

# Theories covered

Valence Bond Theory (Hybridization)

**Molecular Orbital Theory**  
**(Using linear combination of Atomic Orbitals)**

# Theories covered

## Molecular Orbital Theory (Using linear combination of Atomic Orbitals)

### Concept Video

Understanding how Molecular Orbitals Form

Preparing MO diagrams for Period 1

### Concept Video

Prepare MO energy diagrams for simple diatomic molecules (second period).

Fill MO energy diagrams for simple heteronuclear diatomic molecules.

### Concept Video

Using MO theory to explain resonance (delocalized pi systems)

### Concept Video

Describe metallic bonding and physical properties using band theory models.

# Theories of Chemical Bonding

## What will you be learning? Learning Objectives:

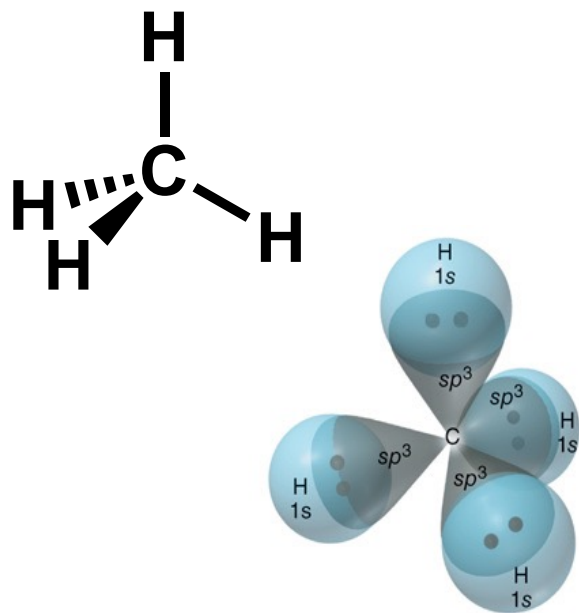
- Explain bonding in diatomic molecules in terms of Valence Bond Theory
- Indicate which orbitals' overlap gives sigma ( $\sigma$ ) bond and/or pi ( $\pi$ ) bonds.
- Sketch pictures of bonding orbitals using valence bond theory.
- Use VSEPR theory to predict hybridization
- Predict hybridization:  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $sp^3d$ ,  $sp^3d^2$
- **Explain molecular orbital theory (MO theory)**
- **Understand that the combination of any two AOs creates a bonding & anti-bonding MO pair.**
- **Prepare MO energy diagrams for simple diatomic molecules (first/second periods).**
- **Fill MO energy diagrams for simple heteronuclear diatomic molecules.**
- **Determine bond orders and predict magnetic properties of diatomics.**
- **Fill  $\pi$  MO energy diagrams for delocalized systems (including benzene and ozone).**
- **Describe metallic bonding and physical properties using band theory models.**

# Valence Bond Theory: What does it tell us

Valence Bond Theory: A covalent bond forms when orbitals of two atoms overlap and a pair of electrons occupy the overlap region

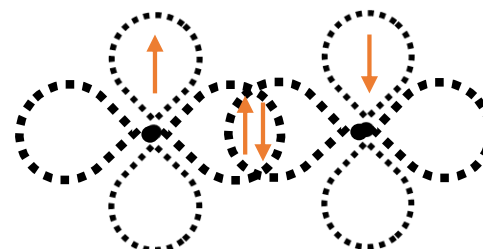
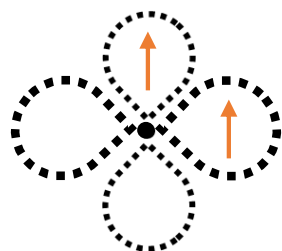
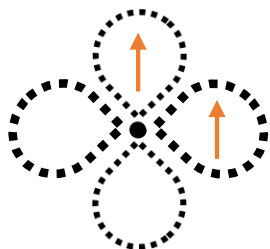
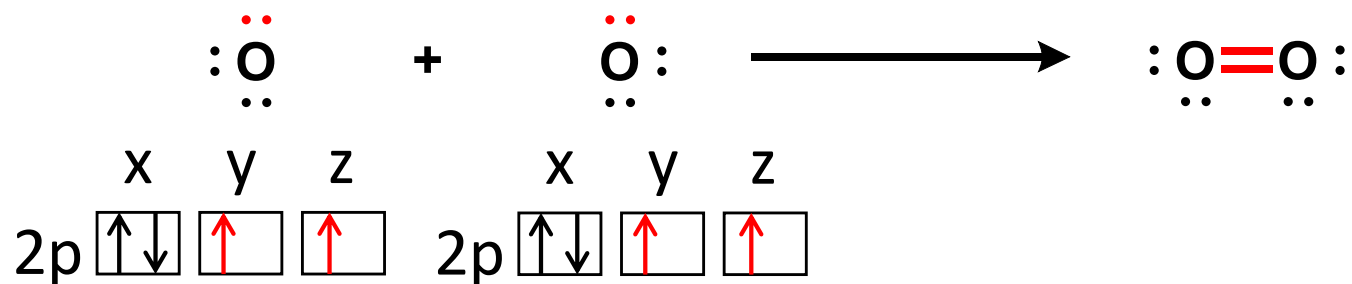
+

Hybridization: Mixing of orbitals to obtain equivalent orbitals

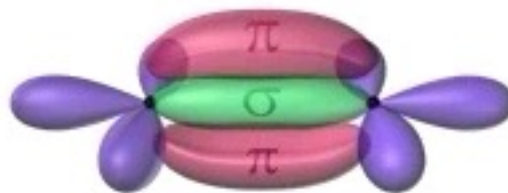


This combination of VBT and hybridization helped explain both nature and geometry of compounds  
But there are limitations

# Valence Bond Theory: What does it tell us



**Formation of s and p bonds**  
**All electrons are paired**



According to valence bond theory: All electrons in  $\text{O}_2$  molecule are paired – so the molecule should be diamagnetic. From experiments:  $\text{O}_2$  molecule is paramagnetic

# But there are limitations

## Limitations of Valence Bond Theory + Hybridization:

1. No conservation of orbital energy.
2. Cannot explain experimental data (magnetic or spectroscopic)  
According to VBT  $O_2$  molecule is diamagnetic (no unpaired electron) – this is not what is observed.
3. Cannot explain resonance (delocalization of electrons).

