*In una molecola EX_n contenente legami singoli E–X ogni coppia elettronica del guscio di valenza di E, **sia di legame σ che solitaria**, è **stereochimicamente attiva***

Table 2.6 The basic arrangement of regions of electron density according to the VSEPR model

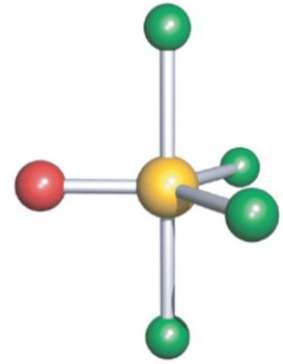
Number of electron regions	Arrangement
2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

Repulsione fra le coppie

coppia solitaria – coppia solitaria > coppia solitaria – coppia di legame > coppia di legame – coppia di legame

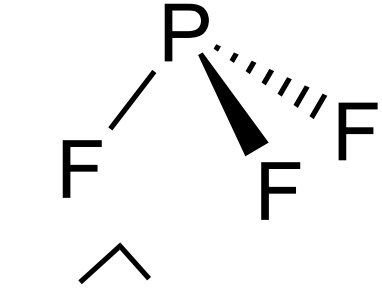
CH_4 (109.5°), NH_3 (107°), H_2O (104.5°)

legame triplo – legame singolo > legame doppio – legame singolo > legame singolo – legame singolo

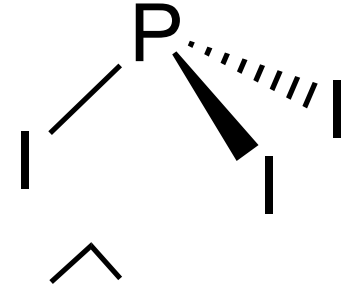


OSF_4

coppie di legame verso atomi (o gruppi) elettronegativi occupano meno spazio di quelle verso atomi più elettropositivi



F-P-F = 97.7°



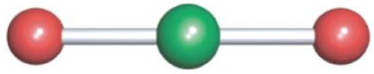
I-P-I = 102°

numero sterico = numero di coppie di legame e di non legame intorno all'atomo centrale. Se non ci sono legami E–H:

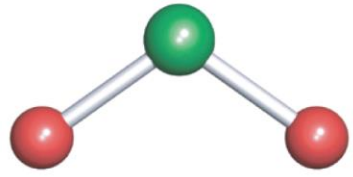
n.s. = $\underbrace{\text{elettroni di valenza } (\pm \text{ carica})/8}_{\text{Legami}} + \underbrace{\text{resto}/2}_{\text{Coppie solitarie}}$

*Il numero sterico determina la **geometria delle coppie**, che non necessariamente coincide con la **geometria molecolare***

2-Coordinate

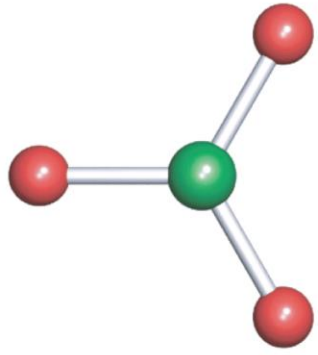


Linear

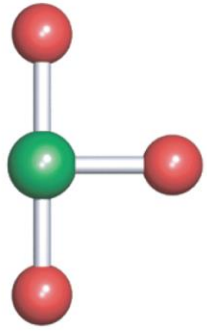


Bent

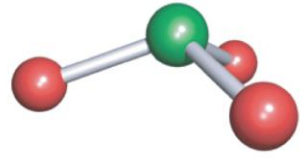
3-Coordinate



Trigonal planar



T-shaped

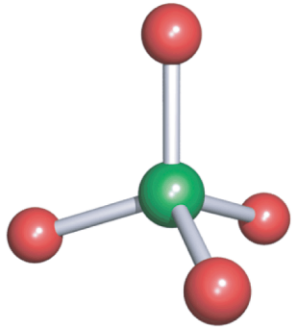


Trigonal pyramidal

BrF_3

n.s. = 5

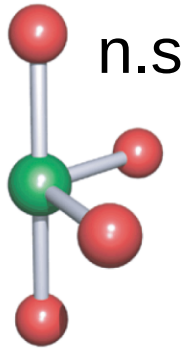
4-Coordinate



Tetrahedral

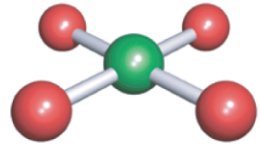
SF_4

n.s. = 5



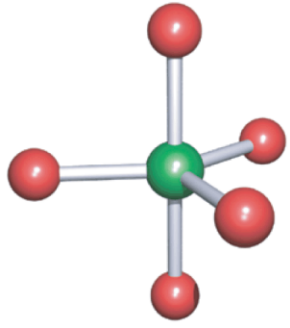
Disphenoidal

ICl_4^- n.s. = 6

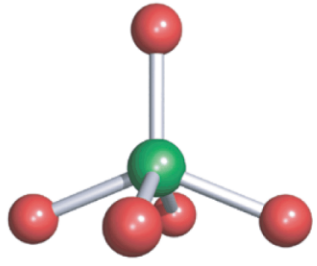


Square planar

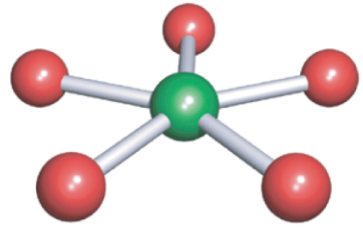
5-Coordinate



Trigonal bipyramidal



Square-based pyramidal

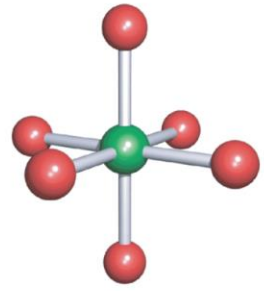


Pentagonal planar

TeF_5^-

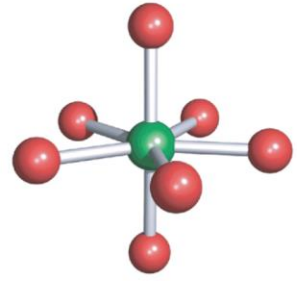
n.s. = 6

6-Coordinate



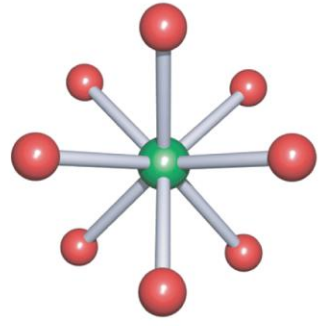
Octahedral

7-Coordinate



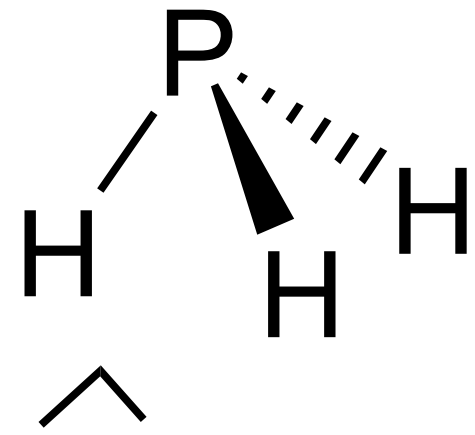
Pentagonal bipyramidal

8-Coordinate



Square antiprismatic

Coppie solitarie stereochimicamente inattive

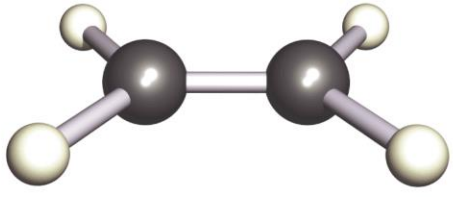


H-P-H ca. 90°

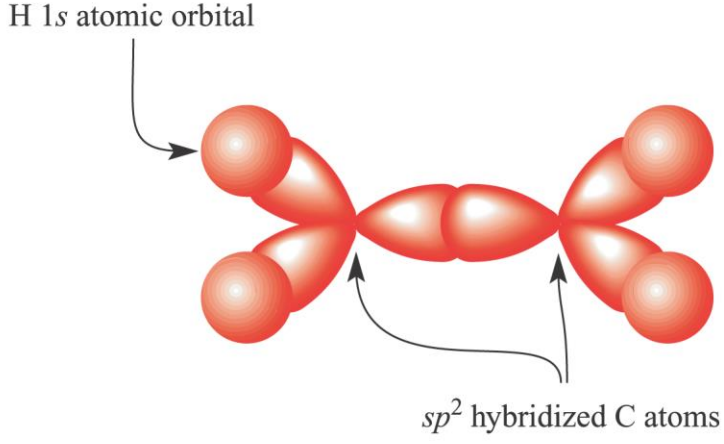
$[SeCl_6]^{2-}$, $[TeCl_6]^{2-}$, $[BrF_6]^{-}$

Molecole poliatomiche secondo la teoria VB

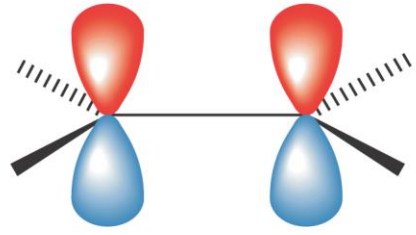
C_2H_4



(a)



(b)

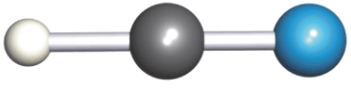


(c)

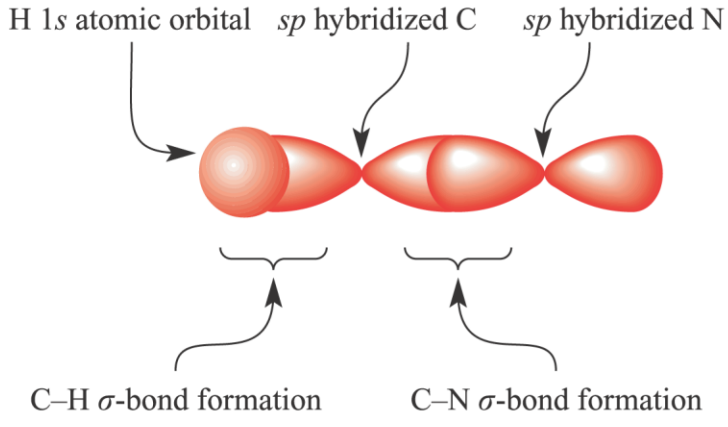
598 kJ mol^{-1} *vs* 2 × 346 kJ mol^{-1}

$\sigma + \pi$ 2σ

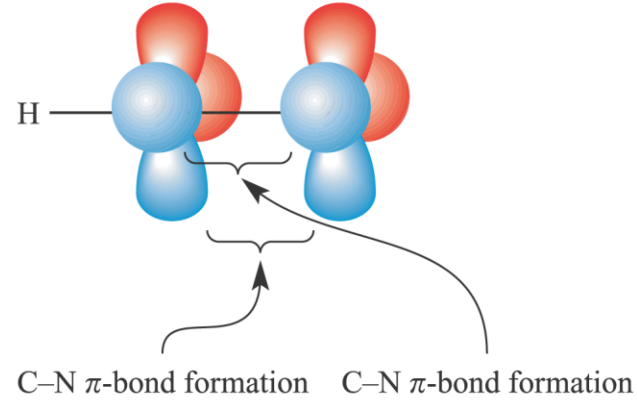
HCN



(a)

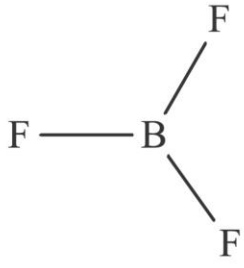

H 1s atomic orbital
sp hybridized C
sp hybridized N
C–H σ-bond formation
C–N σ-bond formation

(b)

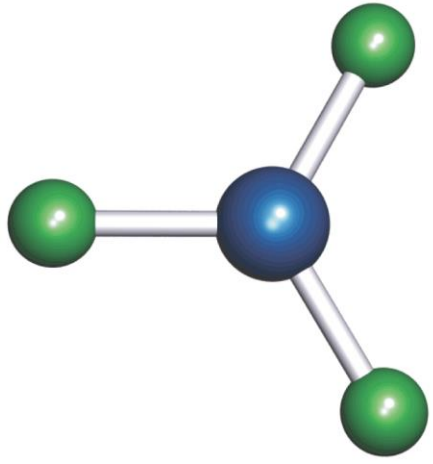

H
C–N π-bond formation
C–N π-bond formation

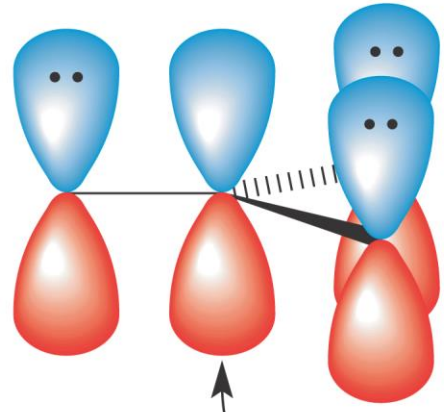
(c)

BF_3



(a)



