Bonding in diatomic molecules

CH101 Fall 2012
Boston University

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Atoms interact by merging *waves*

$$AO + AO \rightarrow 2\ MOs$$
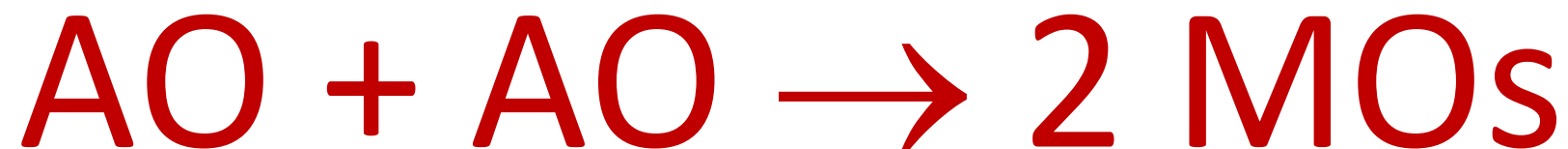
Relative AO phase determines MO character

here the different phases of the p orbital are labelled positive and negative – this can be confusing and so is best avoided
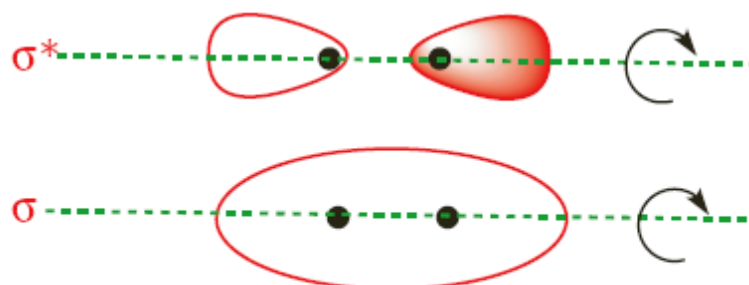
here the different phases of the p orbital are shown by shading one half and not the other
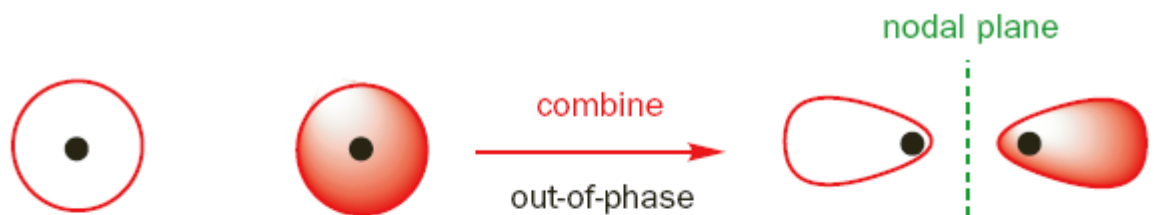
σ MO's have cylindrical symmetry

■

Antibonding orbitals are designated
with a * e.g. σ*, or π*

σ*

σ
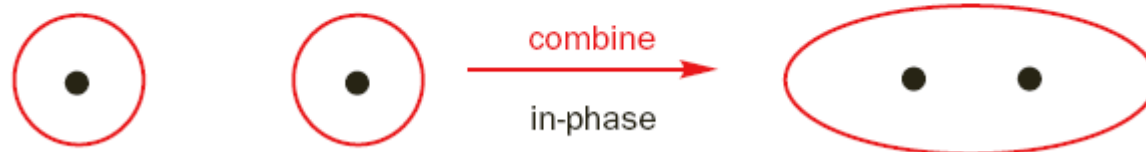
we can rotate
about this axis
without changing
the MOs

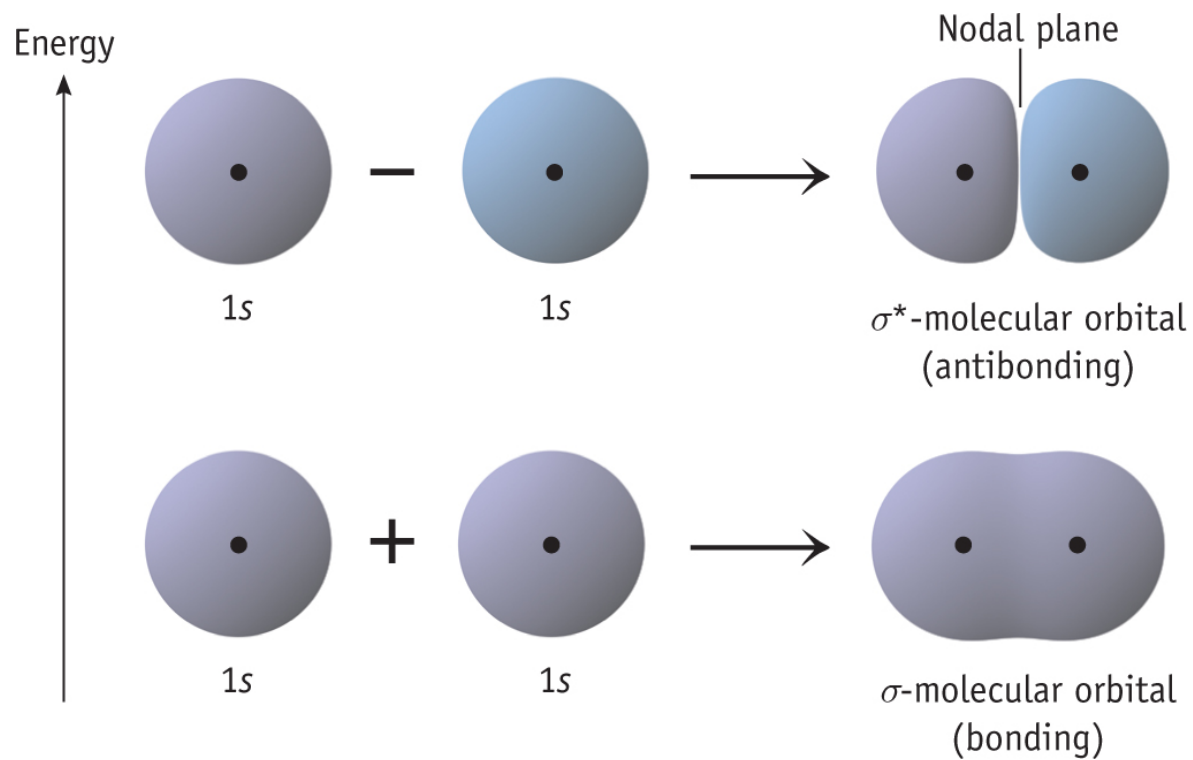both MOs have rotational symmetry about the axis through the two nuclei

