

Fig. 3.6 Successive C_3 rotations in NH_3 are distinguished using the notation C_3 , C_3^2 and C_3^3 . The effect of the last operation is the same as that of the identity operator acting on NH_3 in the initial configuration.

$$S_3 = C_3 \times \sigma_h$$

Point group	Characteristic symmetry elements	Comments
C_s	E , one σ plane	
C_i	E , inversion centre	
C_n	E , one (principal) n -fold axis	
C_{nv}	E , one (principal) n -fold axis, n σ_v planes	
C_{nh}	E , one (principal) n -fold axis, one σ_h plane, one S_n -fold axis which is coincident with the C_n axis	The S_n axis necessarily follows from the C_n axis and σ_h plane. For $n = 2, 4$ or 6 , there is also an inversion centre.
D_{nh}	E , one (principal) n -fold axis, n C_2 axes, one σ_h plane, n σ_v planes, one S_n -fold axis	The S_n axis necessarily follows from the C_n axis and σ_h plane. For $n = 2, 4$ or 6 , there is also an inversion centre.
D_{nd}	E , one (principal) n -fold axis, n C_2 axes, n σ_v planes, one S_{2n} -fold axis	For $n = 3$ or 5 , there is also an inversion centre.
T_d		Tetrahedral
O_h		Octahedral
I_h		Icosahedral

Tabla de caracteres

Un grupo puntual es un conjunto de operaciones de simetría que forman un grupo matemático para el que al menos un punto permanece fijo bajo todas las operaciones del grupo. En tres dimensiones hay 32 grupos, 30 de los cuales son relevantes en química

Las operaciones de simetría pueden representarse de muchos modos. Una representación conveniente es por matrices, donde la composición de operaciones corresponde a la multiplicación de matrices. En el ejemplo C_{2v}

$$\underbrace{\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix}}_{C_2} * \underbrace{\begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix}}_{\sigma_v} = \underbrace{\begin{vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}}_{\sigma'_v}$$

Aunque existe un número infinito de estas representaciones, normalmente se utilizan las representaciones irreducibles, pues las otras representaciones del grupo pueden describirse como combinaciones lineales de las representaciones irreducibles

Para cada grupo puntual, una tabla de caracteres resume la información sobre sus operaciones de simetría y sobre sus representaciones. Dado que siempre existe un número idéntico de representaciones de simetría y de clases de operaciones de simetría, las tablas son cuadradas.

La tabla consiste en una serie de caracteres que representan cómo una representación irreducible se transforma cuando se aplica una cierta operación de simetría.

Si consideramos ahora que la molécula tiene vectores u ORBITALES, al aplicar una operación de simetría puede cambiar la dirección del vector o fase

A, cuando la rotación alrededor del eje principal es simétrica.
B, cuando la rotación alrededor del eje principal es asimétrica.
E y **T** son representaciones doble y triplemente degeneradas respectivamente.

Cuando el grupo puntual tiene un centro de inversión, el subíndice '**g**' (del alemán gerade or even) señala ningún cambio en el signo, y el subíndice '**u**' (ungerade or uneven) un cambio en el signo, en relación con la inversión.

Con los grupos puntuales $C_{\infty v}$ and $D_{\infty h}$ los símbolos se toman prestados de la descripción del momento angular: Σ , Π , Δ .

