

# Announcements for Wednesday, 23OCT2024

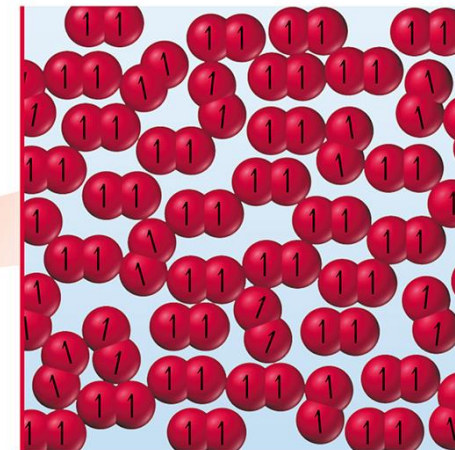
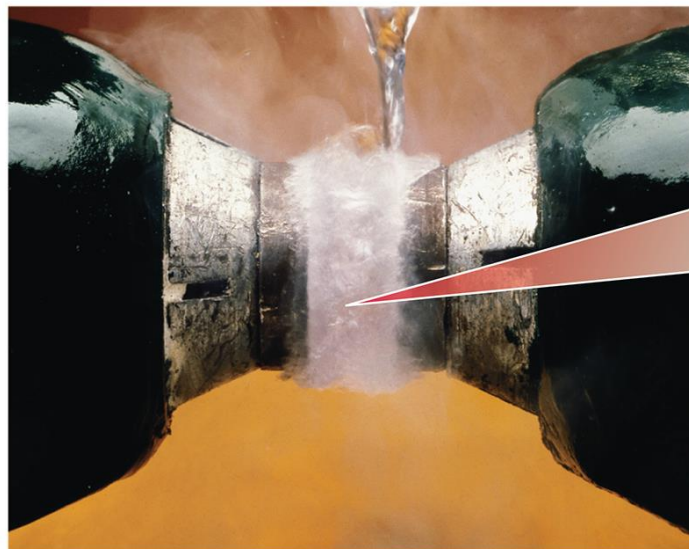
- **Exam 2 Conflict Exam Requests** **due by Friday, 25OCT2024, 11:59 PM (EDT)**
  - for students having Rutgers sanctioned classes and activities during the Exam 2 period (Wednesday, 30OCT2024, 7:45 PM – 9:05 PM)

**ANY GENERAL QUESTIONS?** Feel free to see me after class!

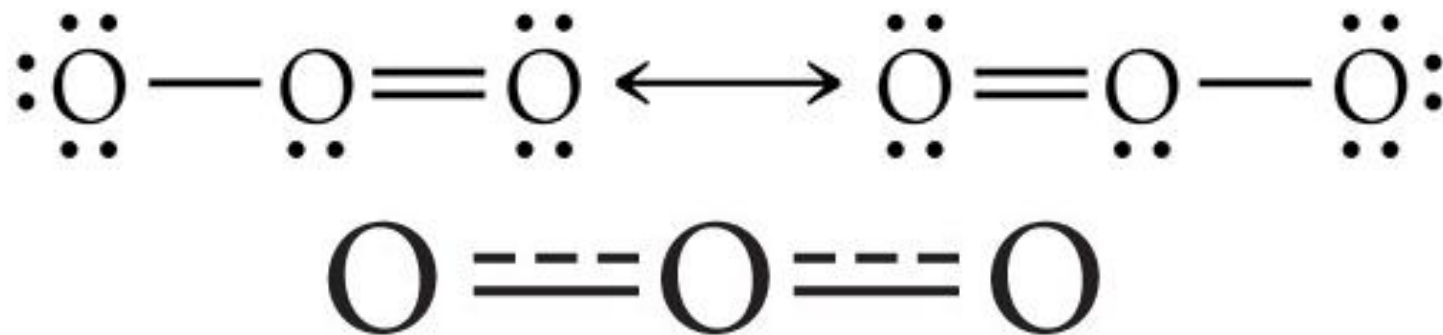
# Some Limitations of Valence Bond Theory – $O_2$ and $O_3$

although relatively successful, the properties of some systems still cannot be adequately accounted for by VB theory

