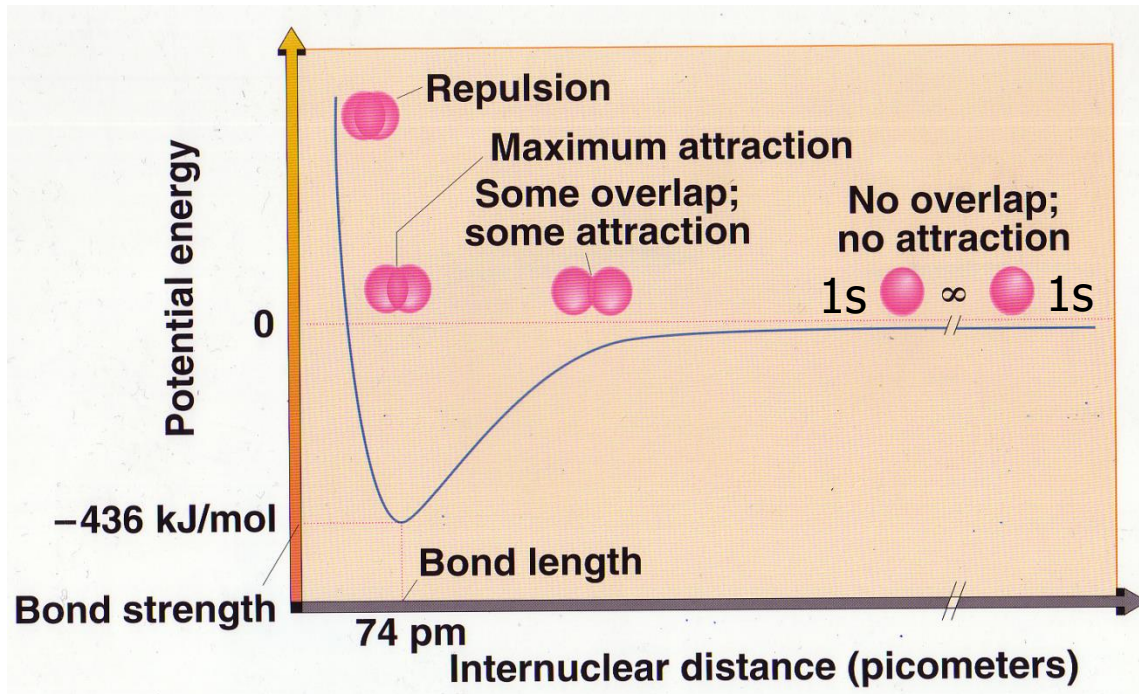


Molecules - Bonding

Atoms are bonded together by **electrons**, but what *is* a **bond**?

A bond forms when two **atomic orbitals overlap** to make a molecule more **stable** than when there was no overlap



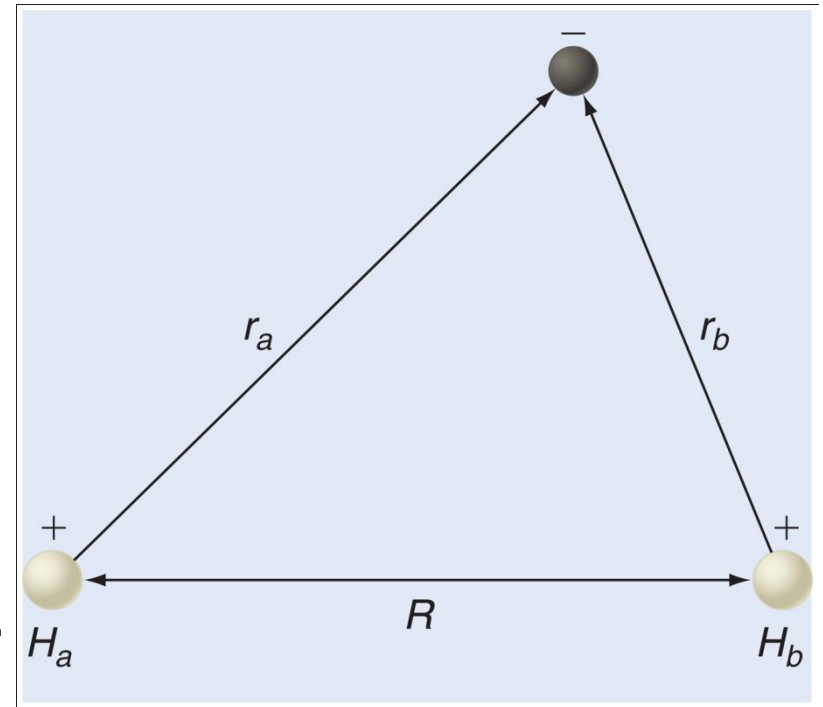
The Quantum Mechanics of H_2^+

Start with the **simplest** molecule, H_2^+ .

What **forces** do we consider?

This is a **three-body** problem,
so there is no **exact** solution.

The nuclei are much more massive
than the electrons (1 u for p; 0.0005u for e).



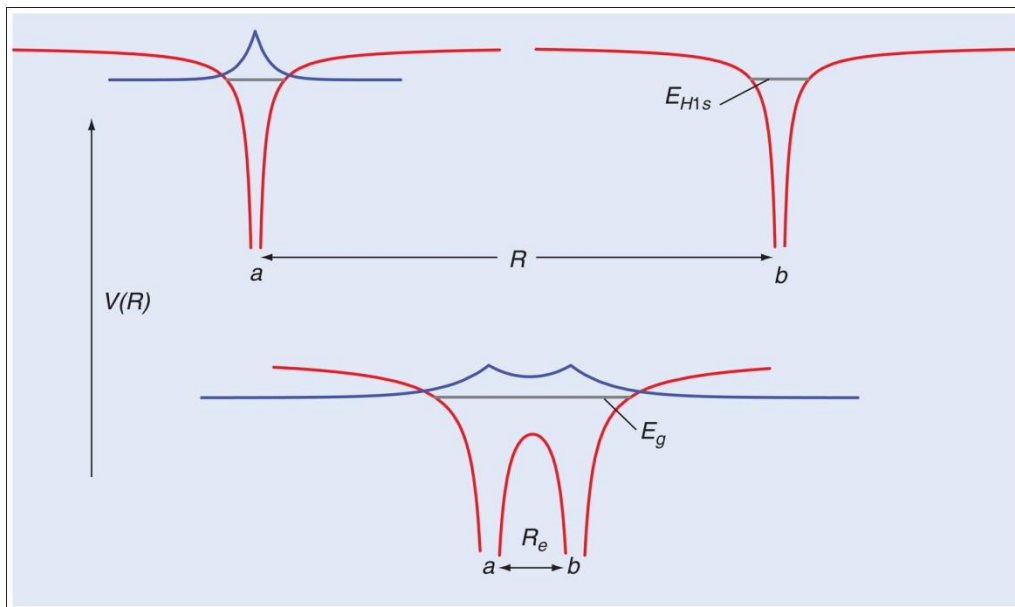
The **Born-Oppenheimer approximation**, assumes that the motion of the nuclei is negligible compared to the motion of the electrons and treat the nuclei as though they were immobile.

By assuming R is **fixed** the problem can be **solved exactly**.

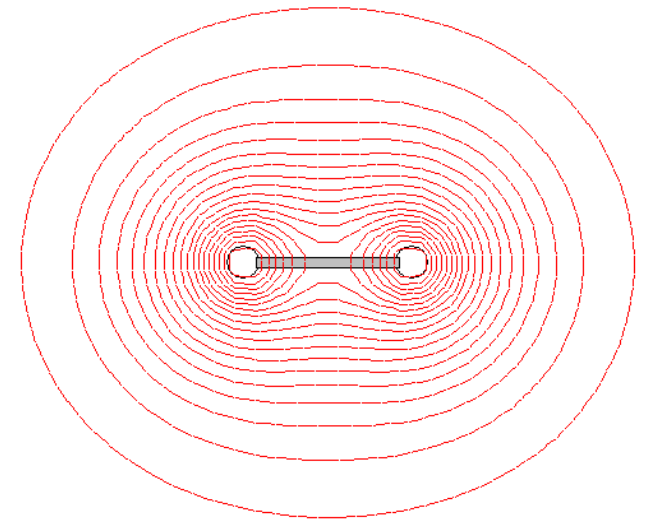
The Quantum Mechanics of H_2^+

For a fixed internuclear distance, \mathbf{R} , the wavefunction of the electron in H_2^+ and its energy can be calculated in manner similar to the energy and orbitals for the H atom.

