Bonding in diatomic molecules

CH101 Fall 2015
Boston University

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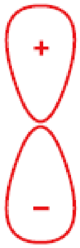
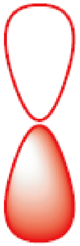
Atoms interact by merging ***waves***

$$\mathrm{AO} + \mathrm{AO} \rightarrow 2\ \mathrm{MOs}$$

Relative AO phase determines MO character



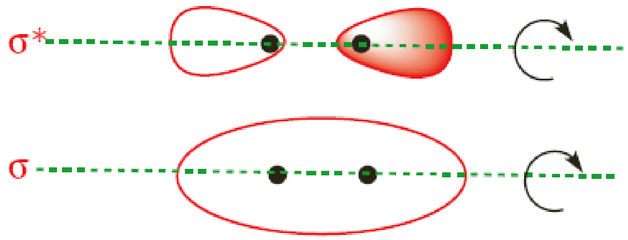
here the different phases of the p orbital are labelled positive and negative – this can be confusing and so is best avoided



here the different phases of the p orbital are shown by shading one half and not the other

σ MO’s have cylindrical symmetry

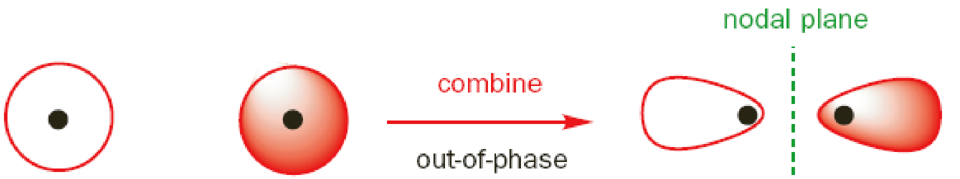
- Antibonding orbitals are designated with a * e.g. σ*, or π*



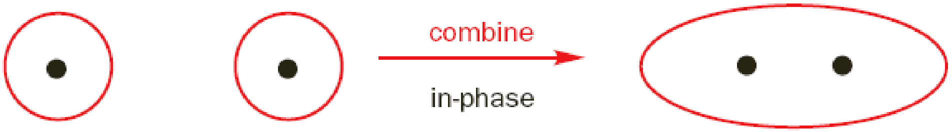
we can rotate about this axis without changing the MOs

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

1sσ and 1sσ*

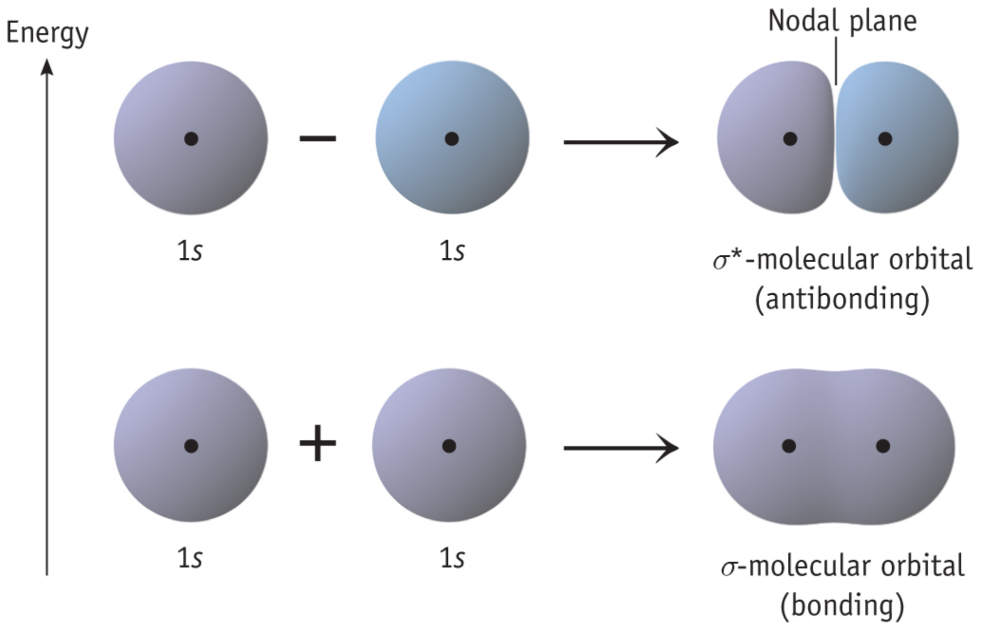


the two 1s orbitals combining out-of-phase to give an **antibonding orbital**



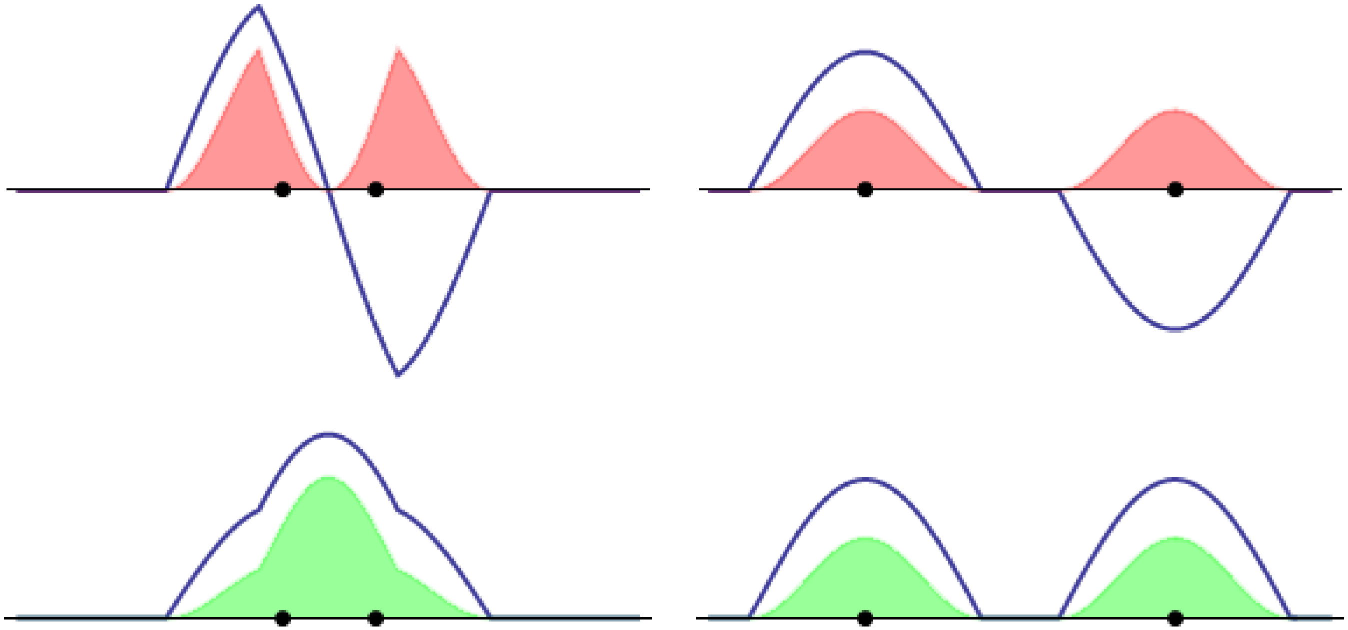
the two 1s orbitals combining in-phase to give a **bonding orbital**