- liquified oxygen ( $O_2(l)$ ) responds to an external magnetic field
  - indicates paramagnetism and the presence of one or more unpaired  $e^-$ s
  - according to VB theory,  $O_2$  should not have unpaired  $e^-$ s
- the O/O bonds in ozone ( $O_3$ ) are identical and some electrons are delocalized

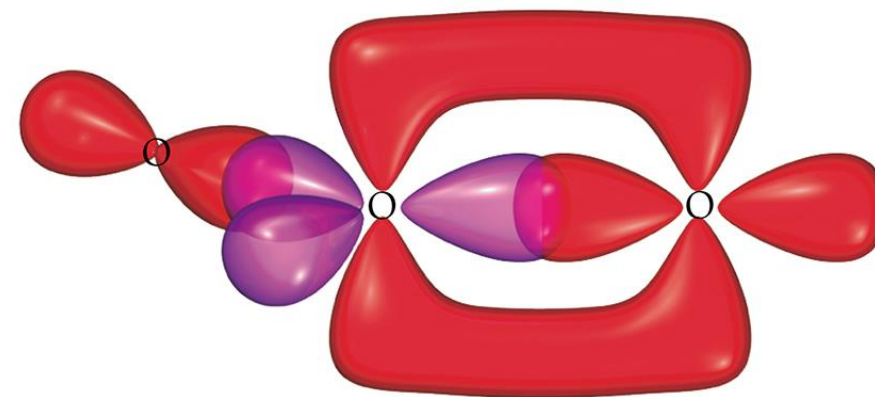


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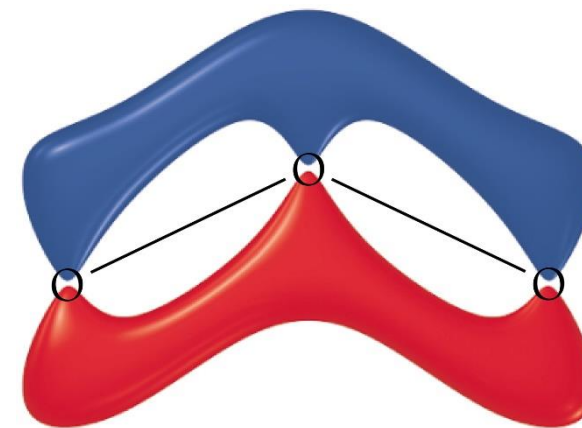
# Molecular Orbital (MO) Theory

- unlike in VB theory, the overlapping of atomic orbitals leads to the formation of **orbitals that extend over the entire molecule**, not localized between two atoms
  - electrons belong to the entire molecule (i.e., delocalized) rather than to individual atoms
- The Schrödinger **wave equation** is applied to the molecule to calculate a set of **molecular orbitals**
  - atomic orbitals are combined to create an initial set of molecular orbitals
  - the MOs are adjusted until their energies are minimized



Valence bond model of O<sub>3</sub>

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Molecular orbital model of O<sub>3</sub>