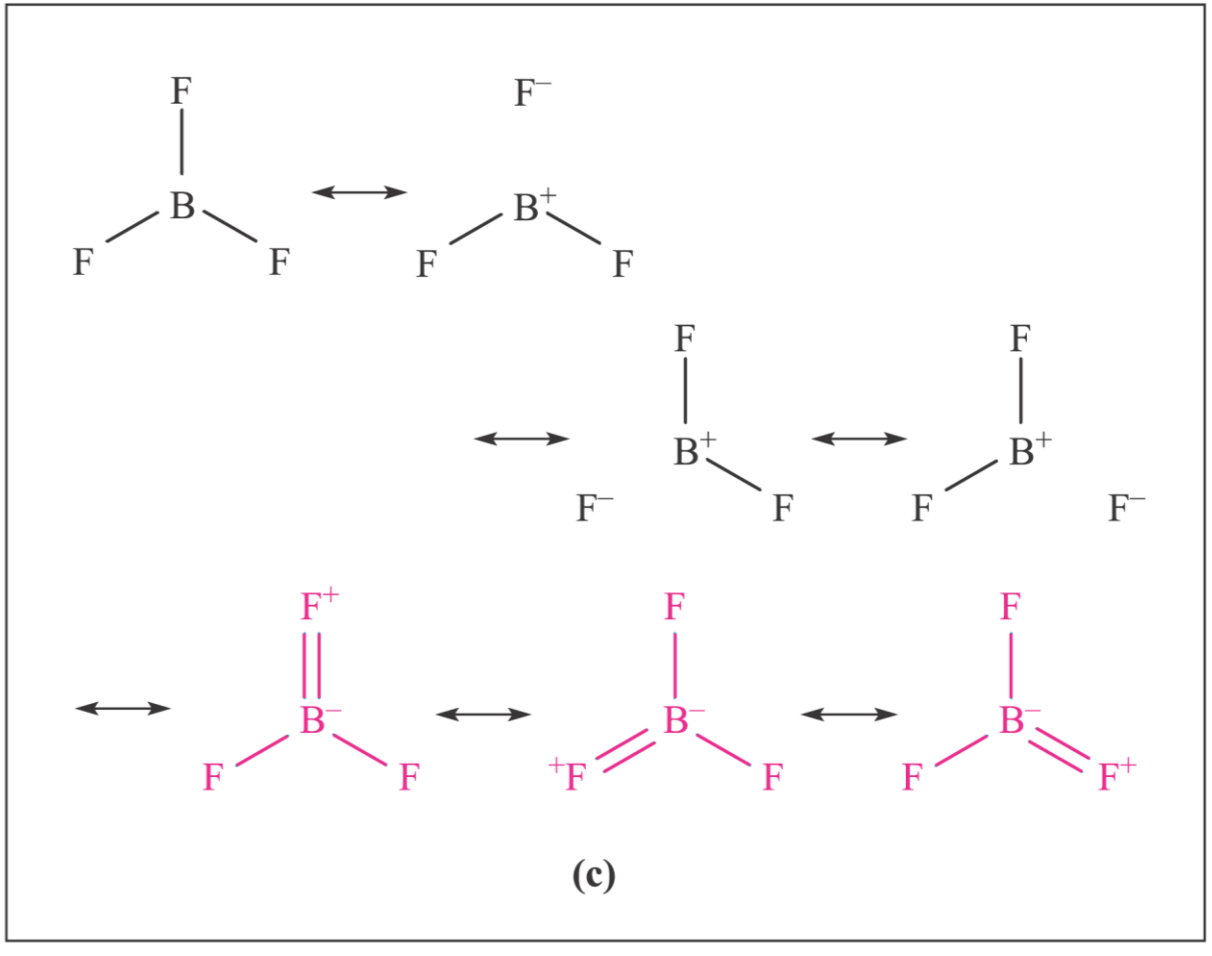


Fully occupied 2*p* atomic orbital on F

Empty 2*p* atomic orbital on B

(b)

BF_3



Molecole poliatomiche secondo la teoria MO

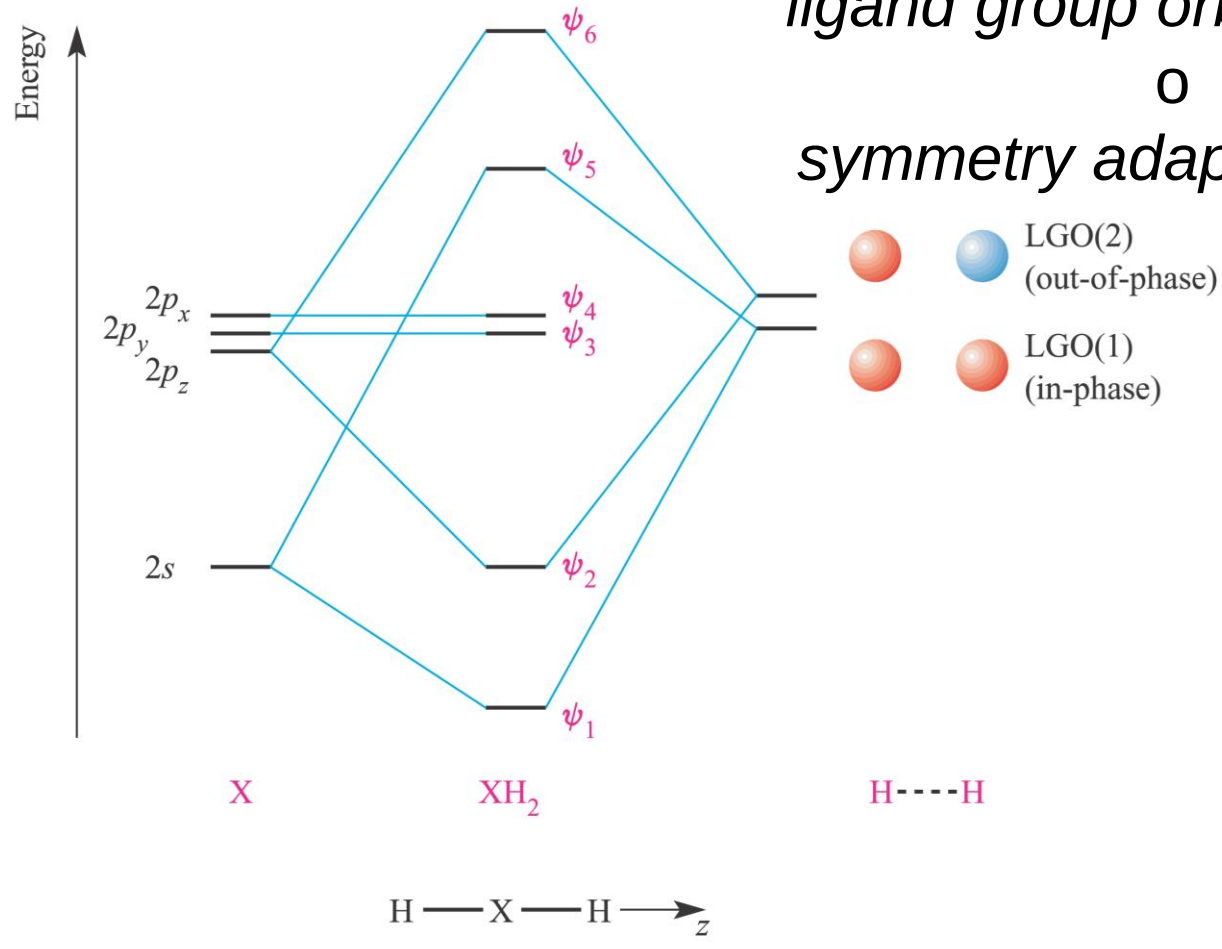
BeH_2

orbitali di gruppo

ligand group orbitals (LGO)

