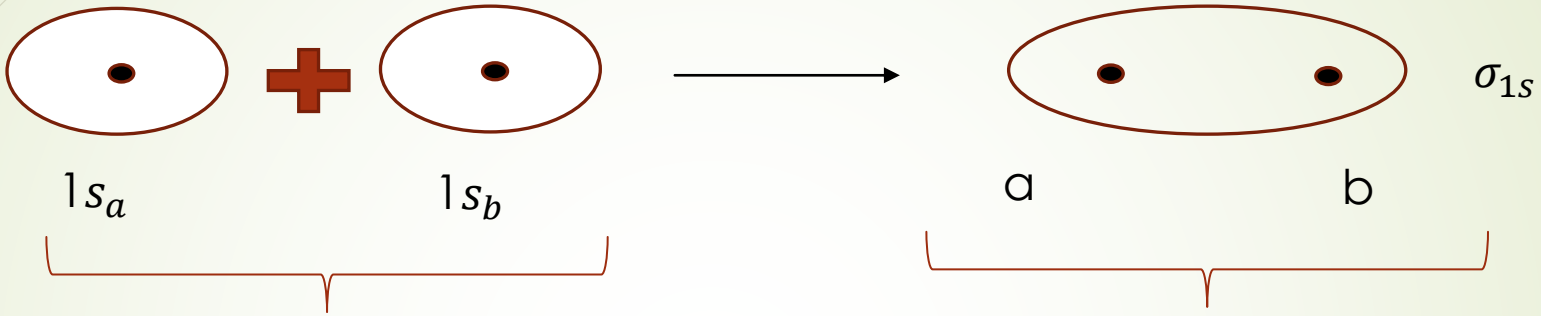
Chapter 3

Molecular Orbital Theory

Approximate Molecular Orbital Theory

- ✓ Molecular orbital theory has become a powerful method for studying the electronic structure of molecules, illuminating many areas of chemistry.
- ✓ In molecular orbital (Mo) theory, valence electrons are delocalized over the entire molecule, not confined to individual atoms or bonds.
- ✓ Molecular orbitals (wavefunctions) arise from the adding together (superimposition) atomic orbitals or wavefunctions.
- ✓ A Linear Commination of Atomic orbitals (LCAO) creates molecular orbitals (bonding and antibonding orbitals).
- ✓ Molecular orbitals can be constructed by $\boldsymbol{N}$ atomic orbitals.

✓ Bonding orbitals result from a linear combination of atomic orbitals (**LCAO**) (constructive interference).



Atomic orbitals

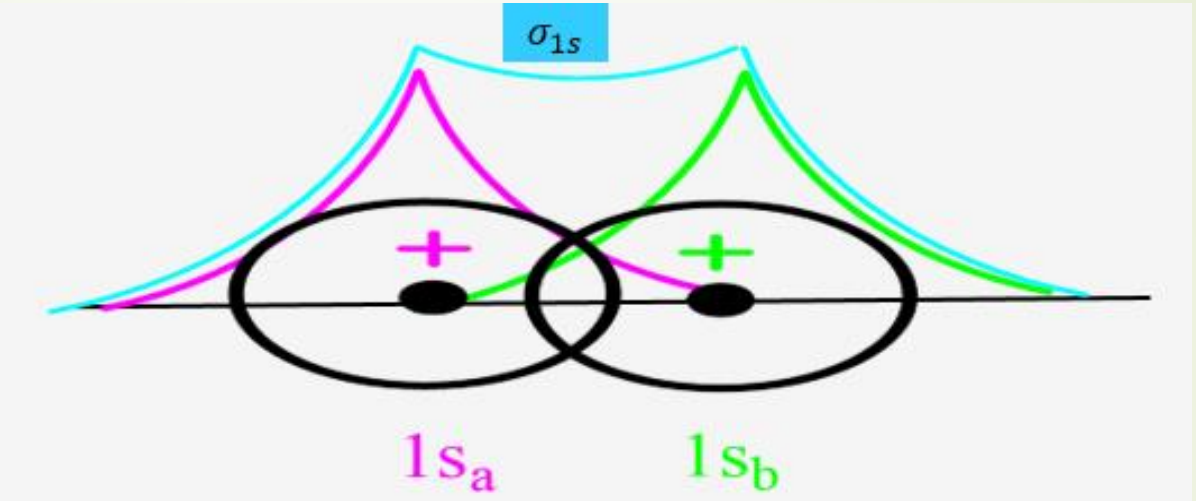
Molecular orbital

σ_{1s} Cylindrically symmetric about the bond axis.

No nodal plane along the bond axis.

$1S_a + 1S_b = \sigma_{1s}$ Bonding molecular orbital (MO).

$1S_a + 1S_b = \sigma_{1s}$ bonding MO and a wavefunction



- ✓ When waves interfere constructively, the amplitude increases where they overlap.
- ✓ Increased amplitude in the internuclear region translates to an enhanced probability density (Ψ^2) between nuclei.
- ✓ An electron in bonding Mo will be attracted to both nuclei. And will be **lower in energy c**ompared to an atomic orbital for a single nuclei.

