Molecular Orbital Theory
(MOT)

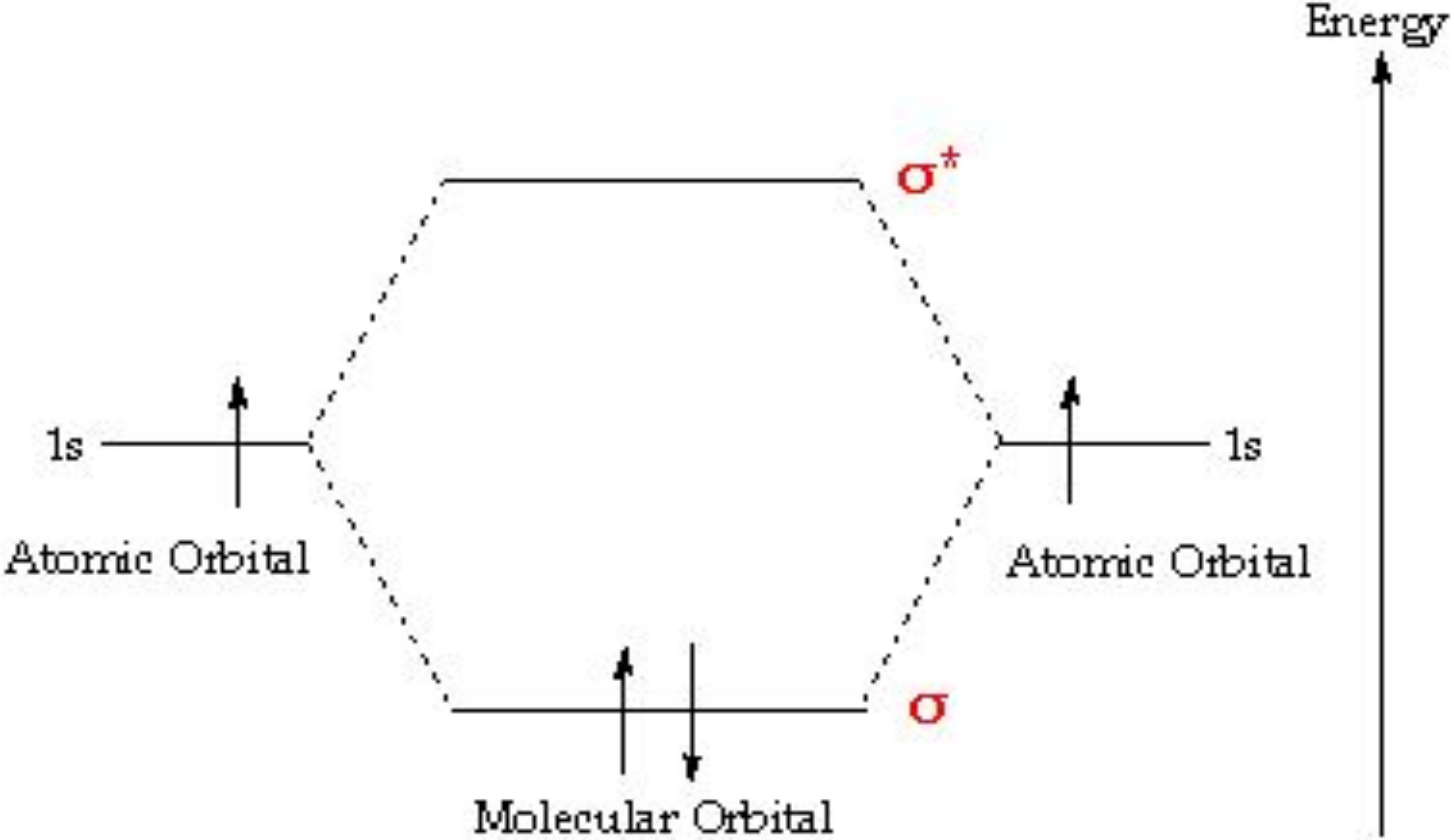
Introduction

The Molecular Orbital Theory (often abbreviated to MOT) is a theory on chemical bonding developed at the beginning of the twentieth century by F. Hund and R. S. Mulliken to describe the structure and properties of different molecules. The valence-bond theory failed to adequately explain how certain molecules contain two or more equivalent bonds whose bond orders lie between that of a single bond and that of a double bond, such as the bonds in resonance-stabilized molecules. This is where the molecular orbital theory proved to be more powerful than the valence-bond theory (since the orbitals described by the MOT reflect the geometries of the molecules to which it is applied)

The key features of the molecular orbital theory are listed below.

- The total number of molecular orbitals formed will always be equal to the total number of atomic orbitals offered by the bonding species.
- There exist different types of molecular orbitals viz; bonding molecular orbitals, anti-bonding molecular orbitals, and non-bonding molecular orbitals. Of these, anti-bonding molecular orbitals will always have higher energy than the parent orbitals whereas bonding molecular orbitals will always have lower energy than the parent orbitals.
- The electrons are filled into molecular orbitals in the increasing order of orbital energy (from the orbital with the lowest energy to the orbital with the highest energy).

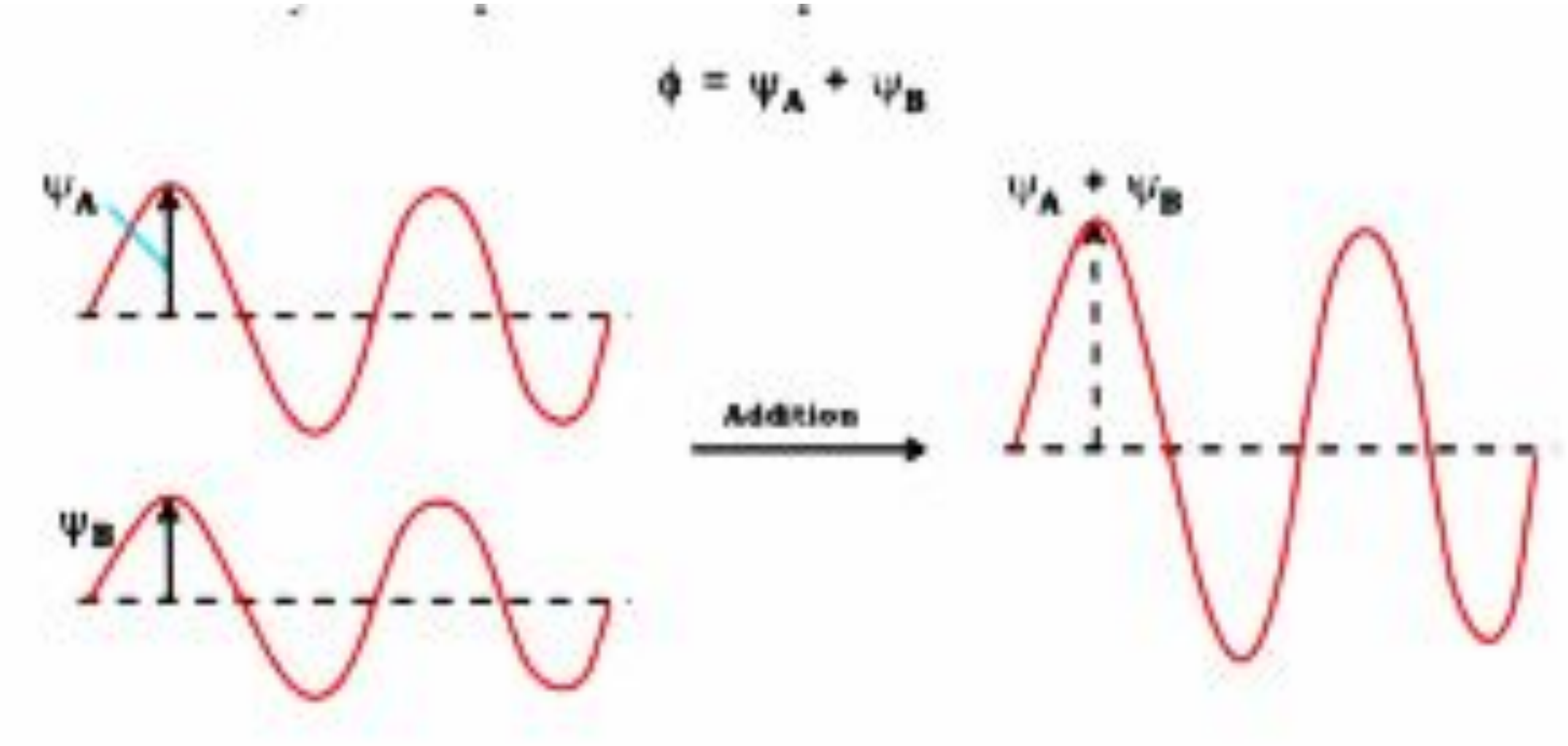
- The most effective combinations of atomic orbitals (for the formation of molecular orbitals) occur when the combining atomic orbitals have similar energies.
  In simple terms, the molecular orbital theory states that each atom tends to combine together and form molecular orbitals. As a result of such arrangement, electrons are found in various atomic orbitals and they are usually associated with different nuclei. In short, an electron in a molecule can be present anywhere in the molecule.
  One of the main impacts of the molecular orbital theory after its formulation is that it paved a new way to understand the process of bonding. With this theory, the molecular orbitals are basically considered as linear combinations of atomic orbitals.