Another Theory to Reconcile the above limitations:  
**Molecular Orbital Theory**

# Concept Videos Recap

**Electrons have wave and particle nature – Quantum mechanics describes this dual behaviour**

**Wave function ( $\Psi$ )** : Wave function is defined by characteristic quantum numbers ( $n, l, m_l$ ), and this mathematical function describes an electron in an atom, or probability of finding the electron (using  $\Psi^2$ )

Wave function (like waves) can have a phase sign ( $\Psi_+$  or  $\Psi_-$ ). These signs **do not imply charge**

**Atomic Orbitals** : Mathematically derived regions of space with 90-95% probability of containing an electron (s, p, and d are atomic orbitals)

# Concept Videos Recap

**Wave function ( $\Psi$ )** : Wave function is defined by characteristic quantum numbers ( $n$ ,  $l$ ,  $m_l$ ), and this mathematical function describes an electron in an atom, or probability of finding the electron (using  $\Psi^2$ )

Wave function (like waves) can have a phase sign ( $\Psi_+$  or  $\Psi_-$ ). These signs **do not imply charge**

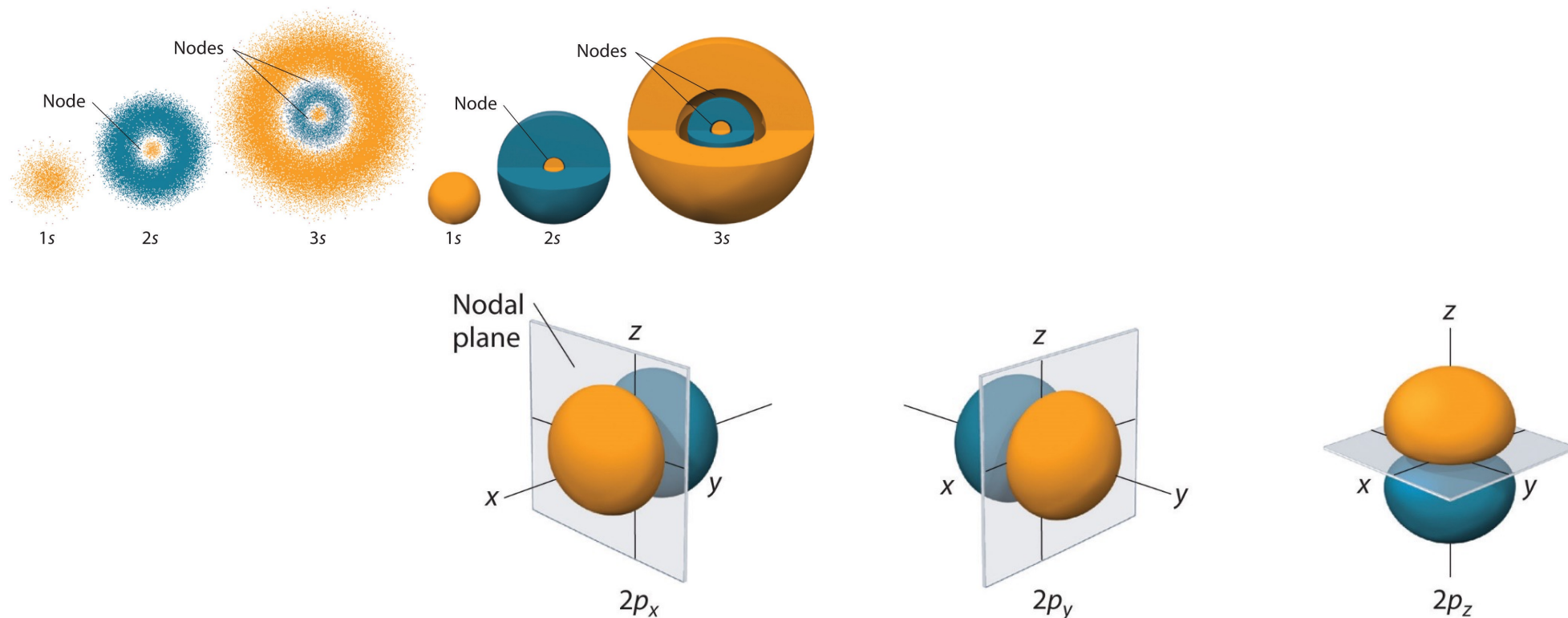


IMAGE COURTESY: [UCDAVIS CHEMWIKI](#), [CC BY-NC-SA 3.0 US](#)

