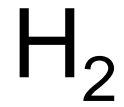
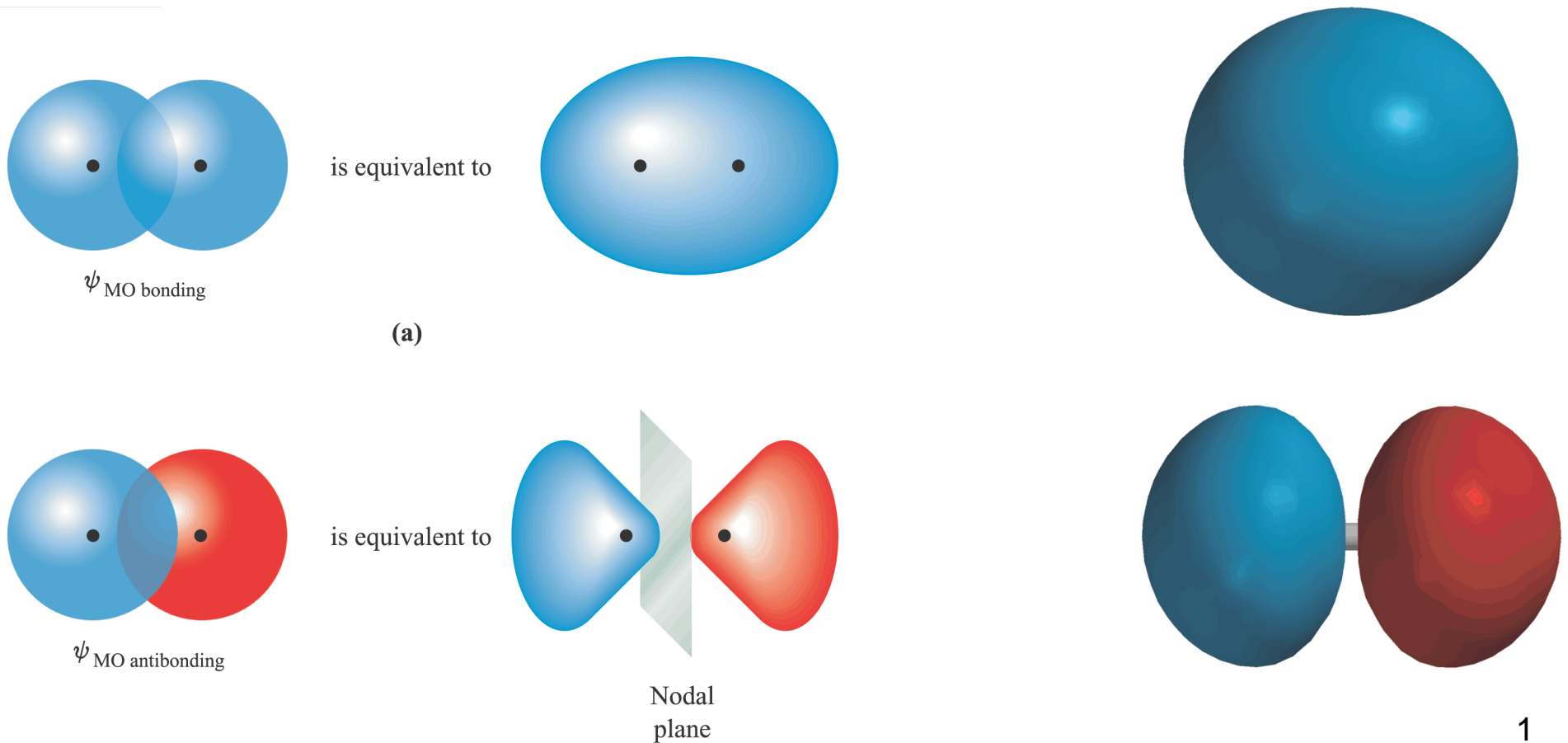


