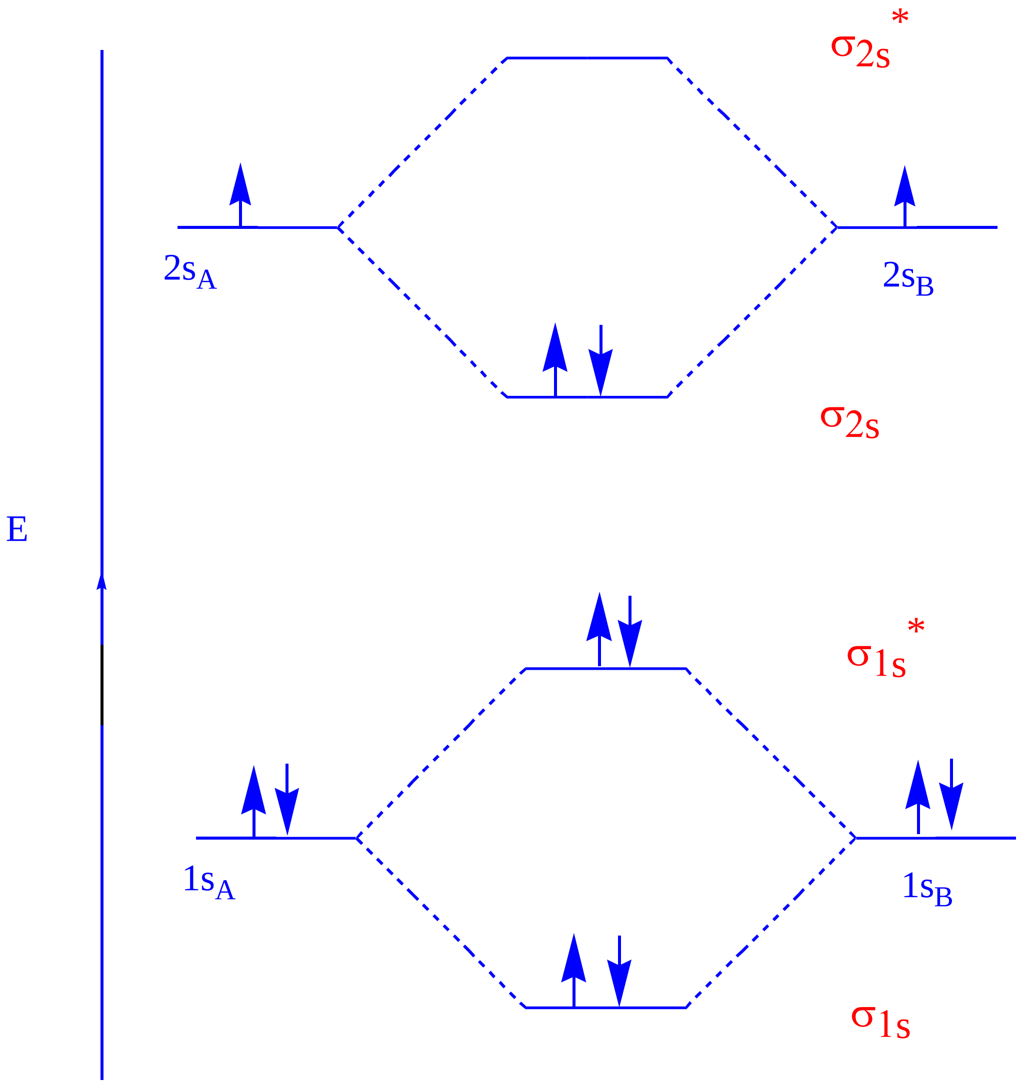
Lecture 15, Oct. 21: Molecular Orbitals

Read: 10.3

Next Online quiz coming soon

Li_2



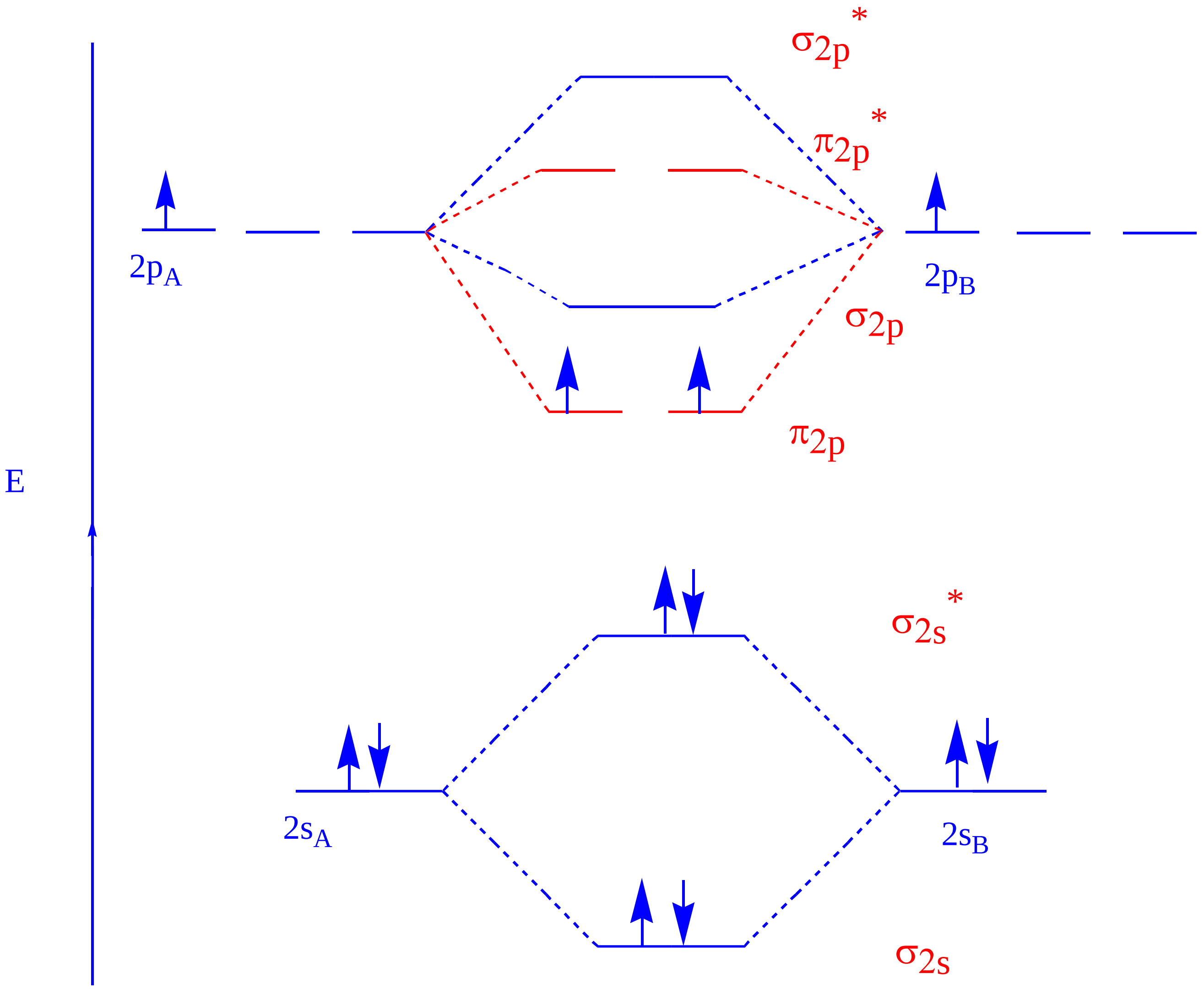
Li_2 stable (in theory) – describes existence as diatomic gas

BO $\frac{4-2}{2} = 1$ or $\frac{2-0}{2} = 1$

Note that we can ignore the σ_{1s} and σ_{1s}* as they cancel out.