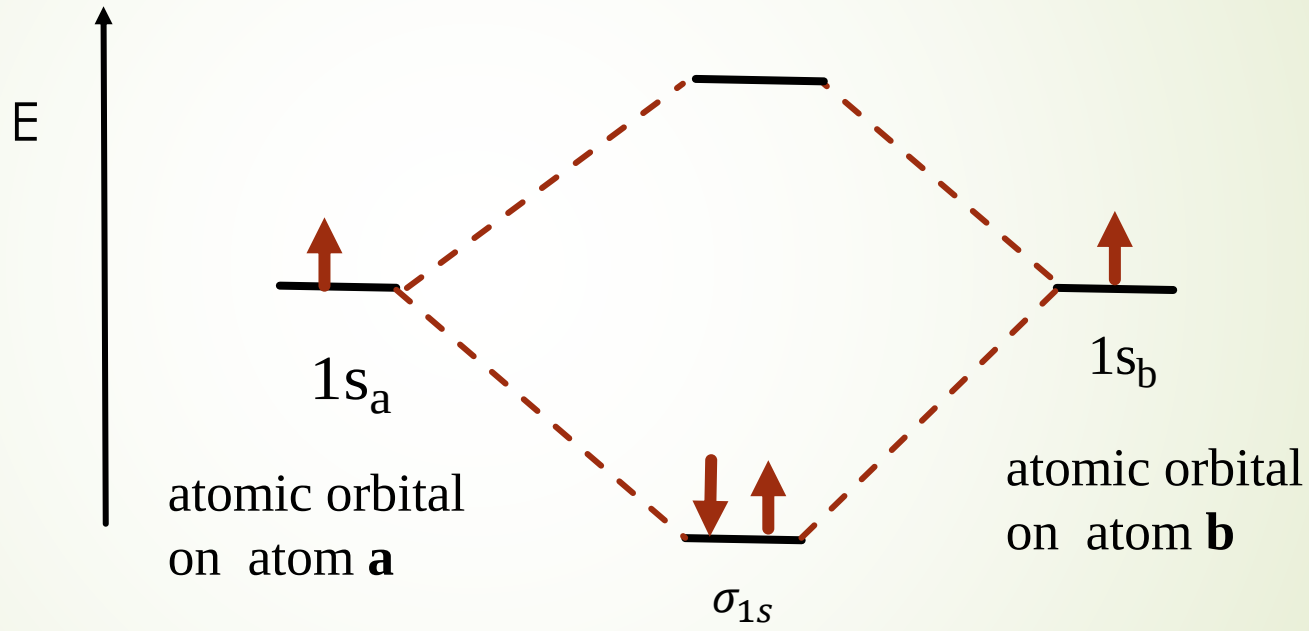
Fill in the blank

An electron in a bonding MO will be **attracted** to both **nuclei**, and will be……..compared to an atomic orbital for a single nuclei.

1. Higher in energy
2. No different in energy
3. Lower in energy.

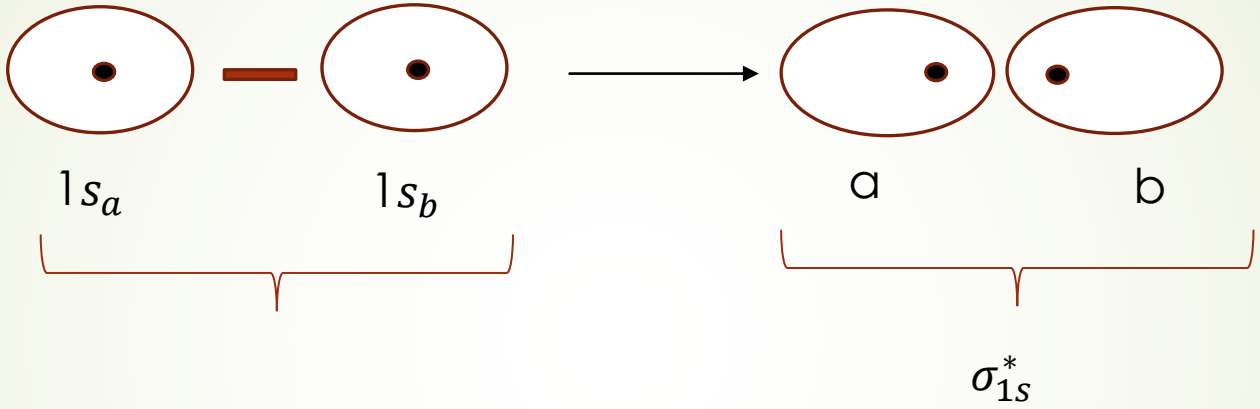
Energy of interaction

✓ The energy of a bonding orbital is decreased compared to the atomic orbitals.



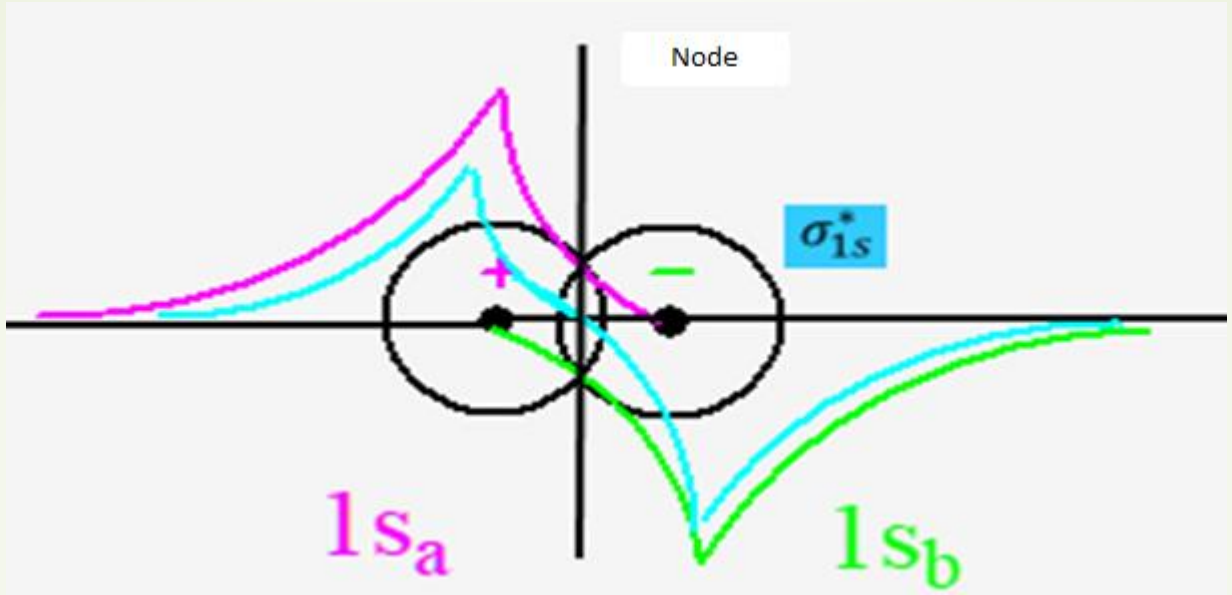
✓ For H_2, when its two electrons both occupy bonding orbital, the molecule is **more** stable.

✓ Antibonding orbitals arise from a linear combination of atomic orbitals (LCAO, destructive interference).



