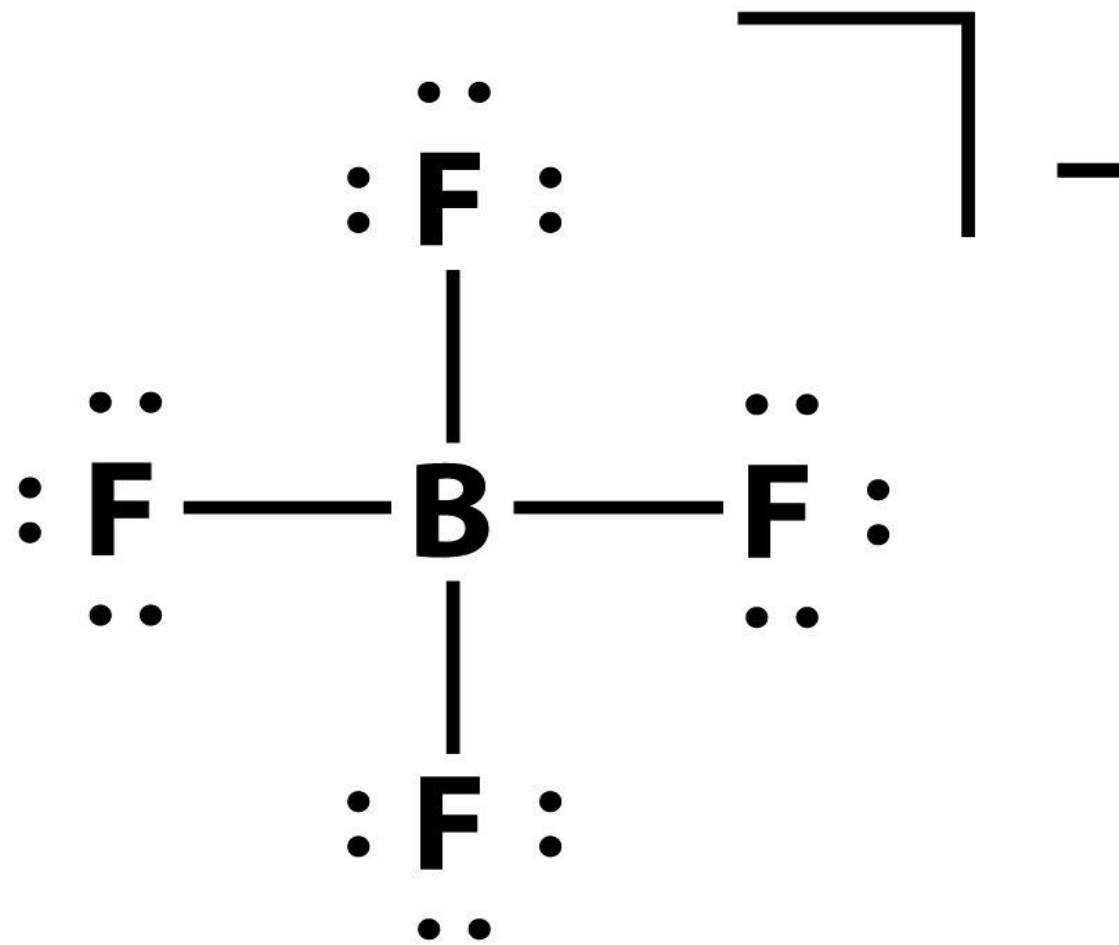
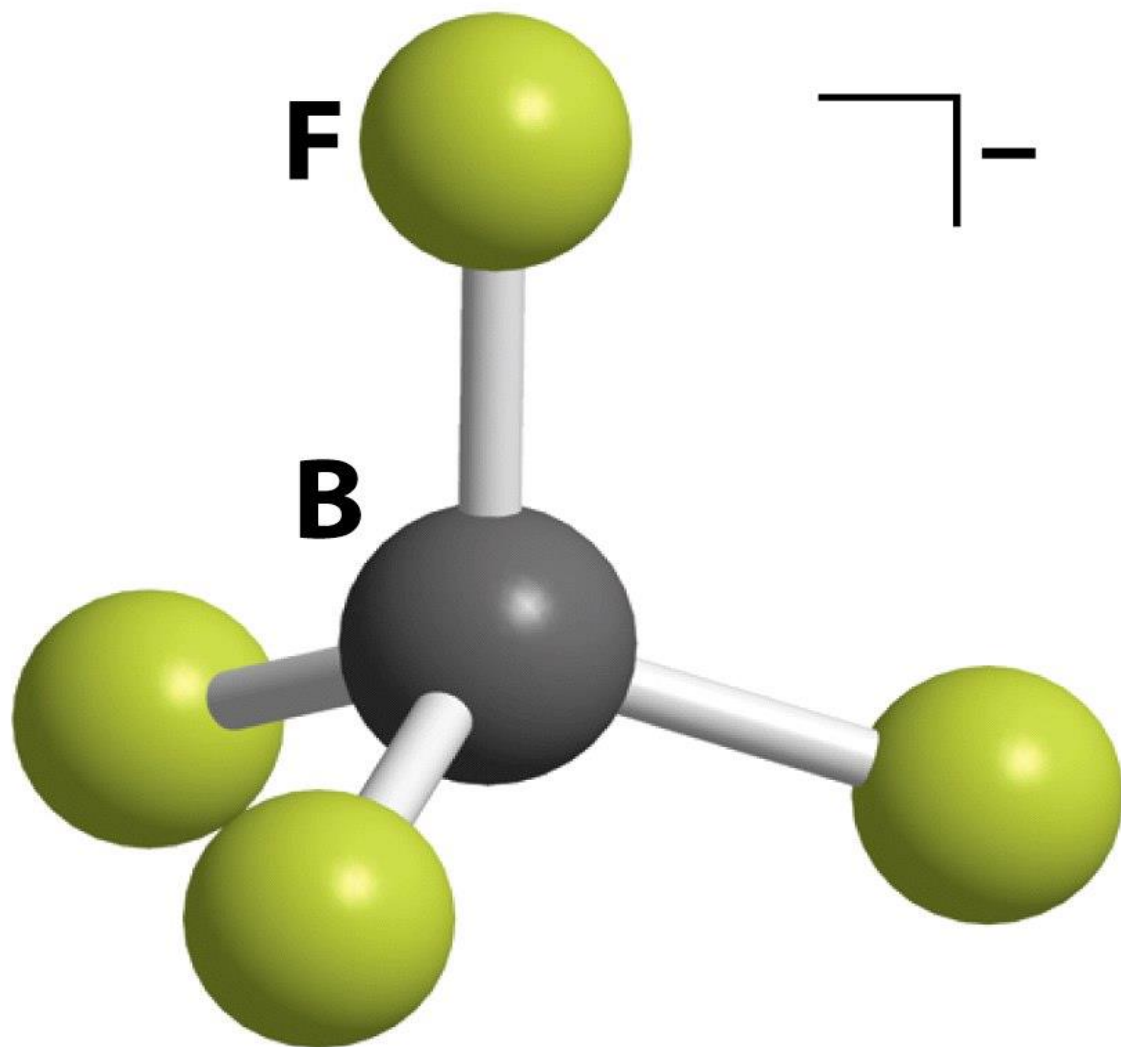


