What will you be learning?

Molecular Orbital Theory
(Using Linear Combination of Atomic Orbitals)

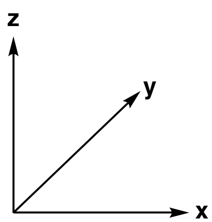
Learning Objectives this week:

Explain molecular orbital theory (MO theory)

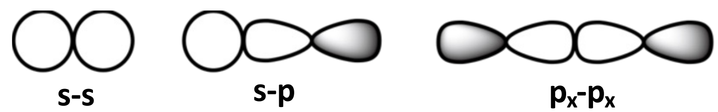
- Understand that the combination of any two AOs creates a bonding & anti-bonding MO pair.
- Prepare MO energy diagrams for simple diatomic molecules (first/second periods).
- Fill MO energy diagrams for simple heteronuclear diatomic molecules.
- Determine bond orders and predict magnetic properties of diatomics.
- Fill π MO energy diagrams for delocalized systems (Resonance).
- Describe metallic bonding and physical properties using band theory models.

Catch up: Theories of Chemical Bonding

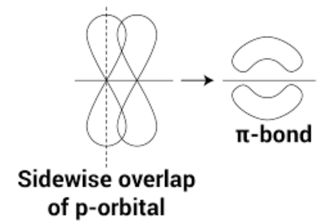
Valence Bond Theory tell us which orbitals are used in bonding but cannot predict geometry.



<u>σ-bond</u> – formed from overlap of two orbitals. Is cylindrically symmetrical around bond axis.



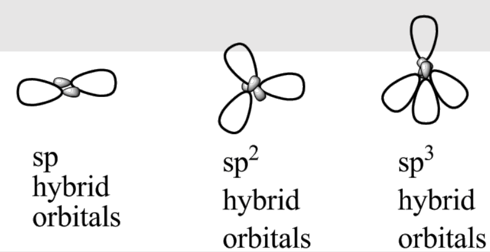
<u>π-bond</u> – formed from overlap of two orbitals. It is not symmetrical around bond axis. Side to side overlap.



VSEPR Theory can predict geometry but does not tell us about orbitals involved in bonding

Combine the two concepts: Hybridization

Mixing of valence orbitals in an element to obtain orbitals with appropriate geometry



Determine the number of electron groups

Number of electron groups = number of hybrid orbitals

Practice Question 1

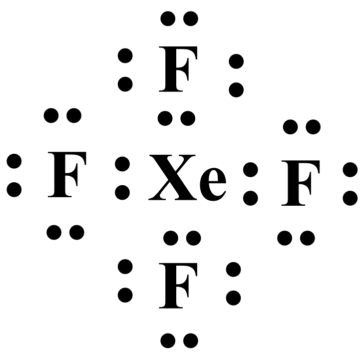
1. Draw the Lewis structure for XeF_4.
2. Predict the VSEPR geometry at xenon.
3. Determine a hybridization scheme to rationalize the geometry.

Practice Question 1

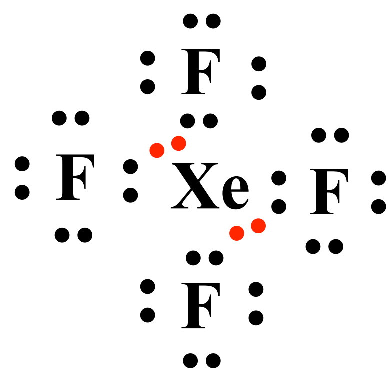
1. Draw the Lewis structure for XeF_4.

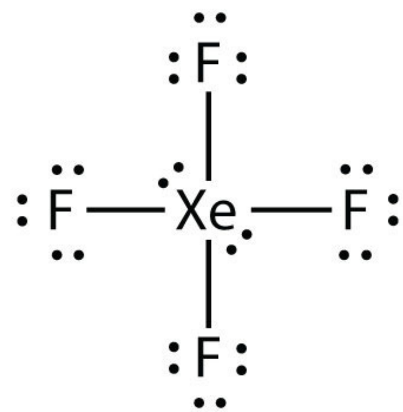
Xe: $5s^2\ 5p^6$ **F: $2s^2\ 2p^5$**

Total number of electrons based on Valence shell electrons in XeF_4 = 8 + 4(7) = 36



Number of electrons = 32





Xe has four bond pairs and two lone pairs

Each of the fluorine atoms have one bond pair, and three lone pairs

Practice Question 1

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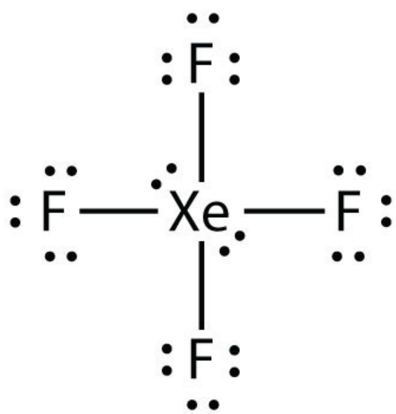
2. Predict the VSEPR geometry at xenon.



Electron geometry requires the count of electron pairs:
bond pairs and lone pairs

Electron pairs on Xe = 6 (four bond and two lone pairs)

Electron geometry on Xe = Octahedral

Molecular geometry on Xe = Square planar
(4 bond pairs and two lone pairs arranged in space)

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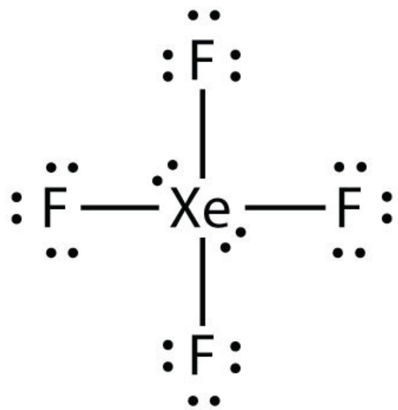
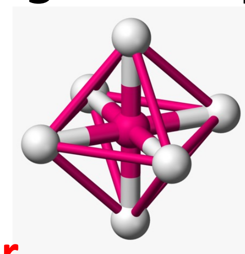
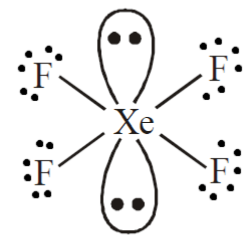


Electron geometry on Xe = Octahedral



Molecular geometry on Xe = Square planar
(4 bond pairs and two lone pairs arranged in space)

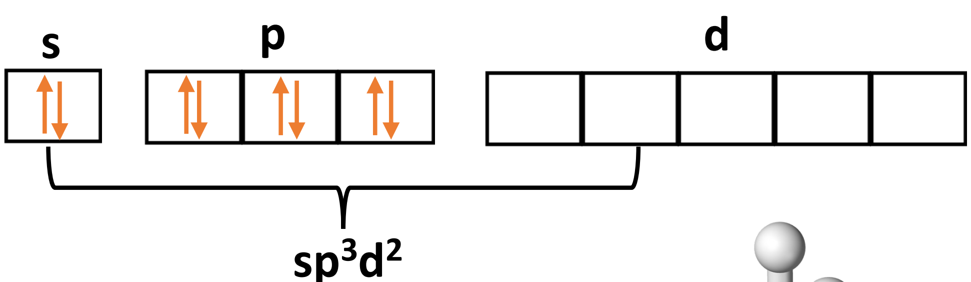


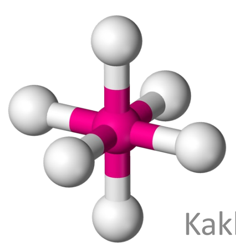
Number of electron groups = number of hybrid orbitals

Number of electron groups on Xe = 6

Number of hybrid orbitals required = 6

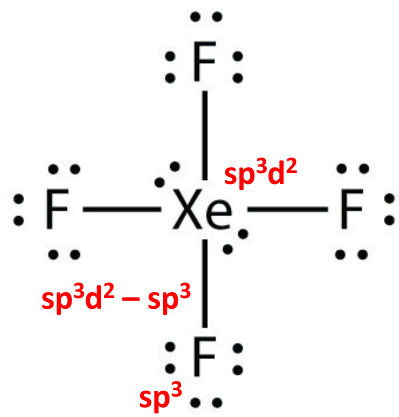
Xe: $5s^2\ 5p^6$





Practice Question 1

1. Draw the Lewis structure for XeF_4.
2. Predict the VSEPR geometry at xenon.
3. Determine a hybridization scheme to rationalize the geometry.
4. Determine hybridization at Fluorine in the molecule.

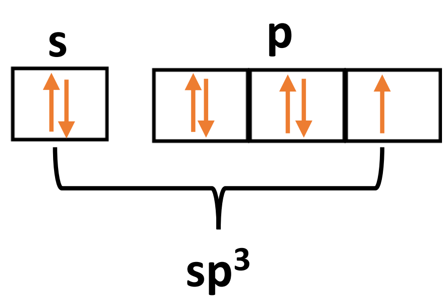


Number of electron groups = number of hybrid orbitals

Number of electron groups on F = 4

Number of hybrid orbitals required = 4

F: $2s^2$ $2p^5$

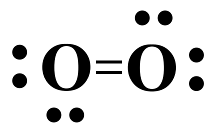


Limitations

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.

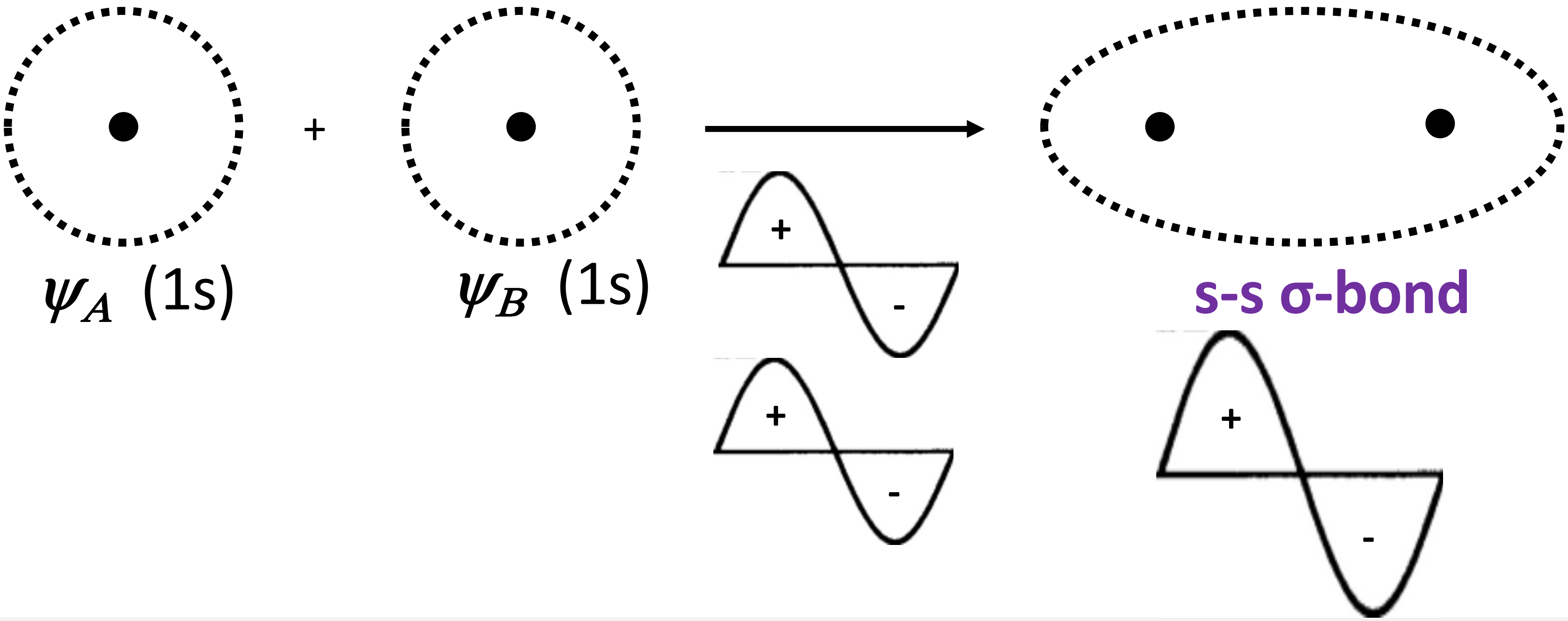
3. **Cannot explain resonance (delocalization of electrons).**