1sσ and 1sσ*



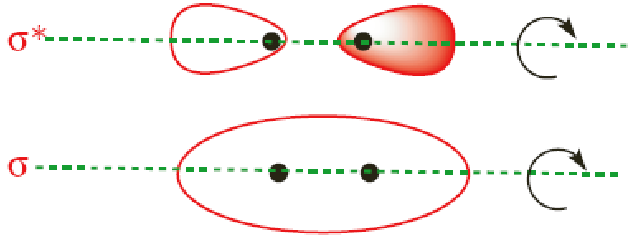
Mahaffy et al., Figure 10.20

1s molecular orbitals:
http://quantum.bu.edu/CDF/101/1sMolecularOrbitals.cdf



σ is “bonding” and σ* is “antibonding”

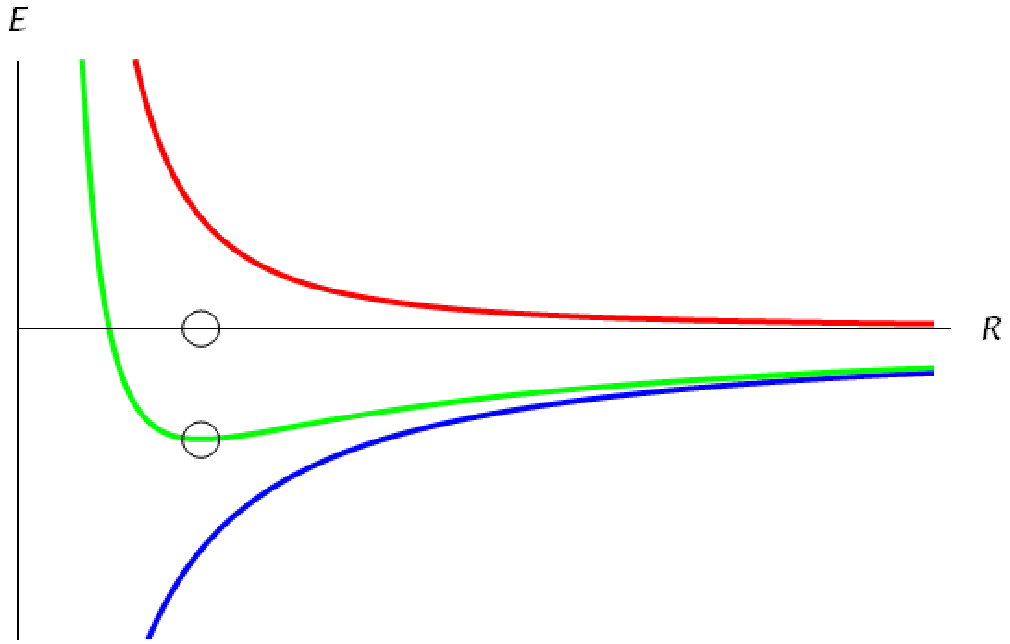
- Antibonding orbitals are designated with a * e.g. σ*, or π*



we can rotate about this axis without changing the MOs

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

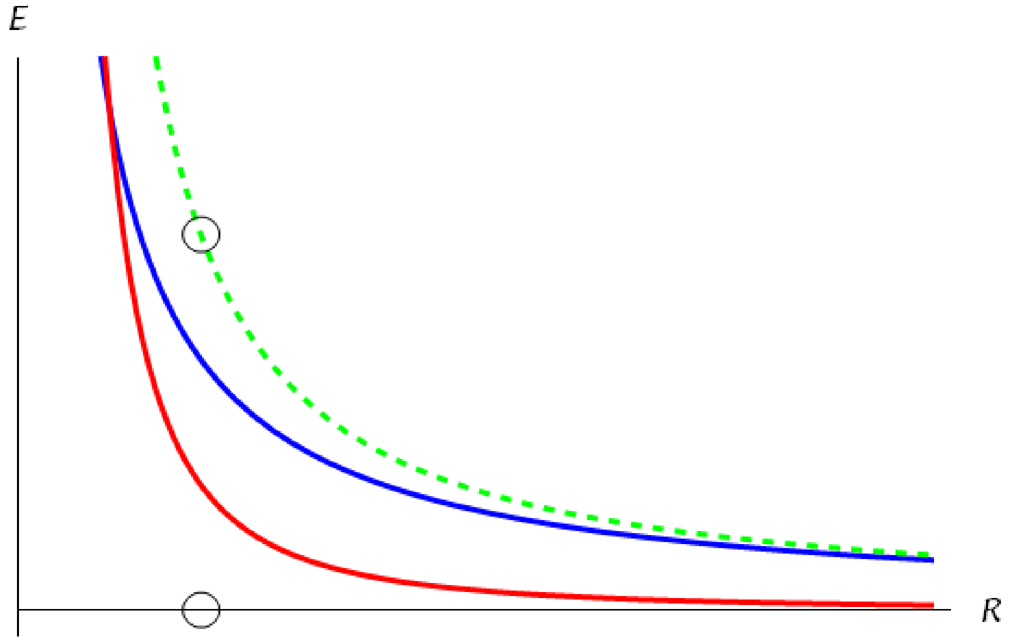
Bonding *PE*, *KE* and total *E*



Attractive (< 0) *PE* is opposed by **repulsive (> 0) *KE***.

Molecular size is at **minimum of total *E***.