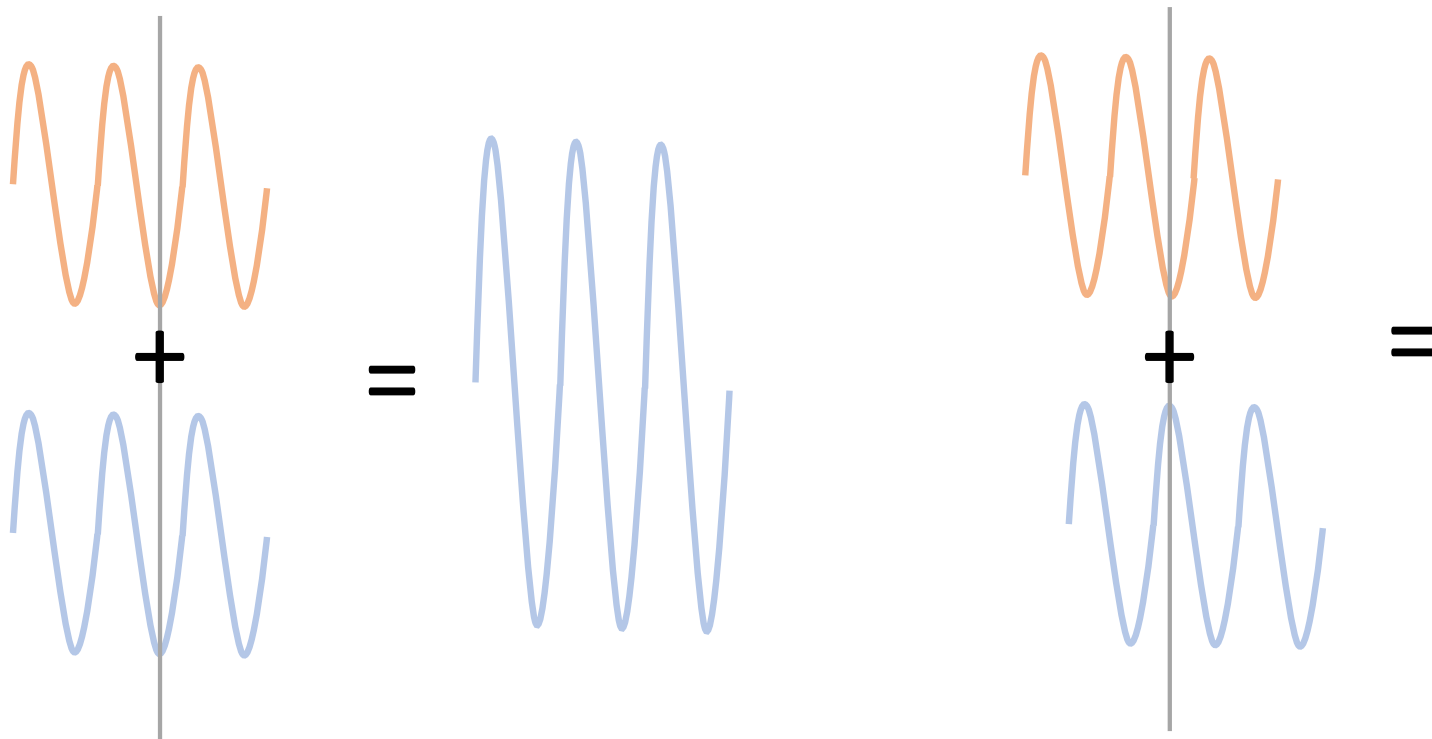


# Wave nature of particles

**Wave function ( $\Psi$ )** : Wave function is defined by characteristic quantum numbers ( $n, l, m_l$ ), and this mathematical function describes an electron in an atom, or probability of finding the electron (using  $\Psi^2$ )

Wave function (like waves) can have a phase sign ( $\Psi_+$  or  $\Psi_-$ ). These signs **do not imply charge**

Waves can have constructive (in-phase) or destructive (out of phase) interference

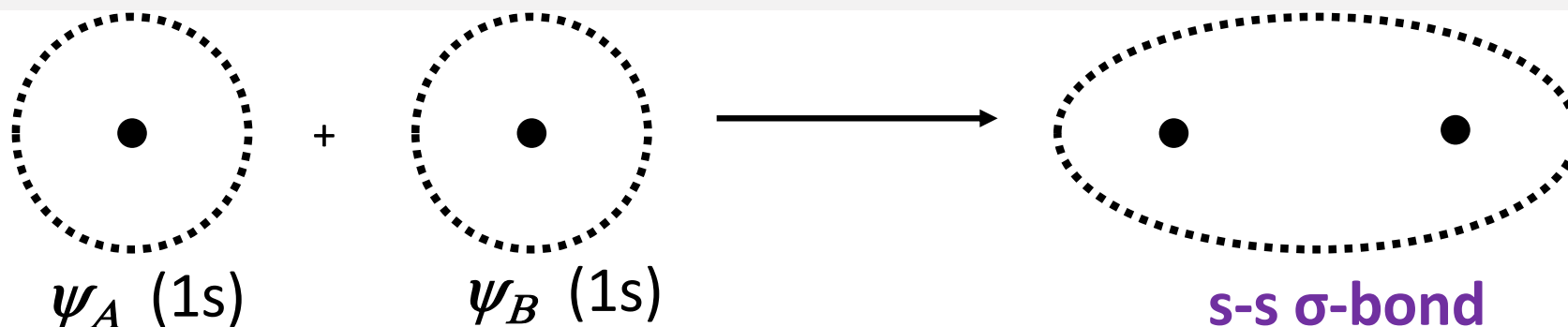


# Molecular Orbital Theory

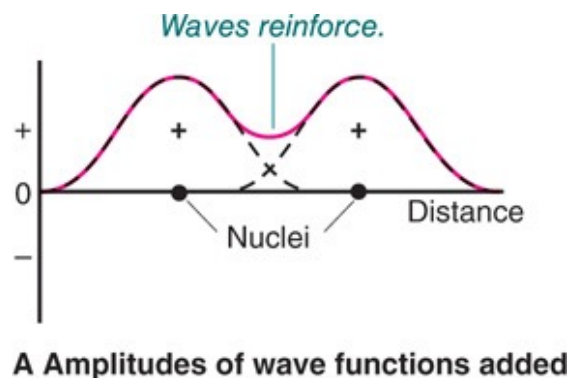
- Molecular Orbitals (MO) result from the Linear Combination of Atomic Orbitals (LCAO).
- This combination may be in-phase (bonding orbitals) or out-of-phase (antibonding orbitals)
- The number of molecular orbitals is always equal to the sum of the number of atomic orbitals that combine

# Molecular Orbital Theory

**Bonding Molecular Orbitals:** These orbitals arise from Linear Combination of Atomic Orbitals (**LCAO**) under conditions of **constructive interference**



