

Molecular Orbital Theory

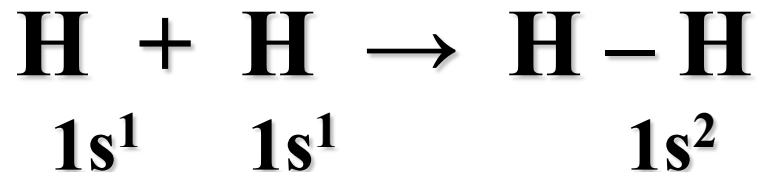
A theory of the electronic structure of molecules in terms of molecular orbitals, that may spread over several atoms or the entire molecule.

- (i) Assumes electronic structure of molecules mimics electronic structure of atoms.*
- (ii) Uses rules similar to Pauli Exclusion Principle.*
- (iii) Molecular orbitals are a combination of atomic orbitals.*
- (iv) Orbital interactions are dependent on
 - (a) energy difference between orbitals*
 - (b) magnitude of overlap**

Molecular Orbital (MO) Theory

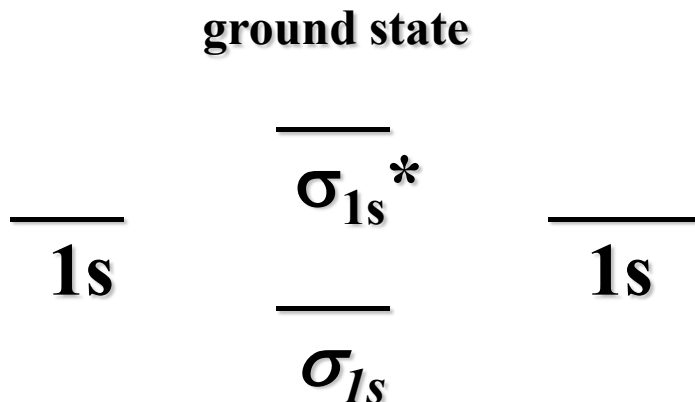
- Wave properties are used to describe the energy of the electrons in a molecule.
- **Molecular orbitals** have many characteristics like atomic orbitals:
 - Maximum of two electrons per orbital
 - Electrons in the same orbital have opposite spin
 - Definite energy of orbital
 - Can visualize electron density by a contour diagram

Molecular Orbital Theory



$\Psi_{1s} + \Psi_{1s} \equiv$ electrons found between 2 nuclei » Bonding orbitals!

$\Psi_{1s} - \Psi_{1s} \equiv$ electrons found elsewhere » Antibonding orbitals *



The following vocabulary terms are crucial in terms of understanding of Molecular Orbital (MO) Theory. Consider the following:

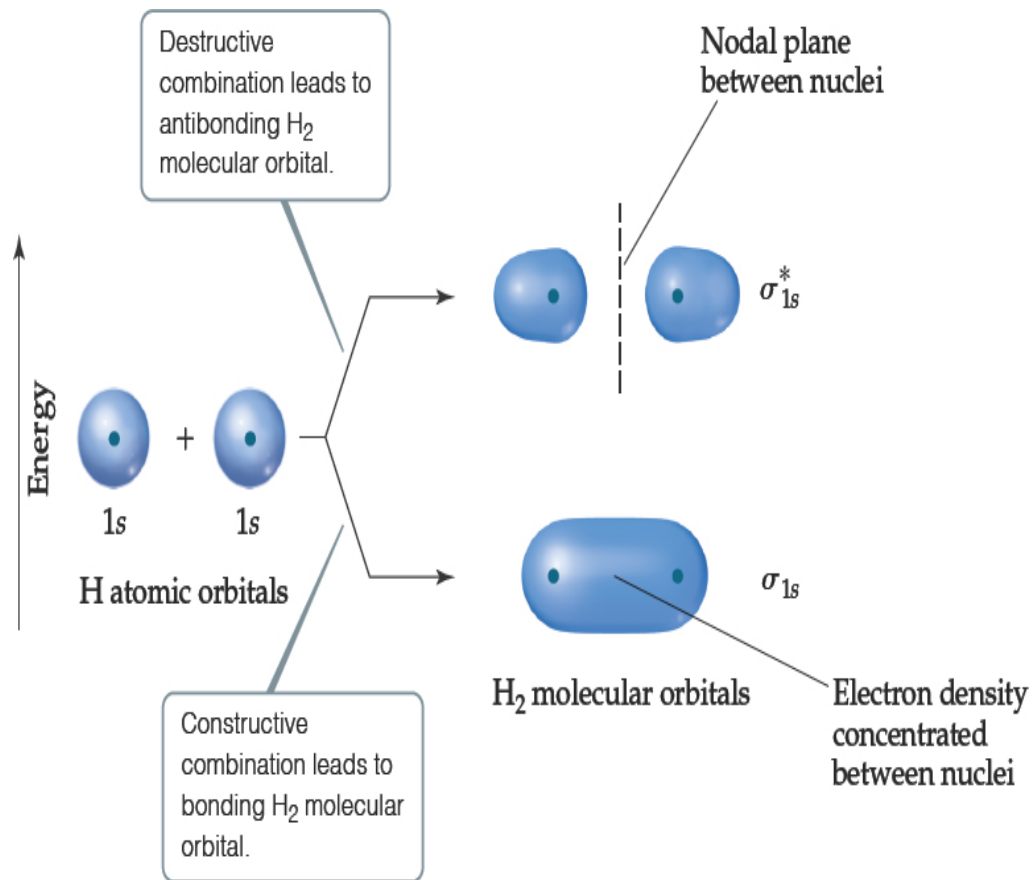
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1. **bonding molecular orbitals**: *lower* in energy than the atomic orbitals of which it is composed. Electrons in this type of orbital favor the molecule; that is, they will favor bonding.
2. **antibonding molecular orbitals**: *higher* in energy than the atomic orbitals of which it is composed. Electrons in this type of orbital will favor the separated atoms. Unstable but can exist!