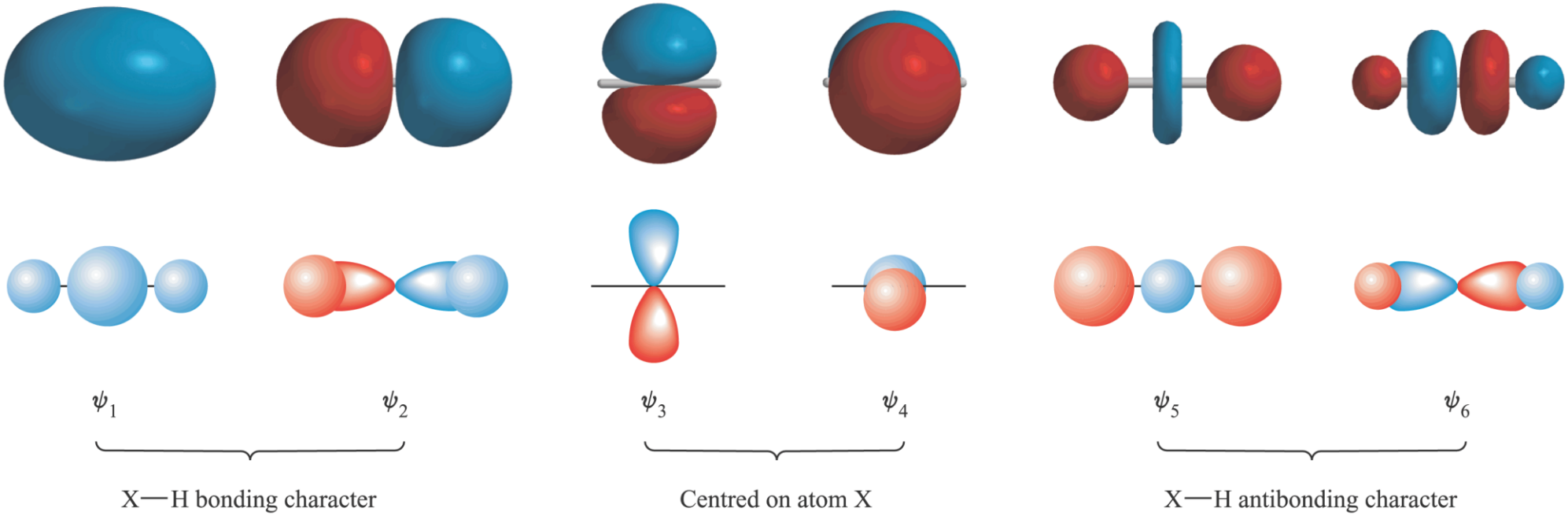
o

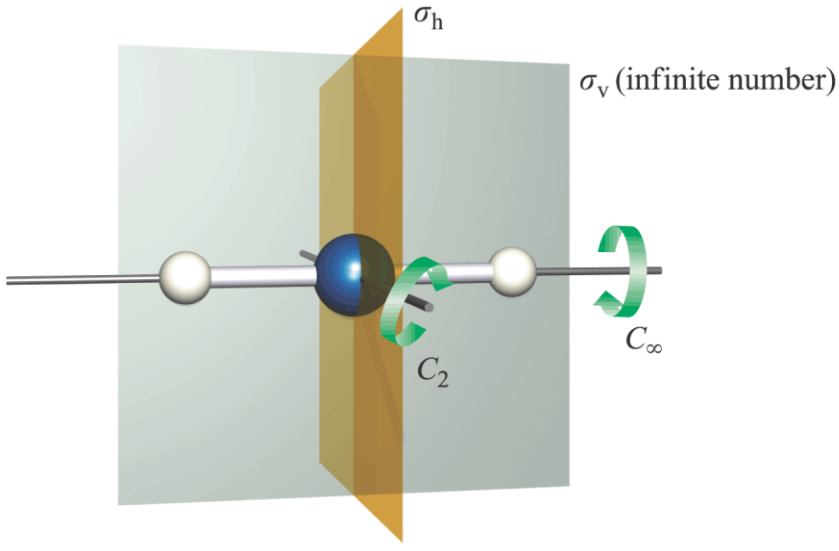
symmetry adapted orbitals



Molecole poliatomiche secondo la teoria MO

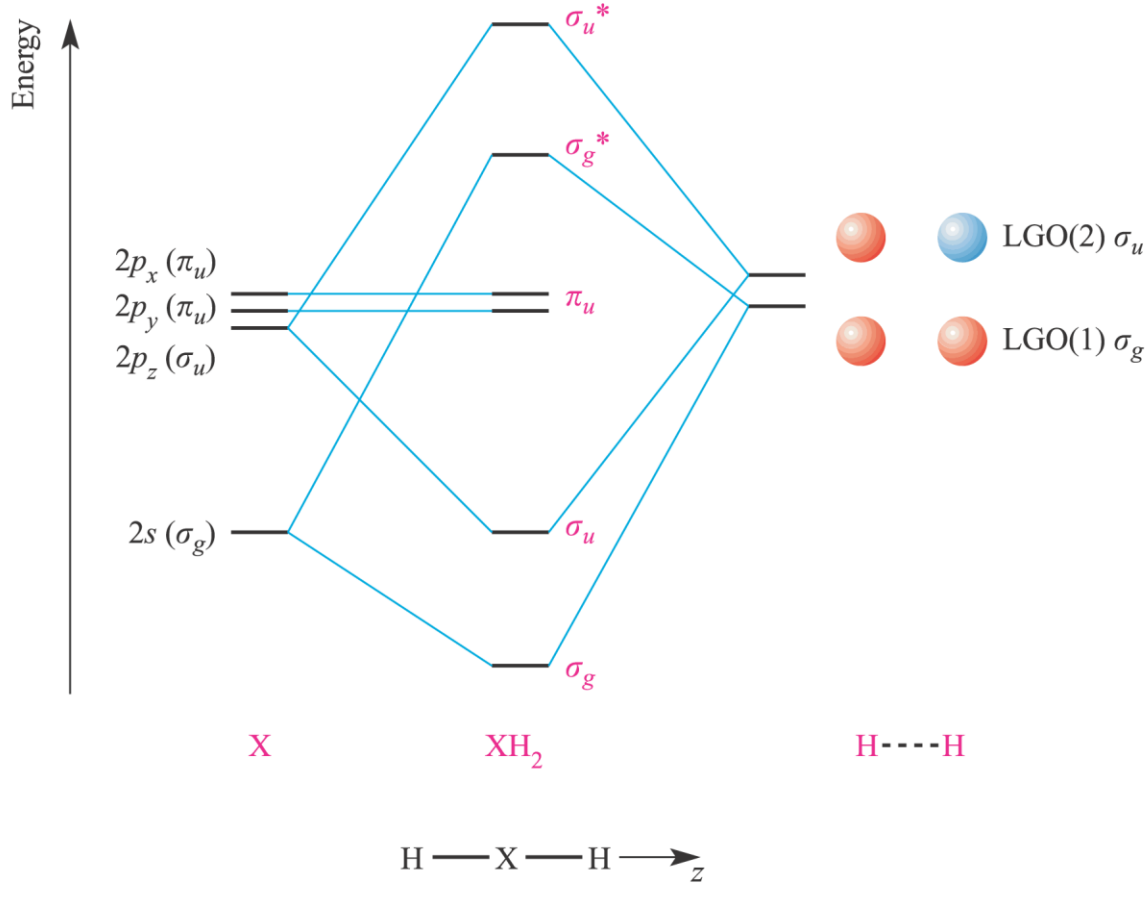
BeH_2



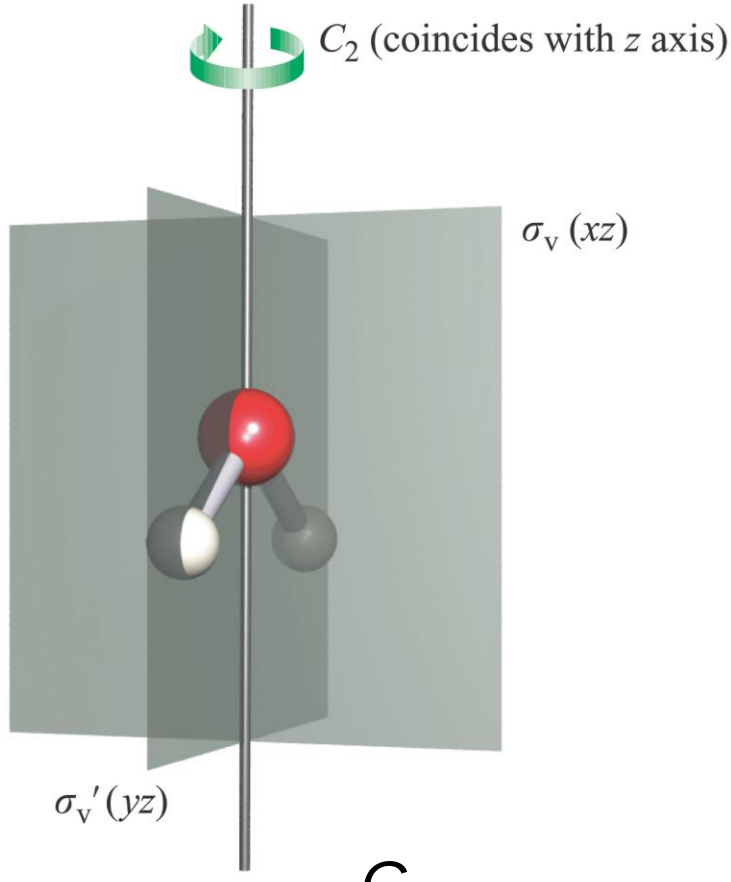

σ_h
σ_v (infinite number)
C_2
C_∞

$D_{\infty h}$

(a)


Energy
σ_u^*
σ_g^*
$2p_x$ (π_u)
$2p_y$ (π_u)
$2p_z$ (σ_u)
π_u
$2s$ (σ_g)
σ_u
σ_g
LGO(2) σ_u
LGO(1) σ_g
X
XH_2
H----H
H — X — H → z

(b)



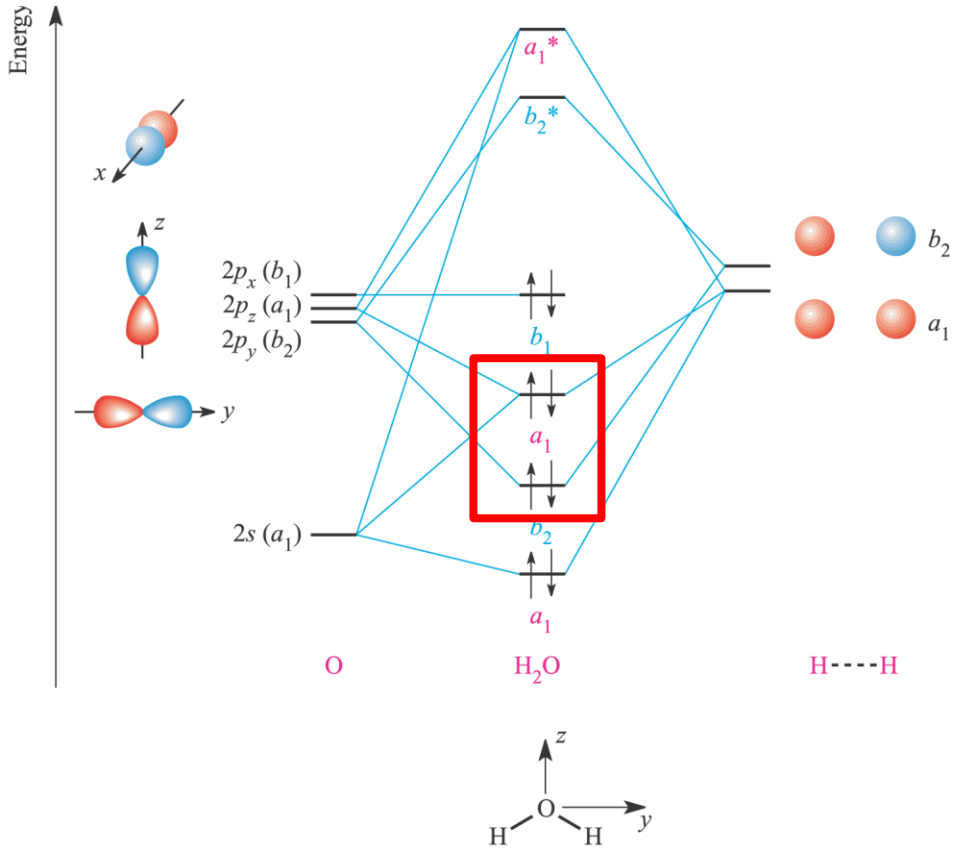
C_{2v}

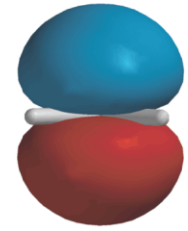
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

2H

2	0	0	2

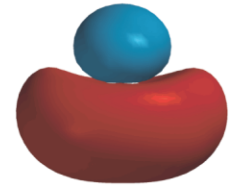
$A_1 + B_2$



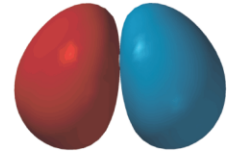


Representation of the b_1 MO

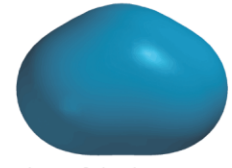
n.l.



Representation of the higher energy a_1 MO



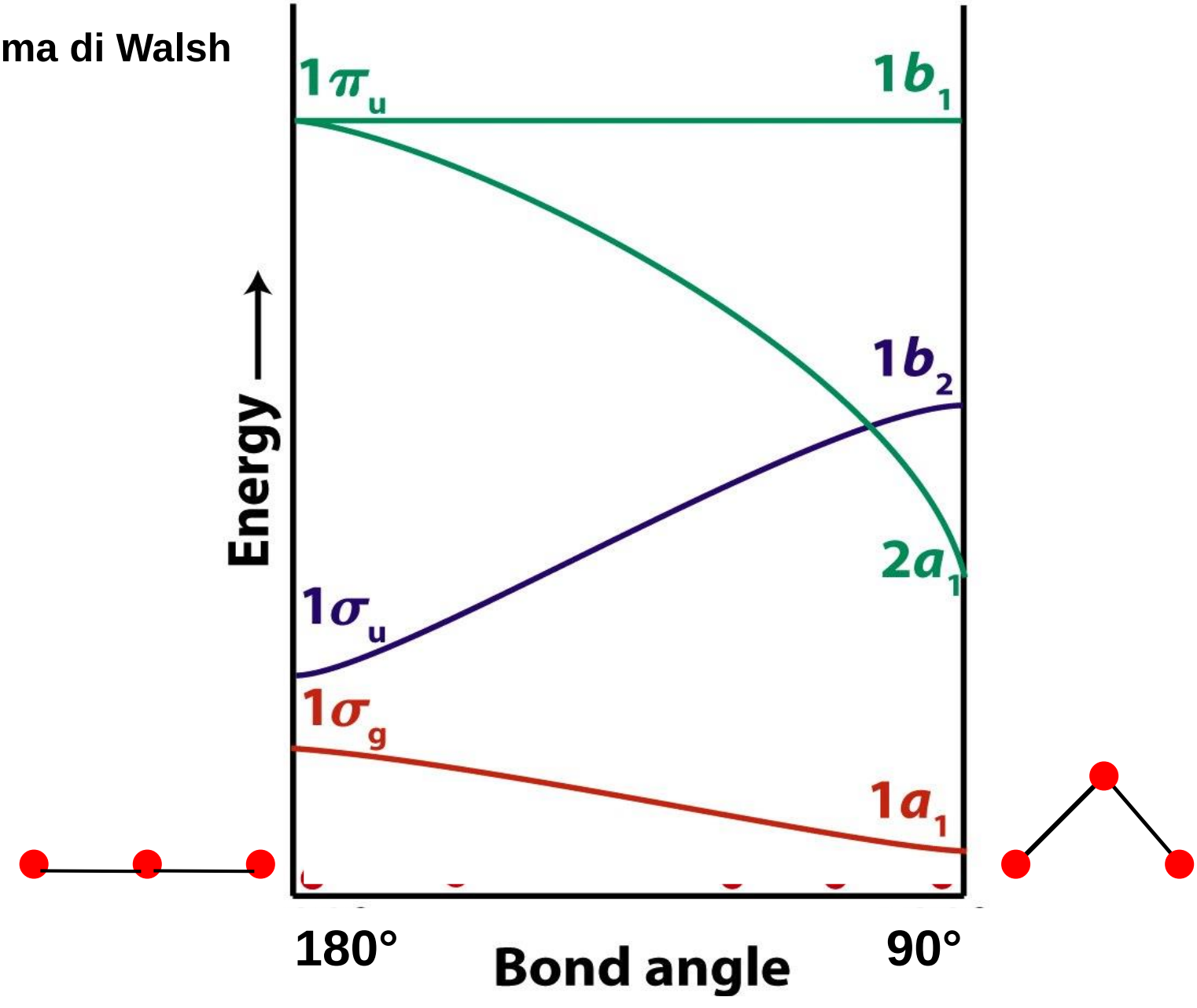
Representation of the b_2 MO

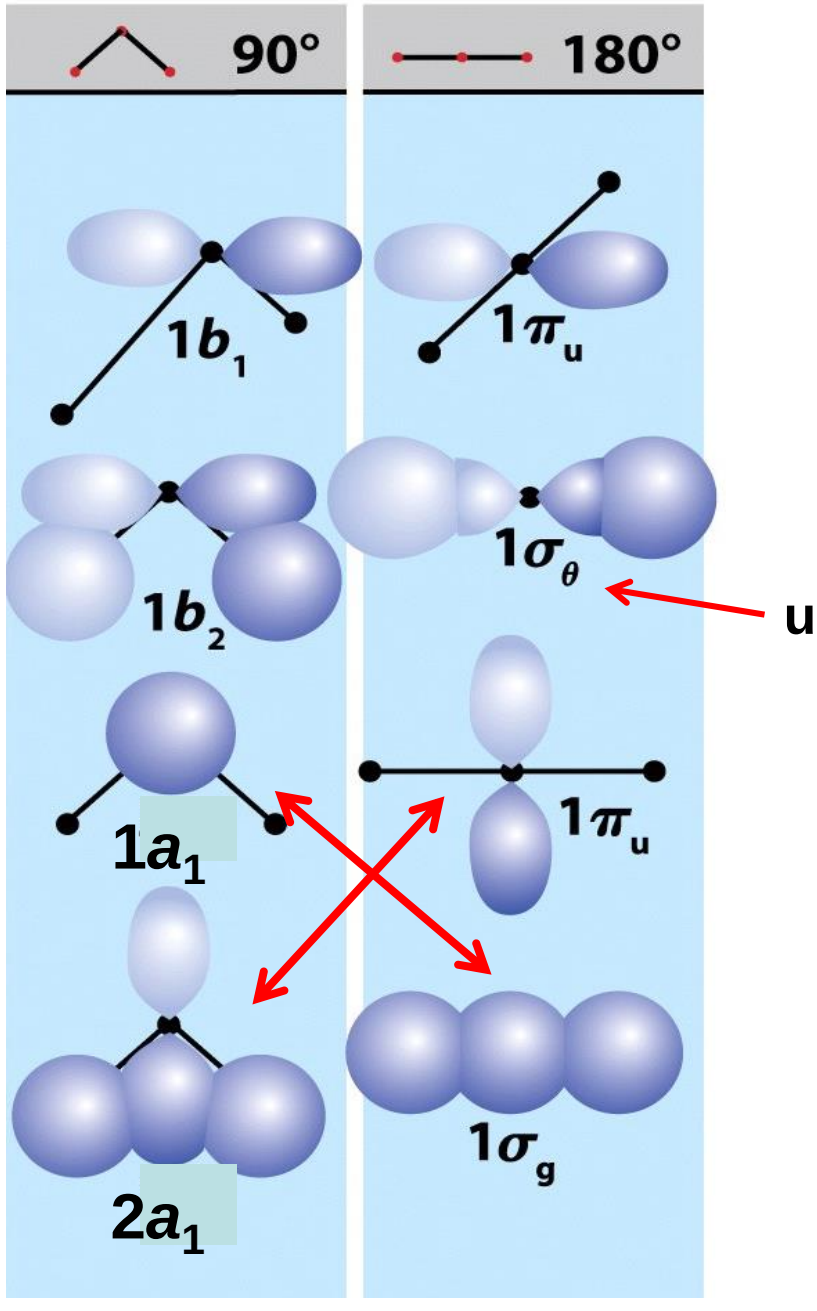


Representation of the lower energy a_1 MO

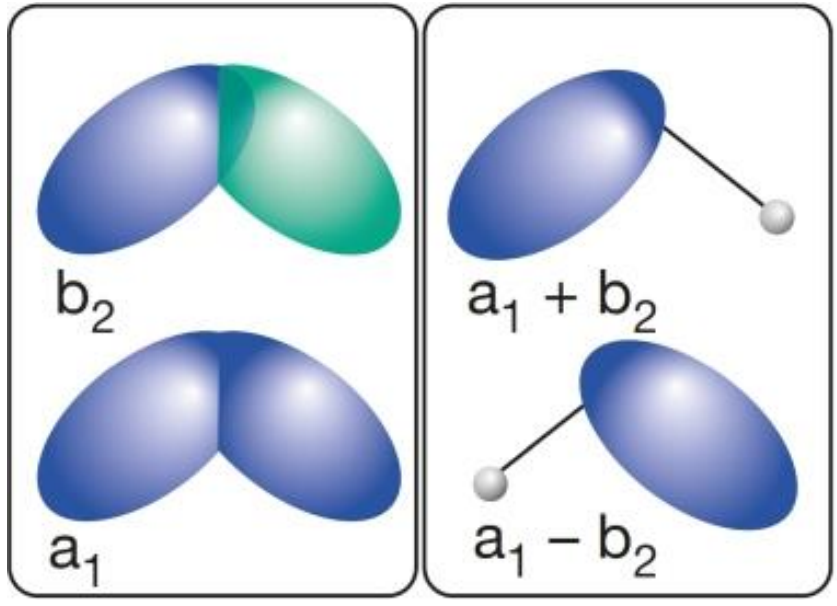
n.l.