Try this for Be and see what happens

B_2

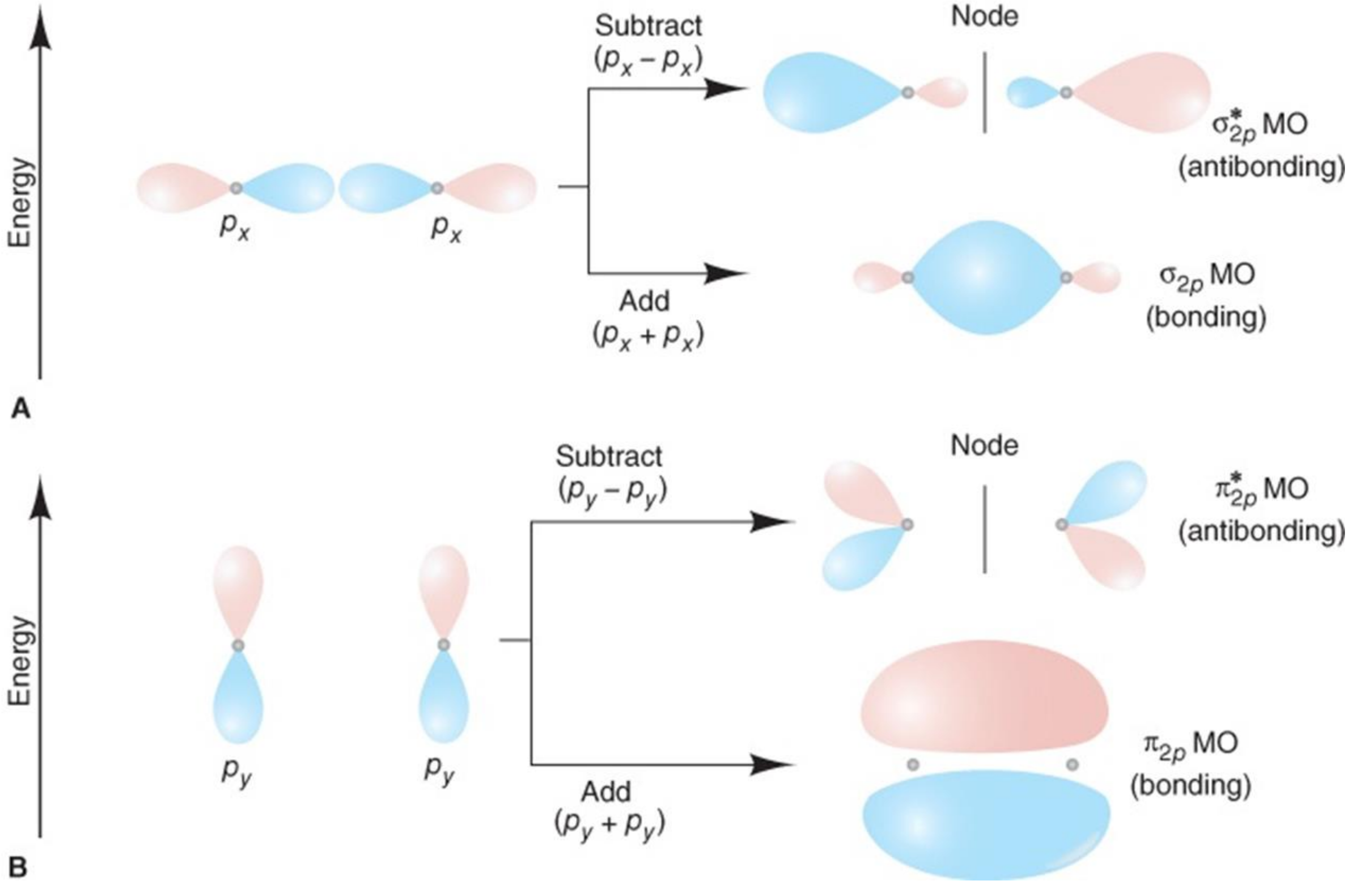


B_2 BO $\frac{4-2}{2} = 1$ or $\frac{2-0}{2} = 1$ stable

unpaired e^- ⇒ paramagnetic = attracted to a magnet

Note that σ_{2s} and σ_{2s}^* cancel out and can be ignored

MOs for p orbitals



Note that the $p_z + p_z$ bonding and $p_z - p_z$ antibonding MOs are not shown on this figure but they also contribute a π_{2p} and π_{2p}* MOs.

C_2

The yellow color seen when burning hydrocarbons is thought to be due to C_2.

Trying to explain the existence of C_2 with previous models fails.