How do we address these limitations:

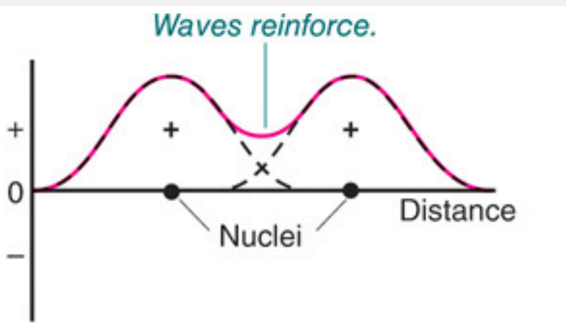
Molecular Orbital Theory

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 (Ψ^2) between the nuclei



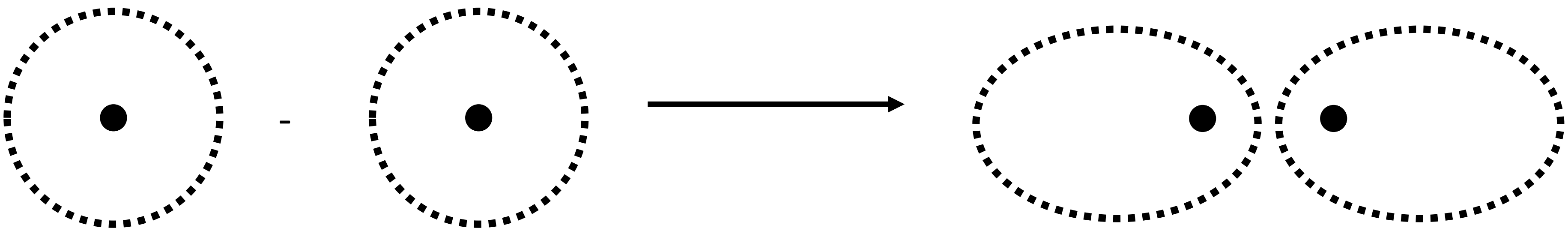
A Amplitudes of wave functions added

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

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

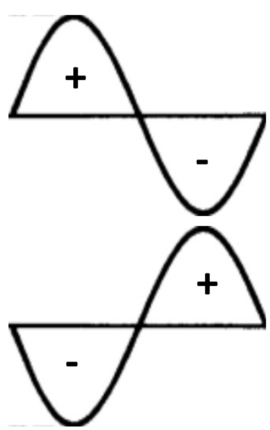
Molecular Orbital Theory

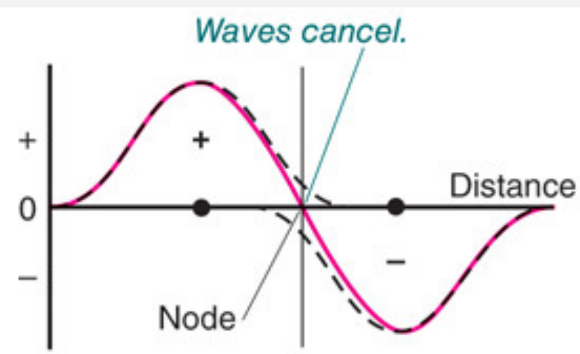
Antibonding Orbitals: These orbitals arise from Linear Combination of Atomic Orbitals (LCAO) under conditions of **destructive interference**



ψ_A (1s) ψ_B (1s) **s-s σ* *anti*bonding**

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

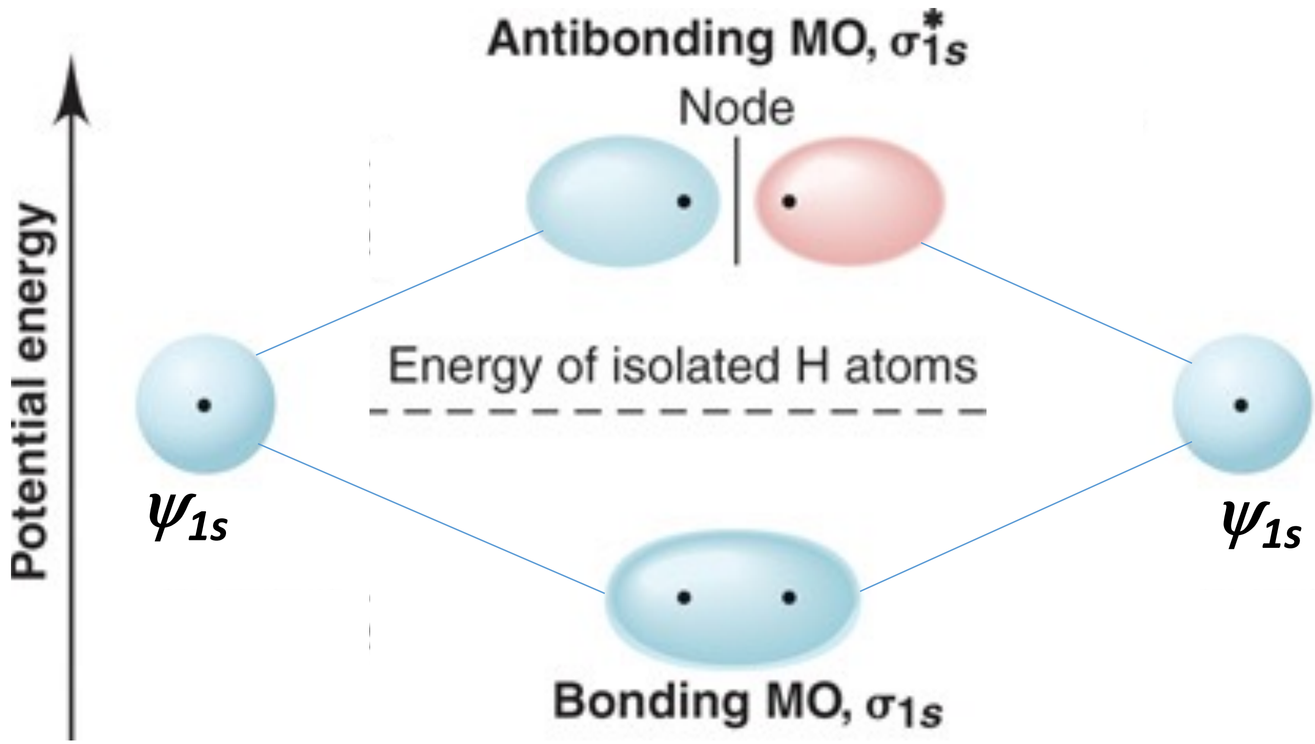




B Amplitudes of wave functions subtracted

Molecular Orbital Theory (Period 1 diatomics)

Linear Combination of Atomic Orbitals



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

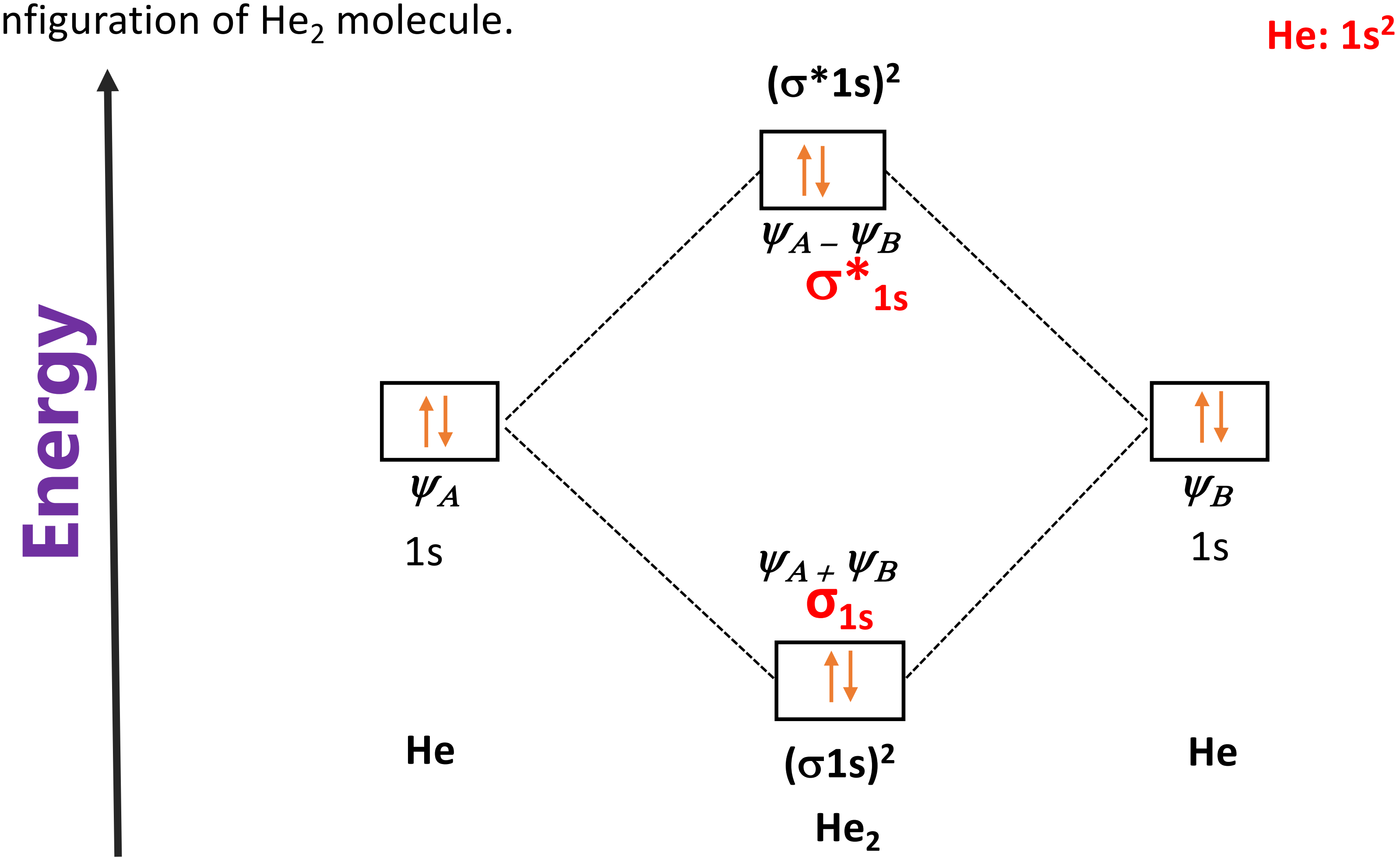
In the above case:

2 atomic orbitals combined to give 2 molecular orbitals

(1 bonding and 1 antibonding)

Practice Question 2

Draw the MO diagram for He_2. Calculate the bond order and show the electronic configuration of He_2 molecule.