Diagramma di Walsh



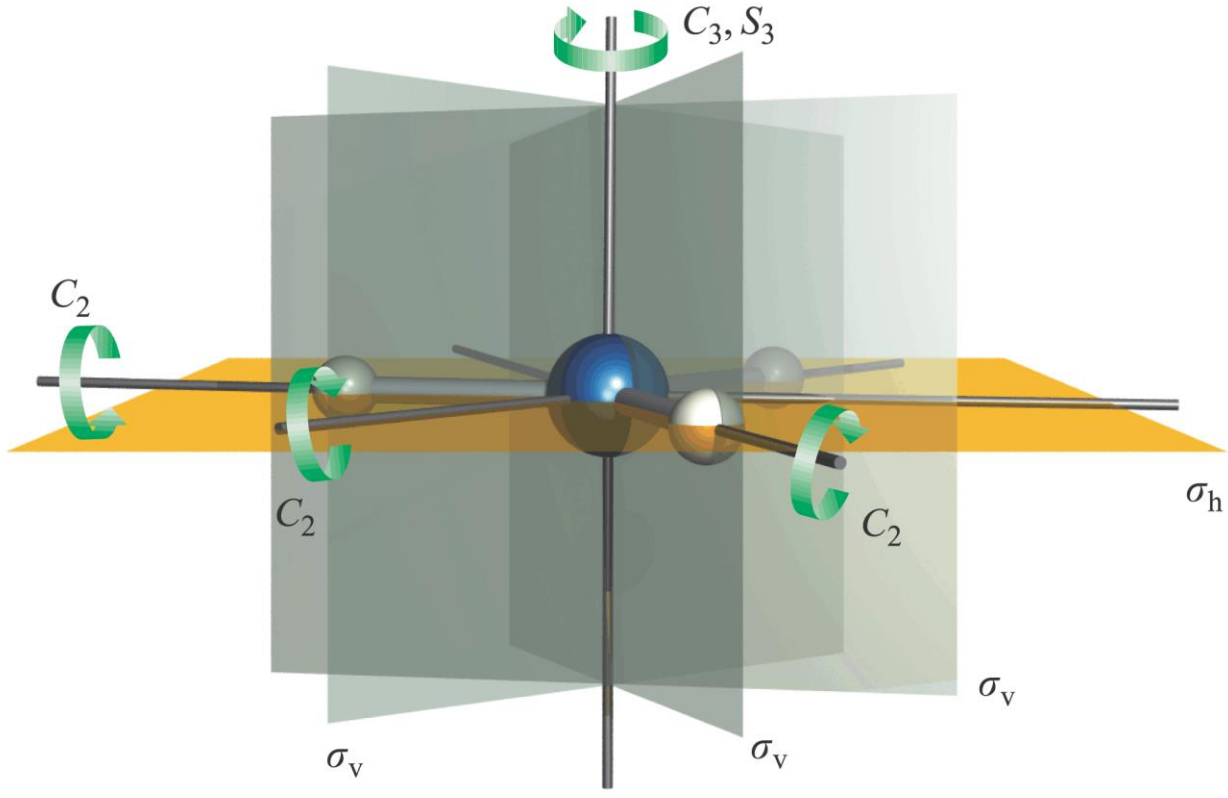

90°
180°
1b1
1πu
1b2
1σθ
u
1a1
1πu
2a1
1σg

Combinazioni lineari di orbitali molecolari



Localizzate	Delocalizzate
Forza dei legami	Spettri elettronici
Costanti di forza	Fotoionizzazione
Lunghezze di legame	Affinità elettronica
Acidità di Brønsted*	Magnetismo
Descrizione VSEPR	Potenziali standard†

BH_3, gruppo puntuale D_{3h}

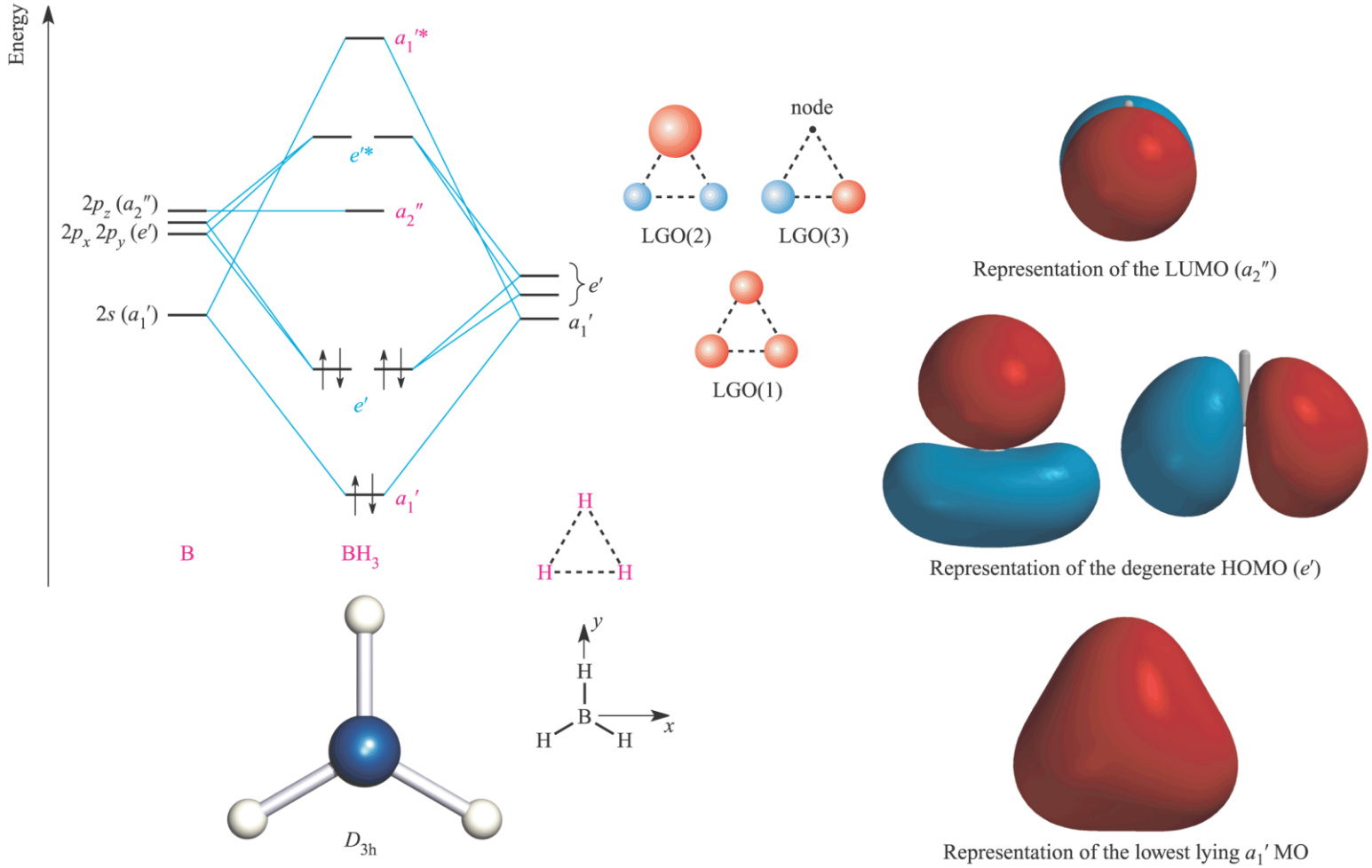


D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

3H

3	0	1	3	0	1

$A_1' + E'$

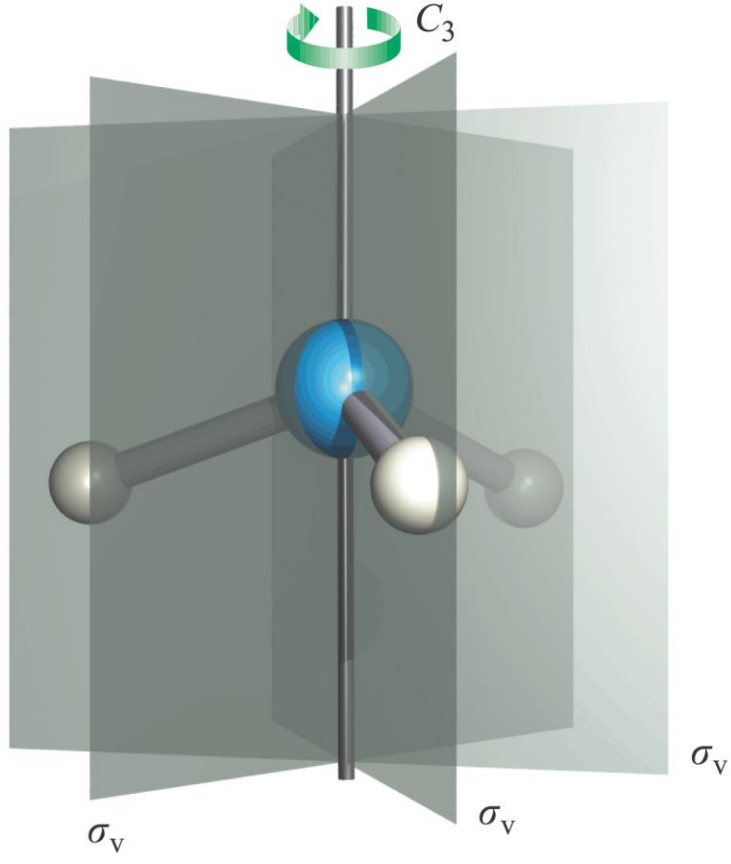


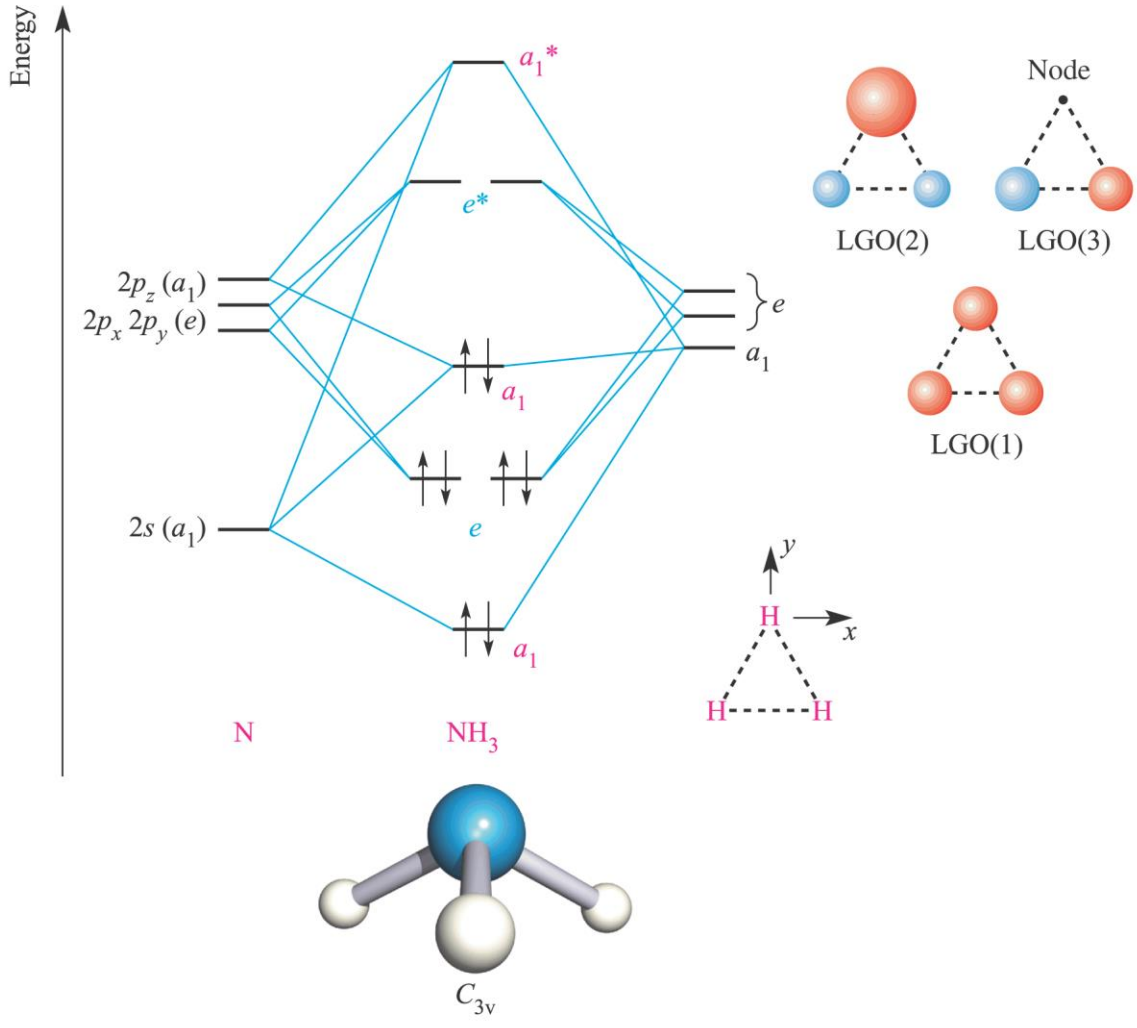
$$\Psi(a_1') = 1/\sqrt{3} \times (\Psi_1 + \Psi_2 + \Psi_3) \qquad \text{(LGO1)}$$