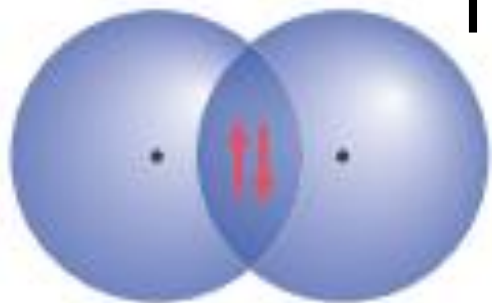
Teoria di Lewis (1916)

Regole di Lewis per gli elettroni di valenza in una molecola :

- di solito per formare un legame si appaiano 2 elettroni (conseguenza del principio di esclusione di Pauli), indicati con due punti o una linea;
- per la maggior parte degli atomi ci saranno al massimo 8 elettroni nel guscio di valenza (**regola dell'ottetto**);
- per gli elementi con orbitali *d* accessibili il guscio di valenza può essere espanso oltre l'ottetto.
- le molecole cercheranno di avere l'energia più bassa possibile, e quindi si formerà il maggior numero di legami possibile e si formeranno i legami più forti possibili.



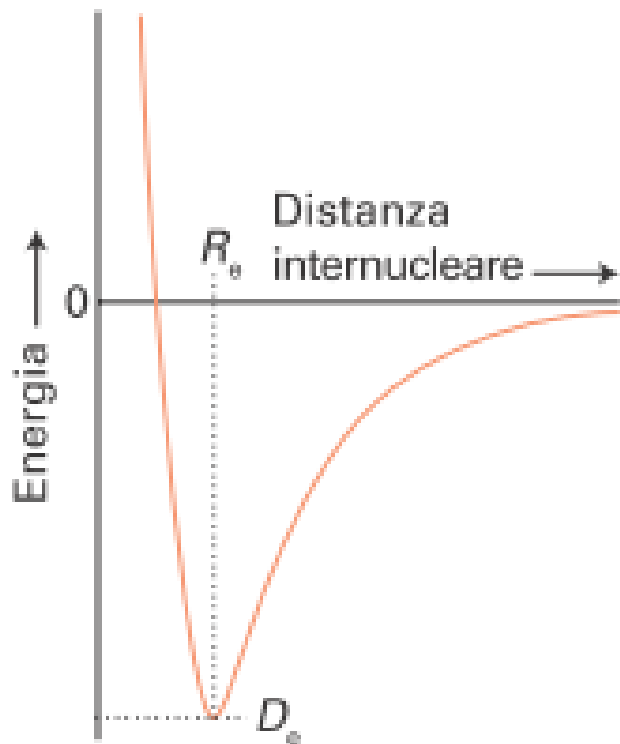




Teoria del legame di valenza (VB) (L. Pauling)

$$\Psi_{\text{cov}} = \Psi_{A(1)}\Psi_{B(2)} + \Psi_{A(2)}\Psi_{B(1)}$$

303 kJ mol⁻¹ a 87 pm



$$\Psi = a\Psi_{\text{cov}} + c\Psi_{A^-}\Psi_{B^+} + c\Psi_{A^+}\Psi_{B^-} = a\Psi_{\text{cov}} + c\Psi_{\text{ion}}$$