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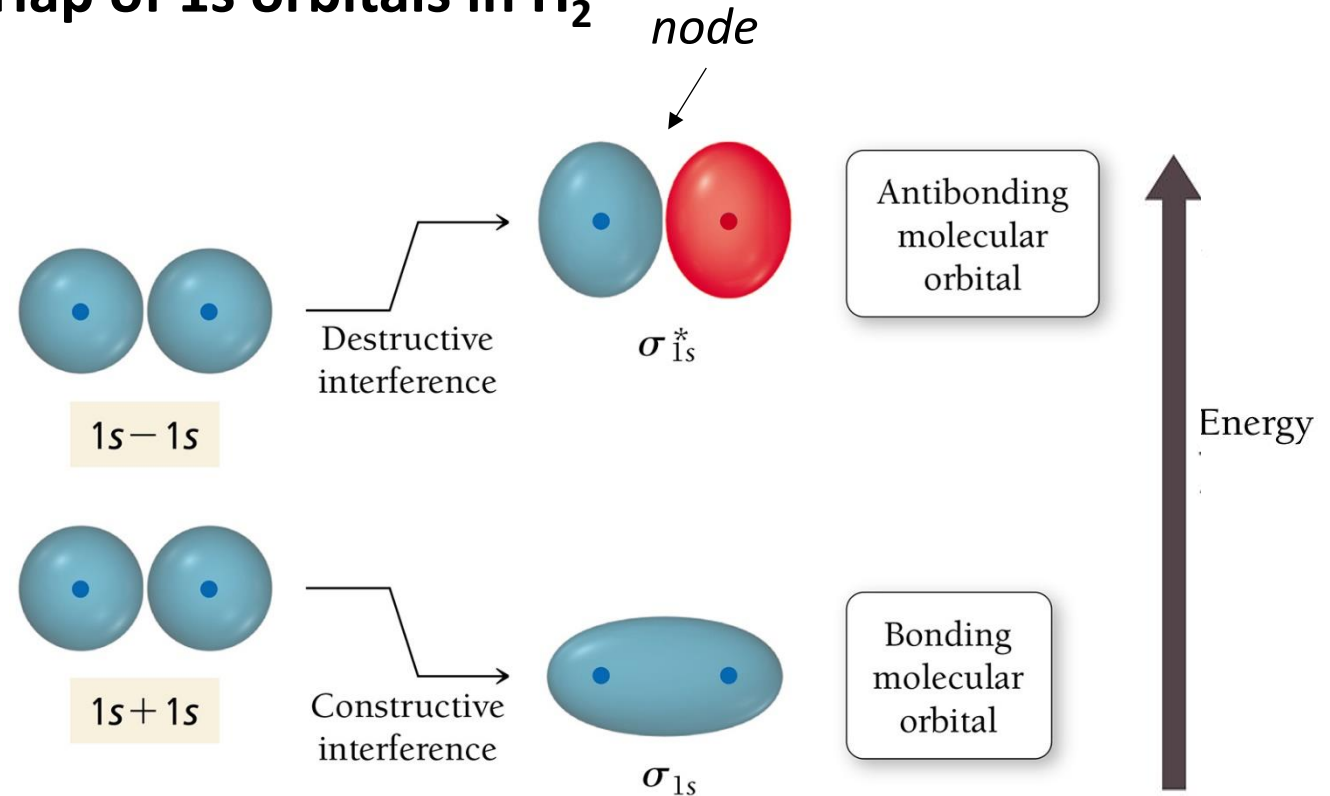
# Linear Combination of Atomic Orbitals (LCAO)

*a method used to create an initial set of molecular orbitals*

consider the overlap of 1s orbitals in H<sub>2</sub>

the atomic orbitals combine:

- **constructively** to form a **bonding** molecular orbital ( $\sigma$  or  $\pi$ )
  - the energy of the MO is **lower** than the individual AOs
  - most electron density **between** nuclei
- **destructively** to form an **antibonding** molecular orbital ( $\sigma^*$  or  $\pi^*$ )
  - the energy of the MO is **higher** than the individual AOs
  - a *node* between nuclei and electron density **outside** inter-nuclei region



## MO Theory (continued)

- the number of atomic orbitals combined equals the number of molecular orbitals formed
- electrons within bonding MOs lower the energy of the system and stabilize it
- electrons within antibonding MOs destabilize the system and cancel the stabilizing effect of electrons in bonding MO

