Molecular orbitals

The molecular orbitals

The **molecular orbitals theory** is quantum-mechanics theory that allows describing some effects that cannot be described with the Valence Band theory.

The combination of different atomic orbitals leads to the formation of new molecular orbitals (MO)
The electrons placed in the MOs are delocalized in the whole molecule an not to the single atoms involved in the bond

In other words the MOs theory is a **polycentric theory** that states that the electrons involved in the molecular orbitals are affected by the **attraction forces of all the nuclei in the molecule**

The molecular orbitals

L.C.A.O. Linear Combination of Atomic Orbitals

The wave functions of the molecular orbitals are obtained by a **linear combination of the atomic orbitals wave functions**

This means that the two wave functions can give rise to **constructive interference (sum) or destructive interference (difference)**

For each bond two molecular orbitals are therefore generated

- Two wave functions

- Two energetic levels

Bonding molecular orbitals

The molecular orbitals generated by the sum of two atomic orbitals has a **smaller energy** compared to the original ones**, with a higher electronic density in between the two atoms nuclei**

Bonging Molecular Orbital Ψ_B

To obtain a boding molecular orbital thw two atomic orbitals interact in phase (same sign of the wave funtion) giving place to constructive interference

interferenze costruttive
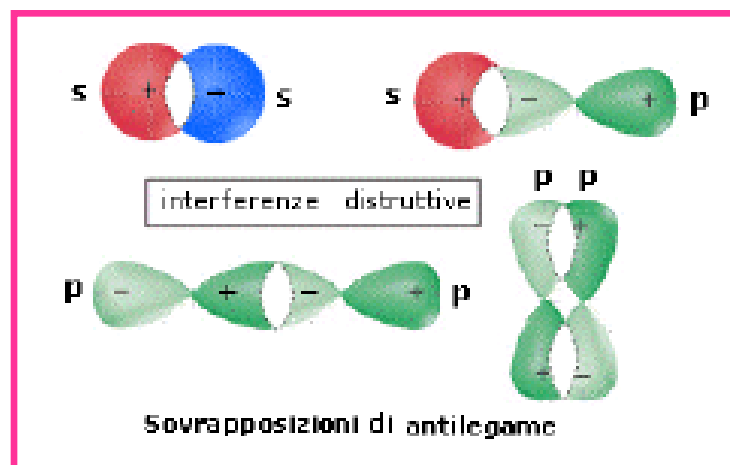
Sovrapposizioni di legame
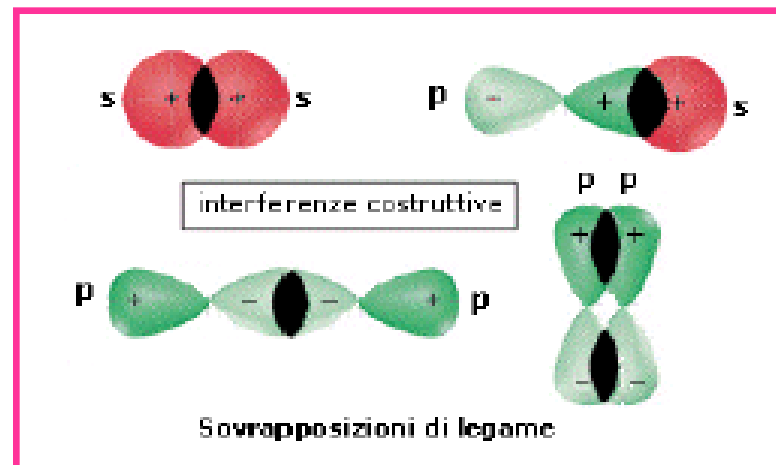
Antibonding molecular orbitals

The molecular orbital generated by the difference between the two original atomic orbitals has a higher energy and the electronic density between the two nuclei axis is zero (node)
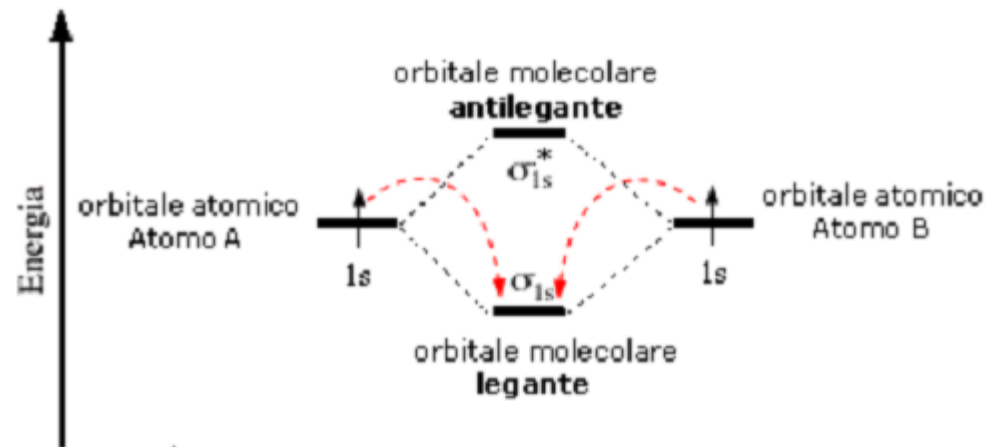
Antibonding Molecular Orbital Ψ*

Opposite phase (opposite sign of the wave function) destructive interference

Molecular orbitals

The bonding between atoms is stronger if the most of the electrons are allocated in the bonding molecular orbitals, lower energy, more stable.
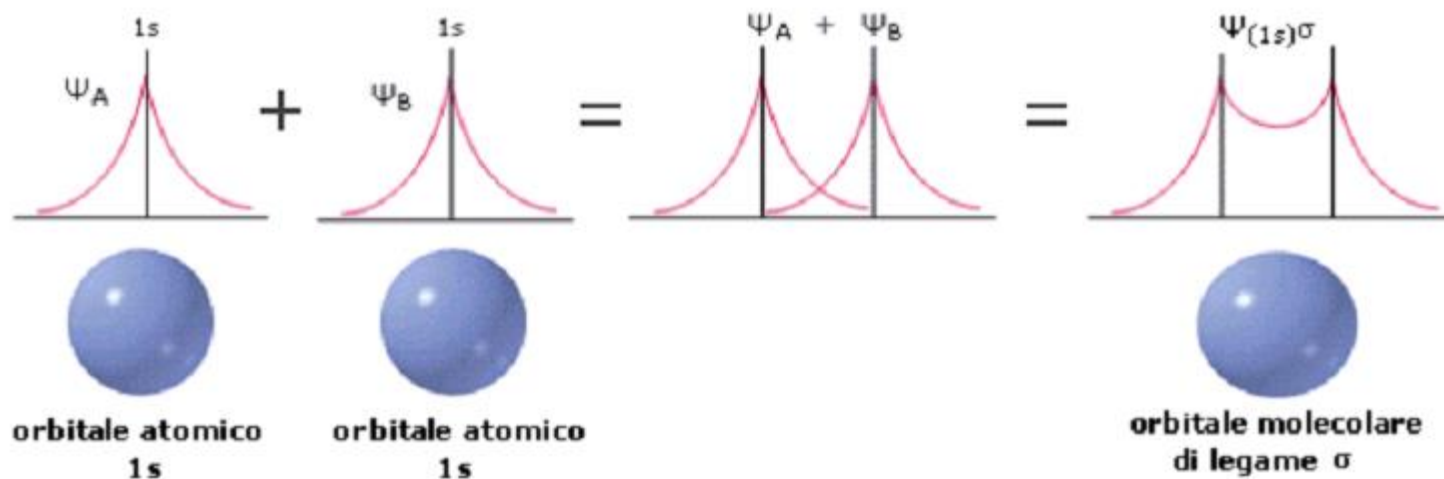