Bond Order = ½ (no. of electrons in bonding orbitals – no. of electrons in antibonding orbitals)

Bond order in He_2 = (2– 2)/2 = 0

Electronic Configuration of He_2 molecule: $(\sigma 1s)^2 (\sigma^*1s)^2$

Practice Question 2

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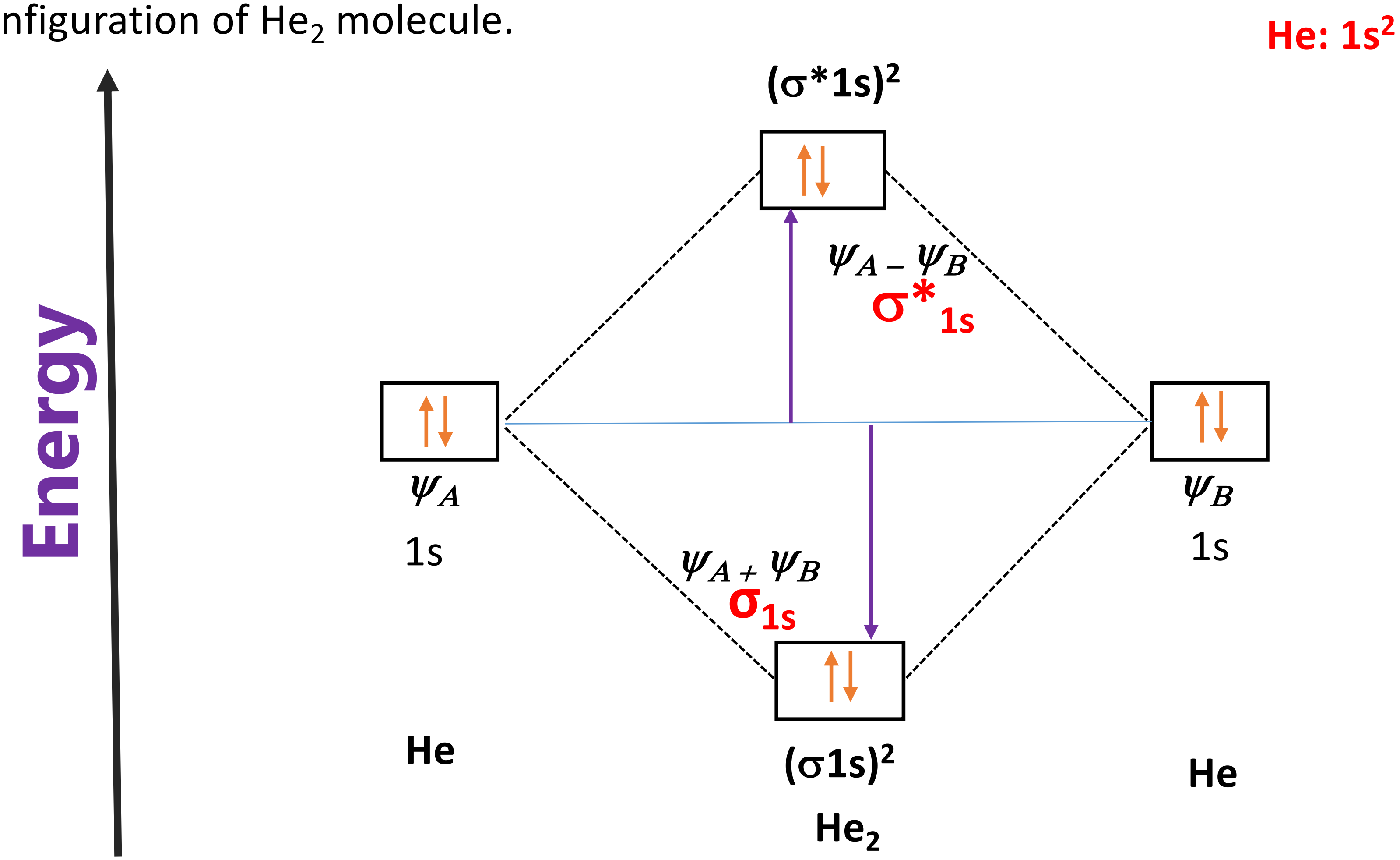

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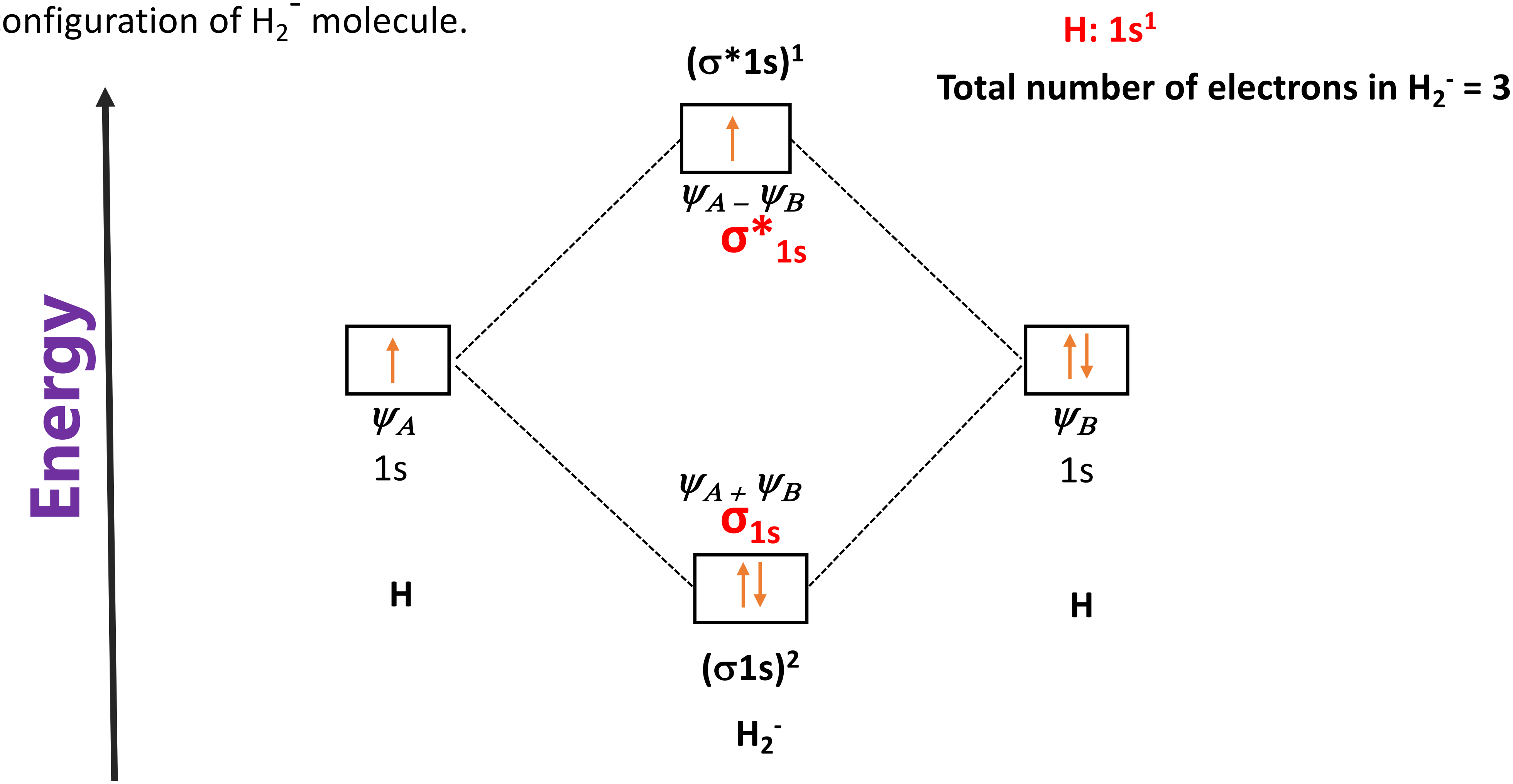
Bond order in He_2 = (2– 2)/2 = 0

Electronic Configuration of He_2 molecule: **$(\sigma 1s)^2 (\sigma^* 1s)^2$**

Practice Question 3

Draw the MO diagram for H_2^-. Calculate the bond order and show the electronic configuration of H_2^- molecule.

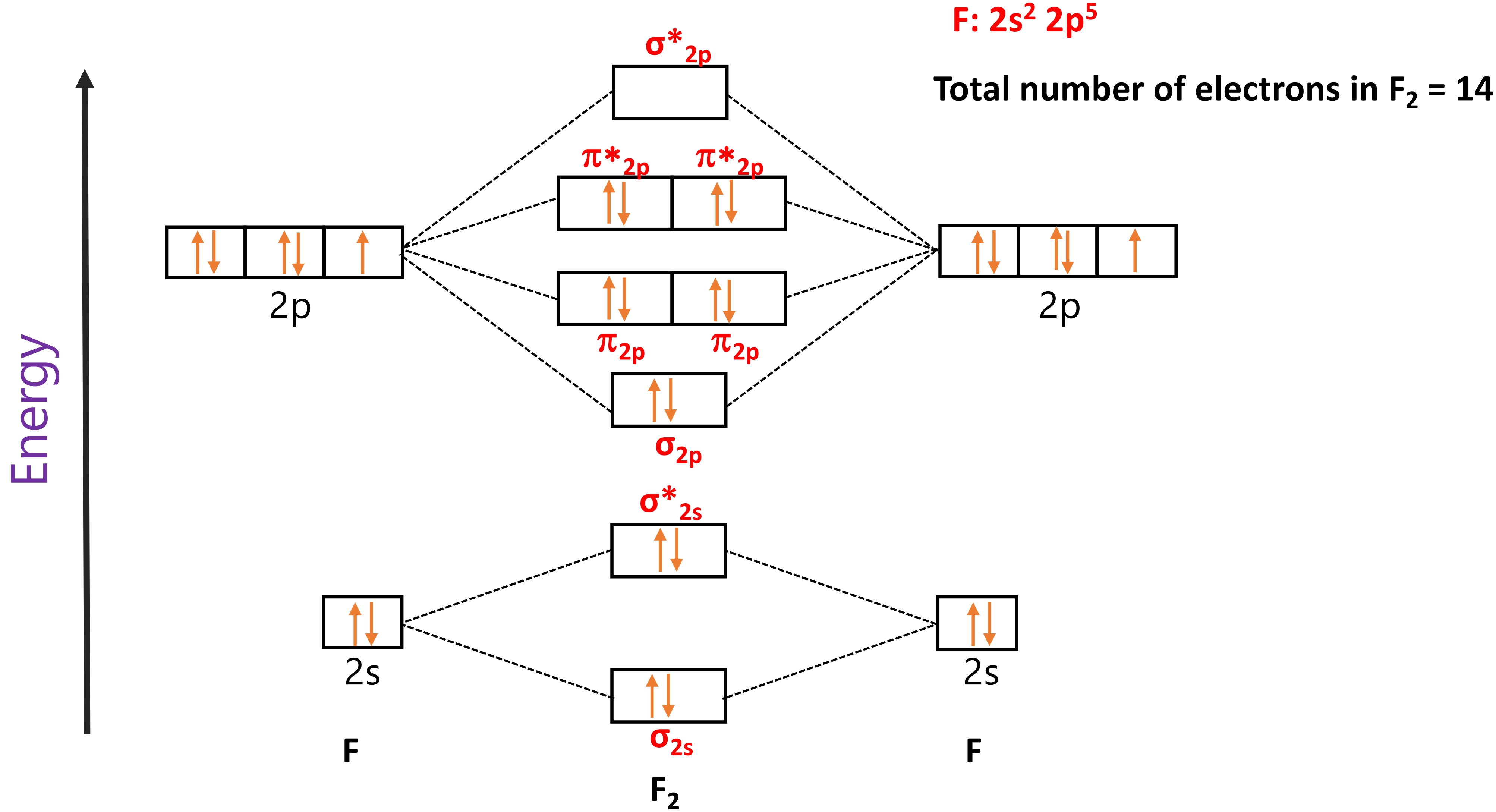


Bond Order = ½ (no. of electrons in bonding orbitals – no. of electrons in antibonding orbitals)

