

From H_2^+ to H_2 molecules

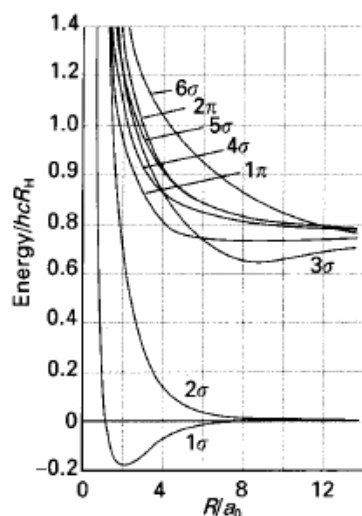


Fig. 8.5 The molecular potential energy curves for the hydrogen molecule-ion.

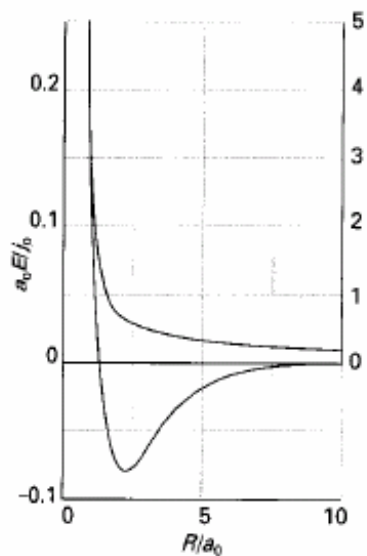


Fig. 8.12 The calculated molecular potential energy curves of the two lowest energy molecular orbitals of the hydrogen molecule-ion within the LCAO approximation. Note the change in scale between the bonding and antibonding curves.

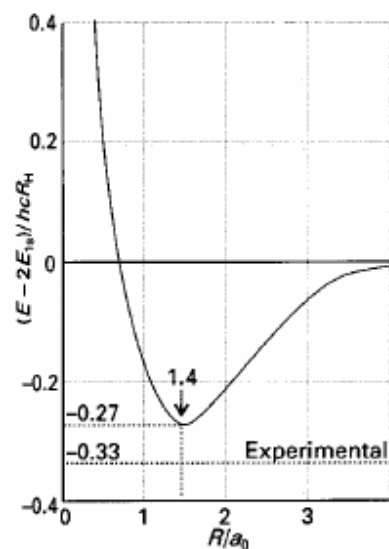


Fig. 8.14 The calculated molecular potential energy curve for the lowest energy orbital of a hydrogen molecule in the LCAO approximation.

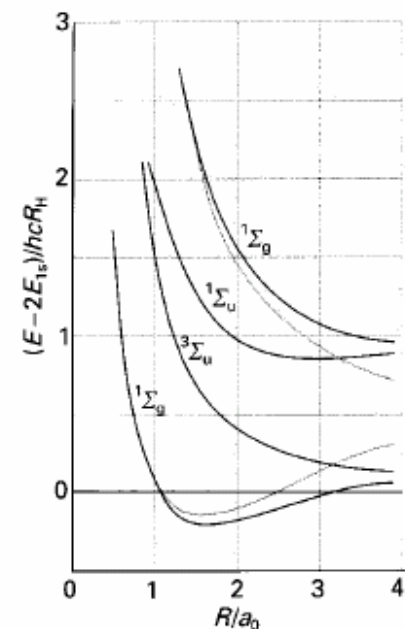


Fig. 8.15 The variation of the energies of four states of the hydrogen molecule with changing internuclear distance and the effect of configuration interaction which pushes the two pale curves apart.

Interazione configurazionale per la molecola H₂

The following configurations are possible:

$$1\sigma_g^2 \quad 1\sigma_g^1 1\sigma_u^1 \quad 1\sigma_u^2$$

The corresponding wavefunctions, including spin, are

$$\Psi_1(1, 2; {}^1\Sigma_g) = \psi_+(1)\psi_+(2)\sigma_-(1, 2)$$

$$\Psi_2(1, 2; {}^1\Sigma_u) = \left(\frac{1}{2}\right)^{1/2} \{\psi_+(1)\psi_-(2) + \psi_+(2)\psi_-(1)\}\sigma_-(1, 2)$$

$$\Psi_3(1, 2; {}^1\Sigma_g) = \psi_-(1)\psi_-(2)\sigma_-(1, 2)$$

$$\Psi_4(1, 2; {}^3\Sigma_u) = \left(\frac{1}{2}\right)^{1/2} \{\psi_+(1)\psi_-(2) - \psi_+(2)\psi_-(1)\}\sigma_+(1, 2)$$

$\Psi_1(1, 2)$ and $\Psi_3(1, 2)$, converge on the same energy as $R \rightarrow \infty$

With CI, the wavefunction of the lower state is

$$\Psi(1, 2) = c_1\Psi_1(1, 2) + c_3\Psi_3(1, 2) = \Phi(1, 2)\sigma_-(1, 2)$$

and the orbital structure of this function is

$$\begin{aligned} \Phi(1, 2) &= c_1\psi_+(1)\psi_+(2) + c_3\psi_-(1)\psi_-(2) \\ &= \frac{1}{2}c_1\{\phi_A(1) + \phi_B(1)\}\{\phi_A(2) + \phi_B(2)\} \\ &\quad + \frac{1}{2}c_3\{\phi_A(1) - \phi_B(1)\}\{\phi_A(2) - \phi_B(2)\} \\ &= \frac{1}{2}(c_1 + c_3)\{\phi_A(1)\phi_A(2) + \phi_B(2)\phi_B(1)\} \\ &\quad + \frac{1}{2}(c_1 - c_3)\{\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)\} \end{aligned}$$

Questa è ancora un combinazione lineare di una configurazione “ionica” (H⁻+p) con una “covalente” (H+H), ma il peso delle due non è 1:1 come nell’LCAO semplice. Esso infatti può variare attraverso i coeff. c_1 e c_3 .

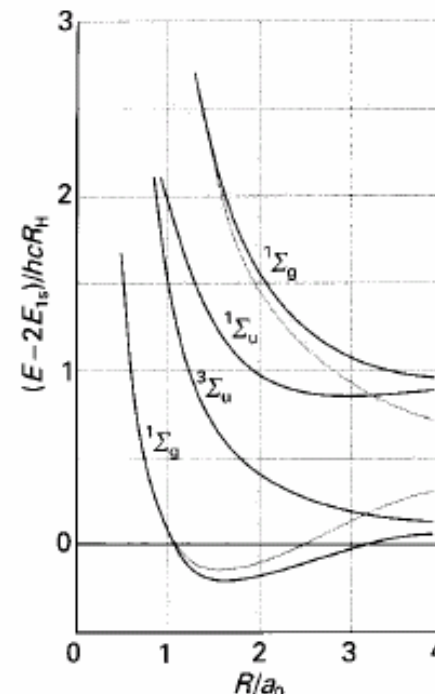


Fig. 8.15 The variation of the energies of four states of the hydrogen molecule with changing internuclear distance and the effect of configuration interaction which pushes the two pale curves apart.

absence of CI (setting $c_1 = 1$ and $c_3 = 0$):

$$\begin{aligned} \Phi(1, 2) &= \frac{1}{2}\phi_A(1)\phi_A(2) + \frac{1}{2}\phi_B(2)\phi_B(1) + \frac{1}{2}\phi_A(1)\phi_B(2) \\ &\quad + \frac{1}{2}\phi_B(1)\phi_A(2) \end{aligned}$$

Teoria delle perturbazioni per un sistema a due livelli (1)

Consider first a system that has only two eigenstates. We suppose that the two eigenstates of $H^{(0)}$ are known, and denote them $|1\rangle$ and $|2\rangle$. The corresponding wavefunctions are $\psi_1^{(0)}$ and $\psi_2^{(0)}$, respectively. These states and functions form a complete orthonormal basis. They correspond to the energies $E_1^{(0)}$ and $E_2^{(0)}$:

$$H^{(0)}\psi_m^{(0)} = E_m^{(0)}\psi_m^{(0)} \quad m = 1, 2$$

The wavefunctions of the true system differ only slightly from those of the model system, and we can hope to solve the equation

$$H\psi = E\psi \quad (6.2)$$

in terms of them by writing

$$\psi = a_1\psi_1^{(0)} + a_2\psi_2^{(0)} \quad (6.3)$$

where a_1 and a_2 are constants to be determined.

To find the constants a_m we insert the linear combination into the Schrödinger equation and obtain (using ket notation)

$$a_1(H - E)|1\rangle + a_2(H - E)|2\rangle = 0$$

When this equation is multiplied from the left by the bras $\langle 1|$ and $\langle 2|$ in turn, and use is made of the orthonormality of the two states, we obtain the two equations

$$\begin{aligned} a_1(H_{11} - E) + a_2H_{12} &= 0 \\ a_1H_{21} + a_2(H_{22} - E) &= 0 \end{aligned} \quad (6.4)$$

where $H_{mn} = \langle m|H|n\rangle$.

Teoria delle perturbazioni per un sistema a due livelli (2)

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

This expression expands to

$$(H_{11} - E)(H_{22} - E) - H_{12}H_{21} = 0$$

and then to

$$E^2 - (H_{11} + H_{22})E + H_{11}H_{22} - H_{12}H_{21} = 0$$

This quadratic equation has the solutions

$$E_{\pm} = \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2} \left\{ (H_{11} - H_{22})^2 + 4H_{12}H_{21} \right\}^{1/2}$$

In the special case of a perturbation for which the diagonal matrix elements are zero ($H_{mm}^{(1)} = 0$, so we can write $H_{mm} = E_m^{(0)}$), this expression simplifies to

$$E_{\pm} = \frac{1}{2}(E_1^{(0)} + E_2^{(0)}) \pm \frac{1}{2} \left\{ (E_1^{(0)} - E_2^{(0)})^2 + 4\varepsilon^2 \right\}^{1/2} \quad (6.6)$$

where $\varepsilon^2 = H_{12}^{(1)} H_{21}^{(1)}$. Because $H^{(1)}$ is hermitian, we can write $\varepsilon^2 = |H_{12}^{(1)}|^2$. When the perturbation is absent, $\varepsilon = 0$ and $E_+ = E_1^{(0)}$, $E_- = E_2^{(0)}$, the two unperturbed energies.