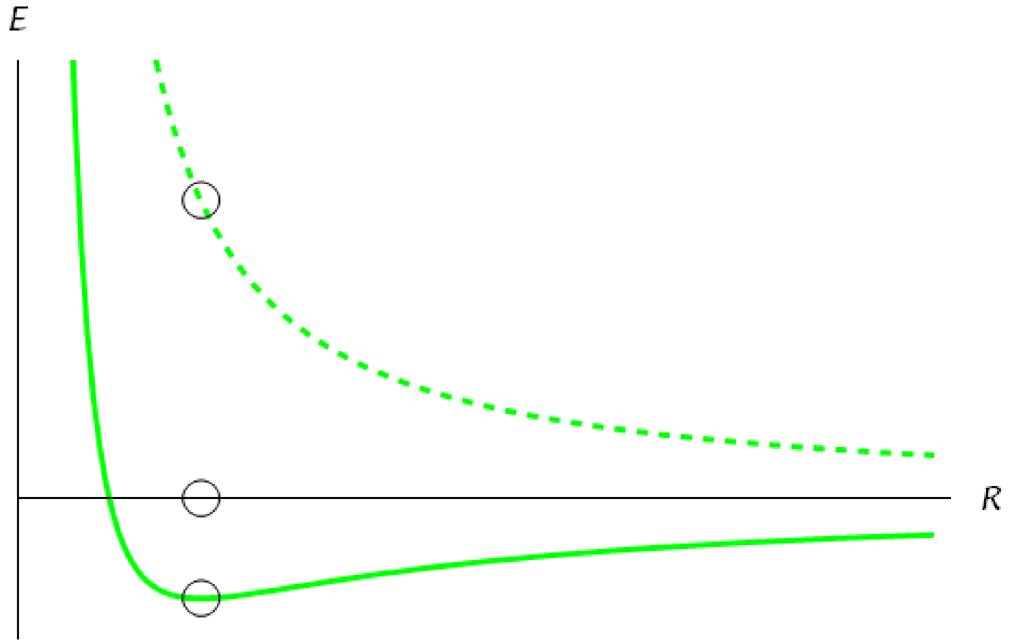
Antibonding *PE*, *KE* and total *E*



Repulsive (> 0) *PE* enhanced by **repulsive (> 0) *KE***.

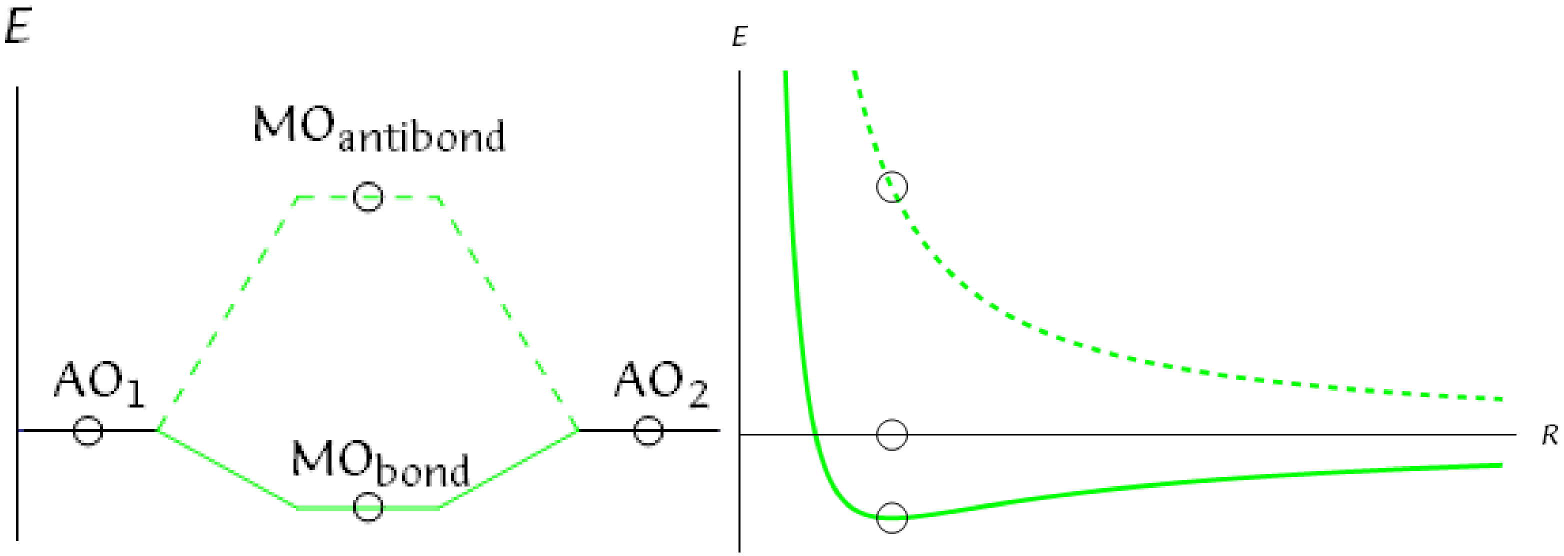
No minimum of total *E* --- **atoms fly apart**!

Bonding and **antibonding** total ***E***



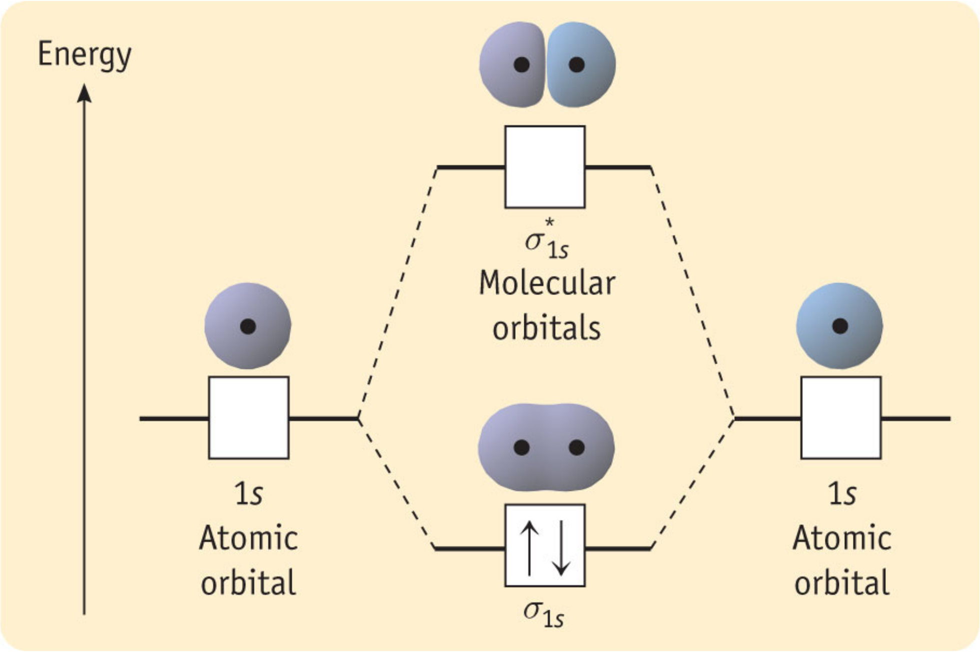
What matters are the total bonding and antibonding ***E*** at the **bonding minimum** versus the **AO energies-**--the energy at infinite separation.