**Bond Order** = one-half of the difference between number of electrons in bonding and antibonding orbitals

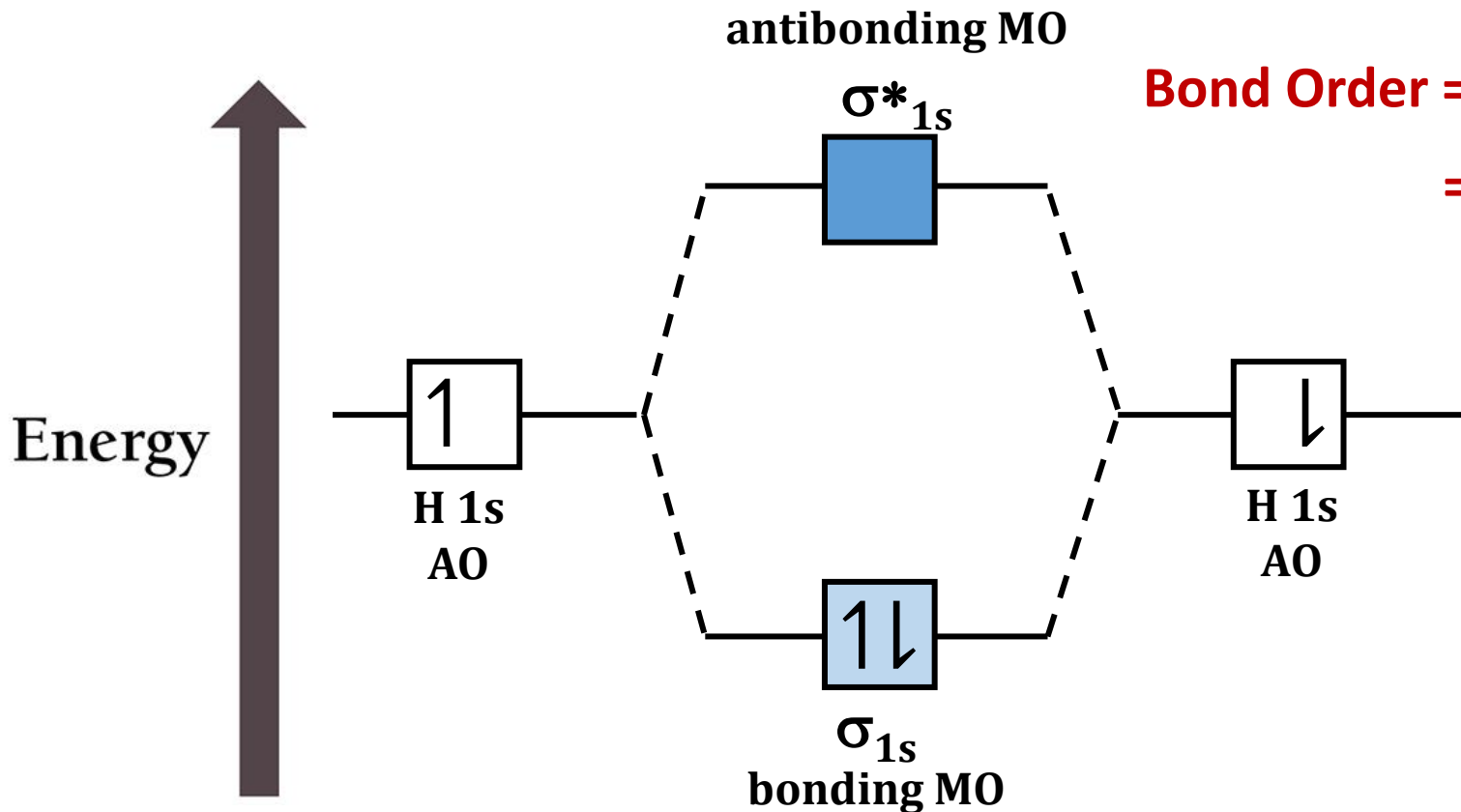
$$\text{Bond Order} = \frac{1}{2} (\# \text{ Bonding Electrons} - \# \text{ Antibonding Electrons})$$

- only need to consider valence electrons
- may be fractional or negative
- higher bond order = **stronger** and *shorter* bonds
- if bond order  $\leq 0$ , then the bond is unstable compared to the individual atoms and **will not form**
- unpaired electrons lead to paramagnetism

# MO Diagrams for *Homonuclear* Diatomic Molecules – **Period 1**

- an *energy diagram* showing the AOs of the atoms composing a molecule, the MOs of the molecule, their relative energies, and the placement of valence e<sup>-</sup>s
- electrons are assigned to molecular orbitals following the same rules from Ch 3
  - **Aufbau principle, Hund's rule, Pauli Exclusion principle**

What is predicted for diatomic hydrogen (H<sub>2</sub>)?