Teoria delle perturbazioni per un sistema a due livelli (3)

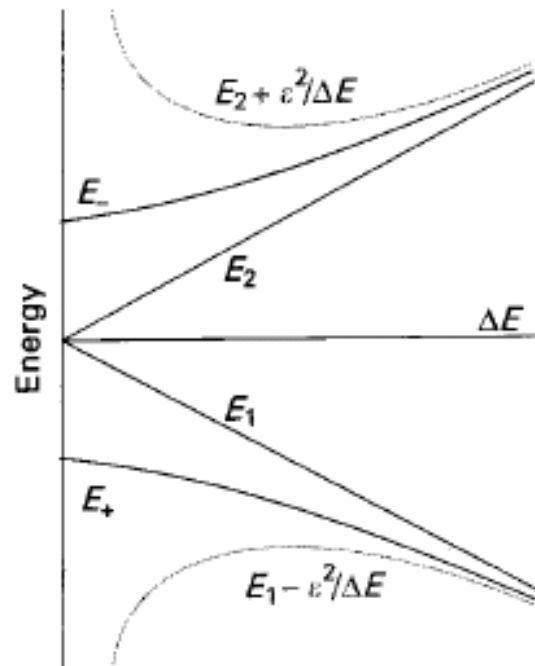


Fig. 6.1 The variation of the energies of a two-level system with a constant perturbation as the separation of the unperturbed levels is increased. The pale lines show the energies according to second-order perturbation theory.

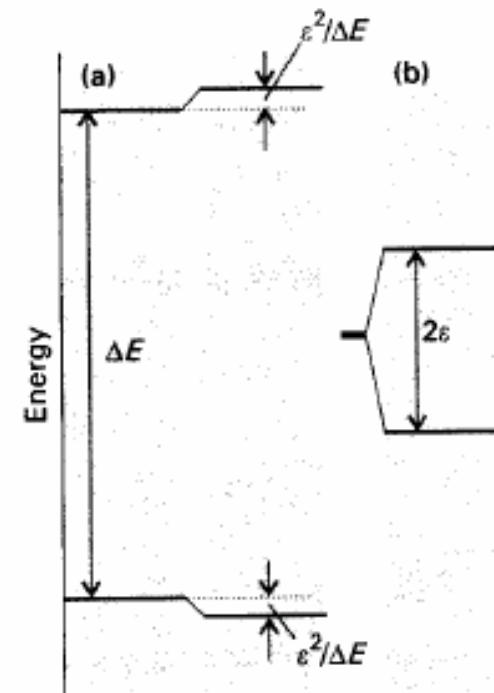


Fig. 6.2 (a) When the unperturbed levels are far apart in energy, the shift in energy caused by a perturbation of strength ϵ is $\pm\epsilon^2/\Delta E$. (b) If the levels are initially degenerate, then the shift in energy is much larger, and is equal to $\pm\epsilon$.

Legame eteropolare

$$\begin{vmatrix} \alpha_A - E & \beta - ES \\ \beta - ES & \alpha_B - E \end{vmatrix} = 0$$

when $|\alpha_A - \alpha_B| \gg \beta$ and $S=0$

$$E_+ = \alpha_A - \frac{\beta^2}{\alpha_B - \alpha_A} \quad E_- = \alpha_B + \frac{\beta^2}{\alpha_B - \alpha_A}$$

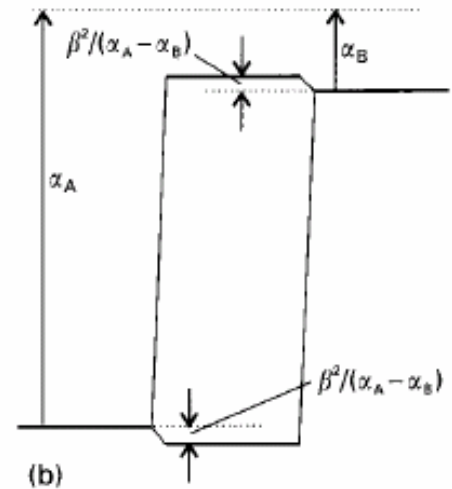
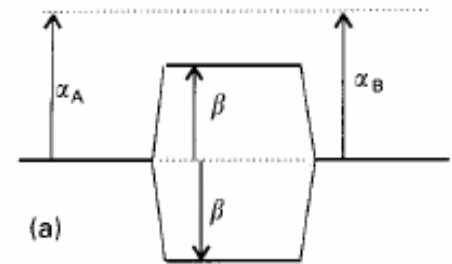


Fig. 8.17 The molecular orbital energy levels stemming from atomic orbitals of (a) the same energy, (b) different energy.

Heteronuclear diatomic molecules

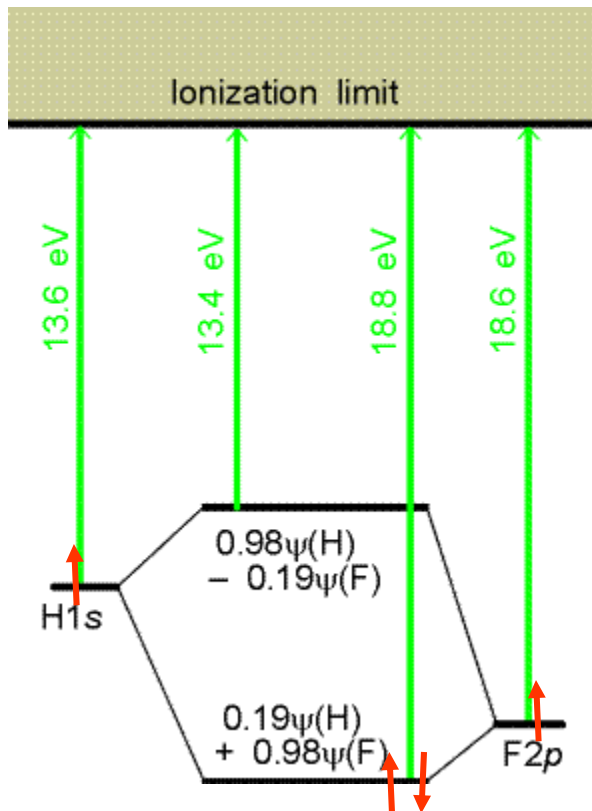
♦ A diatomic molecule with different atoms can lead to *polar bond*, a covalent bond in which the electron pair is shared unequally by the 2 atoms.

Polar bonds

→ 2 electrons in an molecular orbital composed of one atomic orbital of each atom (A and B).

$$\Psi = c_A A + c_B B$$

$|c_i|^2$ = proportion of the atomic orbital “i” in the bond



♦ The situation of covalent polar bonds is between 2 limit cases:

- 1) The *nonpolar bond* (e.g.; the homonuclear diatomic molecule): $|c_A|^2 = |c_B|^2$
- 2) The *ionic bond* in A^+B^- : $|c_A|^2 = 0$ and $|c_B|^2 = 1$

Example: HF

The H1s electron is at higher energy than the F2p orbital. The bond formation is accompanied with a significant partial negative charge transfer from H to F.

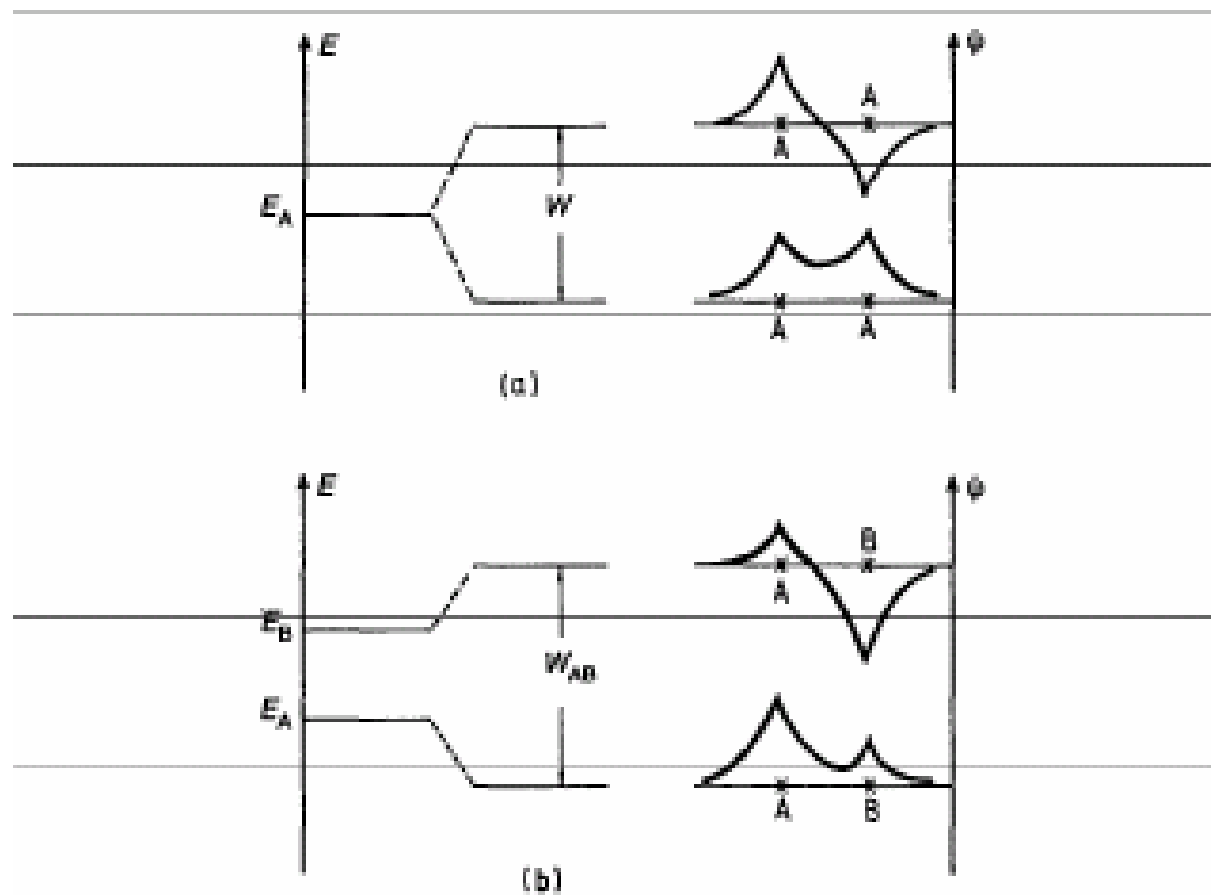
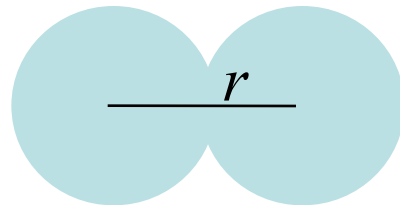


Fig. 3.2 The bonding and antibonding states for (a) the homonuclear and (b) the heteronuclear diatomic molecule. The shift in the energy levels due to overlap repulsion has not been shown.