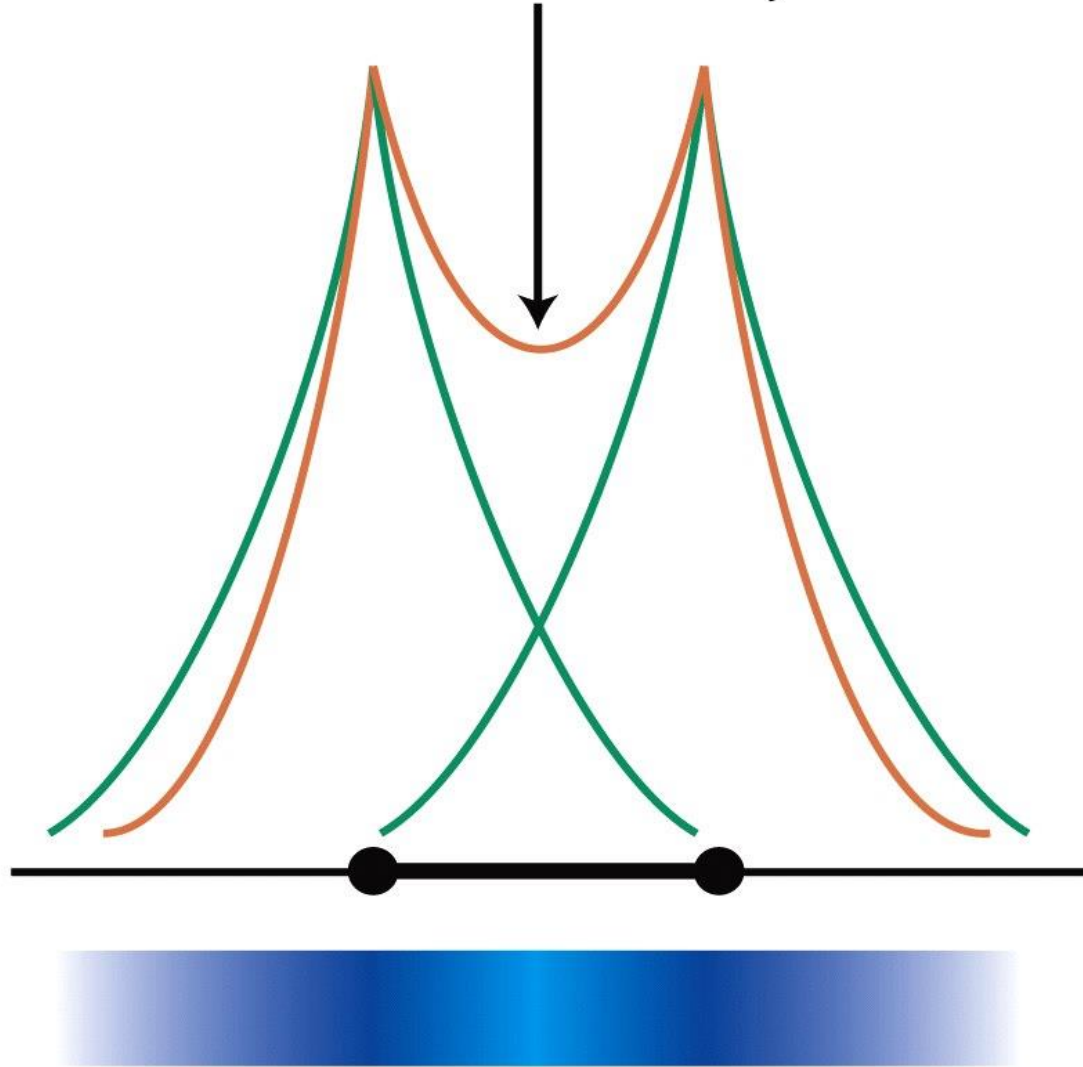
# Teoria dell'Orbitale Molecolare

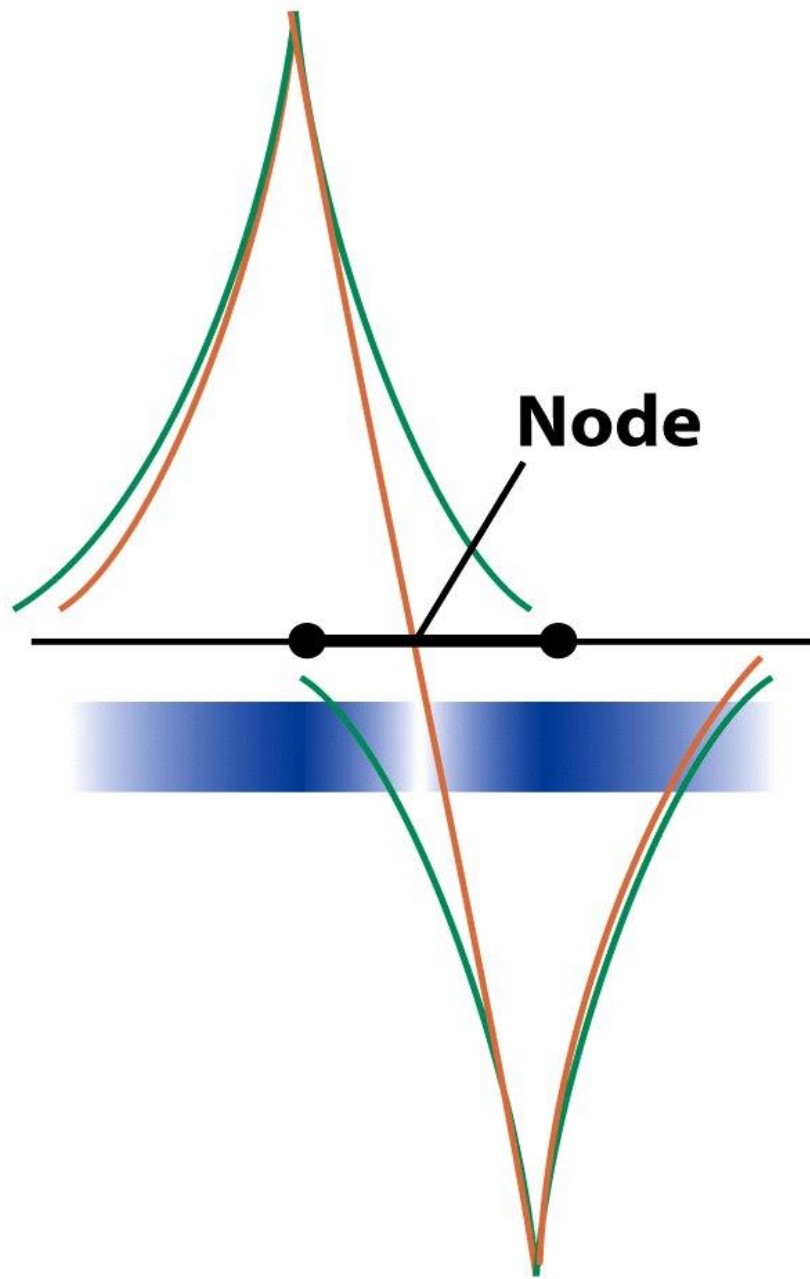


## *Linear Combination of Atomic Orbitals (LCAO)*



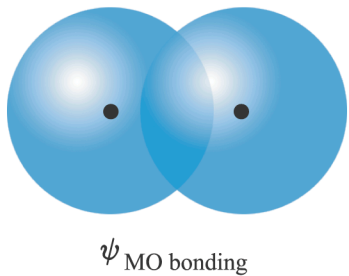
**Enhanced  
density**



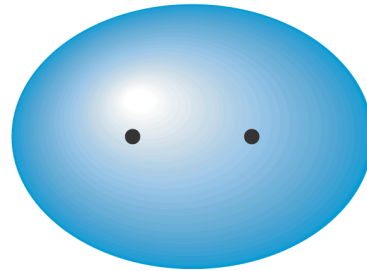


# Teoria dell'Orbitale Molecolare

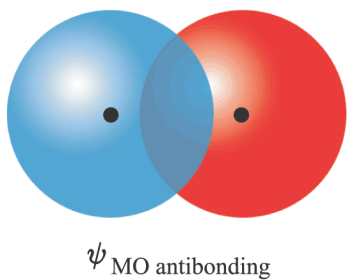
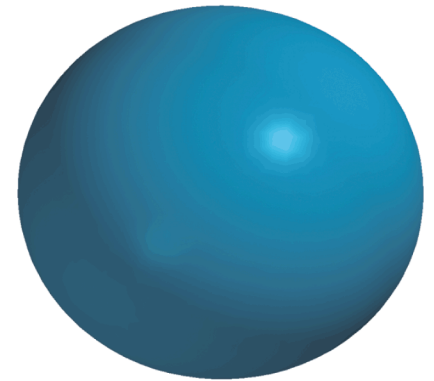
$$\Psi^2_{\text{legante}} = \Psi^2_A + \Psi^2_B + 2\Psi_A\Psi_B$$



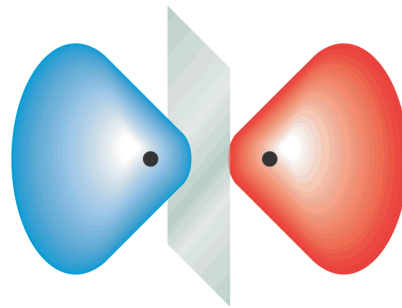
is equivalent to



(a)



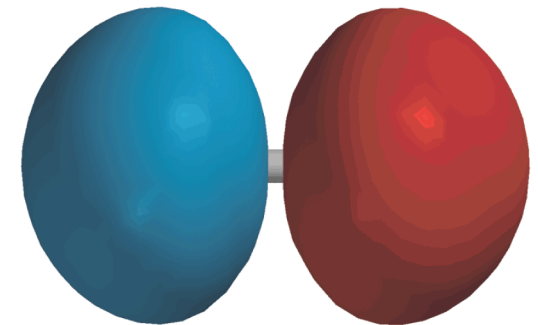
is equivalent to



(b)

$$\Psi^2_{\text{antilegante}} = \Psi^2_A + \Psi^2_B - 2\Psi_A\Psi_B$$

(c)



$$\int \Psi_A \Psi_B d\tau = \text{integrale di sovrapposizione } S$$

$S > 0$  orbitale legante

$S < 0$  orbitale antilegante

$S = 0$  orbitale di nonlegame

$$\int N_b^2 \Psi^2 d\tau = N_b^2 [\int \Psi_A^2 d\tau + \int \Psi_B^2 d\tau + 2\int \Psi_A \Psi_B d\tau] = 1$$

$N_b$  è la **costante di normalizzazione** per l'orbitale legante

$$N_b^2 [1 + 1 + 2S] = 1$$

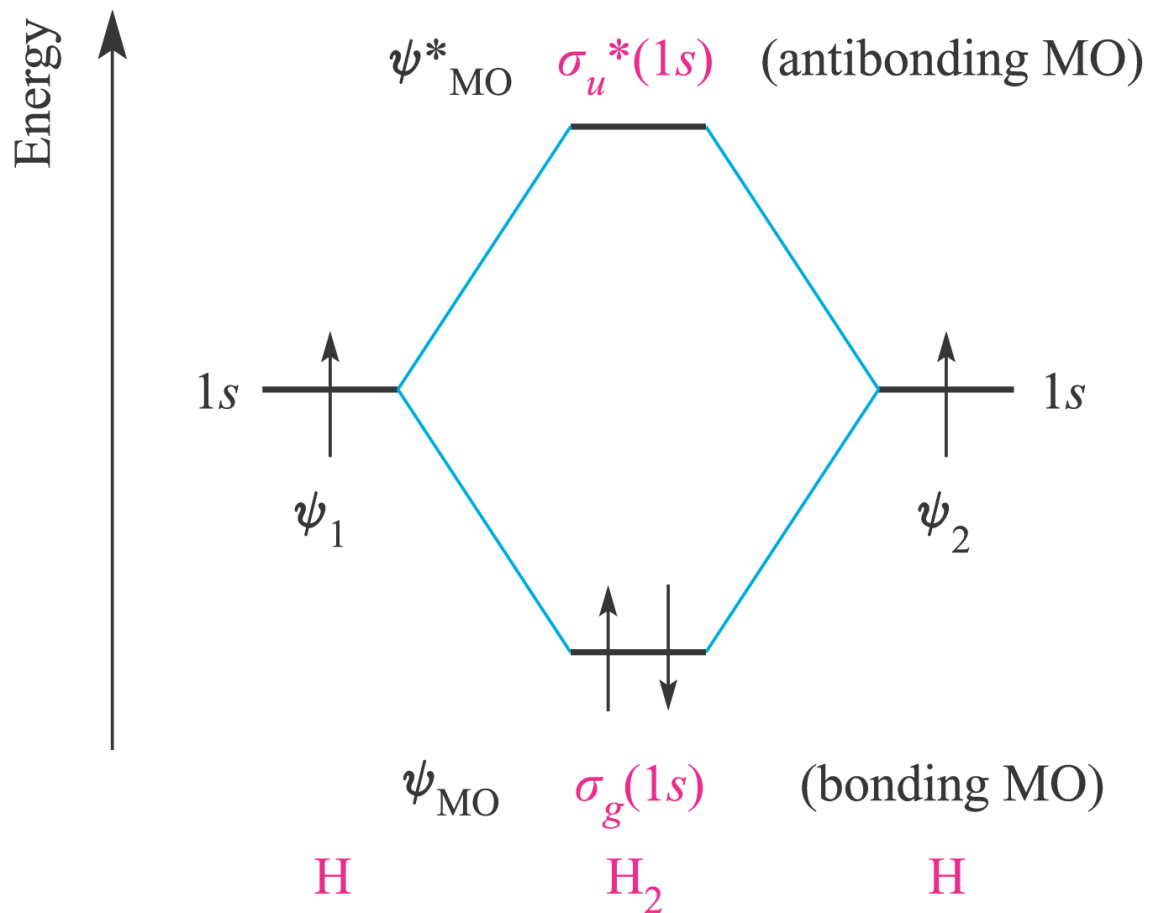
$$N_b = \sqrt{1/(2 + 2S)}$$

$$N_a = \sqrt{1/(2 - 2S)}$$

$N_a$  è la **costante di normalizzazione** per l'orbitale antilegante

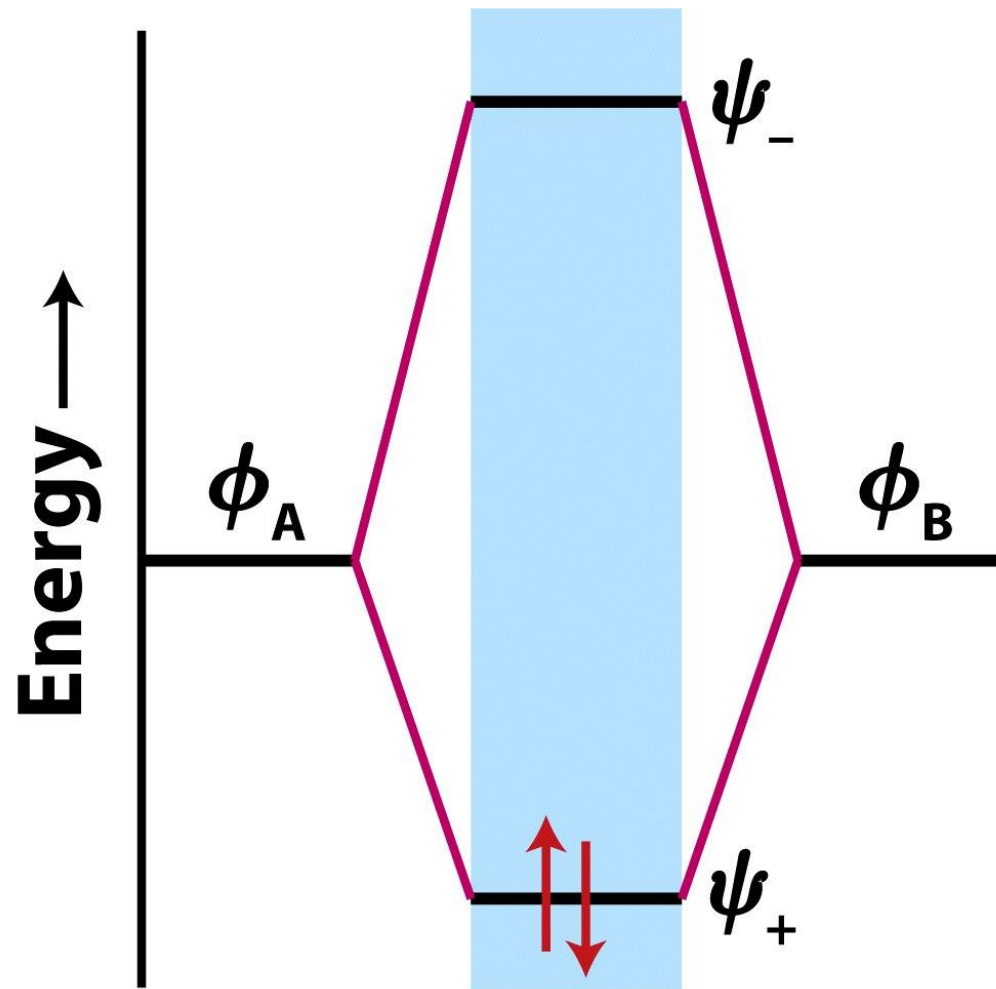
Trascurando l'integrale di sovrapposizione  $S$

