = \psi_1 - \psi_2$$

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

Review: Constructive & Destructive Interference of Waves

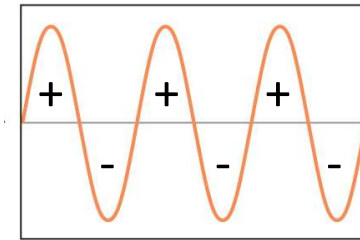
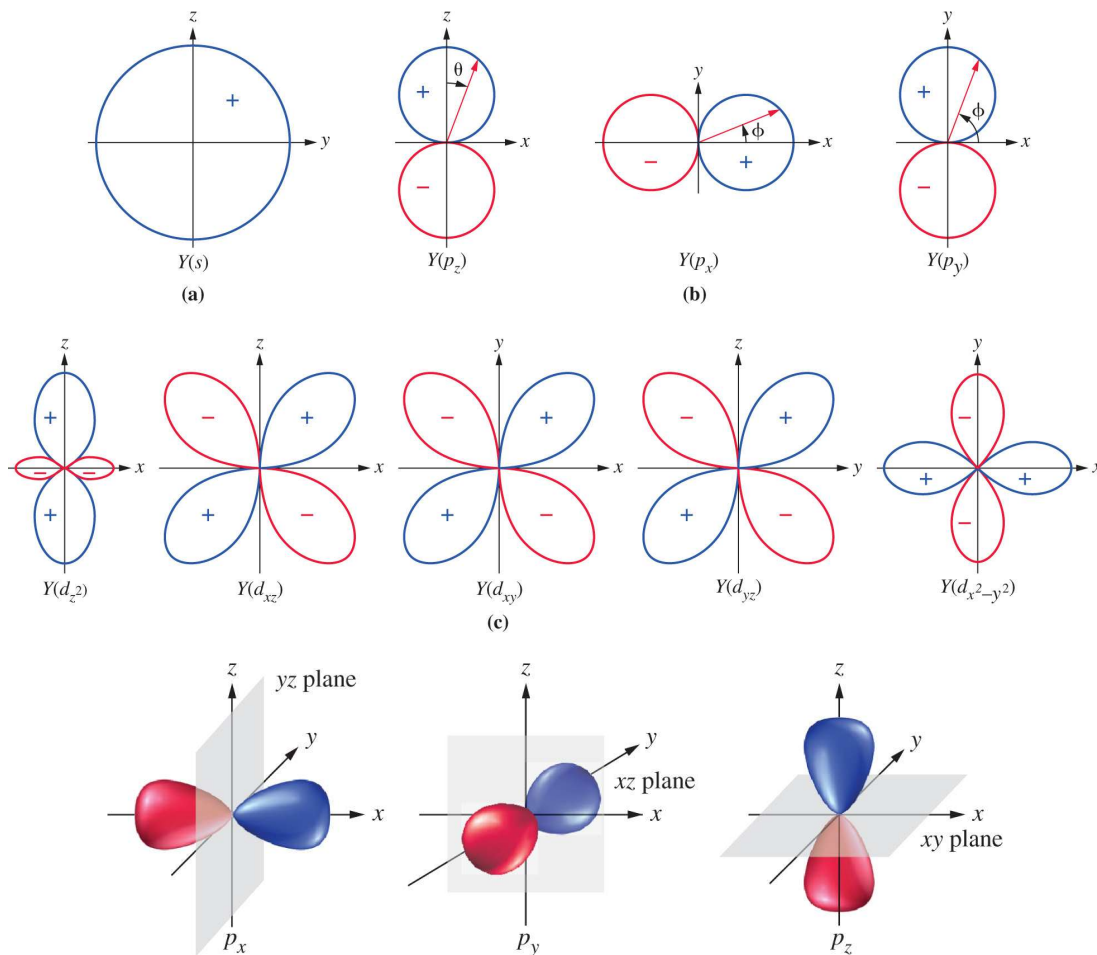


Constructive interference occurs when the troughs and crests are in phase, leading to addition of the two waves.



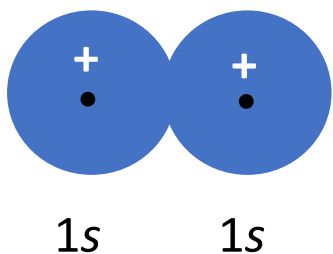
Destructive interference occurs when the troughs and crests are out of phase, leading to cancellation of the two waves.