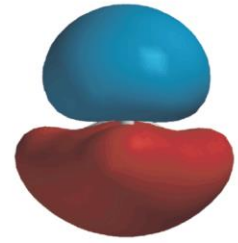
$$\Psi(e')_1 = 1/\sqrt{6} \times (2\Psi_1 - \Psi_2 - \Psi_3) \qquad \text{(LGO2)}$$

$$\Psi(e')_2 = 1/\sqrt{2} \times (\Psi_2 - \Psi_3) \qquad \text{(LGO3)}$$

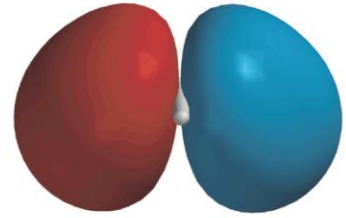
NH_3, gruppo puntuale C_{3v}



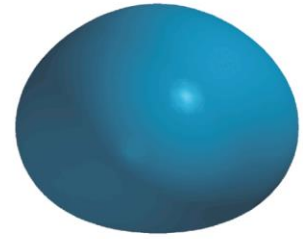




Representation of the HOMO (a_1)

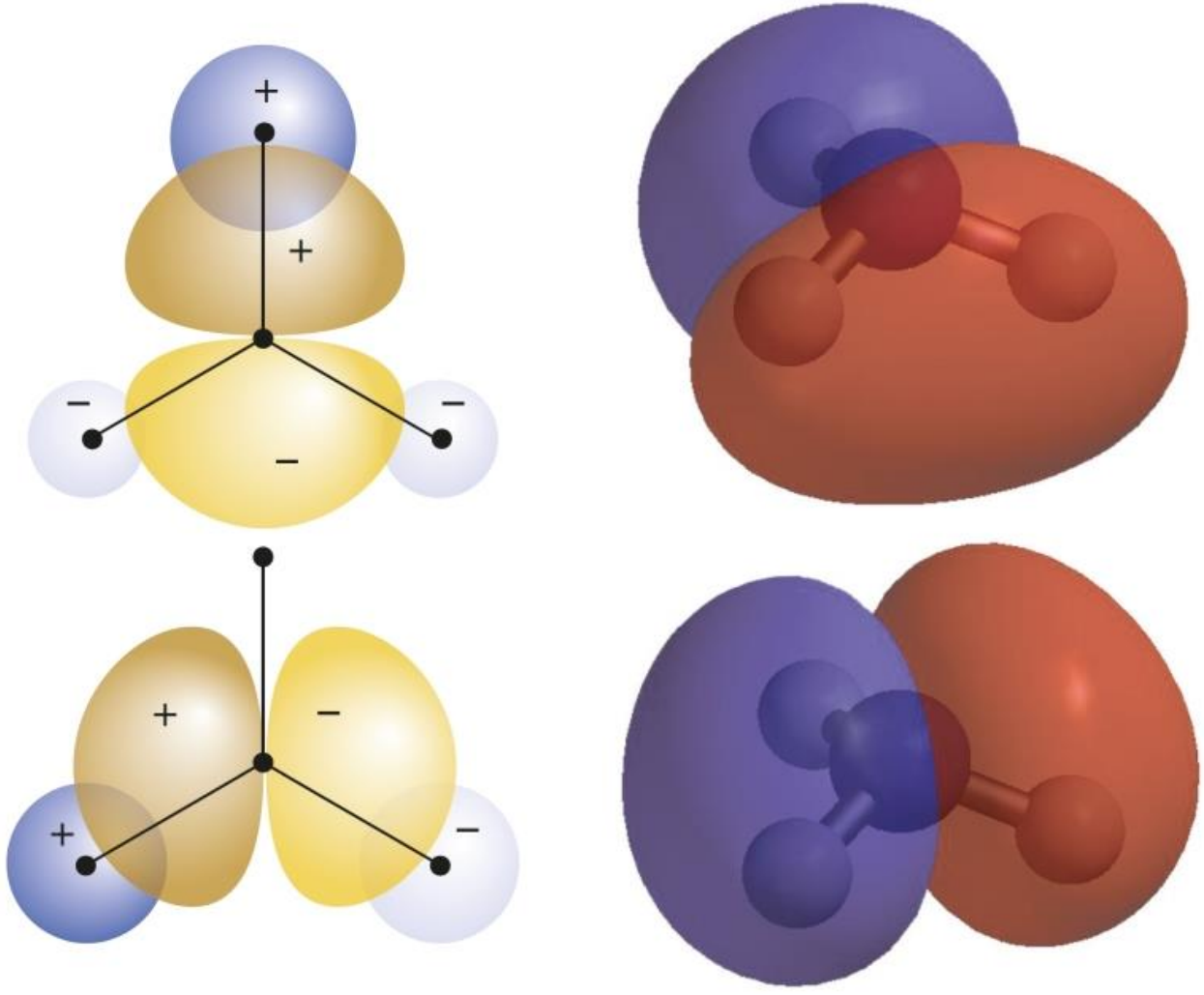


Representation of one of the e MOs

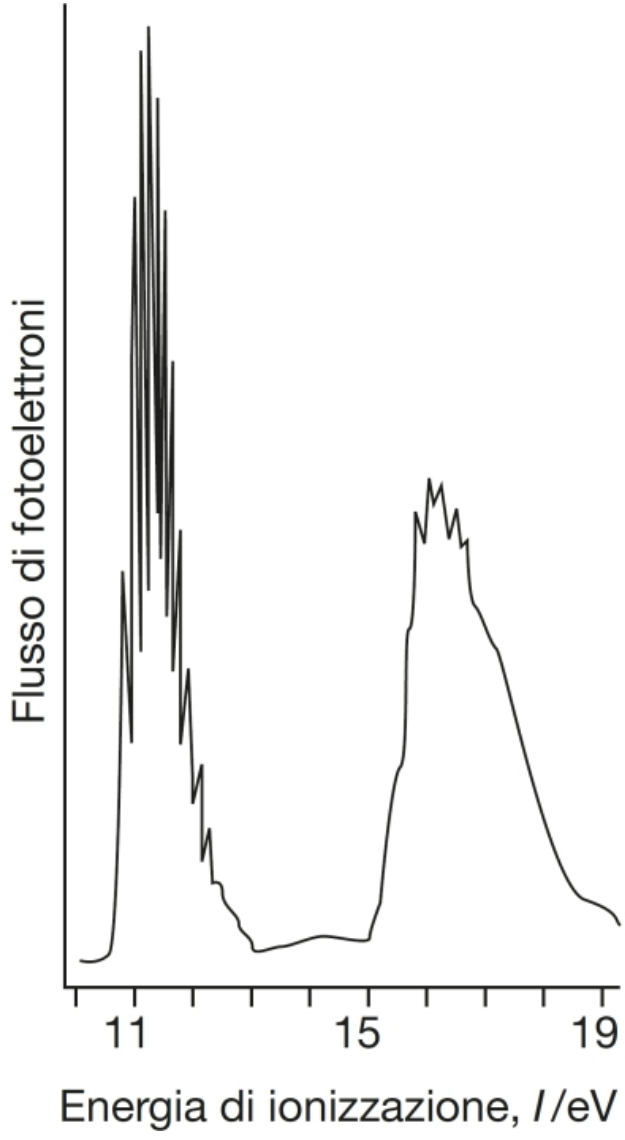


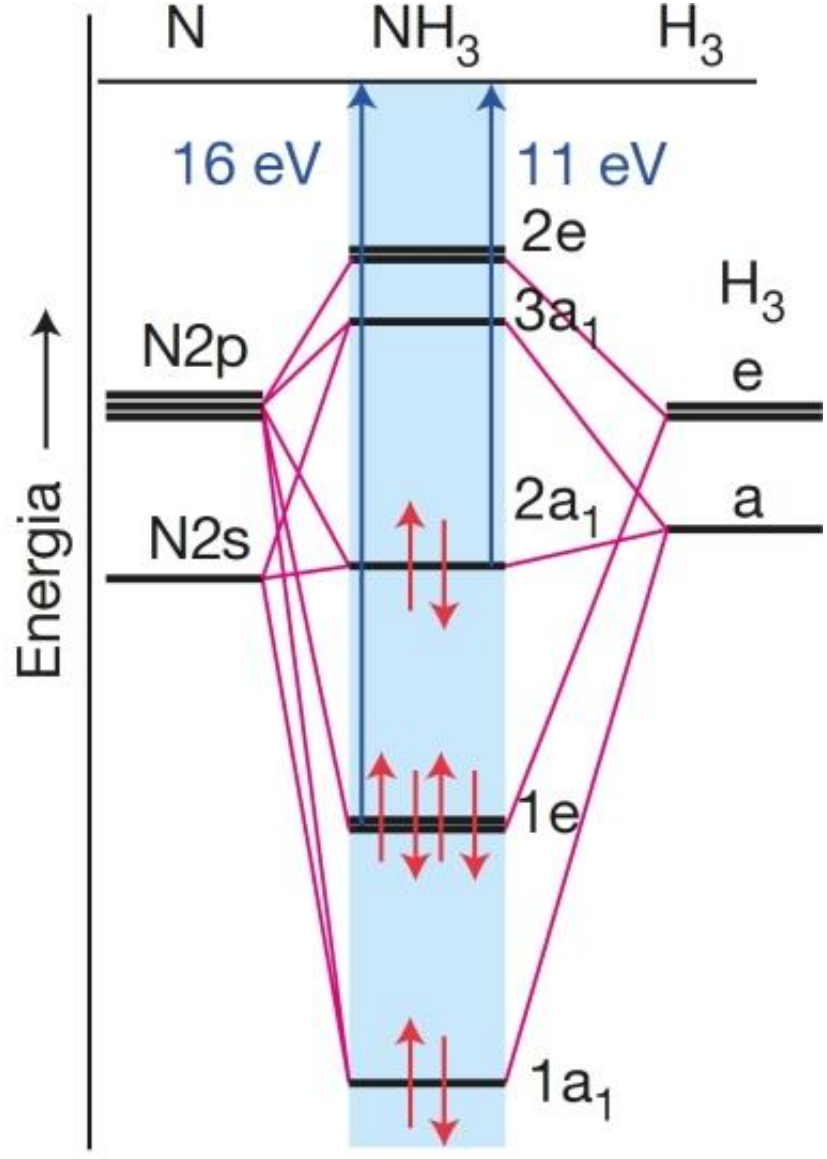
Representation of the lowest lying a_1 MO

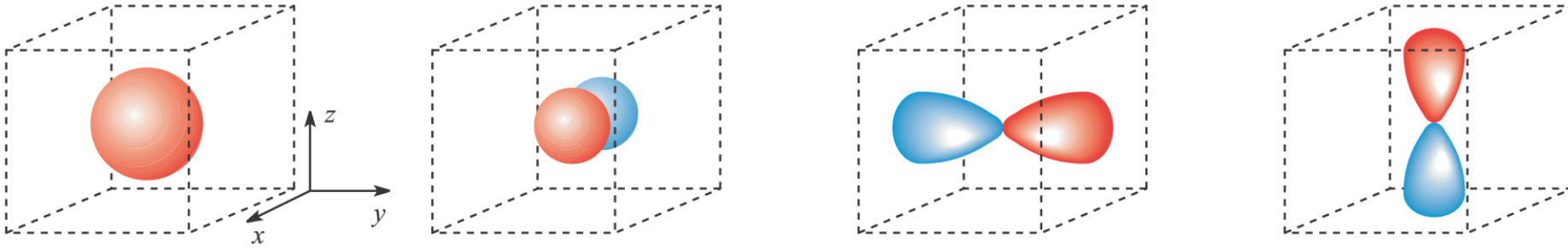
Formazione degli orbitali molecolari leganti e