This constructive interference leads to increased amplitude in the inter-nuclear region - increased probability density ( $\Psi^2$ ) between the nuclei

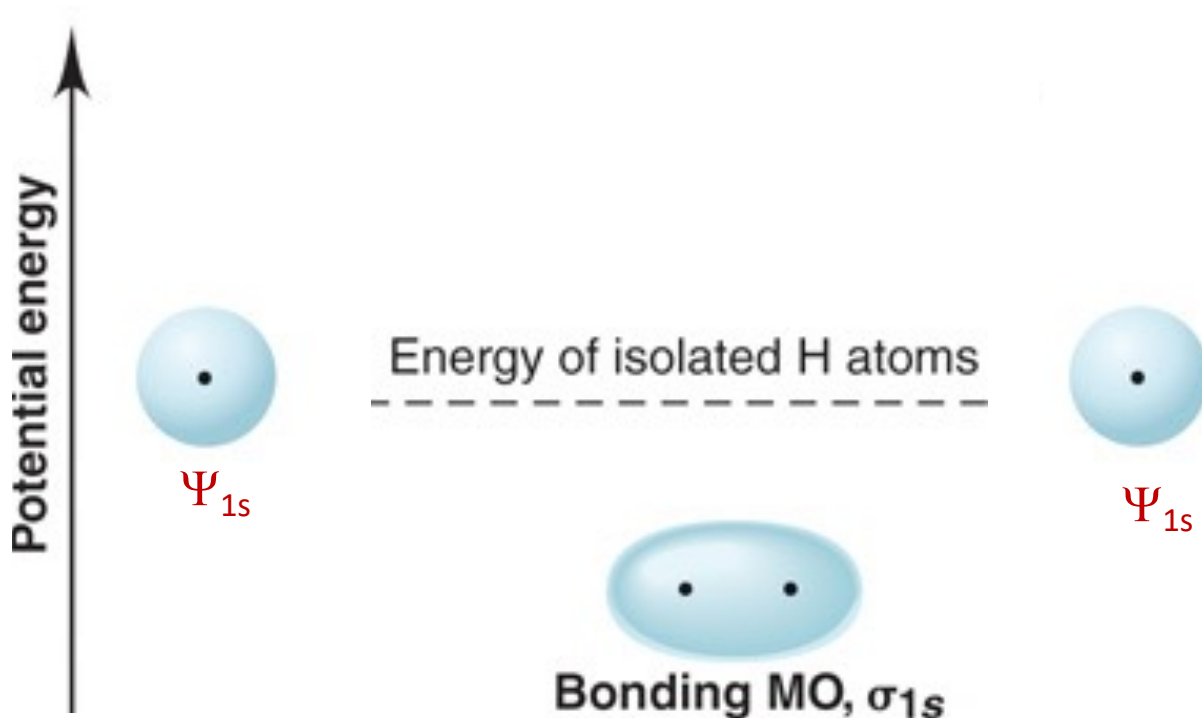


Electrons in this bonding molecular orbital is attracted to BOTH the nuclei

Energy of this bonding molecular orbital is **lower** than the atomic orbitals

# Molecular Orbital Theory

**Bonding Molecular Orbitals:** These orbitals arise from Linear Combination of Atomic Orbitals under conditions of **constructive interference**

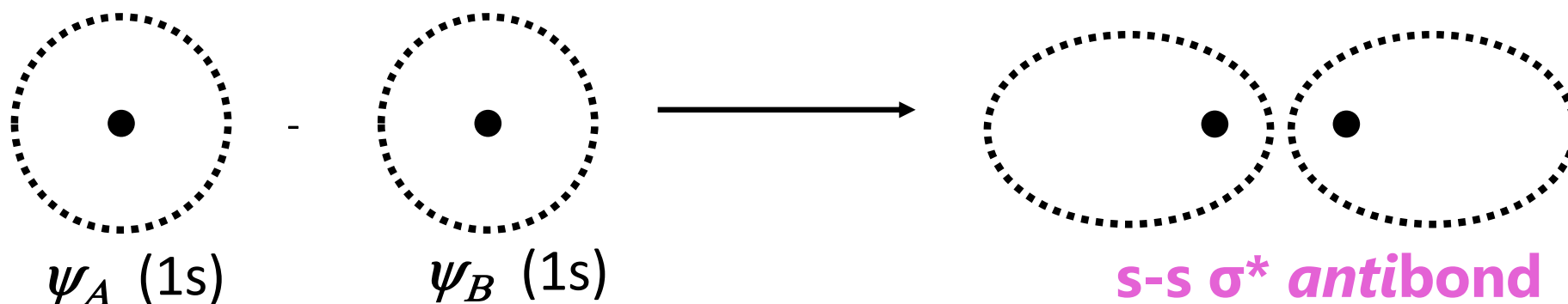


Electrons in this bonding molecular orbital is attracted to BOTH the nuclei

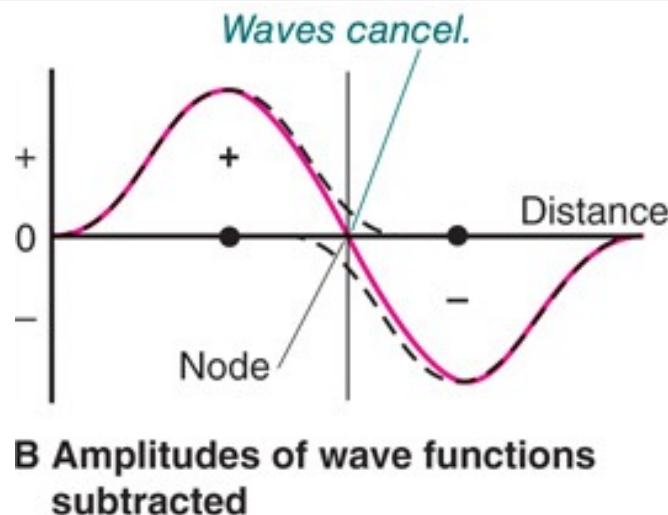
Energy of this bonding molecular orbital is **lower** than the atomic orbitals