Energy
σ^*
1s
1s
Atomic Orbital
Atomic Orbital
σ
Molecular Orbital

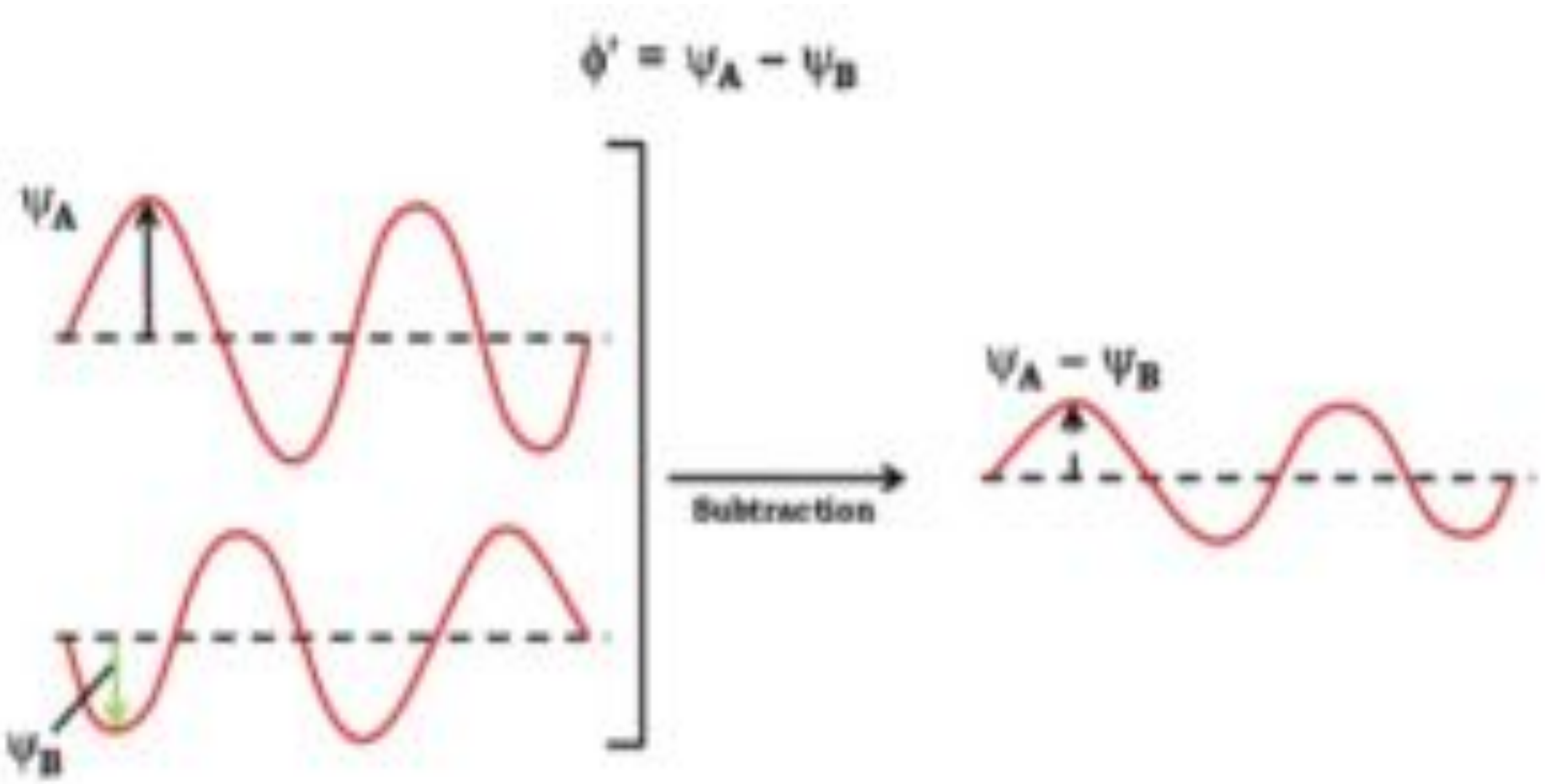
Formation of Molecular Orbitals

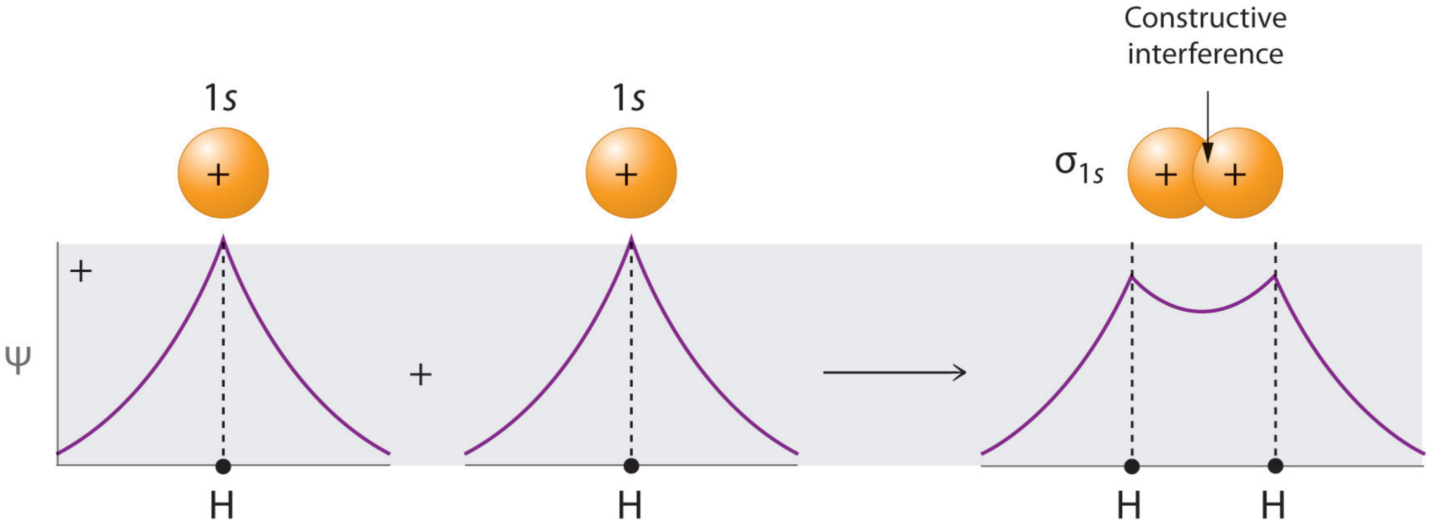
An atomic orbital is an electron wave; the waves of the two atomic orbitals may be in phase or out of phase. Suppose Ψ_A and Ψ_B represent the amplitude of the electron wave of the atomic orbitals of the two atoms A and B.