Spettro di fotoelettroni di NH_3

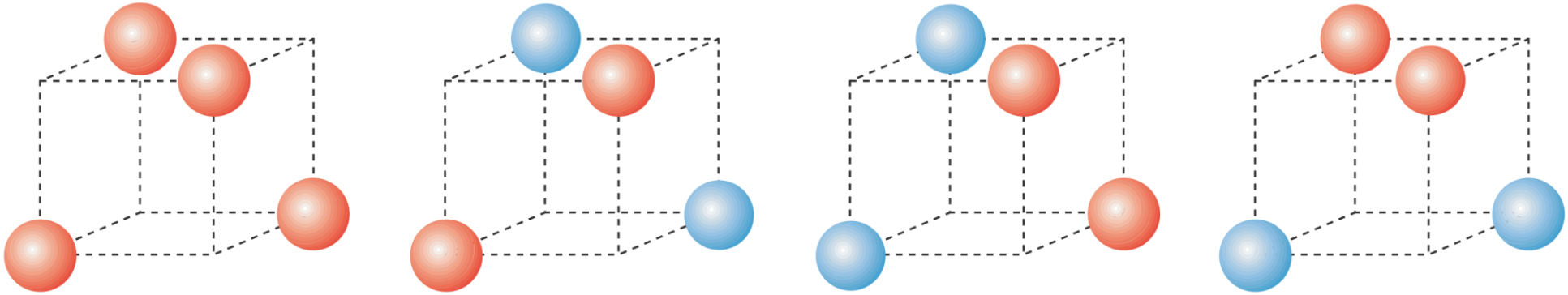






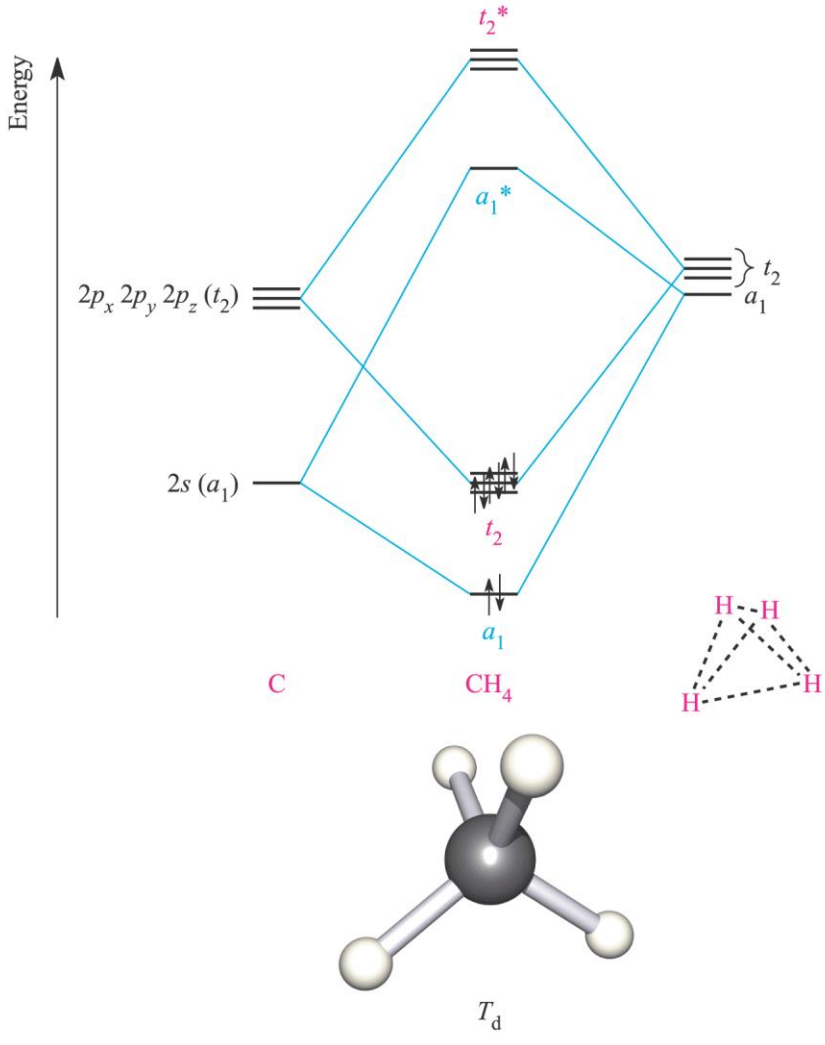
$2s\ (a_1)$ $2p_x\ (t_2)$ $2p_y\ (t_2)$ $2p_z\ (t_2)$

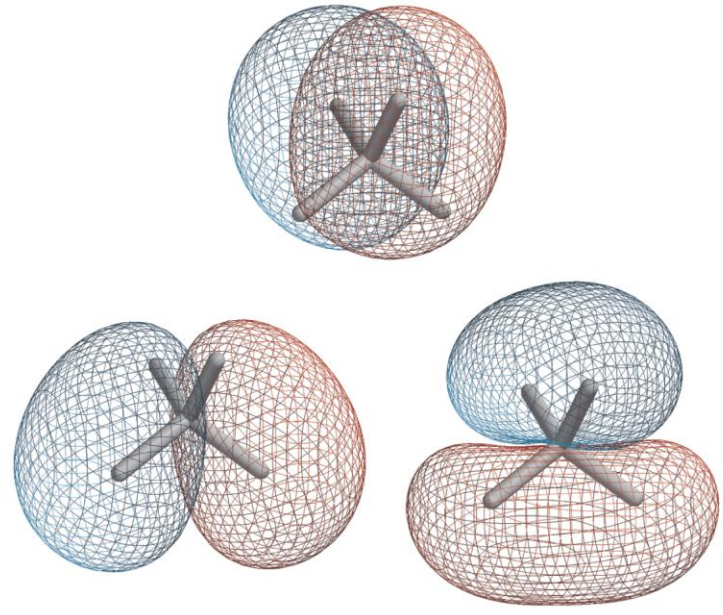
(a)



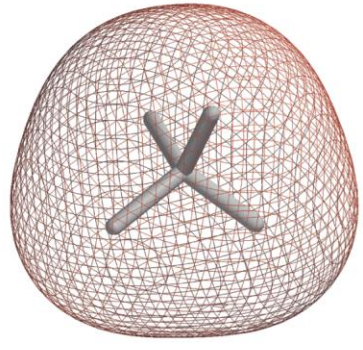
LGO(1) (a_1) LGO(2) (t_2) LGO(3) (t_2) LGO(4) (t_2)

(b)





Representations of the triply degenerate (t_2) bonding MOs

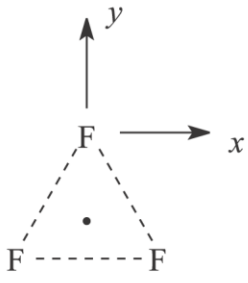


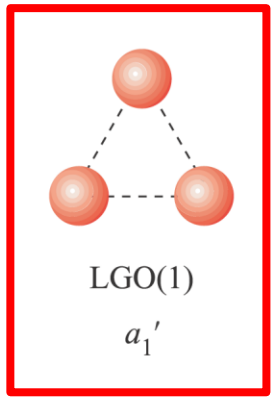
Representation of the a_1 bonding MO

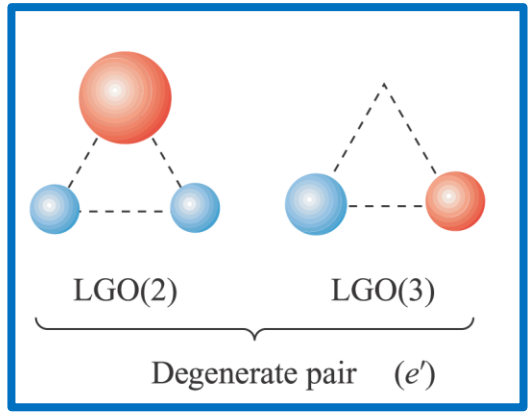
BF_3

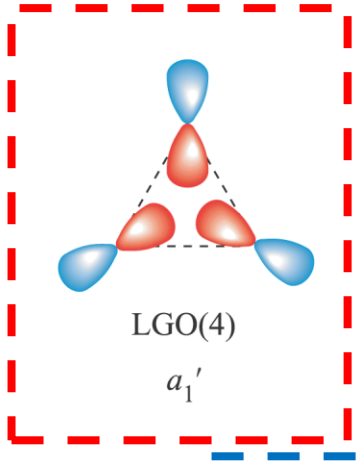
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

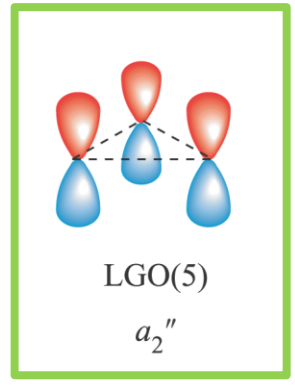
BF_3

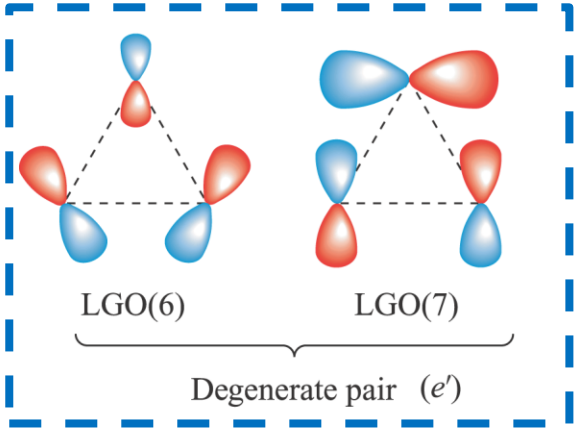


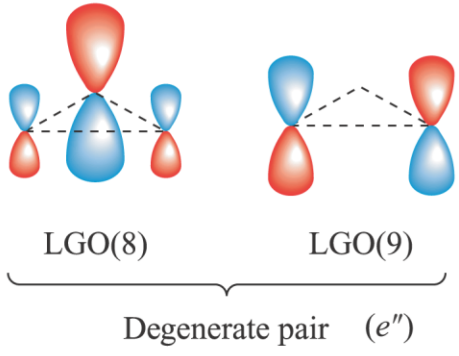


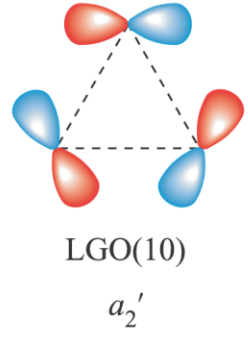


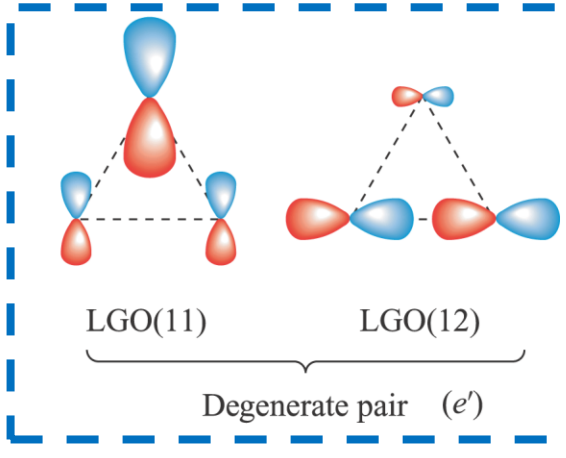










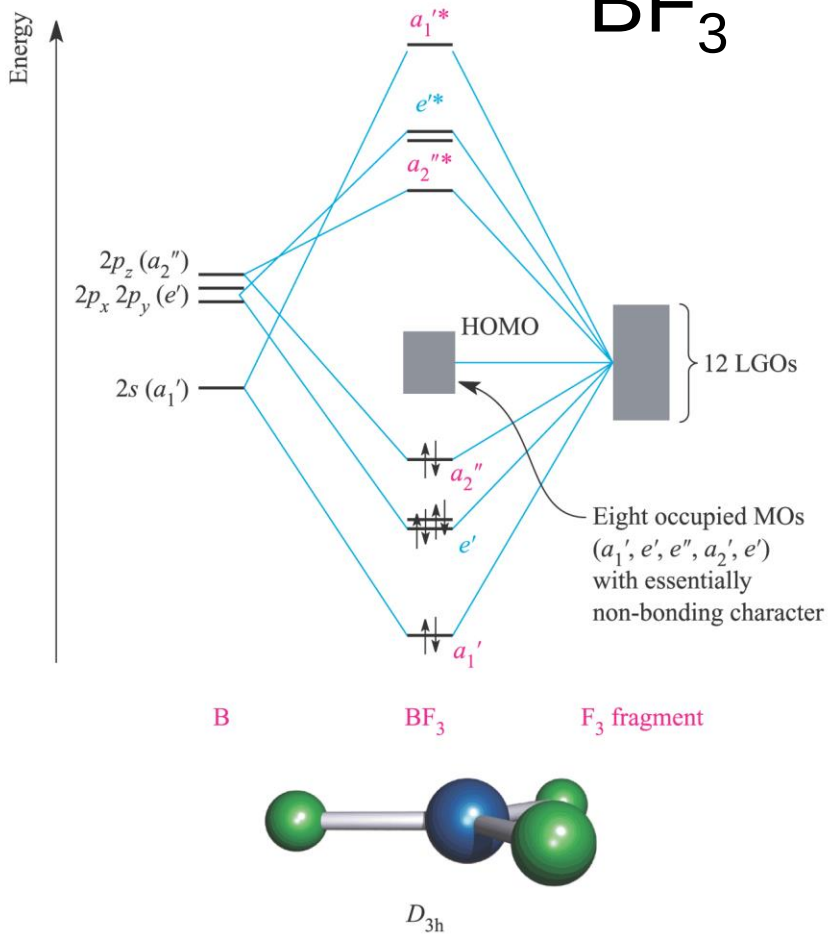


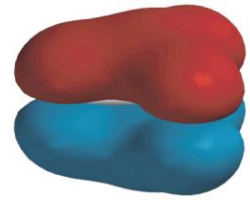
tre $2p_z$

E	C_3	C_2	σ_h	S_3	σ_v
3	0	-1	-3	0	1

$A_2'' + E''$

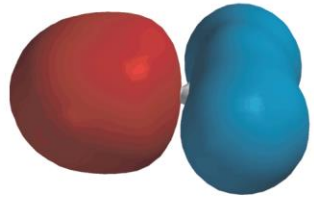
BF_3





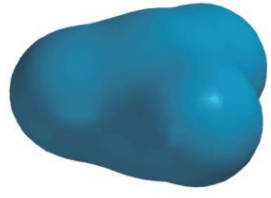
Representation of the a_2'' MO

π



Representation of one of the e' MOs

σ



Representation of the a_1' MO

σ

Ordine di legame 4/3

Molecole ipervalenti: SF_6 (gruppo O_h)