Correlation diagrams …



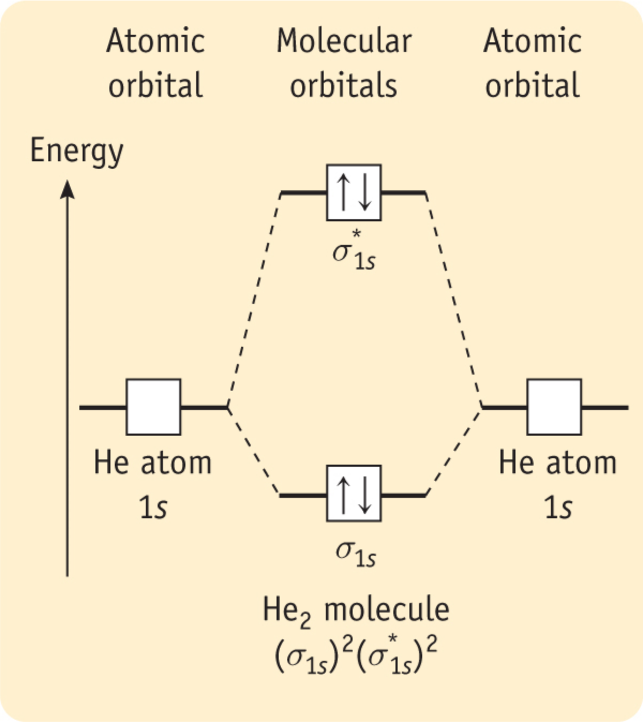
… summarize
bonding and antibonding effects

Filling of MO’s → H_2 MO configuration



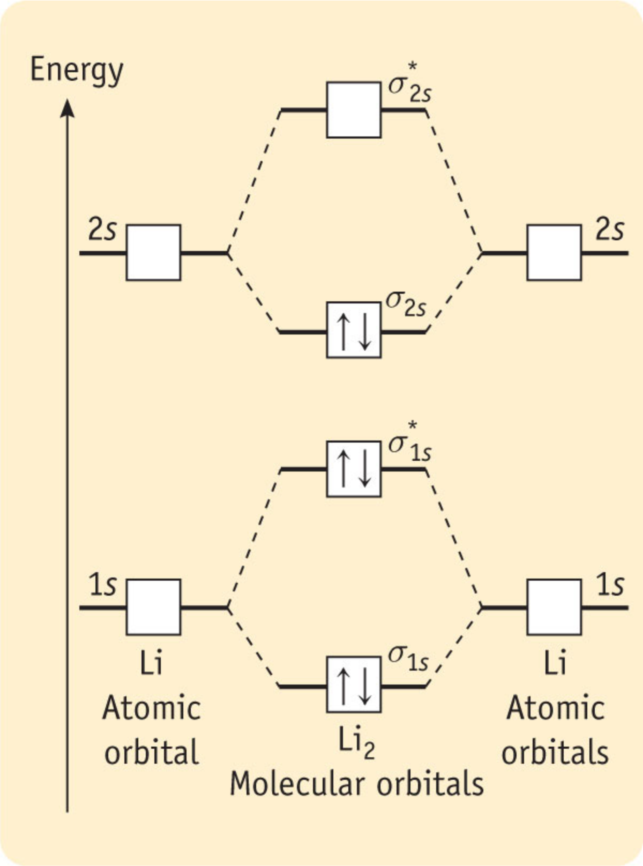
Mahaffy et al., Figure 10.20

Filling of MO's → **He_2** MO configuration



Mahaffy et al., Figure 10.21

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

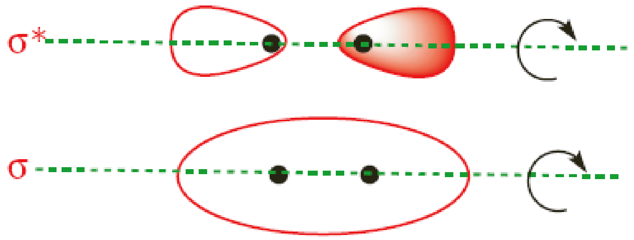
$H_2 = H{:}H \rightarrow$ bond order = 1

$He_2 \rightarrow$ bond order = 0

$He_2^+ \rightarrow$ bond order = …?

1s (and 2s) σ and σ*

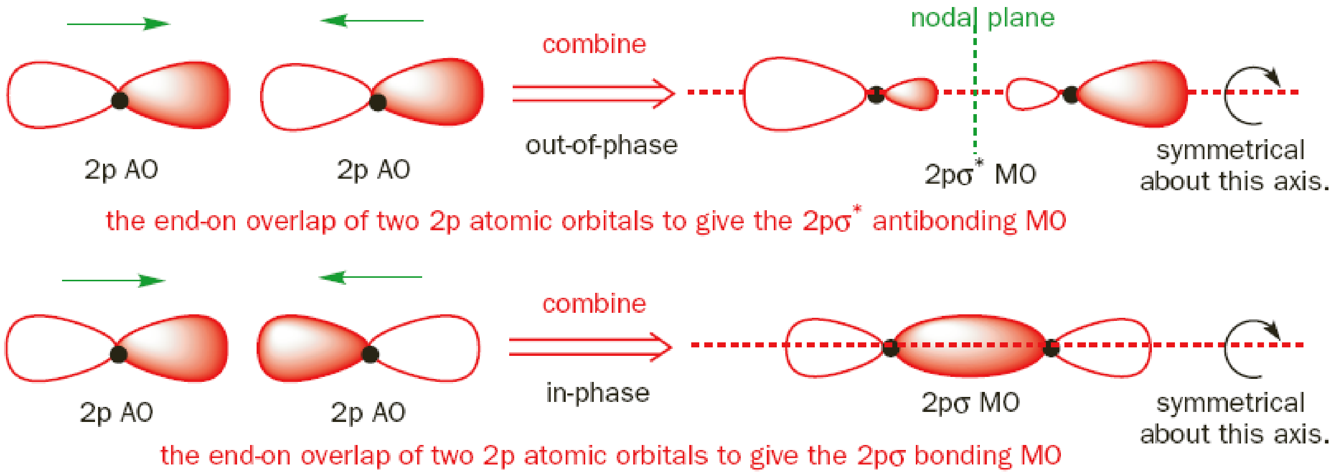
- Antibonding orbitals are designated with a * e.g. σ*, or π*