Let's make a very easy example and let's consider two hydrogen atoms which are forming an H2 molecule

Molecular orbitals

At first we sum the two 1s orbitals, obtaining the bonding molecular orbital $\Psi\sigma1s$.

In this case the Ψ (and also Ψ^2) value increases in the region between the two nuclei

Afetrwards we consider the difference between the two wave functions 1s, obtaining an antibondign molecular orbital $\Psi\sigma^*1s$, it will have a nodal plane between the two nuclei.

In this case Ψ (and also Ψ^2) value decreases down to zero in the region between the two nuclei
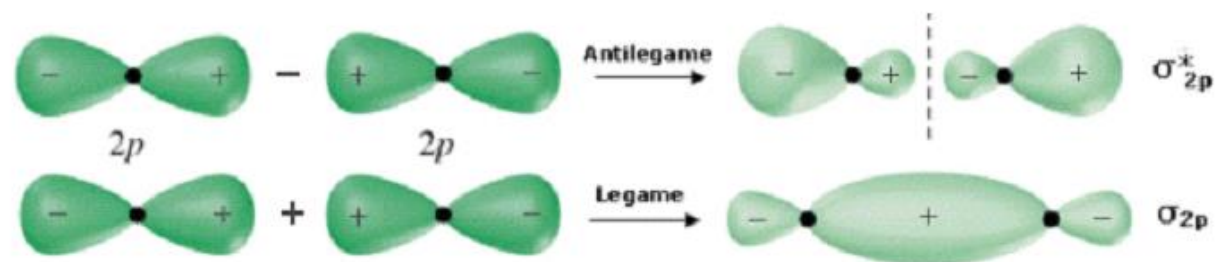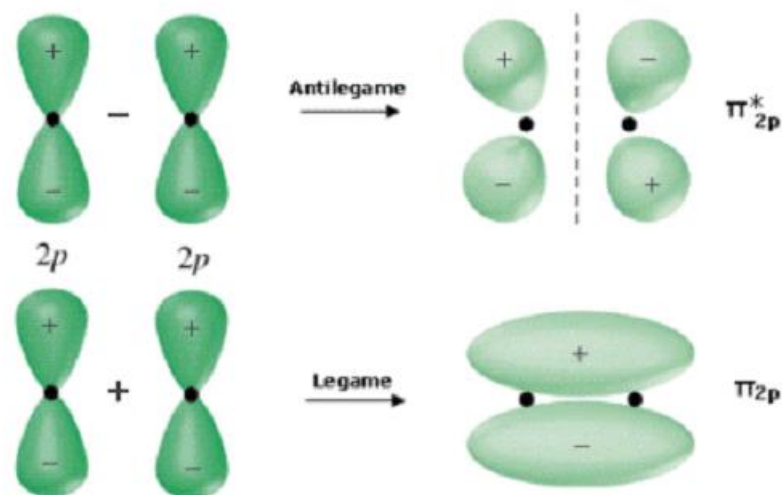

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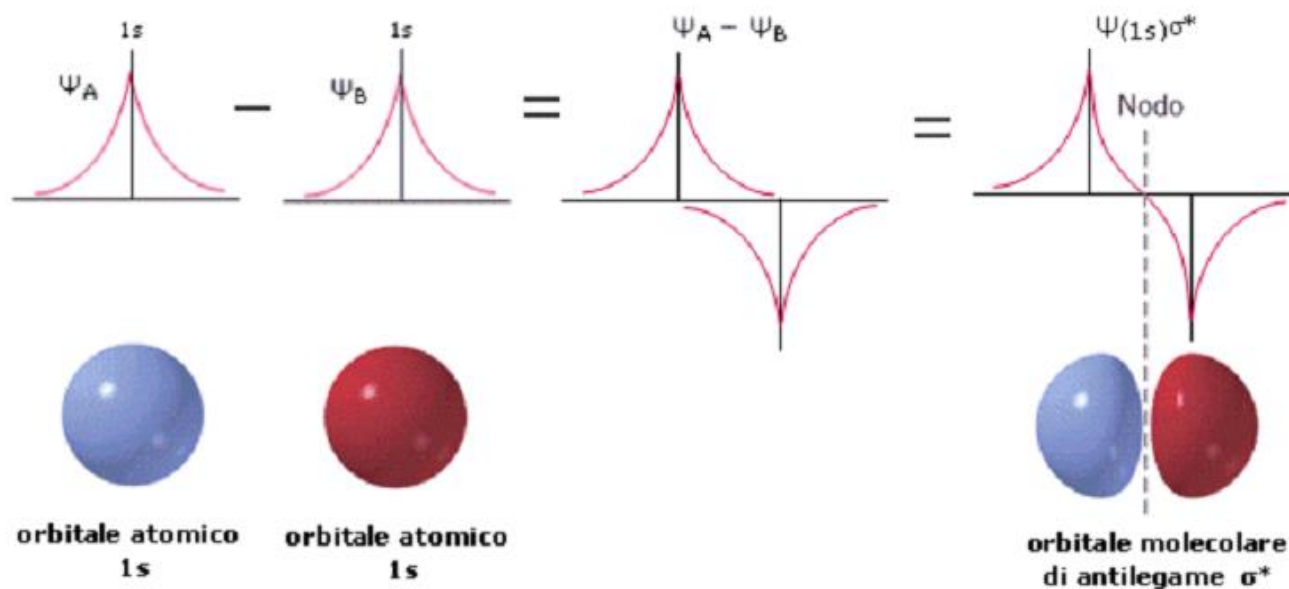
Molecular orbitals

p orbitals can interact in two different ways:

Along the internuclear axis, forming σ e σ* molecular orbitals

Or above and below the internuclear axis creating π e π* molecular orbitals
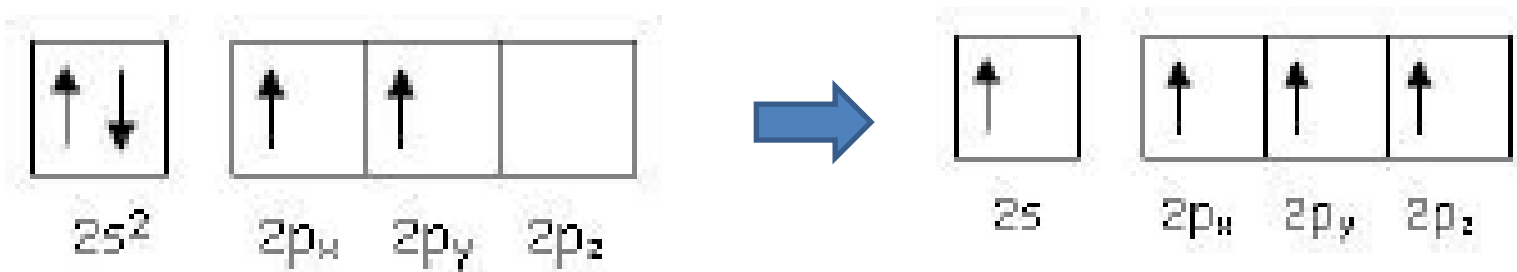
L'atomo di Carbonio

The Carbon Atom

The carbon atom has 6 electrons in the outer shell, with an electronic configuration $1s^1\ 2s^2\ 2p^2$

At a first glance it seem a divalent atom

In the most of the cases the carbon atom (few exceptions CO), tends to form 4 bonds

In order to do that it's electronic configuration changes into: $2s^2$ e $2p^2$

Hybridization of molecular orbitals

In order to give rise to more stable structures, forming bonds with other atoms, the atomic orbitas could change their wave function and recombine, giving rise to so called hybrid molecular orbitals

Hybridization happens noly among valence orbitals (outer shell) with very similar energy

Hybrid orbitals have the same energy and are differently oriented into the space in order to minimize their interaction

Atomic orbitals hybridization: sp

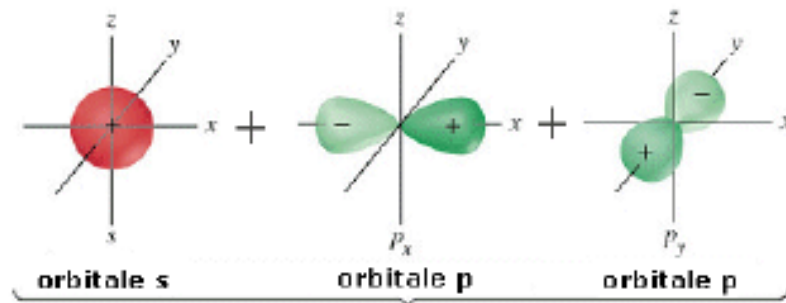The combination of one s orbital and one p orbital give rise to two hybrid **sp orbitals**

sp orbitals lays on the same plane whifted by 180°

The other two p orbitals which are not hybridized will be oriented perpendicularly with respect with the two hydrized ones (y and z axis)
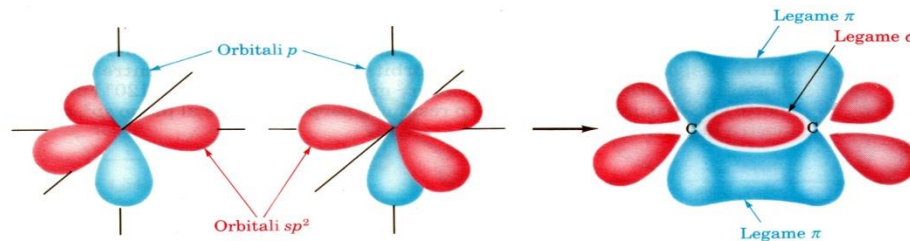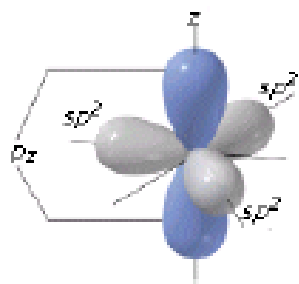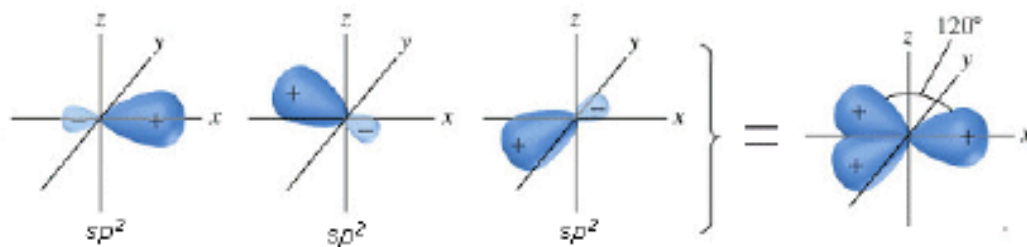

orbitale s   orbitale p   2 orbitali sp
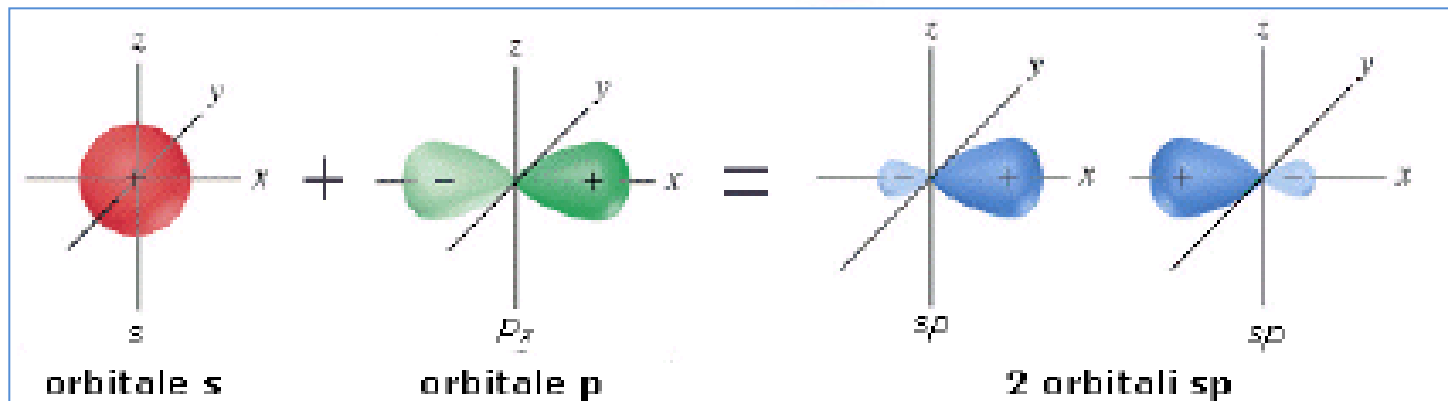
Atomic orbital hybridization: sp²