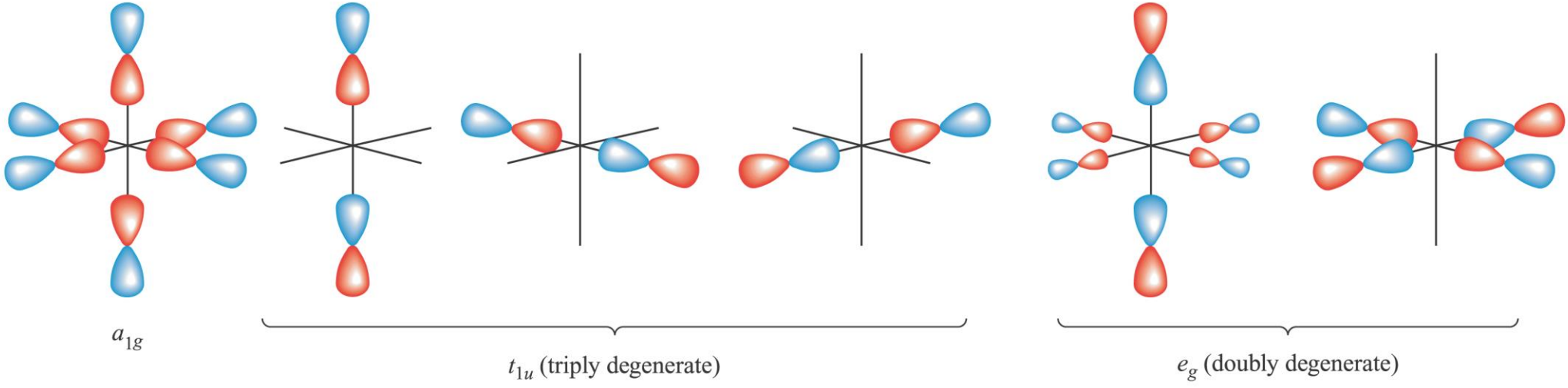
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ $(= C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1
E_g	2	−1	0	0	2	2	0	−1	2	0
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1
E_u	2	−1	0	0	2	−2	0	1	−2	0
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1

sei $2p_z$ radiali

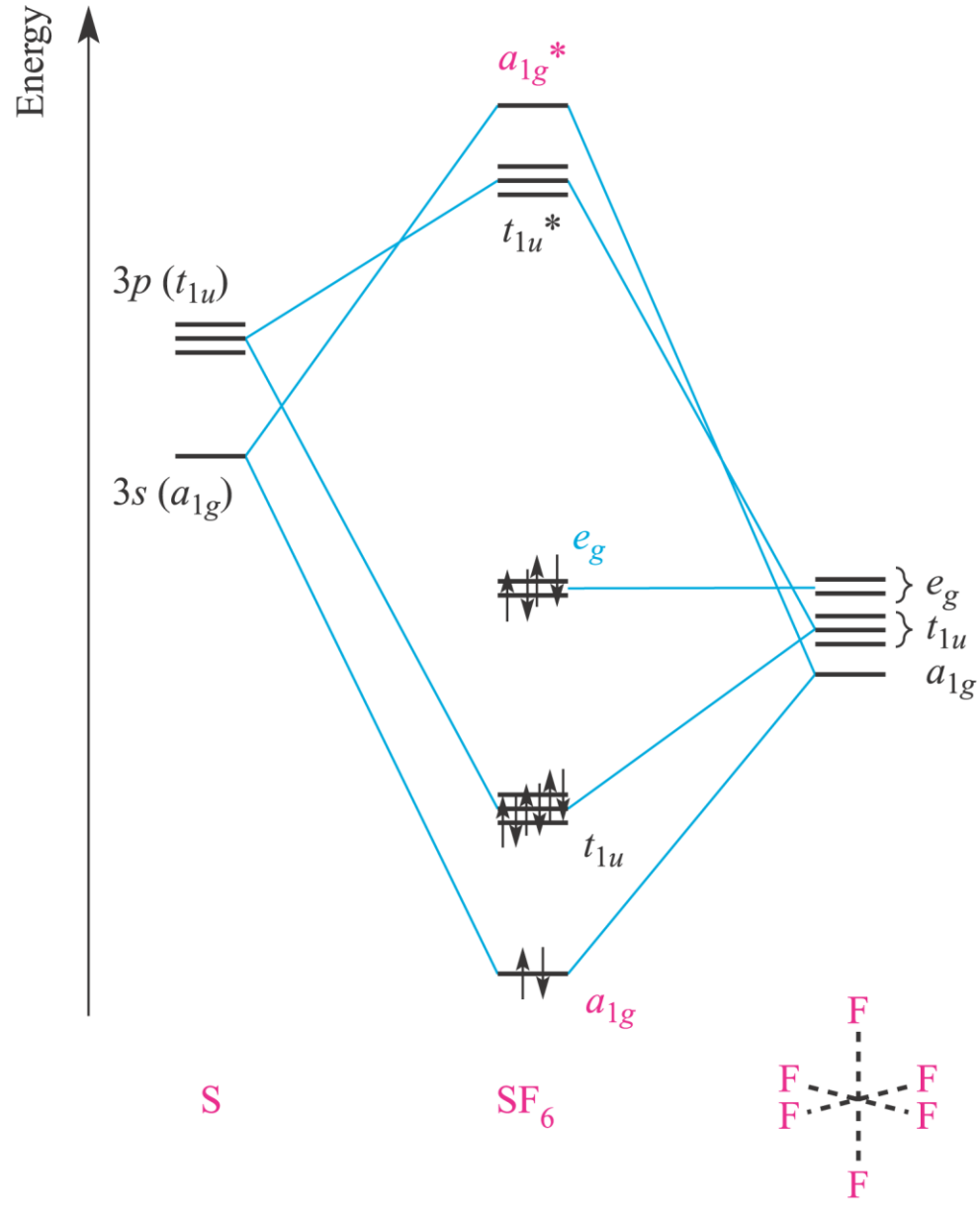
E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
6	0	0	2	2	0	0	0	4	2