For example using LDS

NVE = 2 x 4 = 8 e^-

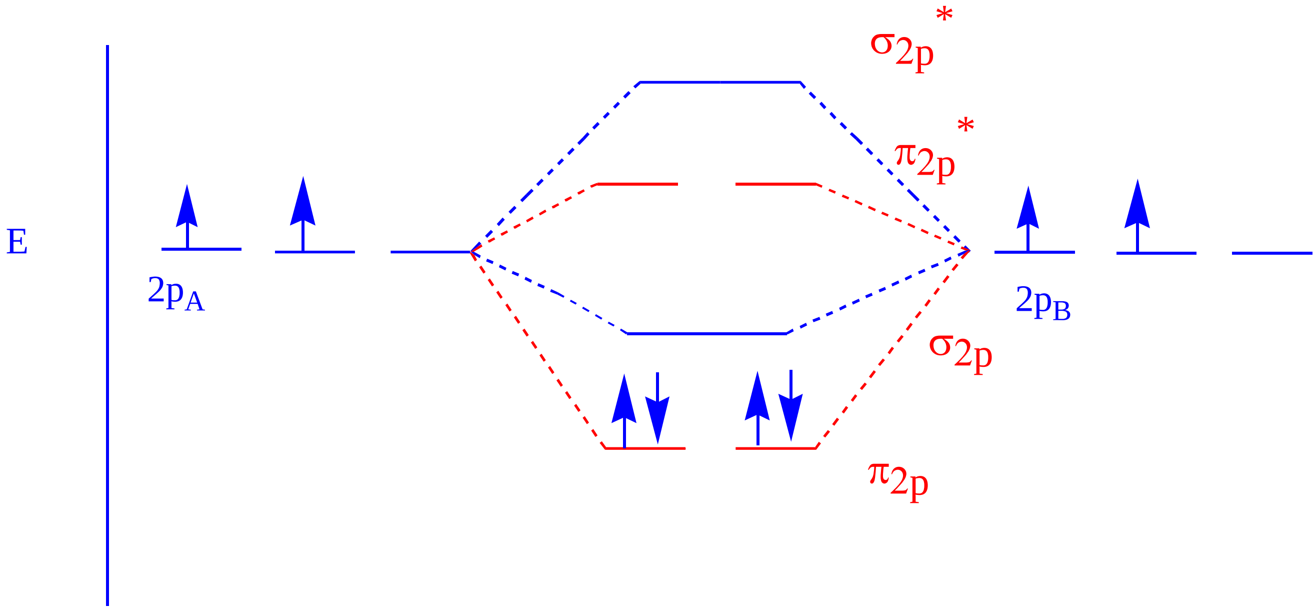
Some possible structures

a) C≣C quadruple bond

b) •C≡C• no octets

c) :C=C: no octets

However the existence can be explained using MO theory



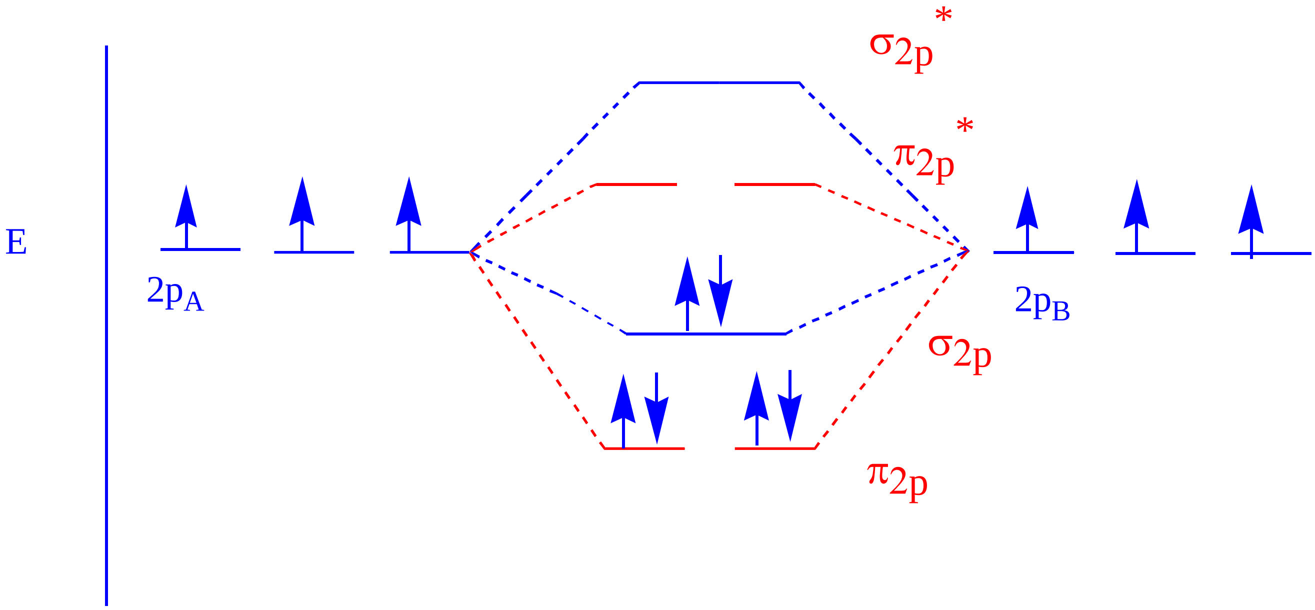
C_2 BO $\frac{4-0}{2} = 2$ and therefore stable

all e^- paired diamagnetic

not attracted to a magnet

(slightly repelled)