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 H₂



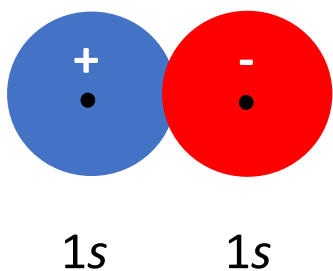
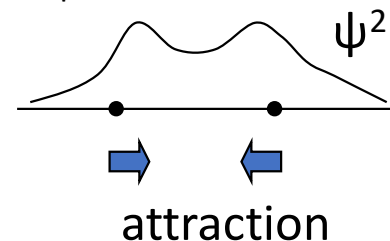
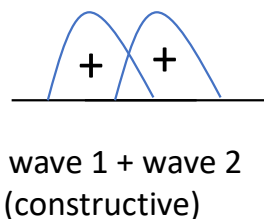
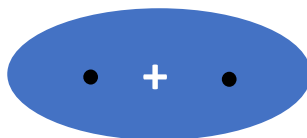
bonding
orbital

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

wave 1 wave 2

High electron density between
nuclei promotes bond formation

σ_{1s}
↑
Origin of AOs
Type of bond

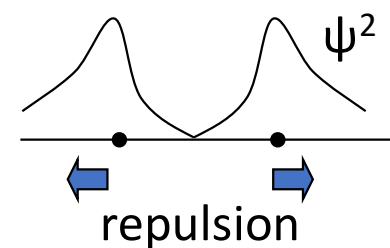
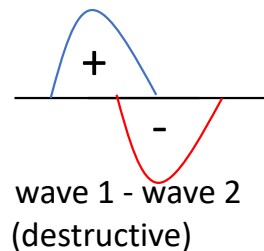
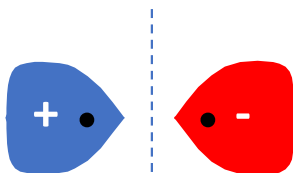