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1sσ and 1sσ*

nodal plane

combine

out-of-phase

the two 1s orbitals combining out-of-phase to give an **antibonding orbital**

combine

in-phase

the two 1s orbitals combining in-phase to give a **bonding orbital**

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1sσ and 1sσ*

Mahaffy et al., Figure 10.20

1sσ (lower) and 1sσ* (upper)
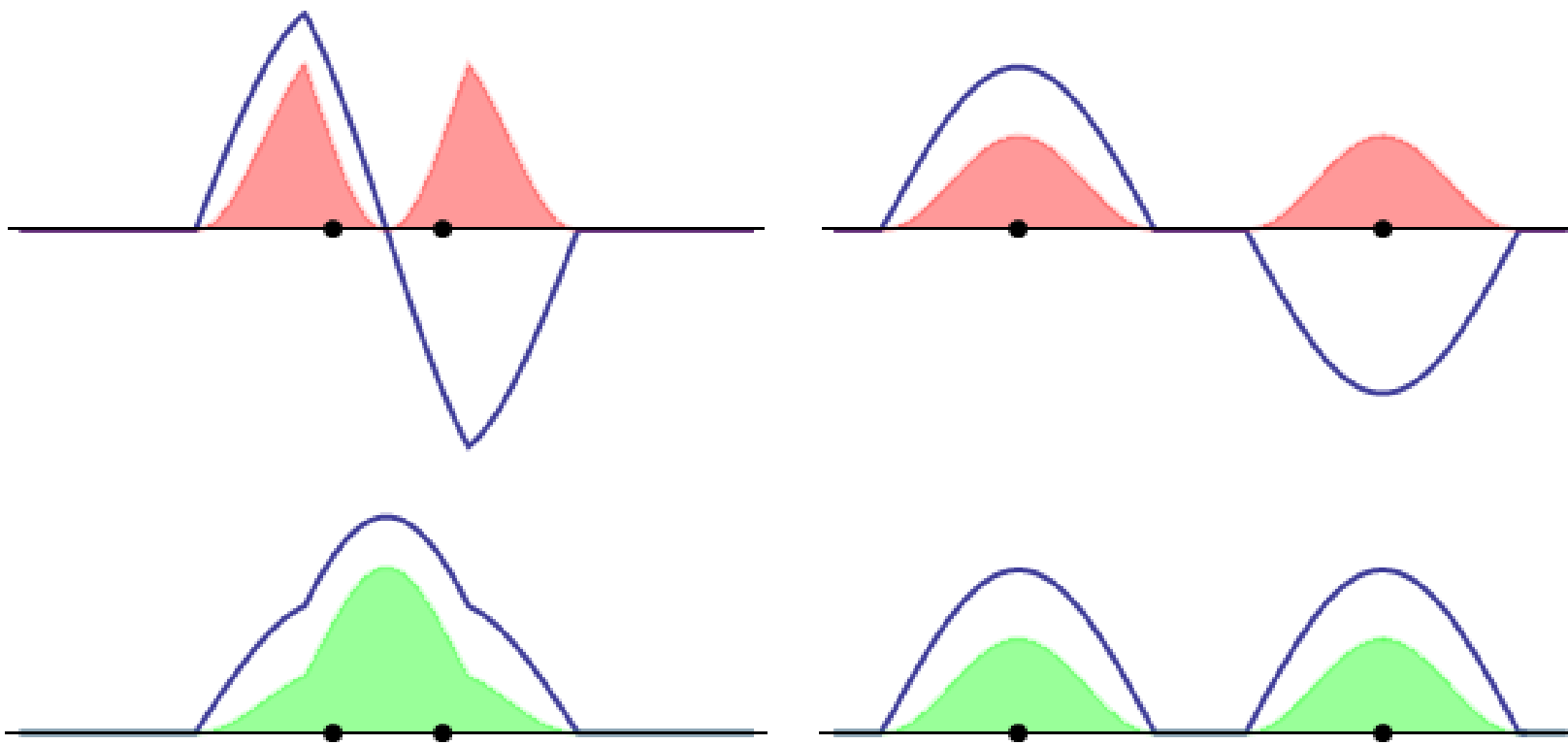
σ is "bonding" and σ* is "antibonding"

■ Antibonding orbitals are designated with a * e.g. σ*, or π*
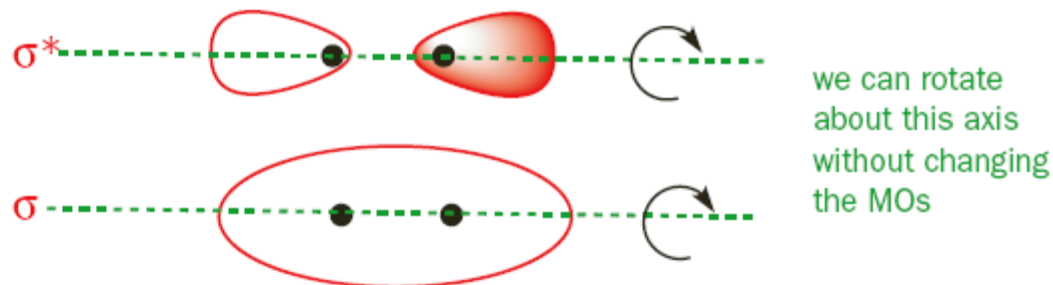
σ*

we can rotate about this axis without changing the MOs

σ

both MOs have rotational symmetry about the axis through the two nuclei

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Bonding *PE*, *KE* and total *E*
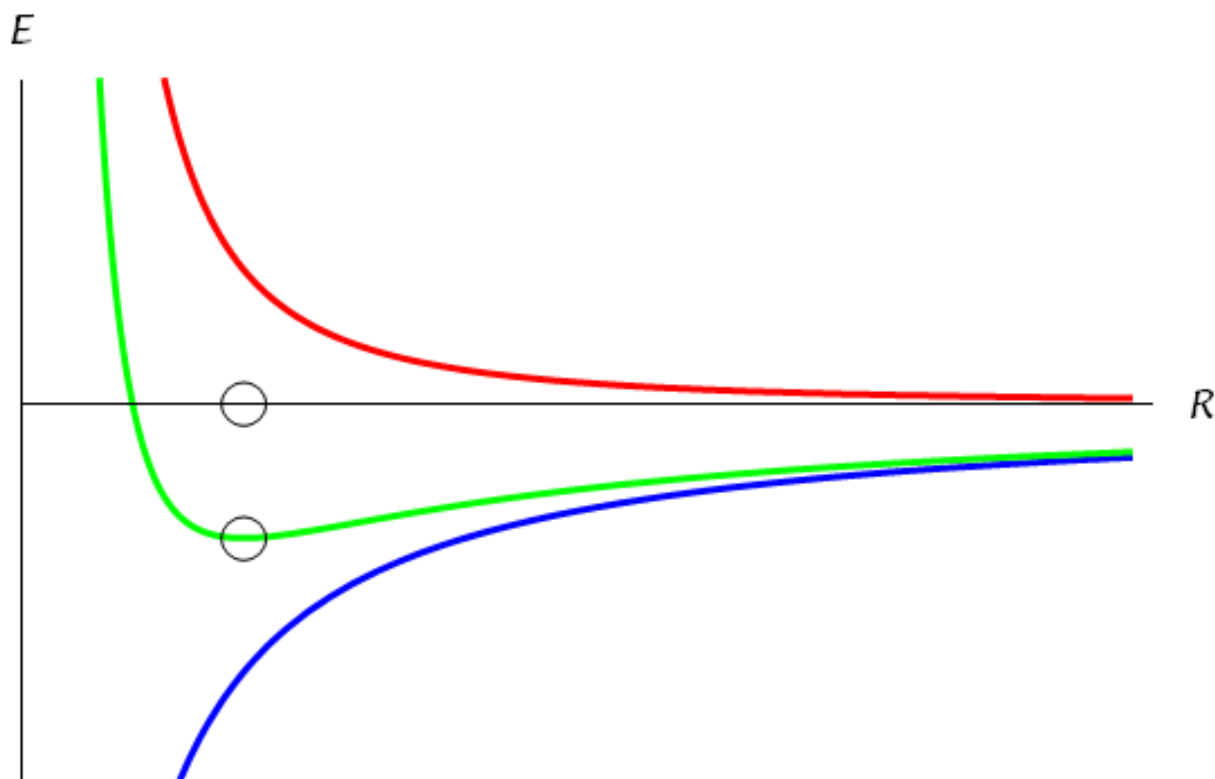
Attractive (< 0) *PE* is opposed by **repulsive (> 0) *KE***.
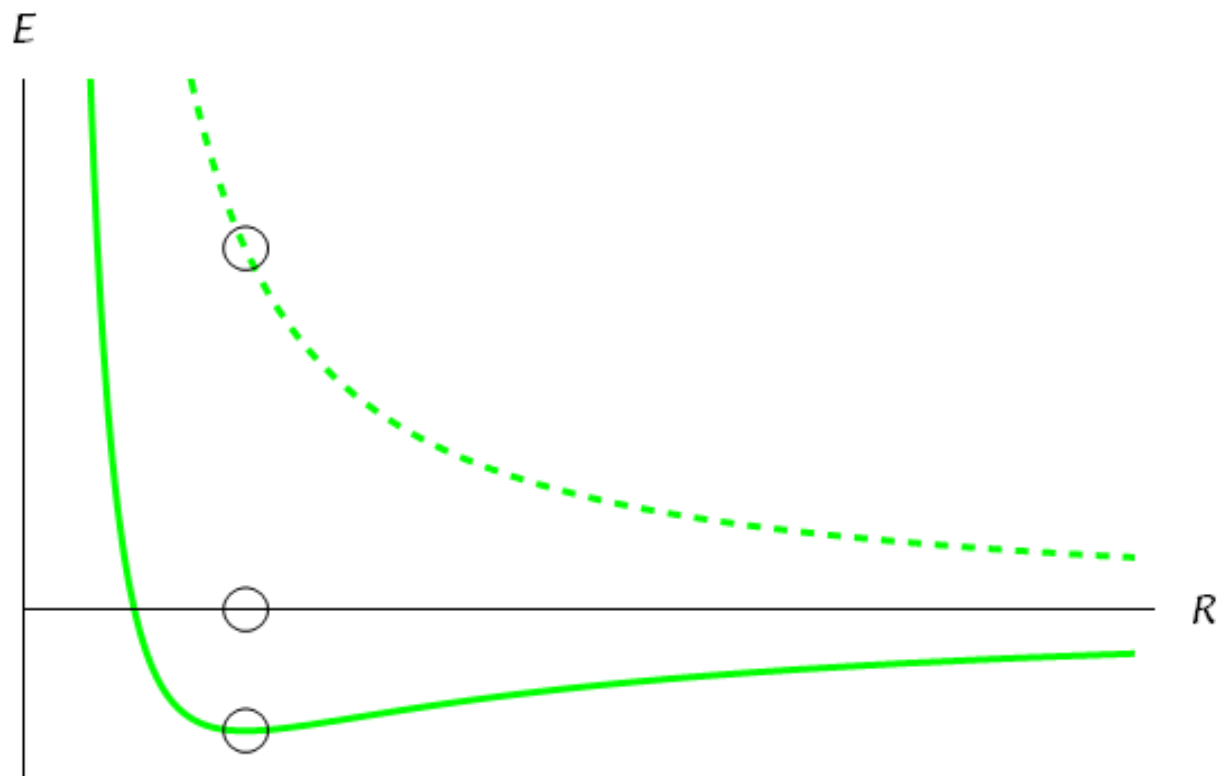
Molecular size is at **minimum of total *E***.