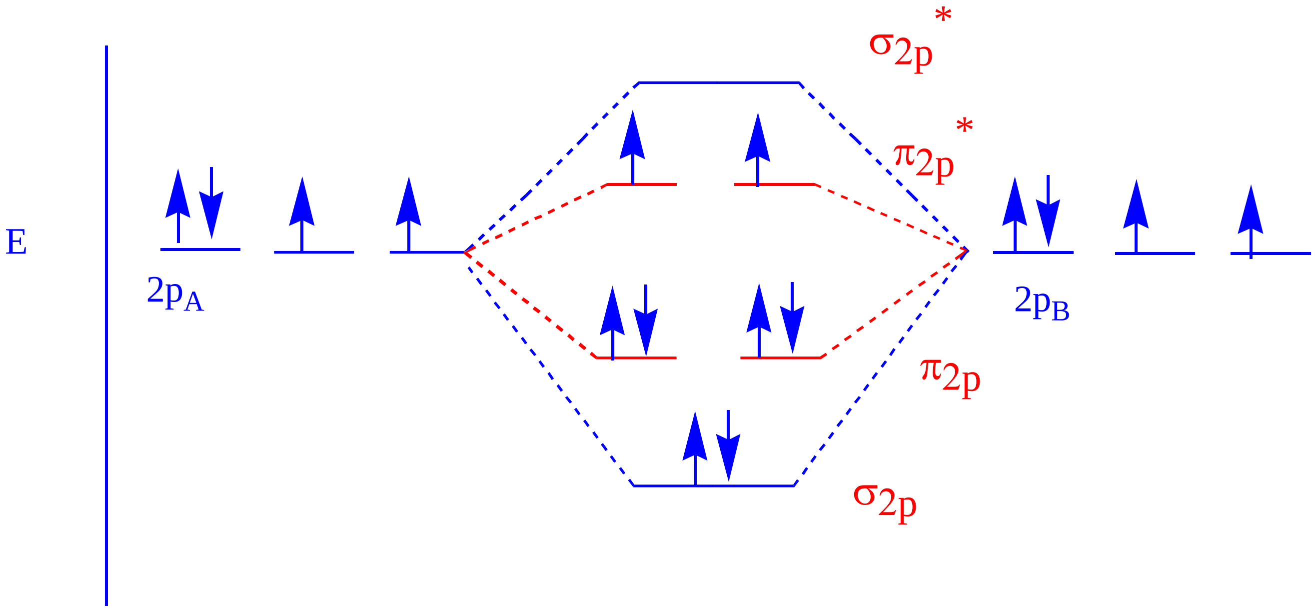
N_2



N_2 BO $\frac{6-0}{2} = 3$stable

all e^- paired diamagnetic

O_2



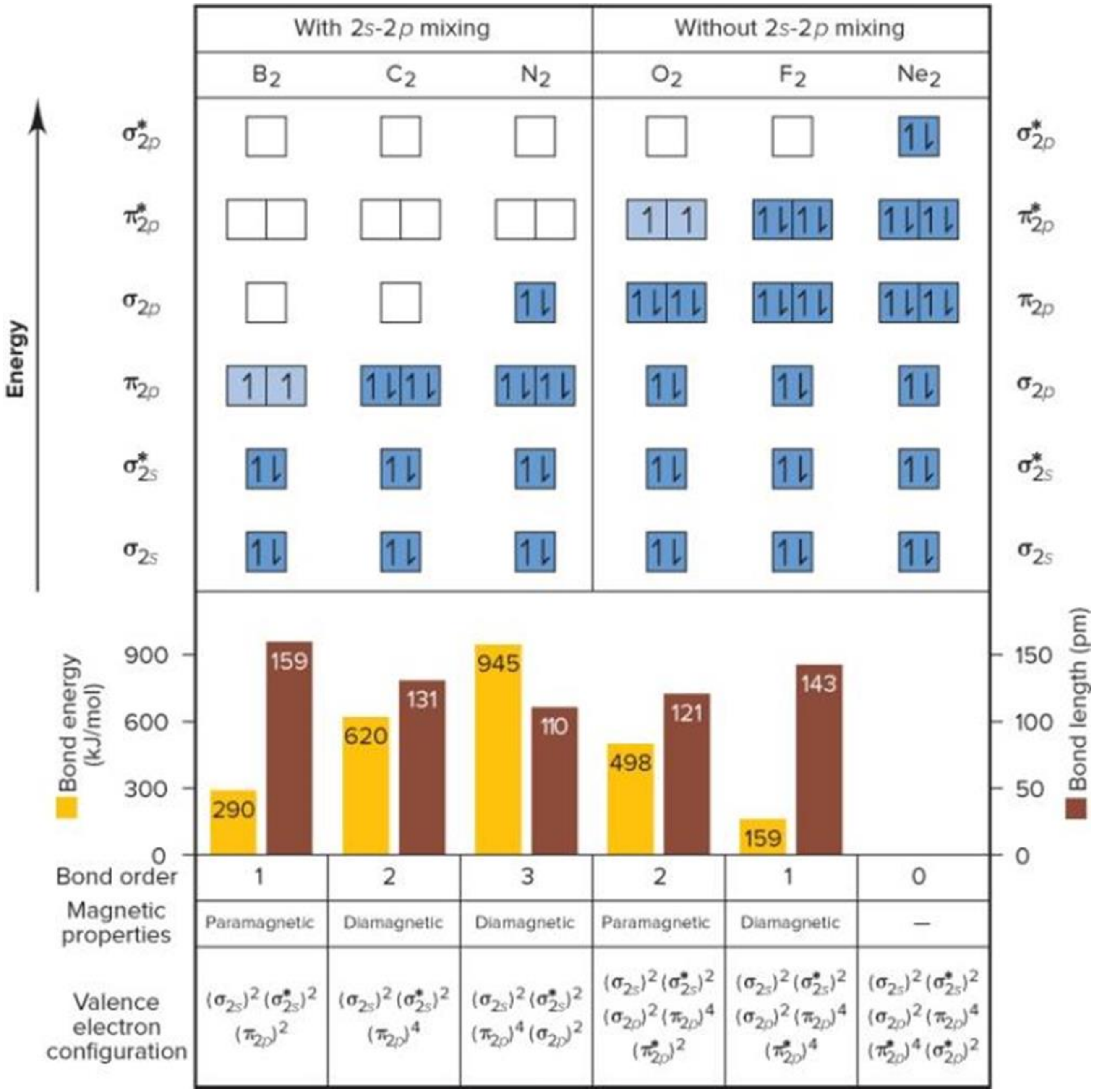
O_2 BO $= \frac{6-2}{2} = 2$ stable unpaired e^- paramagnetic

Note that the MO order is different from that of N_2.

The same pattern in MO is observed for F_2 and Ne_2.

You need to know these two different splitting patterns, where the π_{2p} is either lower in energy than the σ_{2p} (B, C, N) or is higher than the σ_{2p} (O, F, Ne).

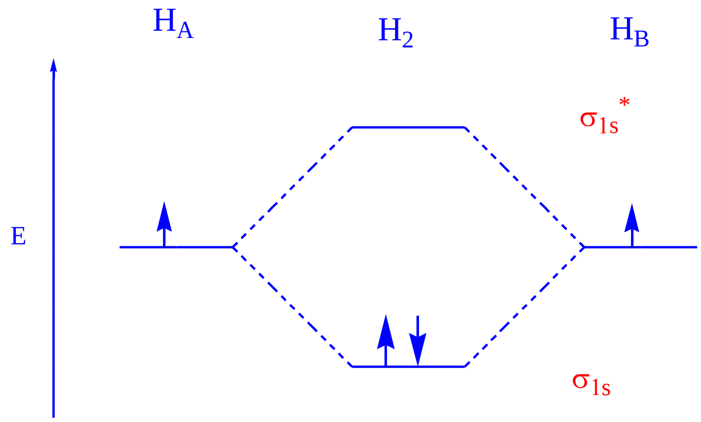
We will not go into the explanation why this happens and will leave it to advanced computational chemistry courses.



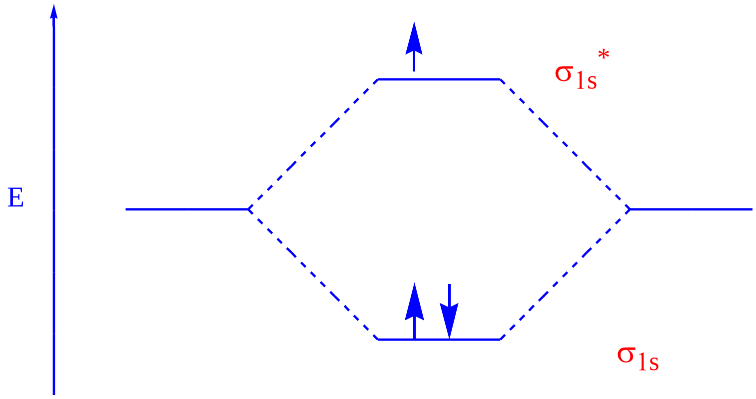
	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Magnetic properties	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—
Valence electron configuration	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi_{2p})^2$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi_{2p})^4$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi_{2p})^4(\sigma_{2p})^2$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\sigma_{2p})^2(\pi_{2p})^4$ $(\pi^*_{2p})^2$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\sigma_{2p})^2(\pi_{2p})^4$ $(\pi^*_{2p})^4$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\sigma_{2p})^2(\pi_{2p})^4$ $(\pi^*_{2p})^4(\sigma^*_{2p})^2$