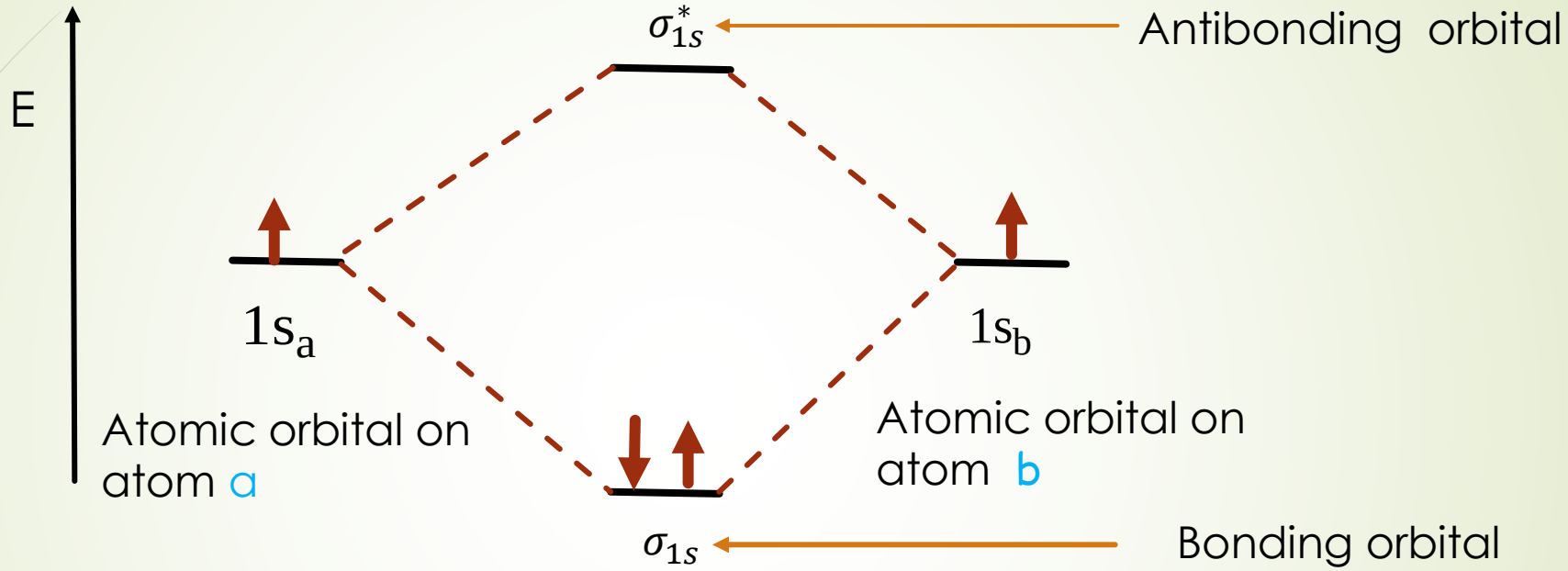
$1S_a - 1S_b = \sigma^*_{1s}$ antibonding molecular orbital

$1S_a - 1S_b = \sigma^*_{1s}$ The antibonding molecular orbital.



- ✓ When wavefunctions interfere destructively, the amplitude decreases where they overlap.
- ✓ Decreased amplitude translates to a diminished probability density betweeen the **nuclei** and a node between the two nuclei.

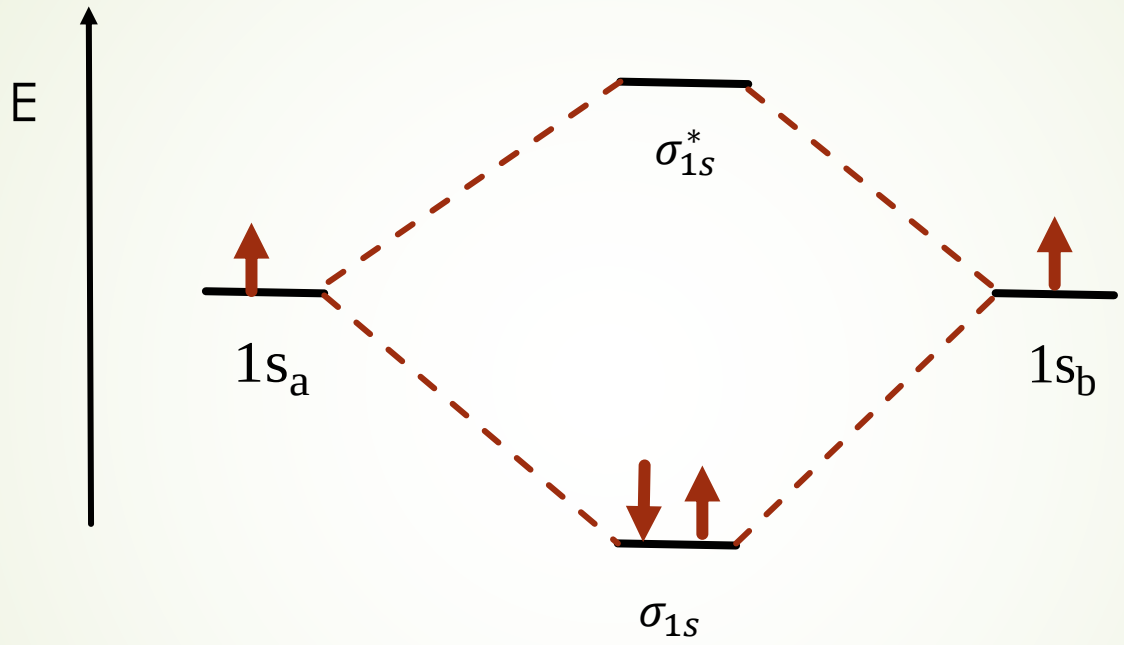
✓ The energy of an anti-bonding orbital is increased compared to atomic orbitals.



✓ The antibonding orbital is raised in E by amount as the bonding orbital is **lowered**.

Two atomic orbitals generate two MO one is bonding (Lower E) and one is antibonding (higher E).

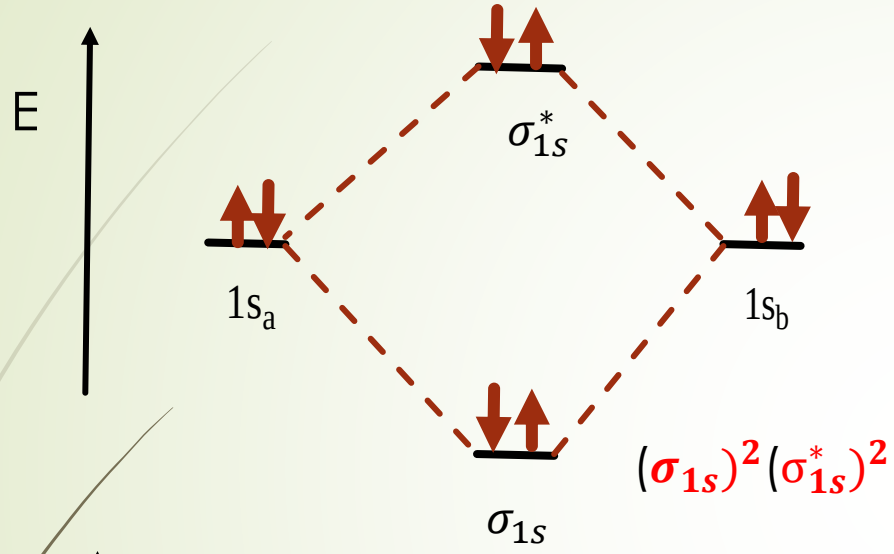
Molecular hydrogen, H_2: $(\boldsymbol{\sigma_{1s}})^{\mathbf{2}}$