Case 1: When the two waves are in phase so that they add up and amplitude of the wave is $\Phi = \Psi_A + \Psi_B$

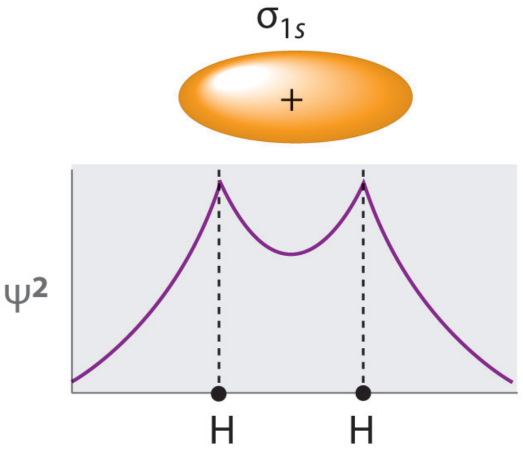

$\phi = \psi_A + \psi_B$
ψ_A
ψ_B
Addition
$\psi_A + \psi_B$

Case 2: when the two waves are out of phase, the waves are subtracted from each other so that the amplitude of the new wave is $\Phi' = \Psi_A - \Psi_B$

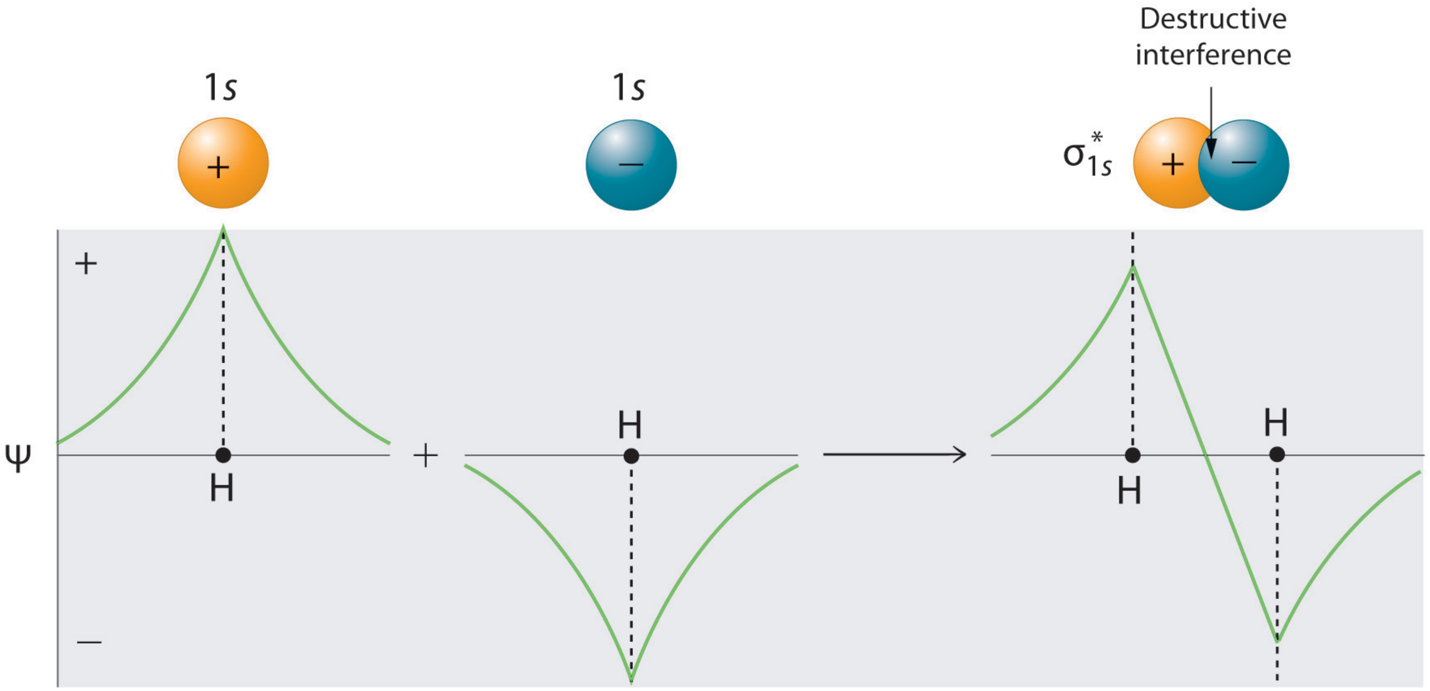

$\phi' = \psi_A - \psi_B$
ψ_A
ψ_B
Subtraction
$\psi_A - \psi_B$