398 kJ mol⁻¹ a 75 pm

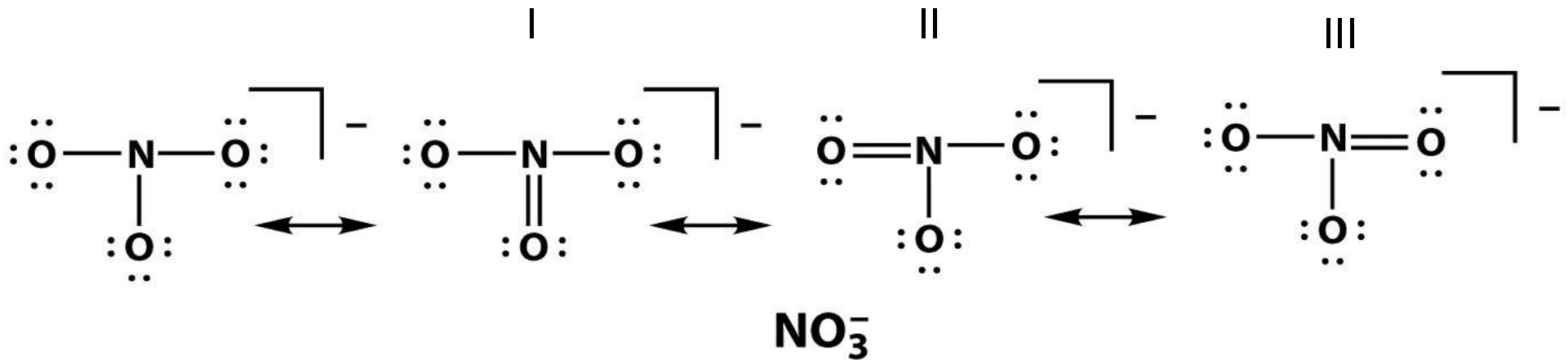


Ibrido di Risonanza
fra strutture canoniche

458 kJ mol⁻¹ a 74 pm

Risonanza

$$\Psi = (1-\lambda)\Psi_{\text{cov}} + \lambda\Psi_{\text{ion}}$$



$$\Psi = a\Psi_{\text{I}} + b\Psi_{\text{II}} + c\Psi_{\text{III}} \quad (\text{con } a = b = c)$$

Strutture canoniche

*L'energia della funzione d'onda risultante è inferiore a quella di ognuna delle funzioni contribuenti (**strutture canoniche**) e la differenza è detta **energia di risonanza***

*Affinché una struttura canonica proponibile contribuisca in modo significativo alla risonanza, essa deve avere il **massimo numero di legami possibili** e la distribuzione delle **cariche formali** deve essere ragionevole.*

Carica formale: la carica che un atomo dovrebbe avere in una molecola se tutti gli atomi avessero la stessa elettronegatività

Elettronegatività = la capacità di un atomo in una molecola di attirare elettroni su di sé

Elettronegatività di Pauling, χ^P

$$D(X-Y)_{\text{misurata}} > \frac{1}{2} [D(X-X) + D(Y-Y)]$$

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</i> -block elements)	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	

$$\Delta\chi = \chi^P(Y) - \chi^P(X) = \sqrt{\Delta D} \quad (D \text{ in eV})$$

Stimare l'energia di legame di Br–F, $D(\text{Br–F})$

$$D(\text{F–F}) = 158 \text{ kJ mol}^{-1}$$

$$\chi^{\text{P}}(\text{F}) = 4.0$$

$$D(\text{Br–Br}) = 224 \text{ kJ mol}^{-1}$$

$$\chi^{\text{P}}(\text{Br}) = 3.0$$

$$\Delta D = [D(\text{Br–F})_{\text{sperimentale}}] - \frac{1}{2}\{[D(\text{Br–Br})] + [D(\text{F–F})]\}$$

$250.2 \text{ kJ mol}^{-1}$

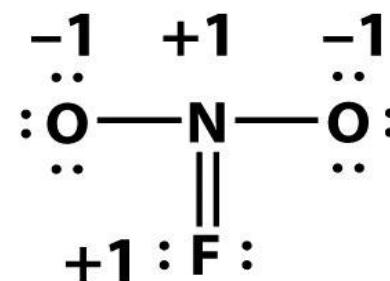
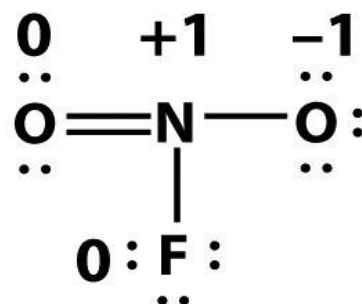
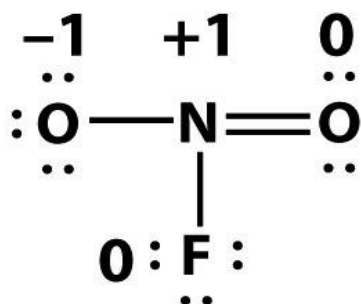
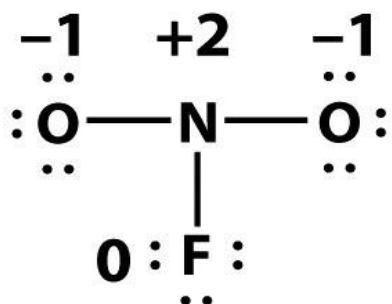
$$\sqrt{\Delta D} = \chi^{\text{P}}(\text{F}) - \chi^{\text{P}}(\text{Br}) = 1.0$$

$$\Delta D = 1.0 \text{ eV} = 96.5 \text{ kJ mol}^{-1}$$

$$[D(\text{Br–F})_{\text{stimato}}] = \Delta D + \frac{1}{2}\{[D(\text{Br–Br})] + [D(\text{F–F})]\}$$

$$[D(\text{Br–F})_{\text{stimato}}] = 96.5 + \frac{1}{2}\{224 + 158\} = 287.5 \text{ kJ mol}^{-1}$$