Molecular Orbital (MO) Theory₂

Whenever there is direct overlap of orbitals, forming a bonding and an antibonding orbital, they are called **sigma (σ) molecular orbitals**. The antibonding orbital is distinguished with an asterisk as σ^* .

Here is an example for the formation of a hydrogen molecule from two atoms.



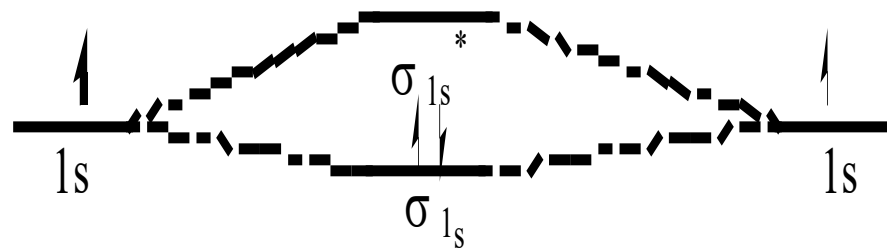
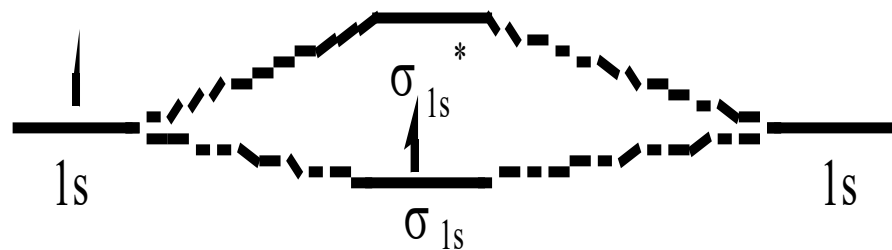
The following vocabulary terms are crucial in terms of understanding of Molecular Orbital (MO) Theory. Consider the following:

4. **sigma (σ) molecular orbitals**: The electron probability of both bonding and antibonding molecular orbitals is centered along the line passing through the two nuclei, where the electron probability is the same along any line drawn perpendicular to the bond axis at a given point on the axis. They are designated σ_s for the bonding MO and σ_s^* for the antibonding MO.

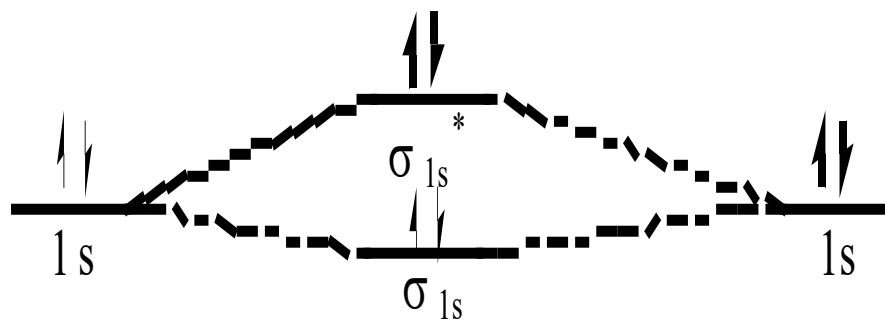
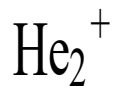
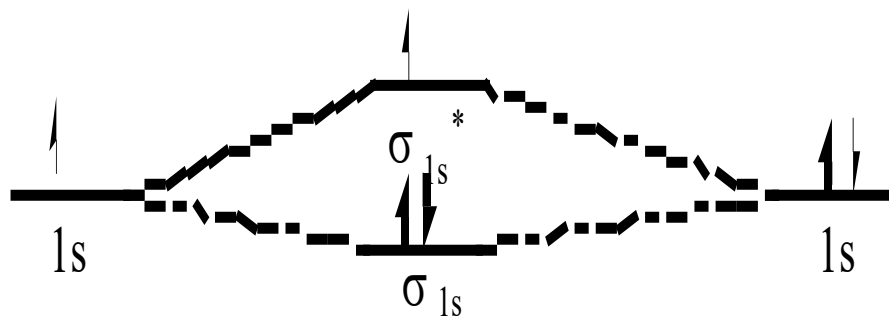
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5. **pi (π) molecular orbitals**: p orbitals that overlap in a parallel fashion also produce bonding and antibonding orbitals, where the electron probability lies above and below the line between the nuclei. They are designated π_p for the bonding MO and π_p^* for the antibonding MO.

Consider the MO diagrams for the diatomic molecules and ions of the first-period elements:



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The following vocabulary terms are crucial in terms of understanding of Molecular Orbital (MO) Theory. Consider the following:

3. **bond order**: the difference between the number of bonding electrons and the number of antibonding electrons, divided by 2. Bond order is an indication of strength.