Electron energy = kinetic energy + electron-nuclear attraction



Side view



Top view

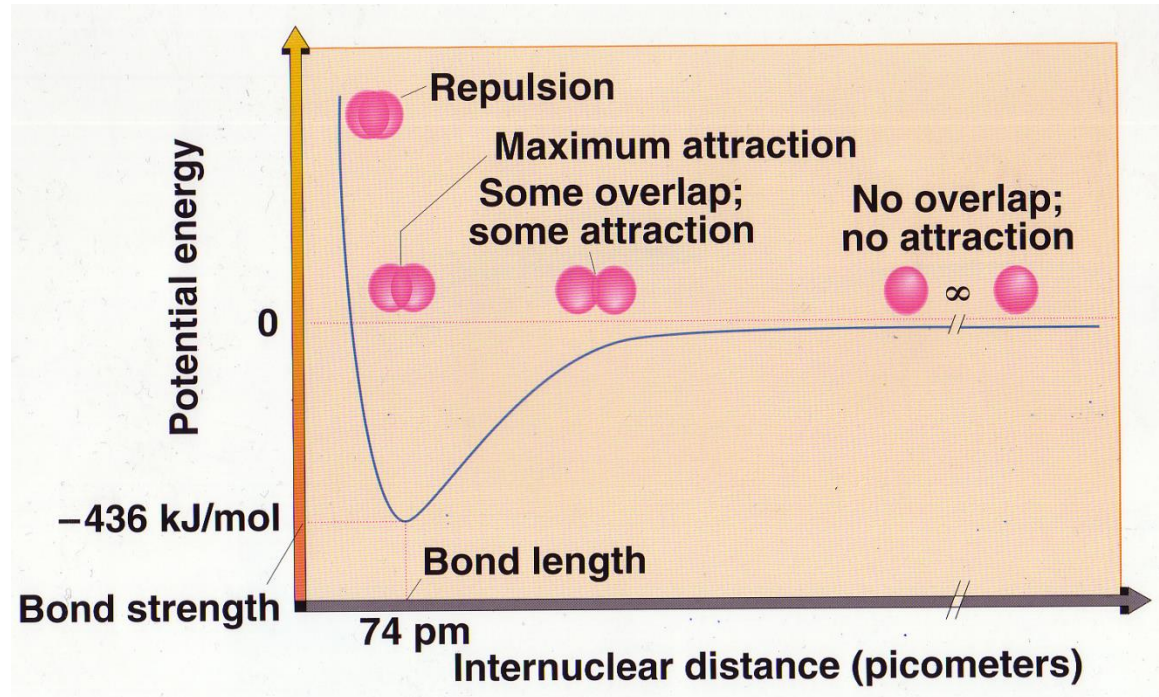
The Quantum Mechanics of H_2^+

Potential energy = **Electron energy** + **Internuclear repulsion energy** at different values of **R**.

The energy of the **ground state** orbital depends on R.

The electron doesn't belong to either atom.

The orbital spans the molecule
" **molecular orbital!** "



Molecules, just like atoms, can have **many orbitals**, where the **lower** energy orbitals are **occupied** and the **higher** energy orbitals are **empty**.

They have **energy level diagrams** similar atoms.

Simple Molecular Orbitals

The simplest atomic orbitals (AO's) are the $1s$ orbitals, which are the **ground state** of hydrogen and helium

H forms bonds: H—H

He does not form bonds

How do we explain this?

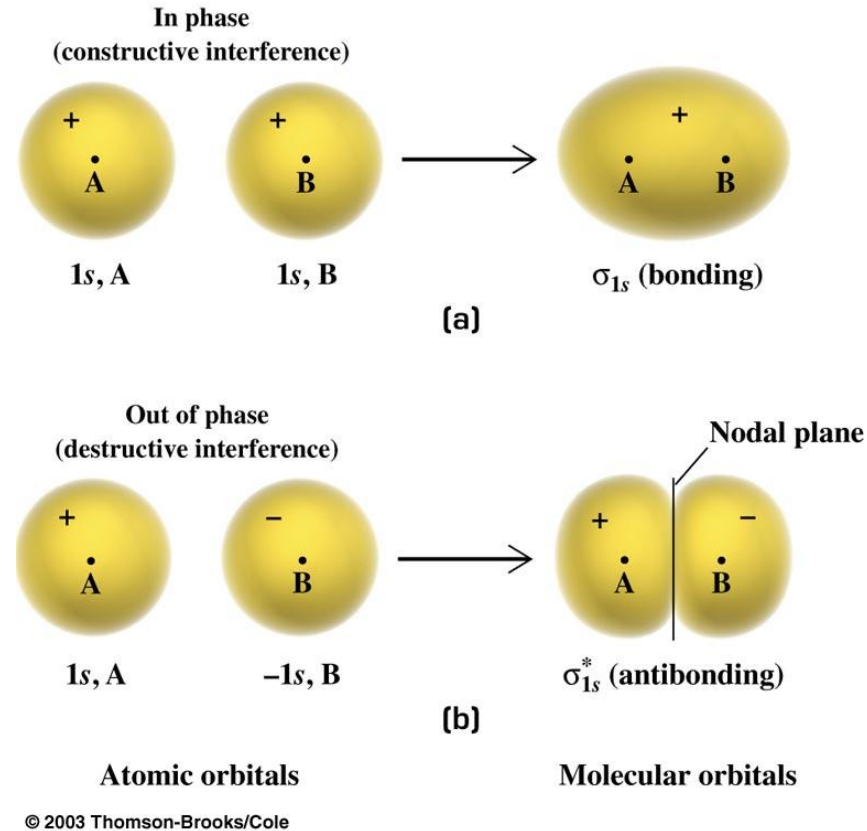
The **exact** wavefunction of *one-electron molecules* such as H_2^+ and He_2^{3+} , are known.

These **exact** wavefunctions can be approximated using **linear combinations of atomic orbitals**, **LCAO**

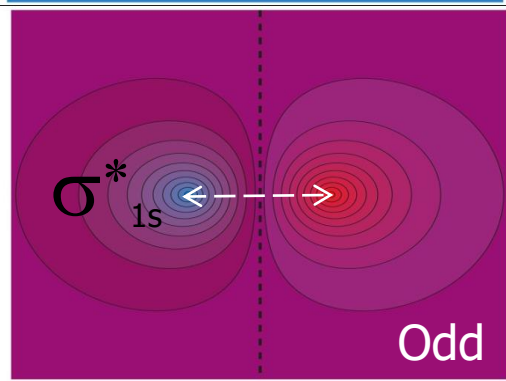
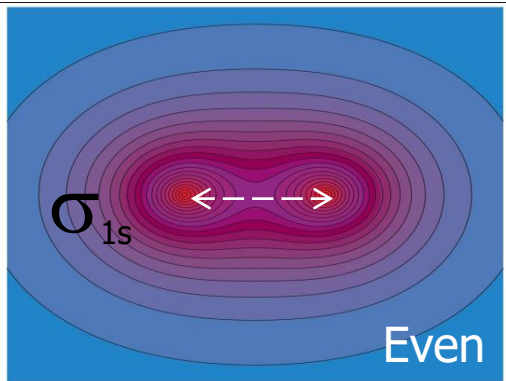
In LCAO, each AO is combined **both** in-phase and out-of-phase, corresponding to **constructive** and **destructive** interference.