Cariche Formali (Q_F)

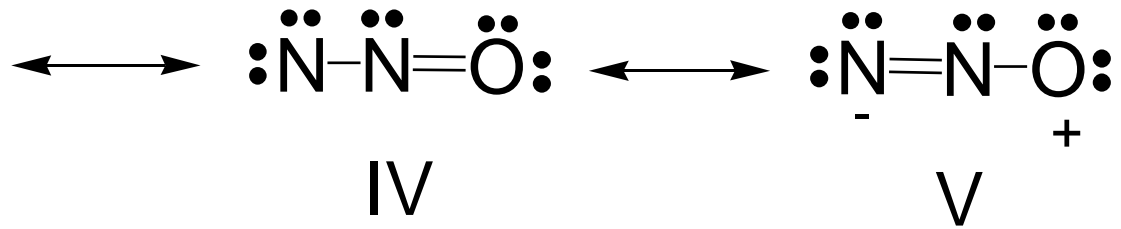
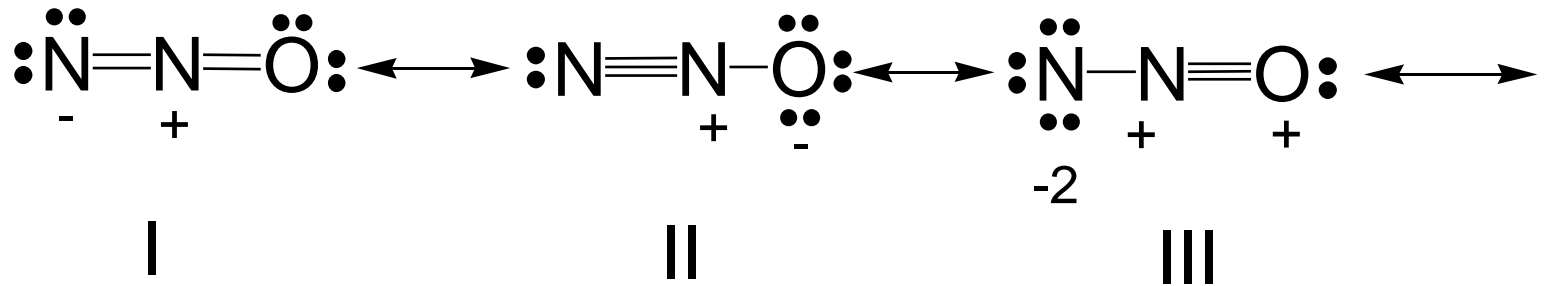


NO₂F

$$Q_F = N_A - N_{LP} - \frac{1}{2}N_{BP}$$

La struttura di Lewis con energia più bassa è quella con le più basse cariche formali sugli atomi (perché tale struttura corrisponde al minimo riarrangiamento degli elettroni)

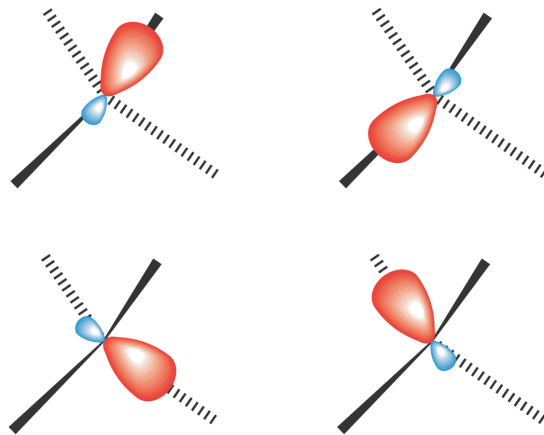
16 elettroni



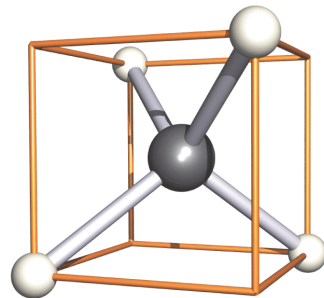
Promozione e Ibridizzazione

(il problema della direzionalità degli orbitali atomici dell'atomo centrale)

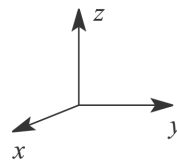
ground state $[\text{He}]2s^22p_x^12p_y^1 \rightarrow$ stato eccitato **di valenza** $[\text{He}] 2s^12p_x^12p_y^12p_z^1$
406 kJ mol⁻¹

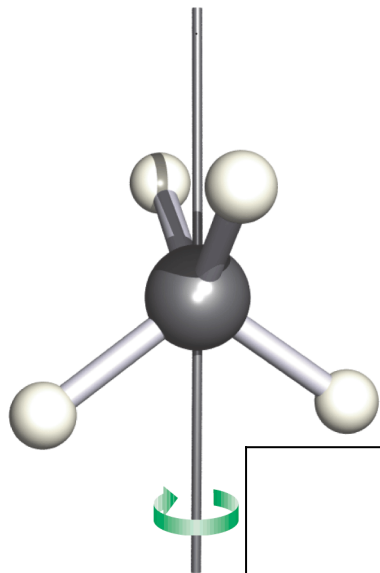


(a)