Constructive interference
1s
1s
σ1s
+
+
+
+
+
+
ψ
H
H
H
H

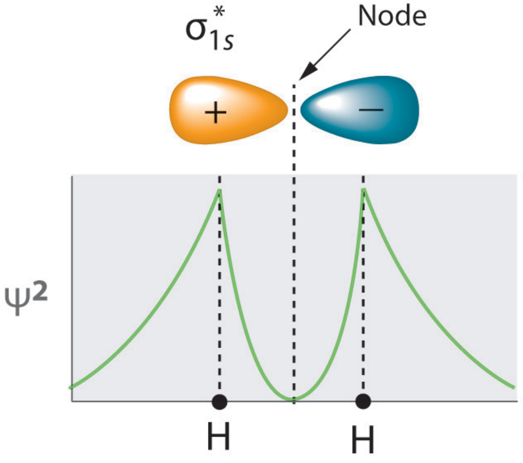
(a) Wave functions combined for σ_{1s}



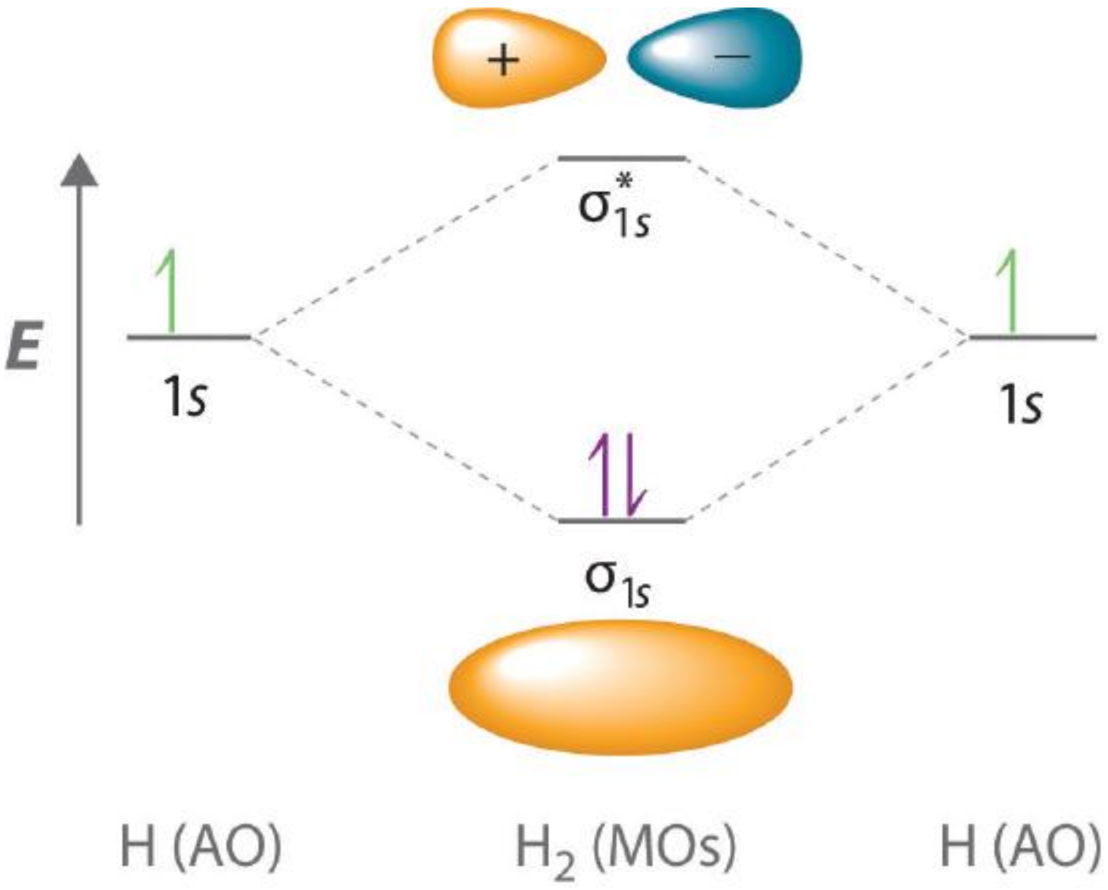
(b) Bonding probability density

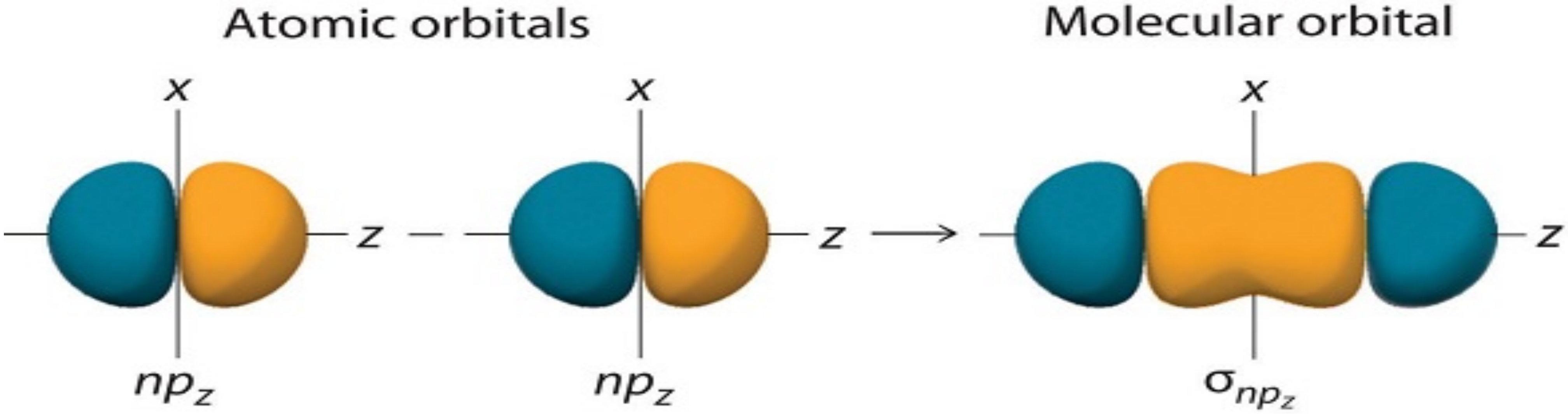

Destructive interference
1s
1s
σ*1s
+
−
+
−
+
−
+
ψ
H
H
H
H

(c) Wave functions combined for σ^*_{1s}

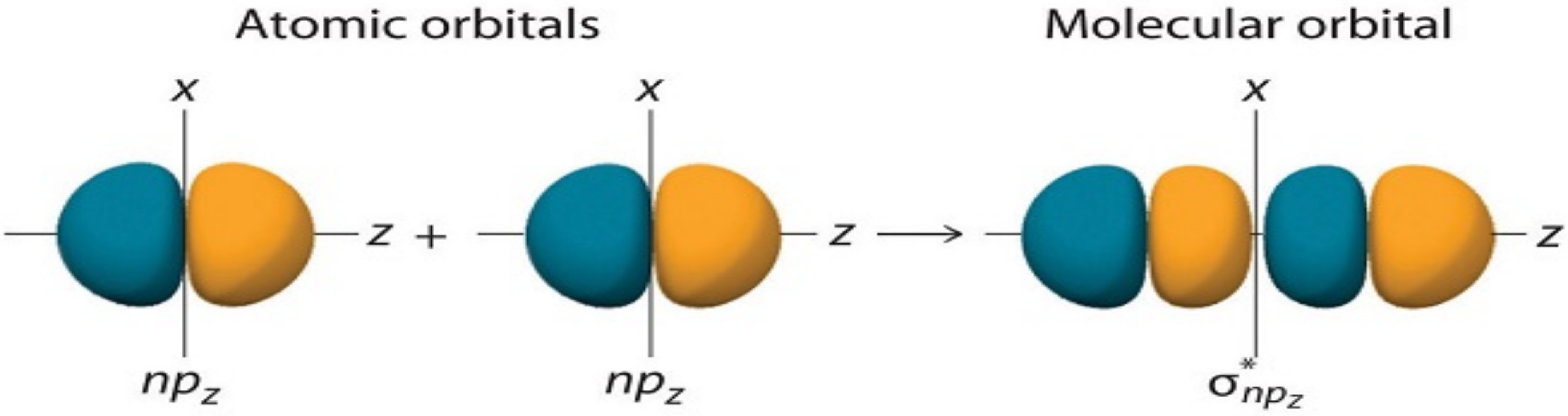

σ*1s
Node
+
−
ψ2
H
H

(d) Antibonding probability density