# Molecular Orbital Theory

**Antibonding Orbitals:** These orbitals arise from Linear Combination of Atomic Orbitals (LCAO) under conditions of **destructive interference**

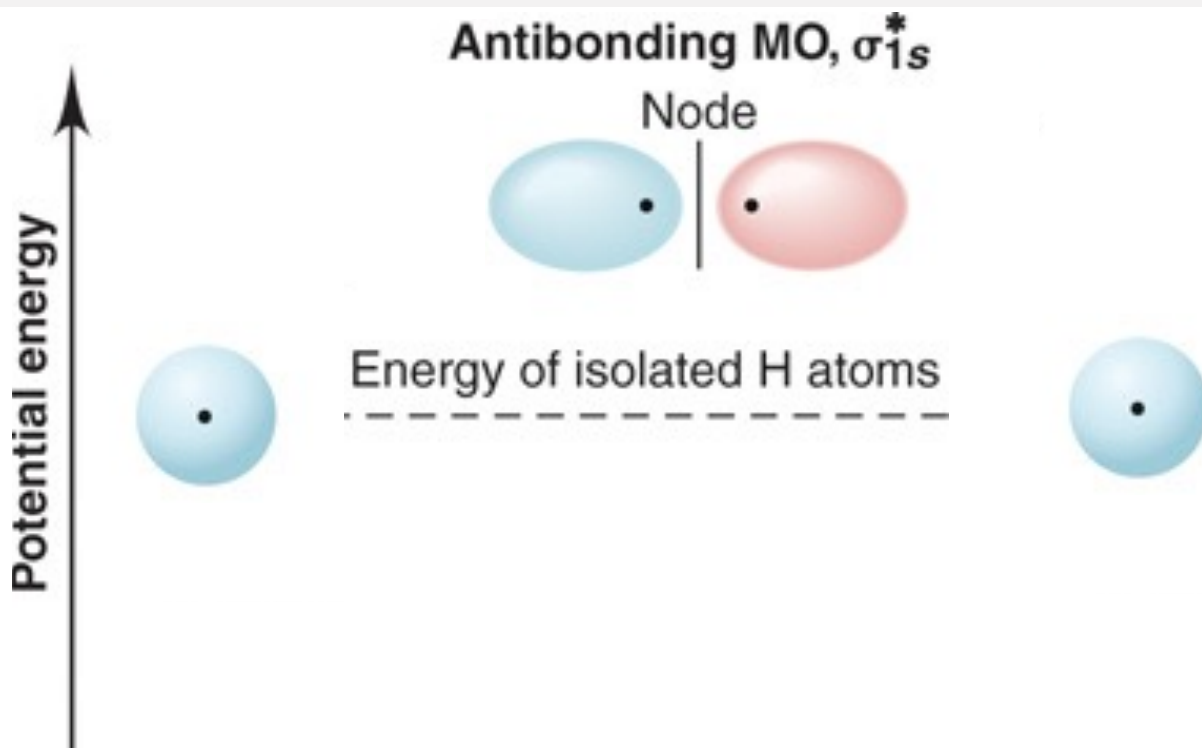


This destructive interference leads to decreased amplitude in the inter-nuclear region - decreased probability density ( $\Psi^2$ ) between the nuclei and a **node** between the nuclei



# Molecular Orbital Theory

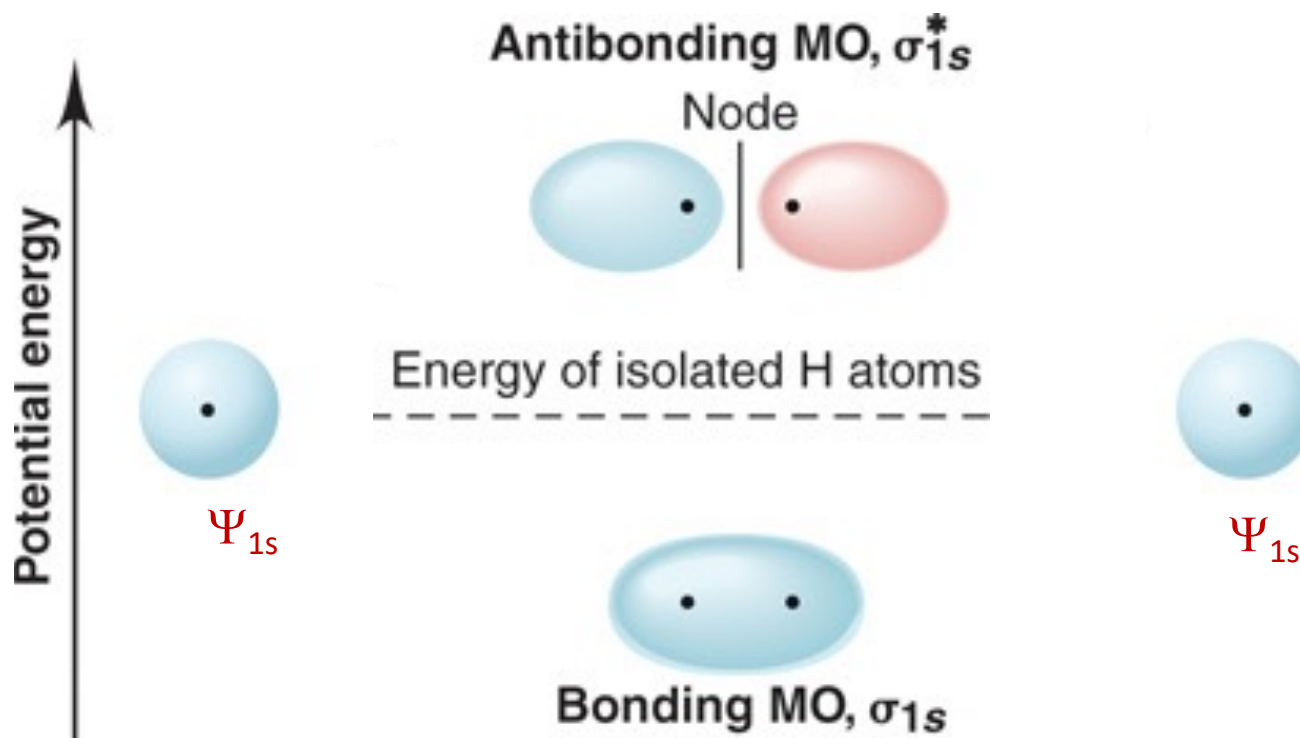
**Antibonding Orbitals:** These orbitals arise from Linear Combination of Atomic Orbitals under conditions of **destructive interference**