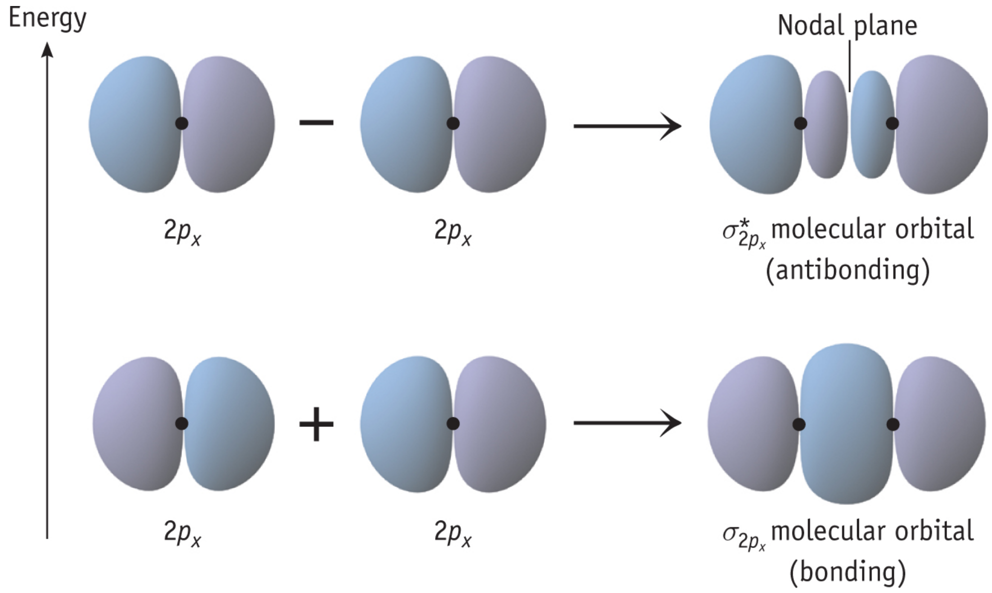
we can rotate about this axis without changing the MOs

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

$2p_z\sigma$ and $2p_z\sigma^*$



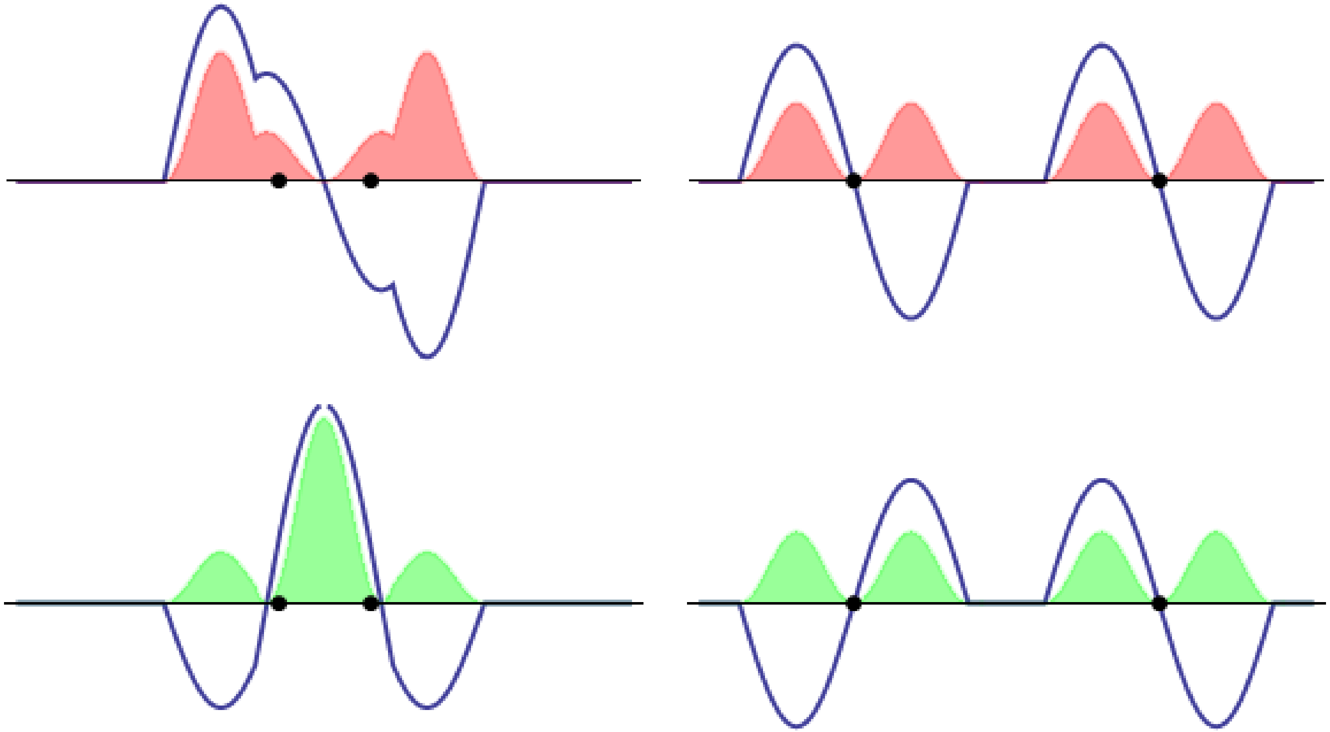
$2p_z\sigma$ and $2p_z\sigma^*$



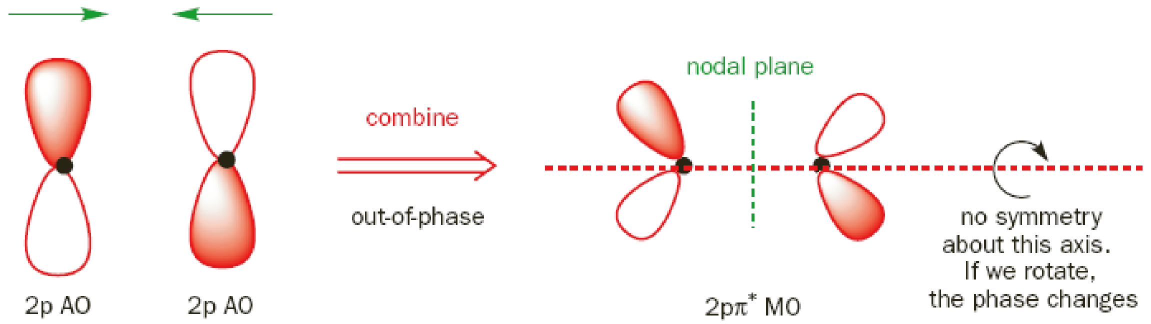
Mahaffy et al., Figure 10.23

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

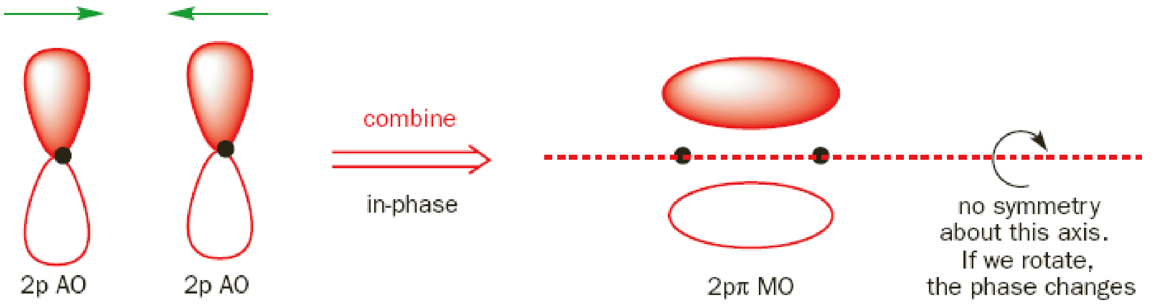
$2p_z$ molecular orbitals:
http://quantum.bu.edu/CDF/101/2pMolecularOrbitals.cdf