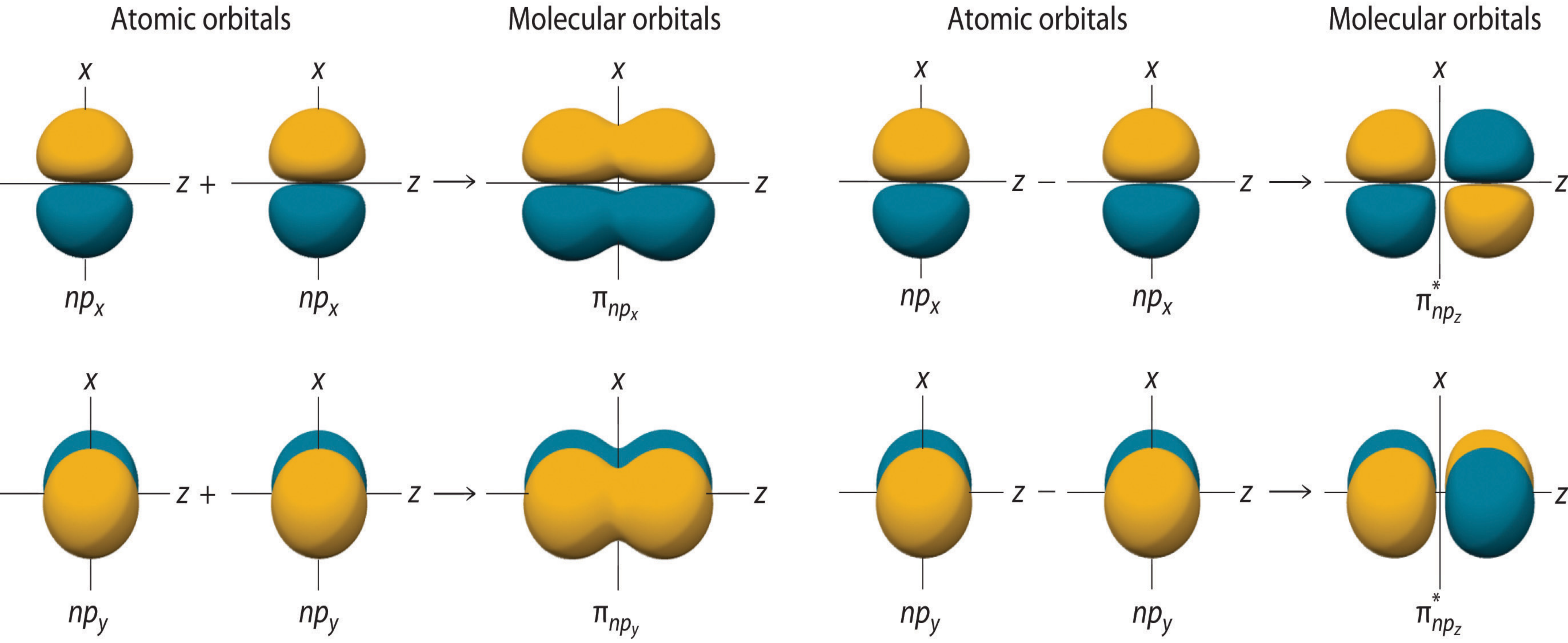
+
−
E
1s
σ^*_{1s}
1s
σ_{1s}
H (AO)
H_2 (MOs)
H (AO)


Atomic orbitals
Molecular orbital
x
x
x
z
−
z
z
np_z
np_z
σ_{np_z}

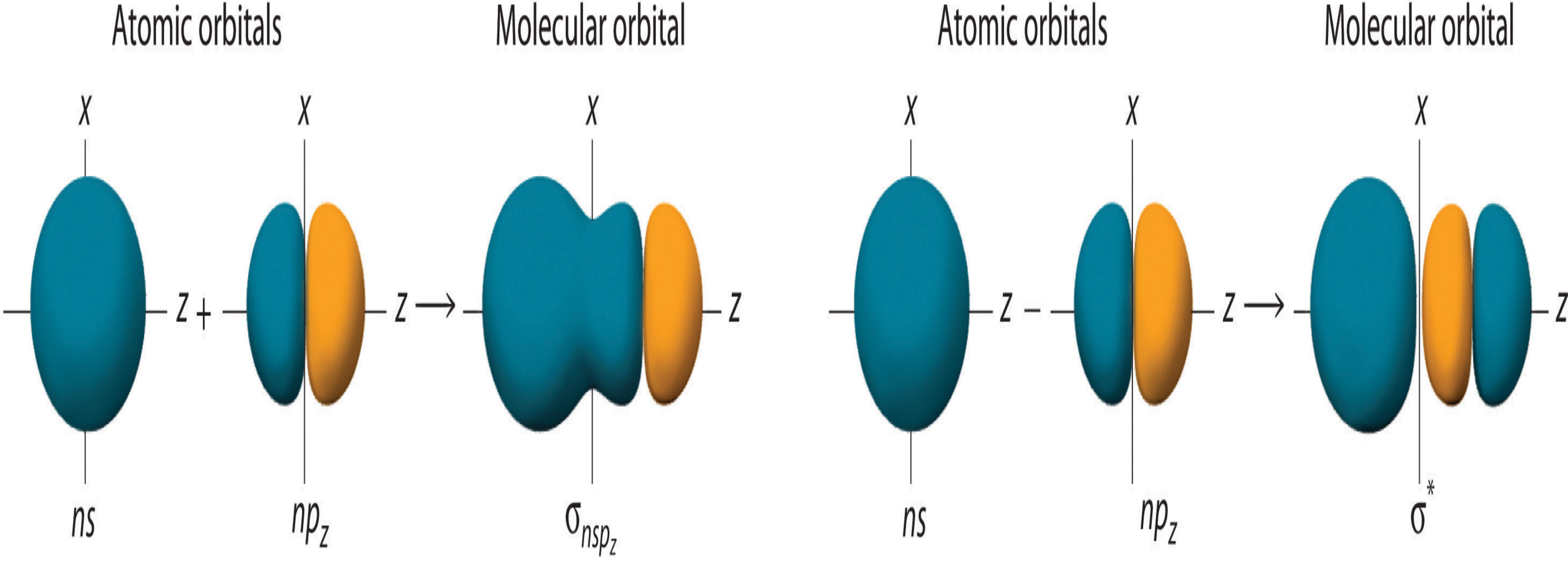
(a) Bonding


Atomic orbitals
Molecular orbital
x
x
x
z
+
z
z
np_z
np_z
$\sigma^*_{np_z}$

(b) Antibonding


Atomic orbitals
Molecular orbitals
Atomic orbitals
Molecular orbitals
x
z
+
$\rightarrow$
np_x
np_x
π_{np_x}
np_y
np_y
π_{np_y}
−
$\pi^*_{np_z}$
$\pi^*_{np_z}$