$$\text{B.O.} = \frac{1}{2} (n_b - n_a)$$

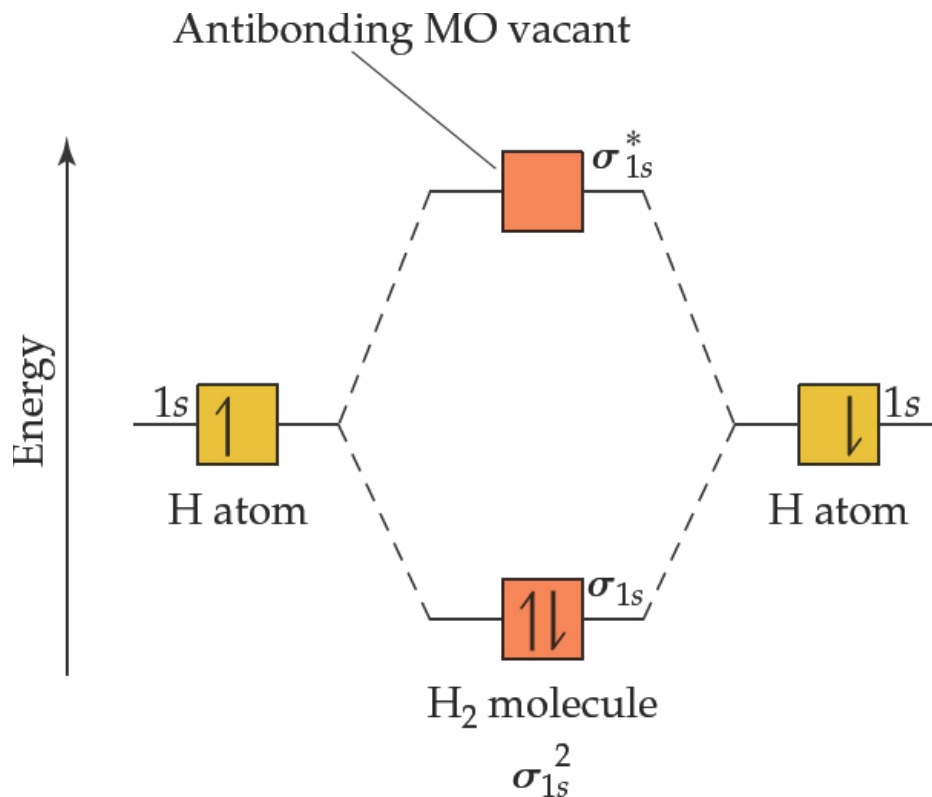
n_b = the number of bonding electrons

n_a = number of antibonding electrons

“Larger bond orders indicate greater bond strength.”

MO Diagram

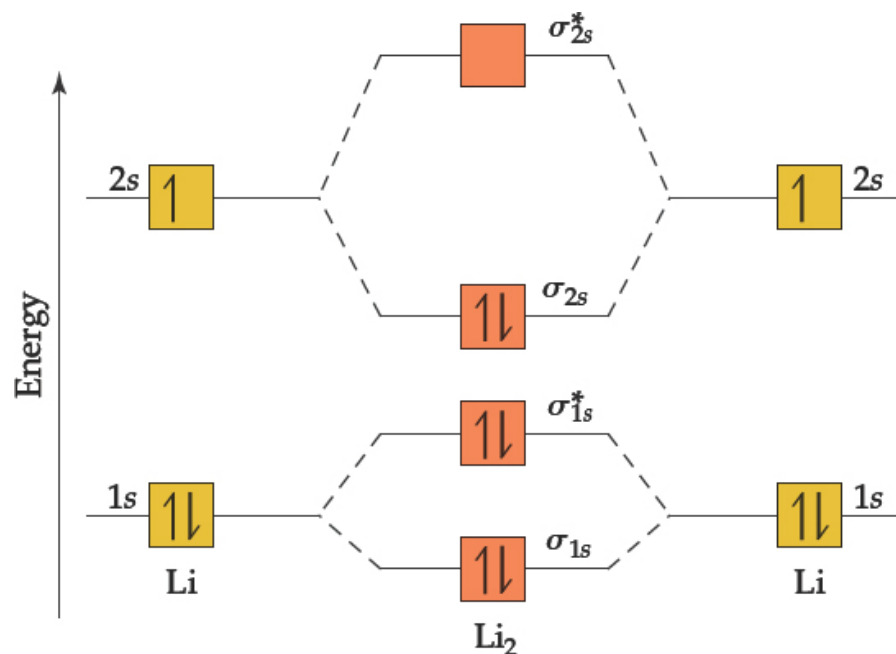
- An **energy-level diagram**, or **MO diagram**, shows how orbitals from atoms combine to form molecular orbitals.
- In H_2 the two electrons go into the bonding molecular orbital (lower in energy).
-



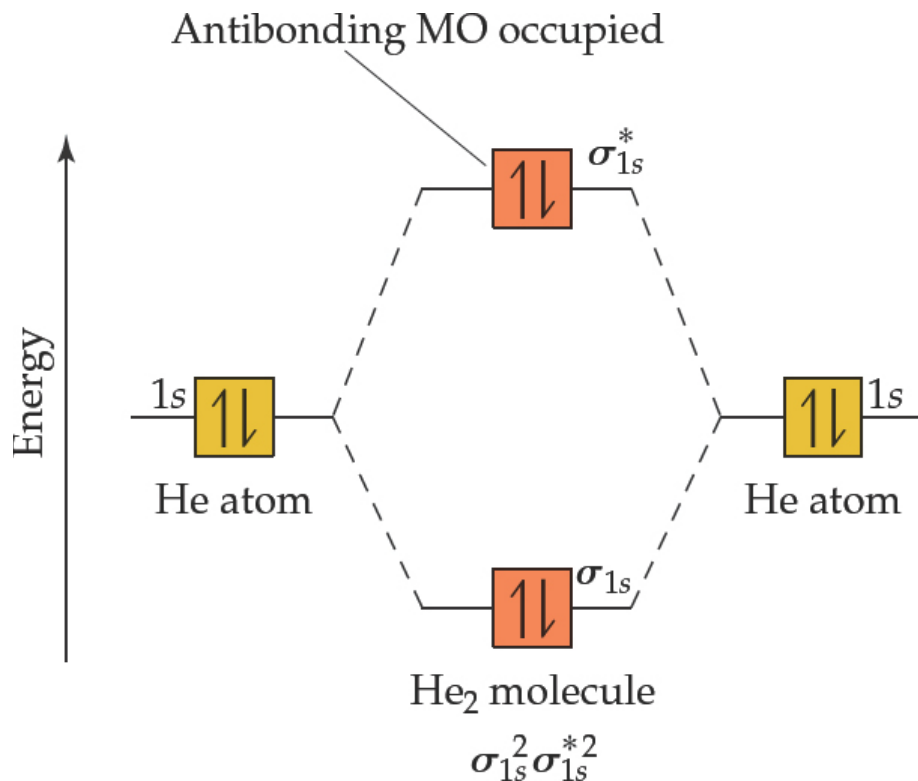
$$\text{Bond order} = \frac{1}{2} \left(\frac{\# \text{ of bonding electrons} - \# \text{ of antibonding electrons}}{\# \text{ of antibonding electrons}} \right) = \frac{1}{2} (2 - 0) = \mathbf{1 \text{ bond.}}$$