The combiation of one s orbital and two p orbitals gives rise to three **sp²** orbitals on the same plane but shifted by **120°**

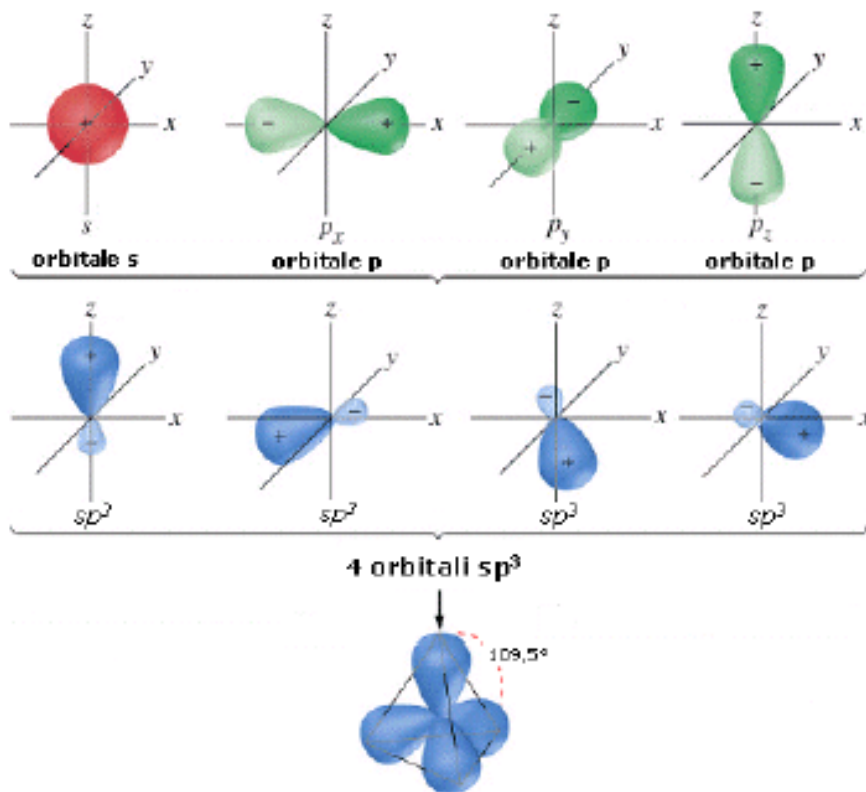orbitale s   orbitale p   orbitale p

The remaining not hybridized p orbital will be orinted perpendicularly

sp^2 sp^2 sp^2

itali sp^2

Atomic orbital hybridization: sp³

The combination between one s orbitals and all the three p orbitals, gives rise t four **sp³** orbitals → **tetraedric strcuture**, shifted by 109,5°

This case is not very interesting for us, just to give an example, Methane molecule has this kind of tetraedric configuration **(CH$_4$)**

Carbon Atom

If we consider the **sp³ hybridization all the four different orbitals are equivalent**
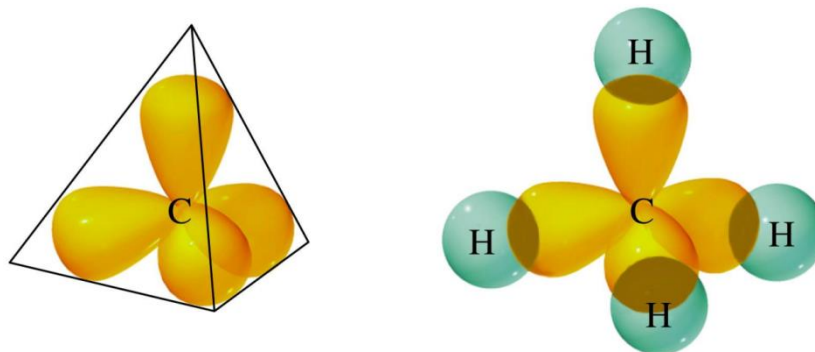
And can form equivalent bonds, typically σ bonds with 4 hydrogen atoms

Crbon Atom

If we consider **sp^2 hybridization, this involves s, p$_x$ e p$_y$ orbitals, so that three equivalent bonds can be formed**

Same plane, shifted by 120°

There will be a fourth not hybridized **p$_z$** orbital perpendicularly oriented and not hybridized

If we try to form a bond betwee two carbon atoms we can at first form a **σ bond,** involving two hybrid orbitals, afterwards a **π bond can be formed between the two not hybridized orbitals**

**A double bond has been formed**
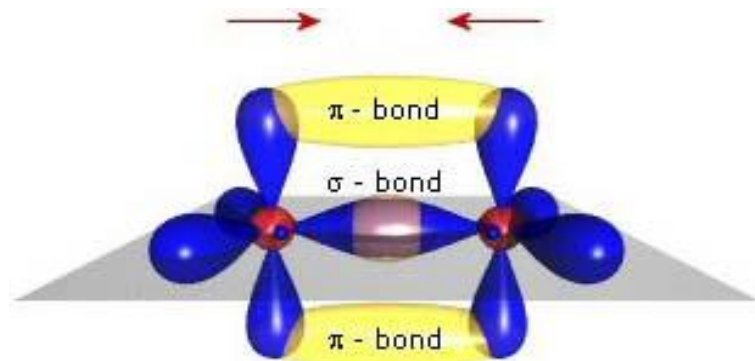
Carbon Atom

Each carbon atom usues two single bonds to bond itself with a hydrogen atom and with a carbon atom and a double bond to bond otself with one more carbon atom Non può esserci un legame doppio tra tutti gli atomi di carbonio adiacenti, ma questi legami si presenteranno alternati