Bond order in H_2^- = (2– 1)/2 = 0.5

Electronic Configuration of H_2^- molecule: **$(\sigma 1s)^2 (\sigma^* 1s)^1$**

Review: MO diagram for O_2 to F_2

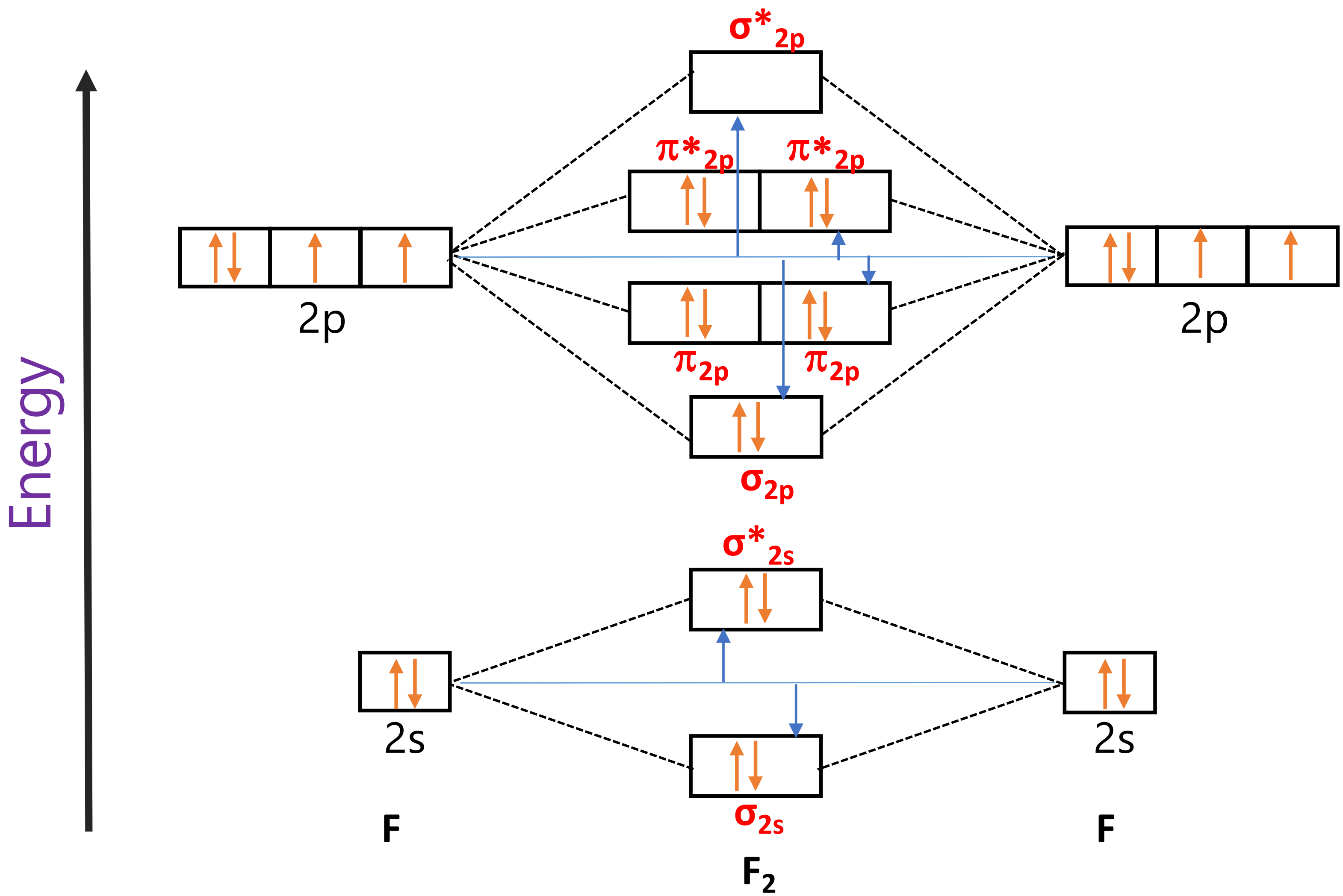


Bond Order = ½ (no. of electrons in bonding orbitals – no. of electrons in antibonding orbitals)

Bond order in F_2 = (8–6)/2 = 1

$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p)^2\ (\pi 2p)^4\ (\pi^* 2p)^4$ **No unpaired electrons** **Diamagnetic**

Review: MO diagram for O_2 to F_2



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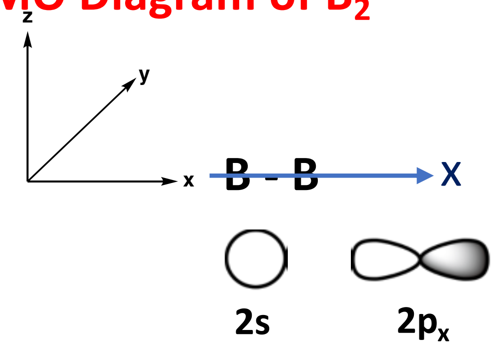
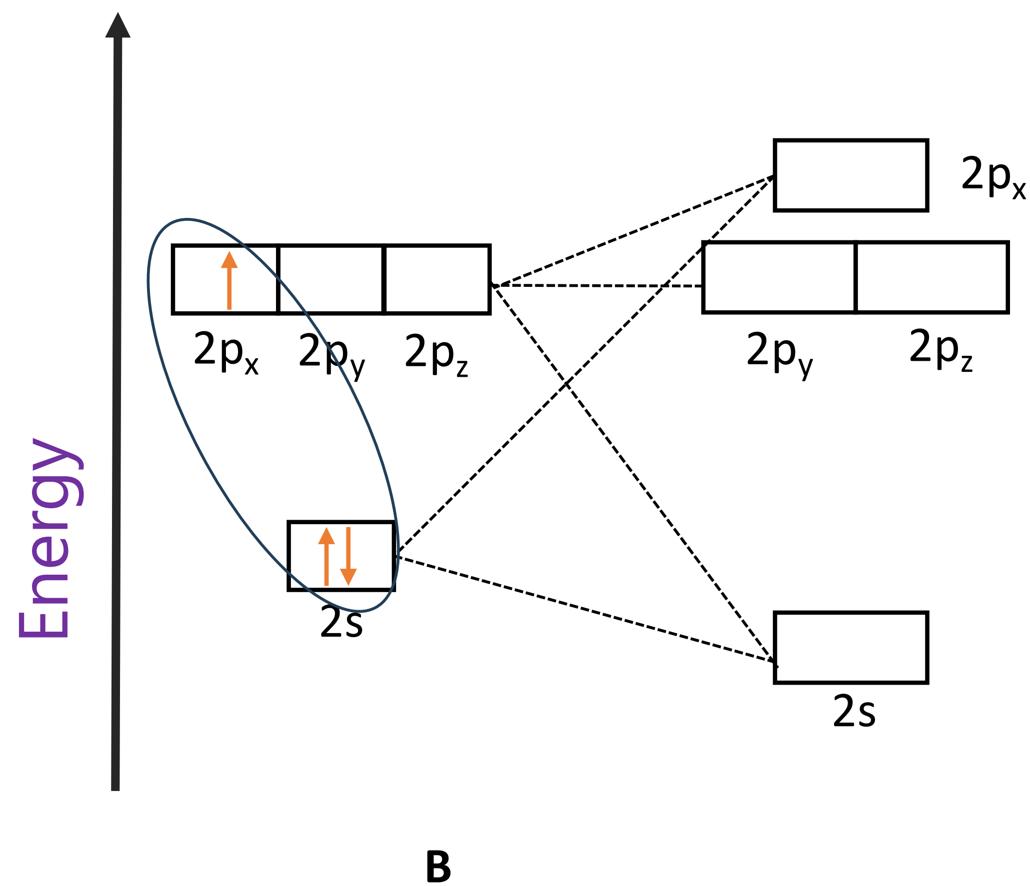
B $2s^2\ 2p^1$

3 electrons in the valence shell

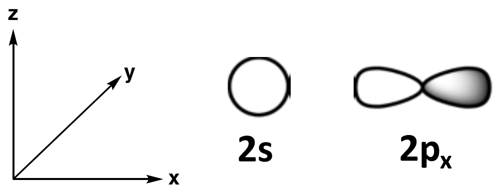


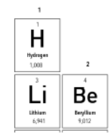


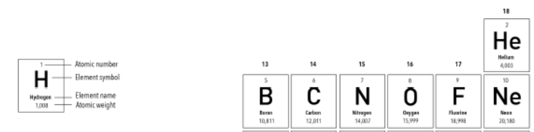
s-p mixing

Review: MO diagram for Li_2 to N_2 (sigma and pi MO)

MO Diagram of B_2







Li $2s^1$ 2p

Be $2s^2$ 2p

B $2s^2$ $2p^1$

C $2s^2$ $2p^2$

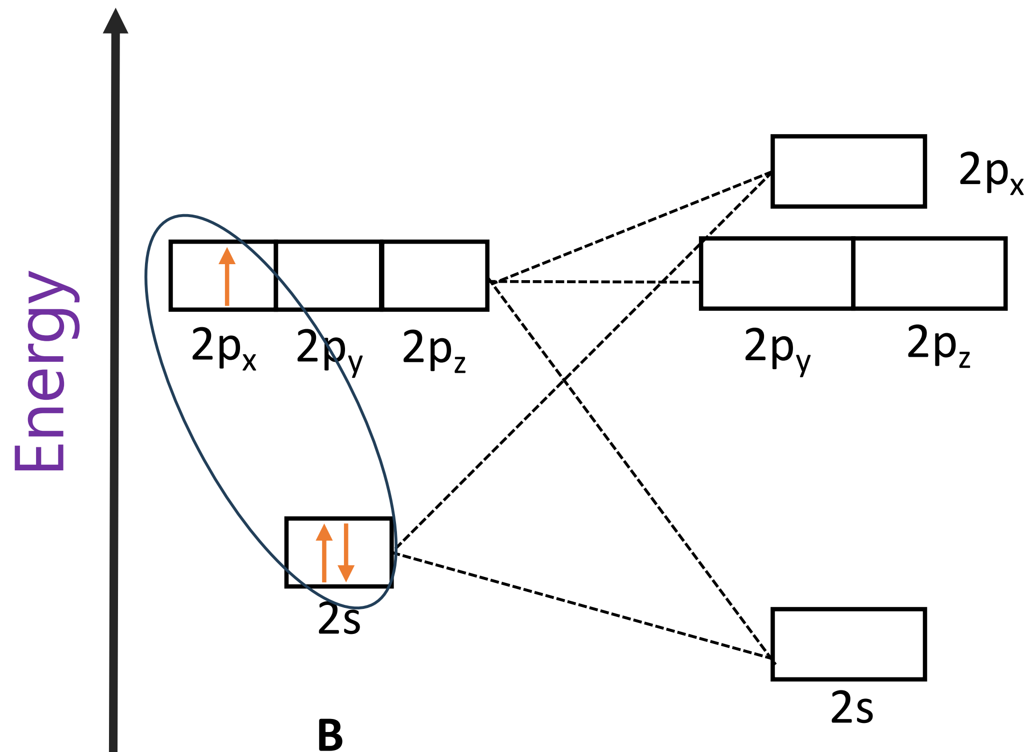
N $2s^2$ $2p^3$

s-p mixing

O $2s^2$ $2p^4$

F $2s^2$ $2p^5$

NO s-p mixing



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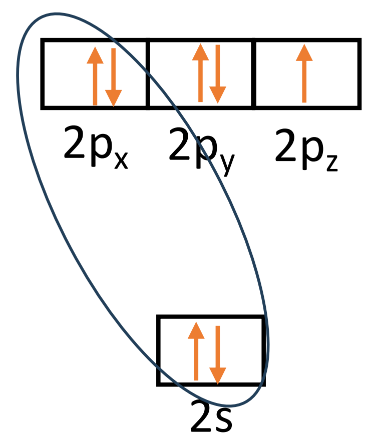

Review: MO diagram for Li_2 to N_2 (sigma and pi MO)