(b)





E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
4	1	0	0	2

$A_1 + T_2$

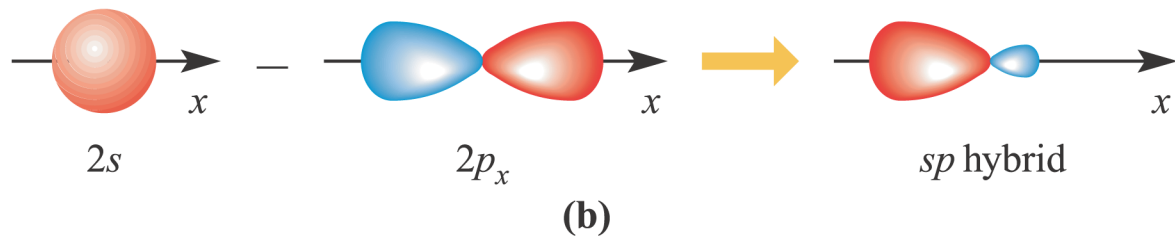
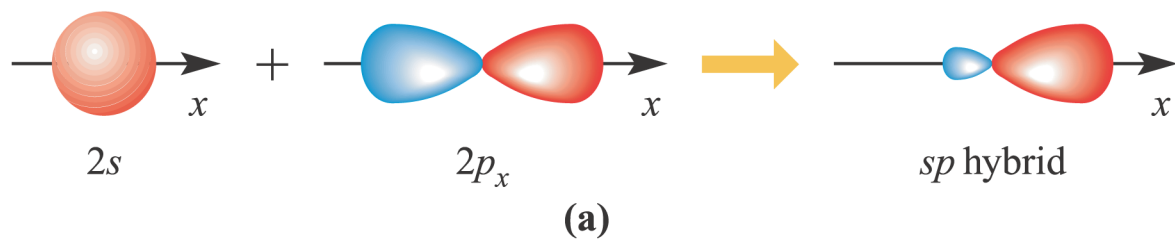
Tabella dei caratteri per il gruppo puntuale T_D

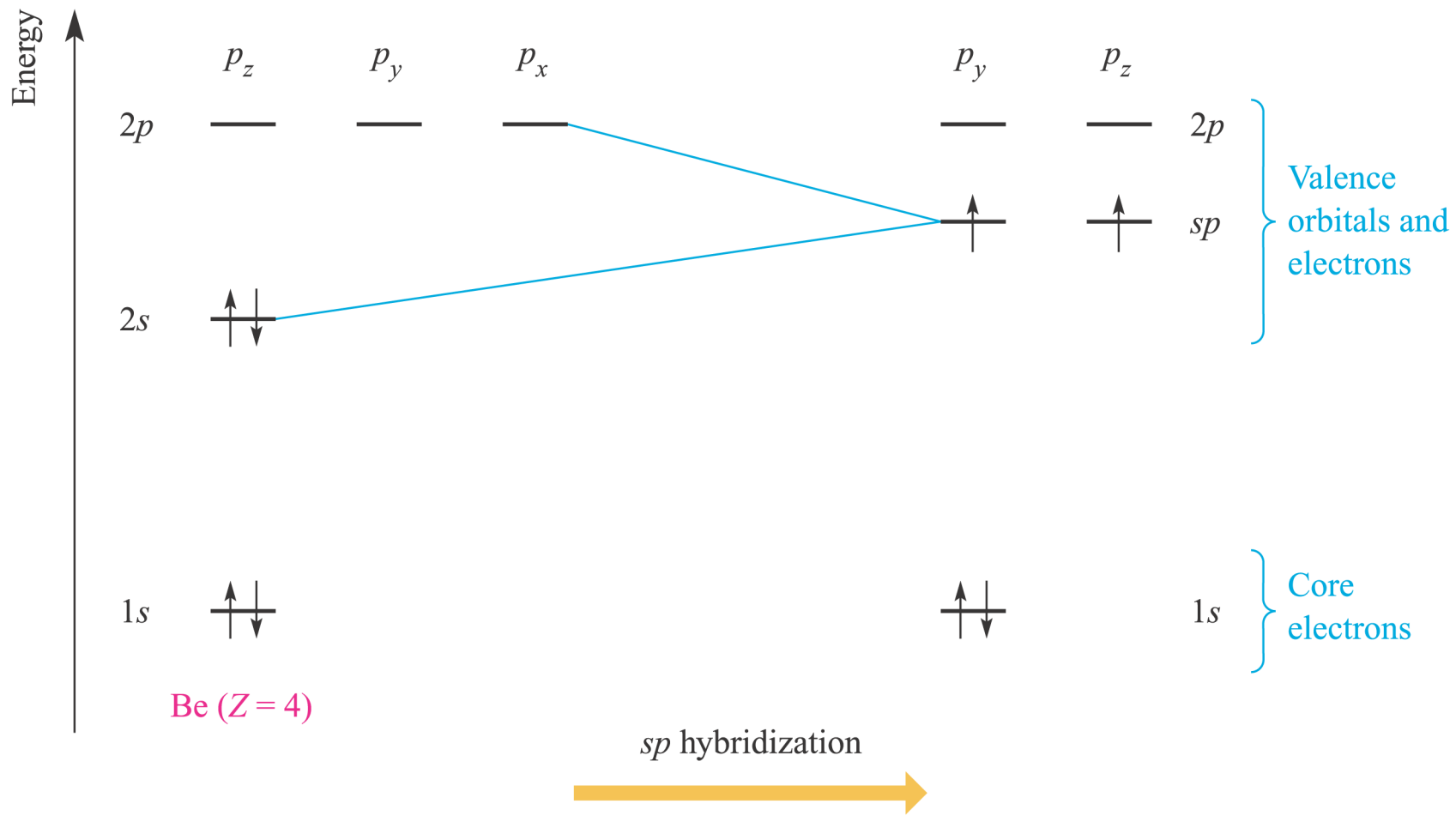
	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