Single and double bonds alternation➔ conjugation

Cnjugation length ➔ length of a molecular chain with a perfect alternation between single and double bonds
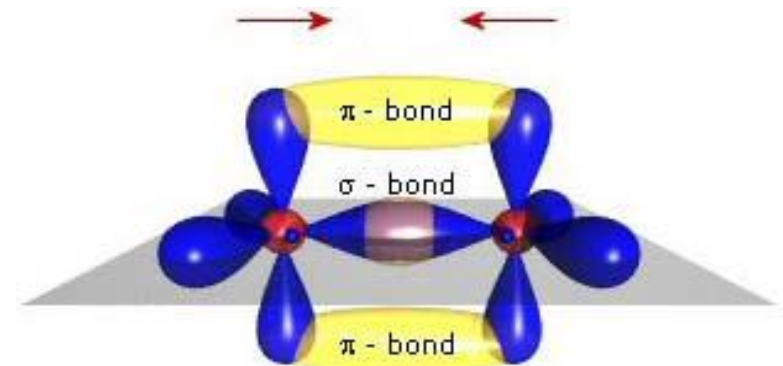

Benzene
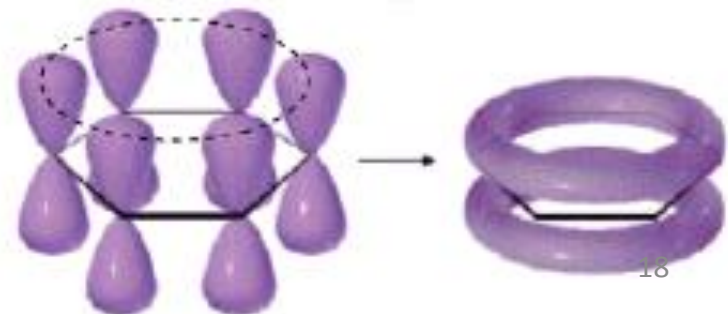
Resonance and Delocalization

When in a molecule there are π electrons (double or triple bonds) it can happen that such molecule can assume two different and equivalent (energetically) configurations.

It cannot be stated , a priori, which one of the two is the most probable structure, the system resonate between the two states

Where are the π electrons placed?
It is impossible to answer, because the chance to get them is equal in all the molecule
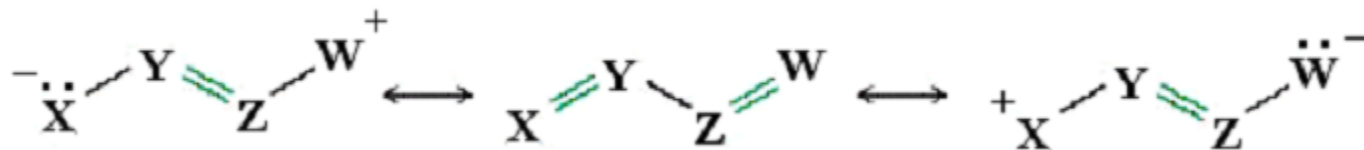
Delocalization of π electrons
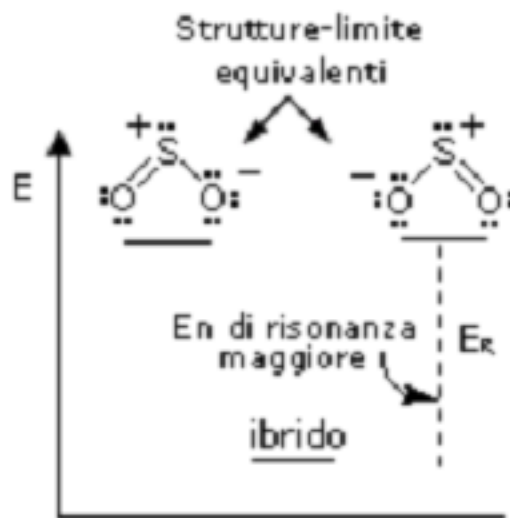
Resonance and Delocalization

Resonance is at the basis of electronic delocalization in conjugated systems

Let's consider a system with a sequence of double $\sigma - p$ bonds, separated by a single σ bond. As long as conjugation is present we have resonance and delocalization
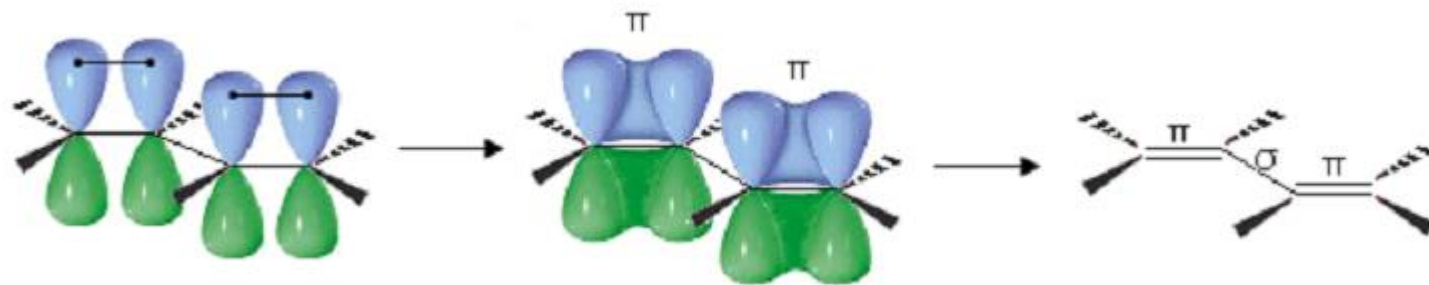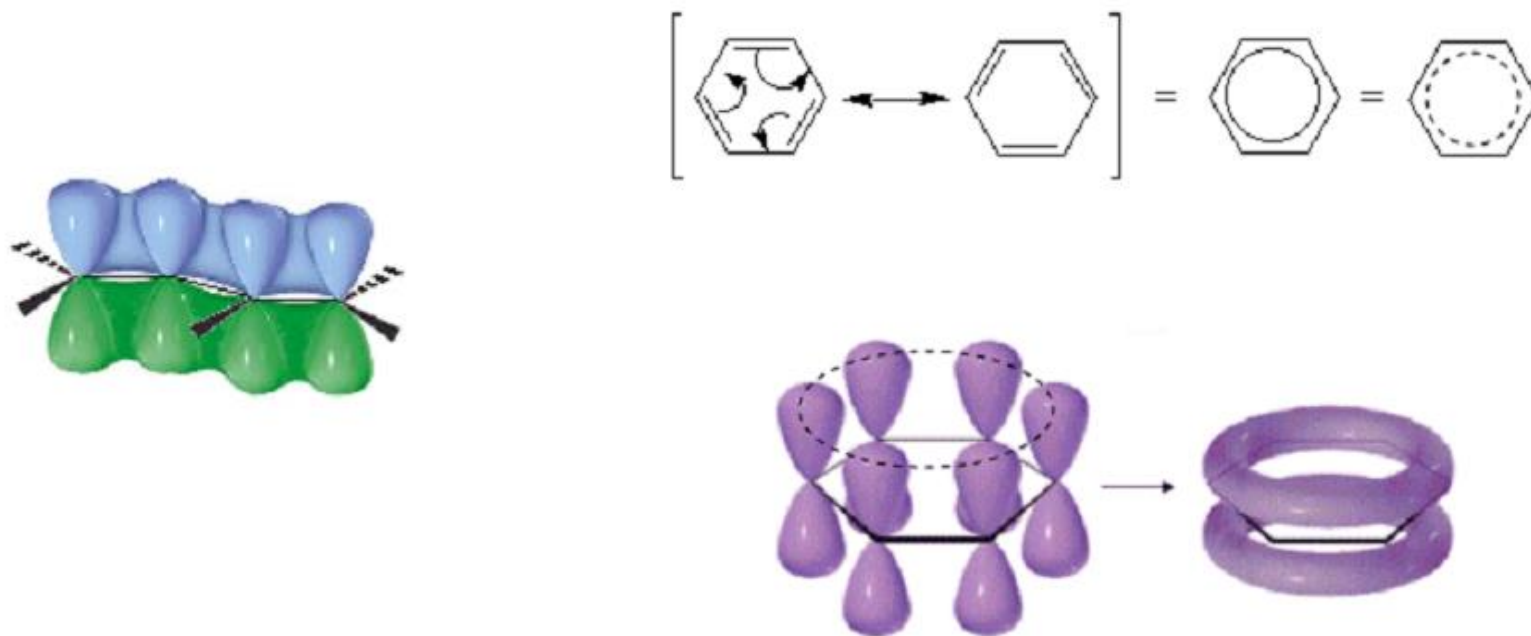