$$N_b = N_a = \sqrt{1/2} = 0.71$$

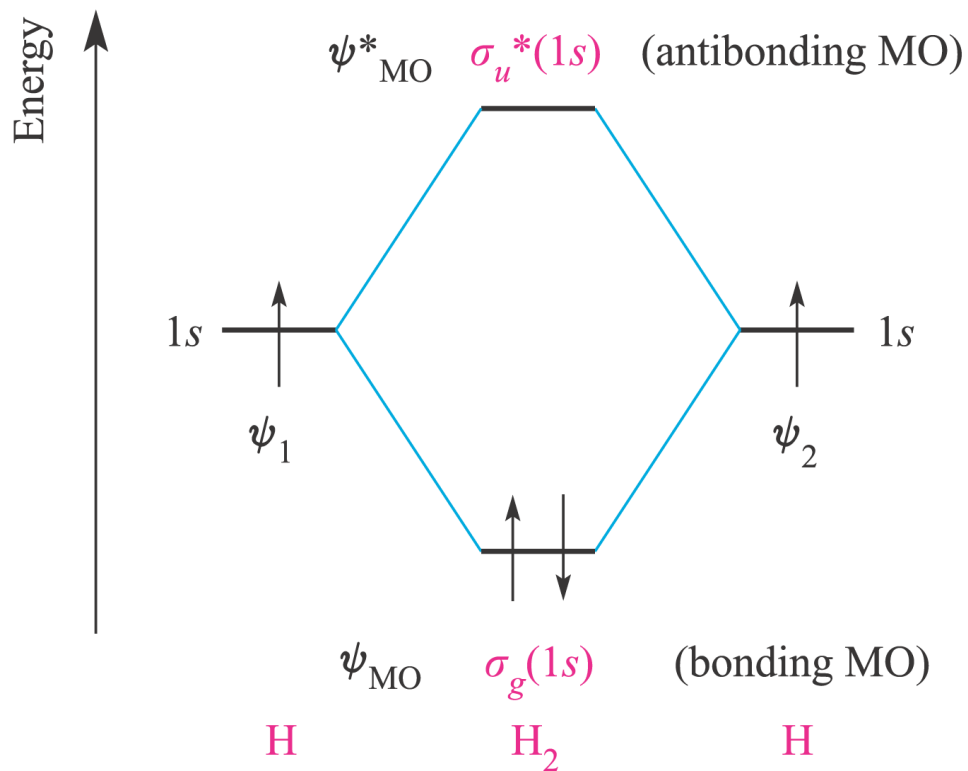


Considerando l'integrale di sovrapposizione  $S$

$$N_b < N_a$$

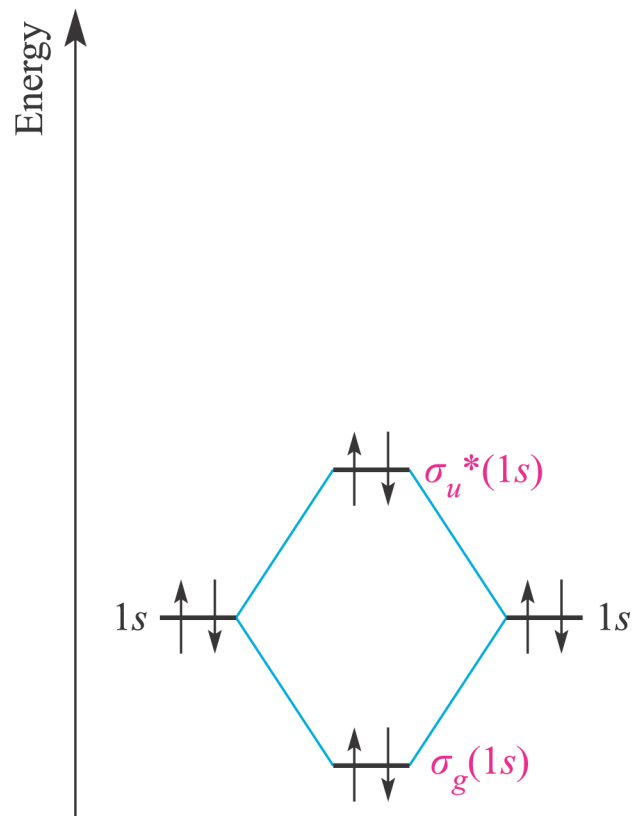


$$\text{ordine di legame} = \frac{1}{2}(n \cdot e_B - n \cdot e_{AB})$$



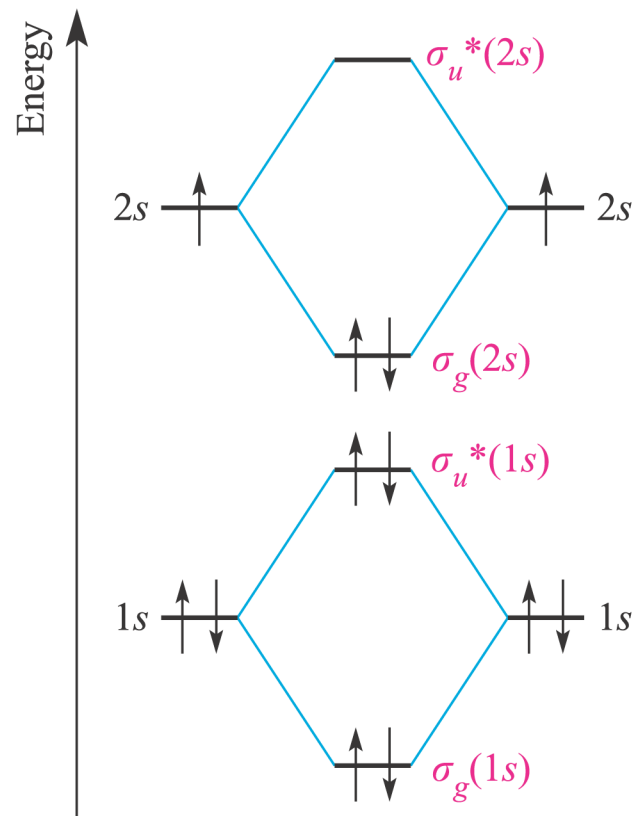
Molecola	Ordine di legame	Energia legame (kJ/mol)	Lunghezza legame (pm)
$H_2$	1	458	74
$H_2^+$	0.5	269	105





He    He<sub>2</sub>    He

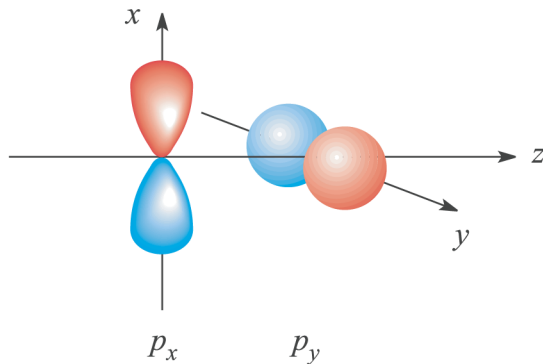
(a)



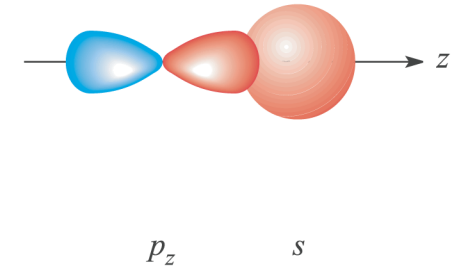
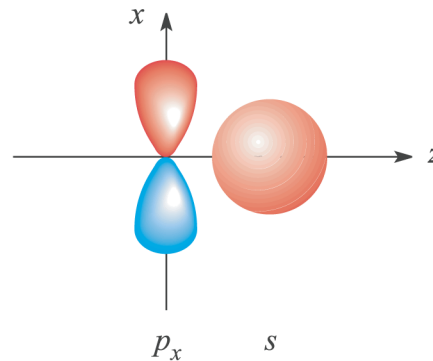
Li    Li<sub>2</sub>    Li

(b)