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Antibonding *PE*, *KE* and total *E*
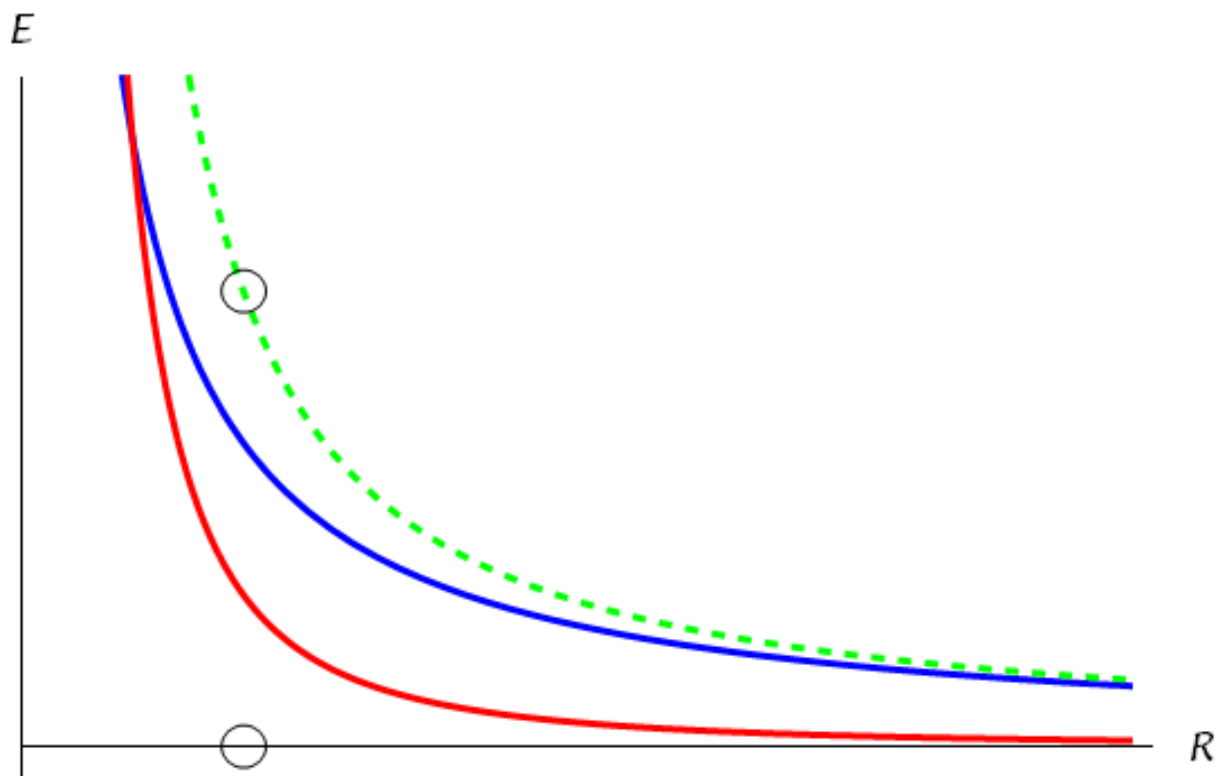
Repulsive (> 0) *PE* enhanced by **repulsive (> 0) *KE***.

No minimum of total *E* --- **atoms fly apart**!

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Bonding and **antibonding** total *E*

What matters are the total bonding and antibonding *E* at the **bonding minimum** versus the **AO energies**---the energy at infinite separation.
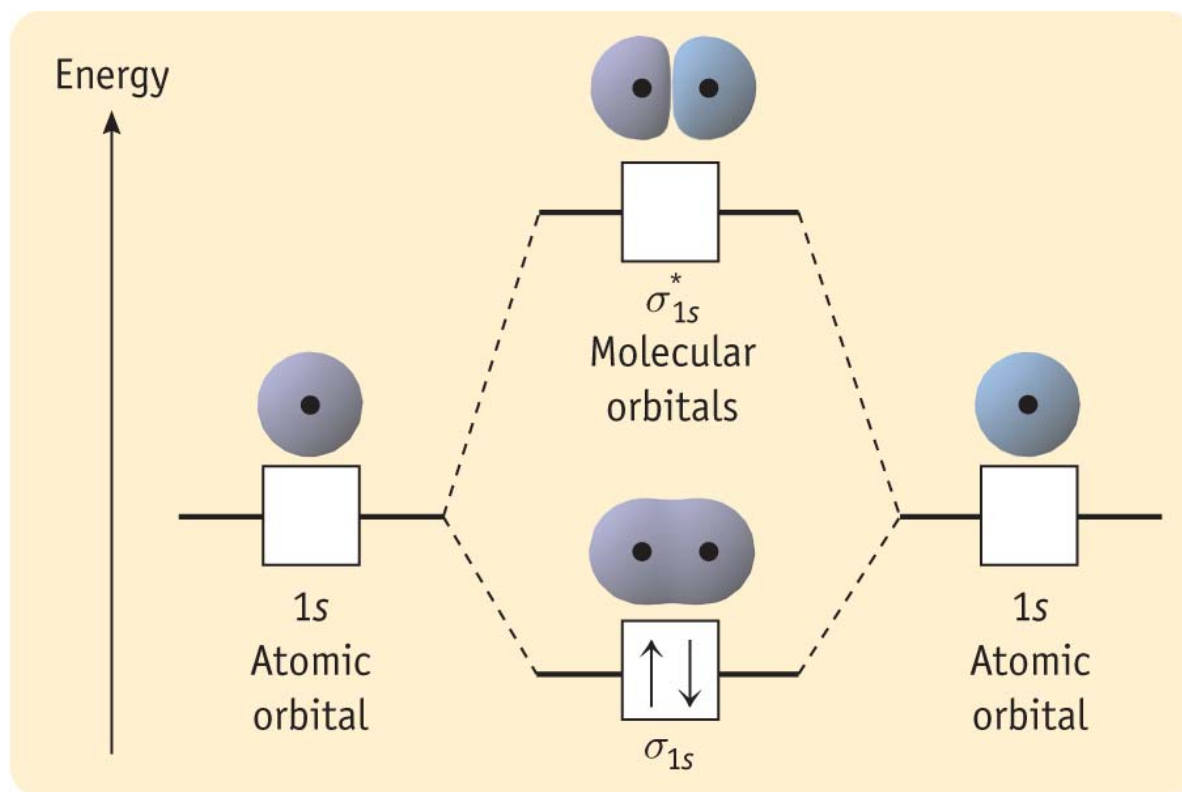
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Correlation diagrams …
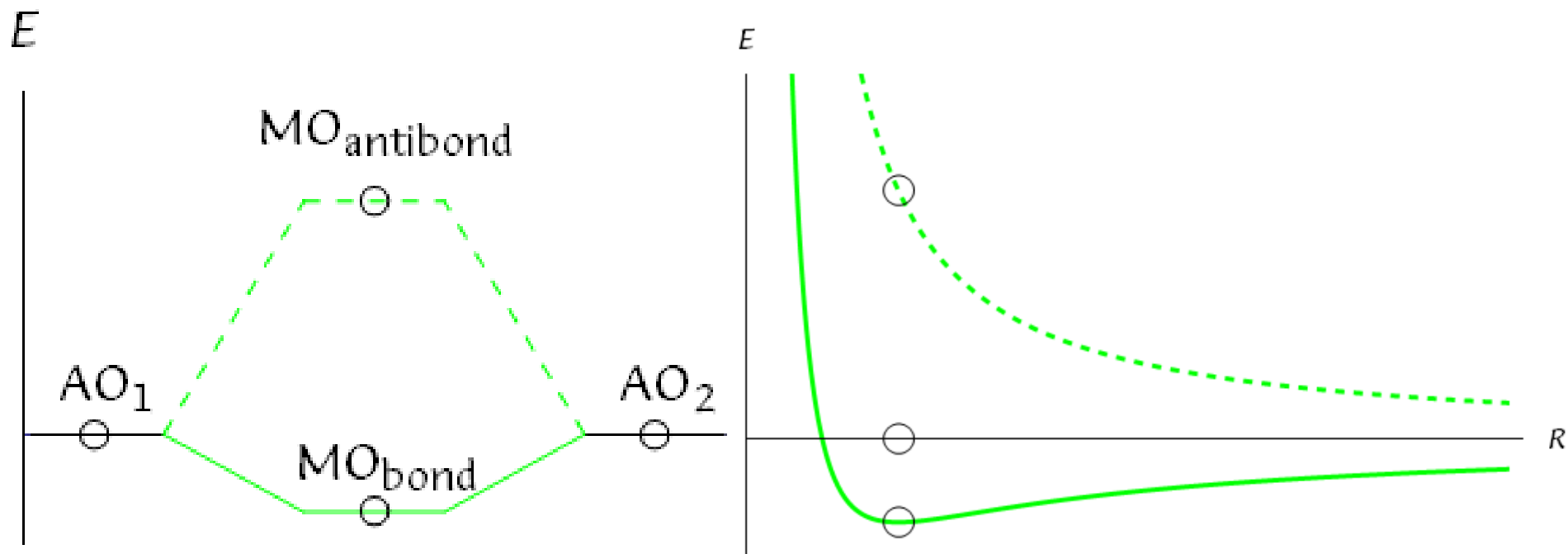
… summarize
bonding and antibonding effects