MO Diagram of B_2

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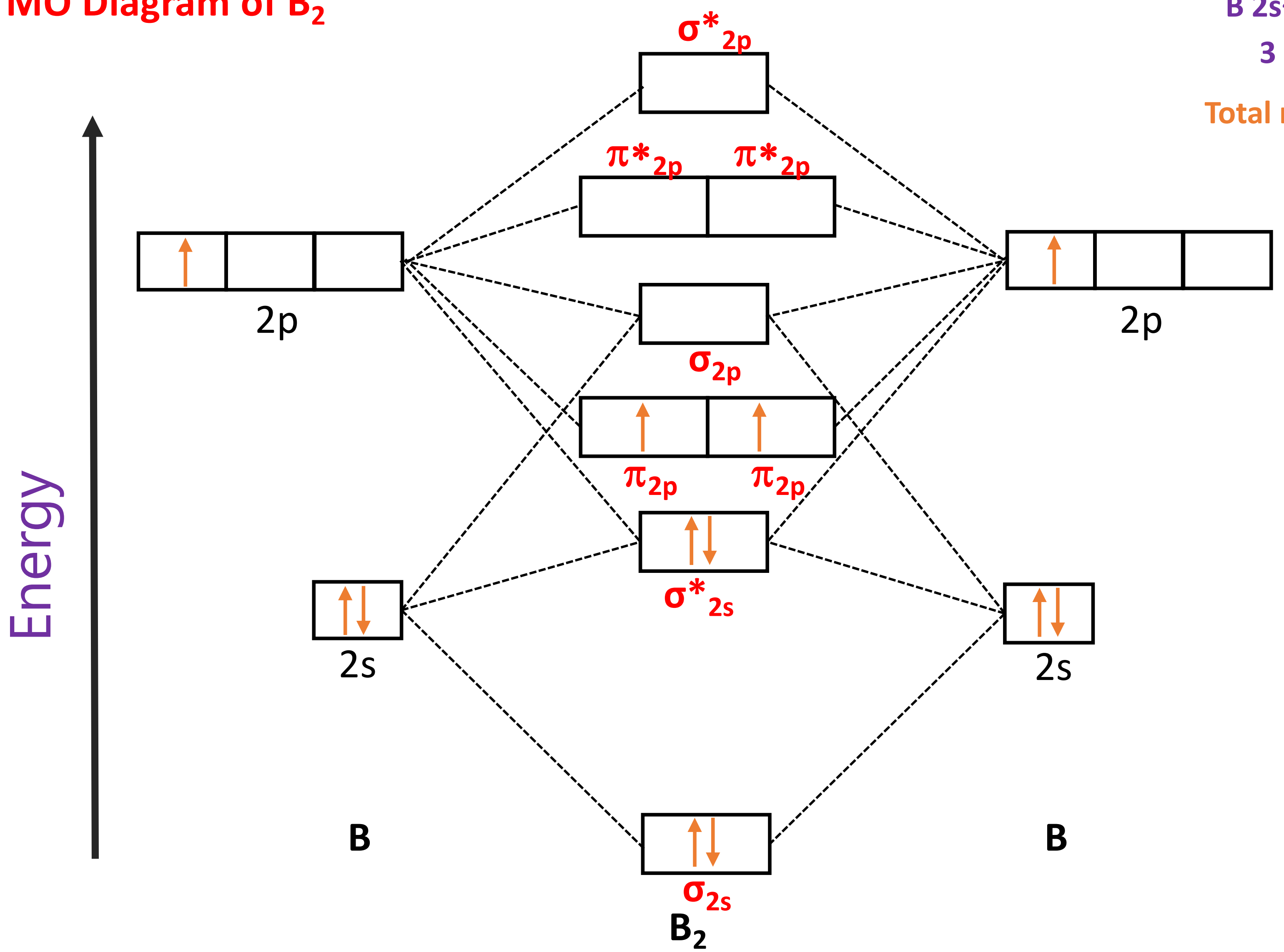
3 electrons in the valence shell

Total number of electrons in B_2 = 6



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Bond order in B_2 = (4–2)/2 = 1

$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p)^2$

Two unpaired electrons

Paramagnetic

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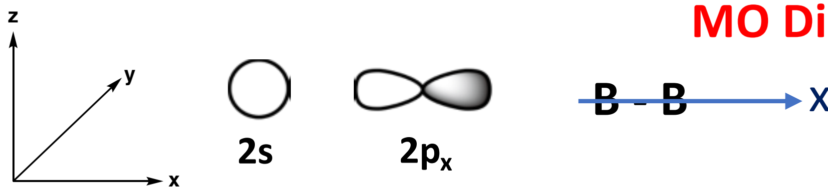

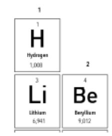

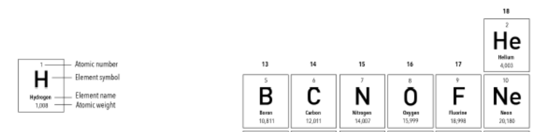

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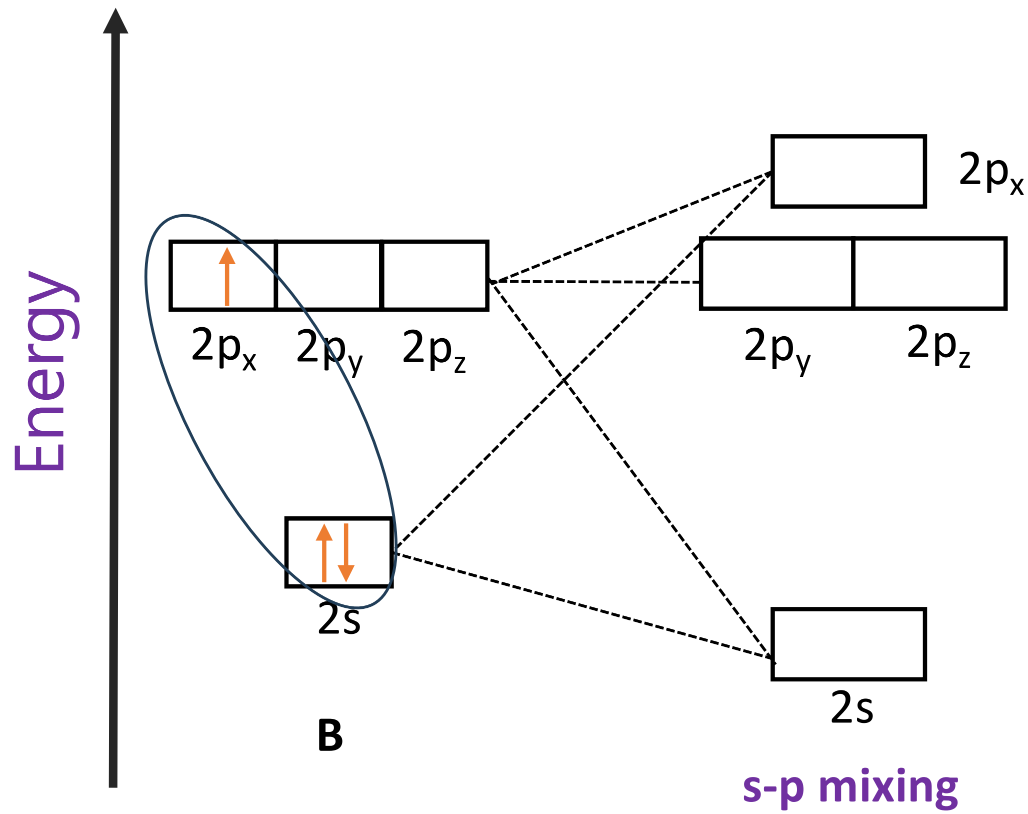
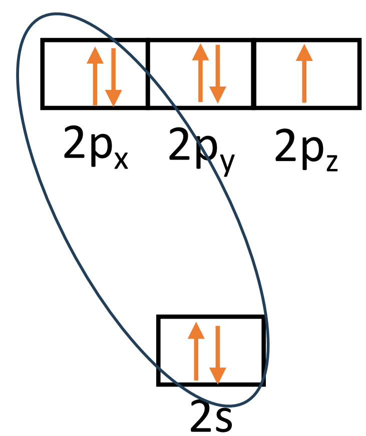
s-p mixing

O $2s^2$ $2p^4$
F $2s^2$ $2p^5$

NO s-p mixing





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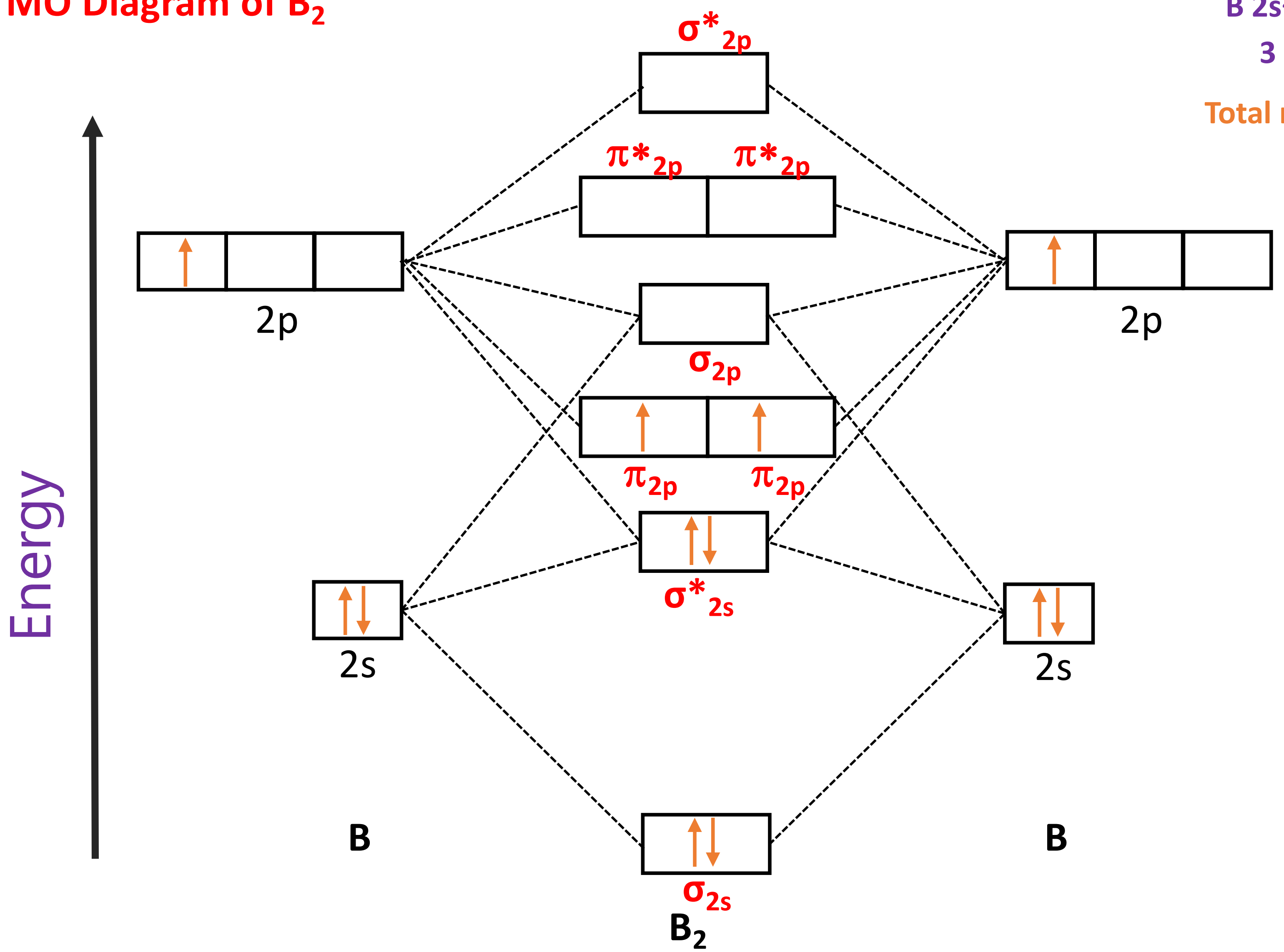

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Bond order in B_2 = (4–2)/2 = 1