Constructive interference - **Bonding orbital**

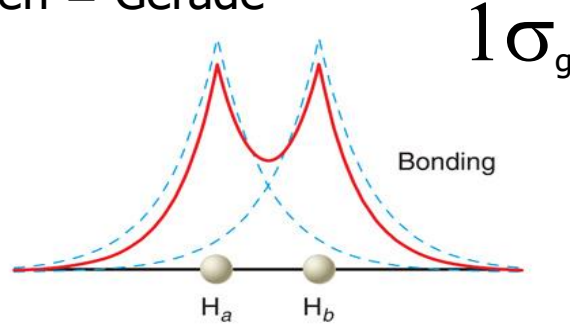
Destructive interference - **Anti bonding orbital** Has a node between atoms



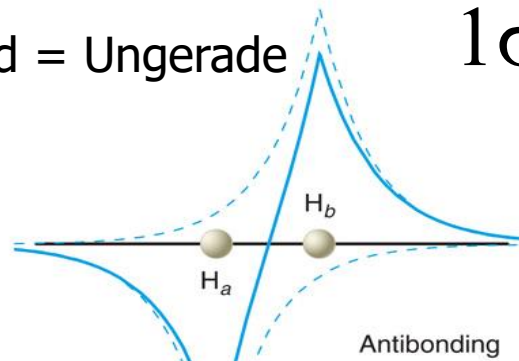
Bonding and Antibonding Orbitals



Even = Gerade

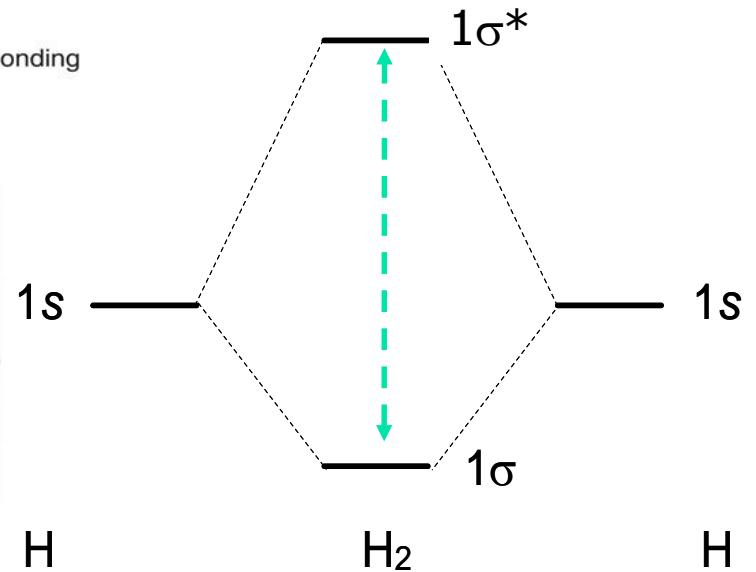
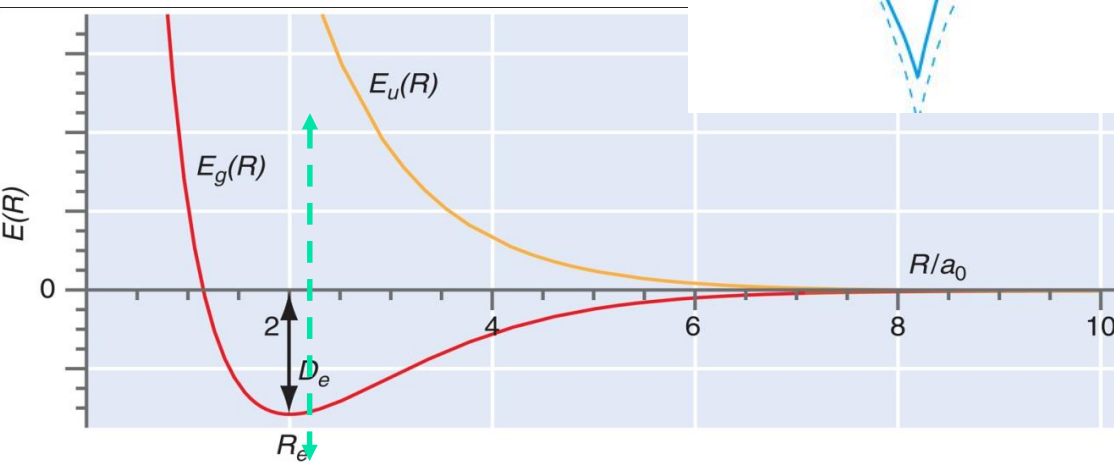


Odd = Ungerade



Energy Gap:
depends on degree of **overlap** possible at the **equilibrium** geometry (R_e)

Energy Level Diagram



Energy Levels of LCAO-molecular orbitals

The MO that forms when two $1s$ orbitals **constructive** interference have **lower** energy than those that **destructively** interfere.

MO's orbitals **energy increases** with number of **nodes**

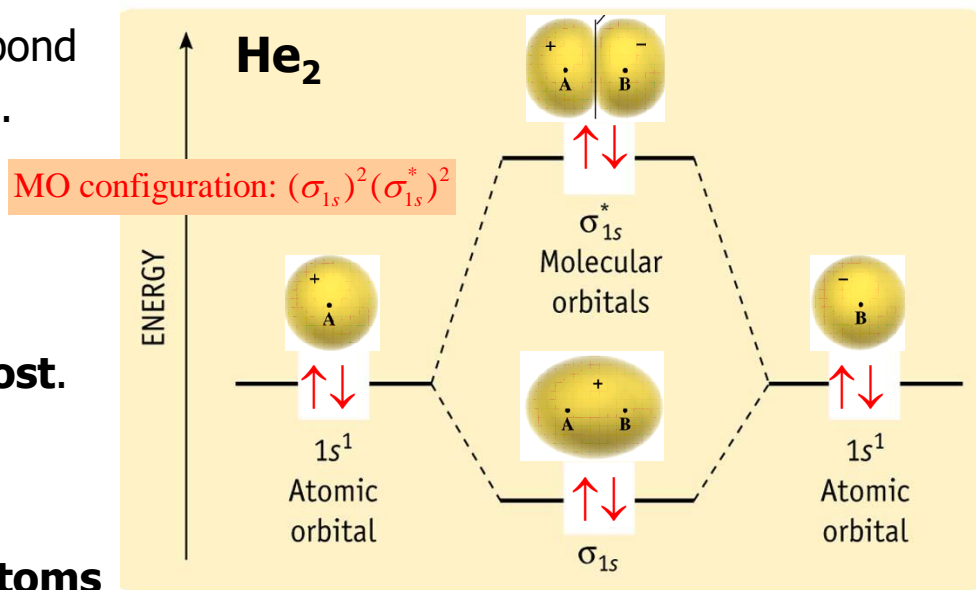
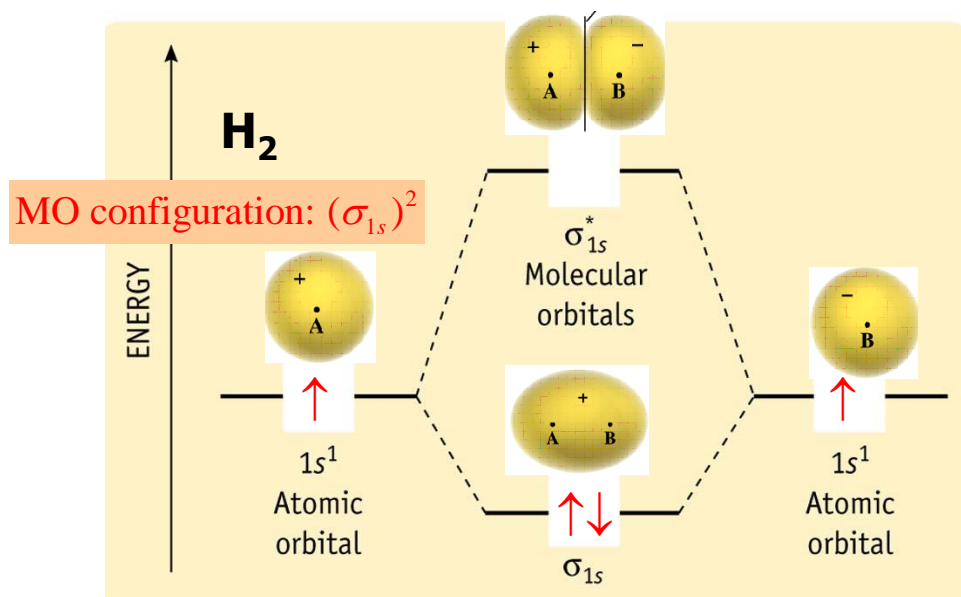
MO energy levels are depicted using a **correlation diagram (Molecular Orbital Diagram)** which relates the energies of the MO's *relative to their constituent AO's*

Adding **both** electrons to H_2 MO diagram a bond is formed ($BO = 1$) by occupying the σ_{1s} MO.

Remember as with atoms the **Pauli Exclusion Principle** and **Hunds rule** apply.

Adding another pair e's for He_2 the bond is **lost**.