Molecole:

H₂



1s

1s

$$\left(\sum H_i\right)\psi_{Mol} = E\psi_{Mol}$$

Difficile da risolvere!
Approssimazioni

$\psi_1(1s)$

$\psi_2(1s)$

Funzioni d'onda atomiche

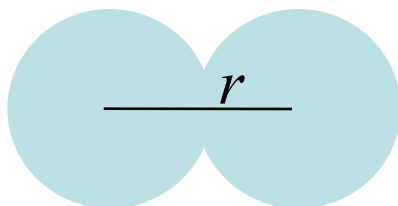
Definiamo gli orbitali molecolari (MO) come:

$$\psi_{Mol} = \psi_1 + \psi_2 \quad \psi_{Mol} = \psi_1 - \psi_2$$

Approssimazione: combinazione lineare degli orbitali atomici
(linear combination of atomic orbitals: LCAO)

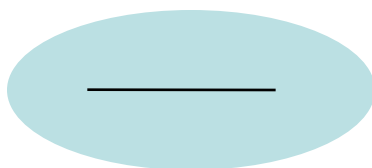
Orbitali molecolari: combinazione lineare di orbitali atomici

H₂



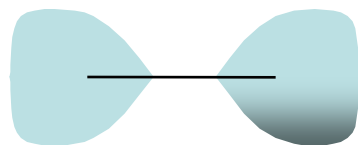
orbitale legante

$1s\sigma$



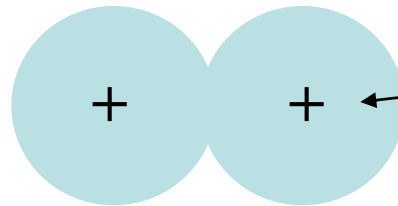
$$\psi_{Mol} = \psi_1 + \psi_2$$

$1s\sigma^*$



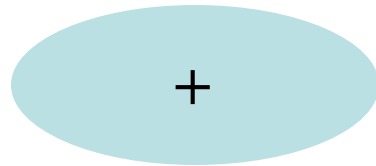
$$\psi_{Mol} = \psi_1 - \psi_2$$

orbitale antilegante



Segno della funzione d'onda

orbitale legante



$$\Psi_{Mol} = \Psi_1 + \Psi_2$$

gerade = pari



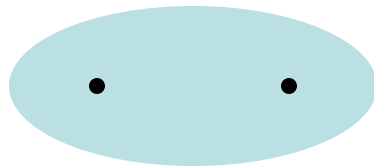
$$\Psi_{Mol} = \Psi_1 - \Psi_2$$

orbitale antilegante

ungerade = dispari

Quale orbitale molecolare MO è più basso in energia?

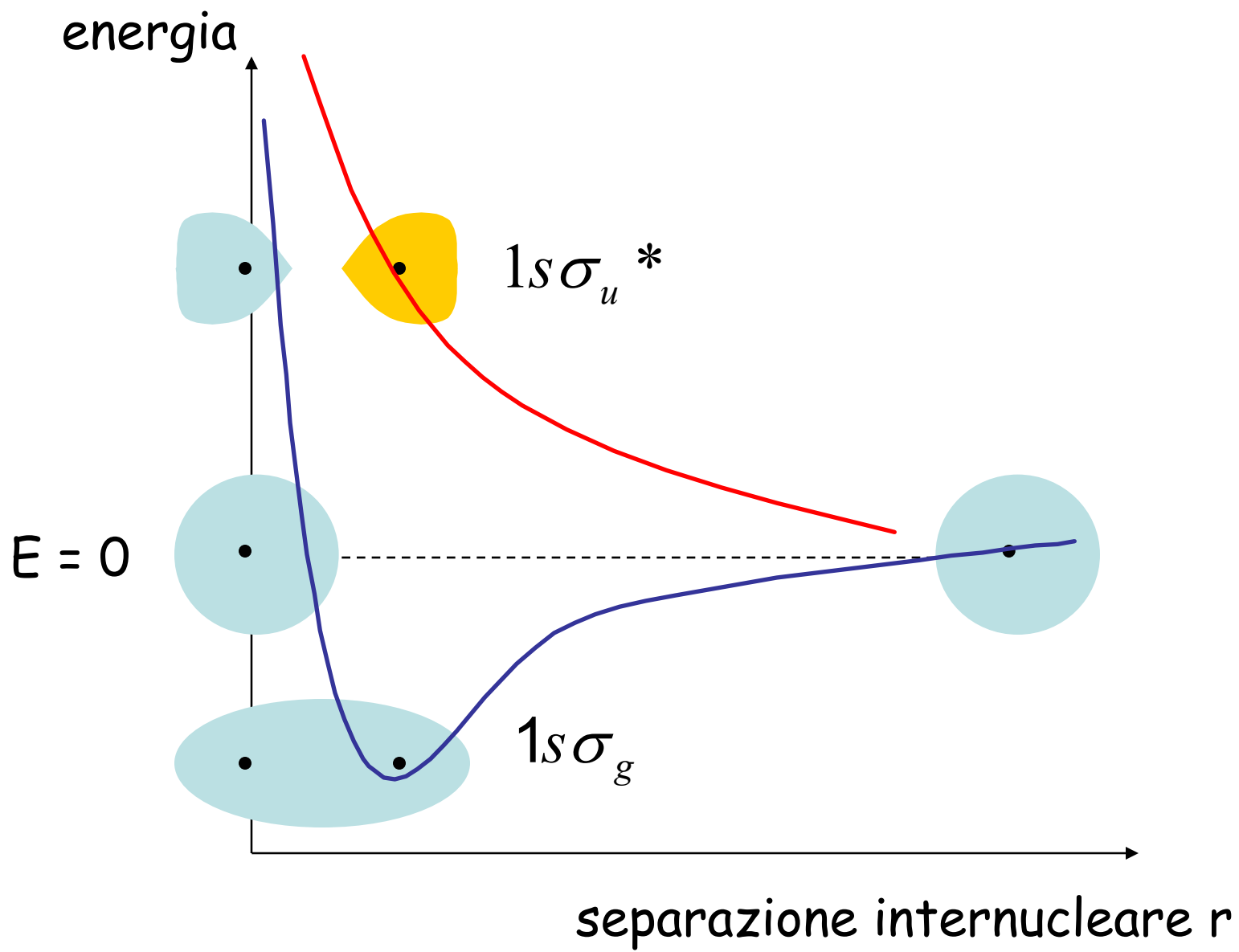
H₂

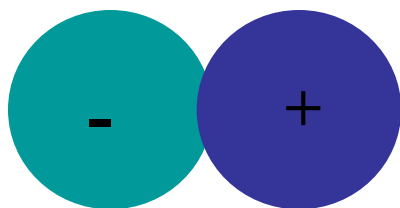


$1s\sigma_g$

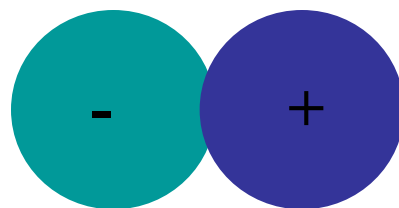


$1s\sigma_u^*$



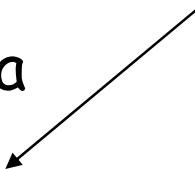


$2p_z$

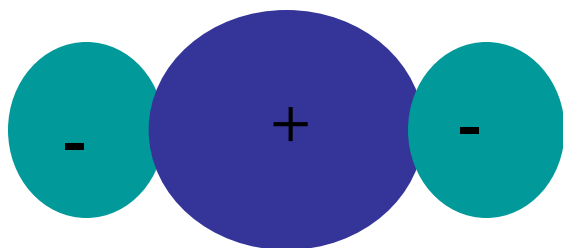
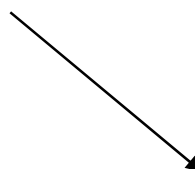