$(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p)^2$

Two unpaired electrons

Paramagnetic

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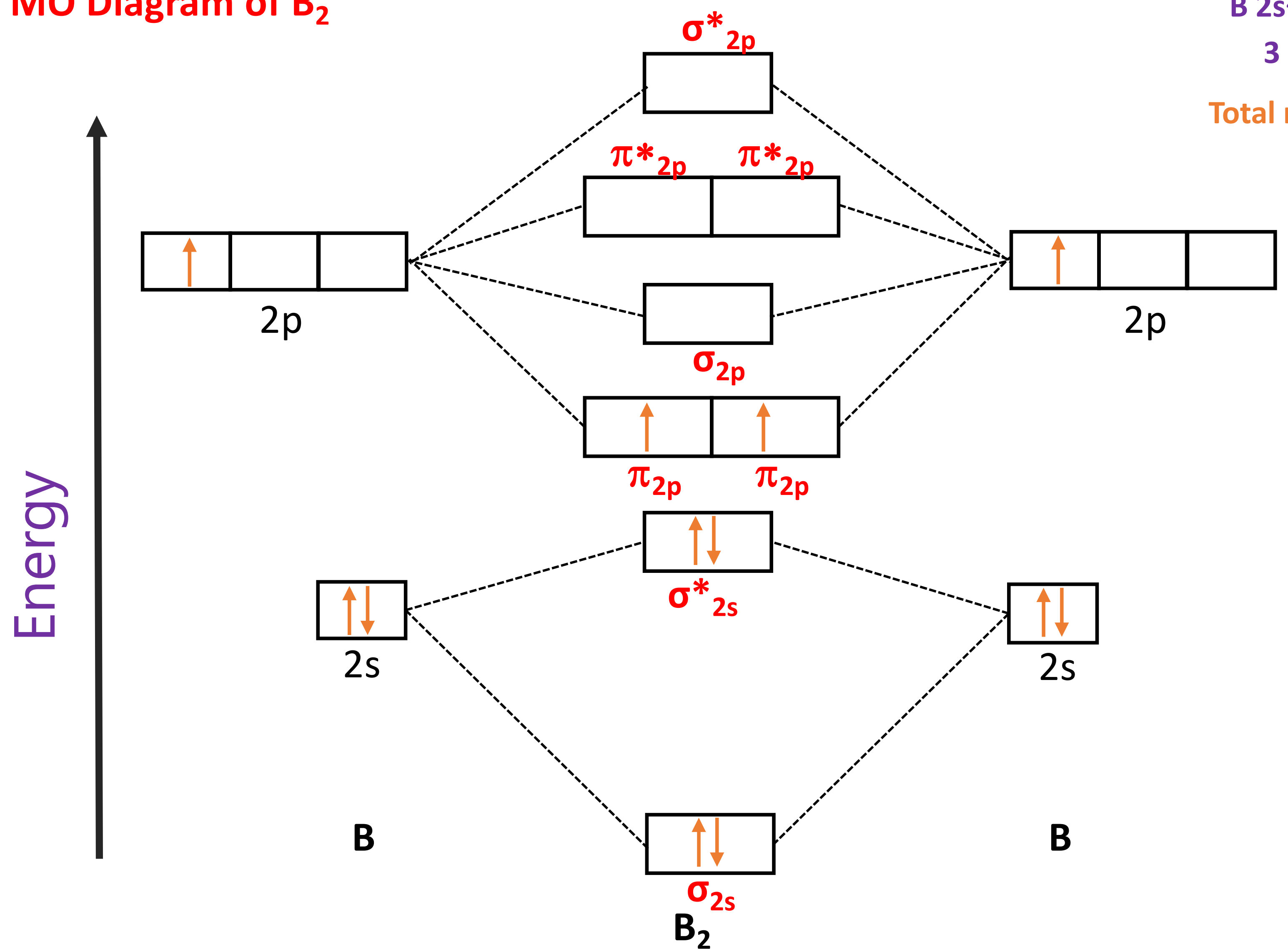

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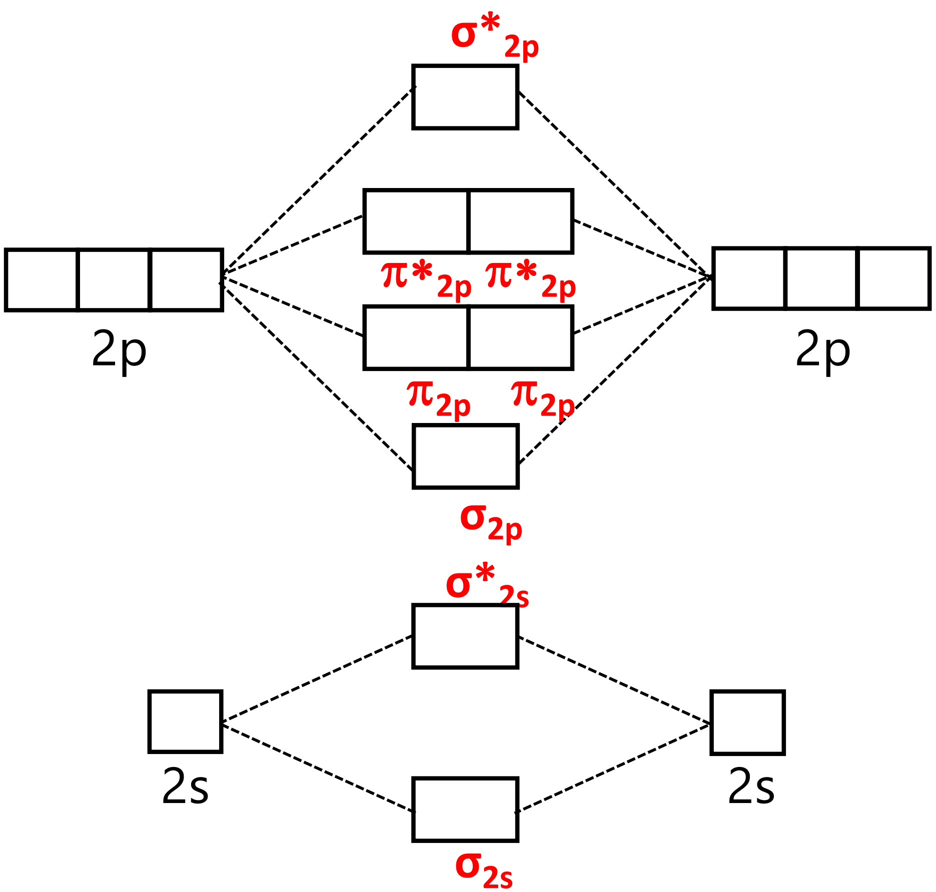
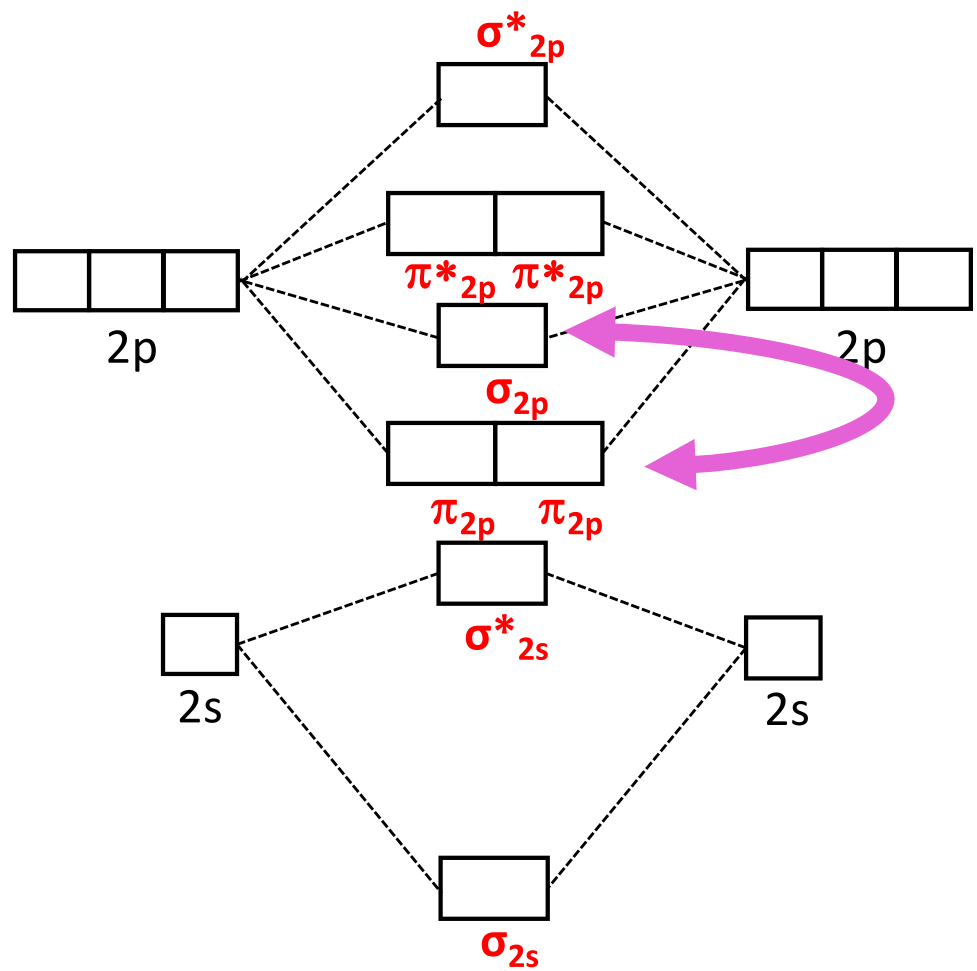
Compare: MO diagrams of O_2 to F_2 to those of Li_2 to N_2

MO Diagram of O_2 to F_2



MO Diagram of Li_2 to N_2



Practice Question 4

Draw the MO energy diagram for O_2^+. What is the bond order? Is it paramagnetic or diamagnetic? Compare the bond length of O_2^-, O_2 and O_2^+

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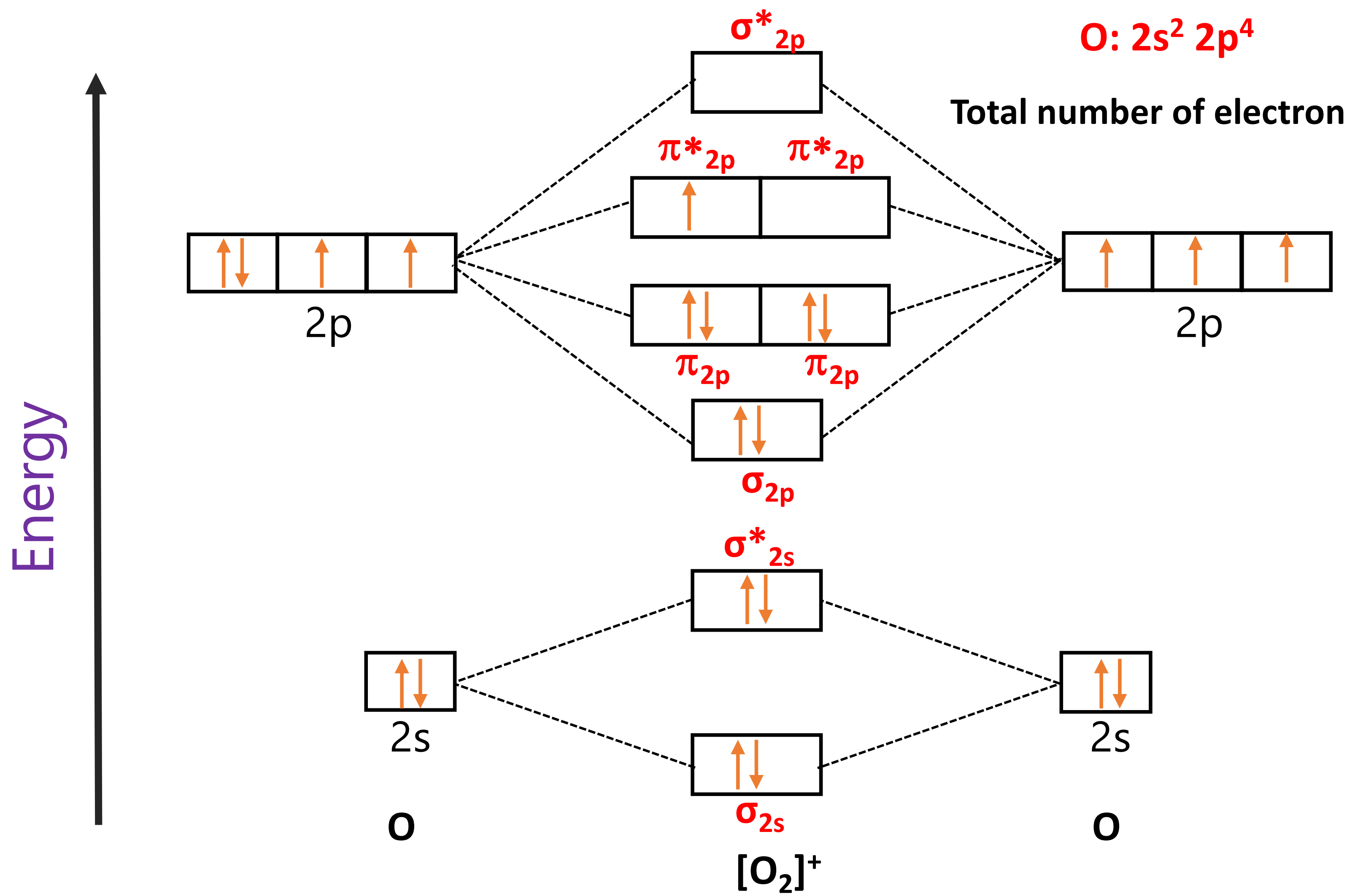
O: $2s^2$ $2p^4$