There are several ways to represent a conjugated π-π systema

In other words, there will be and extended π obrital in all the entire molecule (conjugation length) and the electrons involved in those bonds are delocalized in this new extended molecular orbital

This means that those electrons are delocalized in extended states and therefore a free to move, within this region of space, conjugation length

Insulators: σ bonds

The nature of the chemical bonds, π or σ, determins the energetic gap between the two new created orbitals, bonding and anti-bonding. Therefore, this confers the electronic properties to the final.

σ Bonds are more stable, the electrons are highly localize.

In fact, the energetic distance between bonding and anti-bonding Mos is relatively high, meaning that it will be very difficult for an electron placed in the bonding MO to jump into the higher antibonding level

These materials are generally insulators

Being very strong, σ bonds typically are the one that determine the molecular backbone

If we consider π bonds, the energetic gap between the two bonding and anti-bonding MOs is much smaller than in the previous case.

Therefore, it is much easier for electrons placed in the bonding MOs to receive a sufficient energy to jump into the empty anti-bonding MOs

Such electrons are delocalized and much more free to move

Such energy cna be given by an external field, exposure to light etc.

We have to consider that in a molecule, we have a lot of bonds, therefore the representation of these new energetic levels, MOs, is a little bit more complicated
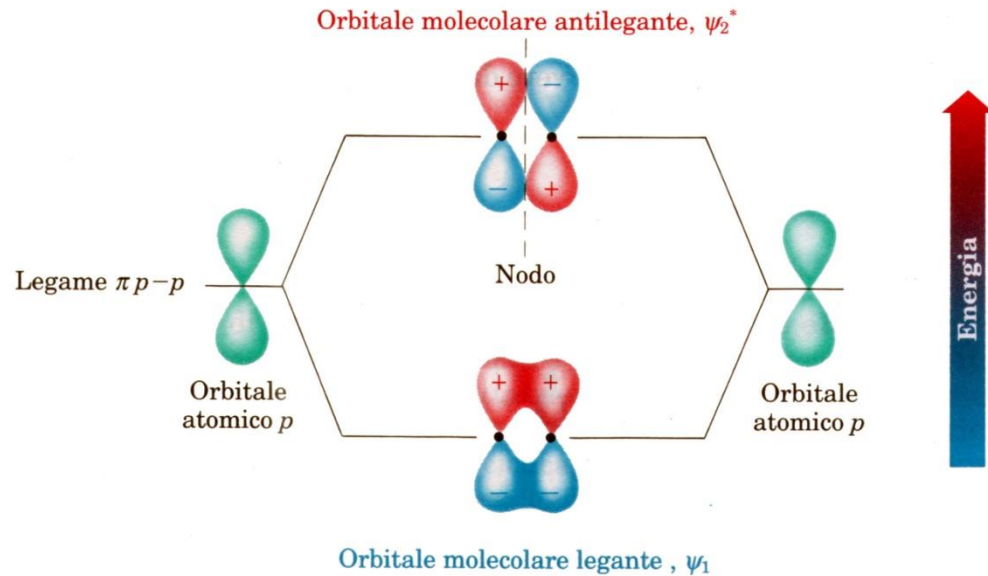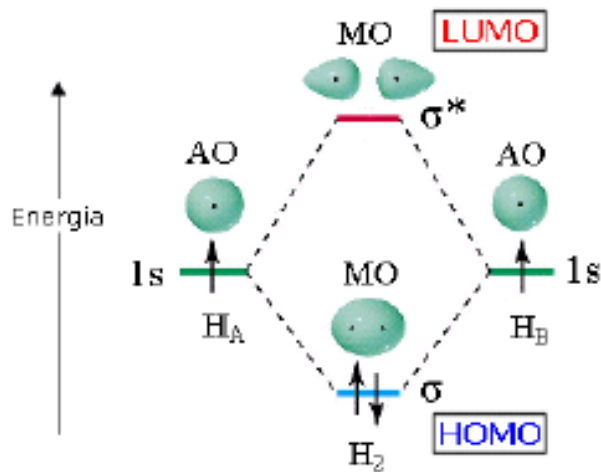
The amount of σ o π bond in one molecule determins the bad gap amplitude, whereas, the number of atoms determines the energetic distance between these new states