$2p_z$

differenza



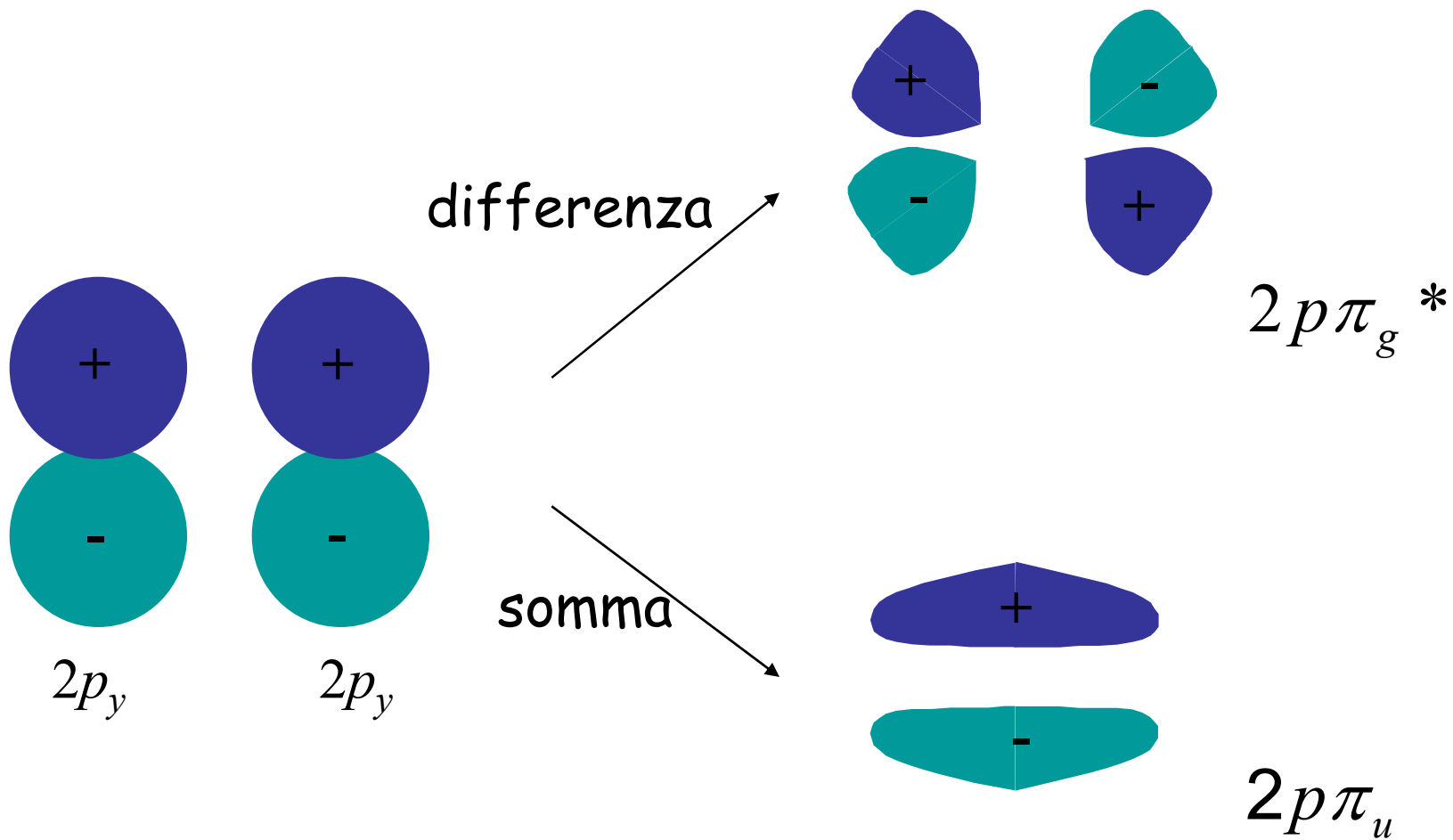
somma



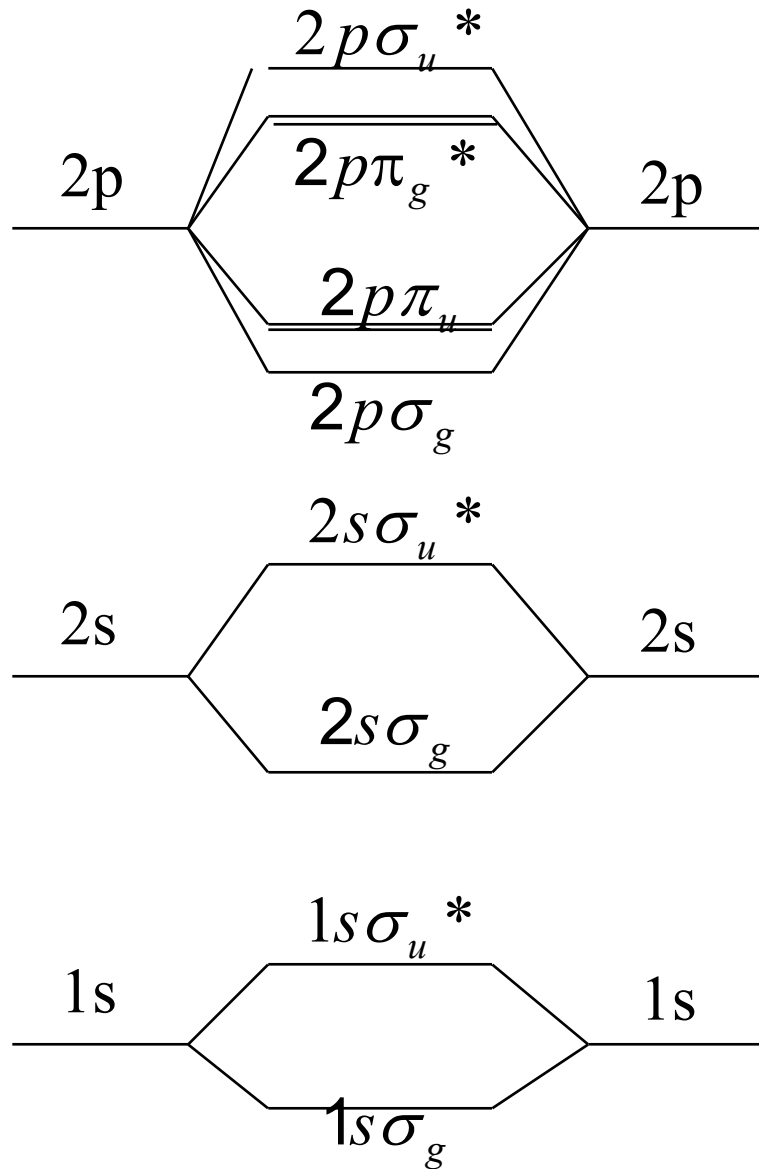
$2p\sigma_g$



$2p\sigma_u^*$

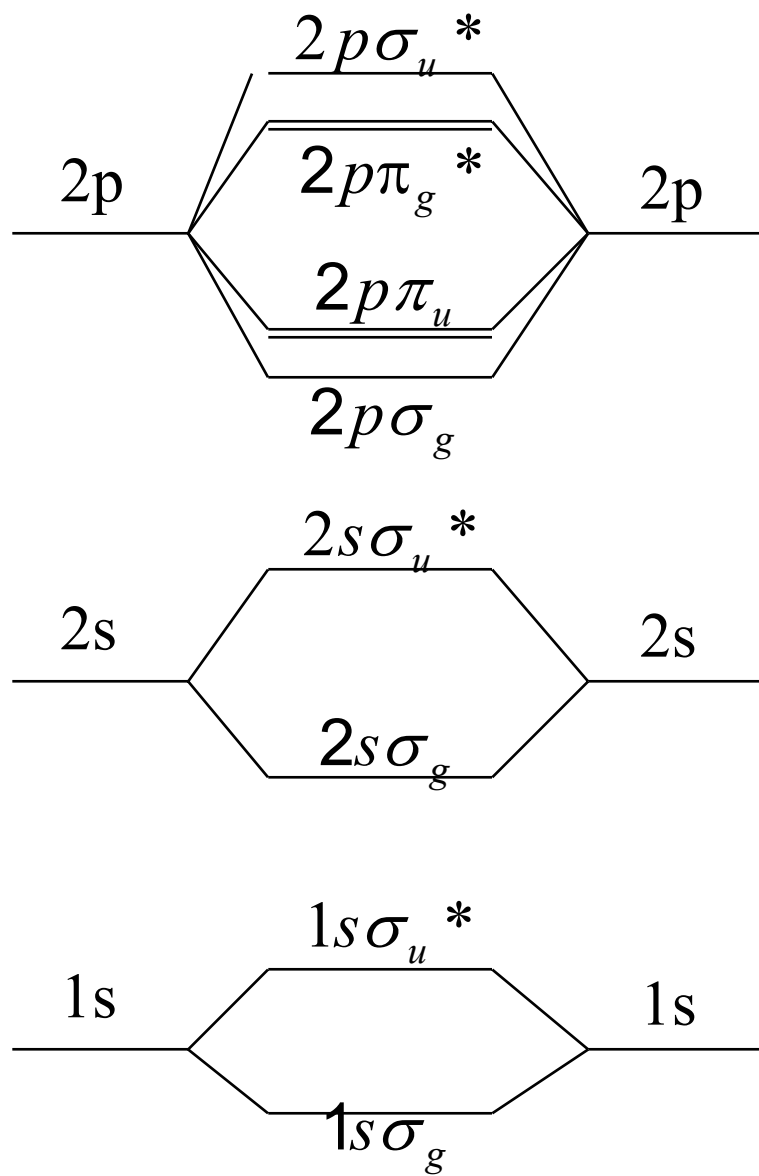


Costruzione di un diagramma dei livelli energetici degli orbitali molecolari

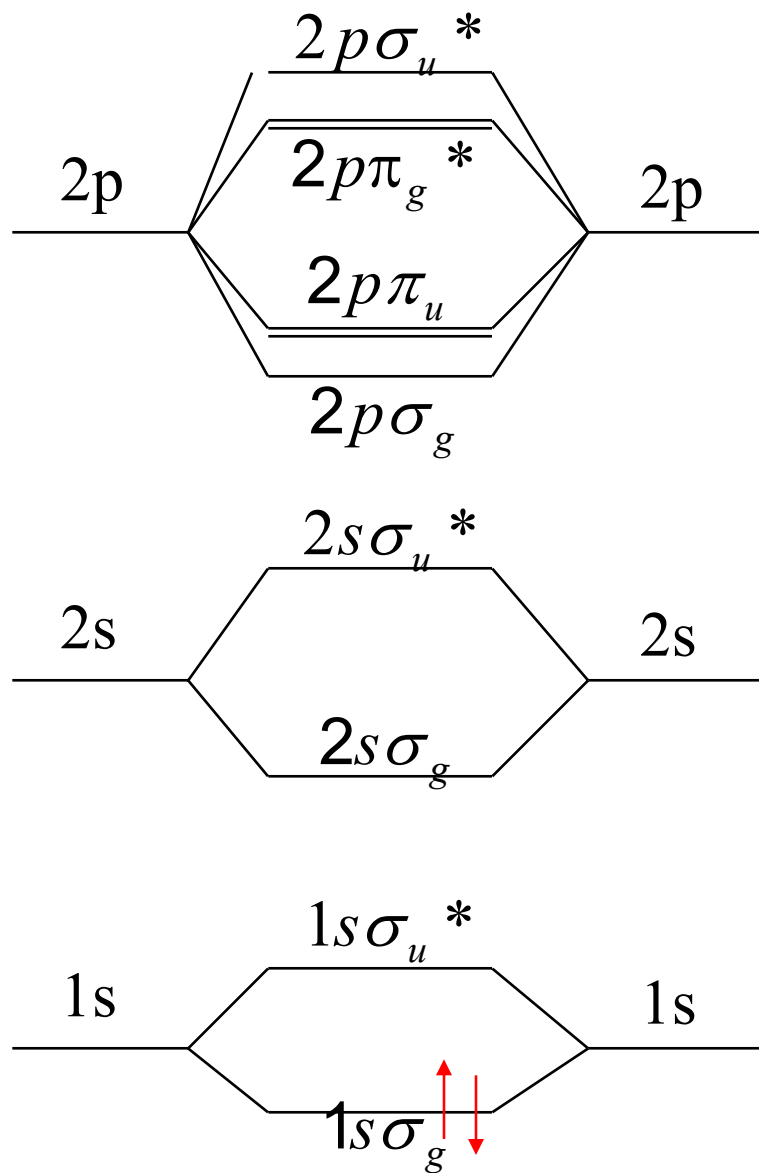


Generica molecola biatomica

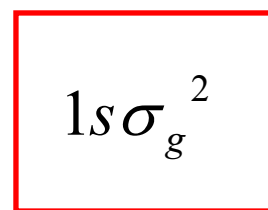
Come distribuire gli elettroni in questi orbitali molecolari ?