Total number of electrons in $[O_2]^+$ = (6x2) -1 = 11



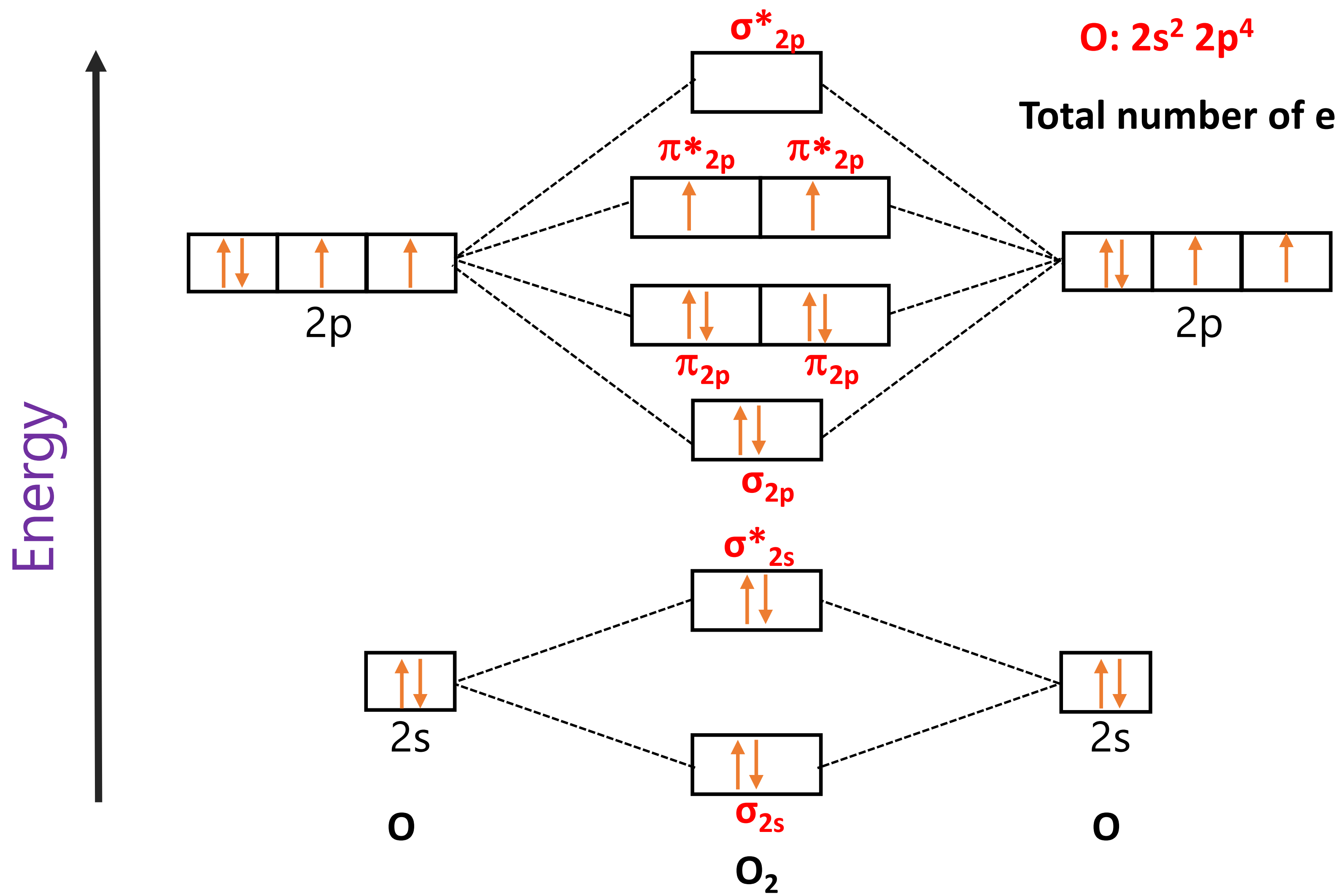
Bond Order = ½ (no. of electrons in bonding orbitals – no. of electrons in antibonding orbitals)

Bond order in $[O_2]^+$ = (8–3)/2 = 2.5

$(\sigma 2s)^2$ $(\sigma^* 2s)^2$ $(\sigma 2p)^2$ $(\pi 2p)^4$ $(\pi^* 2p)^1$ **One unpaired electron** **Paramagnetic**

Practice Question 4

Draw the MO energy diagram for O_2^+. What is the bond order? Is it paramagnetic or diamagnetic? Compare the bond length of O_2^-, O_2 and O_2^+



O: $2s^2\ 2p^4$

Total number of electrons in O_2 = 12

Bond Order = ½ (no. of electrons in bonding orbitals – no. of electrons in antibonding orbitals)

Bond order in O_2 = (8–4)/2 = 2

$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p)^2\ (\pi 2p)^4\ (\pi^* 2p)^2$ **Two unpaired electrons** **Paramagnetic**

Practice Question 4

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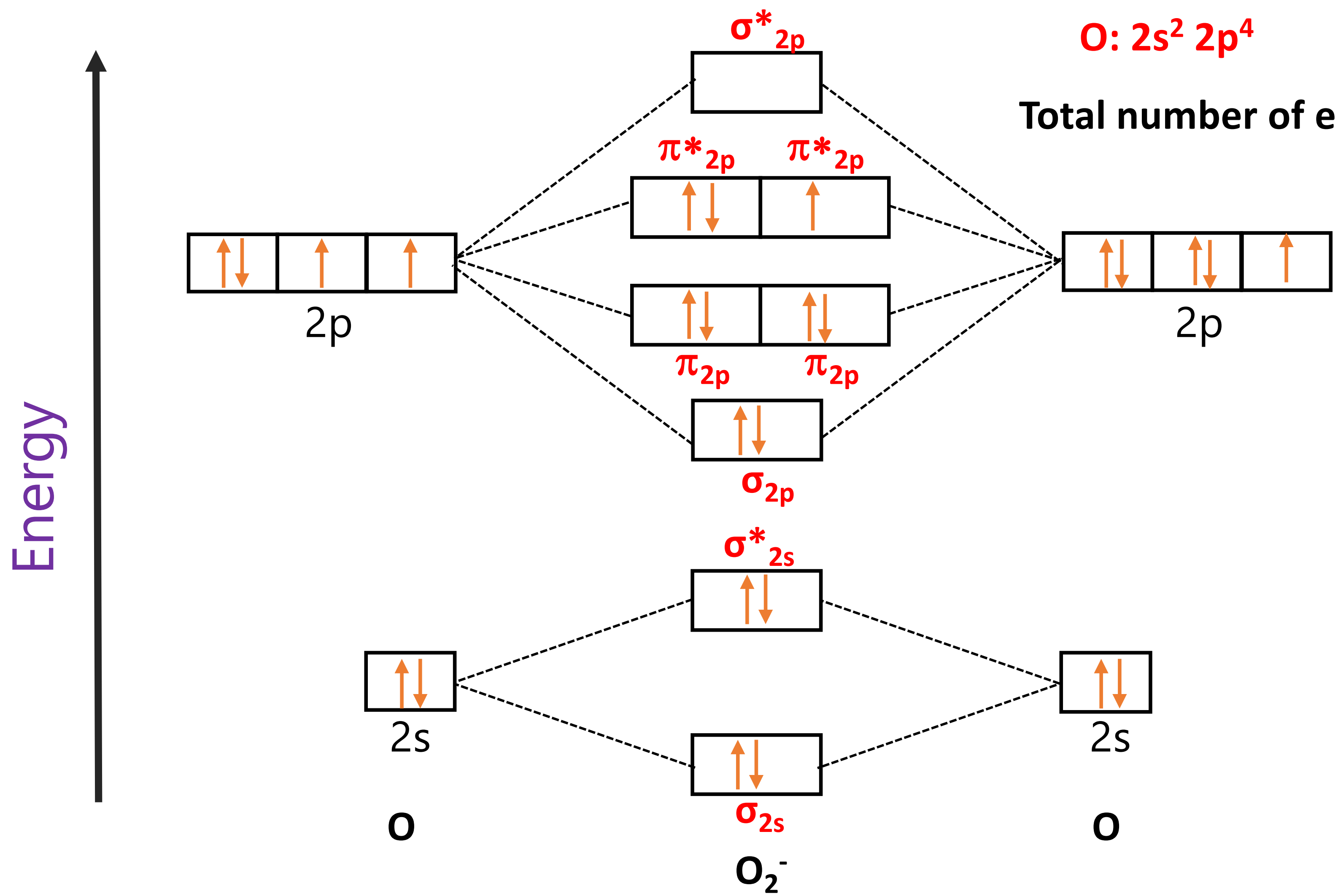

O: $2s^2\ 2p^4$

Total number of electrons in $[O_2]^-$ = 13

Bond Order = ½ (no. of electrons in bonding orbitals – no. of electrons in antibonding orbitals)

Bond order in $[O_2]^-$ = (8–5)/2 = 1.5

$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p)^2\ (\pi 2p)^4\ (\pi^* 2p)^3$ **One unpaired electron** **Paramagnetic**

Practice Question 4

Draw the MO energy diagram for O_2^+. What is the bond order? Is it paramagnetic or diamagnetic? Compare the bond length of O_2^-, O_2 and O_2^+

Bond order in O_2 = 2

Bond order in $[O_2]^-$ = 1.5

Bond order in $[O_2]^+$ = 2.5

Higher the bond order, shorter is the bond length

Bond length order:

$$[O_2]^+ < O_2 < [O_2]^-$$

Practice Question 5

Draw the MO energy diagram for BC. What is the bond order? What is the valence electronic configuration?