Tabla de caracteres

Agua

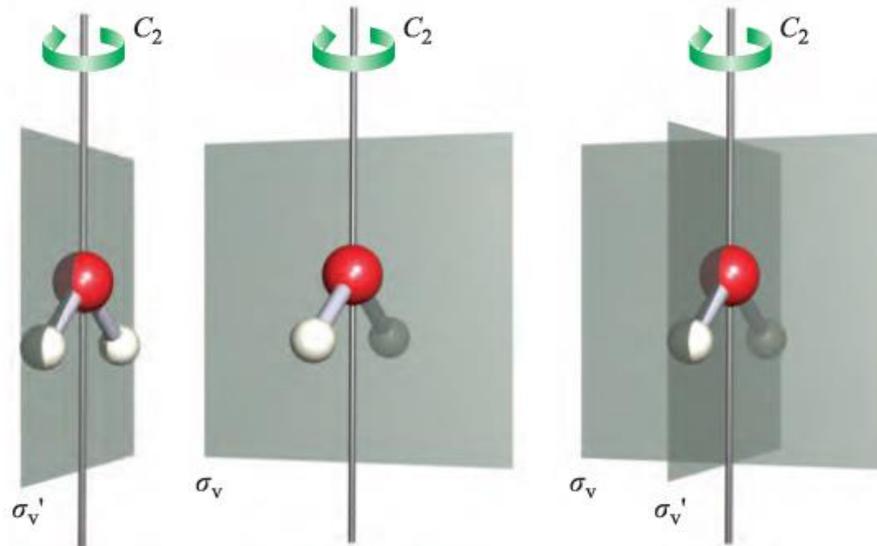
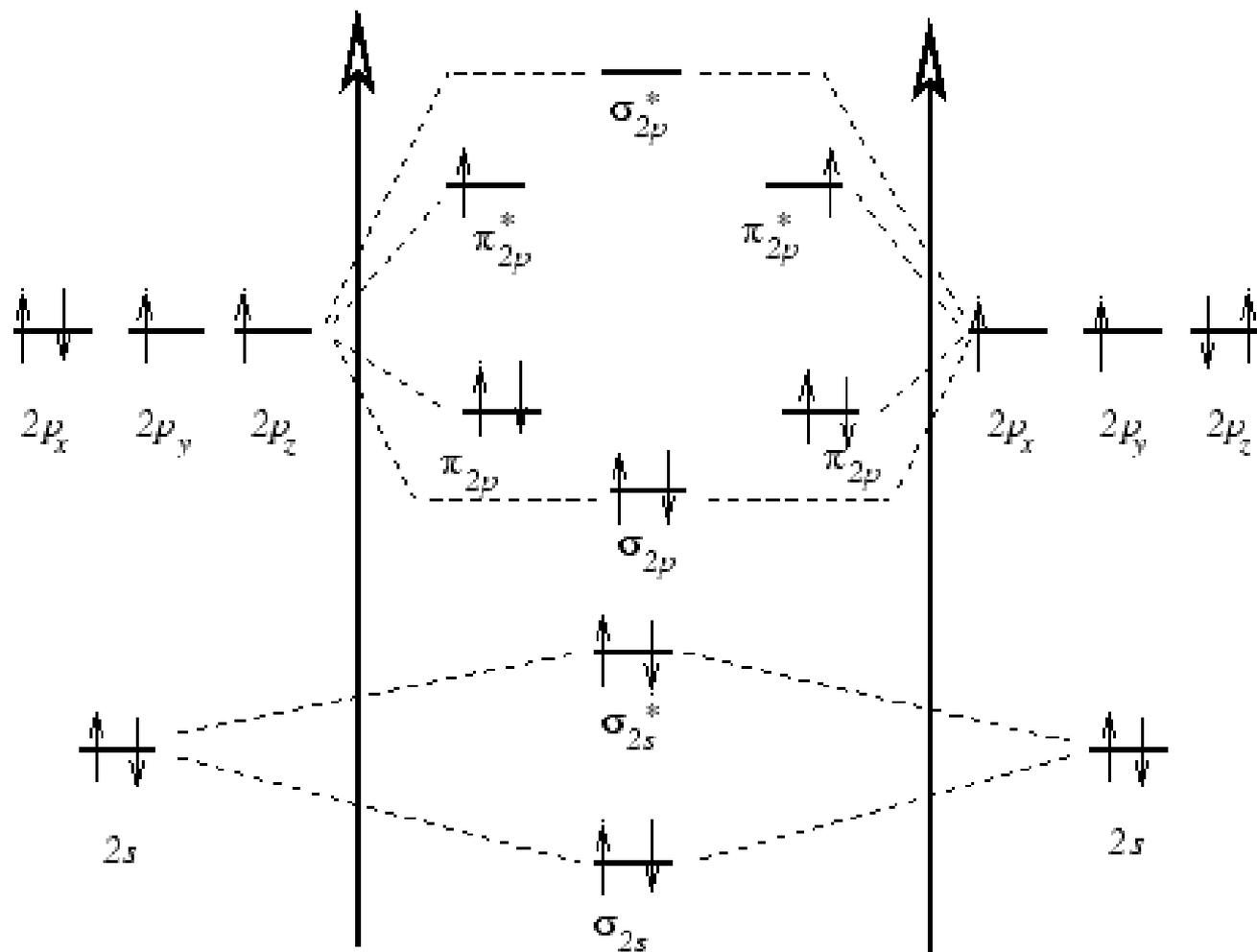