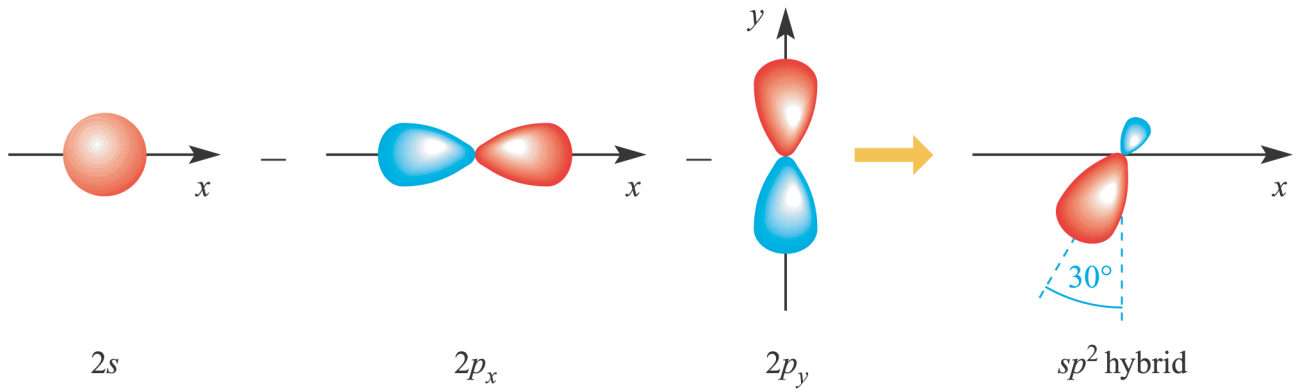
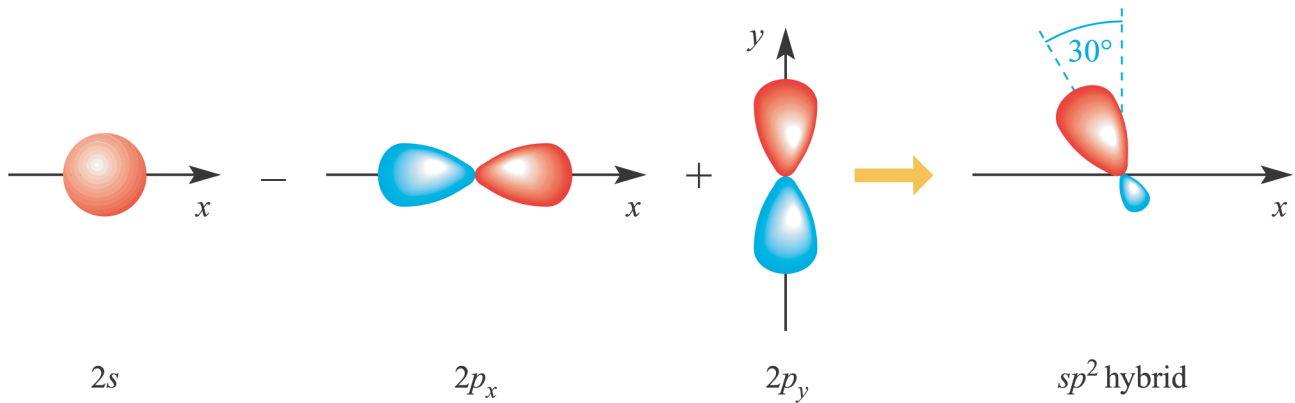
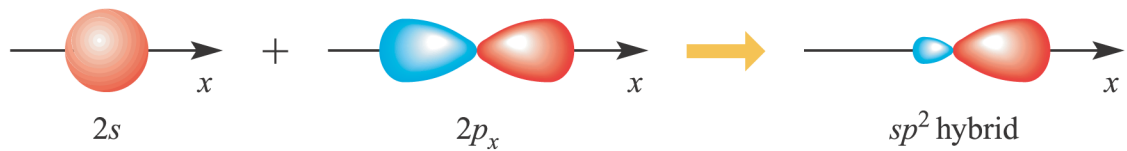
Criteri per l'ibridizzazione

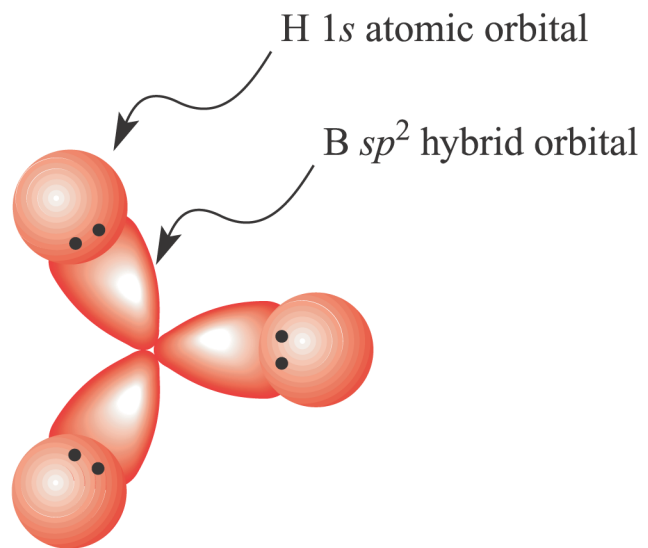
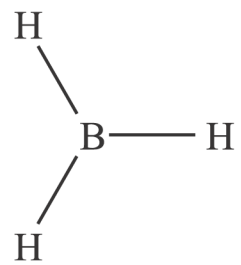
Le funzioni d'onda degli orbitali atomici ibridizzati devono avere:

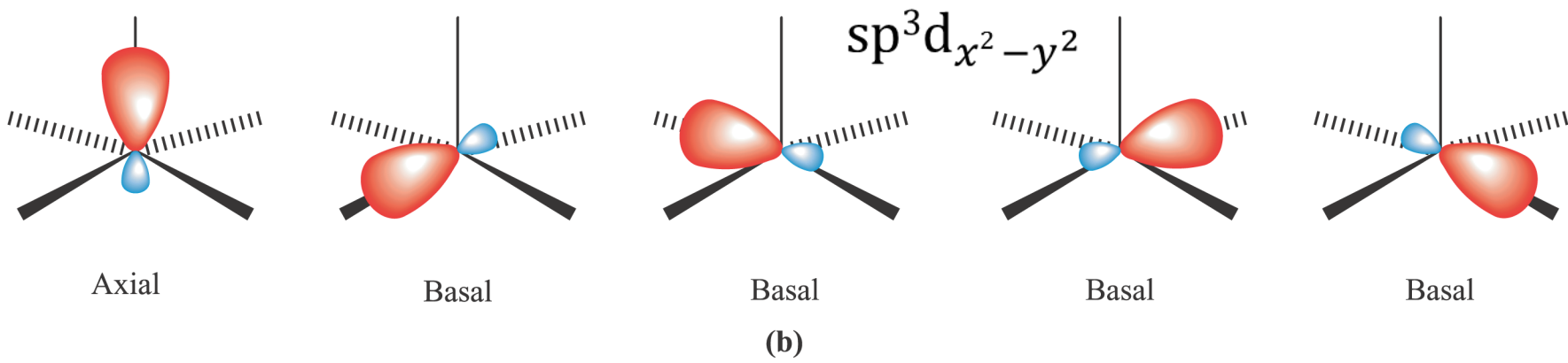
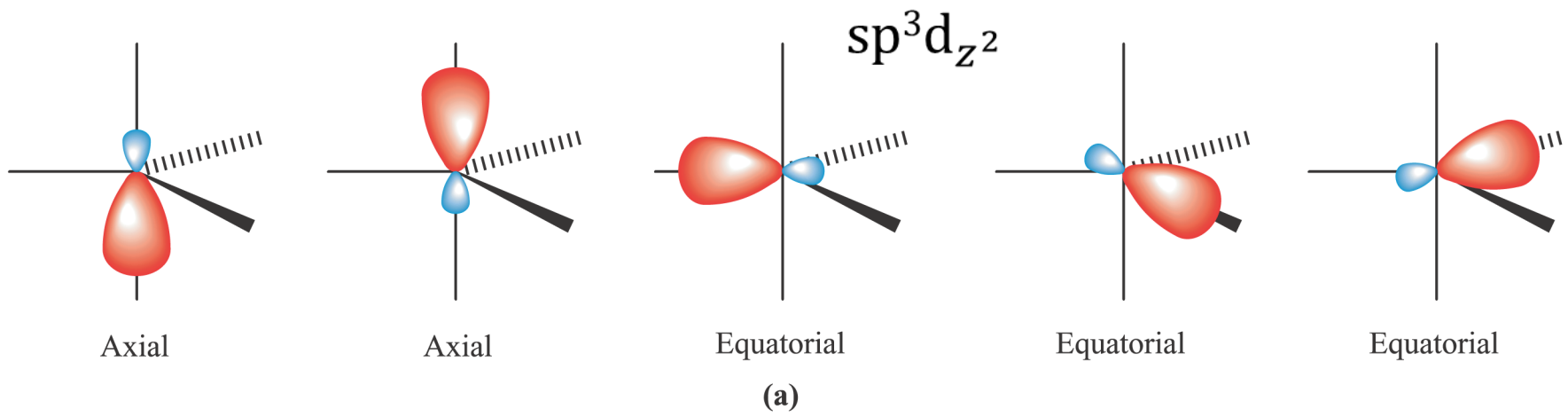
- ***simmetria appropriata***
- ***energia simile***