$2p_x\pi$ and $2p_x\pi^*$

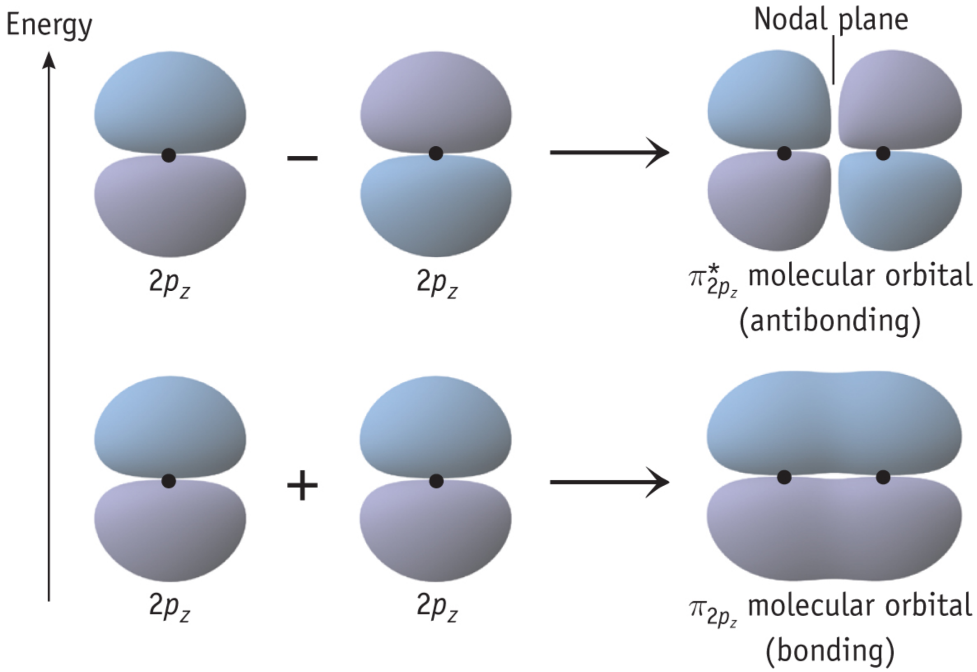


the side-on overlap of two 2p atomic orbitals to give the 2pπ* antibonding MO



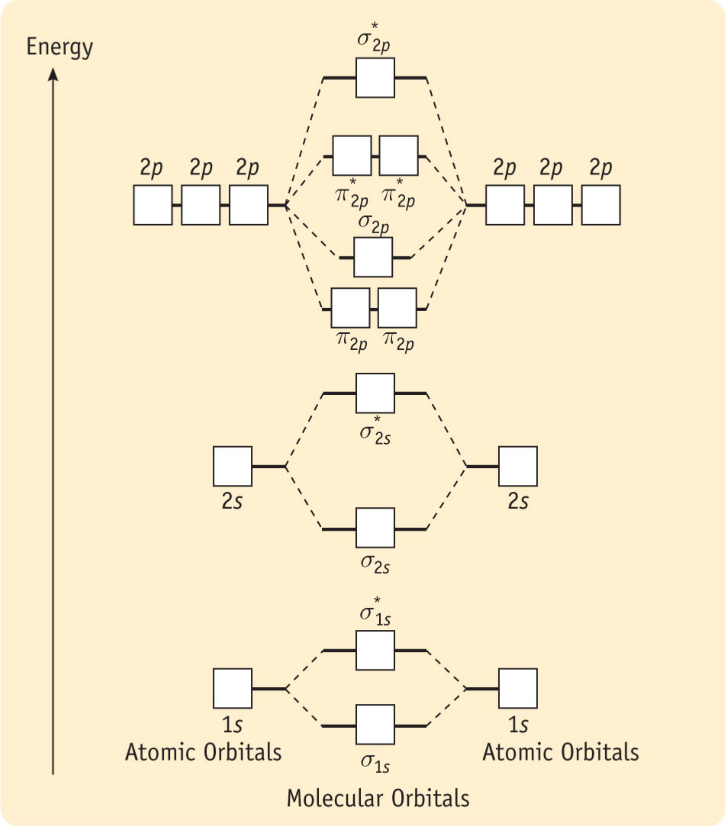
the side-on overlap of two 2p atomic orbitals to give the 2pπ bonding MO