## Interazioni di non-legame

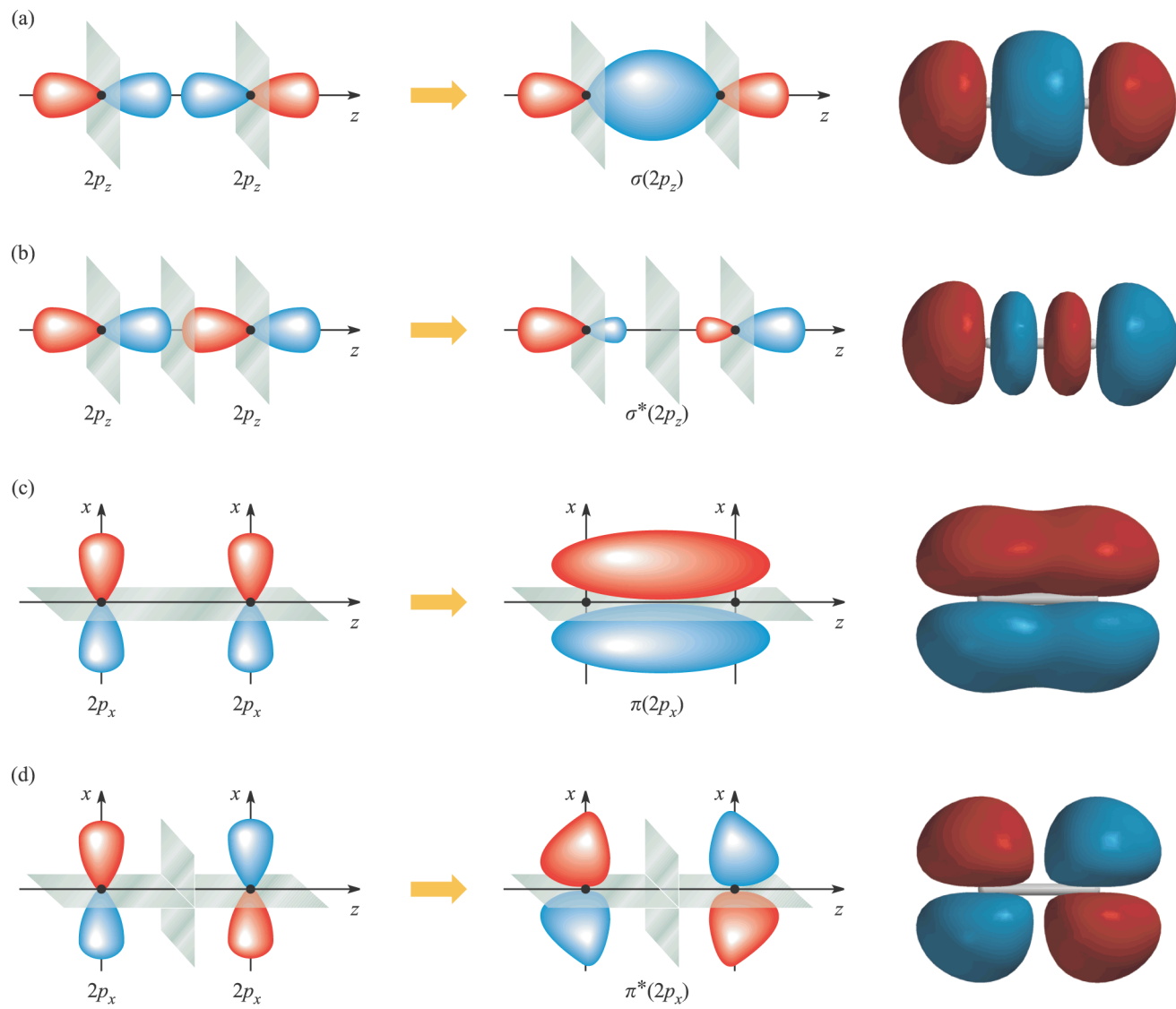


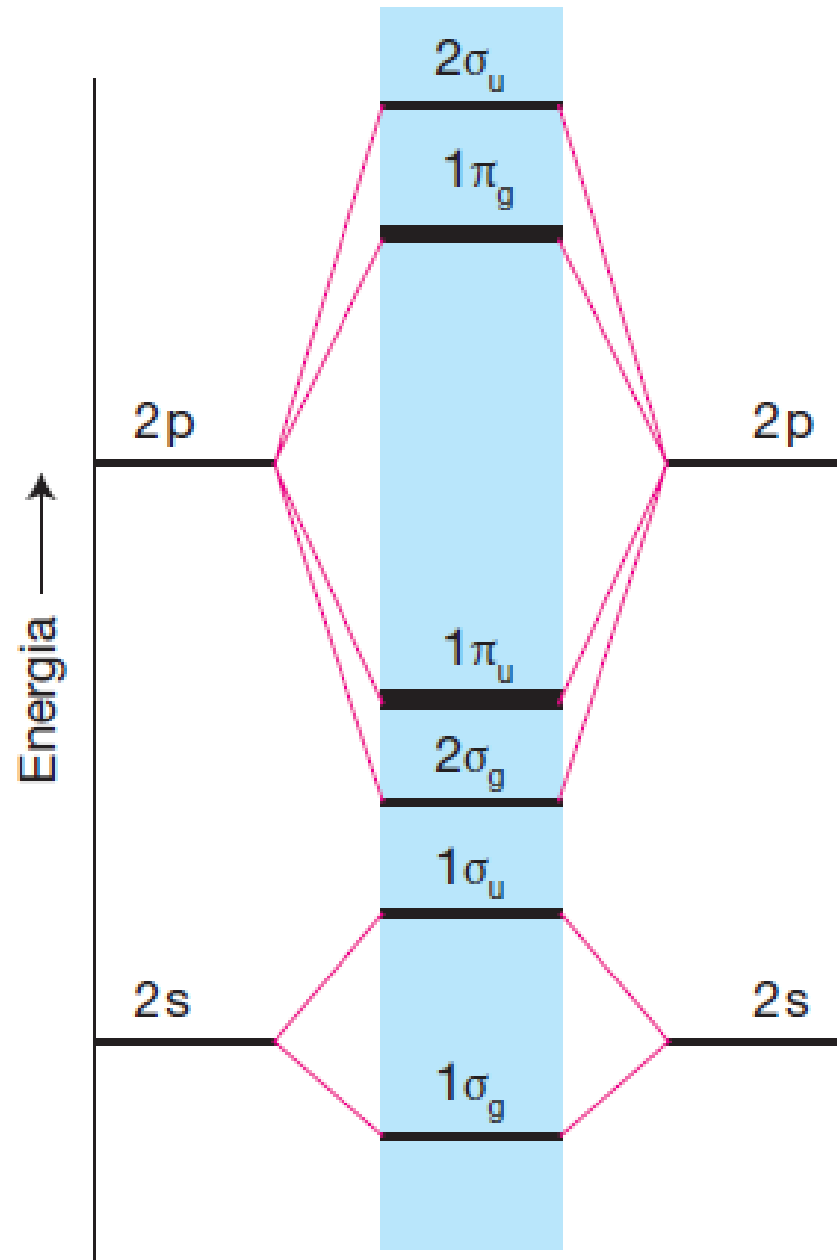
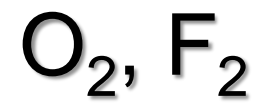
## Interazione di legame



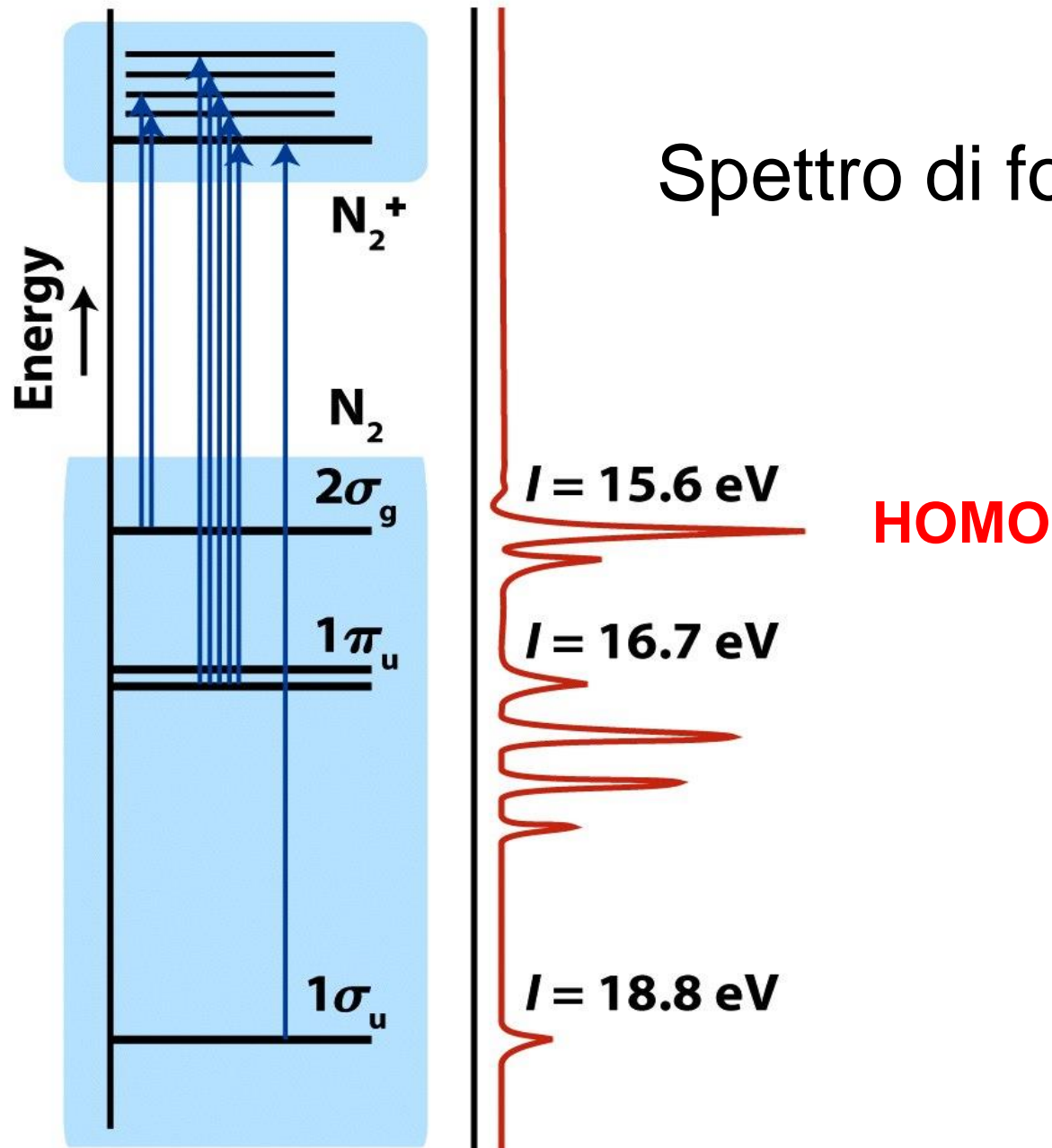
le interazioni tra gli orbitali atomici per dare orbitali molecolari sono:

- **permesse** se le simmetrie degli orbitali atomici sono fra loro compatibili;
- **efficaci** se la regione di sovrapposizione fra gli orbitali atomici è significativa;
- **efficaci** se gli orbitali atomici sono relativamente vicini in energia.