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Filling of MO's → **H₂** MO configuration

Mahaffy et al., Figure 10.20

Filling of MO's → **He$_2$** MO configuration

Atomic orbital | Molecular orbitals | Atomic orbital

Energy

σ^*_{1s}

He atom 1s

He atom 1s

σ_{1s}

He$_2$ molecule
$(\sigma_{1s})^2(\sigma^*_{1s})^2$
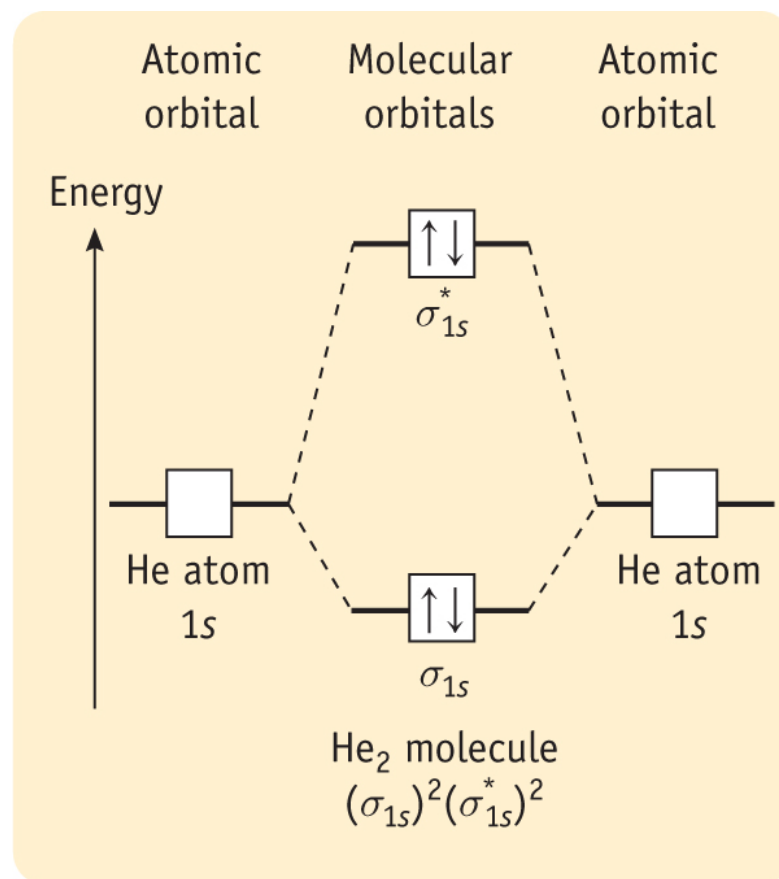
Mahaffy et al., Figure 10.21

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Filling of MO's → Li$_2$ MO configuration