Diatomic ions

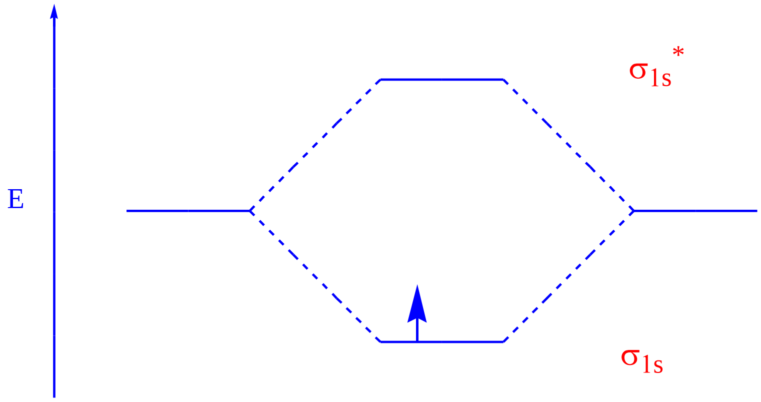
Consider H_2 vs. H_2^+ and H_2^-



H_2^-



H_2^+



H_2 vs. H_2^+ and H_2^-

As shown on the previous diagram, H_2^- has 1 more e^- than H_2

$$BO = \frac{2 - 1}{2} = 0.5 \qquad \text{somewhat stable}$$

And H_2^+ has 1 less e^- than H_2

$$BO = \frac{1 - 0}{2} = 0.5 \qquad \text{somewhat stable}$$

Note that bond orders don't have to be whole numbers.

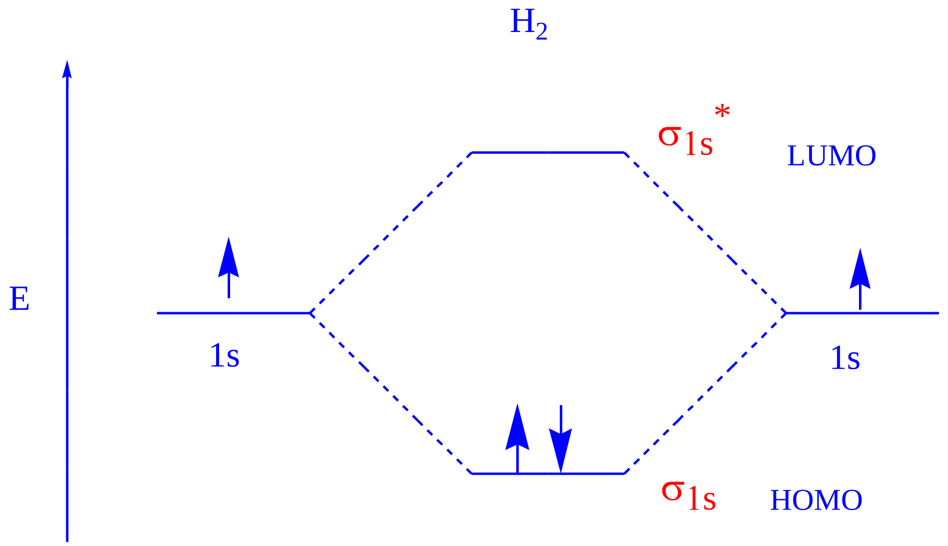
Excited states

For atoms

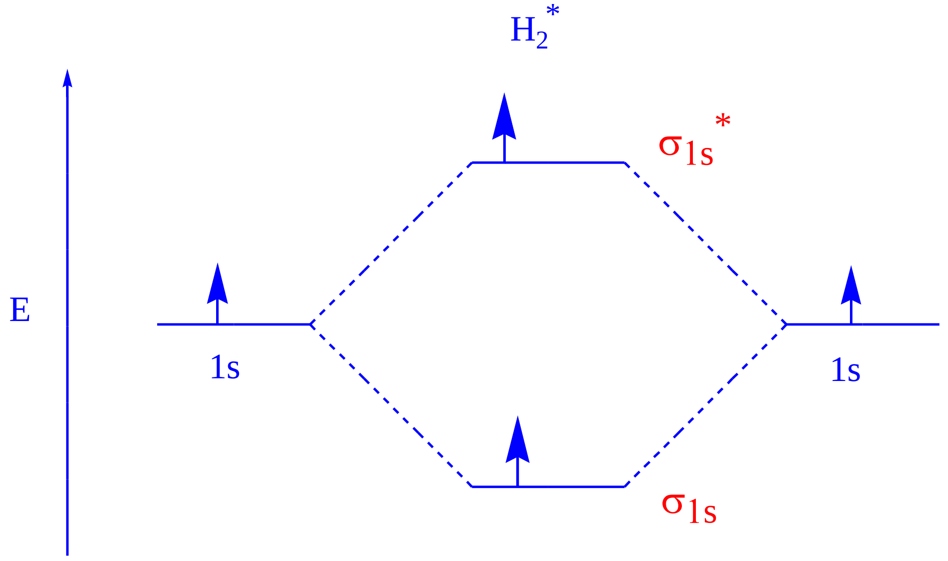
$n = 1$	ground state
$n = 2$	first excited state
$n = 3$	second excited state
…	…
$n = \infty$	ionization

For molecules, normally all of the e^- fill lower MOs which is referred to as the ground state

An e^- can be promoted to a higher energy MO creating an excited state of the molecule.