Electrons in this anti-bonding molecular orbital is excluded from the inter-nuclear region

Energy of this antibonding molecular orbital is **higher** than the atomic orbitals

# Molecular Orbital Theory

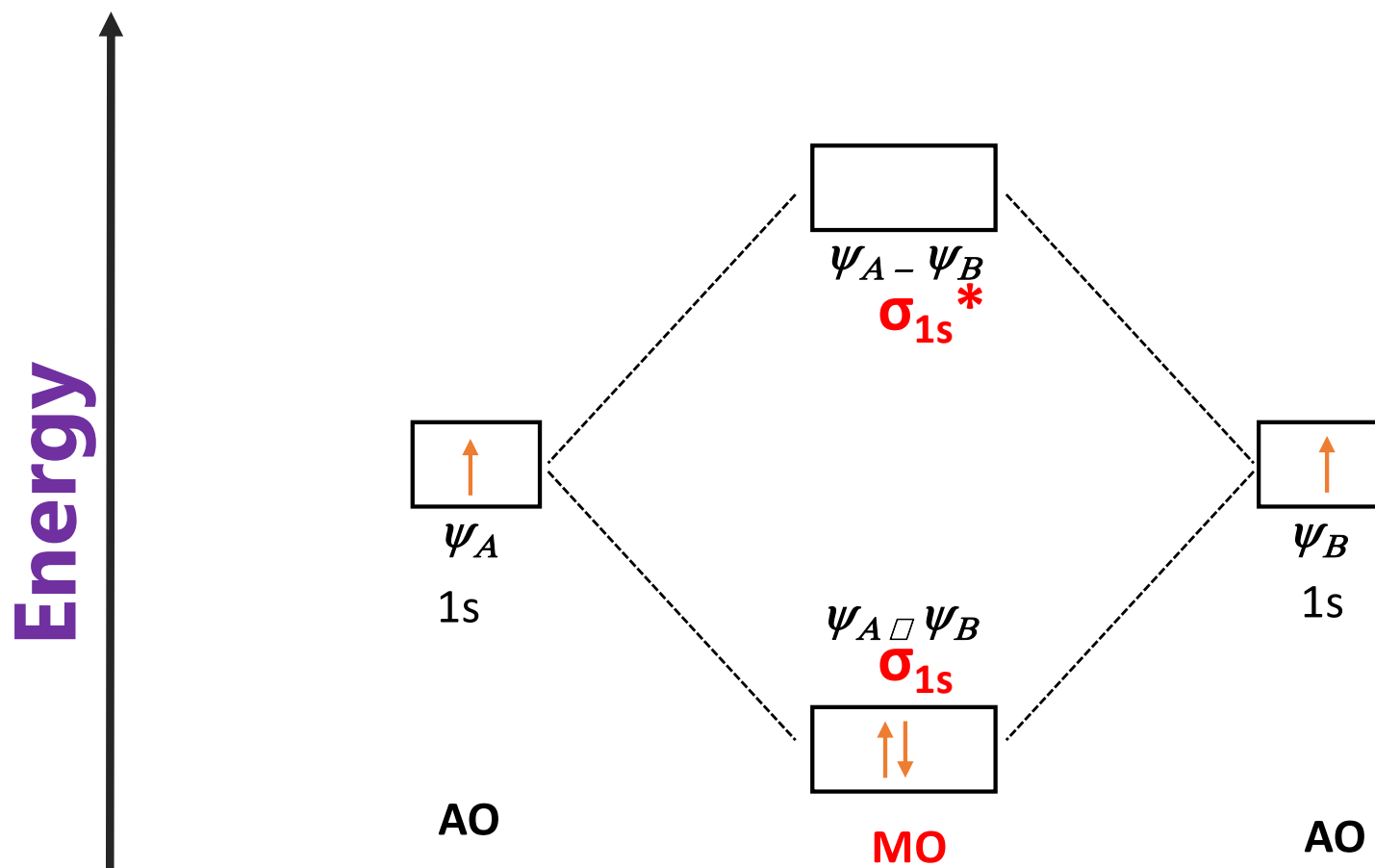


The number of total molecular orbitals is always equal to the number of combined atomic orbitals

In the case above:

2 atomic orbitals combined to give 2 molecular orbitals  
(1 bonding and 1 antibonding)