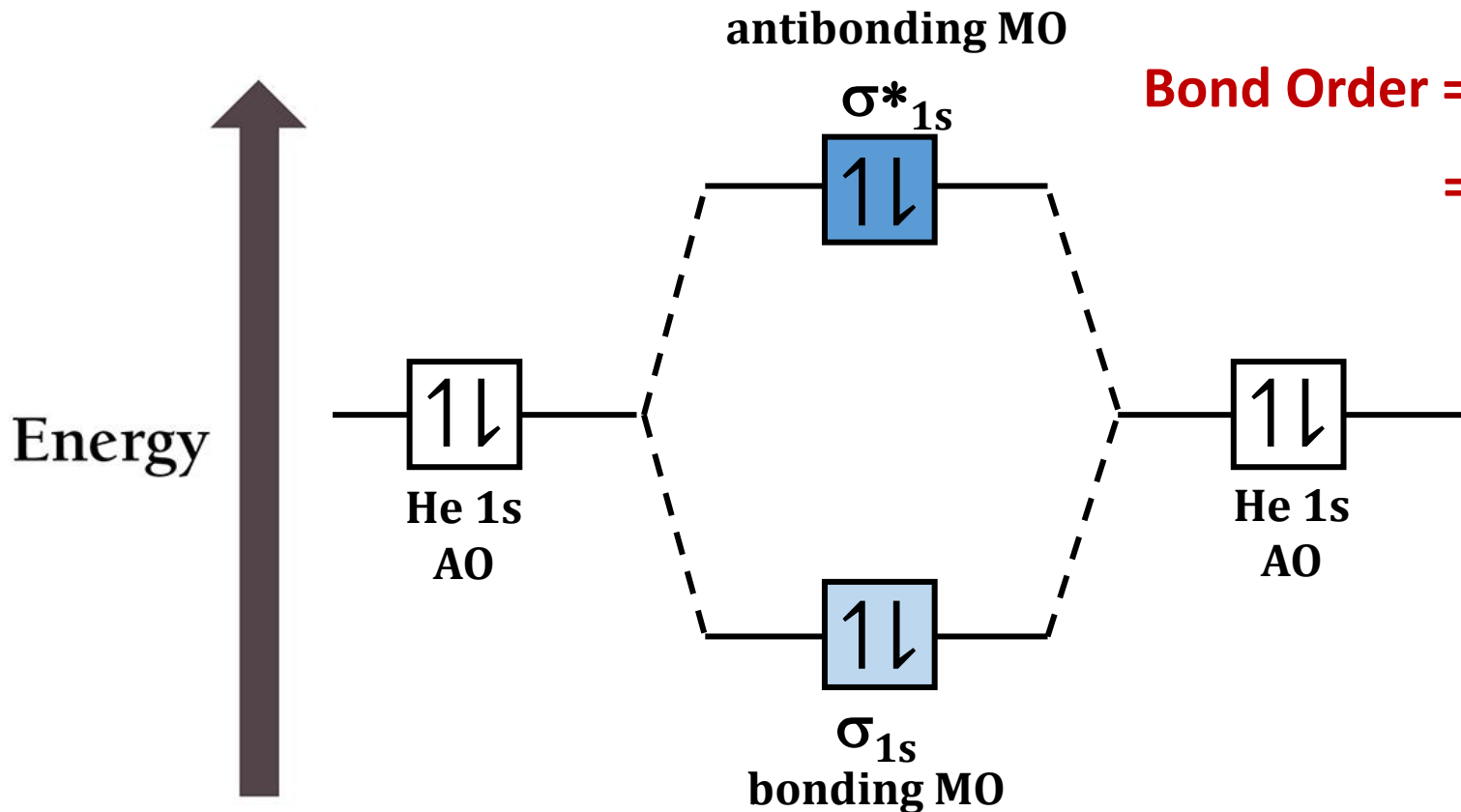
$$\text{Bond Order} = \frac{1}{2} (\# \text{ bonding e}^- \text{s} - \# \text{ antibonding e}^- \text{s})$$
$$= \frac{1}{2} (2 - 0) = 1$$

the H–H bond  
is stable and H<sub>2</sub>  
exists

# MO Diagrams for *Homonuclear* Diatomic Molecules – **Period 1**

- an *energy diagram* showing the AOs of the atoms composing a molecule, the MOs of the molecule, their relative energies, and the placement of valence e<sup>-</sup>s
- electrons are assigned to molecular orbitals following the same rules from Ch 3
  - **Aufbau principle, Hund's rule, Pauli Exclusion principle**