Mahaffy et al., Figure 10.22
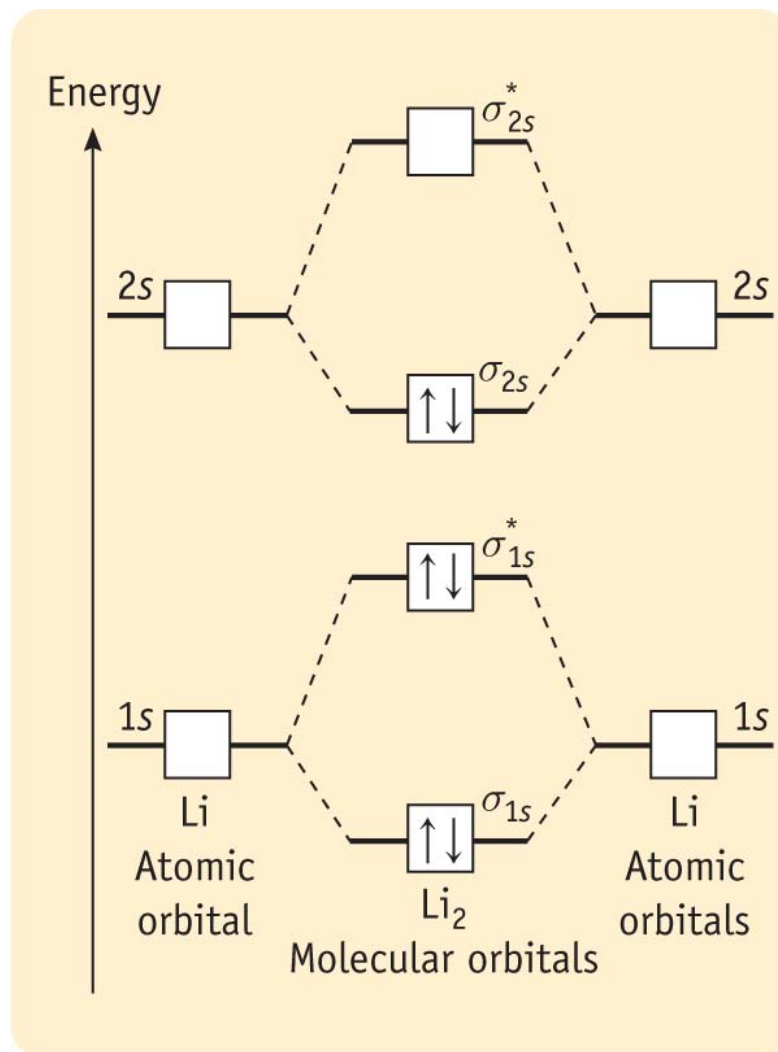
Bond order

(bonding e⁻'s – antibonding e⁻'s)/2

Division by two is because a single bond shares a **pair of electrons**
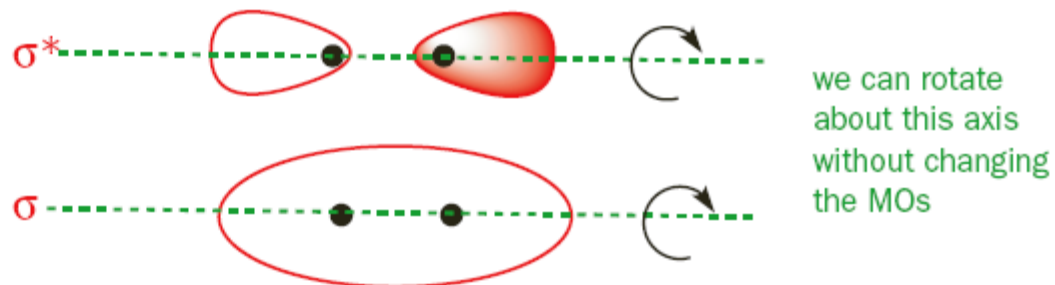
$H_2^+ = H \cdot H^+ \rightarrow$ bond order = 1/2

$H_2 = H:H \rightarrow$ bond order = 1

$He_2 \rightarrow$ bond order = 0

$He_2^+ \rightarrow$ bond order = …?

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1s (and 2s) σ and σ*

■

Antibonding orbitals are designated
with a * e.g. σ*, or π*

σ*

we can rotate
about this axis
without changing
the MOs

σ

both MOs have rotational symmetry about the axis through the two nuclei

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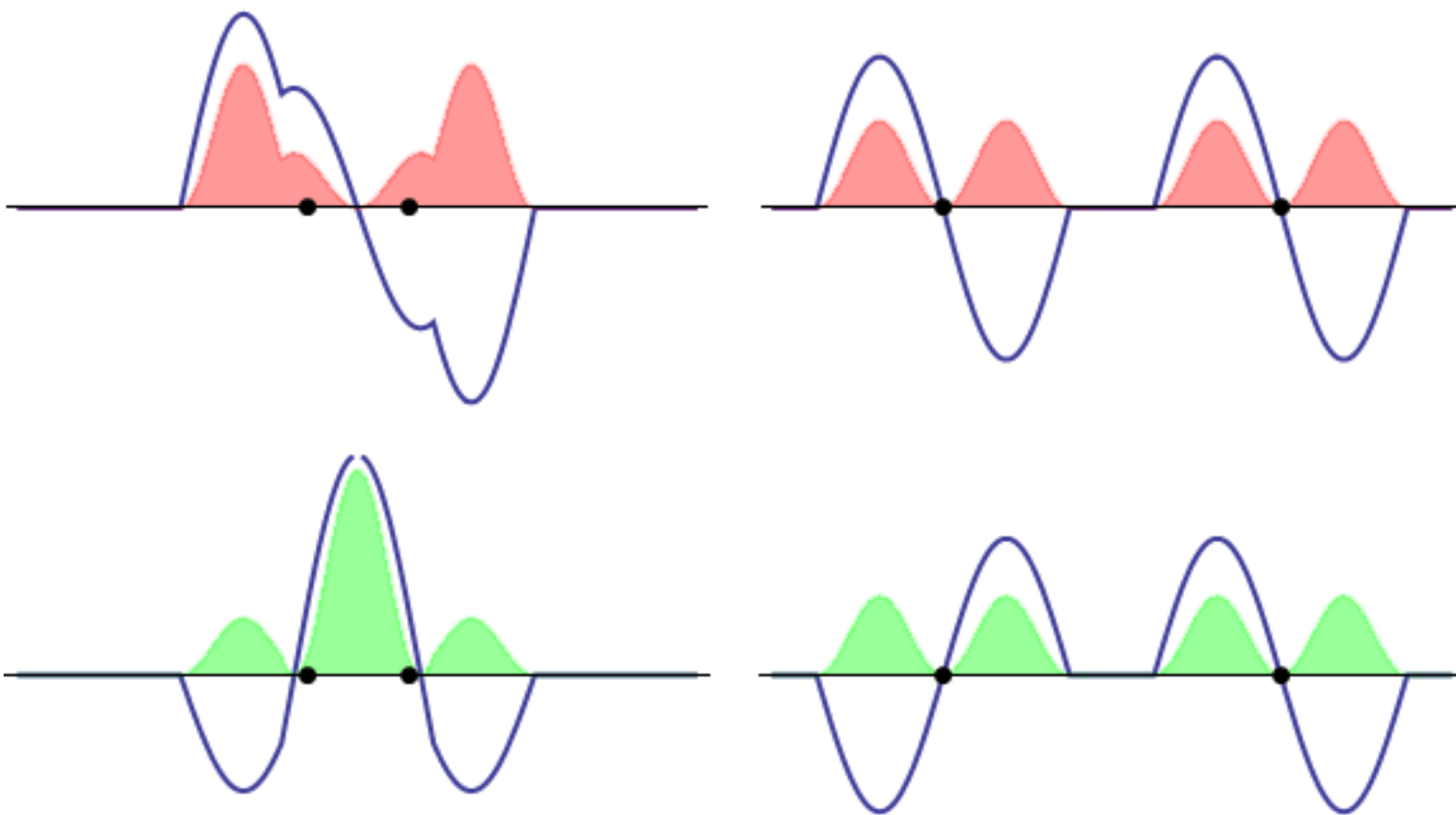UNIVERSITY