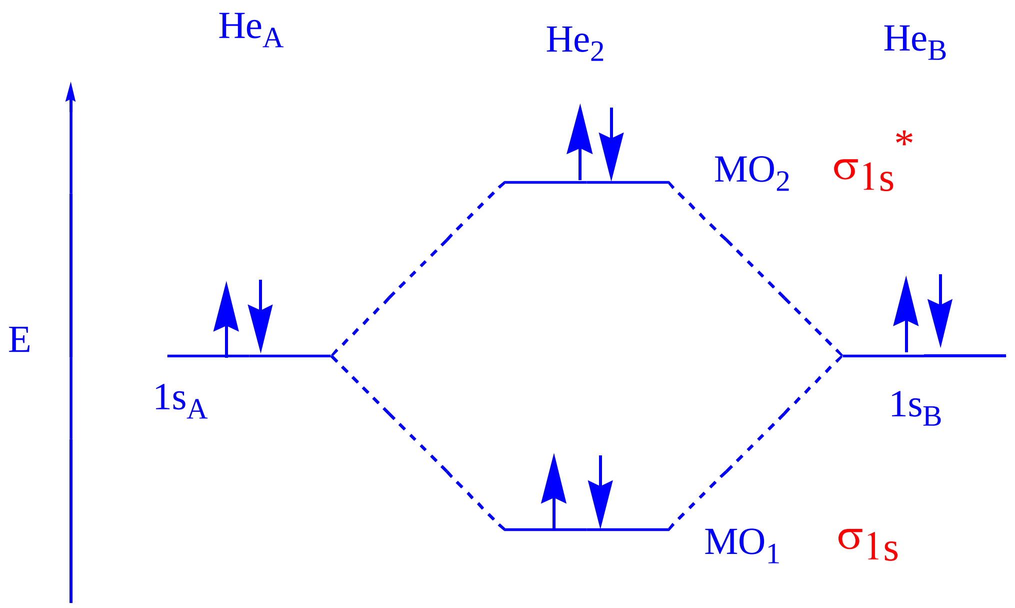
The Highest Occupied MO is usually referred to as **HOMO** while the Lowest Unoccupied MO is called **LUMO**.



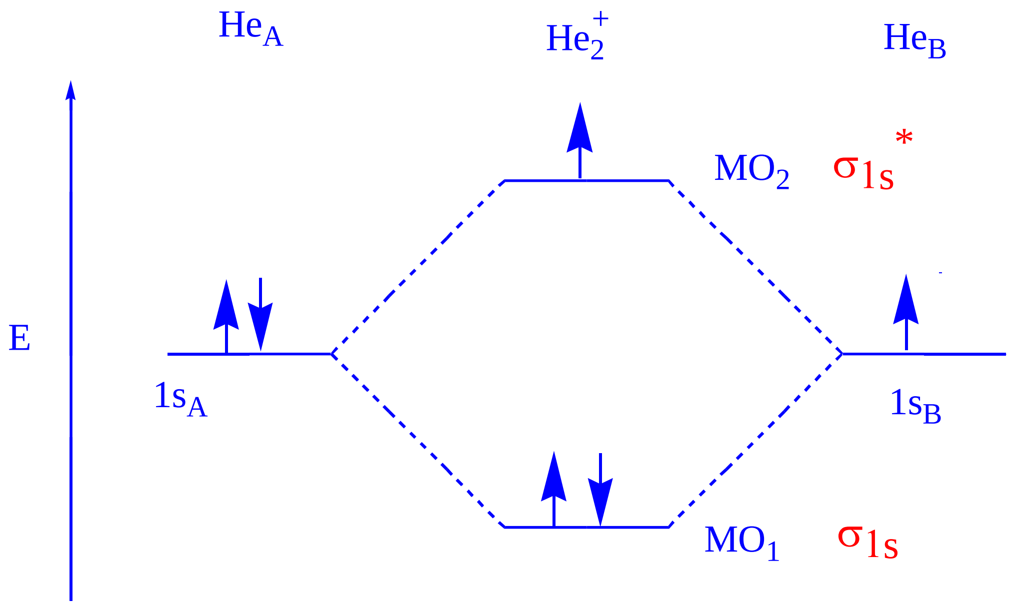
Usually the excitation between the HOMO and LUMO has the highest probability of occurring.

Don’t calculate bond order for excited states as they won’t make much sense as when they did for non-excited species.

Back to Helium: He_2 vs He_2^+



$$\text{Bond order} = \frac{\#\,\text{bonding}\ e^- - \#\,\text{antibonding}\ e^-}{2} = \frac{2-2}{2} = 0 \ \text{unstable}$$



$$\text{Bond order} = \frac{\#\,\text{bonding}\ e^- - \#\,\text{antibonding}\ e^-}{2} = \frac{2-1}{2} = 0.5 \ \text{stable}$$

MO for heterogeneous diatomic molecules

In homogeneous diatomic molecules, the AO energy levels for both atoms are equal.