What about diatomic helium (He<sub>2</sub>)?



$$\text{Bond Order} = \frac{1}{2} (\# \text{ bonding e}^- \text{s} - \# \text{ antibonding e}^- \text{s})$$
$$= \frac{1}{2} (2 - 2) = 0$$

the He–He bond  
is not stable and  
He<sub>2</sub> does not  
exist

## Try This On Your Own

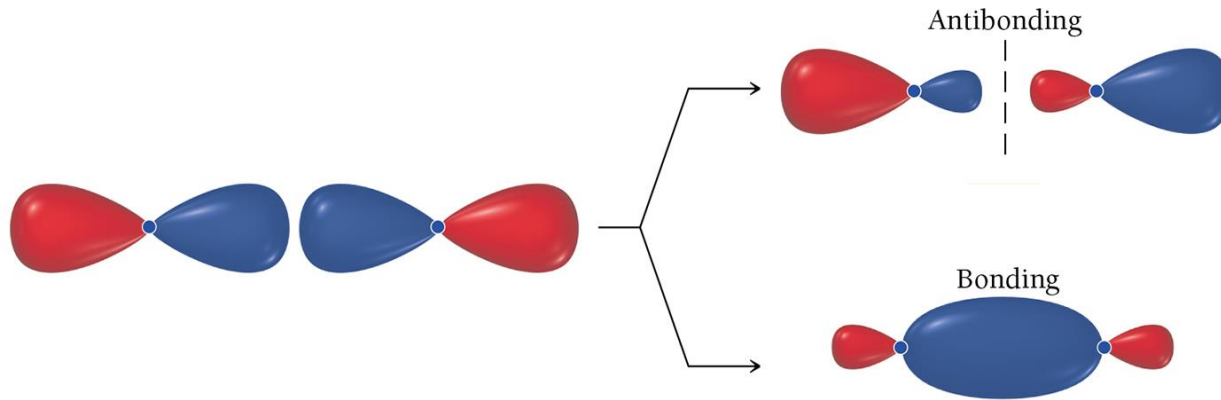
- Draw a molecular orbital diagram for  $\text{He}_2^+$  and determine whether the molecule exists.



# MO Diagrams for *Homonuclear* Diatomic Molecules – **Period 2**

- In addition to s-orbitals, Period 2 atoms have ***p-orbitals*** in their valence shells
- p-orbitals on separate atoms can overlap in two different ways