By filling **both** the **bonding** and the **antibonding** MO leaves the "molecule" in a **higher energy state** ($BO = 0$), than **free atoms**



LCAO for the 2nd Period Elements

The “**dilithium**” molecule can **exist** in very low-pressure vapours, whereas the normal state of lithium is the **metallic solid**

Lewis theory predict Li—Li, with only **two bonding** electrons in its valence

The **net overlap** of the **1s** levels **cancel** out

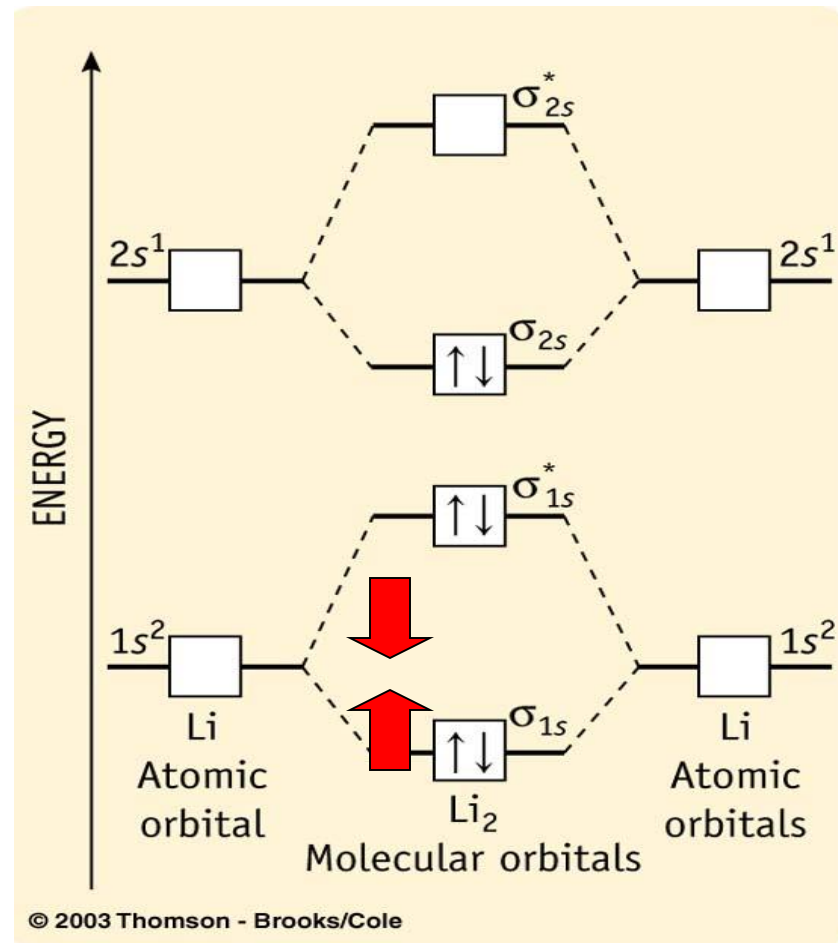
The **net overlap** of the **2s** wave functions leads to a **single bond**, the BO = 1

The Li—Li distance in Li₂ is **159 pm**; at this distance the degree of **overlap** of the 1s orbitals of Li is **negligibly small**

The assumption of “**core**” orbitals is thus valid

The next molecule to consider is **Be₂**, and like He₂ it should **not exist**.

MO configuration: $(\sigma_{2s})^2$



Ignore “core” orbitals in LCAO theory

LCAO from atomic p orbitals: σ -MO's

For B_2 , with 6 valence electrons, we need additional orbitals, made from next lowest atomic orbitals $2p$

Here we must distinguish the **orientation** of the orbitals with respect to each other

Bond axis: z-axis for simple molecules, consider the p_z orbital

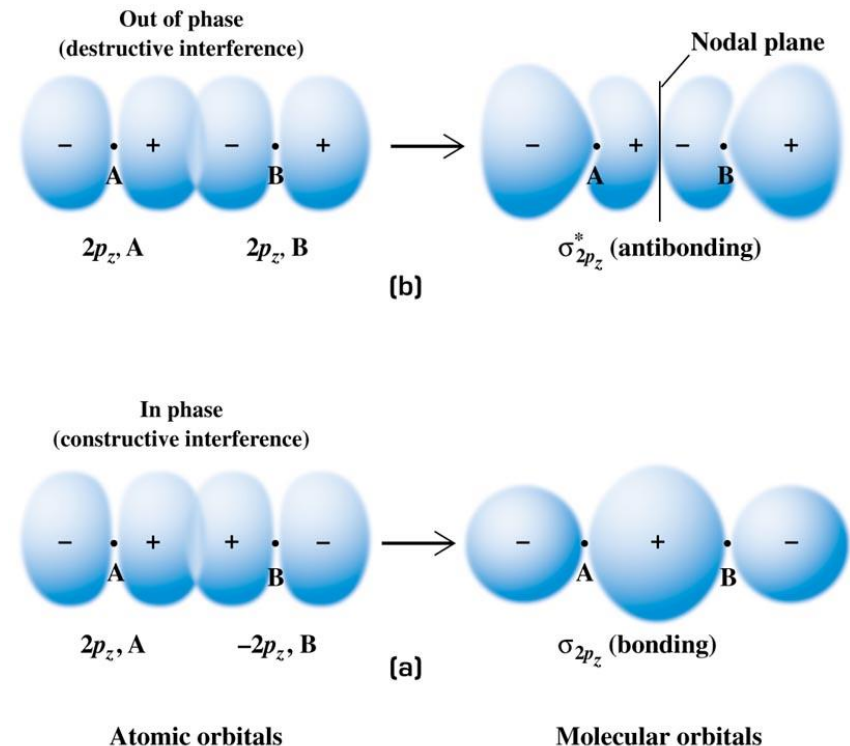
p orbitals **have a node at the nucleus**

In-phase combination between two p_z orbitals will have **two nodes**, at the nuclei but not between them.

Out-of-phase combination will have an **additional node**, between the nuclei

Since **antibonding** orbital has **more nodes** it is higher in energy

Both MO's are defined as $\sigma =$ **cylindrical**



LCAO from atomic p orbitals: π -MO's

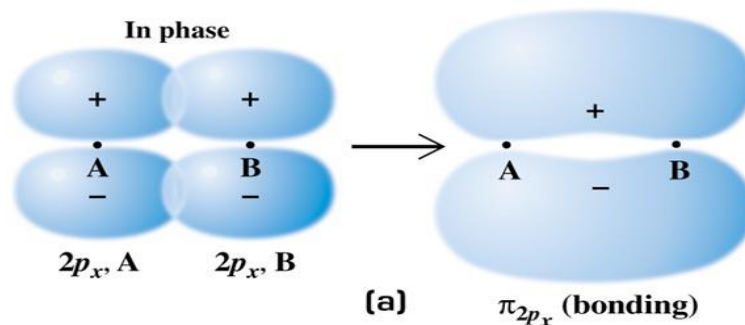
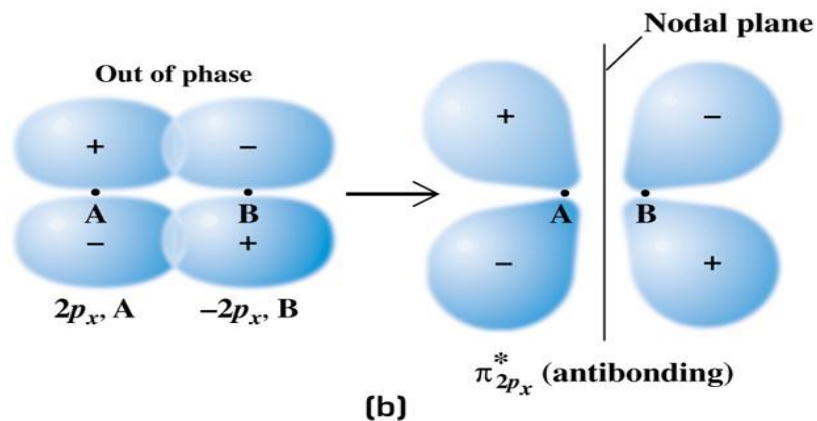
Two orbitals remain at **right angles** to the bond axis on each atom, the p_x and the p_y

Side-on overlap which leads to a new kind of bond, the π -**bond**

The diagram shows the case for p_x

It is called a π -**orbital** because from end-on it resembles an atomic p orbital

π orbitals **contain a nodal plane throughout the molecule**



© 2003 Thomson-Brooks/Cole

The **out-of-phase MO** also has an additional node between the atoms, making it an **antibonding MO**

The p_z orbital were **higher** in energy than p_x and p_y . Therefore, σ_{2p_z} orbitals are **higher** in energy (less stable) than the two $\pi_{2p_{xy}}$ orbitals which are equal in energy

Molecular Orbitals

Atomic orbitals will combine when:

1) Geometry allows for it

They must have compatible shapes

Consider p_x and p_y or $1s$ and $2s$

2) Are close in energy.