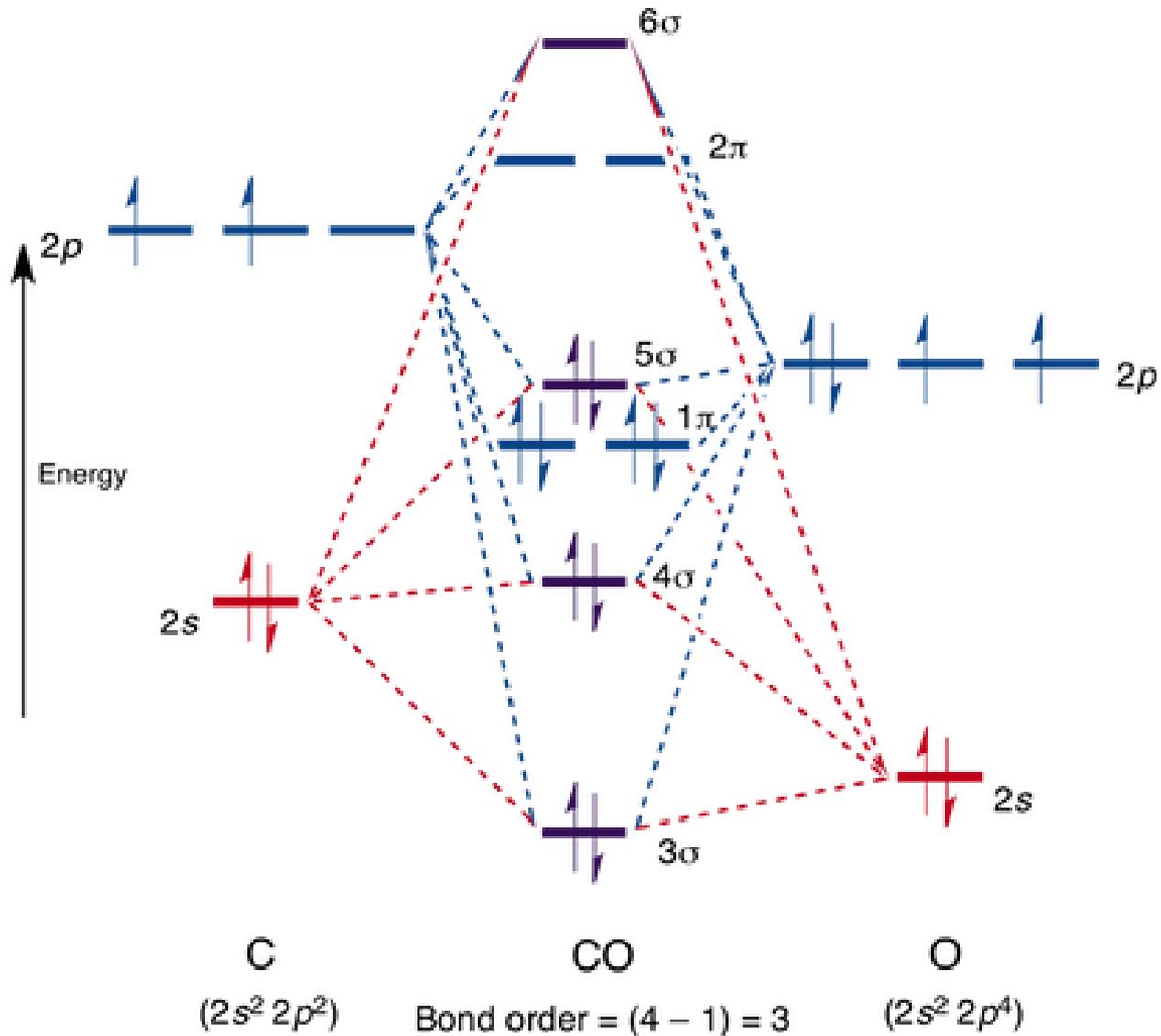
Table 3.2 The character table for the C_{2v} point group. For more character tables, see [Appendix 3](#).