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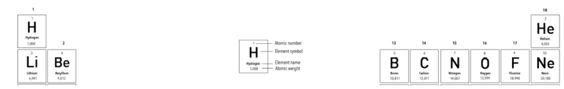
B $2s^2\ 2p^1$

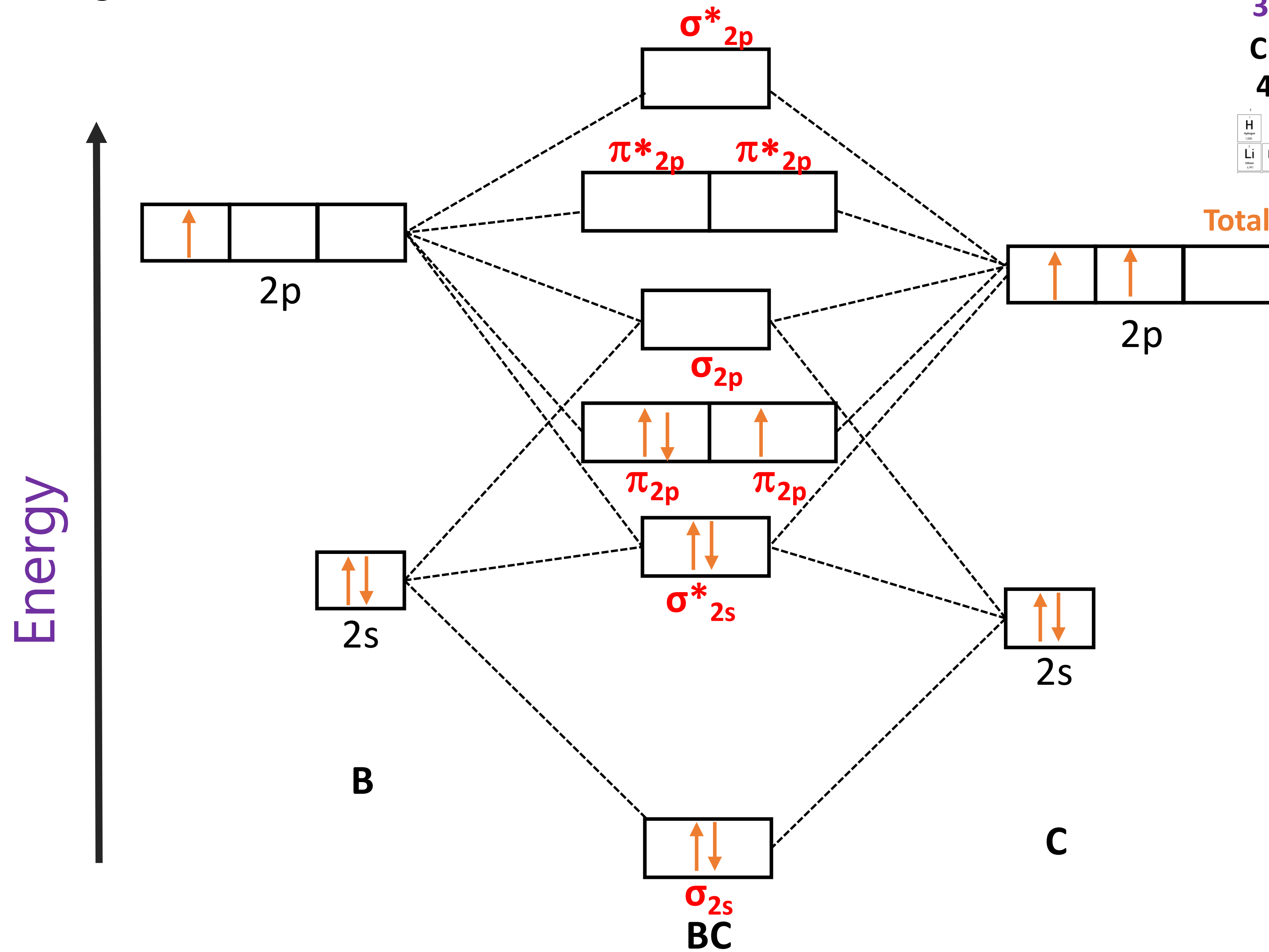
3 electrons in the valence shell

C $2s^2\ 2p^2$

4 electrons in the valence shell



Total number of electrons in BC = 7



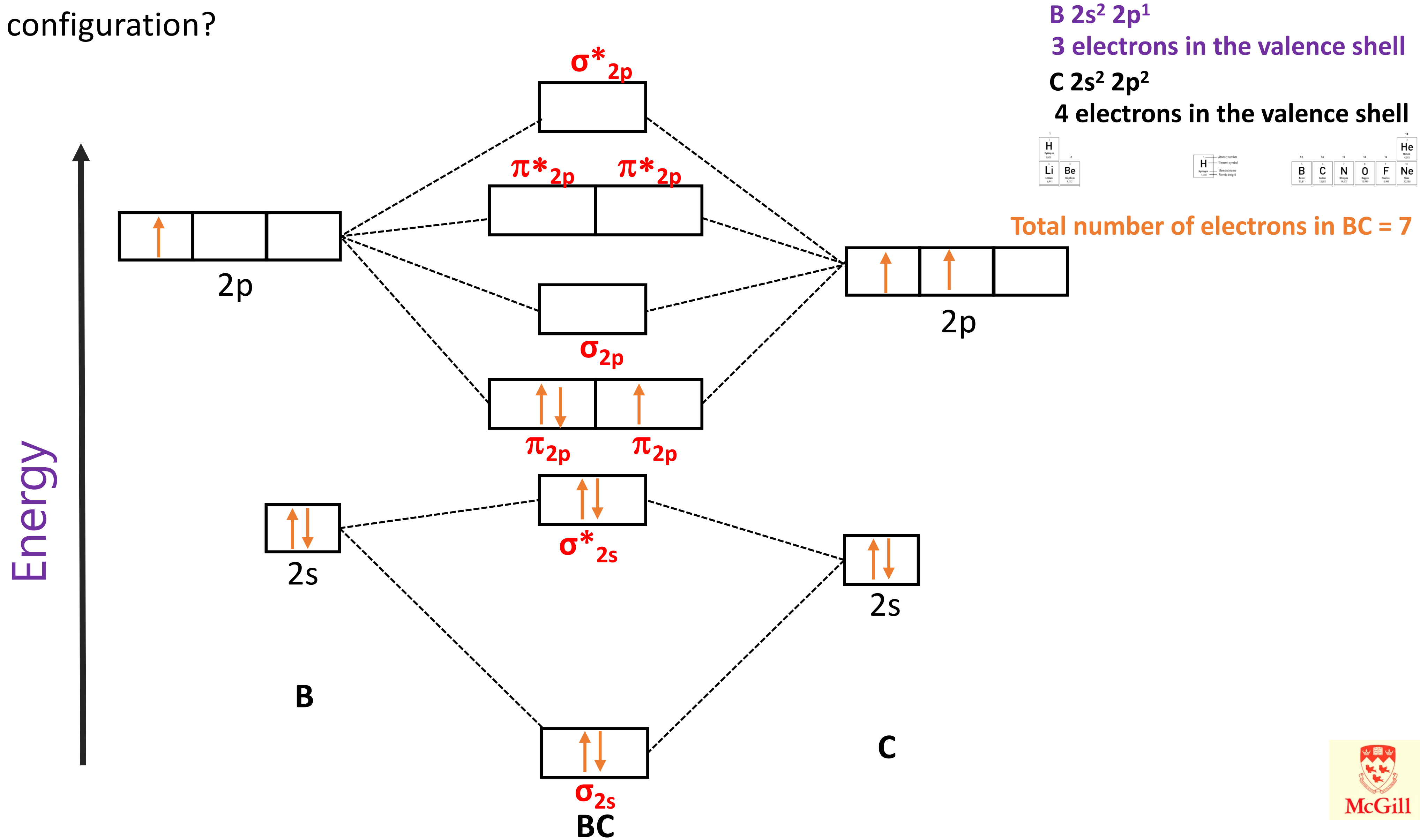
Bond Order = ½ (no. of electrons in bonding orbitals – no. of electrons in antibonding orbitals)

$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p)^3$

Bond order in BC = (5–2)/2 = 1.5

Practice Question 5

Draw the MO energy diagram for BC. What is the bond order? What is the valence electronic configuration?



Bond Order = ½ (no. of electrons in bonding orbitals – no. of electrons in antibonding orbitals)

$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p)^3$

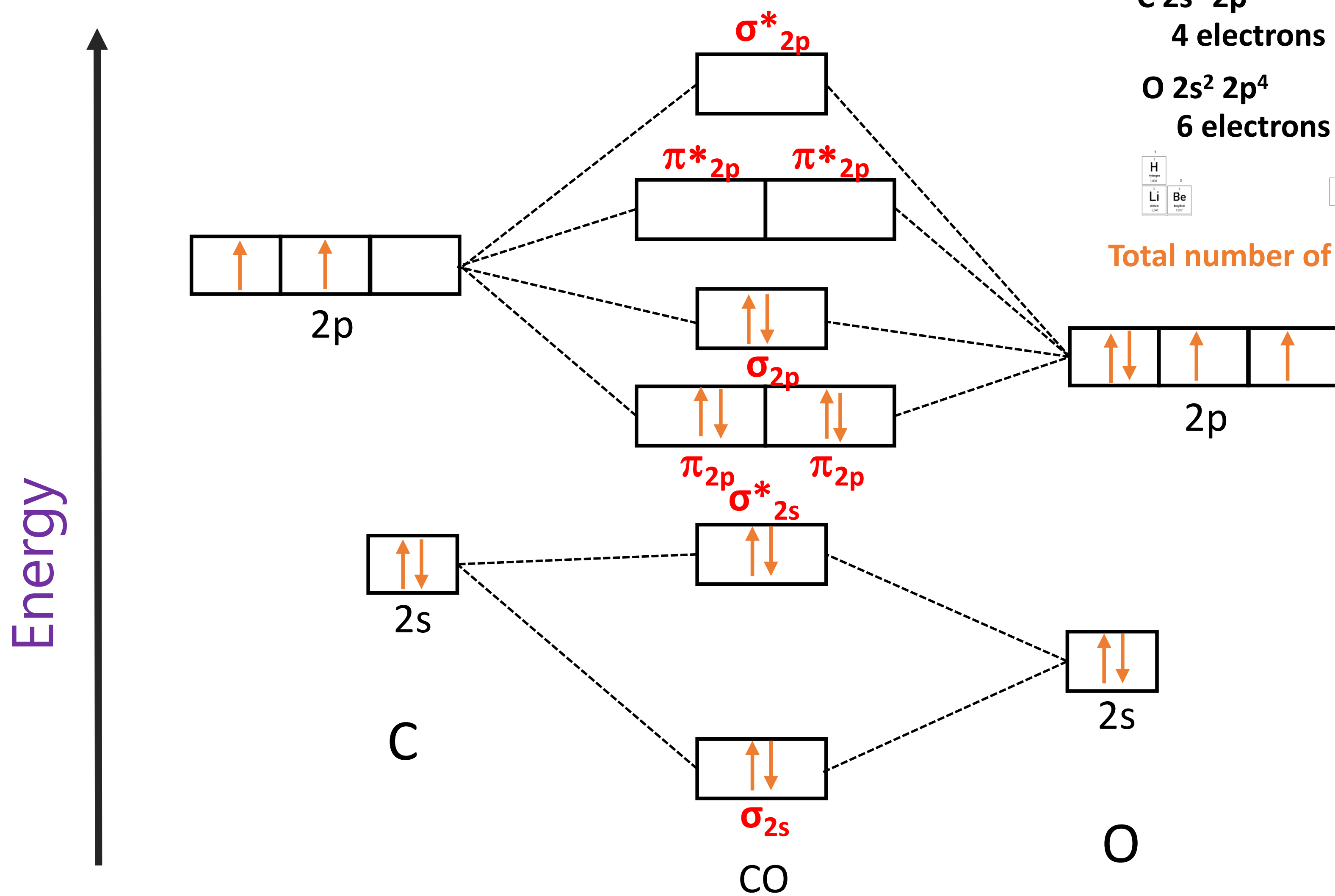
Bond order in BC = (5–2)/2 = 1.5

Practice Question 6

Fill in the MO energy diagram for CO. What is the bond order?

C $2s^2\ 2p^2$
4 electrons in the valence shell

O $2s^2\ 2p^4$
6 electrons in the valence shell



Total number of electrons in CO = 10

Bond Order = ½ (no. of electrons in bonding orbitals – no. of electrons in antibonding orbitals)

$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p)^4\ (\sigma 2p)^2$ **Bond order in CO = (8–2)/2 = 3**   **Diamagnetic**