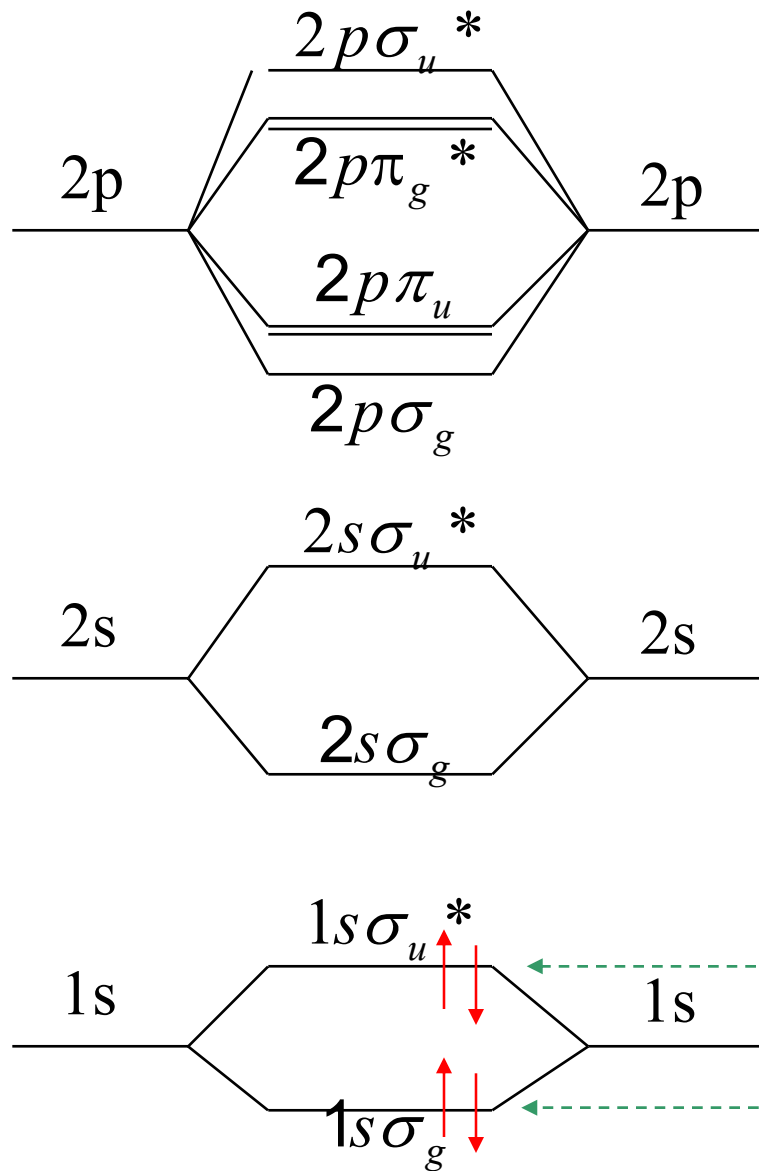
H_2



H_2



Molecola stabile

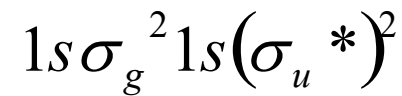


$$E = \frac{H_{AA} \pm H_{AB}}{1 \pm S}$$

$$\psi_b = \frac{1}{\sqrt{2+2S}} (\phi_{1s_A} + \phi_{1s_B})$$

$$\psi^* = \frac{1}{\sqrt{2-2S}} (\phi_{1s_A} - \phi_{1s_B})$$

He₂



Molecola instabile

Energia di destabilizzazione

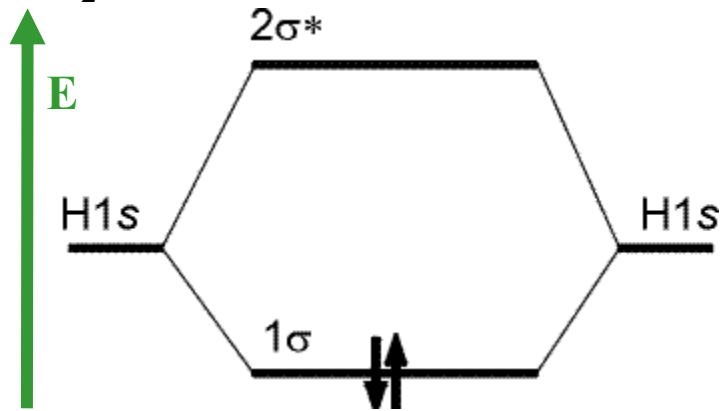
Energia di stabilizzazione

Structure of diatomic molecules

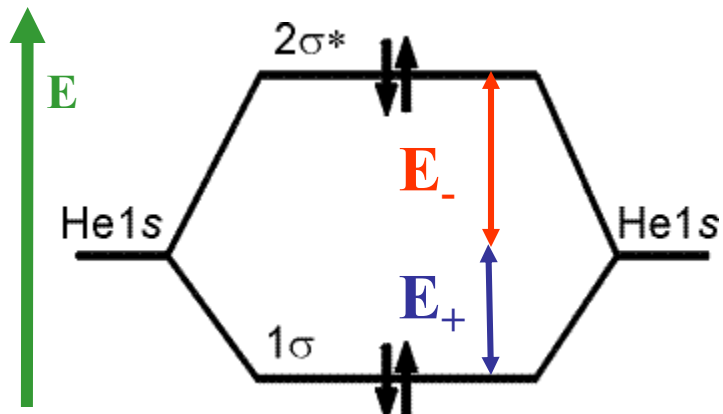
Now, we use the molecular orbitals ($\sigma = \Psi_+$ and $\sigma^* = \Psi_-$) found for the one-electron molecule $H-H^+$; in order to describe many-electron diatomic molecules.

The hydrogen and helium molecules

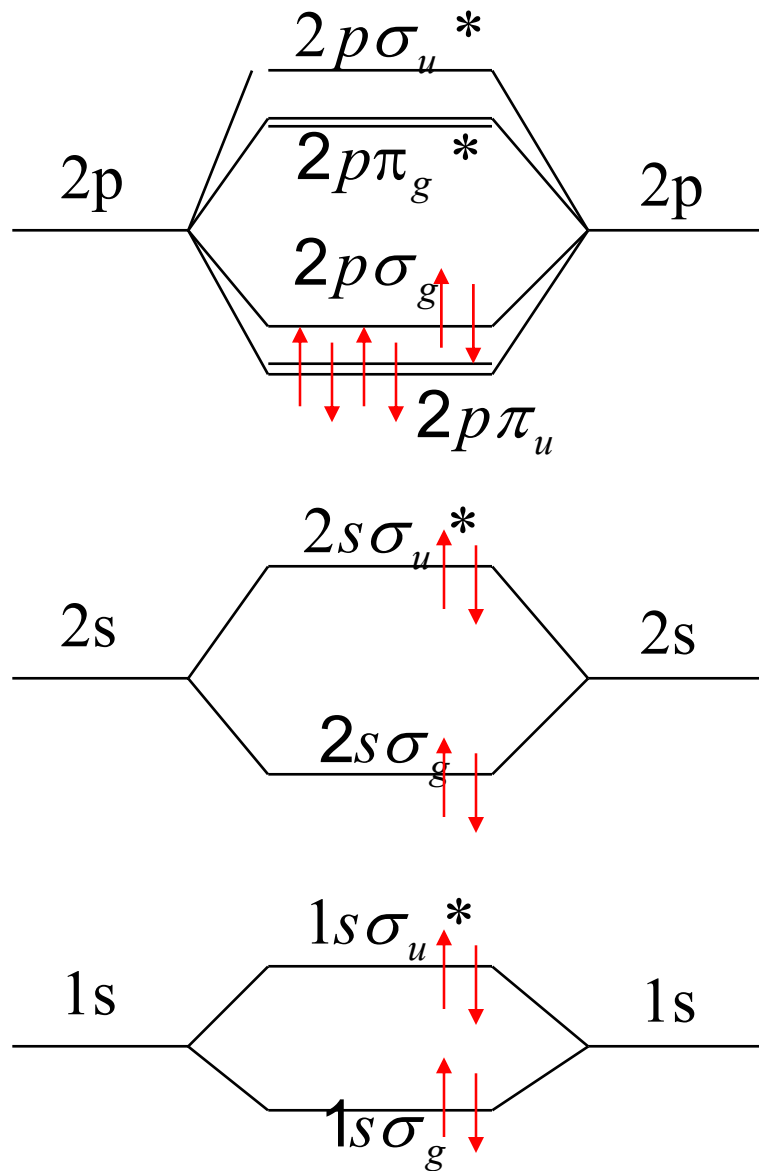
H_2 : 2 electrons \rightarrow ground-state configuration: $1\sigma^2$



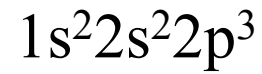
He_2 : 4 electrons \rightarrow ground-state configuration: $1\sigma^2 2\sigma^{*2}$



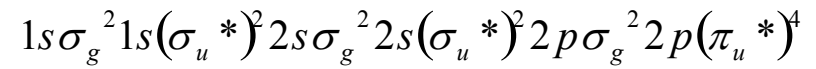
$E_+ < E_- \rightarrow He_2$ is not stable and does not exist