MOs, Bonding, and Core Electrons

- Li_2 (g) occurs at high temperatures.
- Lewis structure: $\text{Li} - \text{Li}$.
- The MO diagram is on the right.
- Notice that core electrons don't play a major part in bonding, so we usually don't include them in the MO diagram.



Can He₂ Form? Use MO Diagram and Bond Order to Decide!



**Therefore He₂
does not exist.**

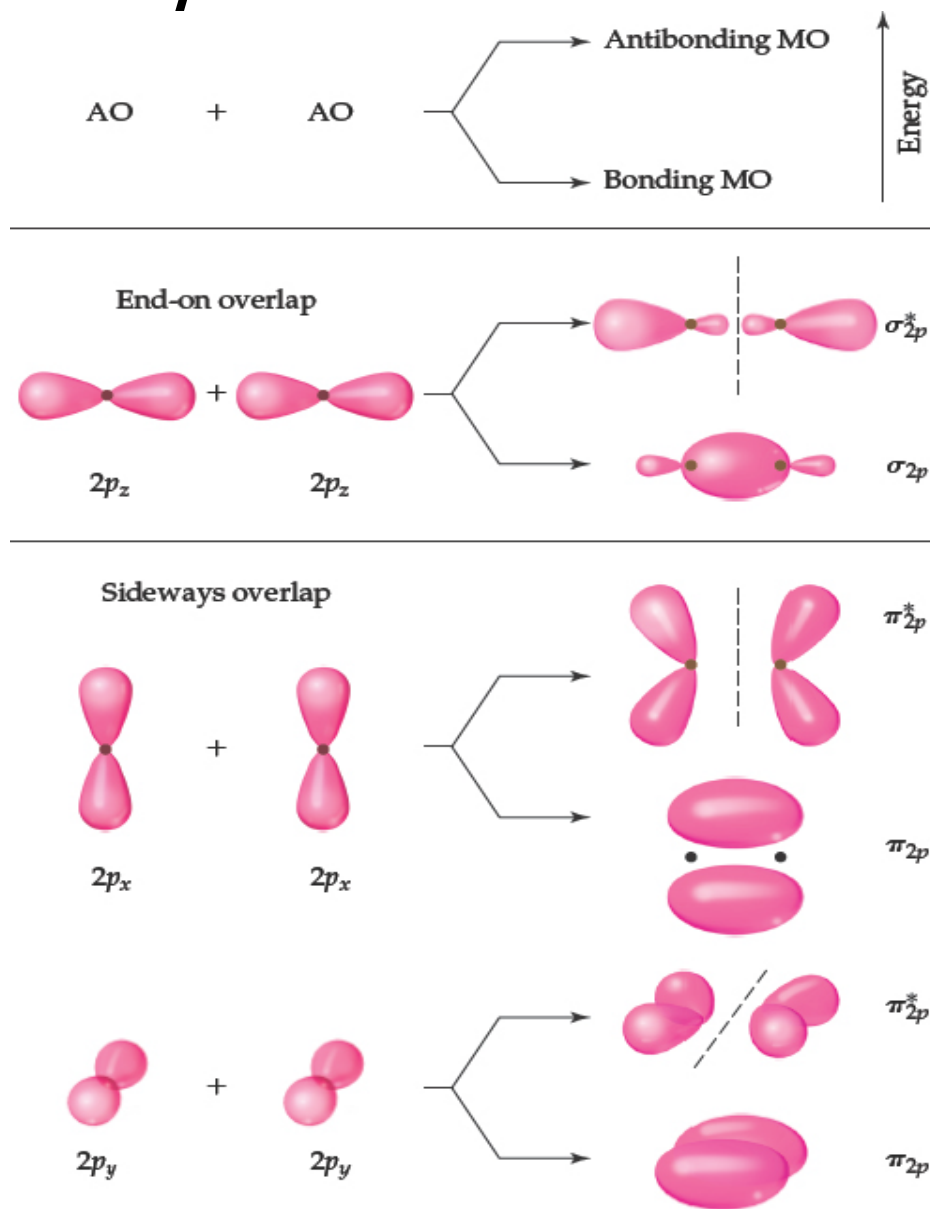
$$\text{Bond order} = \frac{1}{2}(2 - 2) = 0 \text{ bonds.}$$

Guiding Principles for the Formation of Molecular Orbitals

- 1) The number of MOs formed equals the number of AOs combined.**
- 2) AOs combine with AOs of similar energy.**
- 3) The effectiveness with which two AOs combine is proportional to their overlap.**
- 4) Each MO can accommodate at most two electrons with opposite spin. (They follow the Pauli exclusion principle.)**
- 5) When MOs of the same energy are populated, one electron enters each orbital (same spin) before pairing. (They follow Hund's rules.)**