$2p_x\pi$ and $2p_x\pi^*$



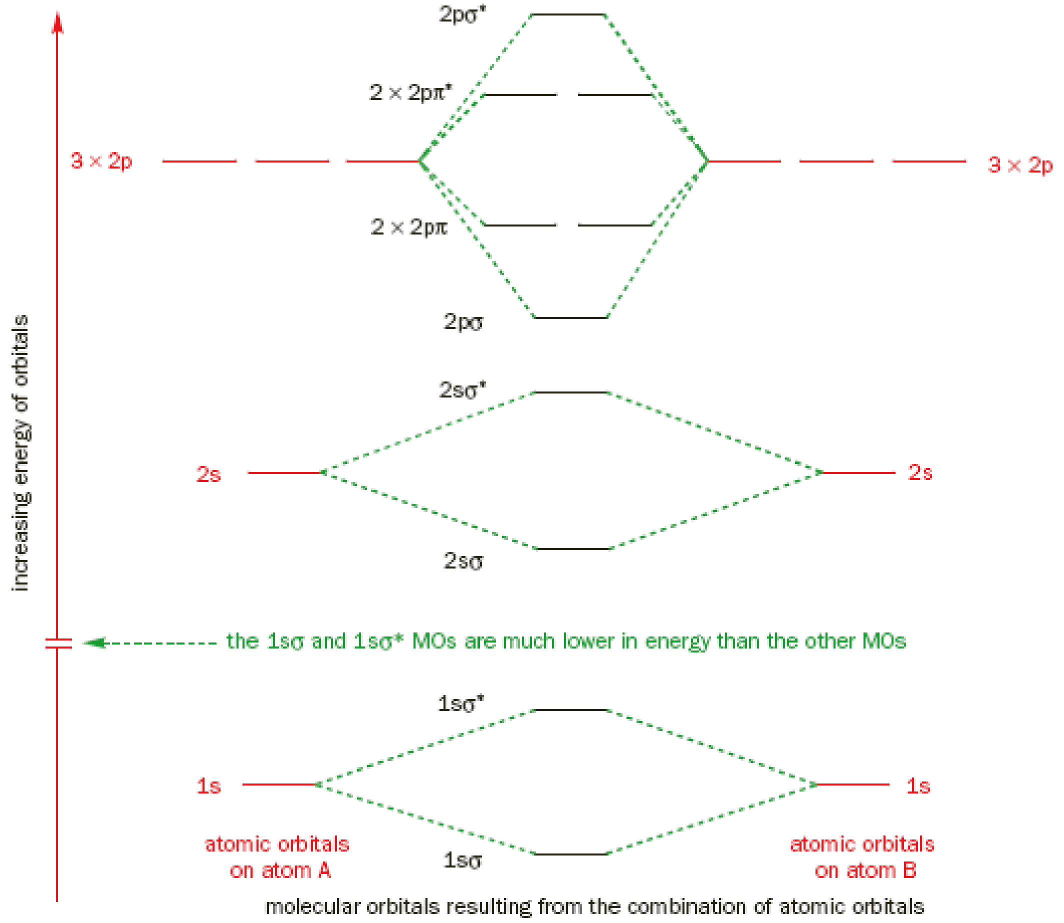
Mahaffy et al., Figure 10.24

Homonuclear diatomics, up to N_2

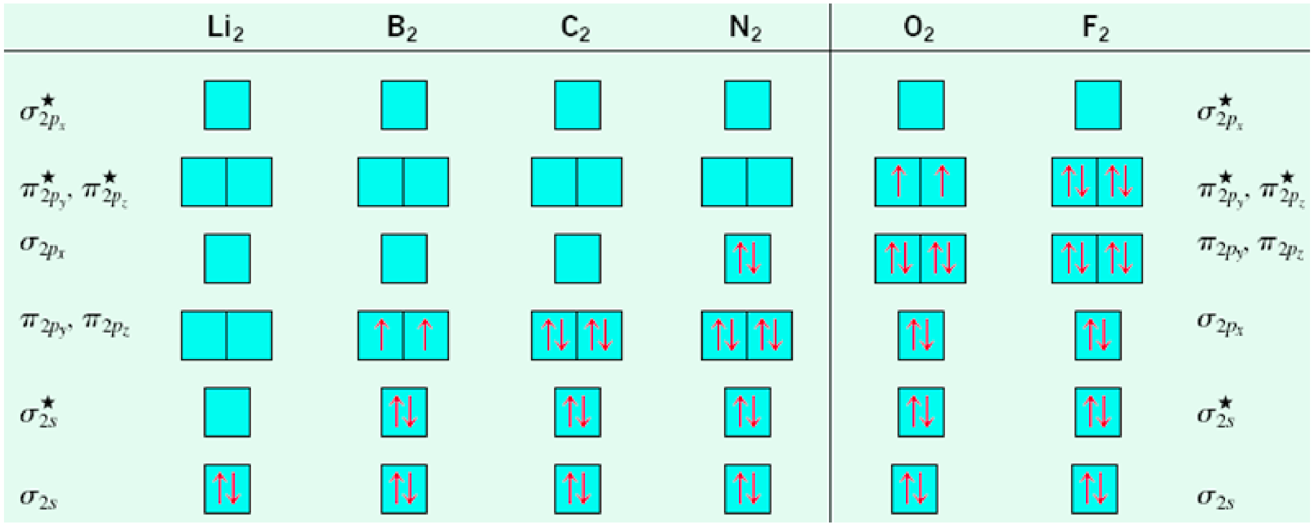


Mahaffy et al., Figure 10.25

Homonuclear diatomics, after N_2



Homonuclear diatomics



	Li_2	B_2	C_2	N_2	O_2	F_2	
$\sigma^{\star}_{2p_x}$	☐	☐	☐	☐	☐	☐	$\sigma^{\star}_{2p_x}$
$\pi^{\star}_{2p_y}, \pi^{\star}_{2p_z}$	☐ ☐	☐ ☐	☐ ☐	☐ ☐	↑ ↑	↑↓ ↑↓	$\pi^{\star}_{2p_y}, \pi^{\star}_{2p_z}$
σ_{2p_x}	☐	☐	☐	↑↓	↑↓ ↑↓	↑↓ ↑↓	π_{2p_y}, π_{2p_z}
π_{2p_y}, π_{2p_z}	☐ ☐	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	↑↓	↑↓	σ_{2p_x}
$\sigma^{\star}_{2s}$	☐	↑↓	↑↓	↑↓	↑↓	↑↓	$\sigma^{\star}_{2s}$
σ_{2s}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	σ_{2s}

Laird, University Chemistry, Figure 3.4

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?

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**.