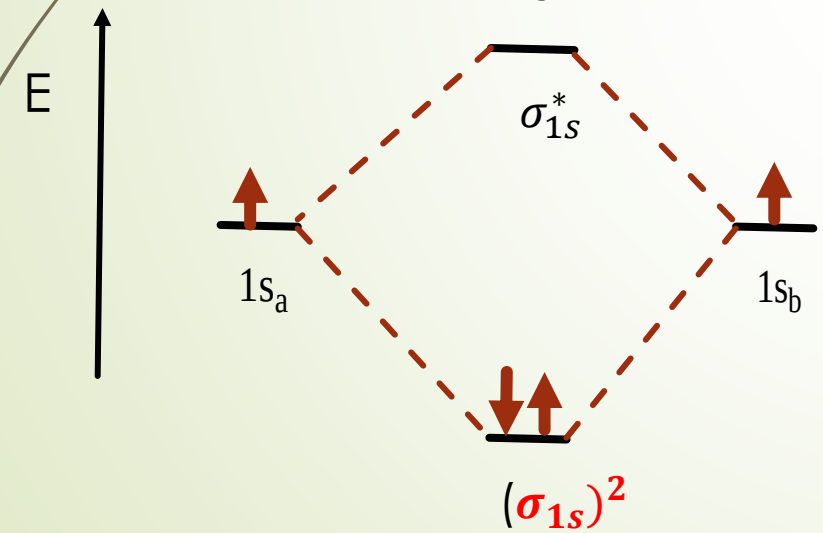
Electronic configuration of H_2: $(\boldsymbol{\sigma_{1s}})^{\mathbf{2}}$

✓ Pick the correct answer for the MO diagram of He_2

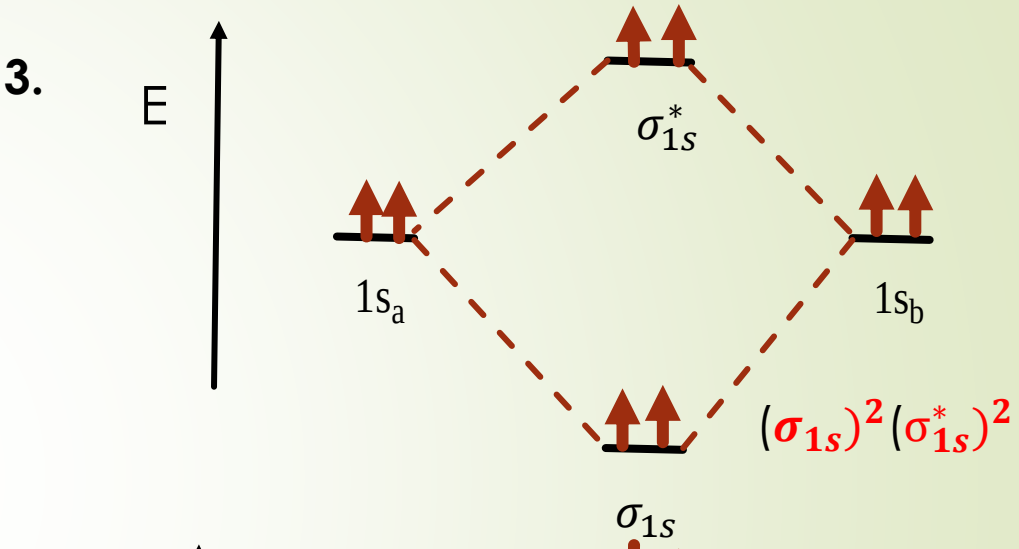
1.



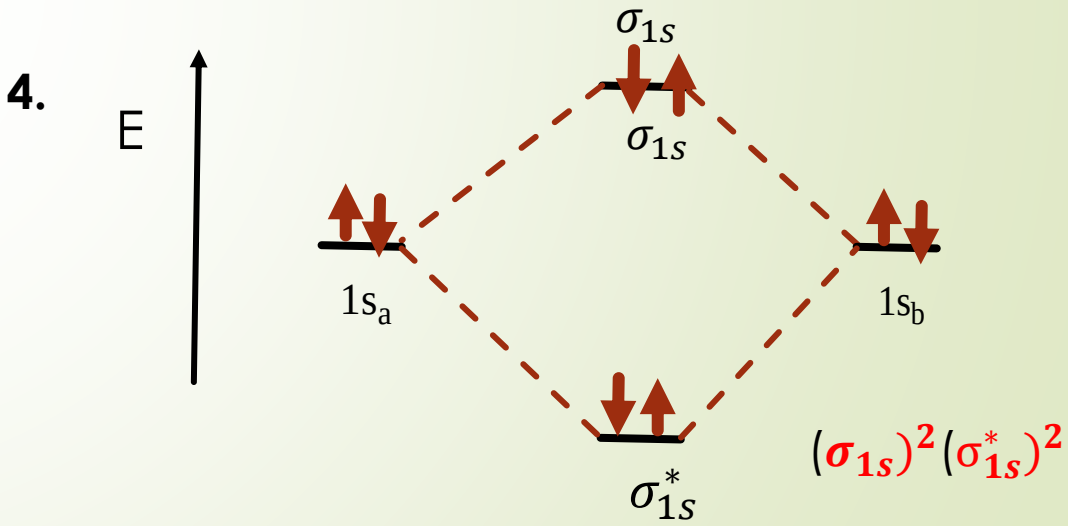
2.