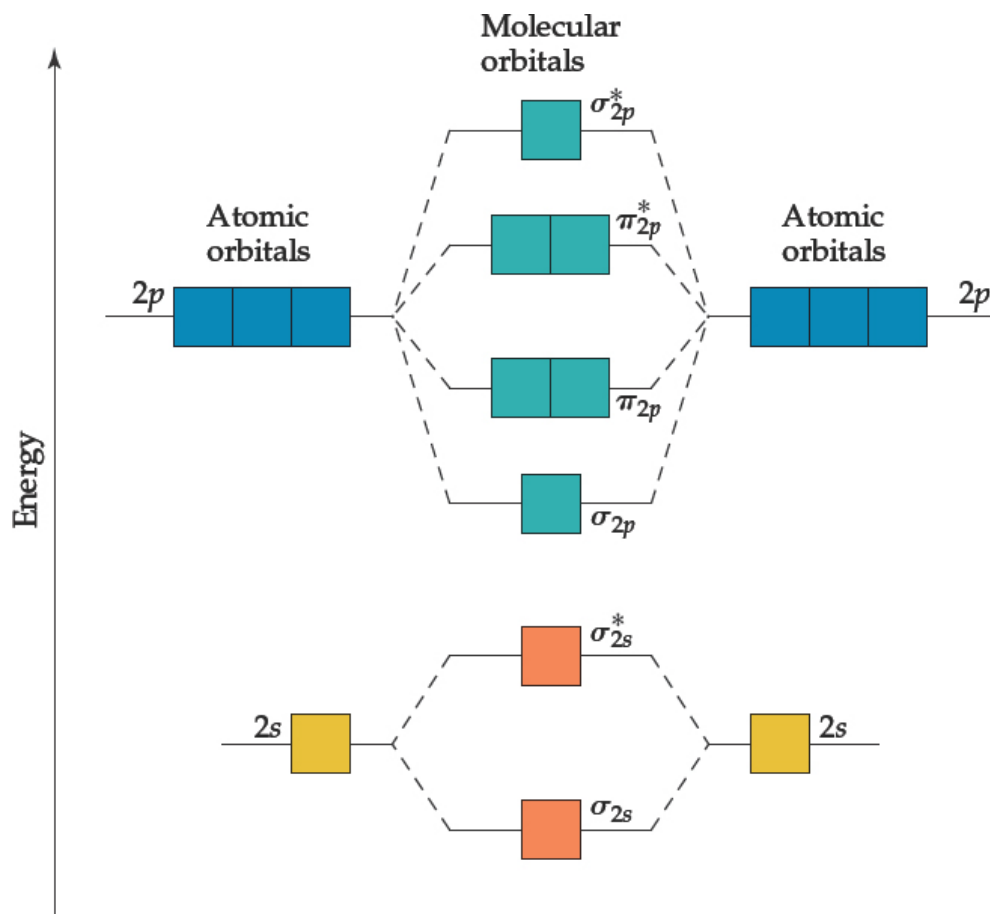
MOs from p -Orbitals

- p -orbitals also undergo overlap.
- They result in either direct or sideways overlap.



MO Diagrams for the Second Period p -Block Elements

- There are σ and σ^* orbitals from s and p atomic orbitals.
- There are π and π^* orbitals from p atomic orbitals.
- Since direct overlap is stronger, the effect of raising and lowering energy is greater for σ and σ^* .