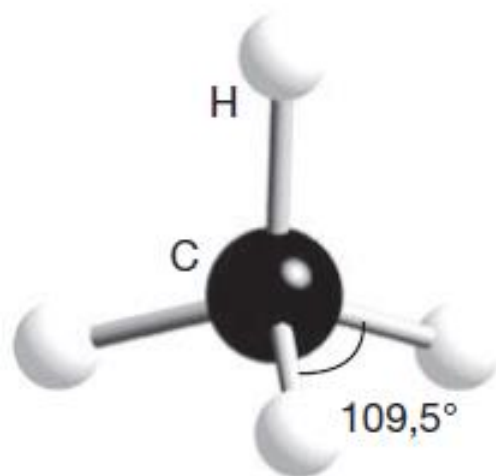




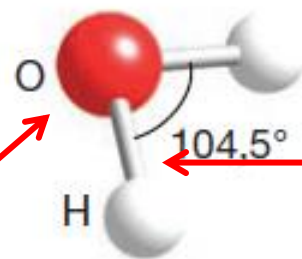
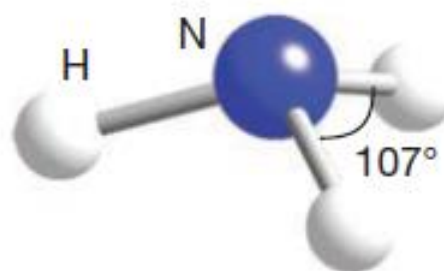




Negli ibridi sp^n non necessariamente tutti gli orbitali contribuiscono in modo eguale all'ibrido

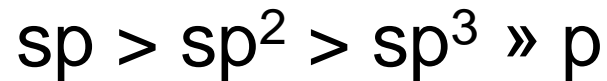


30% s + 70%p



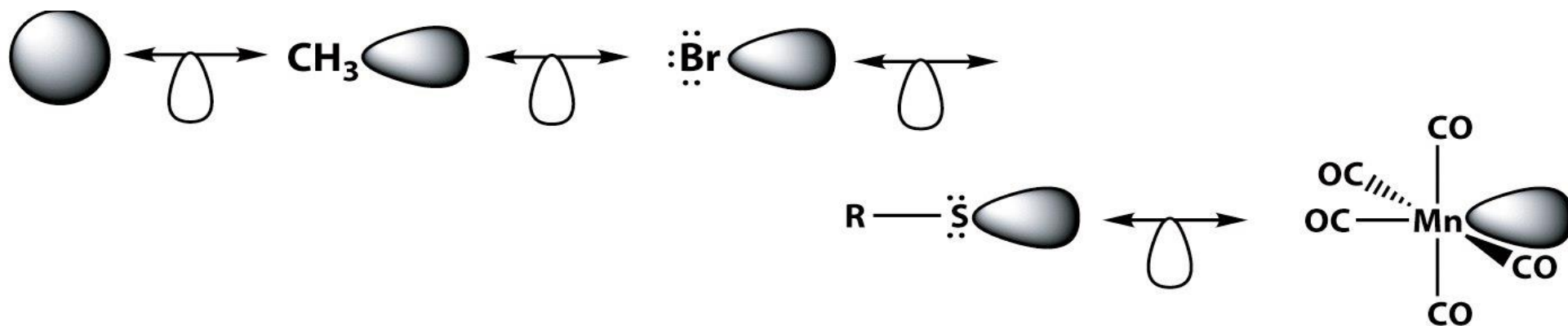
20% s + 80%p

Sovrapposizione



Molecola	Ibridizzazione	Energia legame C-H (kJ/mol)	Lunghezza legame C-H (pm)
Acetilene	sp	500	106.1
Etilene	sp ²	400	108.6
Metano	sp ³	410	109.3

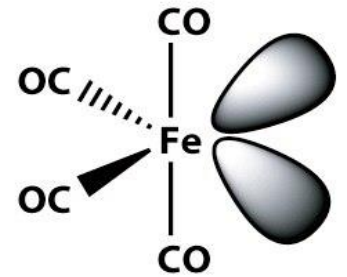
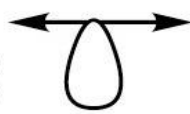
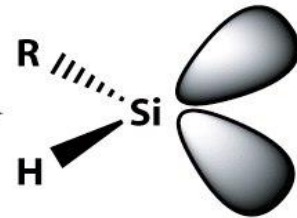
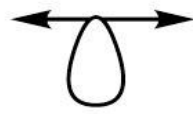
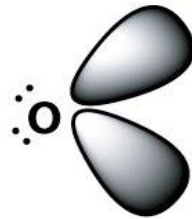
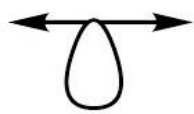
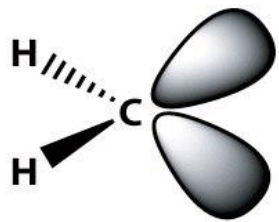
Serie di frammenti isolobali



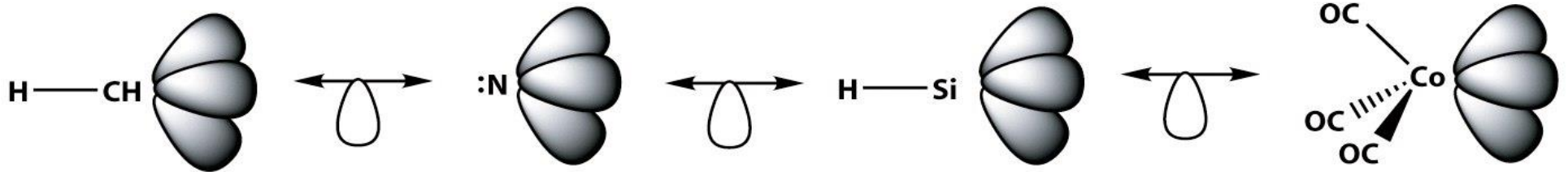
I frammenti hanno:

- stessa simmetria
- energie simili
- stessa occupazione elettronica

Serie di frammenti isolobali



Serie di frammenti isolobali



Il frammento BH^- è isolobale a CH