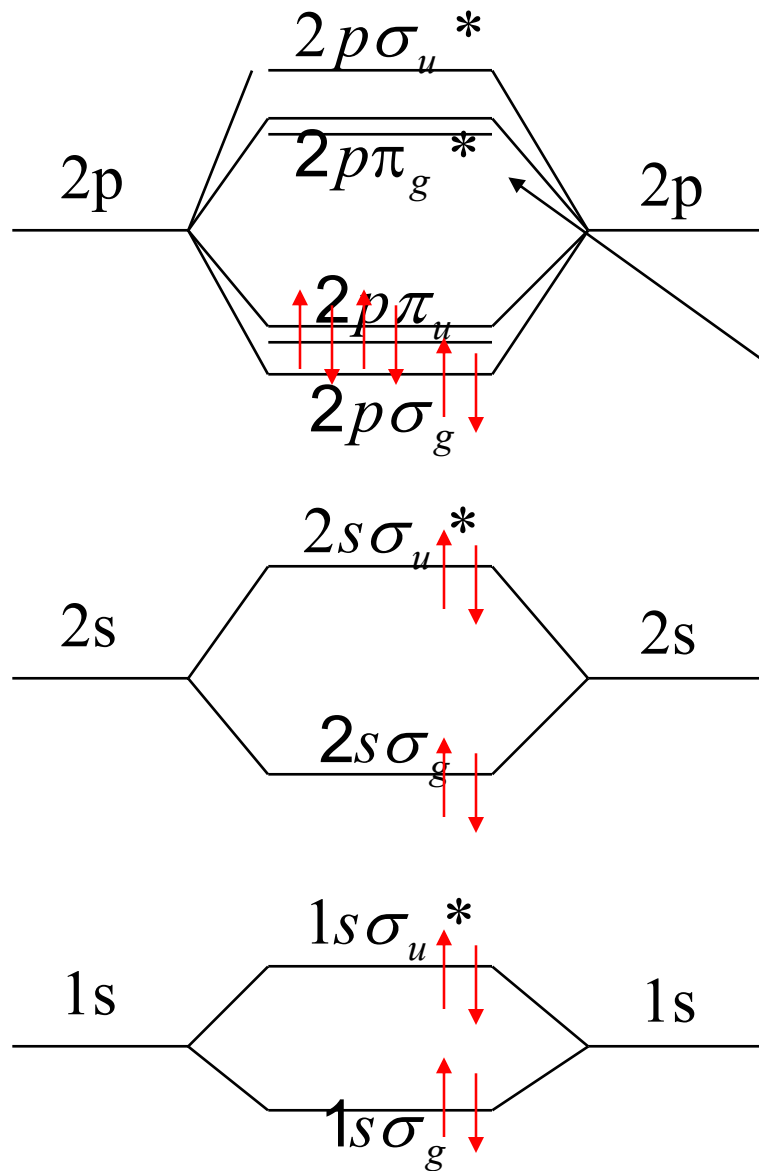


Atomo di azoto

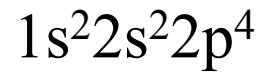


$N_2 \rightarrow 14$ elettroni

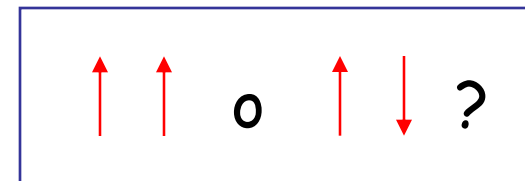




Atomo di ossigeno

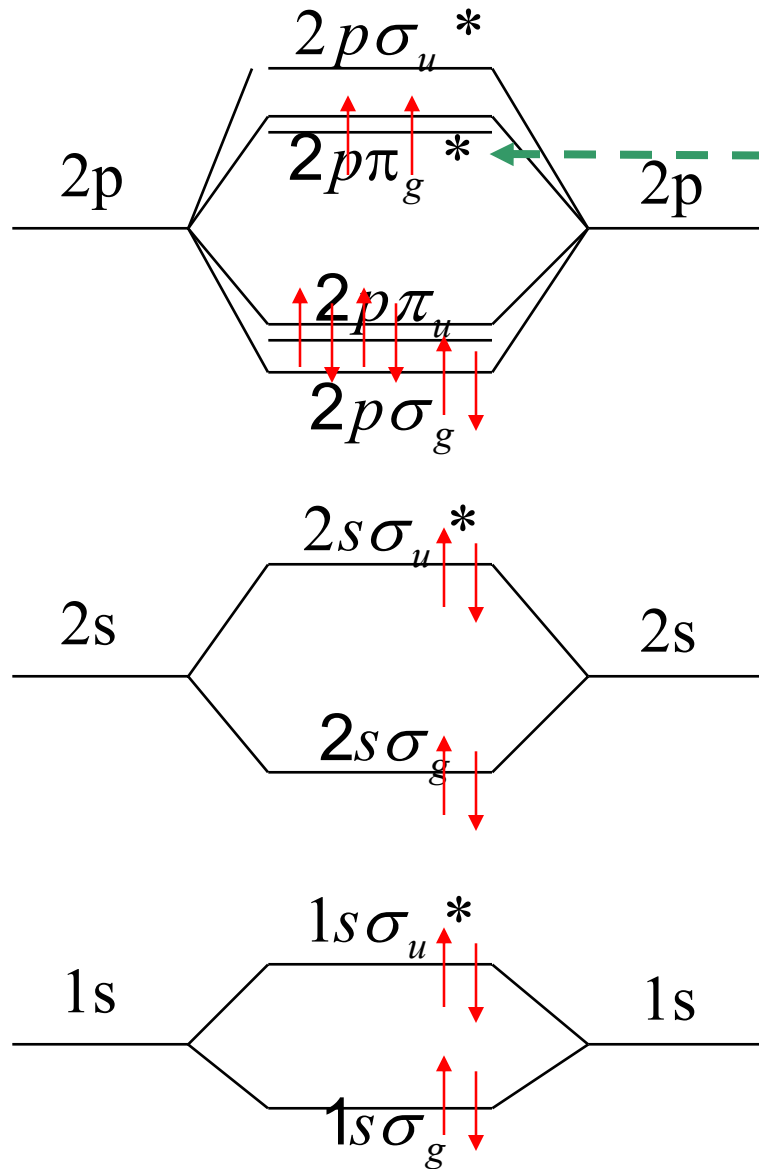


O_2 \Rightarrow 16 elettroni



- Come distribuiamo due elettroni nei due orbitali degeneri?

Atomo di ossigeno $1s^2 2s^2 2p^4$



Regola di Hund per due elettroni equivalenti

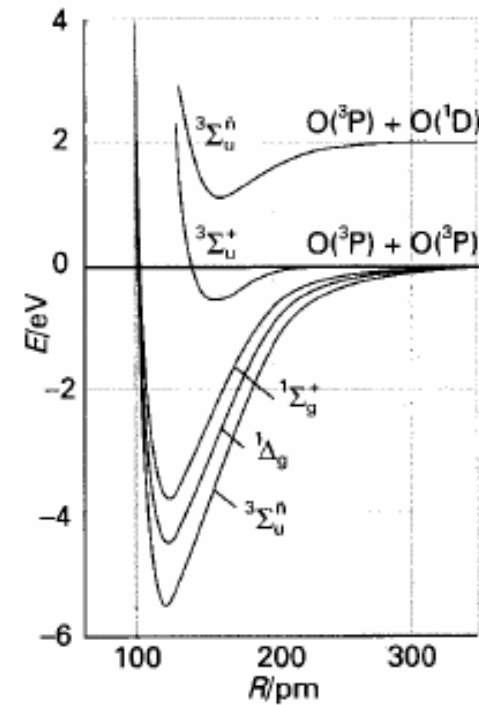
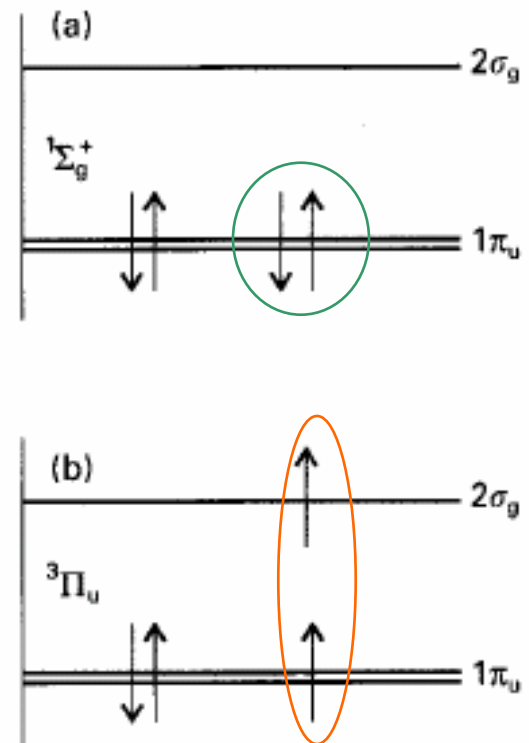
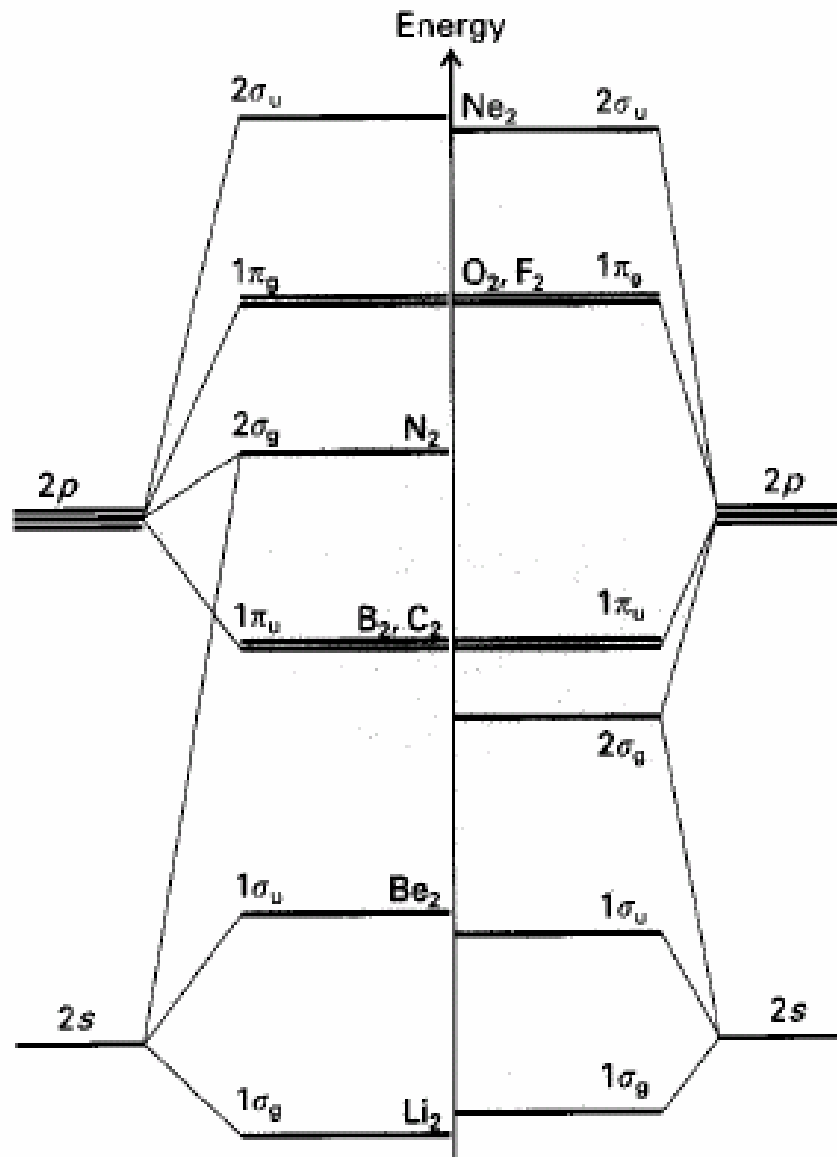