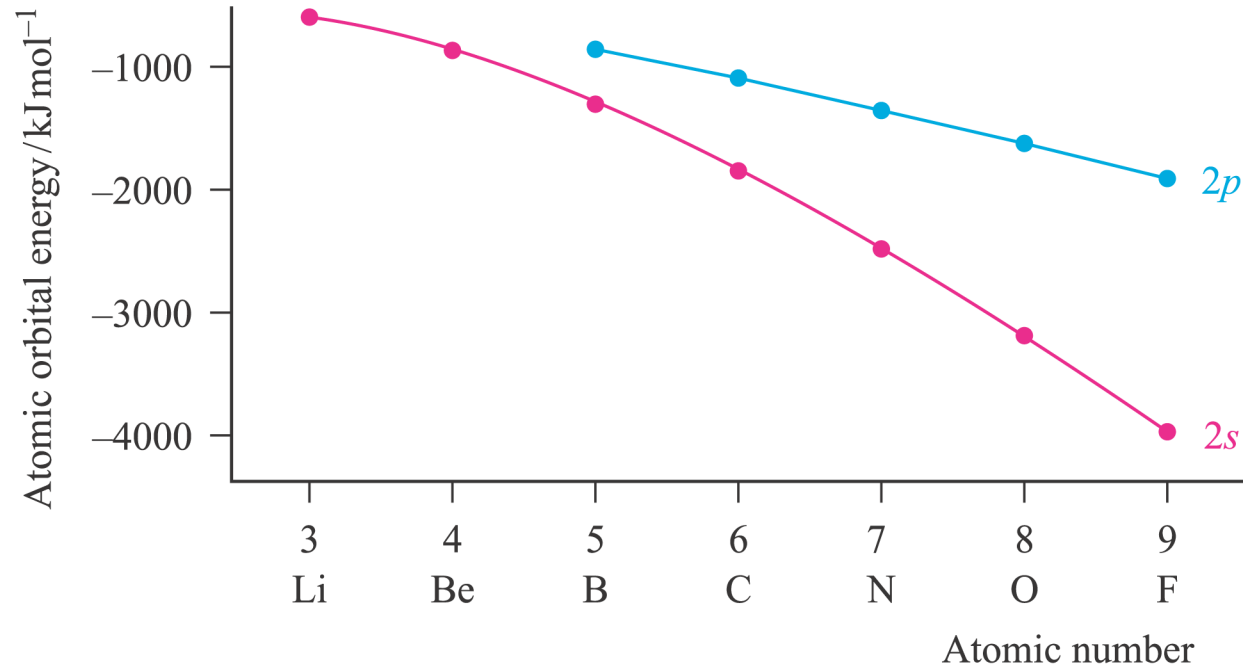




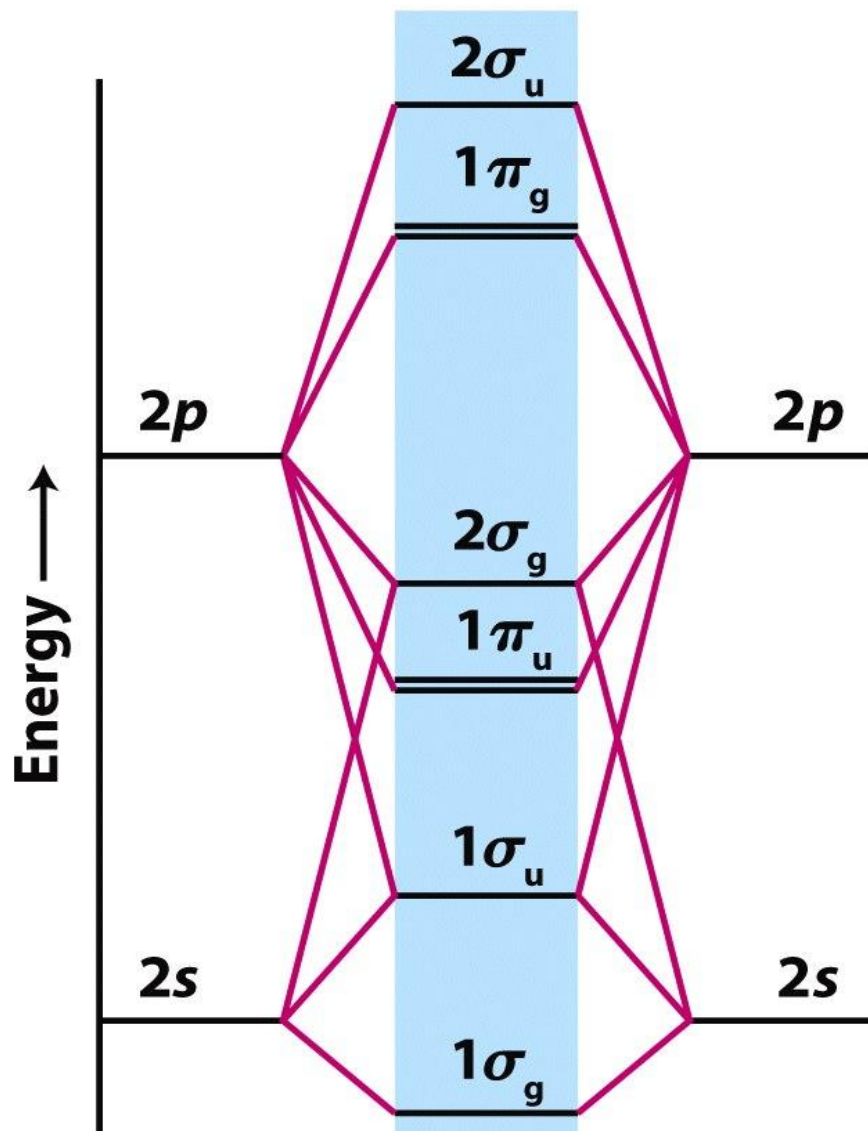
# Spettro di fotoelettroni di $N_2$



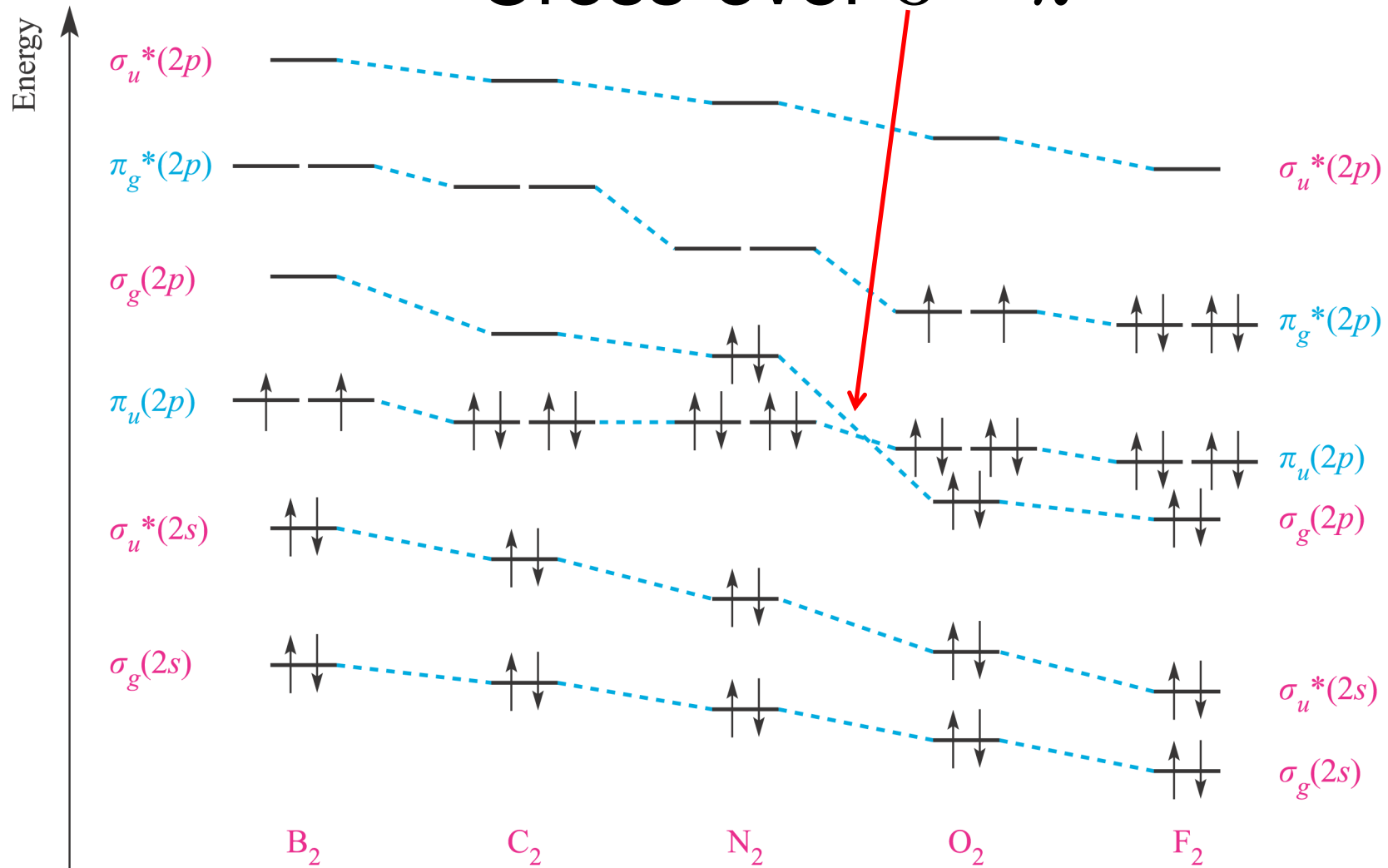
# Energia degli orbitali atomici 2s e 2p in funzione di $Z$



# $B_2, C_2, N_2$



# Cross-over $\sigma - \pi$





Diatomic	Bond distance / pm	Bond dissociation enthalpy / $\text{kJ mol}^{-1}$	Bond order	Magnetic properties
$\text{Li}_2$	267	110	1	Diamagnetic
$\text{Be}_2^\dagger$	—	—	0	—
$\text{B}_2$	159	297	1	Paramagnetic
$\text{C}_2$	124	607	2	Diamagnetic
$\text{N}_2$	110	945	3	Diamagnetic
$\text{O}_2$	121	498	2	Paramagnetic
$\text{F}_2$	141	159	1	Diamagnetic

Molecola	Energia di ionizzazione (kJ mol <sup>-1</sup> )
O <sub>2</sub>	1164
N <sub>2</sub>	1503

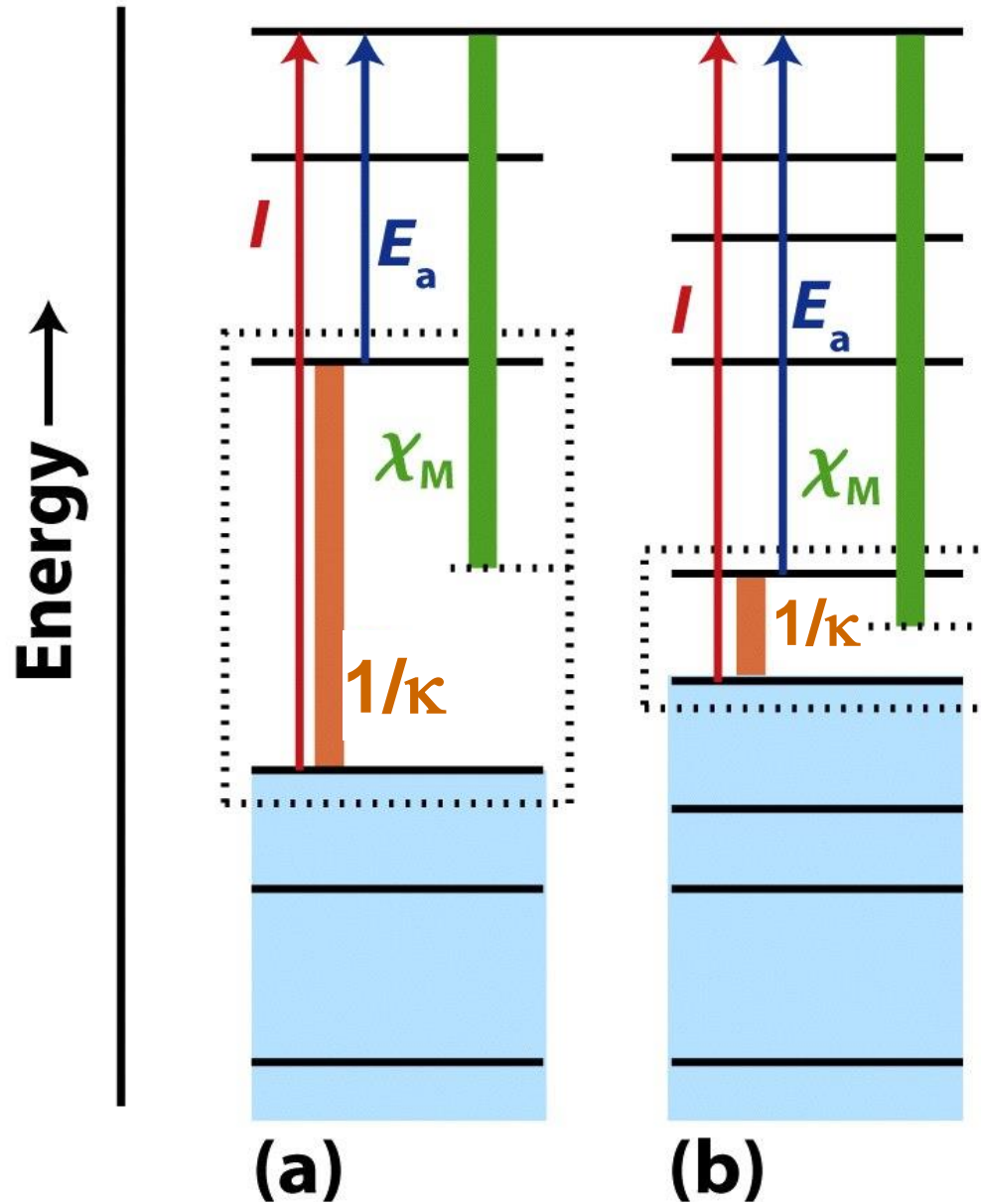
Molecola	Ordine di legame	Lunghezza di legame (pm)
O <sub>2</sub>	2	121
O <sub>2</sub> <sup>-</sup>	1.5	126
O <sub>2</sub> <sup>2-</sup>	1	149
O <sub>2</sub> <sup>+</sup>	2.5	112