Heterogeneous diatomic molecules

⇓

Starting AO levels are no longer equal

⇓

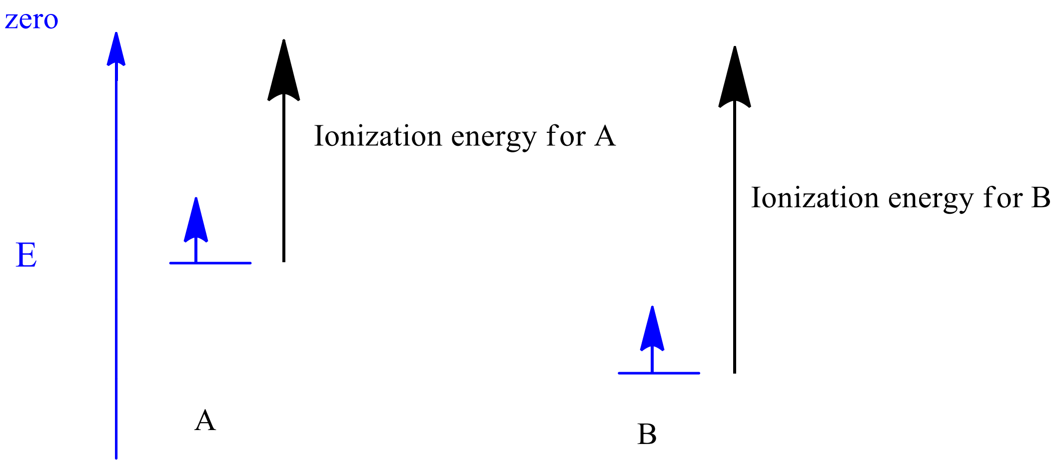
Energy levels in diagram "distorted" (unsymmetrical)

Higher ionization energy leads to lower energy

Arbitrary decision

Assume MO energy pattern follows that of the atom with greater ionization energy.

Explanation of higher IE leading to lower energy



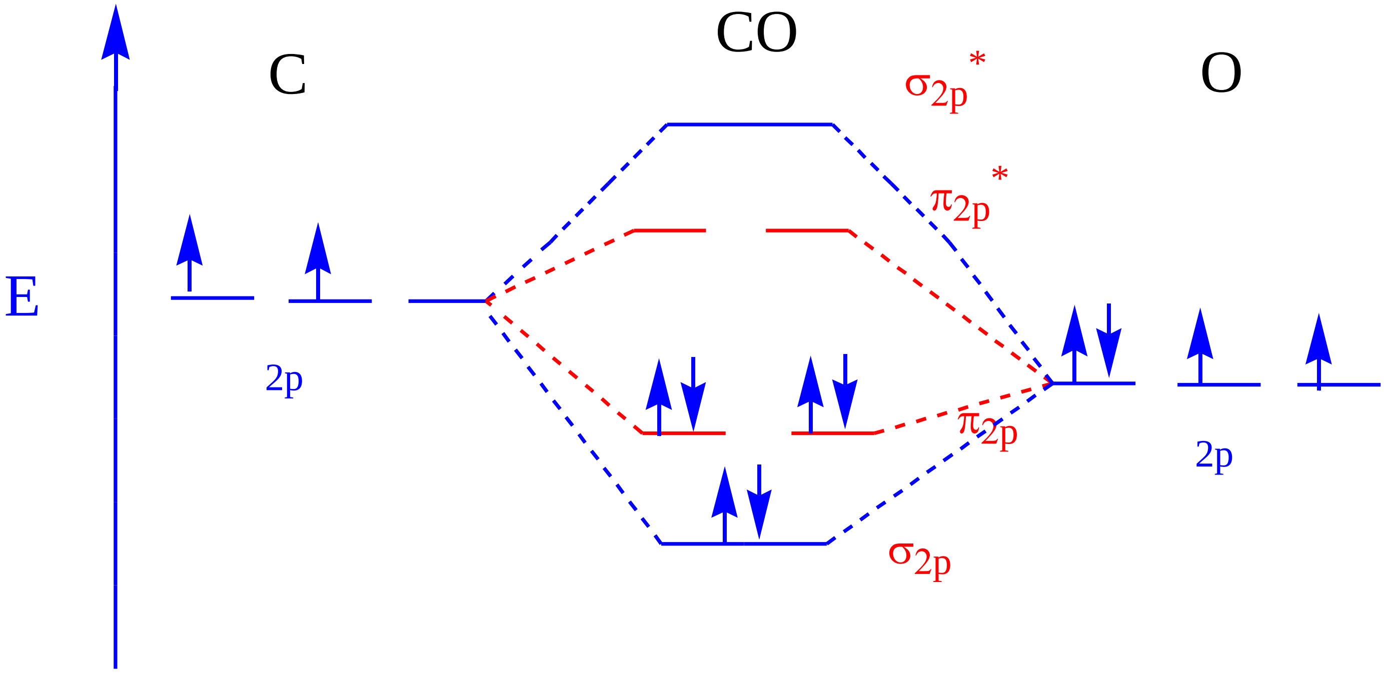
Ionization energy is the complete removal of the electron.

On the graph it is the transition from the given energy level all the way to the top where zero energy is. The greater the distance on the graph, the larger the ionization energy.

Hence in this diagram, atom B, with a higher ionization energy, will have a lower starting energy level.

Carbon monoxide CO C [He]$2s^2$**$2p^2$**

O [He]$2s^2$**$2p^4$**



IE (O) > IE (C)

(remember periodic trend L→R in IE from unit 1?)

Assume MO splitting pattern follows that of O.

CO BO $\frac{6-0}{2} = 3$ stable

all e^- paired diamagnetic