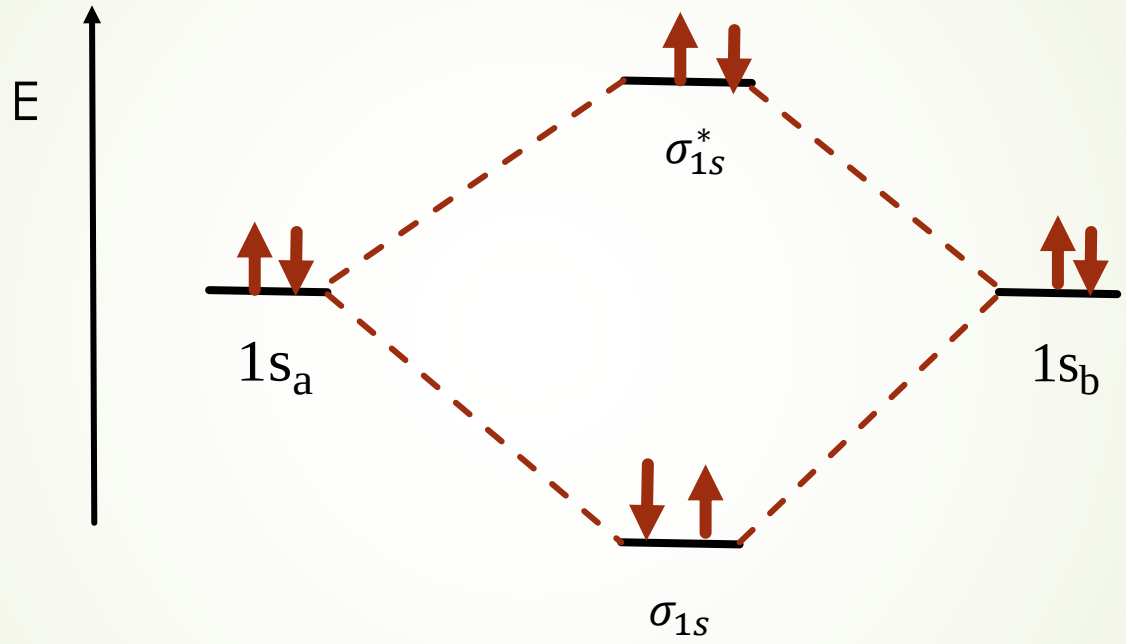
3.



4.



Molecular orbital of He_2



Electron configuration of He_2 : $(\sigma_{1s})^2(\sigma^*_{1s})^2$

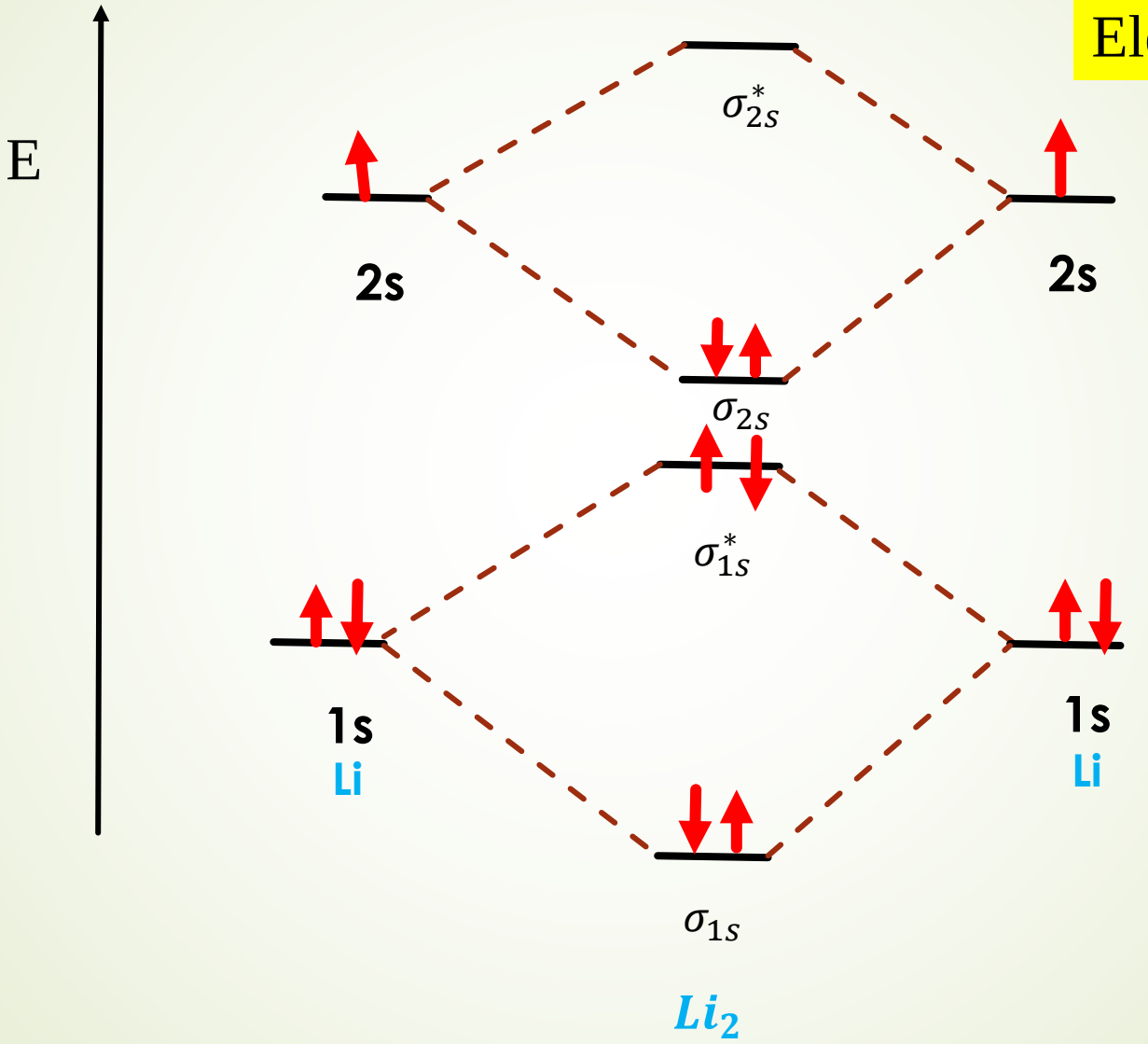
✓ Molecular orbital theory predicts that $\boldsymbol{He_2}$ does not exist.

$$\text{Bond order} = \frac{1}{2}\left[n_{\text{bonding electrons}} - n_{antiboding\ electrons}\right]$$

Example: For He_2; $B.O = \frac{1}{2}(2-2) = 0$ no bond, the molecule does not exist (helium is a monatomic gas).

Molecule or ion	Electronic configuration	Bind order
He_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2$	0
He_2^+ (2-1)1/2	$(\sigma_{1s})^2(\sigma^*_{1s})^1$	0,5
H2 (2-0)1/2	$(\sigma_{1s})^2$	1
H2+ (1-0)1/2	$(\sigma_{1s})^1$	0,5
Li2 (4-2)1/2	$\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{1s})^2$	1

✓ The MOs formed by LCAO for 2s orbitals are analogous to those formed by1s.