The degree of mixing depends on energy difference

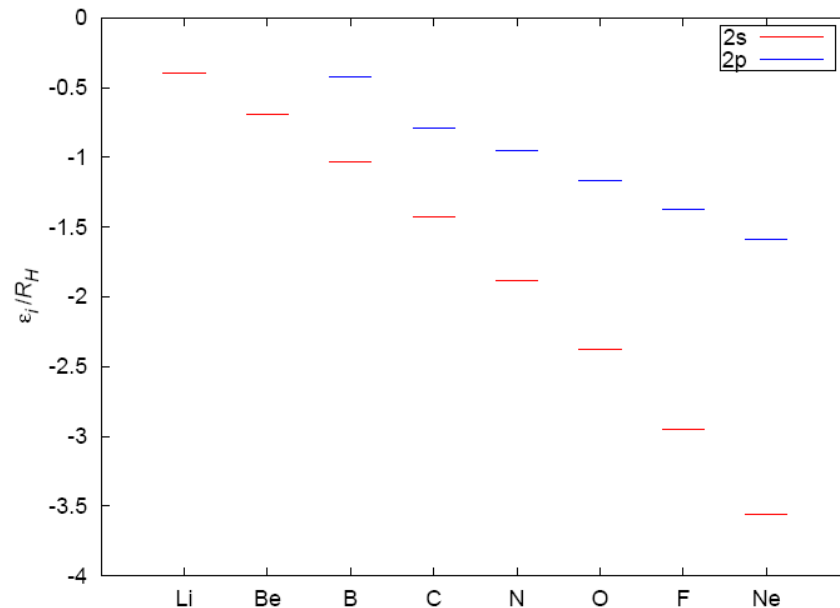
Consider $2s$ and $2p$ orbitals of H and F

3) If they have the right phase

Same phase – constructive interference

Opposite phase – destructive interference

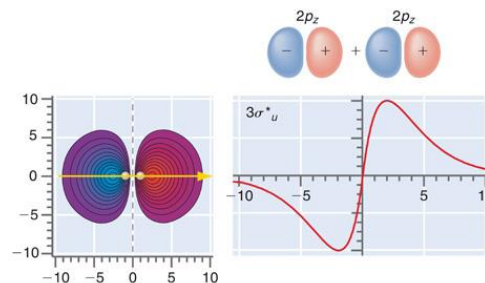
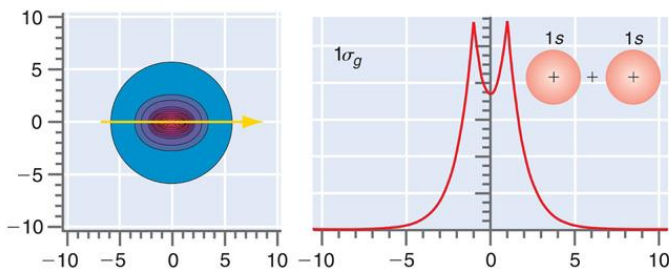
Consider $2s$ and $-2p_z$



$$\text{Bond Order} = [(\# \text{ bonding e's}) - (\# \text{ anti-bonding e's})]/2$$

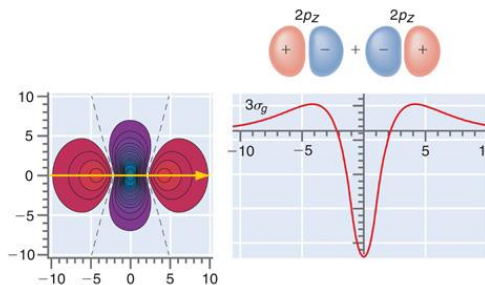
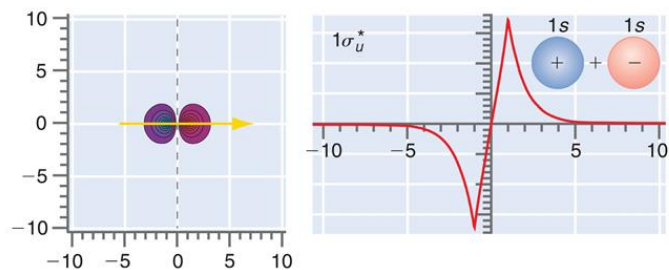
MO's for the Diatomics

$1\sigma_{1s}$



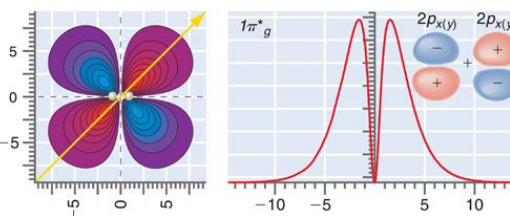
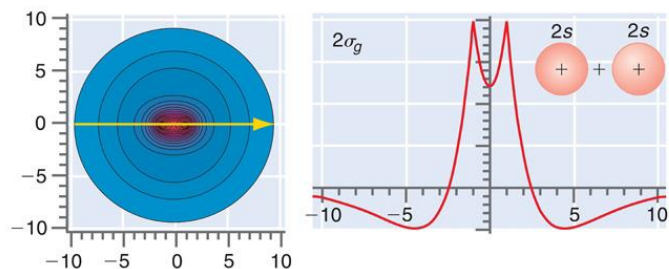
$3\sigma^*_{2p} = 4\sigma^*$

$1\sigma^*_{1s}$



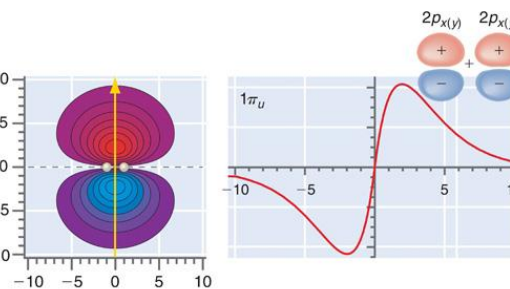
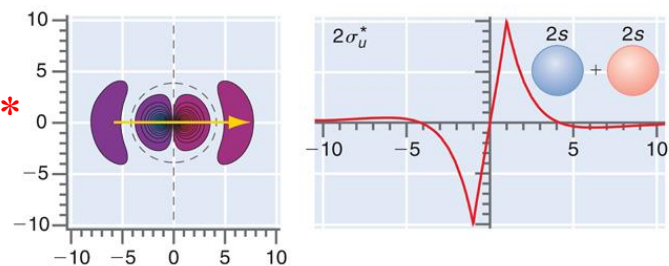
$3\sigma_{2p} = 3\sigma$

$2\sigma_{2s} = 1\sigma$



$1\pi^*_{2p} = 2\pi^*$

$2\sigma^*_{2s} = 2\sigma^*$



$1\pi_{2p} = 1\pi$

Correlation Diagrams for Diatomics of 2nd period

The MO energy reflects those of the AO's when atoms are aligned along the **bond axis**. **Why?**