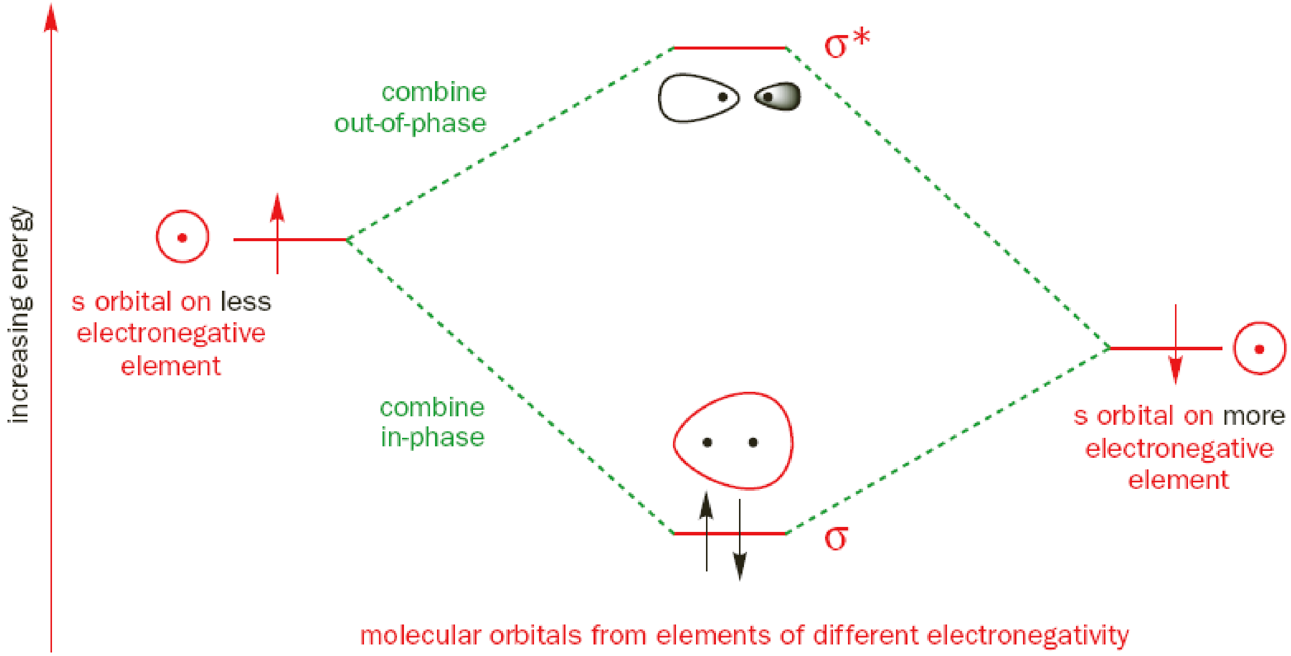
Overlap: Greater the better

- 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

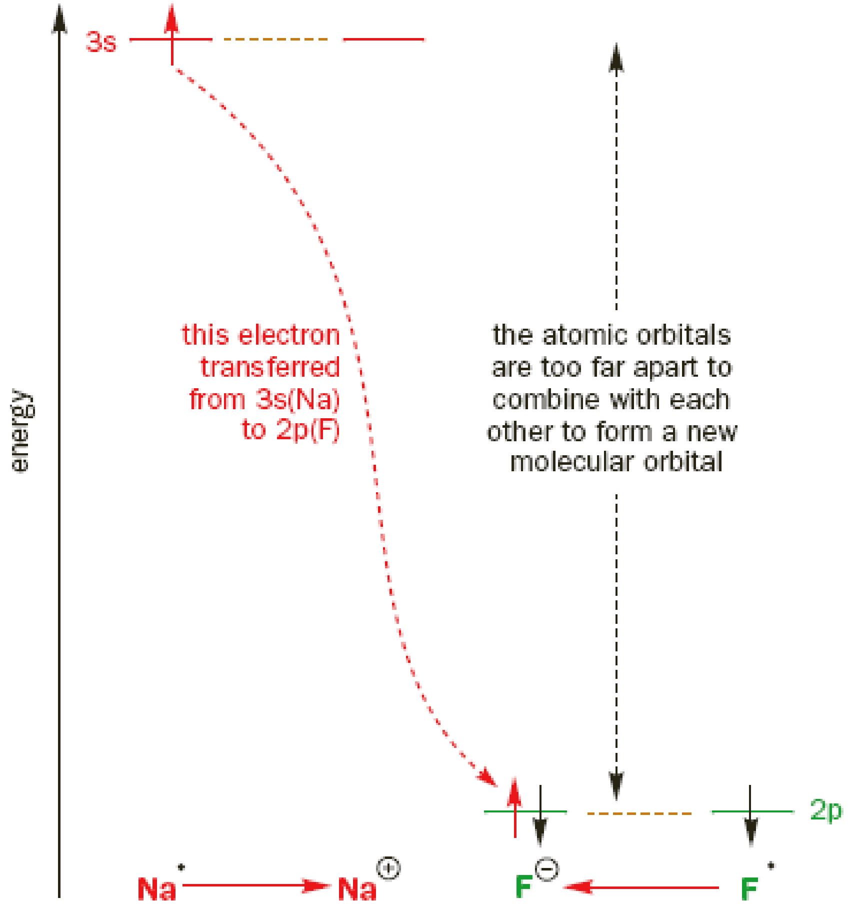
- The **closer** AO’s are in energy, the **greater** the bonding/antibonding effect.
- If AO’s have **same energy** (identical atoms, homonuclear bond), MO’s will be **50% of each AO**.
- If AO’s have **different energy** (different atoms, heteronuclear bond), …
  - **Bonding MO → more lower energy AO**
  - **Antibonding MO → more higher energy AO**

Energy: Closer the better



molecular orbitals from elements of different electronegativity

Energy: Closer the better

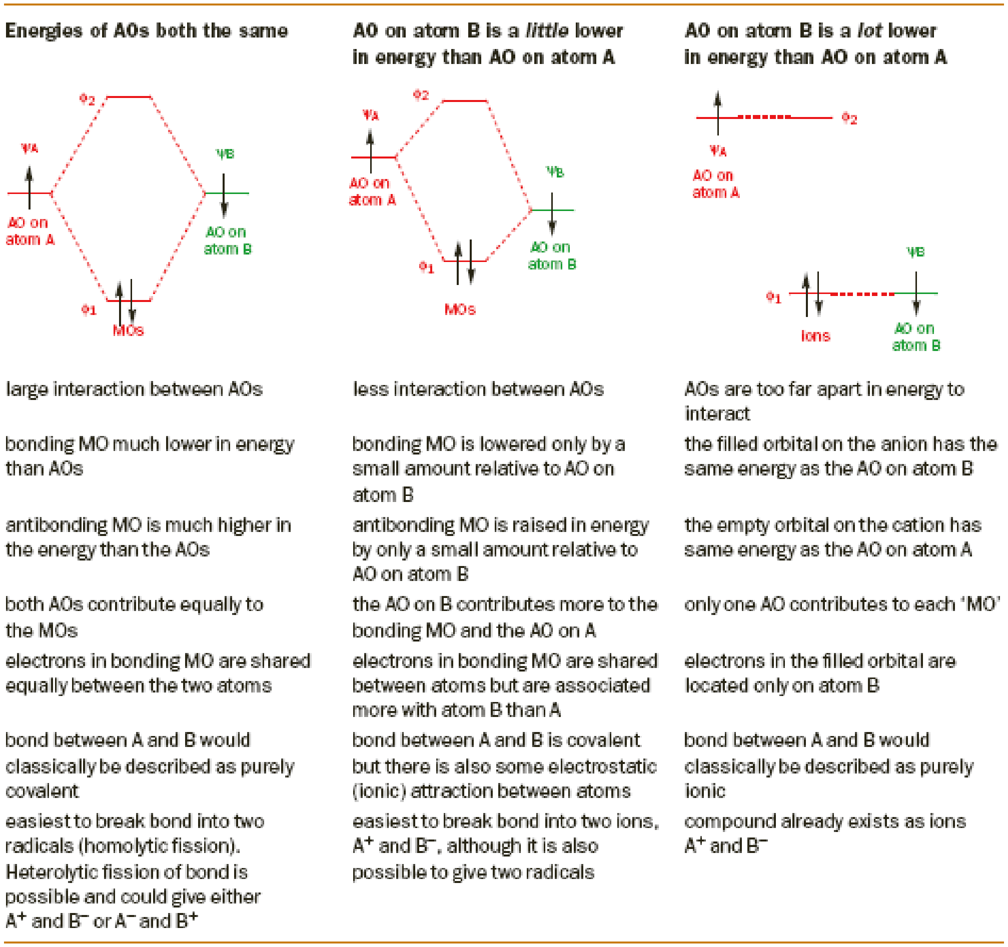


this electron transferred from 3s(Na) to 2p(F)

the atomic orbitals are too far apart to combine with each other to form a new molecular orbital

sodium atom
sodium ion
fluoride ion
fluorine atom

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^-

Practice

Questions on Symmetry, Overlap, Energy

http://goo.gl/oYEf3b