$$A_{1g} + T_{1u} + E_g$$

LGO del frammento F_6 in SF_6



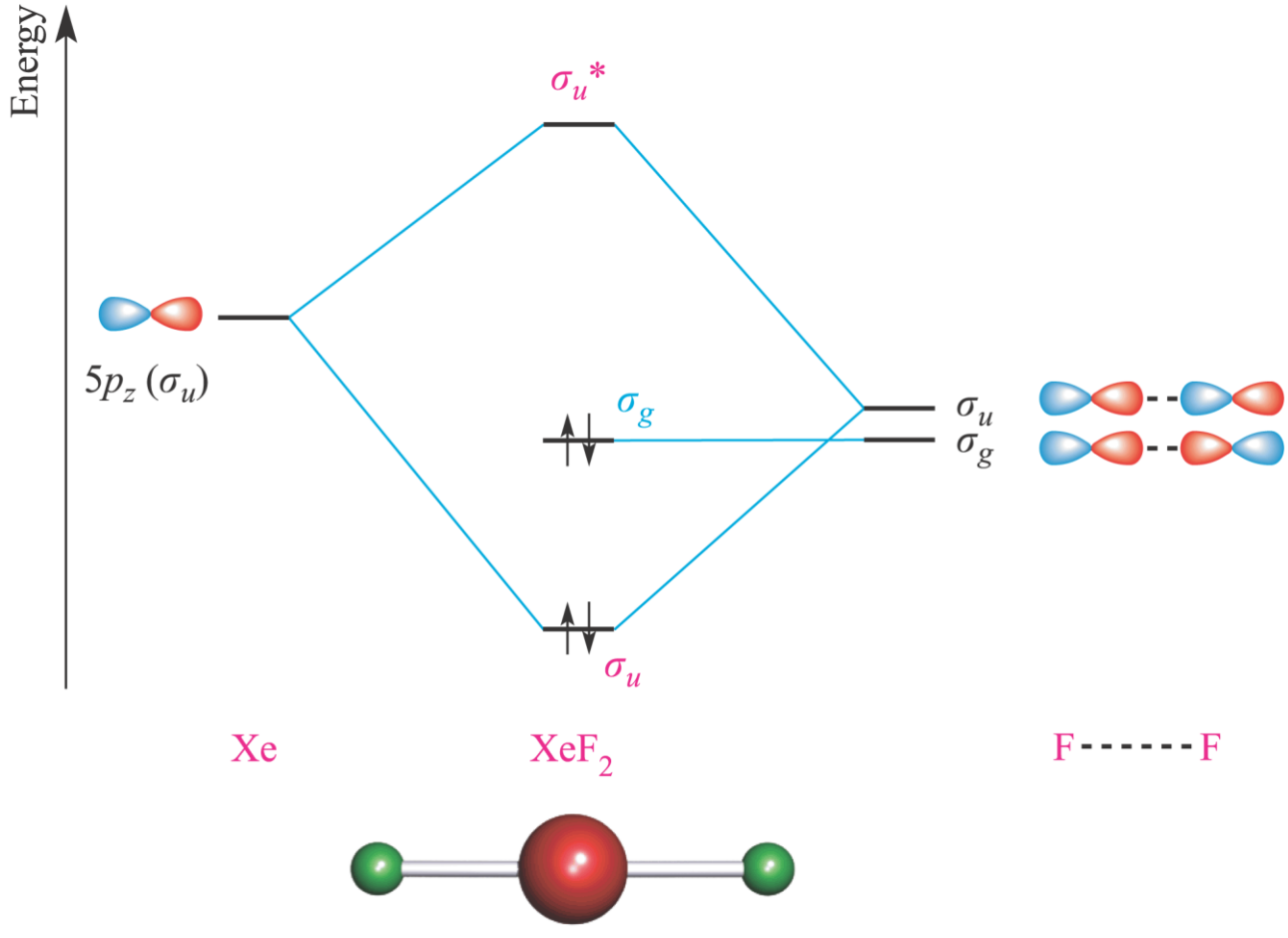
nonlegame



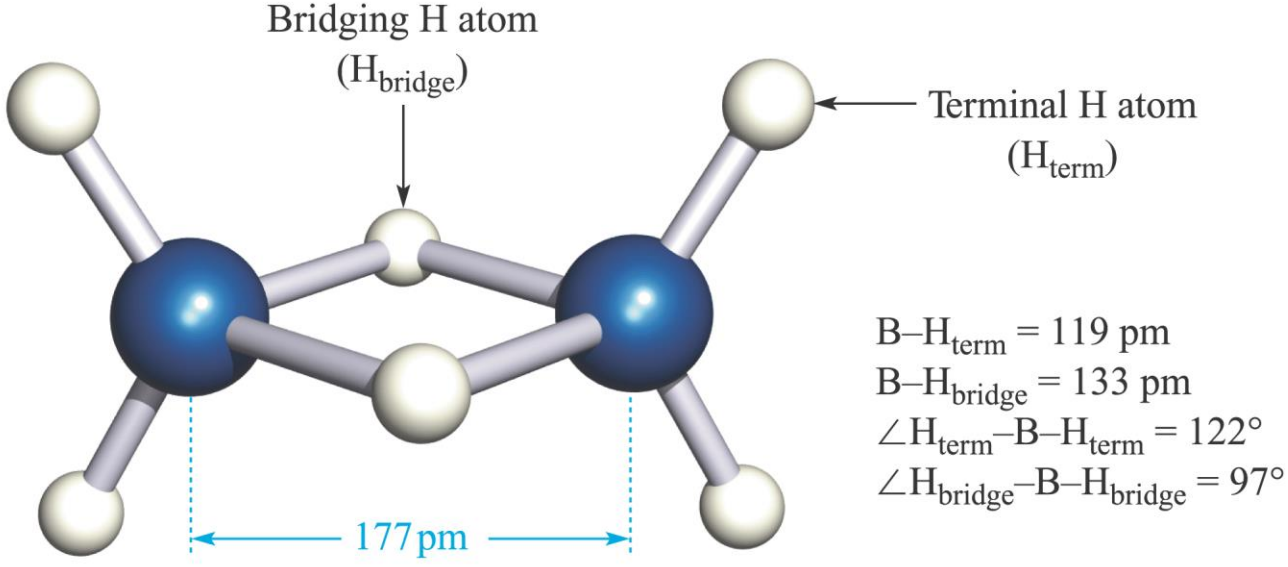
+ 18 MO di nonlegame

Ordine di legame 2/3, nessun orbitale d

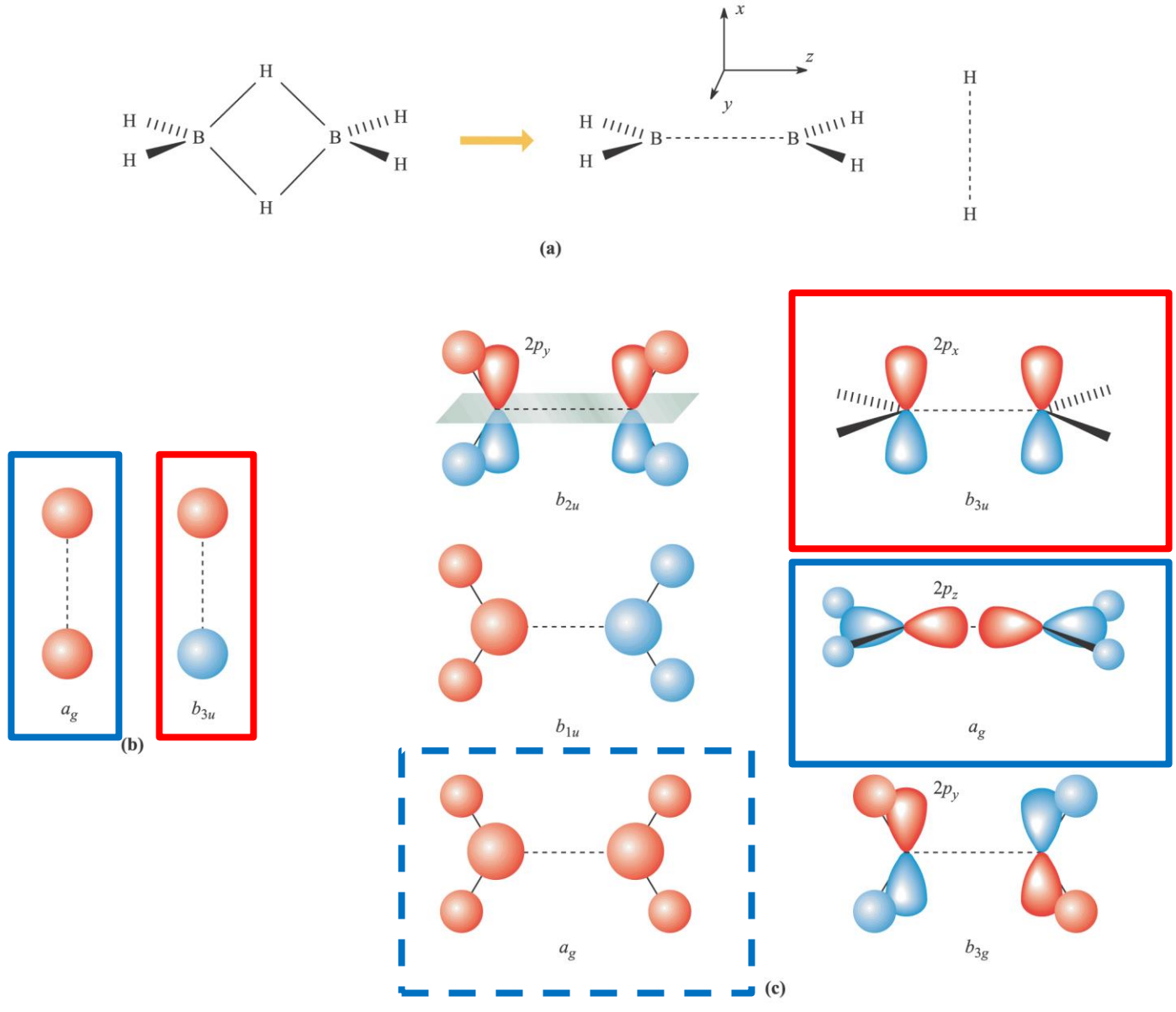
XeF_2: Interazione 3*c* – 2*e*



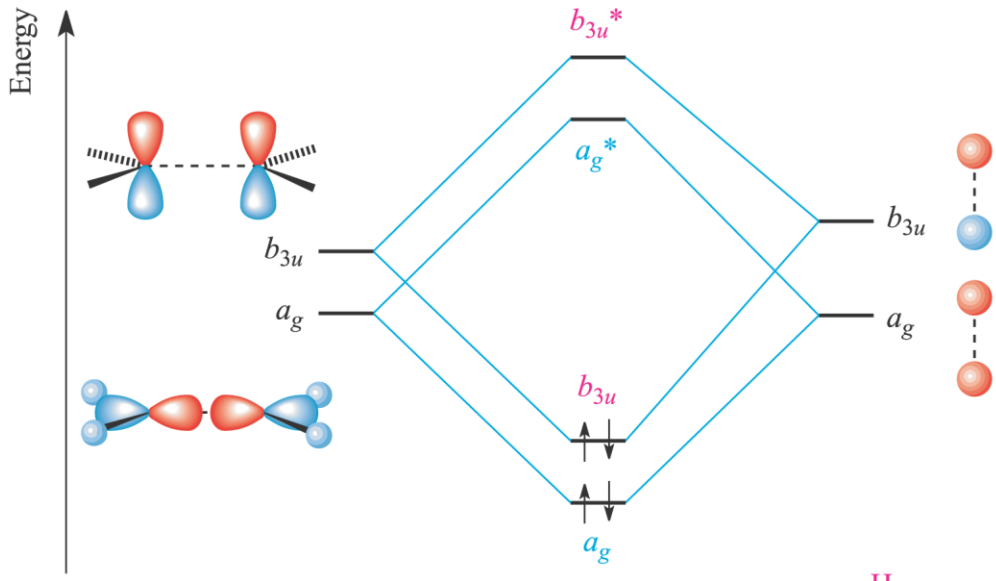
Diborano, B_2H_6



D_{2h}

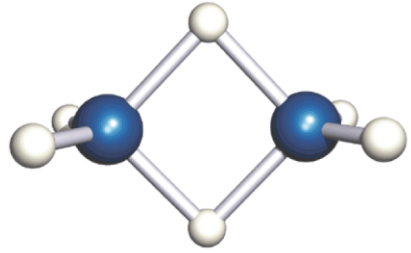


6 LGO (su 12) a energia più bassa del frammento B_2H_4

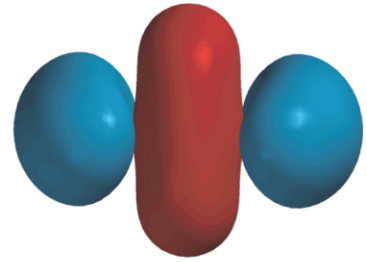


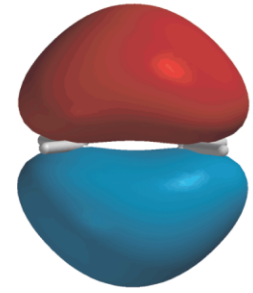
H_2B ----- BH_2 B_2H_6

H
H



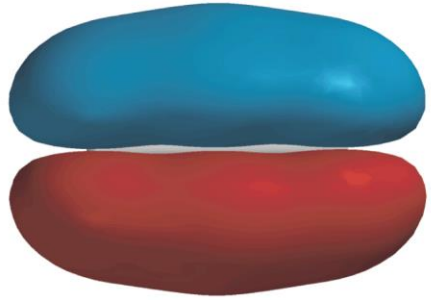
D_{2h}



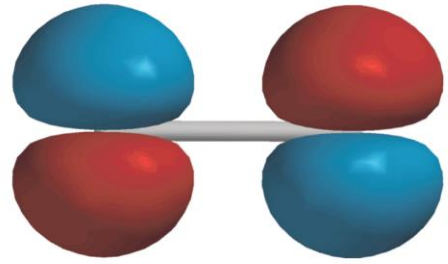


Representation of the a_g (top) and b_{3u} MOs which contain B–H–B bonding character

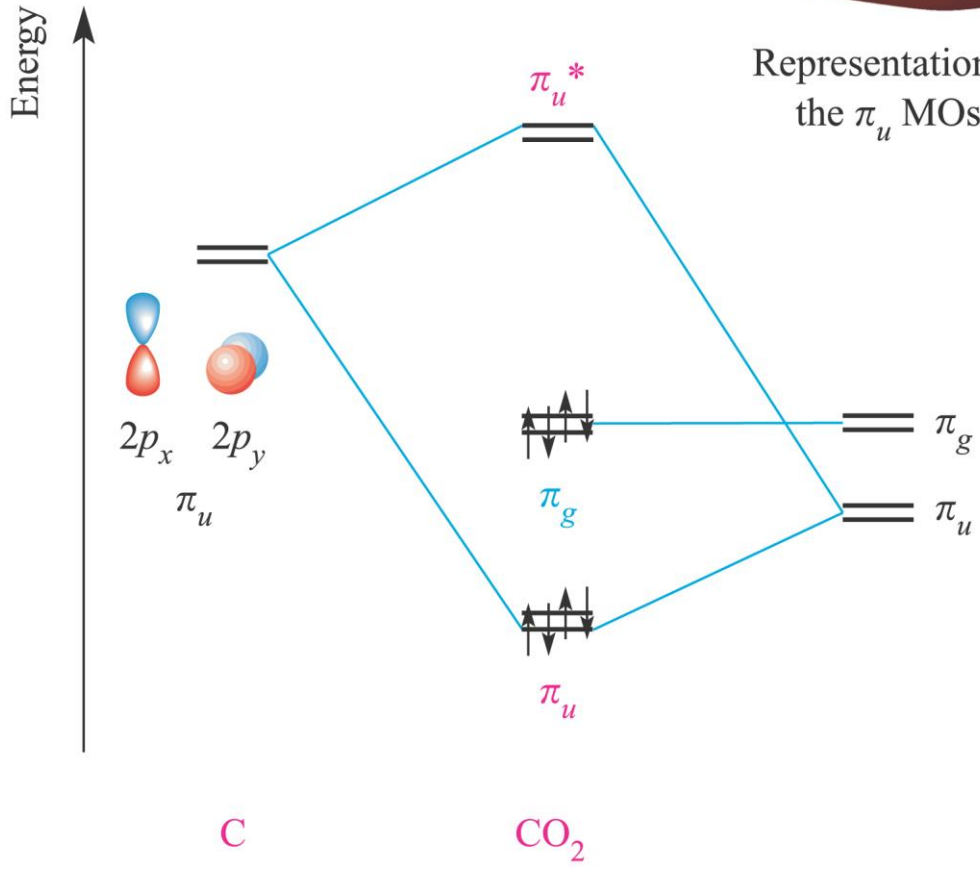
Diagrammi MO parziali: CO_2

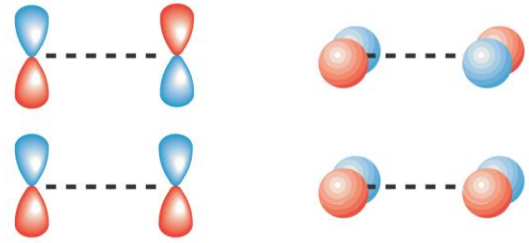


Representation of one of the π_u MOs in CO_2



Representation of one of the π_g MOs in CO_2



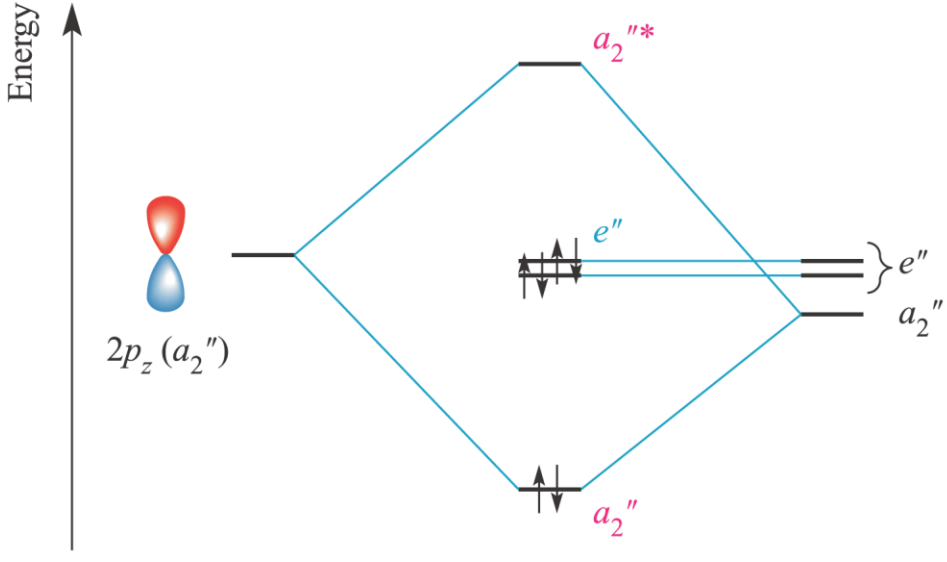


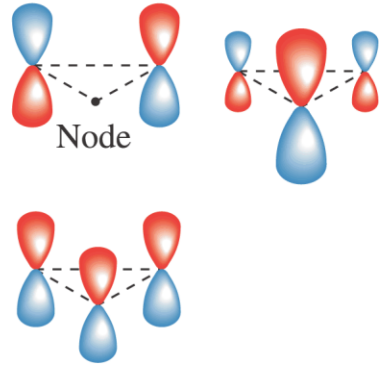
Combination of $2p_x$ orbitals

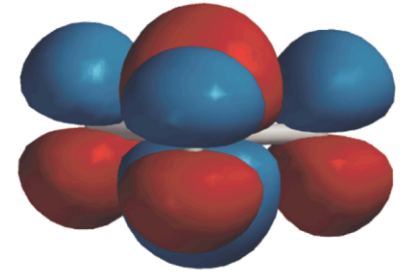
Combination of $2p_y$ orbitals

O------O

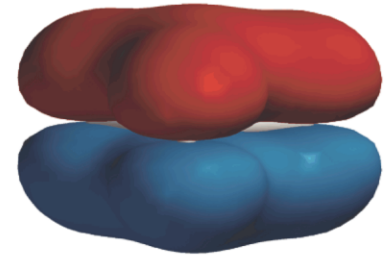
NO_3^-





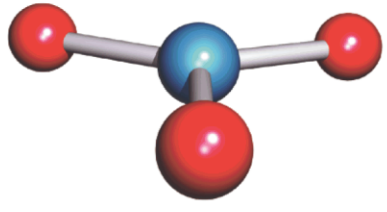


A representation of the $a_2''^*$ MO



A representation of the a_2'' MO showing the delocalization of π-character over the N and O centres

N $[NO_3]^-$



D_{3h}