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2p$_z$σ and 2p$_z$σ*
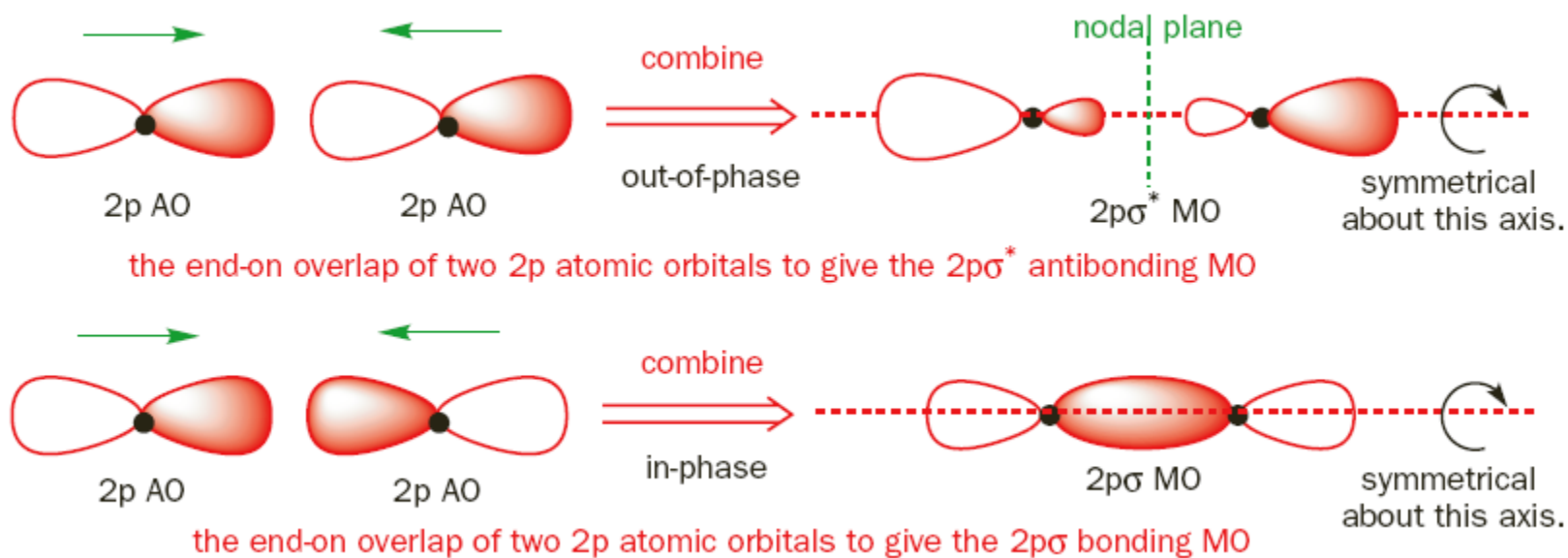
$2p_z\sigma$ and $2p_z\sigma^*$
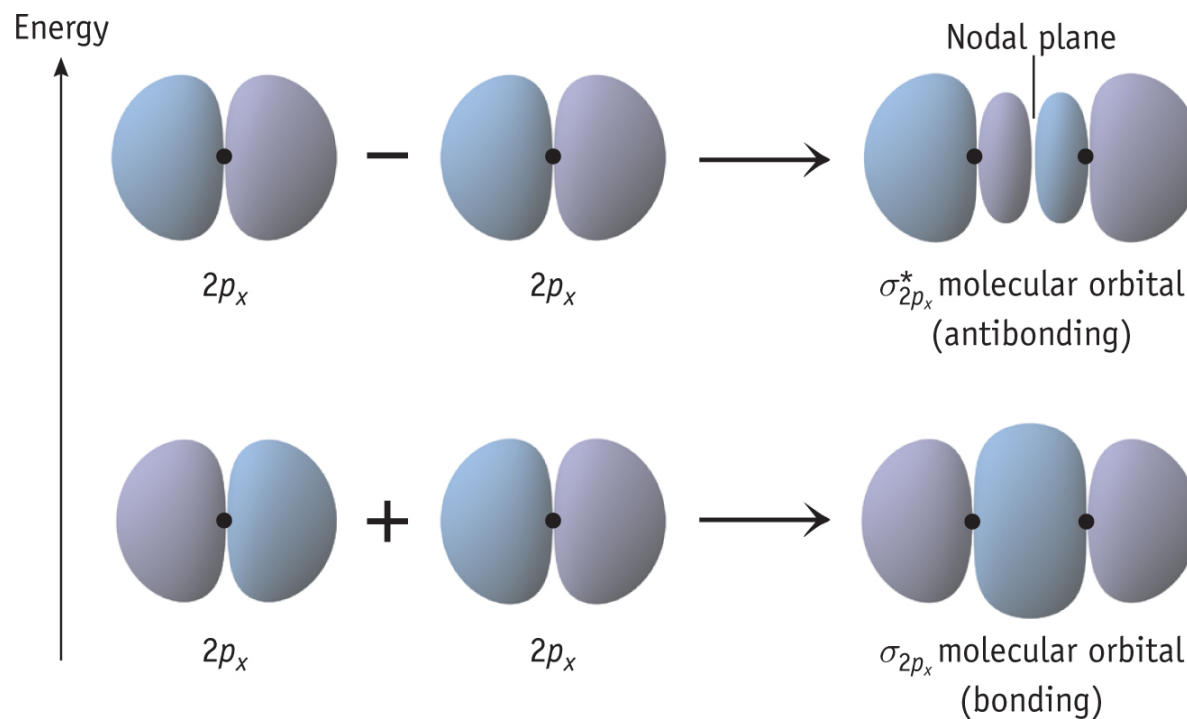
Mahaffy et al., Figure 10.23

$2p_z\sigma$ (lower) and $2p_z\sigma^*$ (upper)

2p$_x$π and 2p$_x$π*
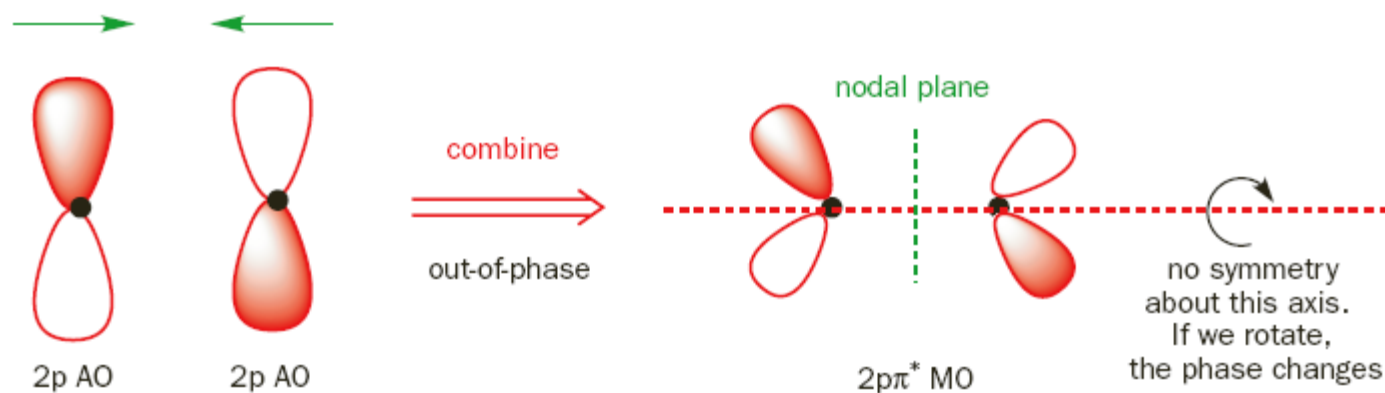
nodal plane

combine

out-of-phase

no symmetry about this axis. If we rotate, the phase changes

2p AO   2p AO   2pπ* MO

the side-on overlap of two 2p atomic orbitals to give the 2pπ* antibonding MO

combine

in-phase

no symmetry about this axis. If we rotate, the phase changes

2p AO   2p AO   2pπ MO

the side-on overlap of two 2p atomic orbitals to give the 2pπ bonding MO

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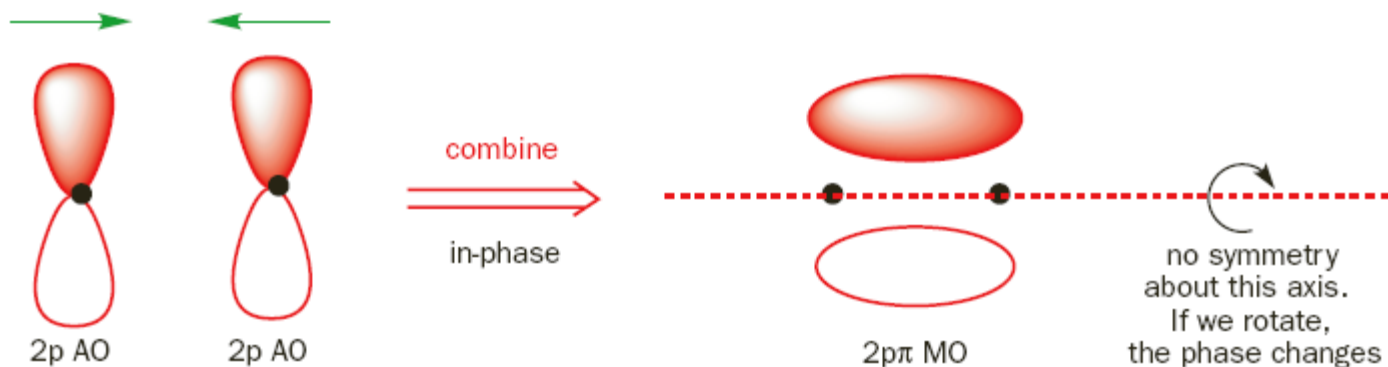
$2p_x\pi$ and $2p_x\pi^*$
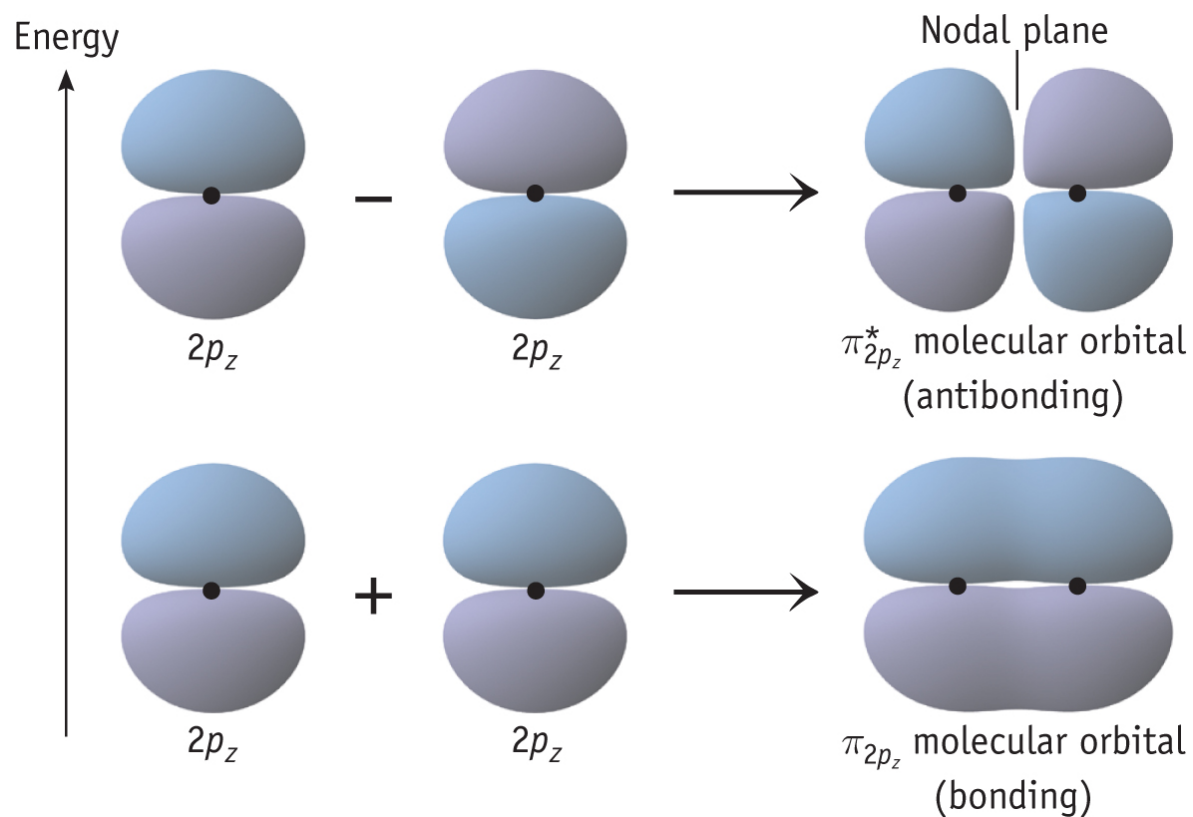
Mahaffy et al., Figure 10.24