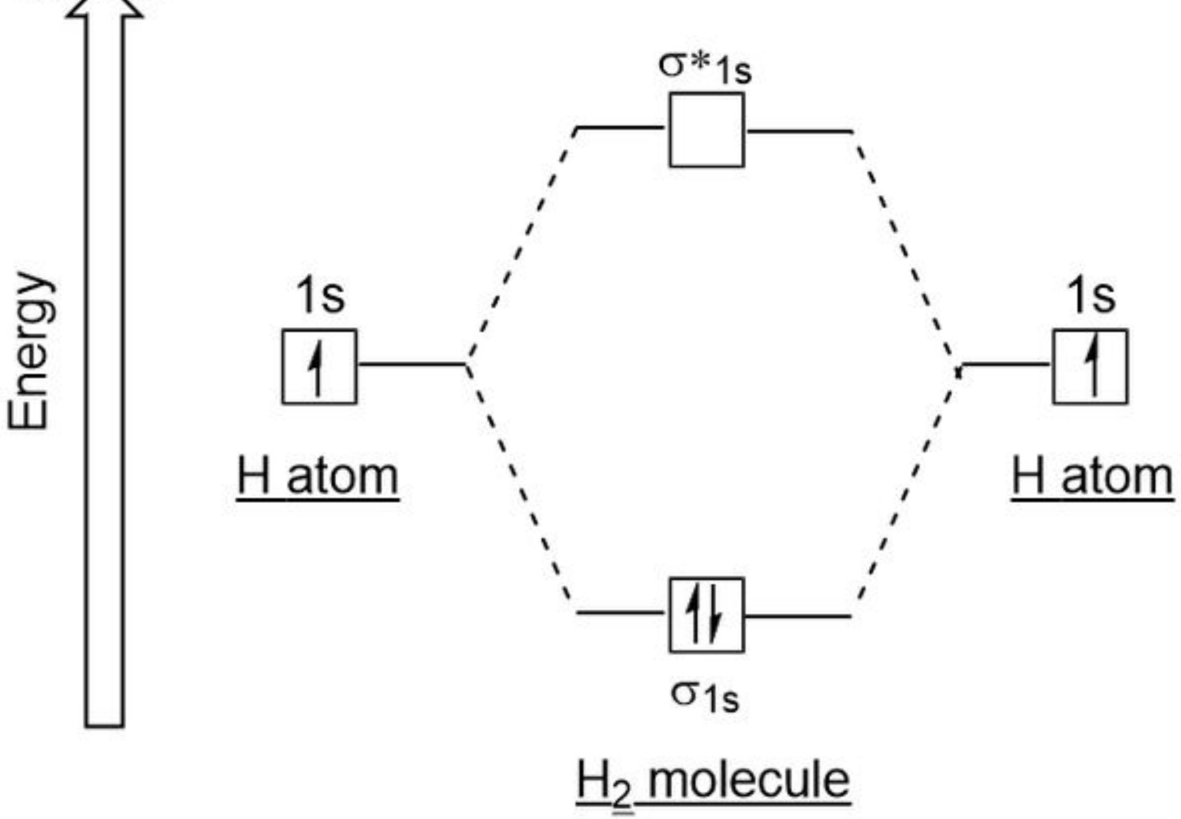
(a) Bonding **(b) Antibonding**

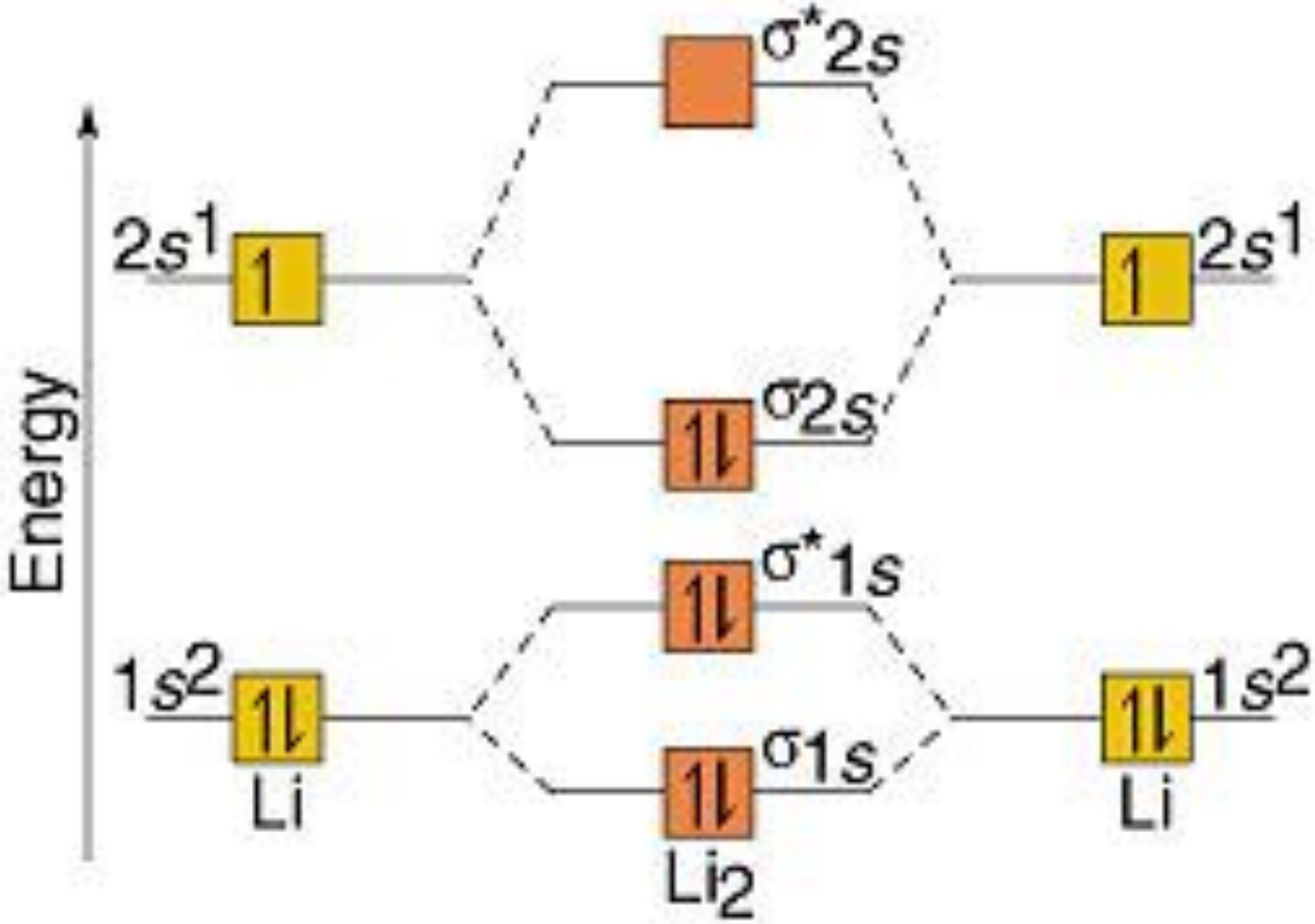

Atomic orbitals
Molecular orbital
Atomic orbitals
Molecular orbital
x
z
+
ns
np_z
→
σ_{nsp_z}
−
σ^*