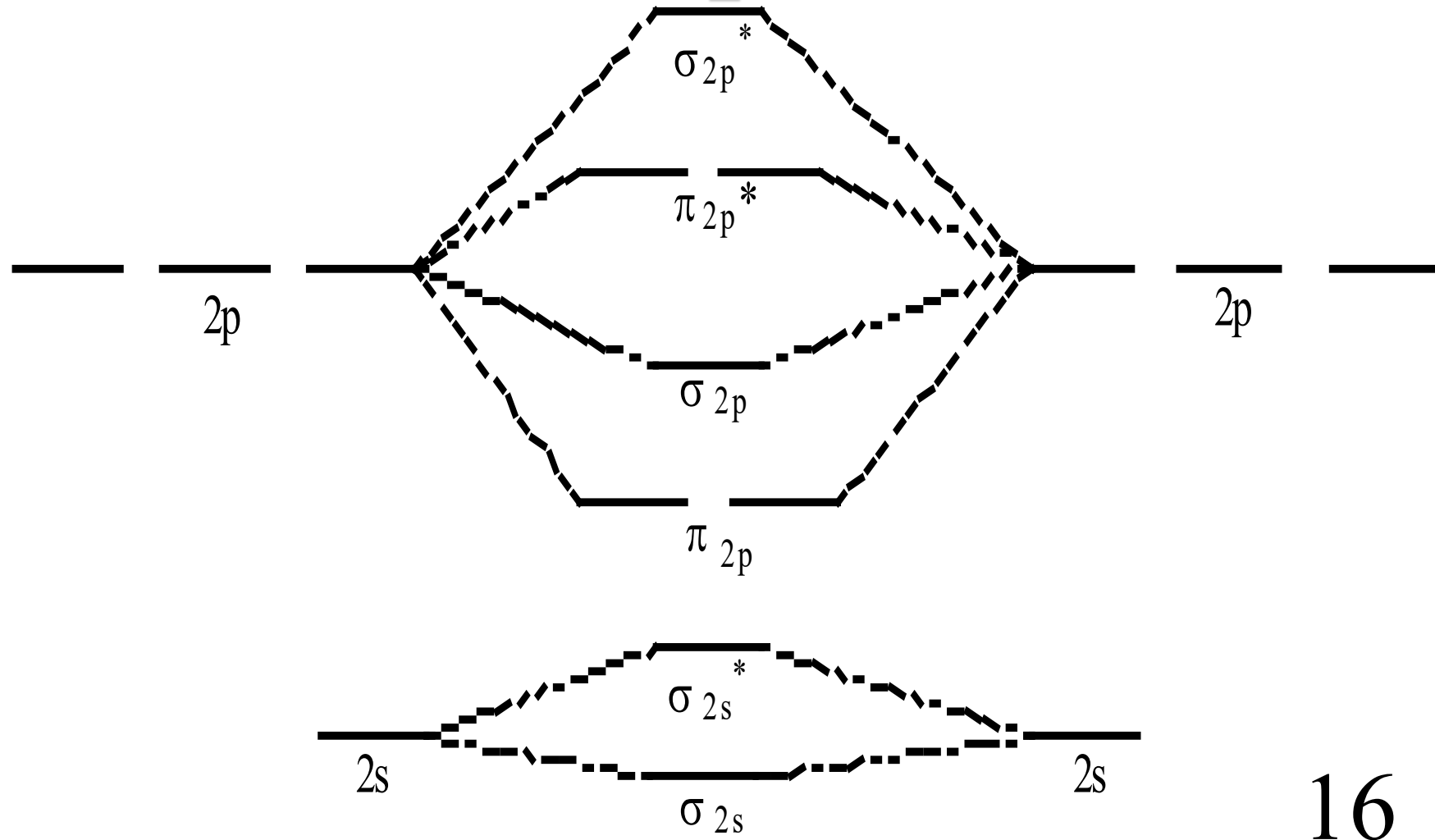
2nd row

Energy ↑	Large 2s–2p interaction			Small 2s–2p interaction		
	B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂
σ_{2s}^*	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
π_{2p}^*	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$
σ_{2p}^*	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
π_{2p}	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$
σ_{2p}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
π_{2p}^*	\uparrow \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	\uparrow \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$
σ_{2p}^*	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

Consider one of the possible molecular orbital energy-level diagram for diatomic molecules of the second-period elements:

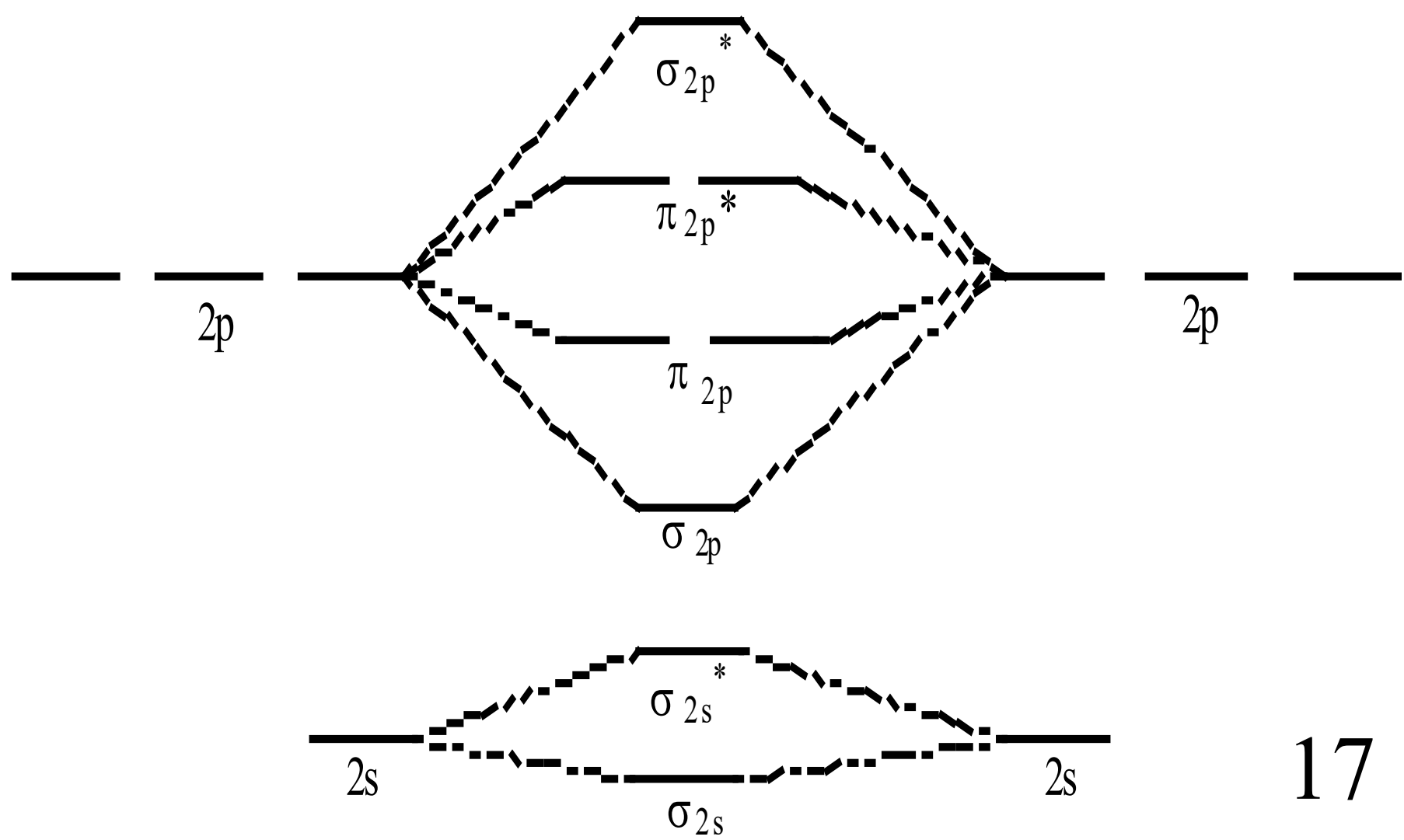
$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^2 \pi_{2p}^{*4} \sigma_{2p}^{*2}$$

$$Z \leq 7$$











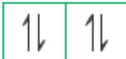
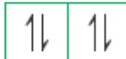



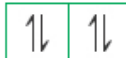
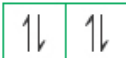
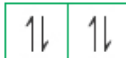

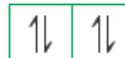
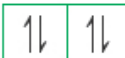

















The other possible molecular orbital energy-level diagrams for diatomic molecules of the second-period elements:

$Z \geq 8$



M O Diagrams for Diatomic Molecules of Second Period Elements

Energy ↑	Large 2s–2p interaction			Small 2s–2p interaction		
	B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂
σ_{2p}^*						
π_{2p}^*						
σ_{2p}						
π_{2p}						
σ_{2s}^*						
σ_{2s}						
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

MO Diagrams and Magnetism

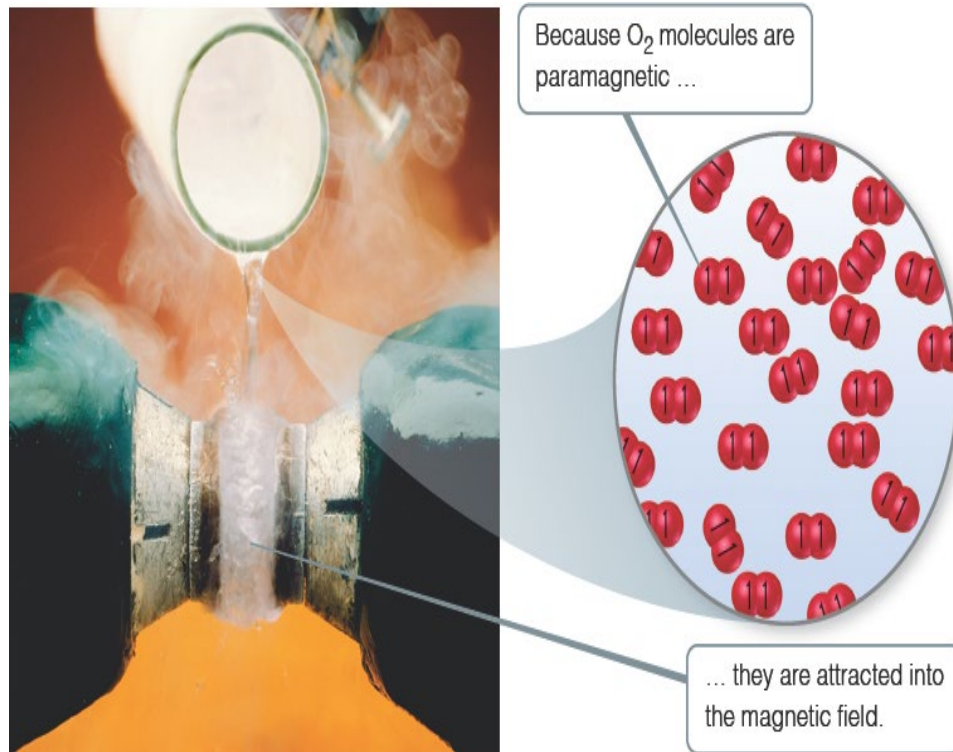
- **Diamagnetism** is the result of all electrons in every orbital being spin-paired. These substances are weakly repelled by a magnetic field.
- **Paramagnetism** is the result of the presence of one or more unpaired electrons in an orbital.

Is oxygen (O_2) paramagnetic or diamagnetic? Look back at the MO diagram!

It is paramagnetic.

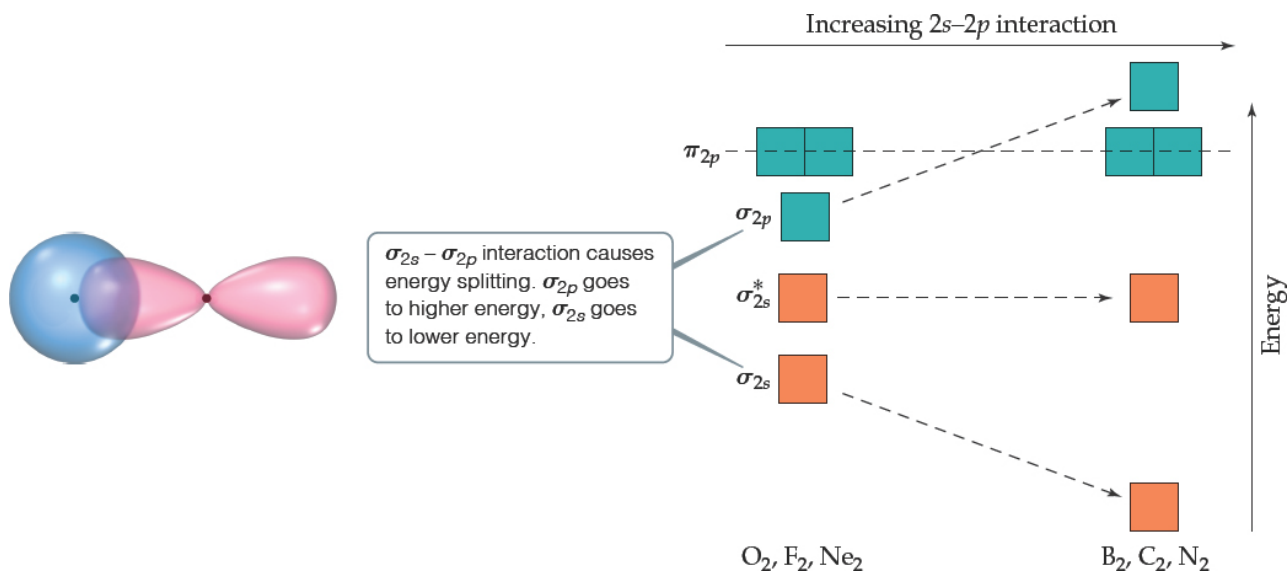
Paramagnetism of Oxygen

- Lewis structures would **not** predict that (O_2) is paramagnetic.
- The MO diagram clearly shows that (O_2) is paramagnetic.
- Both show a double bond (bond order = 2).