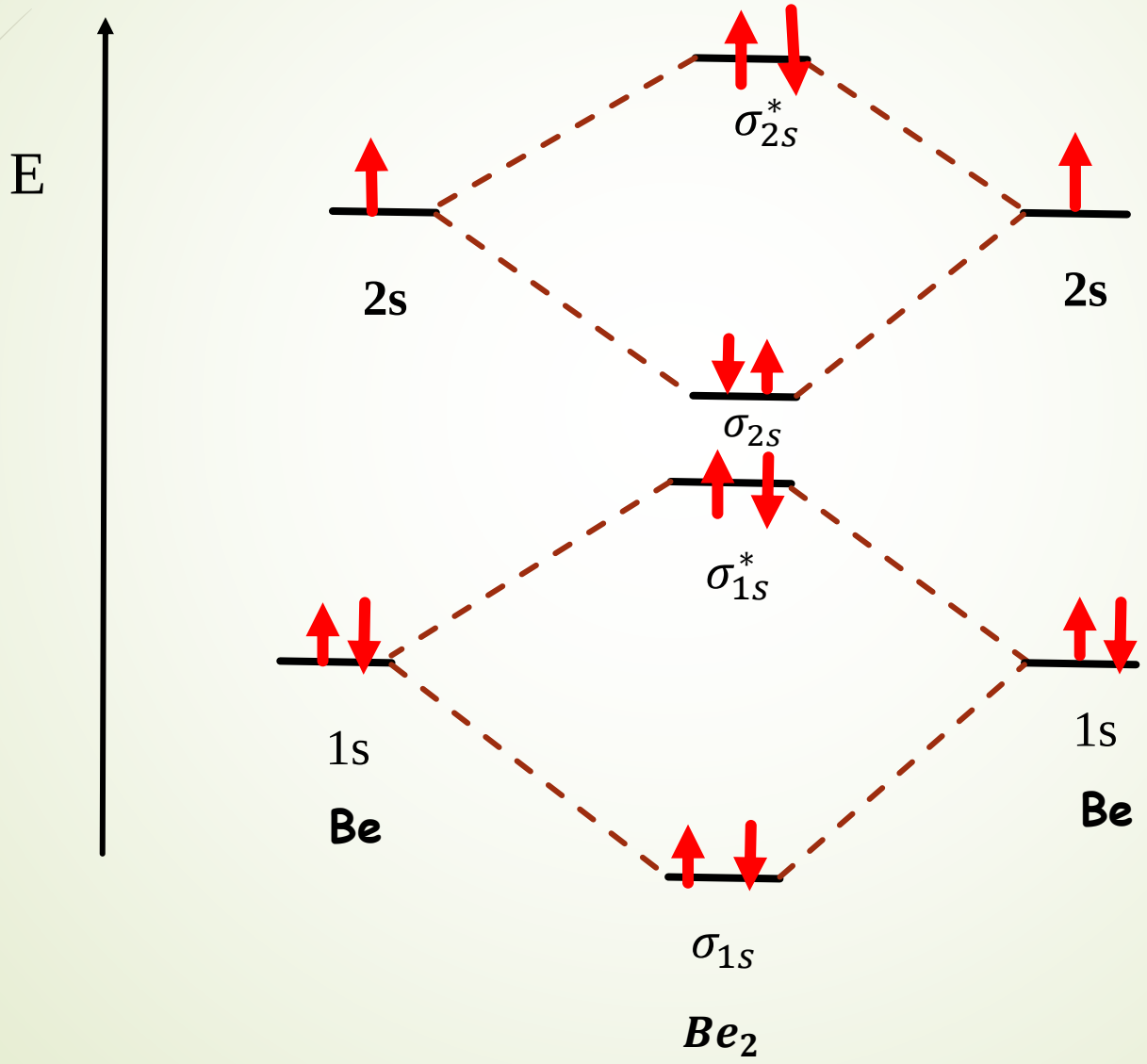
Li_2

Electronic configurations:

$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2$

B.O=$\frac{1}{2}$(4-2)=1

Electronic configurations for Be_2: $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2$