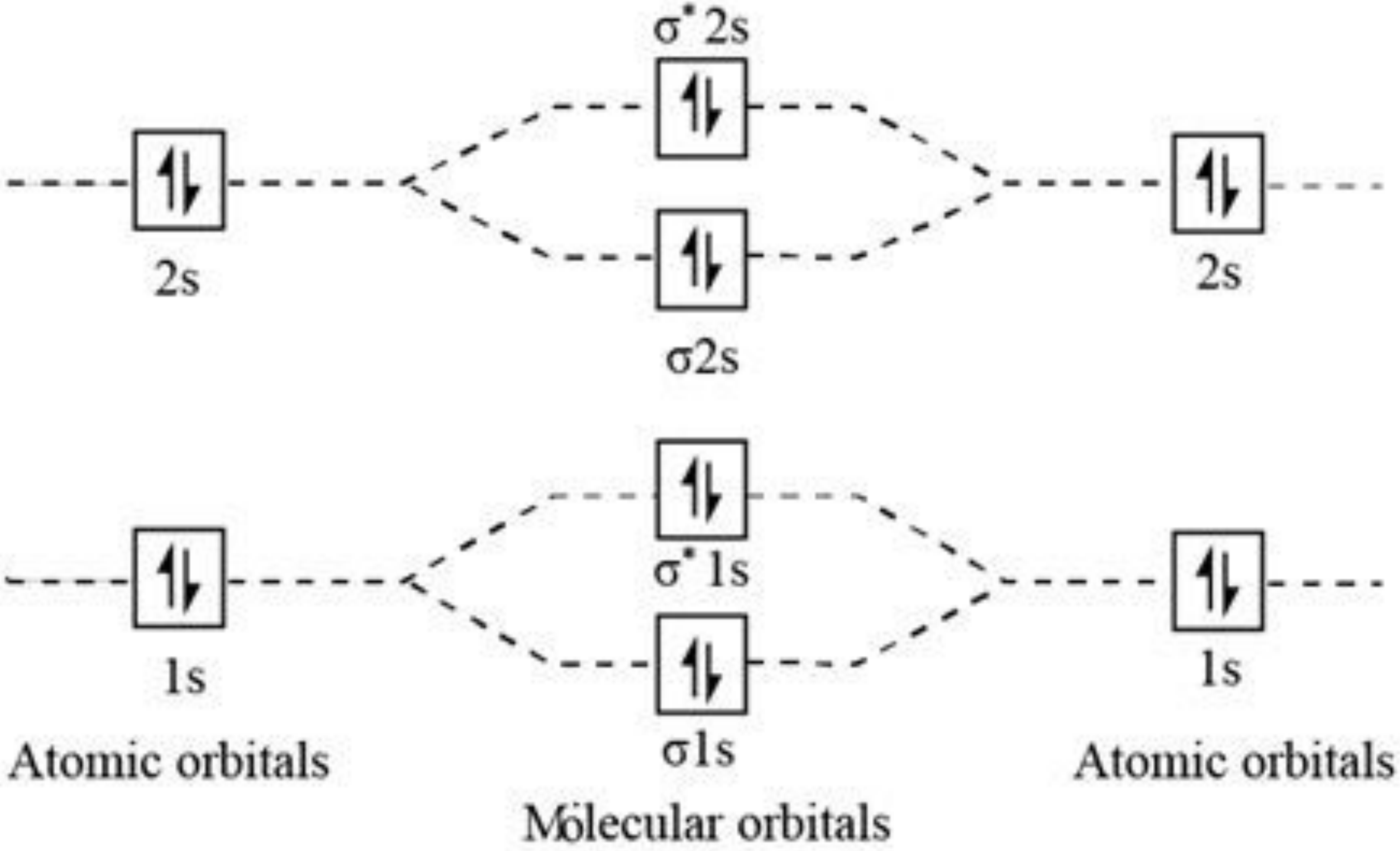
(a) Bonding

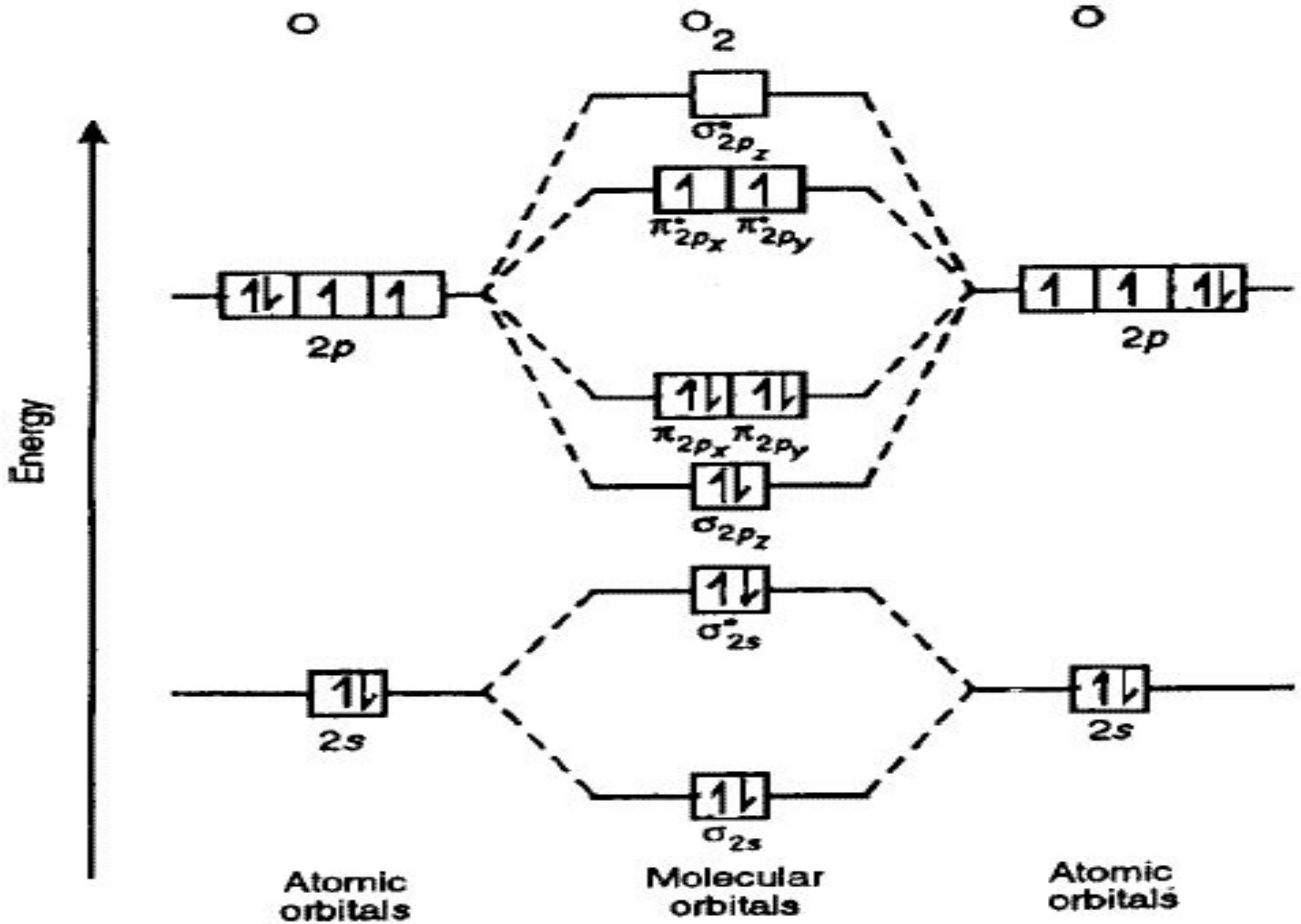
(b) Antibonding

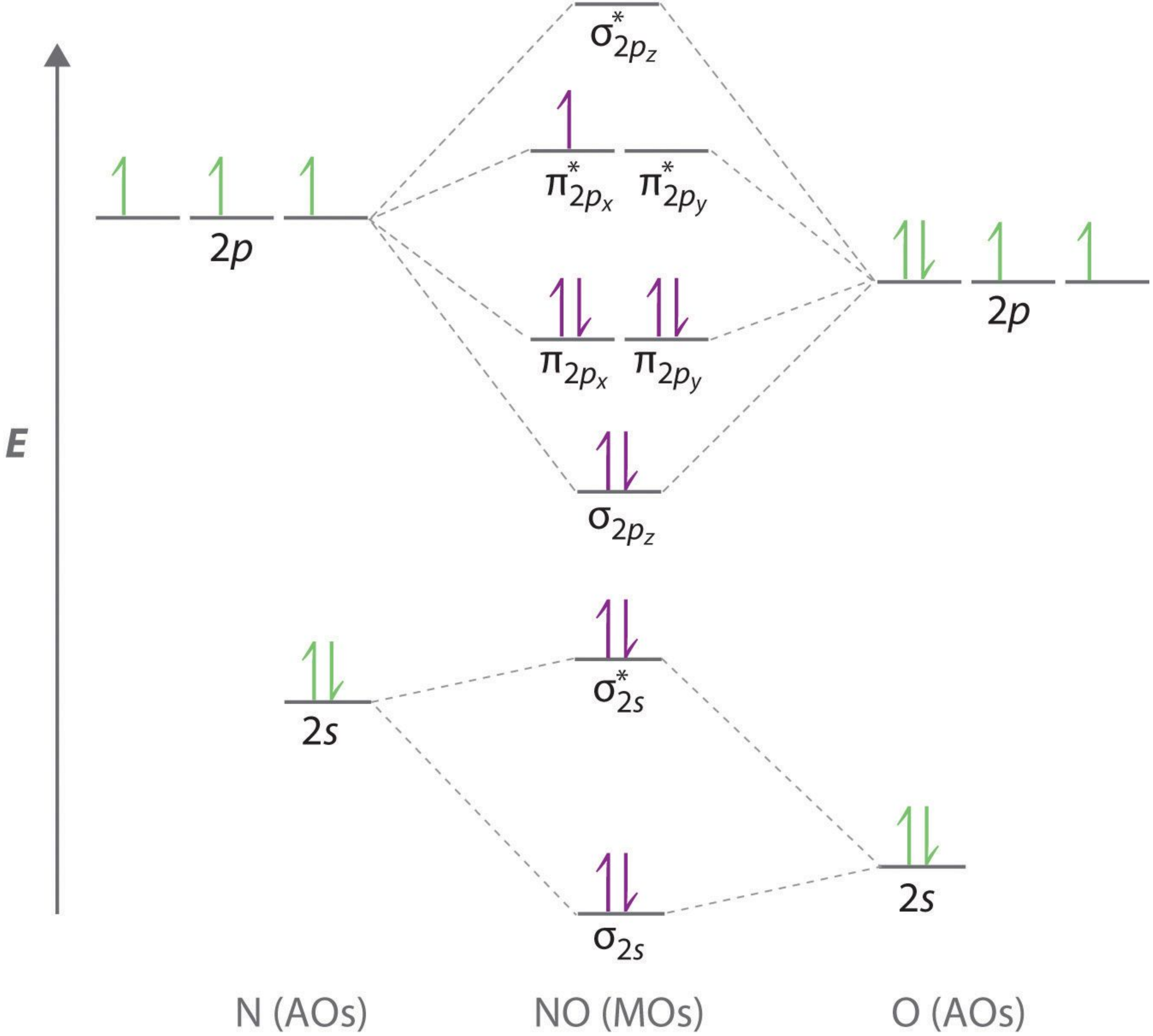
SAMPLE ONLY


Energy
σ*1s
1s
1s
H atom
H atom
σ1s
H_2 molecule


Energy
σ*2s
2s¹
2s¹
σ2s
σ*1s
1s²
1s²
σ1s
Li
Li
Li₂


σ* 2s
2s
2s
σ2s
σ* 1s
1s
1s
σ1s
Atomic orbitals
Atomic orbitals
Molecular orbitals

O
O₂
O
Energy
σ*2pz
π*2px π*2py
2p
2p
π2px π2py
σ2pz
σ*2s
2s
2s
σ2s
Atomic orbitals
Molecular orbitals