# H<sub>2</sub> Molecular Orbital Energy Diagram

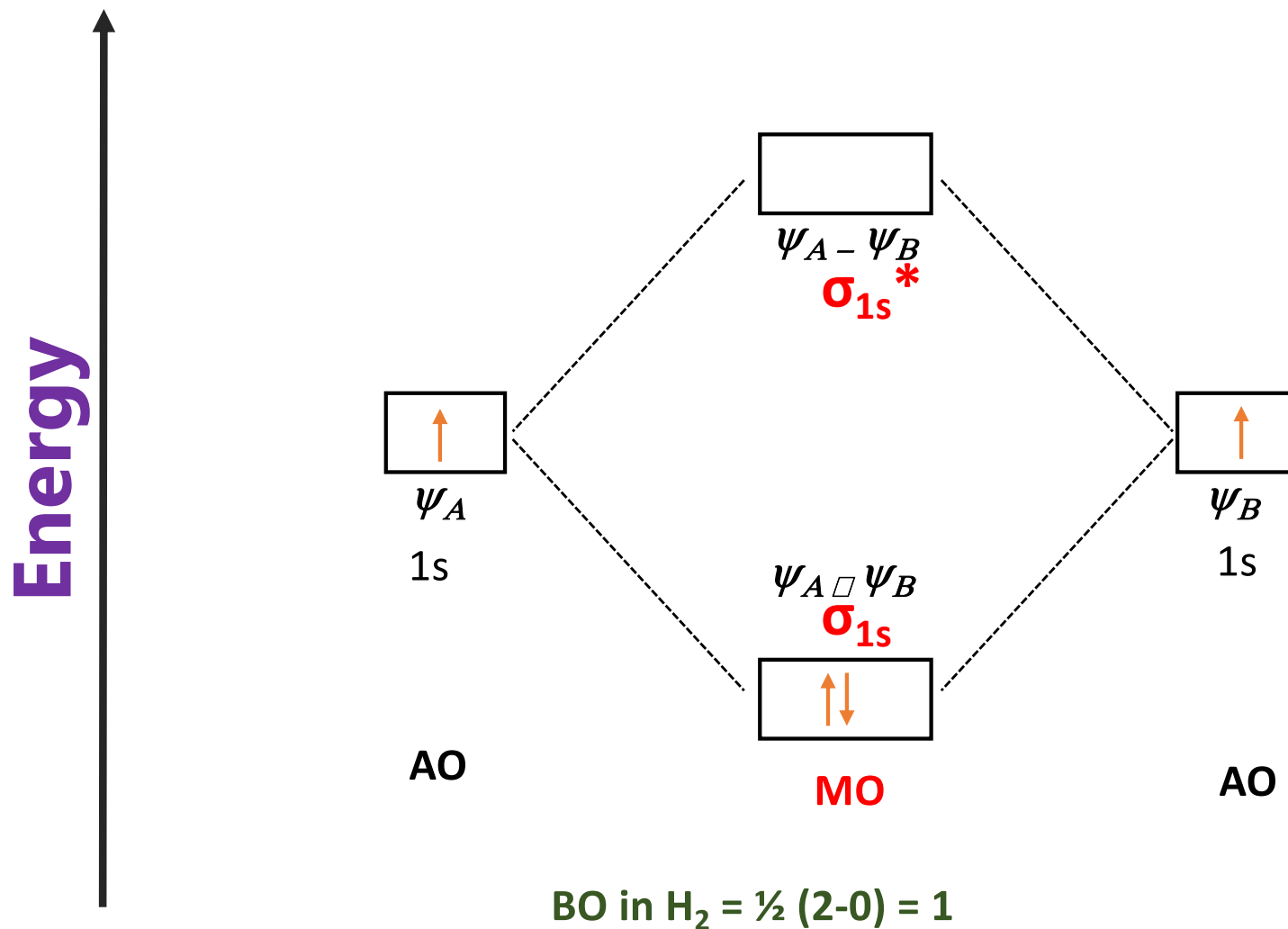


Use Aufbau and Pauli's exclusion principle to fill the electrons in the bonding orbital.

Electron fill lower energy orbital first. An orbital can occupy a maximum of 2 electrons



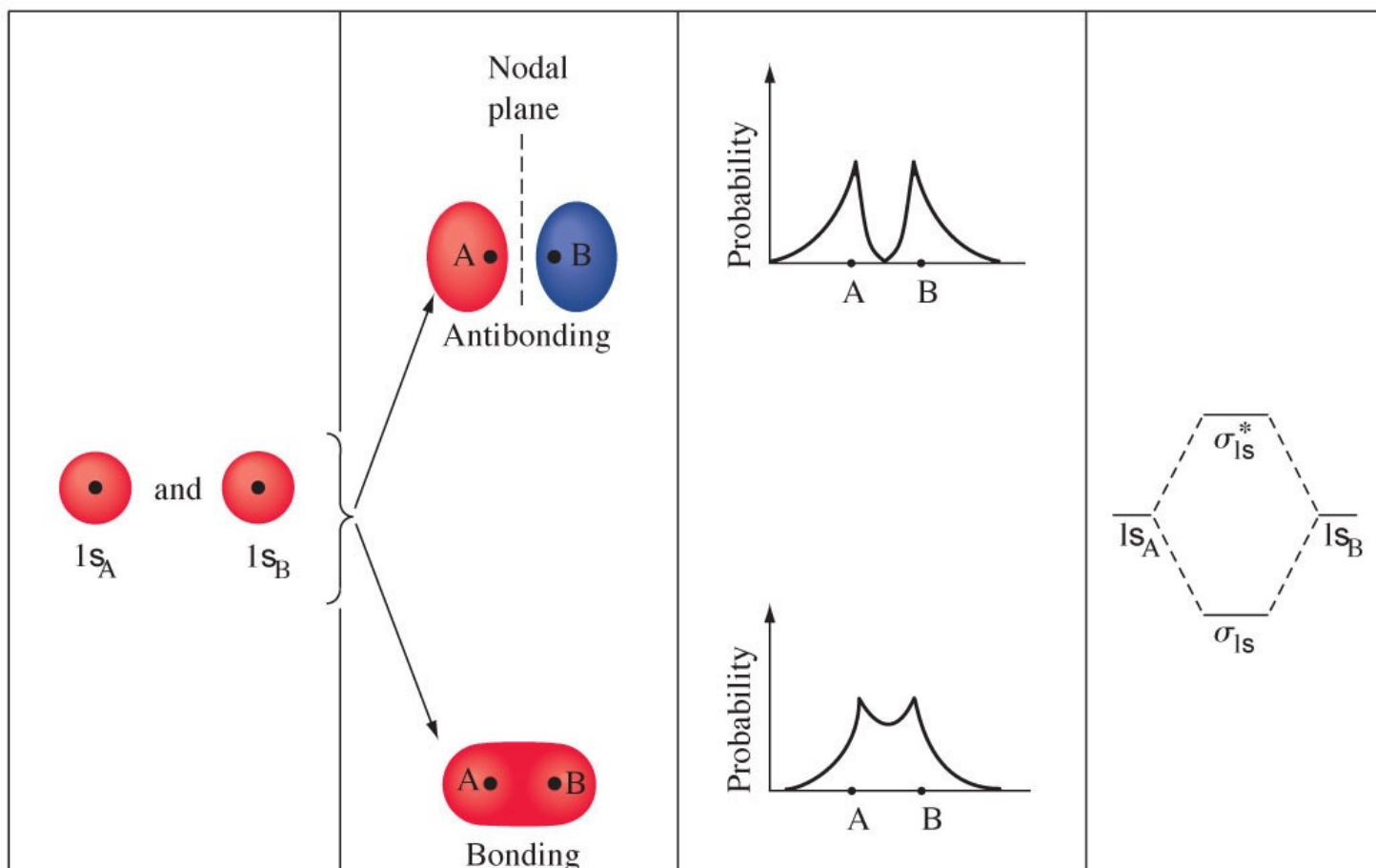
# Using MO theory to determine bond order: H<sub>2</sub>