Hence P_z is **higher** than P_x and P_y

Similarly σ_{2p} **is higher** than π_{2p}

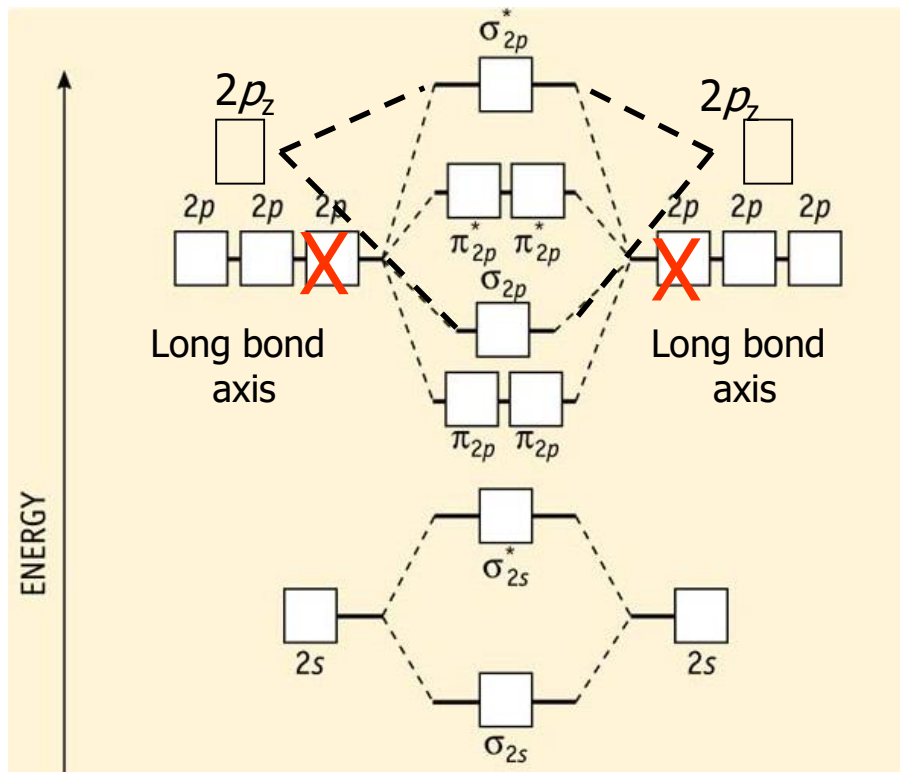
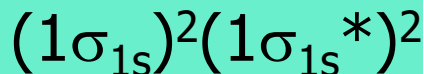
Bonding behavior of diatomic molecules can be **predicted** by sequentially filling the energy levels of the M.O.

Recall that the **Pauli Exclusion** Principle and **Hunds** rule apply.

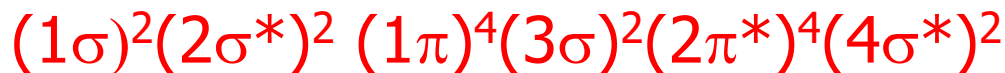
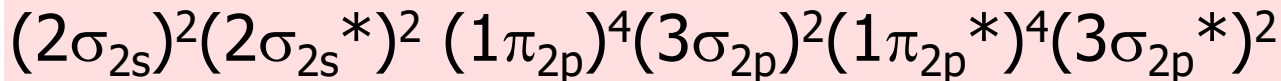
The **electron configurations** of the diatomic molecules are analogous to the atom.

Electrons fill in the order of MO energies from **lowest to highest**

Core



Valence



The complete energy level diagram

All the orbitals in the ground-state 2nd period elements have been considered

Bonding between these elements can be predicted by adding electrons to this orbital correlation energy level diagram

Li_2 - bond order 1

Be_2 - fills the σ_{2s}^* (a.k.a $2\sigma^*$), BO = 0

B_2 - partially fills π_{2p} (a.k.a 1π), BO = 1
- 2 e's parallel i.e. paramagnetic

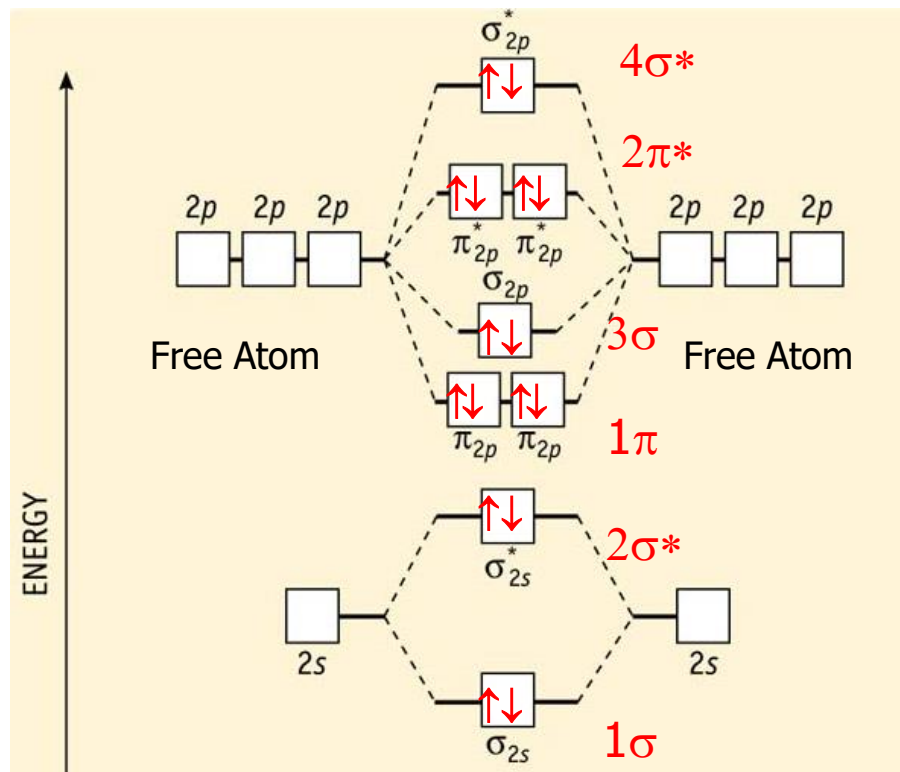
C_2 - fills π_{2p} , - BO = 2
- diamagnetic

N_2 - fills σ_{2p} (a.k.a 3σ) - BO = 3
- diamagnetic

O_2 - partially fills π_{2p}^* (a.k.a $2\pi^*$), BO = 2
- paramagnetic

F_2 - fills π_{2p}^* levels - BO = 1

Ne_2 - fills σ_{2p}^* (a.k.a $4\sigma^*$), BO = 0, does not exist



Molecular Orbitals of Homonuclear Diatomics

Li, Be, B, C and N have smaller energy gaps between the $2s$ and $2p$ orbitals, hence some mixing between them occurs when forming the σ and σ^* orbitals, primarily $2\sigma^*$ and 3σ :

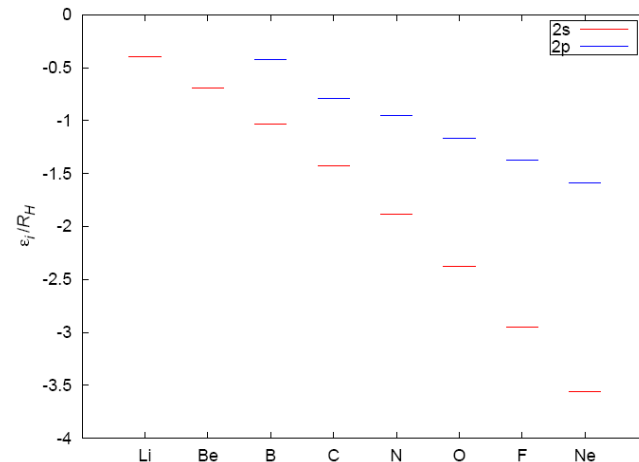
" p character" in $2\sigma^*$ lowers its energy.



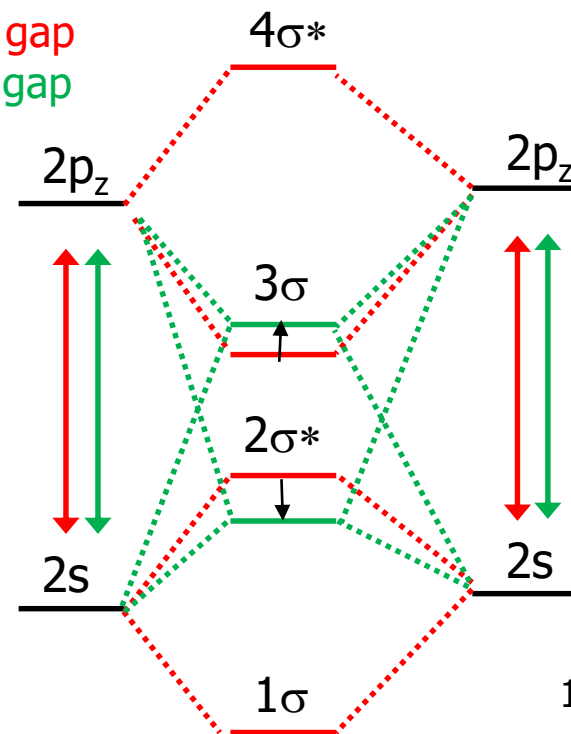
" s character" in 3σ raises its energy



This effect can cause the 3σ orbital to be higher in energy than the 1π orbital. This is the case in Li_2 , Be_2 , B_2 , C_2 and N_2 .