Au<sub>2</sub>(g) (221 kJ/mol)

## Elettronegatività di Pauling, $\chi^P$

Group 1	Group 2		Group 13	Group 14	Group 15	Group 16	Group 17
H 2.2							
Li 1.0	Be 1.6		B 2.0	C 2.6	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3		Al(III) 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8	Ca 1.0	<i>(d-block elements)</i>	Ga(III) 1.8	Ge(IV) 2.0	As(III) 2.2	Se 2.6	Br 3.0
Rb 0.8	Sr 0.9		In(III) 1.8	Sn(II) 1.8 Sn(IV) 2.0	Sb 2.1	Te 2.1	I 2.7
Cs 0.8	Ba 0.9		Tl(I) 1.6 Tl(III) 2.0	Pb(II) 1.9 Pb(IV) 2.3	Bi 2.0	Po 2.0	At 2.2

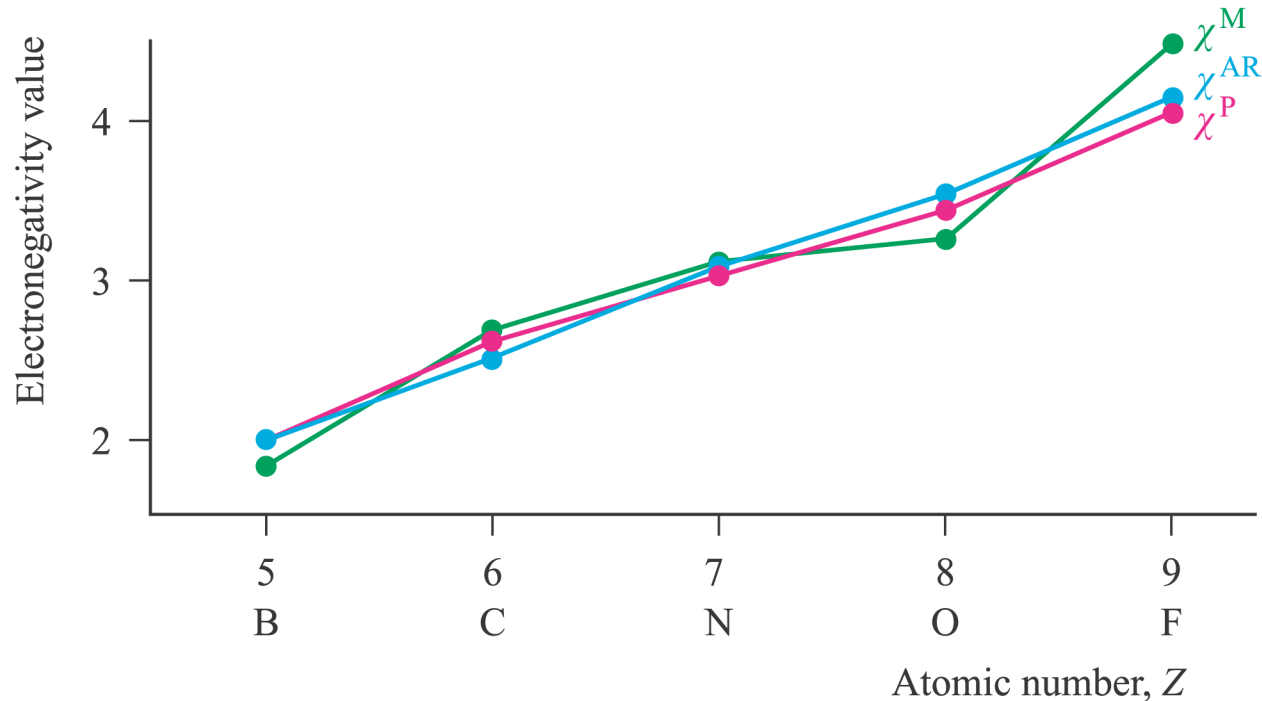
# Ionization limit



Elettronegatività di Mulliken,  $\chi^M$

$$\chi^M = \frac{1}{2}(I_v + E a_v)$$

$$\chi^{AR} = (3590 \times Z_{\text{eff}}/r_{\text{cov}}^2) + 0.744$$



$\chi^M$  = Mulliken (v = stato di valenza)

$\chi^{AR}$  = Allred e Rochow (elettronegatività = forza elettrostatica esercitata dal nucleo sugli elettroni di valenza)

Dipendenza di  $\chi^M$  da carica parziale  $\delta$  e ibridizzazione

$\chi = a + b\delta$  **equazione di Mulliken-Jaffè** (b = coefficiente di carica)  
 $b = 1/\kappa$  ( $\kappa$  = capacità di carica o **polarizzabilità**)

orbitali ibridi aventi maggiore carattere s sono più elettronegativi

	Ibridizzazione C	$\chi^M$
HC≡CH	sp (50% s)	2.99
CH <sub>4</sub>	sp <sup>3</sup> (25% s)	2.48

	Ibridizzazione N	$\chi^M$	pK <sub>b</sub>
Me <sub>3</sub> N	sp <sup>3</sup> (25% s)	3.04	4.2
C <sub>5</sub> H <sub>5</sub> N	sp <sup>2</sup> (33% s)	3.26	8.8

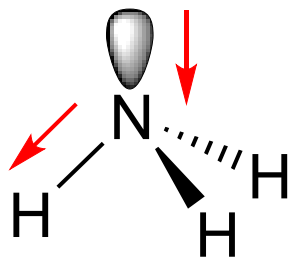
Tabella 5.6. Elettronegatività degli elementi.

Elemento	Mulliken-Jaffe, $\chi_{MJ}^a$							
	Pauling $\chi_P^b$	Sanderson $\chi_S^c$	Allred Rochow $\chi_{AR}^d$	Allen $\chi_{AM}^e$	Orbitale o ibrido	a		Volt/ elettrone
						Scala di Pauling <sup>f</sup>	Volt	
1. H	2.20	2.59	2.20	2.30	s	2.25	7.17	12.84
2. He			5.50 <sup>g</sup>		s	3.49 <sup>h</sup>	12.98 <sup>i</sup>	23.22
						4.86 <sup>j</sup>	15.08 <sup>k</sup>	
3. Li	0.98	0.89	0.97	0.91	s	0.97	3.00	4.77
4. Be	1.57	1.81	1.47	1.58	sp	1.54	4.65	6.58
5. B	2.04	2.28	2.01	2.05	sp <sup>2</sup>	2.04	6.37	8.74
					sp <sup>3</sup>	1.90	5.86	8.64
6. C	2.55	2.75	2.50	2.54	sp	2.59	10.42	11.70
					sp <sup>2</sup>	2.66	8.91	11.50
					sp <sup>3</sup>	2.43	8.15	11.39
7. N	3.04	3.19	3.07	3.07	sp	3.63	14.00	13.32
					sp <sup>2</sup>	3.26	11.78	13.22
					sp <sup>3</sup>	3.04	10.66	13.16
					20% <sub>s</sub>	2.90	10.00	13.13
					p	2.28	7.32	13.00
8. O	3.44	3.65	3.50	3.61	sp <sup>2</sup>	3.94	15.48	15.62
					sp <sup>3</sup>	3.68	14.02	15.55
					17% <sub>s</sub>	3.41	12.55	15.47
					p	2.82	9.63	15.33
9. F	3.98	4.00	4.10	4.19	sp <sup>3</sup>	4.30	17.63	17.99
					14% <sub>s</sub>	3.91	15.30	17.81
					p	3.35	12.20	17.57
10. Ne		4.50 <sup>l</sup>	4.84 <sup>l</sup>	4.79	sp <sup>3</sup>	4.49	18.86	18.92
					12% <sub>s</sub>	3.98	15.71	18.50
					p	3.41 <sup>m</sup>	12.56 <sup>n</sup>	18.08
						4.26 <sup>o</sup>	13.29 <sup>p</sup>	—
11. Na	0.93	0.56 <sup>q</sup>	1.01	0.87	s	0.91	2.84	4.59
12. Mg	1.31	1.32	1.23	1.29	sp	1.37	4.31	5.27
13. Al(I)		0.84			p	0.91	2.86	6.23
Al(III)	1.61	1.71	1.47	1.61	sp <sup>2</sup>	1.83	5.61	6.12
					sp <sup>3</sup>	1.71	5.21	5.92
14. Si	1.90	2.14 <sup>r</sup>	1.74	1.92	sp <sup>3</sup>	2.28	7.30	7.13
15. P	2.19	2.52	2.06	2.25	sp <sup>3</sup>	2.41	7.84	9.53
					20% <sub>s</sub>	2.30	7.41	9.30
					p	1.84	5.67	8.83
16. S	2.58	2.96	2.44	2.59	sp <sup>3</sup>	2.86	9.84	10.36
				v <sup>s</sup>	17% <sub>s</sub>	2.69	9.04	10.20
					p	2.31	7.44	10.12
17. Cl	3.16	3.44	2.83	2.87	14% <sub>s</sub>	3.10	12.15	11.55
					p	2.76	10.95	11.40
18. Ar		3.31 <sup>t</sup>	3.20 <sup>t</sup>	3.24	sp <sup>3</sup>	3.49	12.98	12.38
					12% <sub>s</sub>	3.19	11.41	12.18
					p	2.85 <sup>u</sup>	9.83 <sup>v</sup>	11.98
						3.11 <sup>w</sup>	9.87 <sup>x</sup>	—
19. K	0.82	0.45	0.91	0.73	s	0.73	2.42	3.84
20. Ca	1.00	0.95	1.04	1.03	sp	1.08	3.29	3.08