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Homonuclear diatomics, up to N$_2$
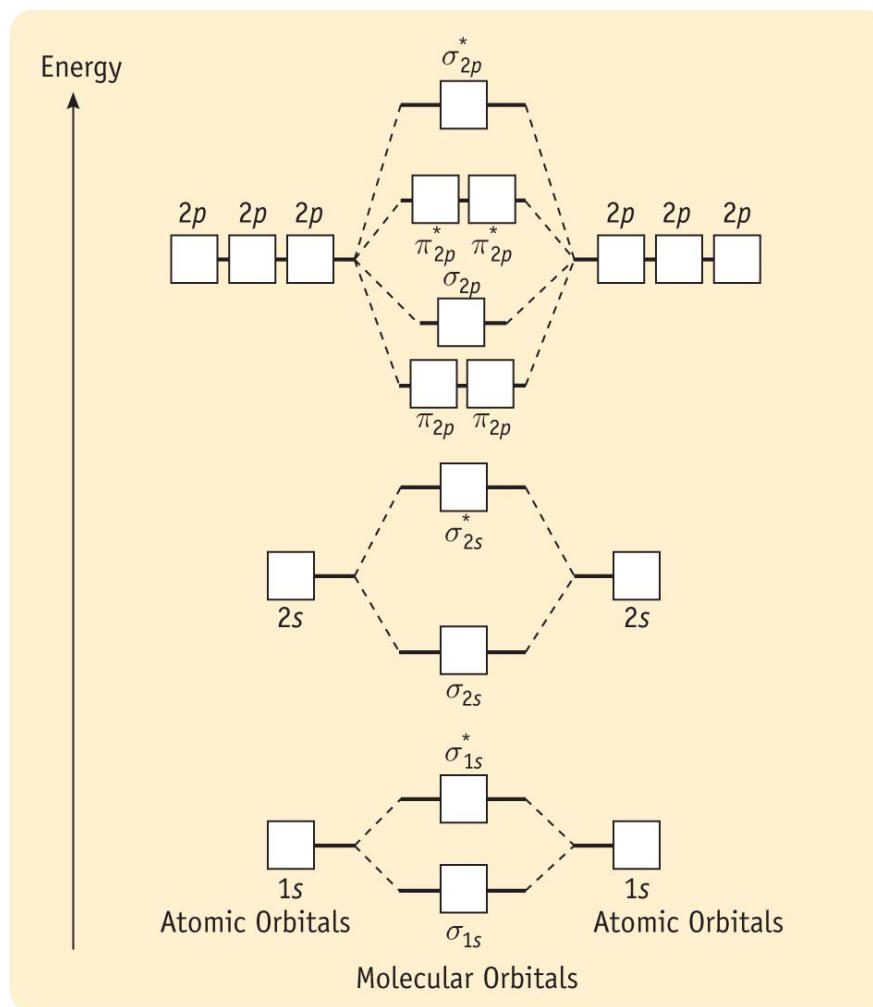
Mahaffy et al., Figure 10.25

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Homonuclear diatomics, after N$_2$

Homonuclear diatomics

Laird, University Chemistry, Figure 3.4

Homonuclear diatomics

Challenge: Of H_2, Li_2, and Be_2, which is/are most stable?

Challenge: In Li_2, what contribution to bonding is due to MO's made from 1s AO's?

Challenge: N_2, O_2, F_2, Ne_2

TurningPoint lesson:

Homonuclear diatomic molecules

http://goo.gl/404yQ

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Which AO's combine?

SOE: Symmetry, Overlap, Energy

- **Symmetry**: Which AO's can combine to form MO's?

- **Overlap**: Which AO's combine with the greatest bonding/antibonding effect?

- **Energy**: How does relative AO energy affect composition of MO's?

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Symmetry: Net overlap or not?

- For a pair of AO's to give a (**bonding/antibonding**) pair of MO's, there must be **net overlap** (in-phase or net out-of-phase).

- If in-phase and out of phase overlap **exactly balance**, the AO's remain uncombined, as **nonbonding orbitals**.

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Overlap: Greater the better

- The **more** net overlap, the **greater** the bonding/antibonding effect.

- **Core** AO's have **least** overlap

- **Valence** AO's have **greatest** overlap

- **Bonding due** to MO's made from **valence AO's**

Energy: Closer the better

- The **closer** AO's are in energy, the **greater** the bonding/antibonding effect.

- If AO's have **same energy** (identical atoms, homonuclear bond), MO's will be **50% of each AO**.