Bond Order =  $\frac{1}{2}$  (no. of bonding electrons – no. of antibonding electrons)

Electronic Configuration of H<sub>2</sub> molecule:  $(\sigma 1s)^2$

# Linear Combination of 1s orbital

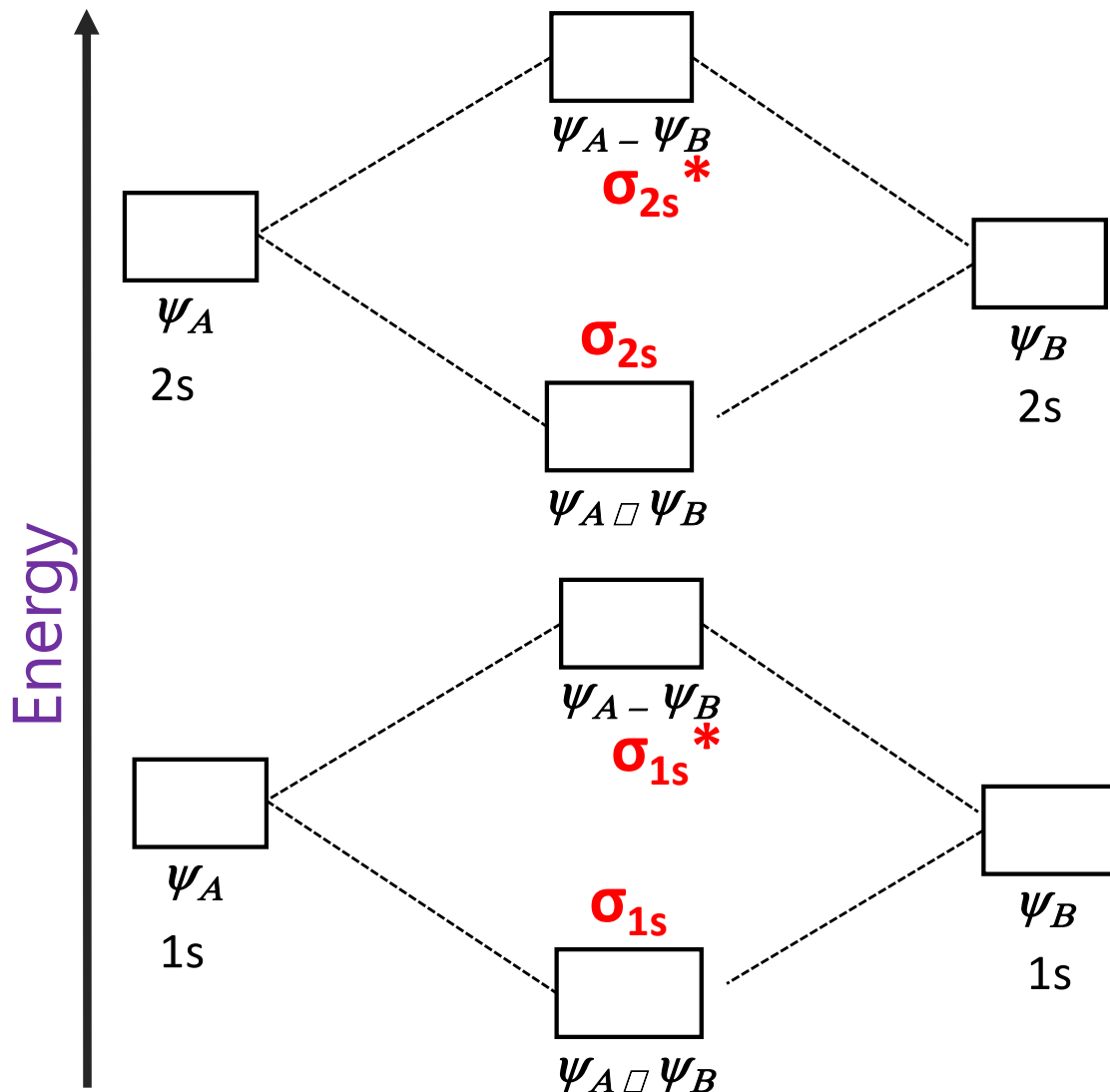


**Solving molecular orbitals becomes quite difficult for molecules that are not first period diatomics**

**We assume that other molecules create MOs in a similar way (though we cannot explicitly solve MOs for anything but first-period diatomics)**

# MO theory: 2s orbital LCAO

The MOs formed by LCAO of 2s orbitals are formed in the same way as those from 1s orbital



Bond order can be calculated using all the electrons or just the valence electrons