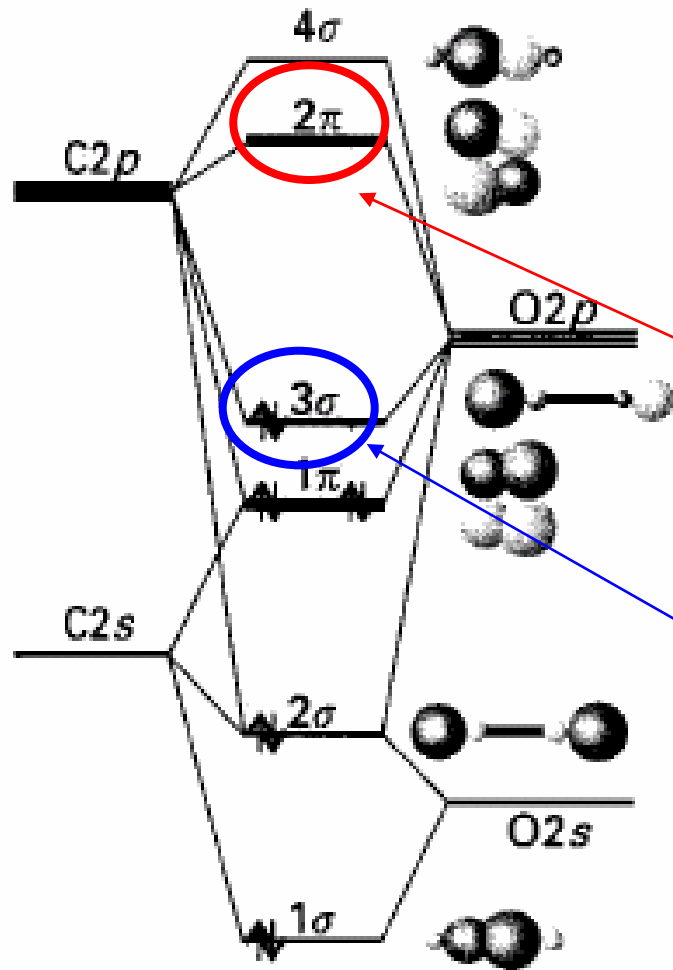
Fig. 8.19 The experimentally determined molecular potential energy curves of some of the lower energy states of dioxygen.

Stato fondamentale delle molecole biatomiche



C₂: competizione tra energia degli orbitali e correlazione di spin

Legame eteropolare: molecola di CO



Stato fondamentale



LUMO
Lowest Unoccupied
Molecular Orbital

HOMO
Highest Occupied
Molecular Orbital

Il Metodo di Huckel

Utilizzato spesso per il calcolo degli orbitali Π .

Approssimazioni ulteriori rispetto al metodo LCAO:

$$H_{ij} = \beta, \text{ se } |i-j|=1$$

$$S_{ij} = 1, \text{ se } i=j$$

$$H_{ij} = 0, \text{ altrimenti}$$

$$S_{ij} = 0, \text{ se } i \neq j$$

Inoltre definiamo $H_{ii} = \alpha$

Molecola di **butadiene**: 4 orbitali 2p sui 4 atomi di carbonio.
Pertanto la funzione d'onda di prova sar :

$$\psi = a_1 2p_1 + a_2 2p_2 + a_3 2p_3 + a_4 2p_4$$

dove i termini fuori diagonale (β) sono definiti come:

$$H_{ij} = \int (2p_i) \mathcal{H} (2p_j) d\tau.$$

molecole
 poliatomiche:
 butadiene (C₄H₆)

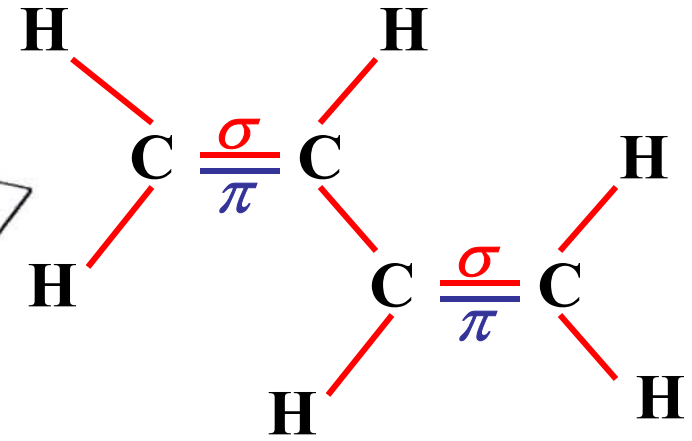
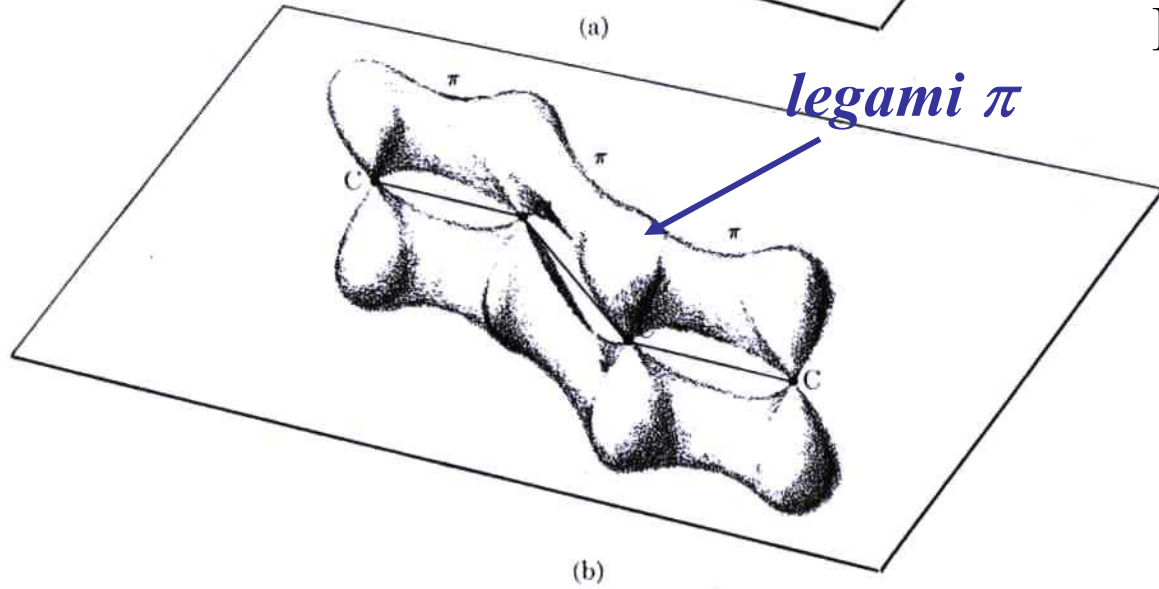
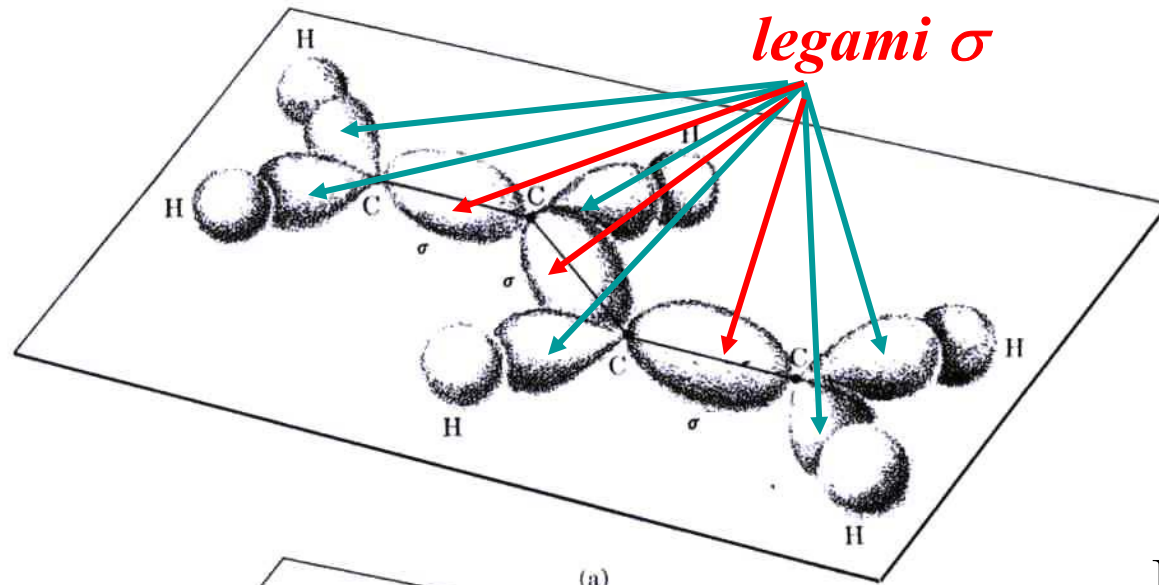
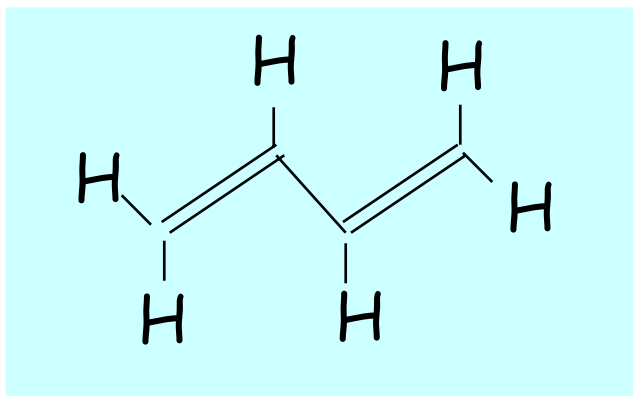
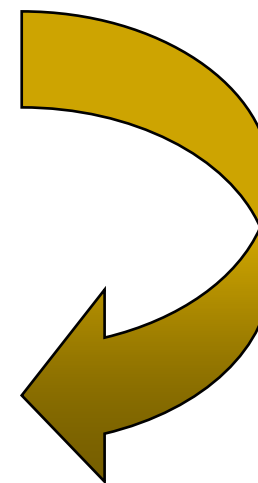


Fig. 5-24. Electronic distribution in butadiene. (a) Localized σ -bonds; (b) unlocalized π -bonds.