antibonding
orbital

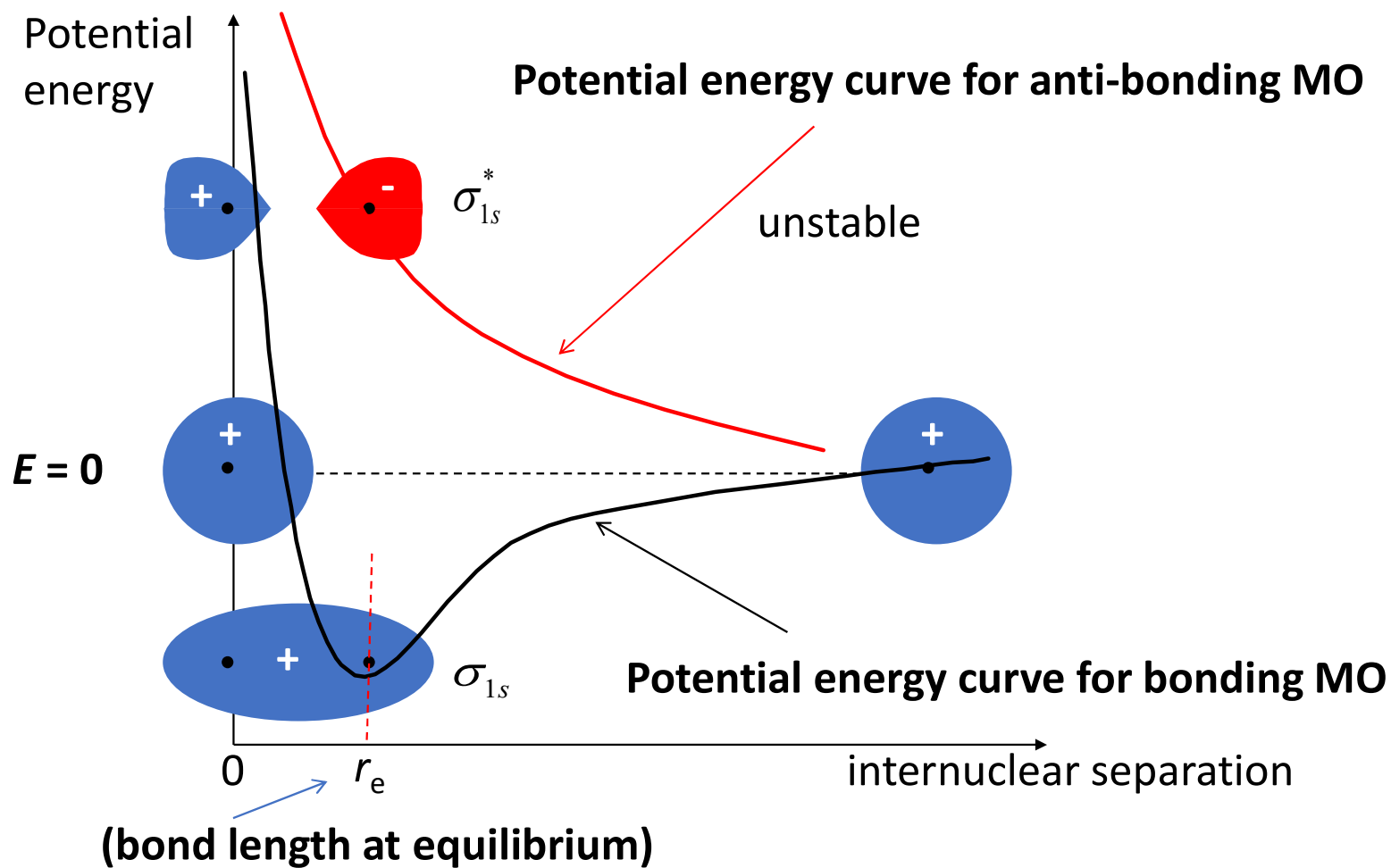
$$\psi_{Mol} = \psi_1 - \psi_2$$

High electron density in outer regions
of nuclei favors bond dissociation

σ_{1s}^*



MO and Potential Energy



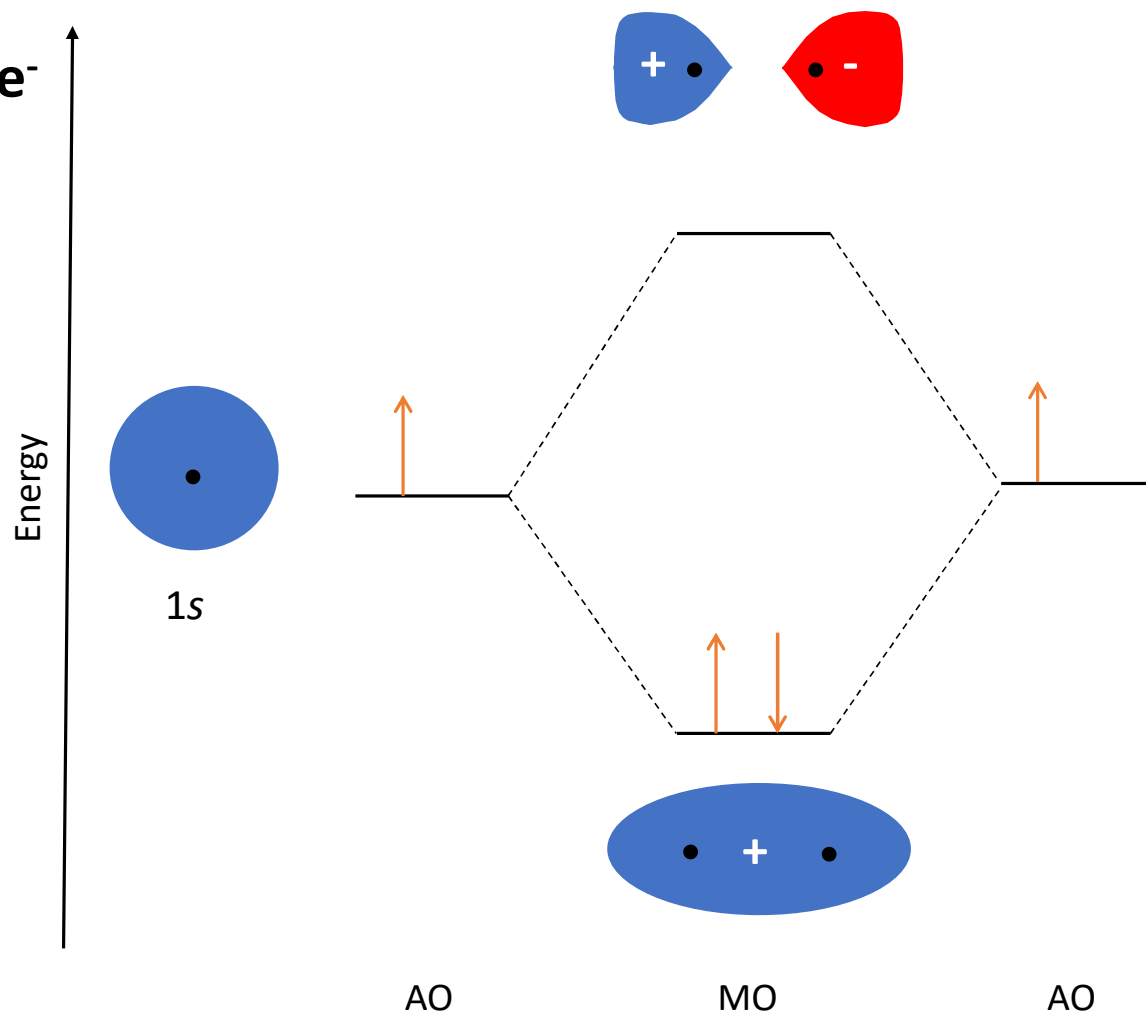
Basic Rules in MO Theory

- 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.

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

Diatomic Molecules in the 1st Period

H₂ has 2 e⁻



$$\text{Bond Order} = \frac{2-0}{2} = 1$$

Therefore, a single bond in H₂

Diatomic Molecules in the 1st Period

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

This means that He₂ **will not** be formed by covalent bonding!

Note, He₂ pairs do exist at extremely low temperatures where the two He atoms are held together by weak van der Waals forces. MO theory is limited to interactions through covalent bonds.