# momento di dipolo elettrico $\mu$

$$\mu = q \times e \times d$$

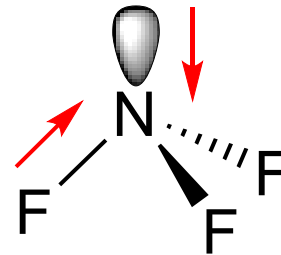
$$1\text{D} = 3.336 \times 10^{-30} \text{ C}\times\text{m}$$



$$\chi_{\text{N}} = 3.0$$

$$\chi_{\text{H}} = 2.2$$

1.47 D

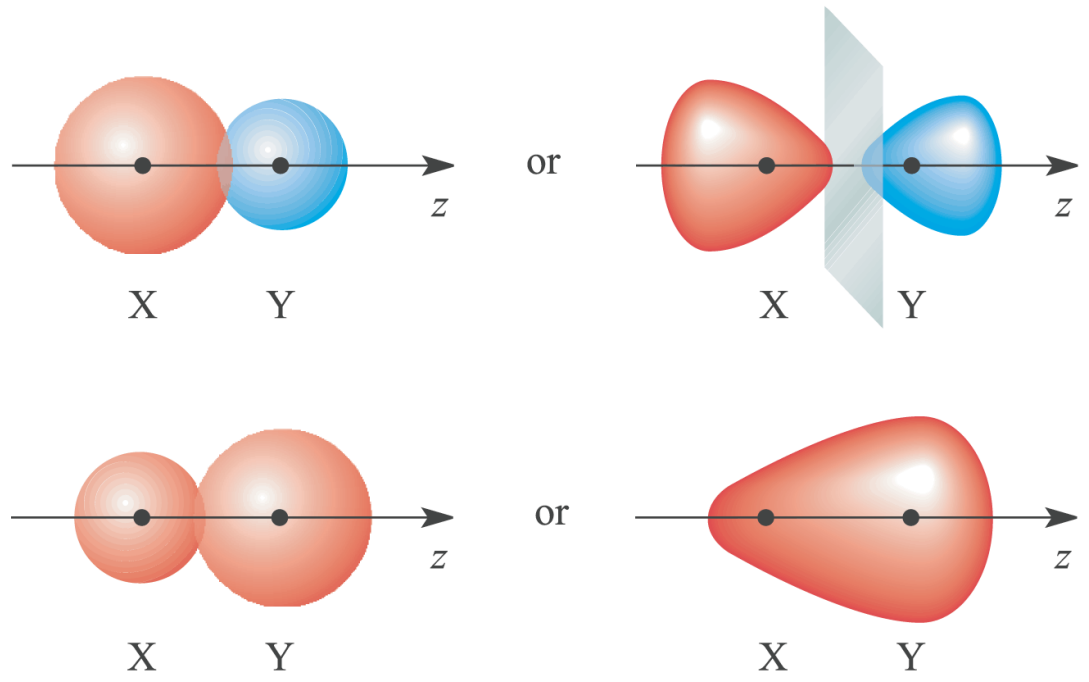
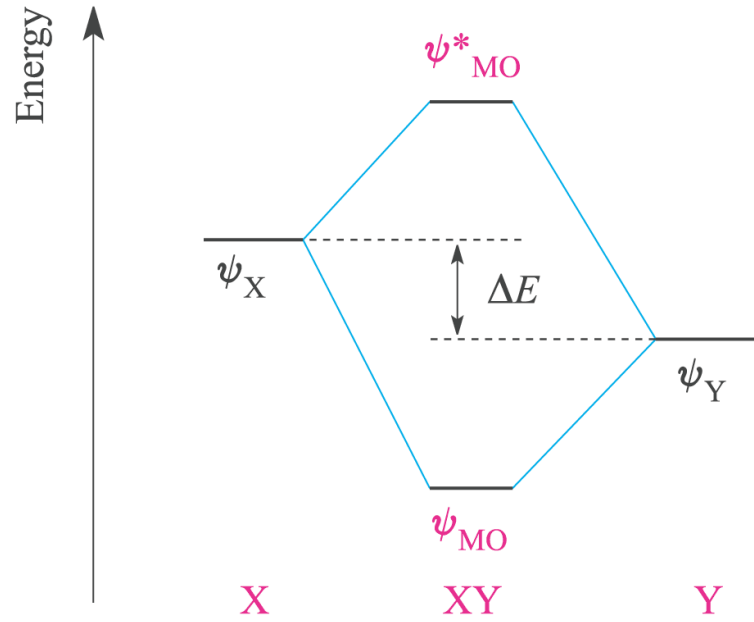


$$\chi_{\text{N}} = 3.0$$

$$\chi_{\text{F}} = 4.0$$

0.24 D

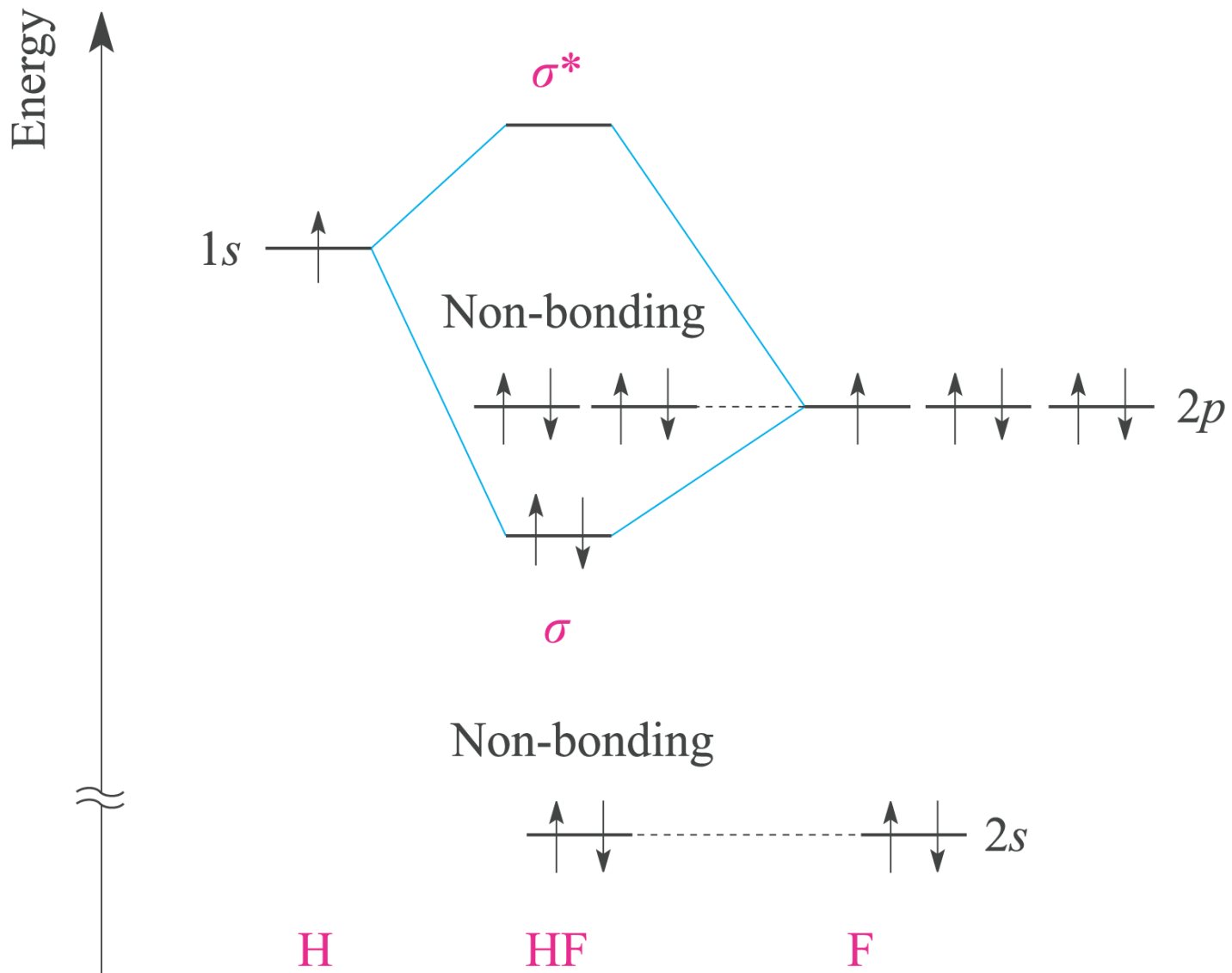




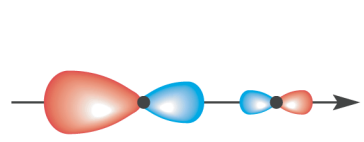
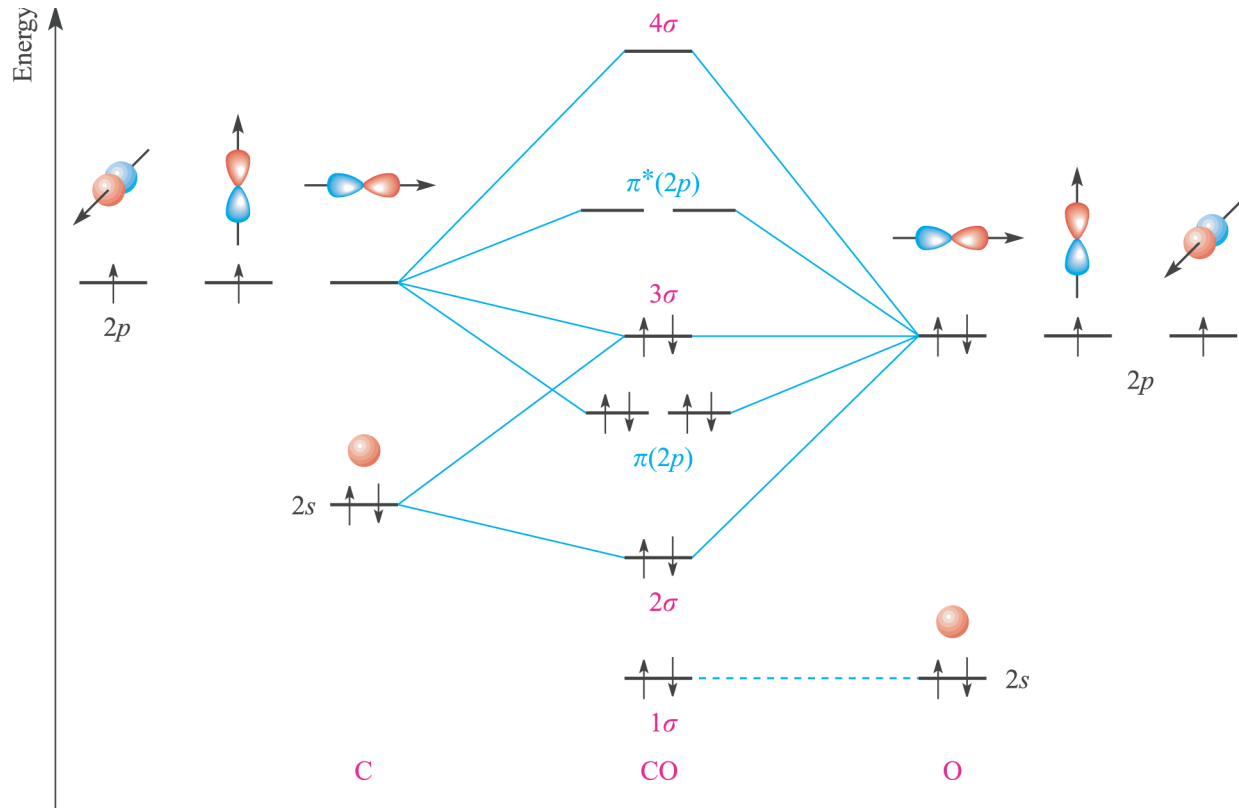
$$\Psi_{MO} = N[(c_1 \times \Psi_X) + (c_2 \times \Psi_Y)] \text{ con } c_2 > c_1$$