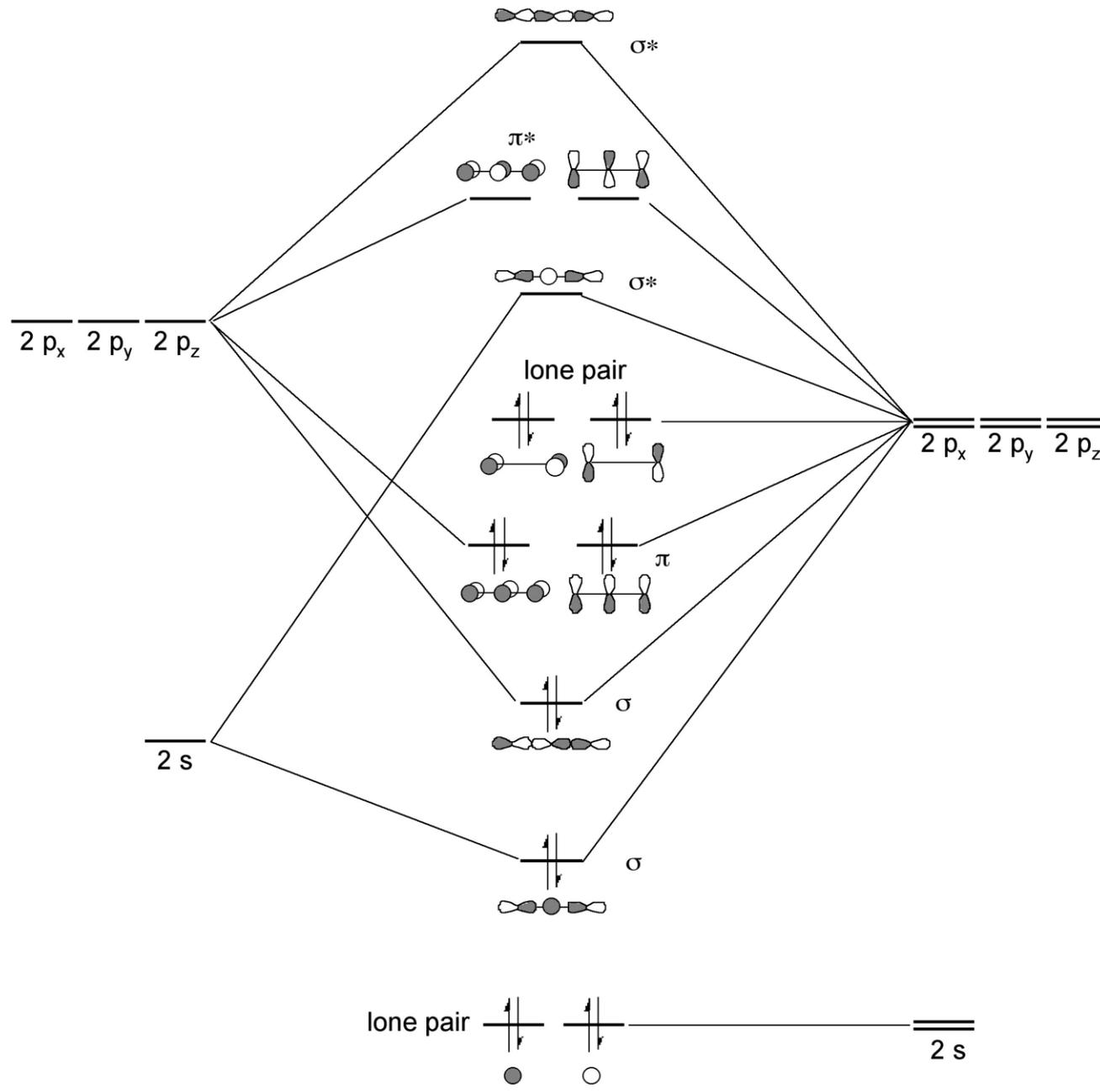
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	x, xz
B_2	1	-1	-1	1	y, R_x	y, yz