- If AO's have **different energy** (different atoms, heteronuclear bond), …

  - **Bonding MO $\rightarrow$ more lower energy AO**

  - **Antibonding MO $\rightarrow$ more higher energy AO**

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Energy: Closer the better

molecular orbitals from elements of different electronegativity
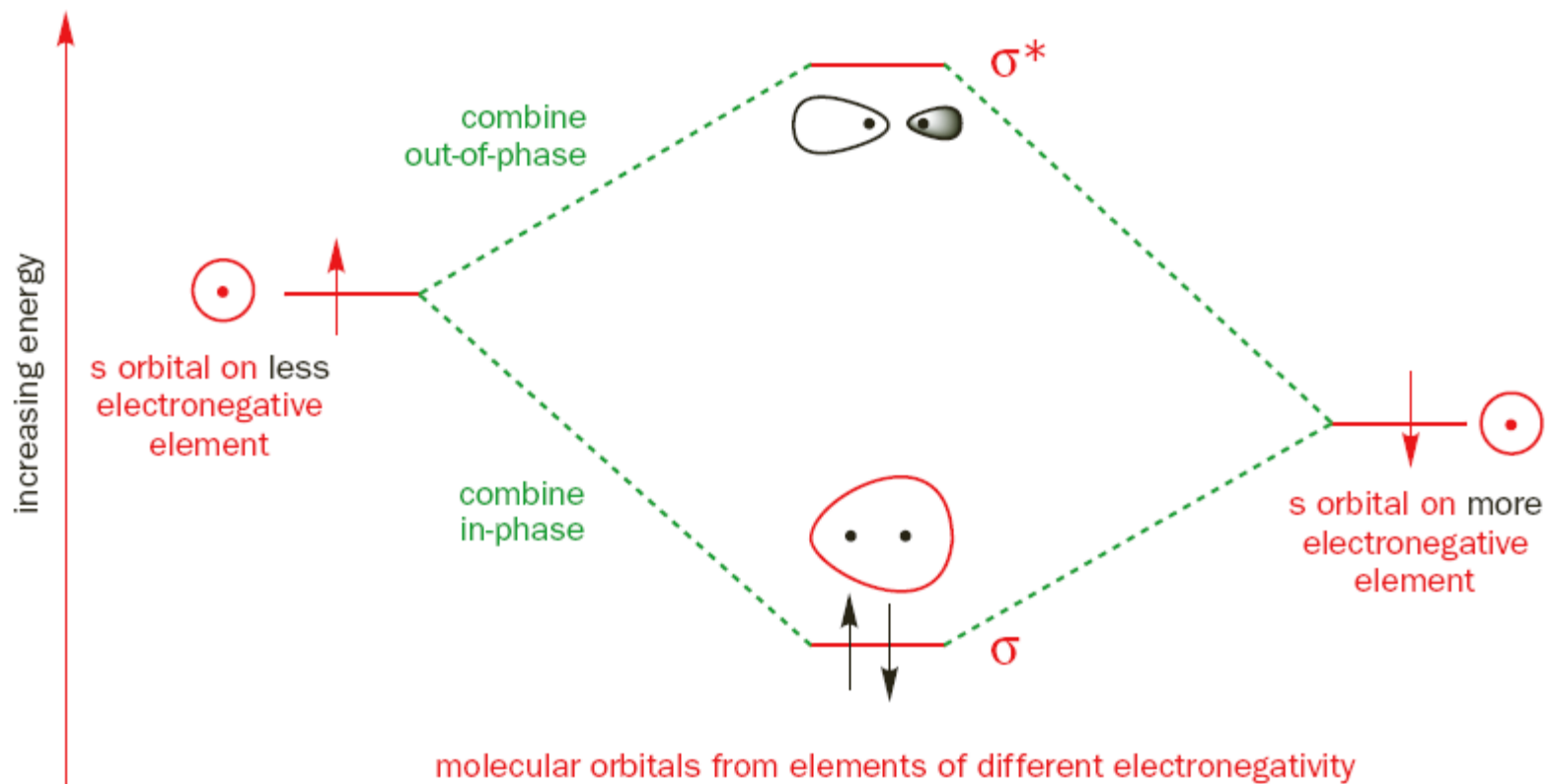
Energy: Closer the better
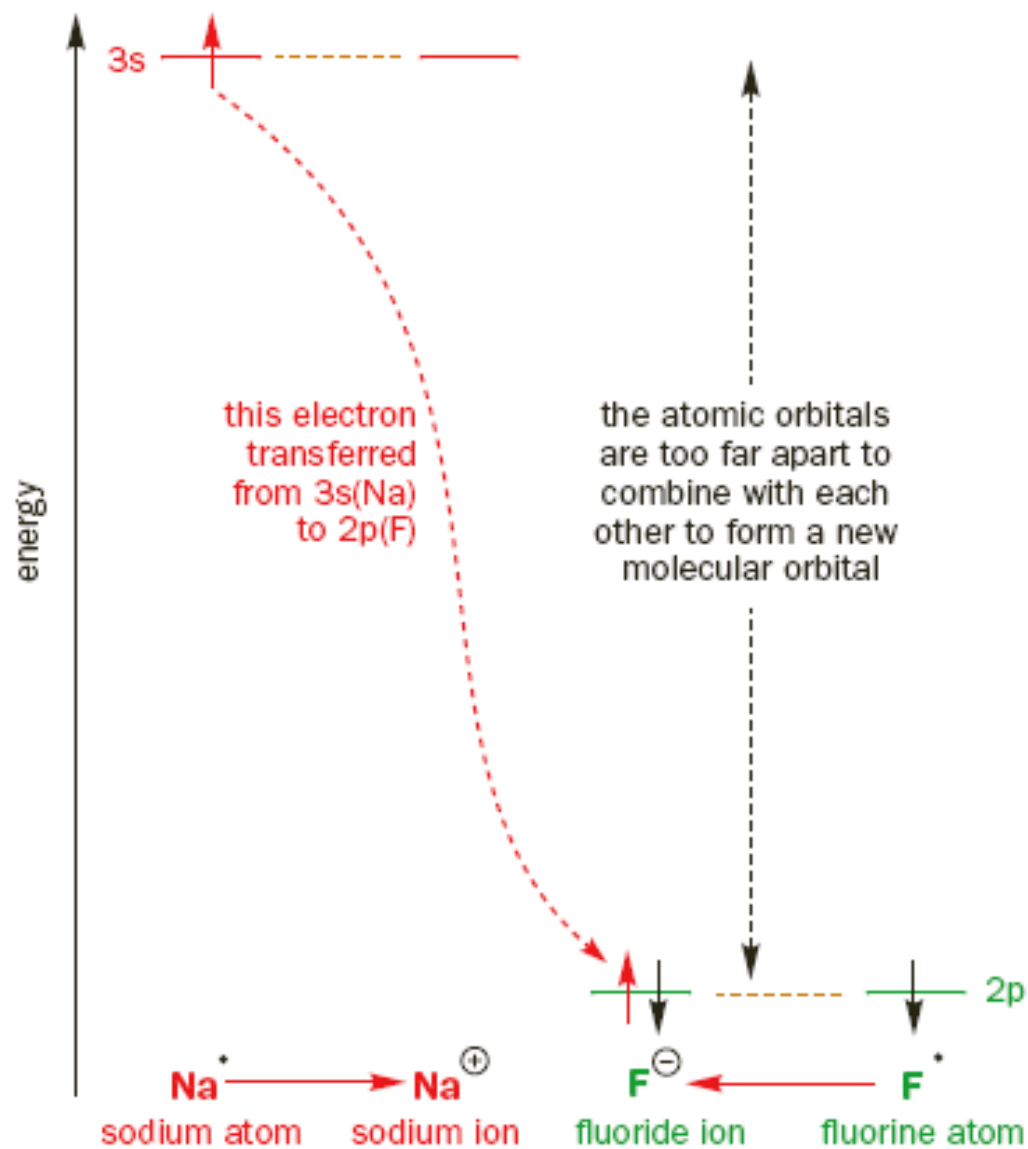
Energy: Closer the better

Energies of AOs both the same	AO on atom B is a *little* lower in energy than AO on atom A	AO on atom B is a *lot* lower in energy than AO on atom A
large interaction between AOs	less interaction between AOs	AOs are too far apart in energy to interact
bonding MO much lower in energy than AOs	bonding MO is lowered only by a small amount relative to AO on atom B	the filled orbital on the anion has the same energy as the AO on atom B
antibonding MO is much higher in the energy than the AOs	antibonding MO is raised in energy by only a small amount relative to AO on atom B	the empty orbital on the cation has same energy as the AO on atom A
both AOs contribute equally to the MOs	the AO on B contributes more to the bonding MO and the AO on A	only one AO contributes to each 'MO'
electrons in bonding MO are shared equally between the two atoms	electrons in bonding MO are shared between atoms but are associated more with atom B than A	electrons in the filled orbital are located only on atom B
bond between A and B would classically be described as purely covalent	bond between A and B is covalent but there is also some electrostatic (ionic) attraction between atoms	bond between A and B would classically be described as purely ionic
easiest to break bond into two radicals (homolytic fission). Heterolytic fission of bond is possible and could give either A^+ and B^- or A^- and B^+	easiest to break bond into two ions, A^+ and B^-, although it is also possible to give two radicals	compound already exists as ions A^+ and B^-
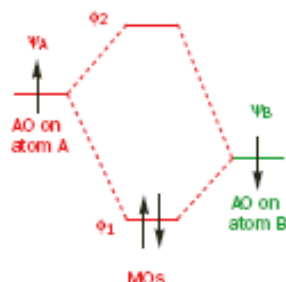
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TurningPoint lesson:
Symmetry – Overlap – Energy
http://goo.gl/tQiAj

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