$$\Psi^*_{MO} = N[(c_2 \times \Psi_X) + (c_1 \times \Psi_Y)]$$

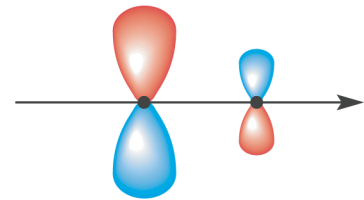
# HF



# CO

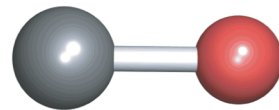
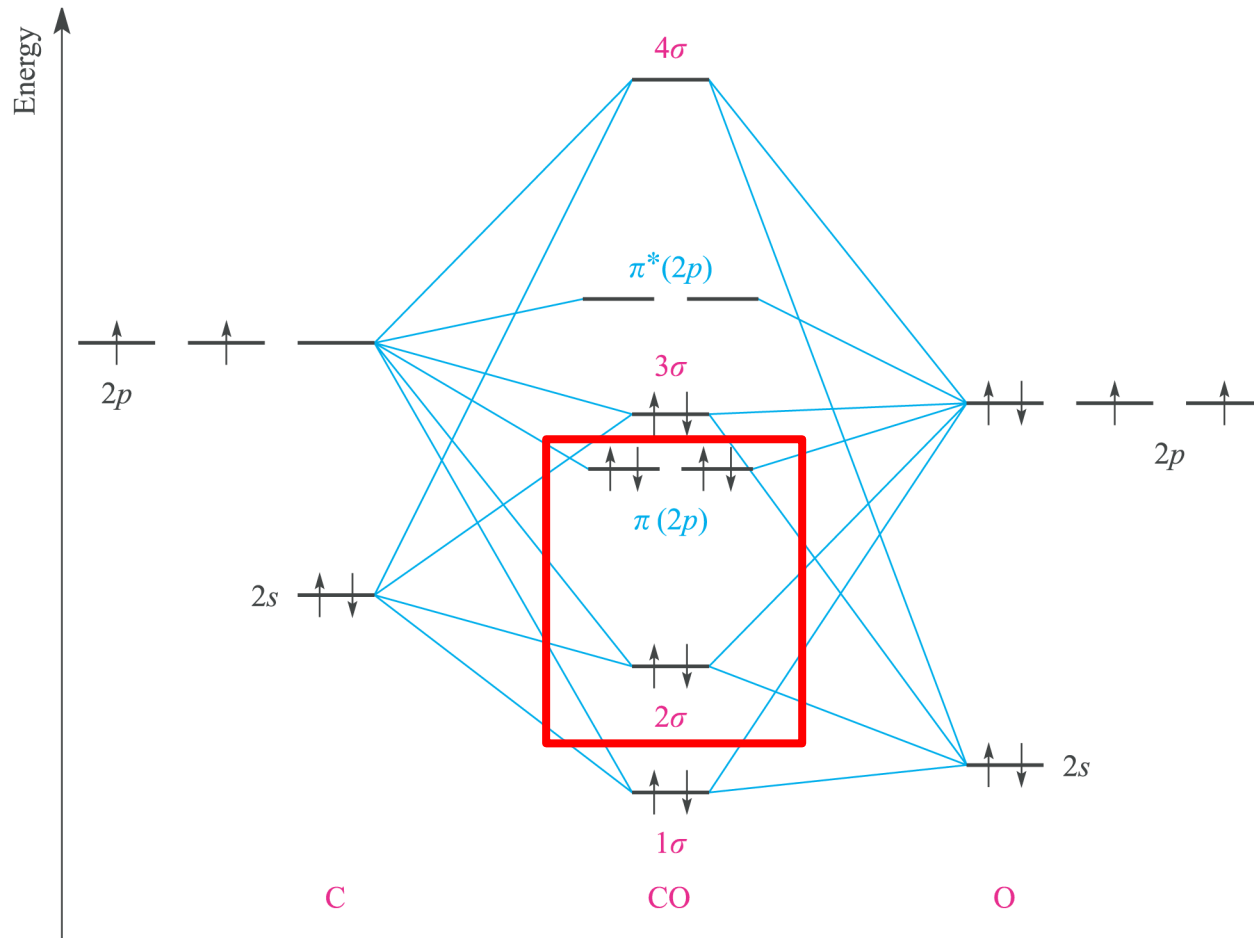


HOMO

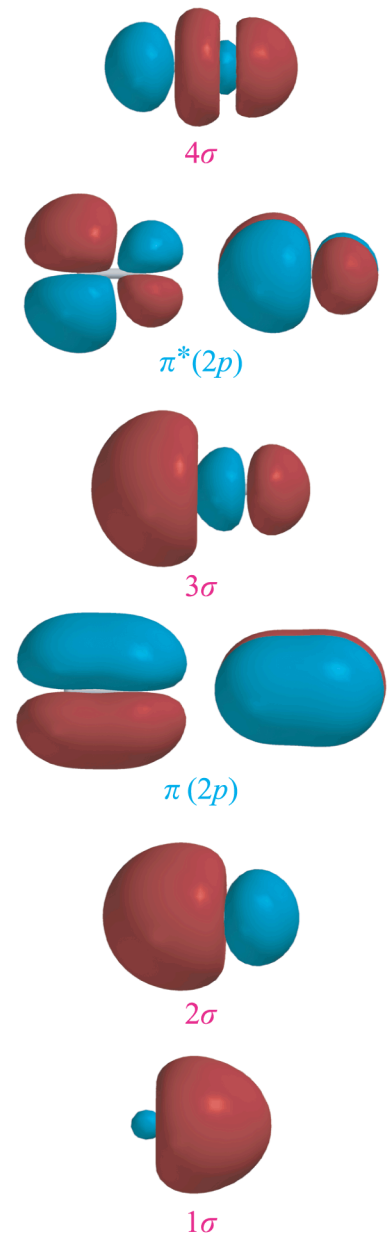


LUMO

# CO



(b)



# Dov'è l'errore?

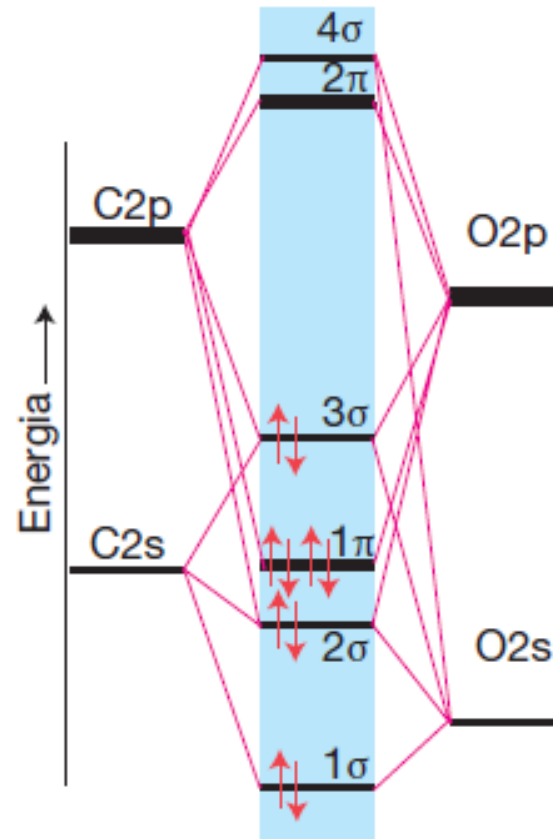
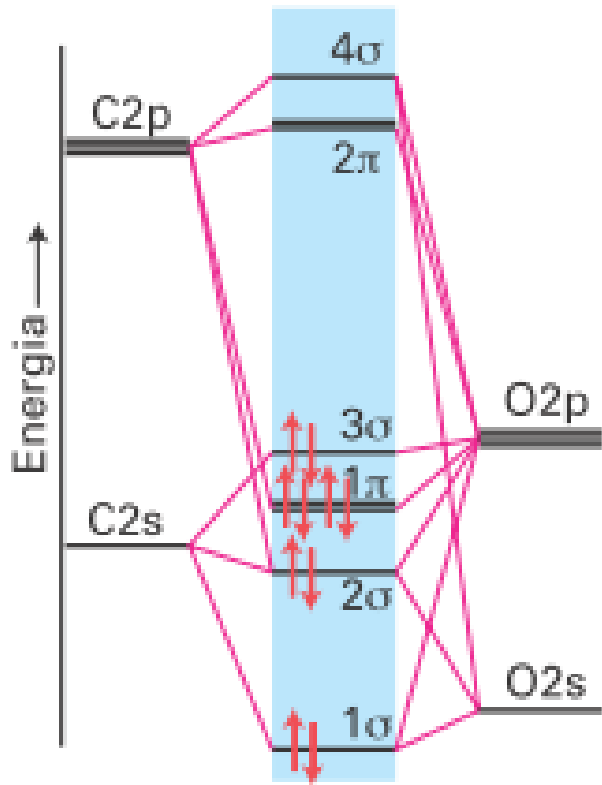


Figura 2.22, pag. 51 Atkins et al.,  
Chimica Inorganica, ed. italiana

Figura 2.22, pag. 45 Weller et al.,  
Chimica Inorganica, ed. italiana