Fo all electrons

B.O=$\frac{1}{2}$(4-4)=0

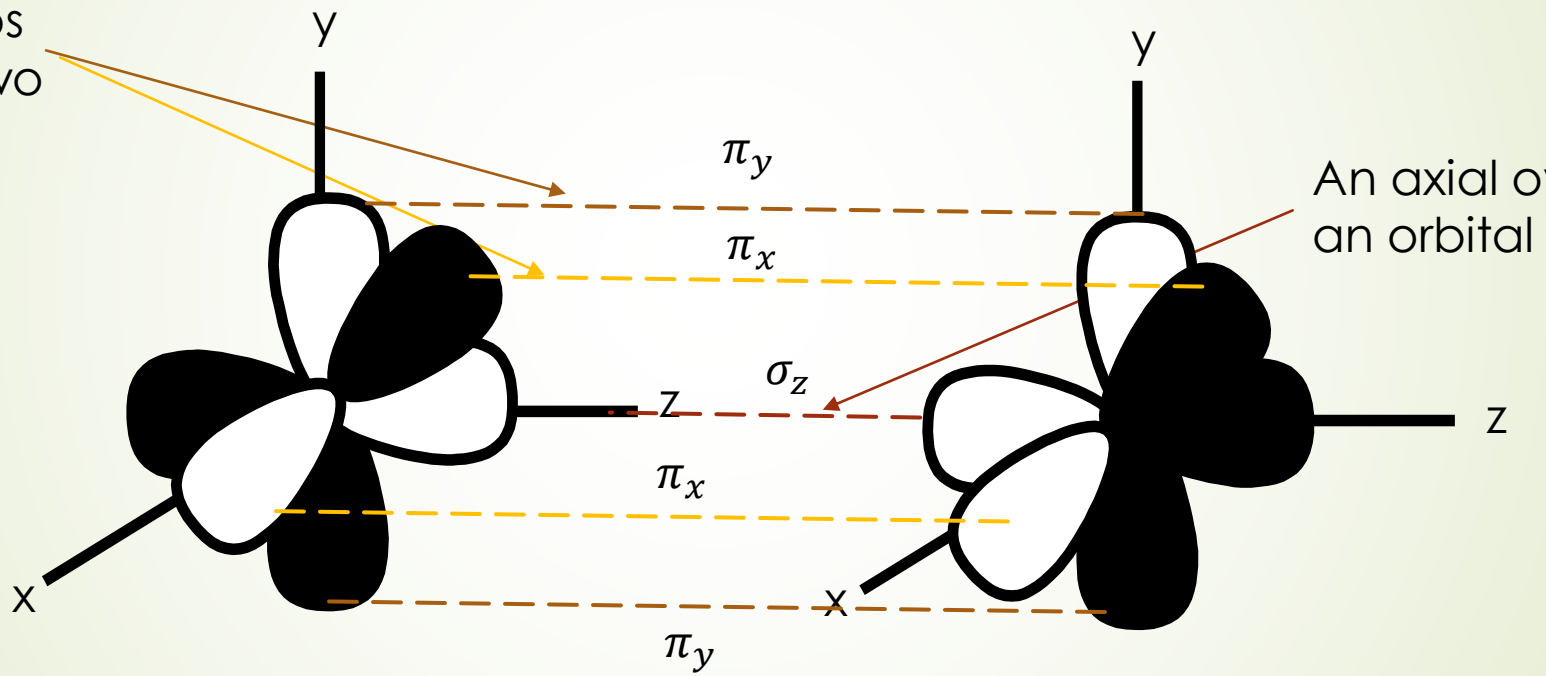
Or for valence electrons

B.O=$\frac{1}{2}$(2-2)=0

$\Delta E_{dissociation}$=9 KJ/MOL

- Mononuclear diatomic molecules with MO originating from s and p orbitals

Two side overlaps (2px, 2py) form two π orbitals

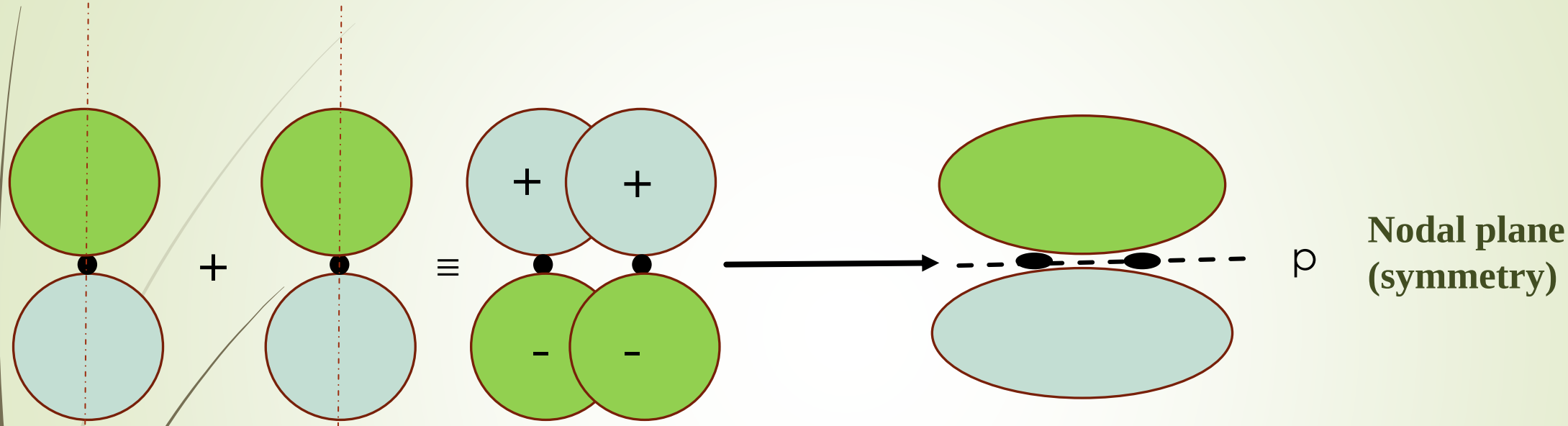


2Px, 2Py and 2Pz orbitals

2Px, 2Py and 2Pz orbitals

✓ Bonding orbitals formed by LCAO of 2px and 2py via constructive interference.

Interference increases probability density



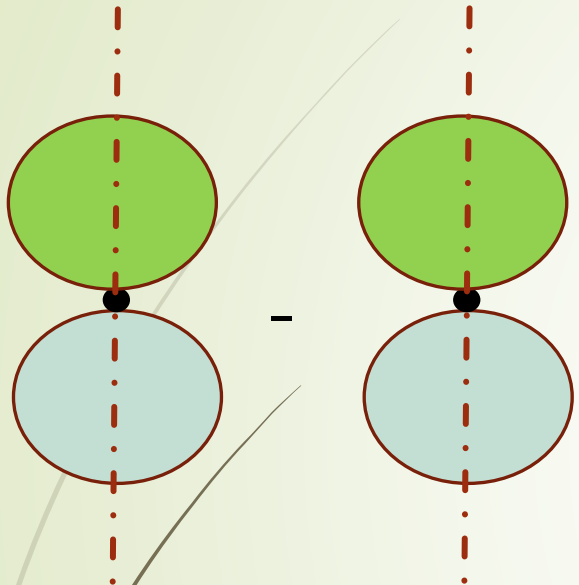
$2p_{xa}$ ou $2p_{ya}$

$2p_{yb}$ ou $2p_{yb}$

π_{2p_x} ou π_{2p_y}

π-orbital: molecular orbital (MO) resulting from the lateral overlap of two p orbitals with a nodal plane passing through the bond axis.

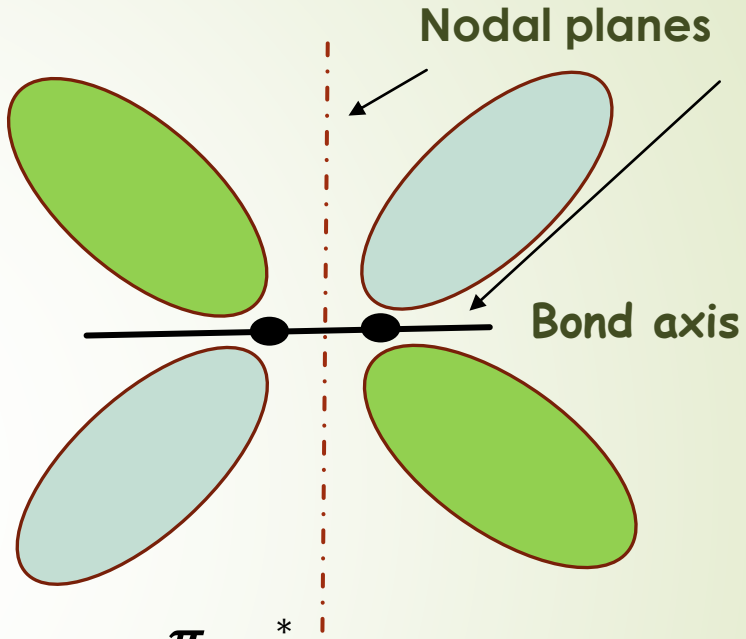
✓ Antibonding orbitals formed by LCAO of 2Px and 2Py via **destructive** interference.