Large gap
Small gap

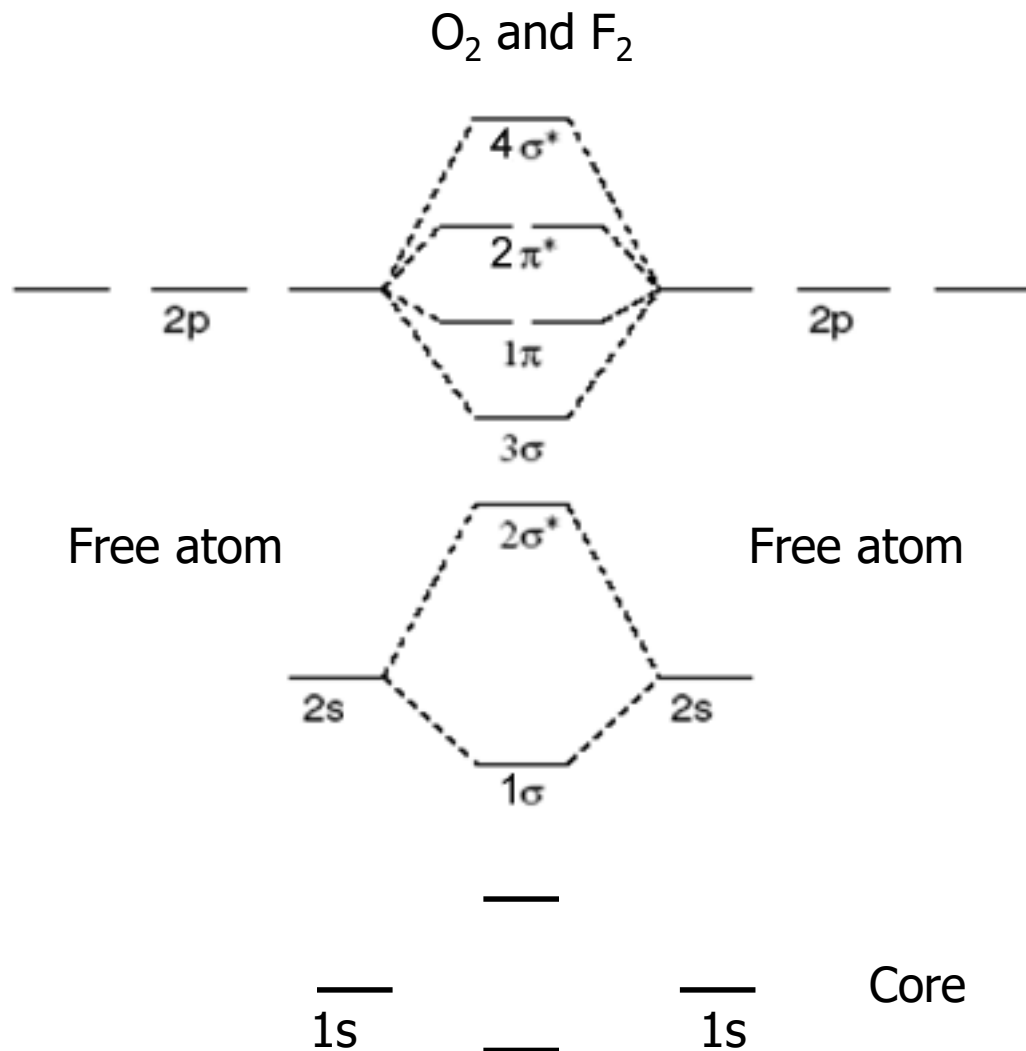


Molecular Orbital Order in Homonuclear Diatomics

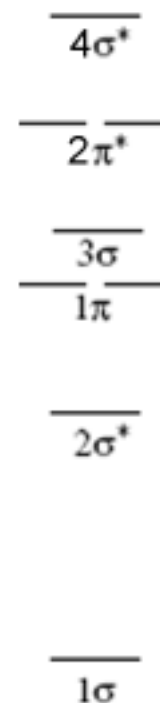
In general the labels valence MOs are numbered in the order of appearance starting at 1.