Nel caso della molecola di idrogeno avevamo:

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{AB} - ES & H_{BB} - E \end{vmatrix} = 0$$

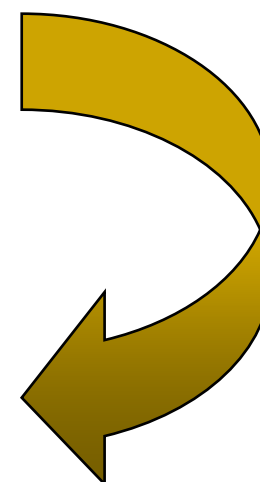
$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$



Molecola di butadiene

$H_{11}-E$	$H_{12}-ES_{12}$	$H_{13}-ES_{13}$	$H_{14}-ES_{14}$
$H_{21}-ES_{21}$	$H_{22}-E$	$H_{23}-ES_{23}$	$H_{24}-ES_{24}$
$H_{31}-ES_{31}$	$H_{32}-ES_{32}$	$H_{33}-E$	$H_{34}-ES_{34}$
$H_{41}-ES_{41}$	$H_{42}-ES_{42}$	$H_{43}-ES_{43}$	$H_{44}-E$

$\alpha-E$	β	0	0
β	$\alpha-E$	β	0
0	β	$\alpha-E$	β
0	0	β	$\alpha-E$



Diagonalizzando la matrice si ottengono i seguenti autovalori:

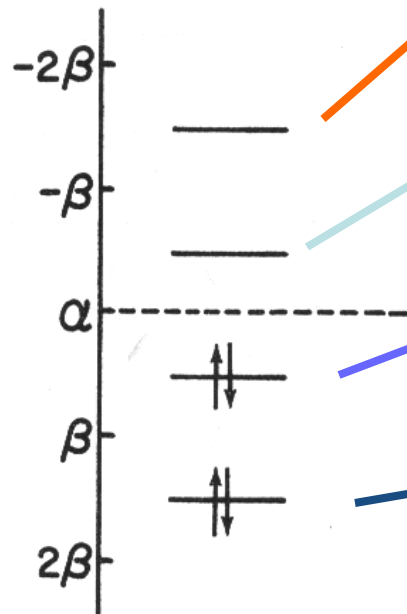
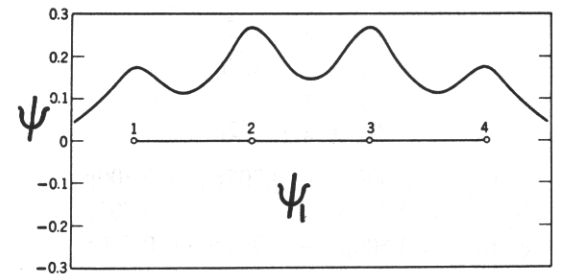
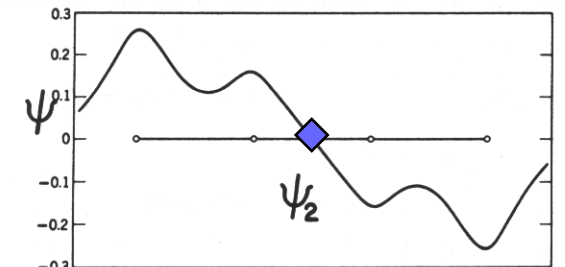
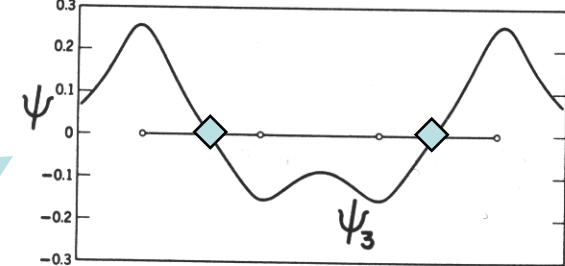
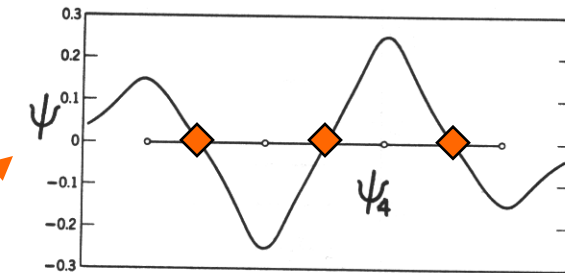
$$E_1 = \alpha + \beta \left(\frac{3 + \sqrt{5}}{2} \right)^{\frac{1}{2}} = \alpha + 1.62\beta$$

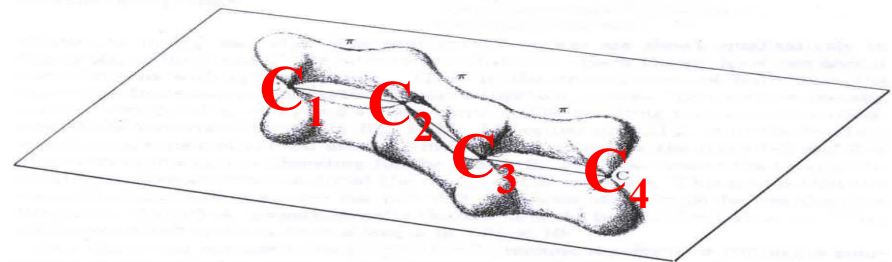
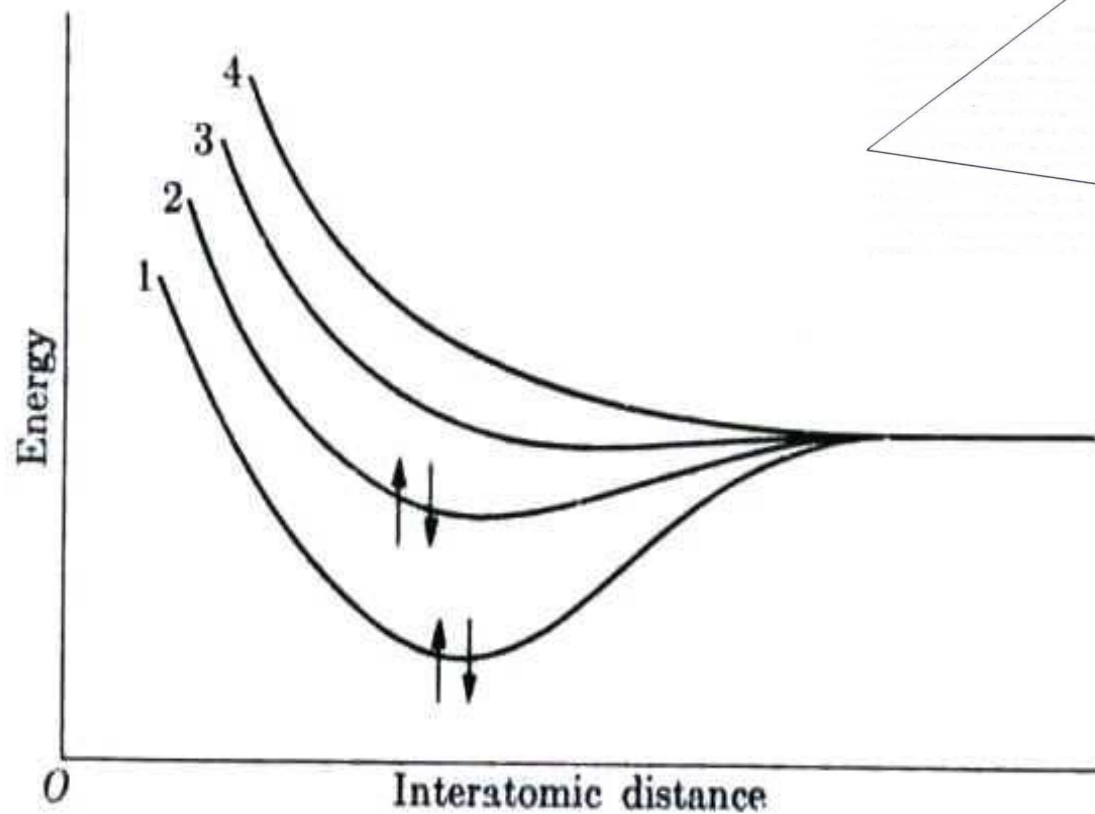
$$E_2 = \alpha + \beta \left(\frac{3 - \sqrt{5}}{2} \right)^{\frac{1}{2}} = \alpha + 0.62\beta$$

$$E_3 = \alpha - \beta \left(\frac{3 - \sqrt{5}}{2} \right)^{\frac{1}{2}} = \alpha - 0.62\beta$$

$$E_4 = \alpha - \beta \left(\frac{3 + \sqrt{5}}{2} \right)^{\frac{1}{2}} = \alpha - 1.62\beta$$

Le funzioni d'onda corrispondenti sono:





*gli orbitali π
del butadiene
in funzione
della distanza
interatomica*

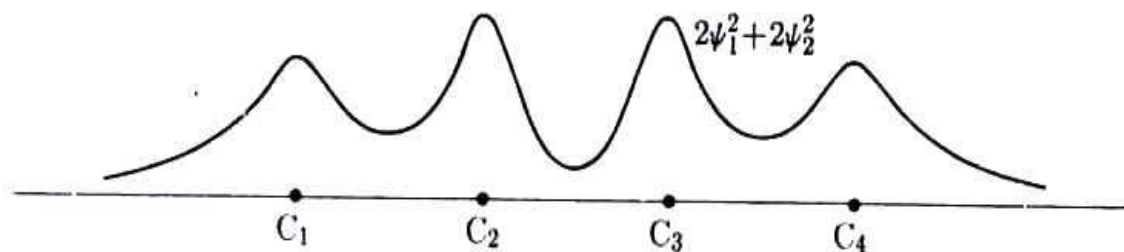


Fig. 5-27. Total probability distribution of π -electrons in butadiene.