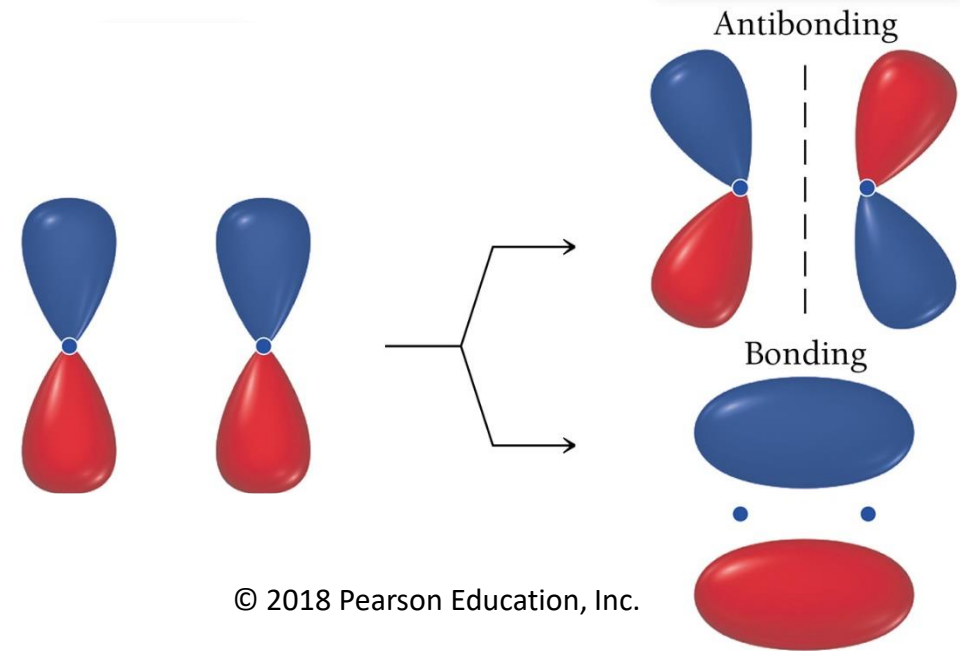
head-to-head ( $\sigma$ ) overlap



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- formation of  $\sigma_{2p}$  and  $\sigma_{2p}^*$  MOs

side-to-side ( $\pi$ ) overlap



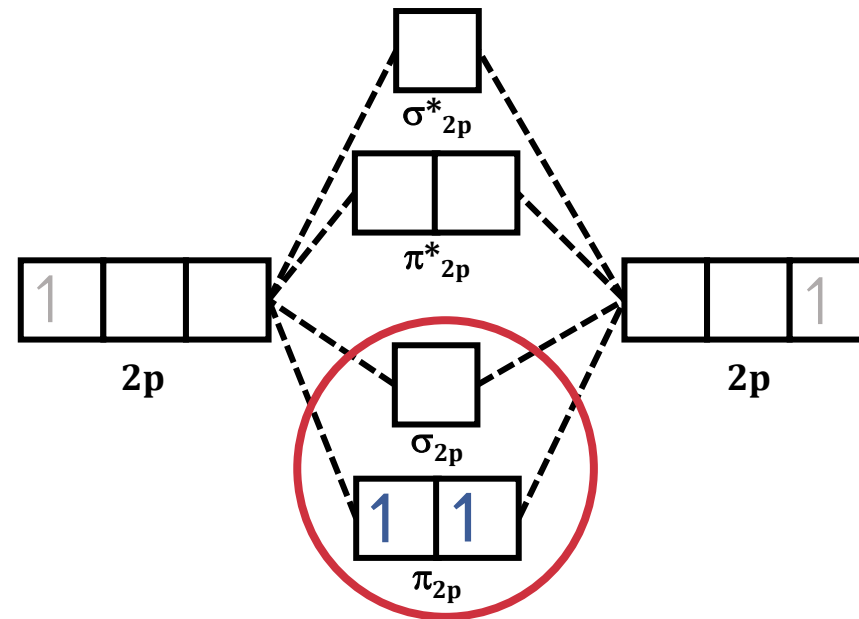
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- formation of  $\pi_{2p}$  and  $\pi_{2p}^*$  MOs (2 sets)

# MO Diagrams for *Homonuclear* Diatomic Molecules – **Period 2**

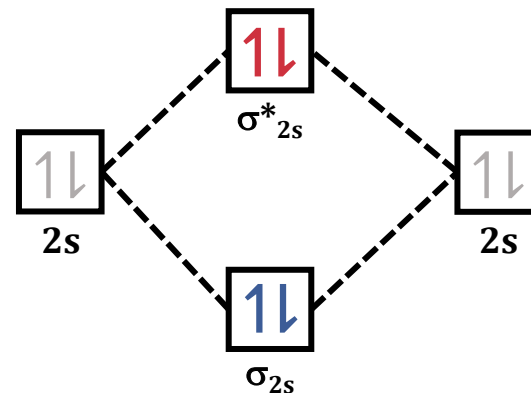
Does the B<sub>2</sub> molecule exist?