Molecules with few atoms are characterized by discrete states, when the number of atomes is big enough sugh dscrete states ar so energetically close that can be considered as and energetic band
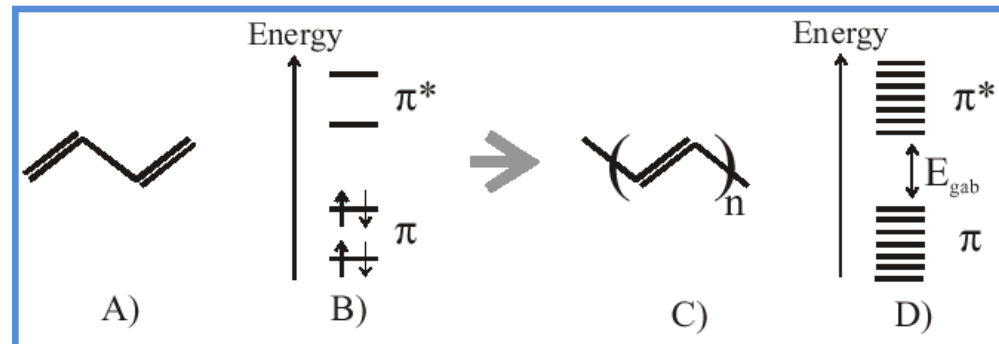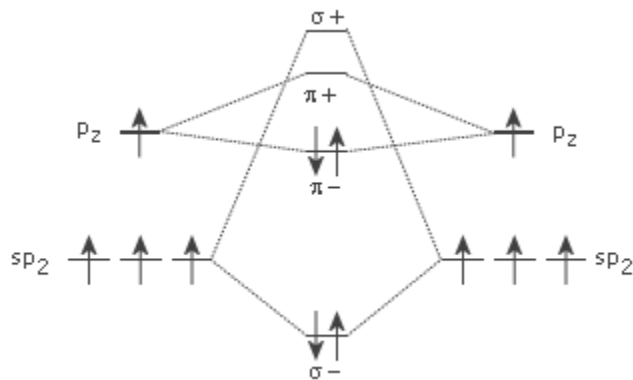
HOMO (Highest Occupied Molecular Orbital)

LUMO (Lowest Unoccupied Molecular Orbital)

The energetic distance between HOMO and LUMO determines the band gap of the molecule

The band gap

It is possible to estimate the band gao of one conjugated molecule by considering the **π electron as an electron in a box with infinite walls and with a length L given by the cnojugation length of the molecule**

The conjugation length is the part of the molecule where a perfect alternation between double and single bond exsists

The π electron, being confined in such a well can be represented as a sinusoidal wave with a wavelength $\lambda_n = 2L/n$
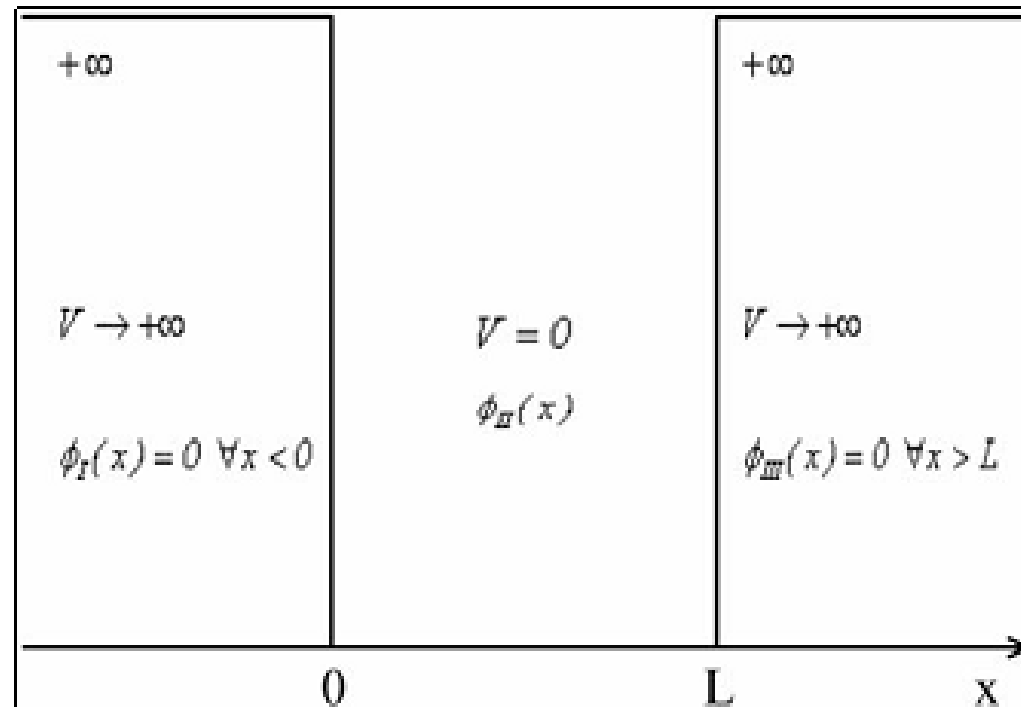
Where n represent the nth state

(b)
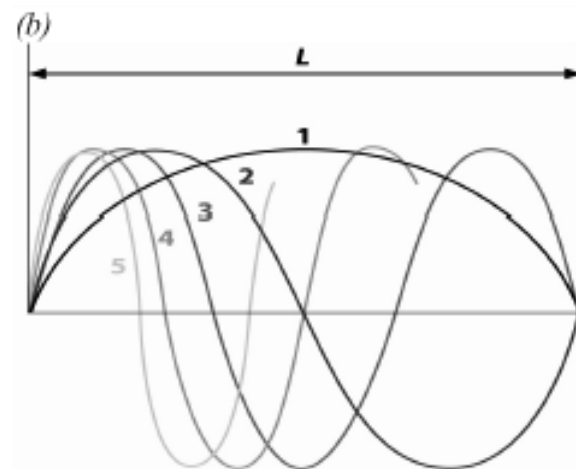
Let's consider this example again

The electron inside the box can be represented as a free electron, but we have some border conditions

$+\infty$

$V \to +\infty$

$\phi_I(x) = 0 \; \forall x < 0$

$V = 0$

$\phi_{II}(x)$

$+\infty$

$V \to +\infty$

$\phi_{III}(x) = 0 \; \forall x > L$

0   L   X

Unidimensional case

The potential energy inside the box is 0

Which will be the eigenvalue equation?

$$E_T = E_{cin} = \frac{p^2}{2m} \Rightarrow H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \Rightarrow \frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + E\psi(x) = 0$$

Which could be the solutions for this equation?

$$\psi_1(x) = A\cos(kx)$$

$$\psi_2(x) = B\sin(kx)$$

$$\psi_1(x) = A\cos(kx)$$

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + E\psi(x) = 0$$

$$-\frac{\hbar^2}{2m}Ak^2\cos(kx) + EA\cos(kx) = 0$$

$$k = \sqrt{\frac{2mE}{\hbar^2}} = \frac{\sqrt{2mE}}{\hbar}$$

The most general solution is given by a linear combination of the previous two:

$$\psi(x) = A\cos(kx) + B\sin(kx)$$

$$\psi(x) = A\cos(kx) + B\sin(kx)$$

$$\psi(0) = 0 \Rightarrow A\cos(0) = 0 \Rightarrow A = 0$$

$$\psi(L) = 0 \Rightarrow B\sin(kL) = 0$$

$$kL = n\pi$$

B=0 is not acceptable

Therefore, we obtain

$$\frac{\sqrt{2mE_n}}{\hbar}L = n\pi \qquad\qquad E_n = \frac{\pi^2\hbar^2}{2mL^2}n^2 = \frac{h^2}{8mL^2}n^2$$

$$E_n = \frac{n^2 h^2}{8mL^2}$$

n = number of states; h Planck constant; m electron mass; L conjugation length.