$2p_{xa}$ – $2p_{ya}$

or

$2p_{ya}$ – $2p_{yb}$



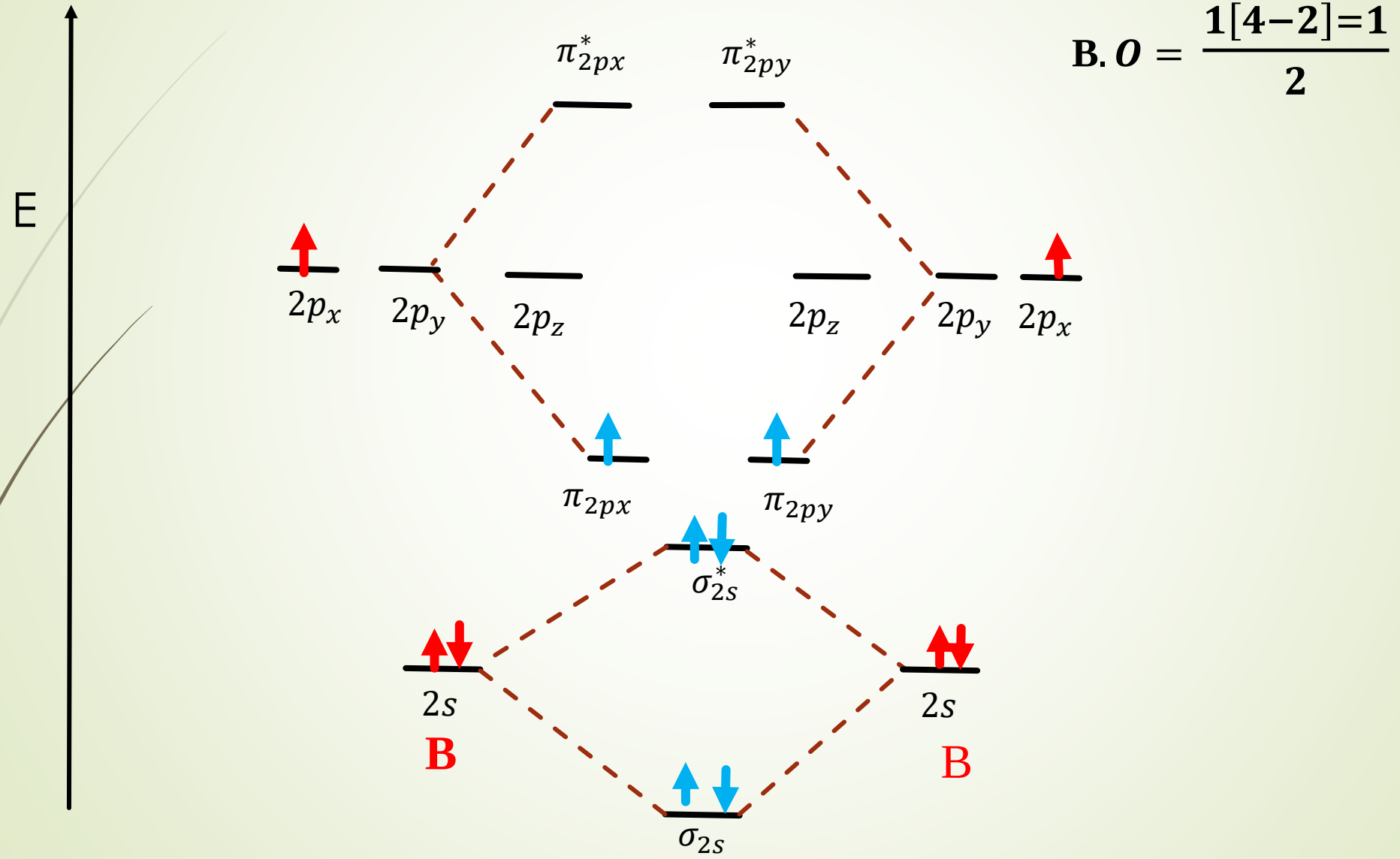
$\pi_{2p_x}{}^*$

or

$\pi_{2p_y}{}^*$

✓ The two p orbitals interact negatively with each other and this generates a nodal plane between the molecules (the phase must change).

B_2 valence electron configuration: $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi^*_{2px}\ \pi^*_{2pY}$



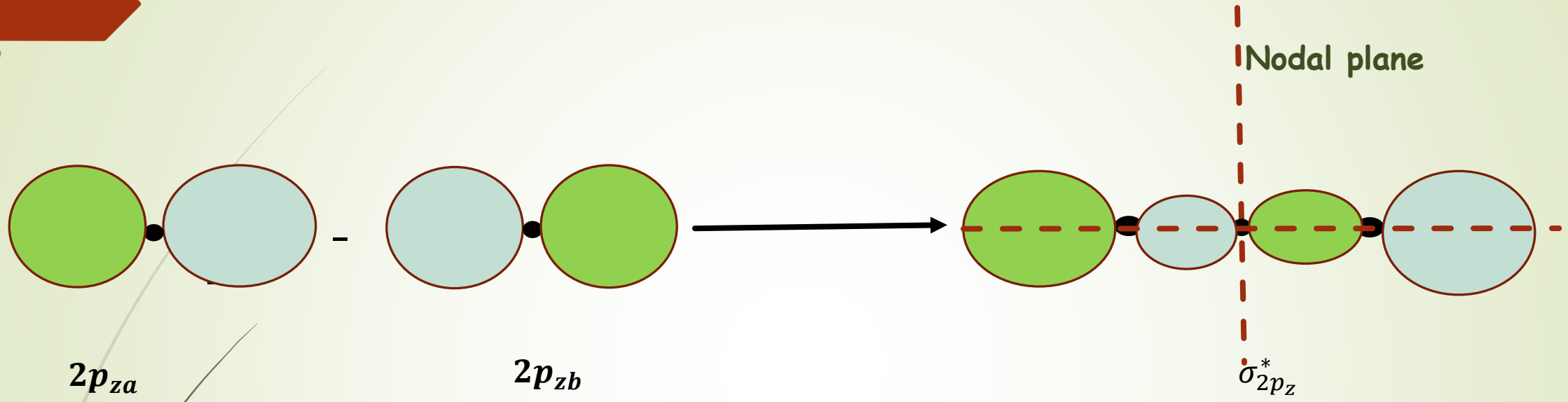
$$\text{B. } O = \frac{1[4-2]=1}{2}$$

Binding orbitals formed by LCAO of 2Pz

$2p_{za}$ $2p_{zb}$ σ_{2p_z}

- ✓ σ: Cylindrically symmetric with no nodal plane along the link axis, **nodes** pass through the nuclei, but no nodes along the bond axis.
- ✓ Constructive interference.

Anti-bonding orbitals formed by 2Pz LCAO



σ: cylindrically symmetric with no nodal plane about the bond axis nodes pass pass through and between the nuclei, but not along the bond axis.

✓ Destructive interference.

Reference

- Principles of Chemical Science catherine drennan Lecture 13: Molecular orbital Theory.