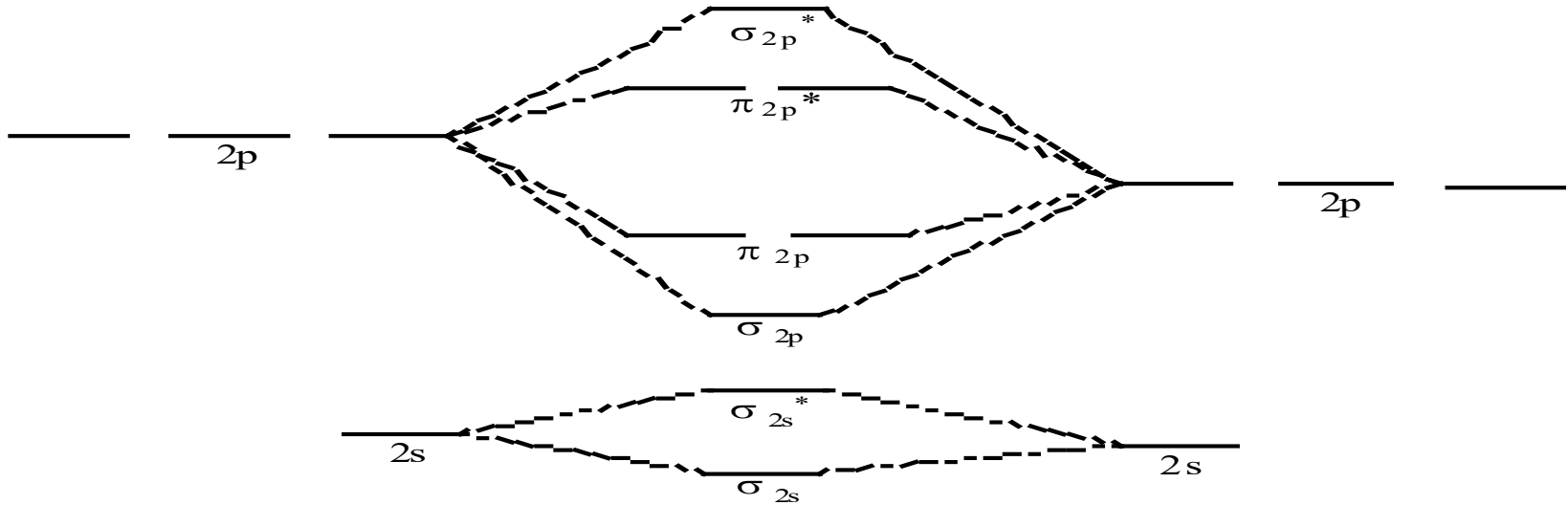


s and p Orbital Interactions

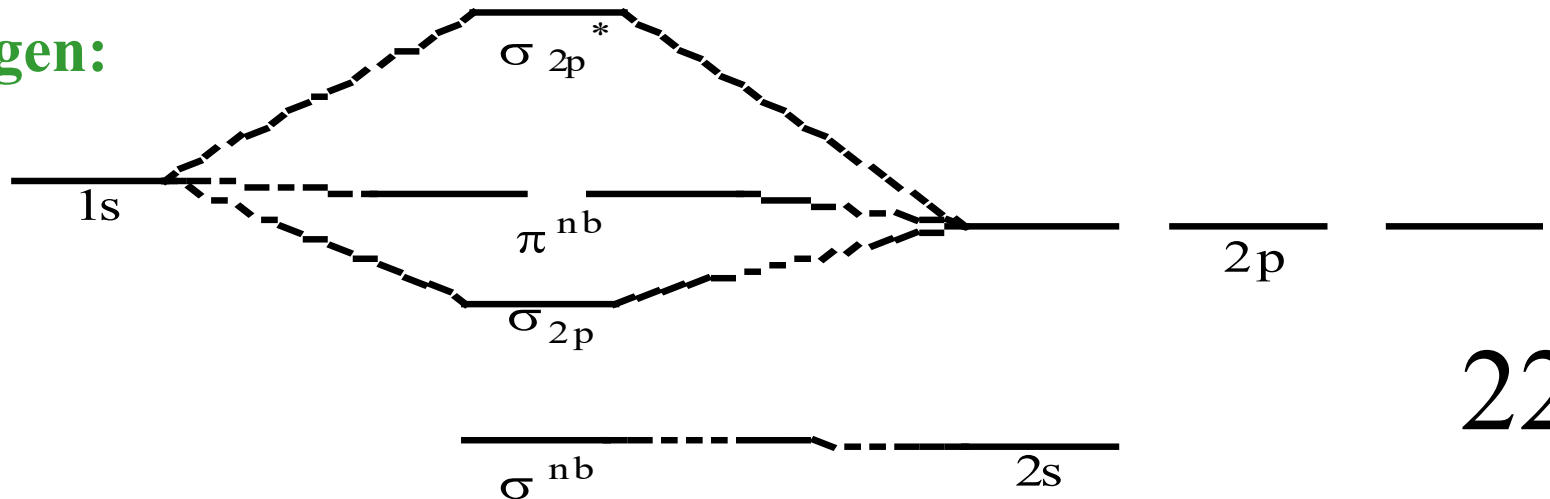
- In some cases, s orbitals can interact with the p_z orbitals more than the p_x and p_y orbitals.
- It raises the energy of the p_z orbital and lowers the energy of the s orbital.
- The p_x and p_y orbitals are degenerate orbitals.



What if the two diatomic elements (or ions) are different? Then you must take electronegativity into account when constructing the molecular orbital energy diagram:



Finally, consider a diatomic molecule where one of the bonded atoms is hydrogen:



Heteronuclear Diatomic Molecules

- Diatomic molecules can consist of atoms from different elements.
- How does a MO diagram reflect differences?
- The atomic orbitals have different energy, so the interactions change slightly.
- The more electronegative atom has orbitals lower in energy, so the bonding orbitals will more resemble them in energy.