B: [He] 2s<sup>2</sup> 2p<sup>1</sup>

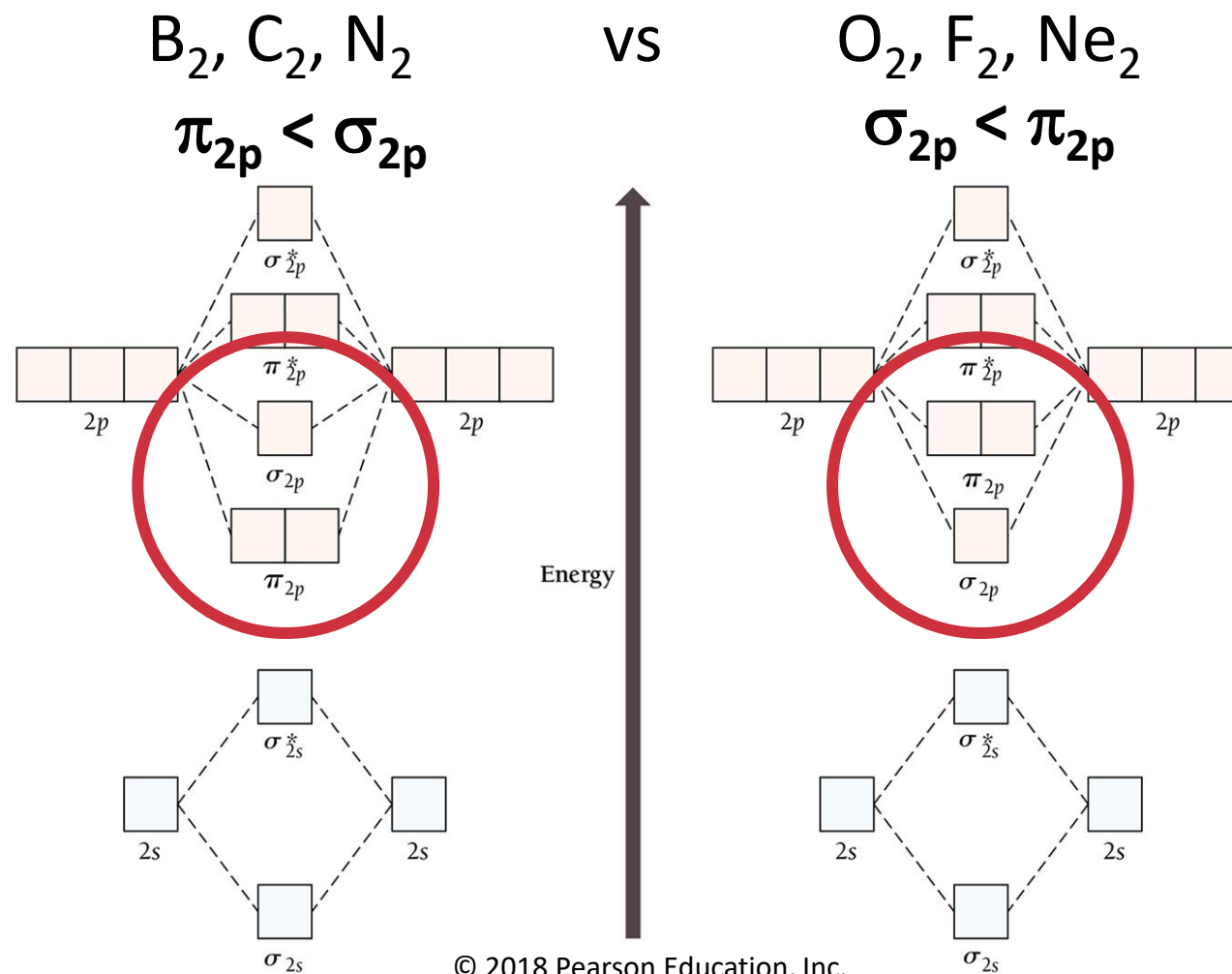


$$\text{Bond Order} = \frac{1}{2} (4 - 2) = 1$$

**B<sub>2</sub> exists**



# Molecular Orbital Energy Ordering – Period 2



- the relative energy orderings are usually determined computationally
- **Don't Memorize:** energy orderings can be found on the *Formula Sheet*