*Imagine we have **N** atoms within the conjugation length **L**, each one involves a π orbital with two electrons*

If d is the distance between atoms **L will be (N-1)d**, for N>>1 it becomes Nd

N atoms will form N/2 π bonds, i.e. there will be N π molecular orbitals (N/2 bonding and N/2 antibonding)

Considering the Pauli exclusion principle, only two electrons can occupy the single orbital
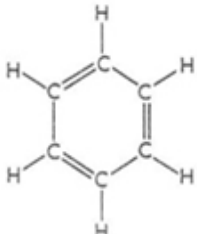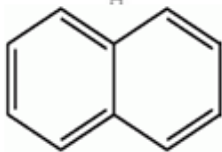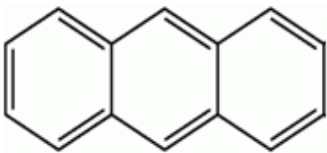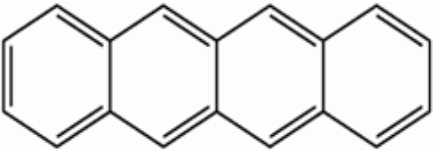
Ithe number of occupied states n will be N/2
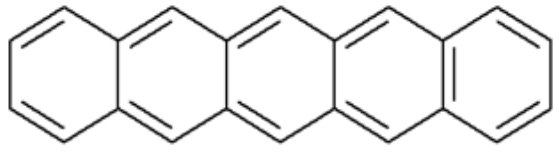
$$E(HOMO) = \frac{\left(\dfrac{N}{2}\right)^2 h^2}{8m(Nd)^2} \qquad E(LUMO) = \frac{\left(\dfrac{N}{2}+1\right)^2 h^2}{8m(Nd)^2}$$

$$E_G = E(LUMO) - E(HOMO) = \frac{(N+1)h^2}{8m(Nd)^2}$$
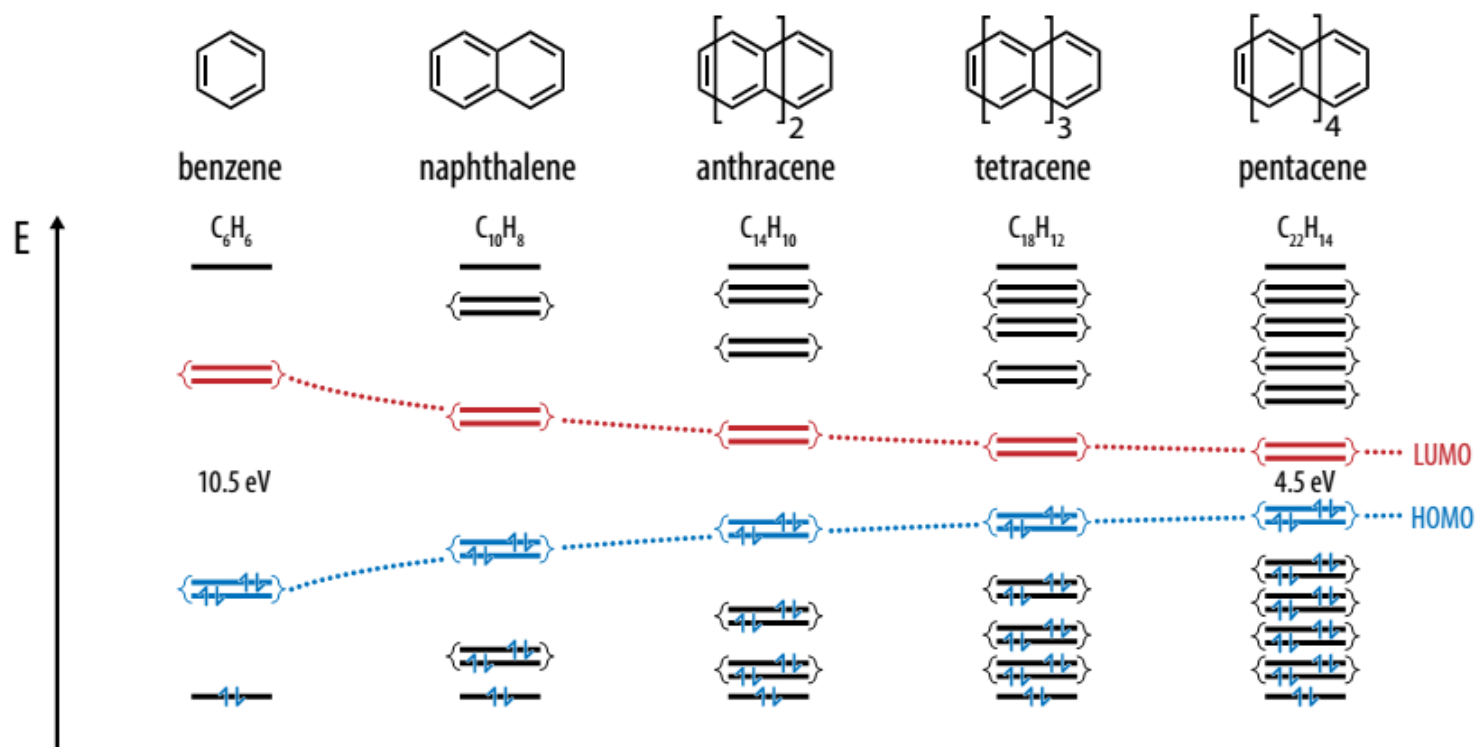
the band gap decreases when the molecule conjugation length (Nd) increases

Band Gap in organic conjugated polymers

		Band Gap
Benzene		6.0 eV
Naphtalene		4.3 eV
Anthracene		3.3 eV
Tetracene		2.6 eV
Pentacene		2.1 eV

The higher the conjugation length the smaller the band gap