The Core orbitals are ignored

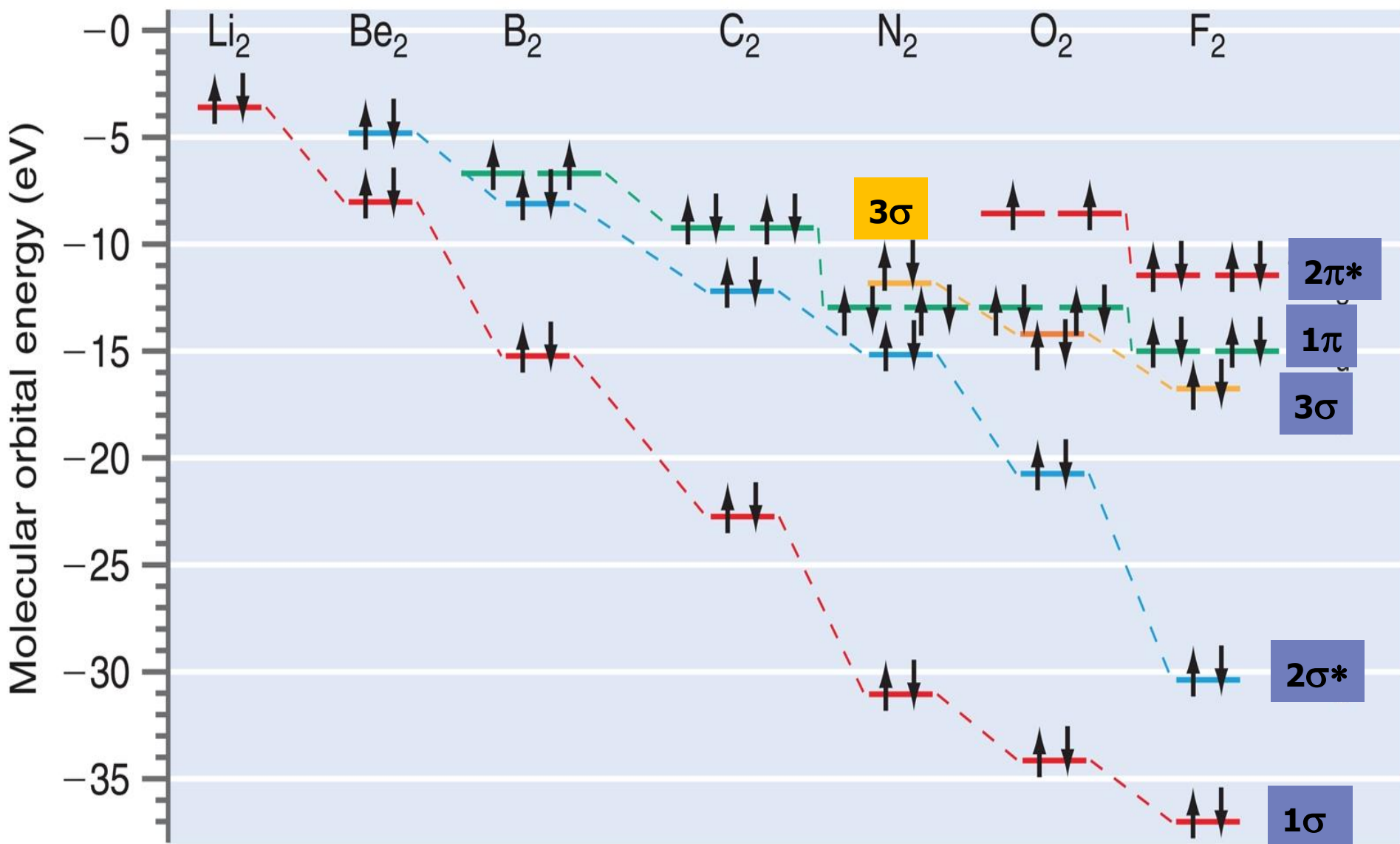
The parent AOs are not indicated



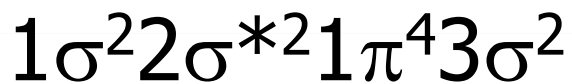
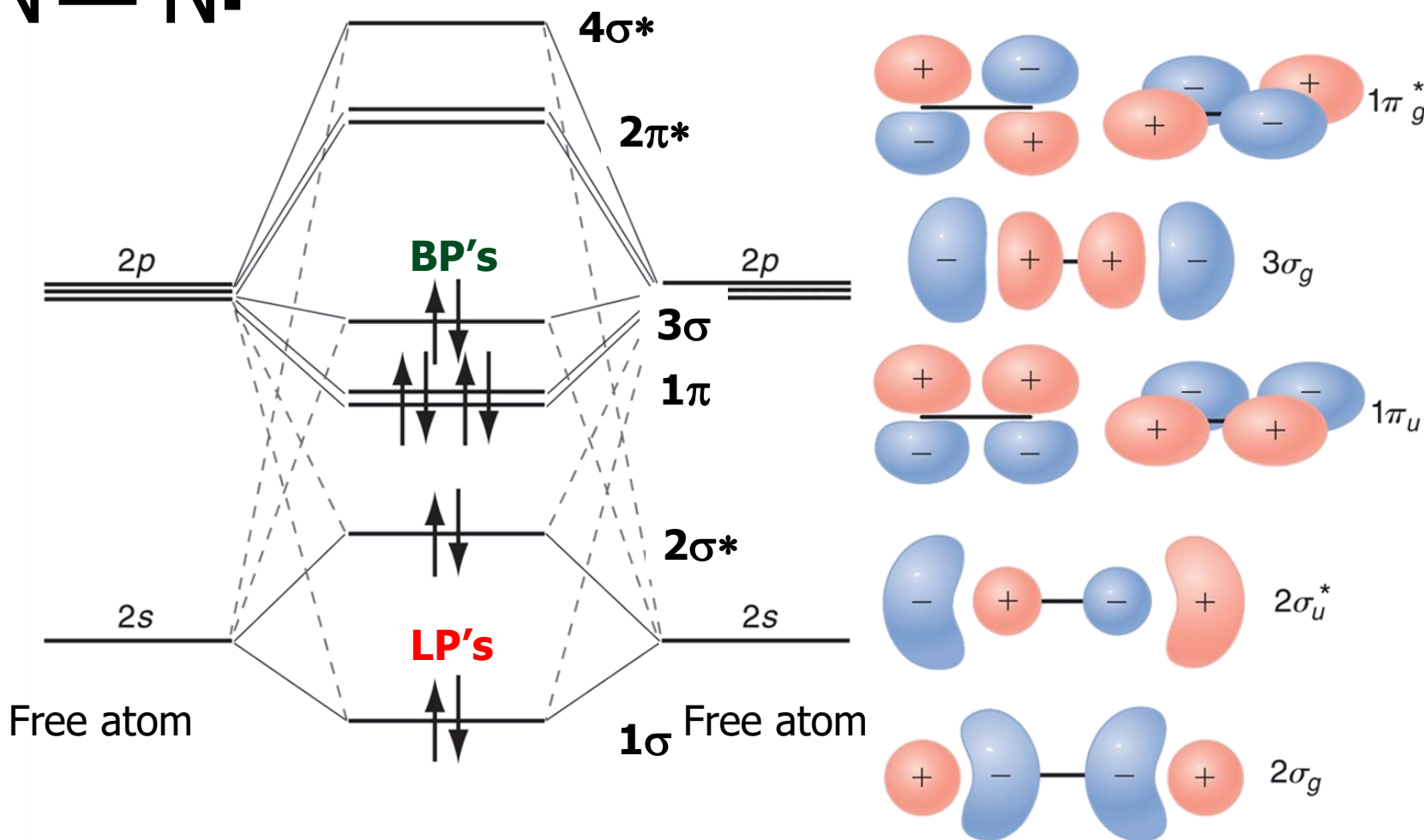
Li₂, Be₂, C₂ and N₂



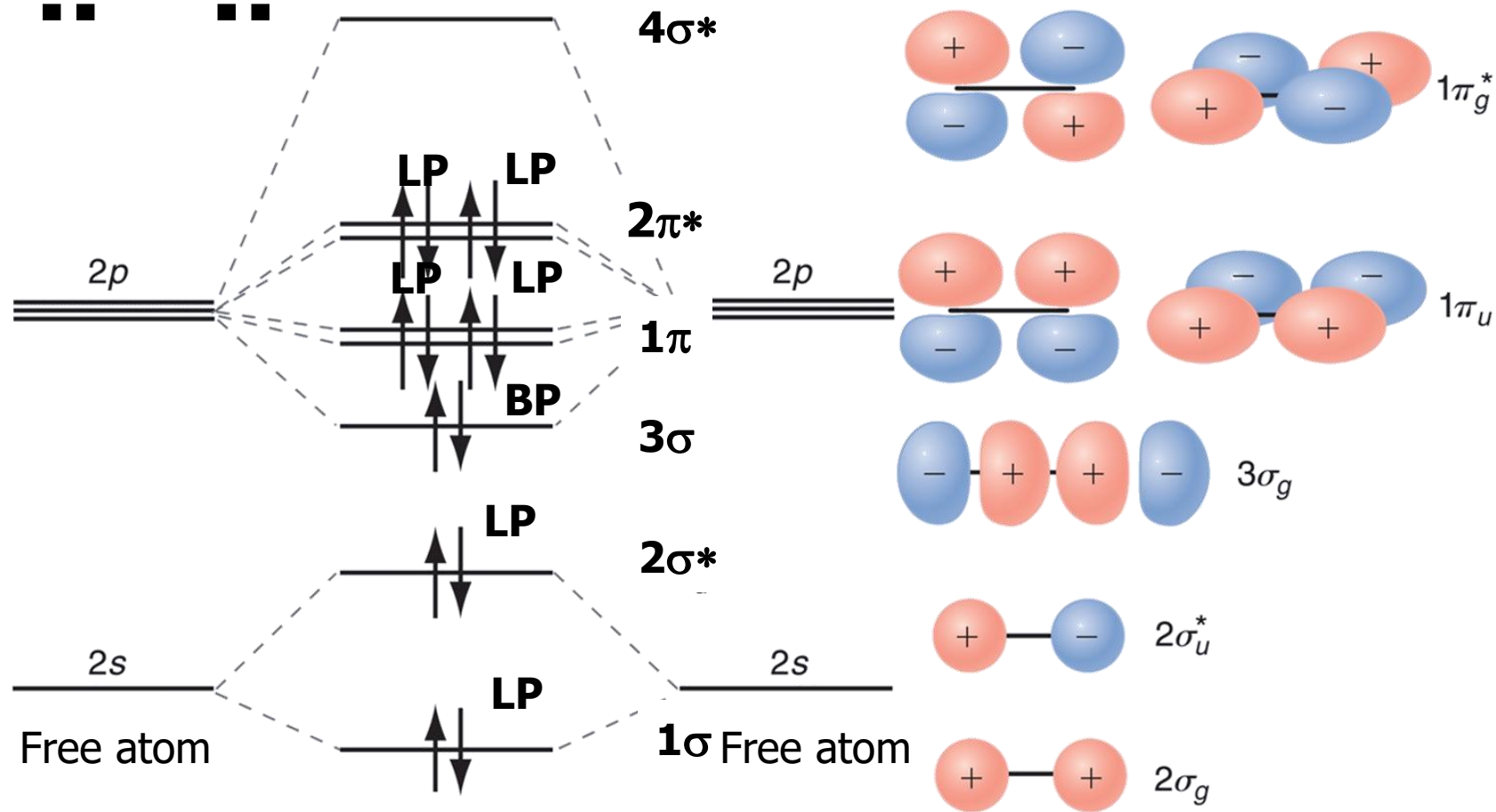
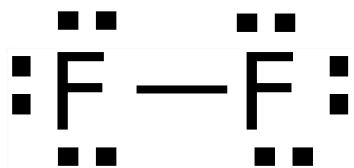
Electron Configurations of the Diatomics



Electron Configuration of N₂



Electron Configuration of F₂



Properties of Diatomics

Valence electrons only