Atomic orbitals



$\sigma^*_{2p_z}$
$\pi^*_{2p_x}$
$\pi^*_{2p_y}$
$2p$
π_{2p_x}
π_{2p_y}
$2p$
E
σ_{2p_z}
σ^*_{2s}
$2s$
$2s$
σ_{2s}
N (AOs)
NO (MOs)
O (AOs)

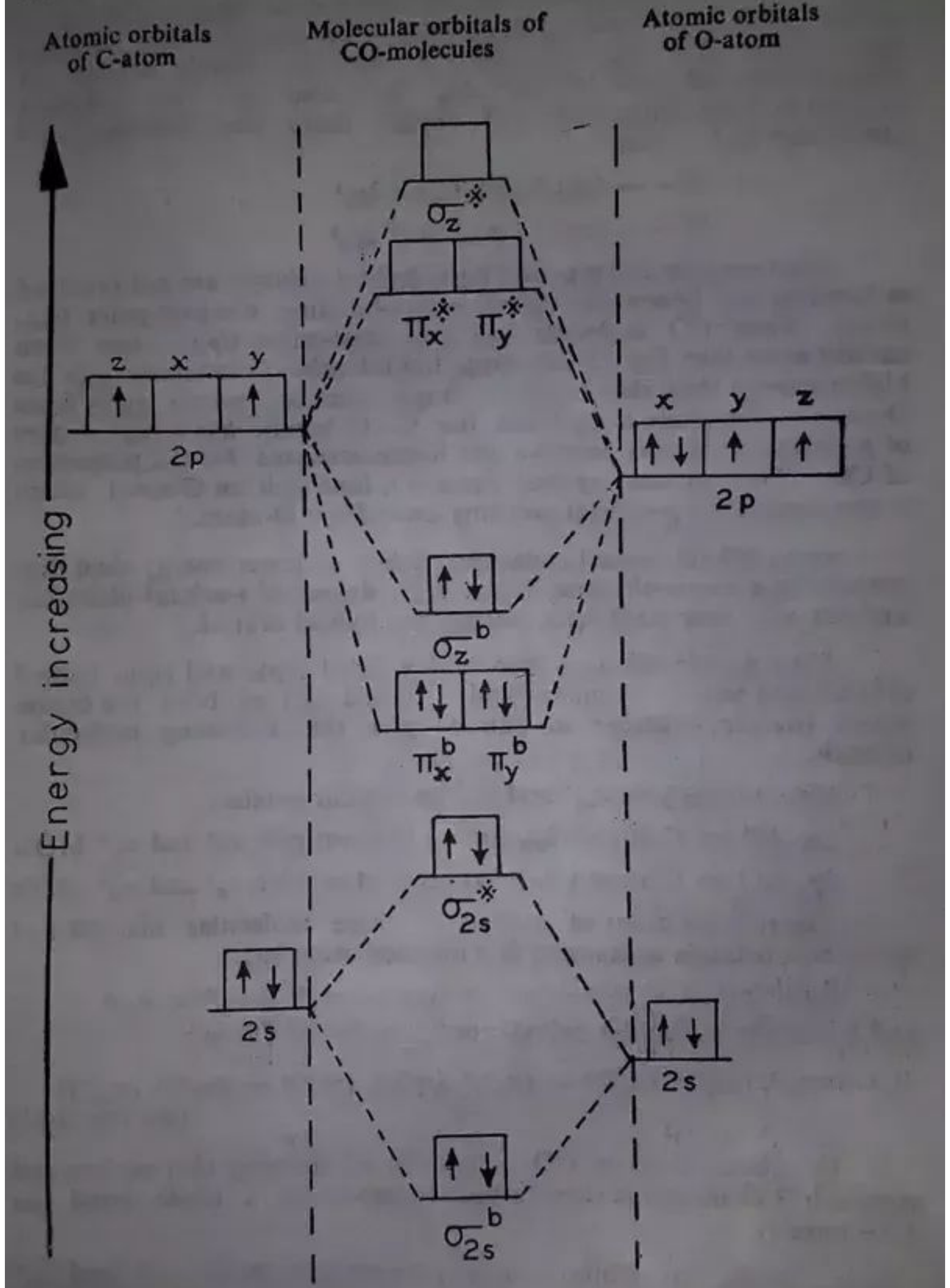

Atomic orbitals of C-atom
Molecular orbitals of CO-molecules
Atomic orbitals of O-atom
Energy increasing
z x y
2p
σ_z^*
π_x^* π_y^*
σ_z^b
π_x^b π_y^b
σ_{2s}^*
σ_{2s}^b
2s
x y z
2p
2s

Fig. 5·20. Molecular orbital energy level diagram (drawn not to scale) of CO molecule.