Orbitales moleculares



Monóxido de carbono

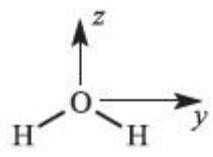
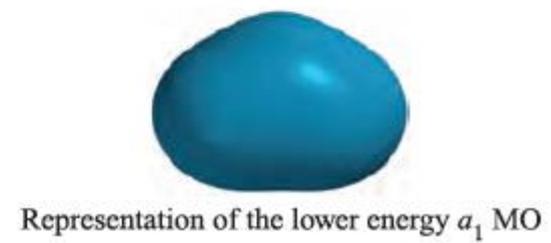
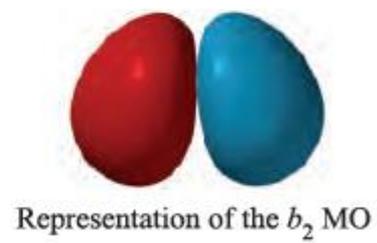
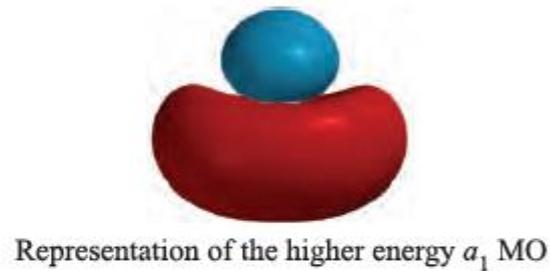
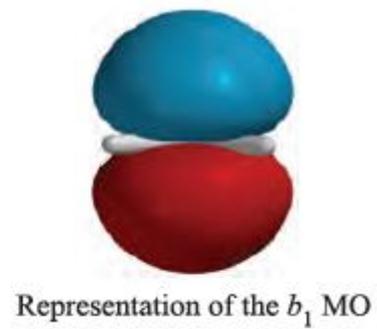
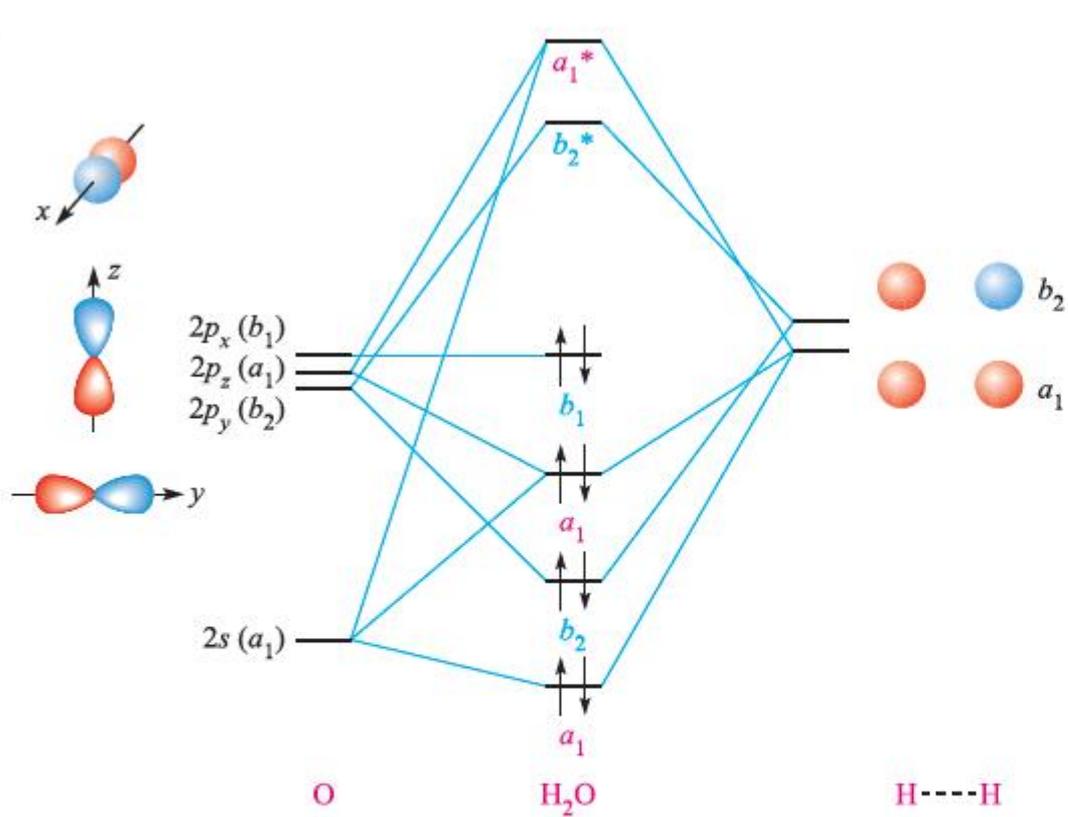




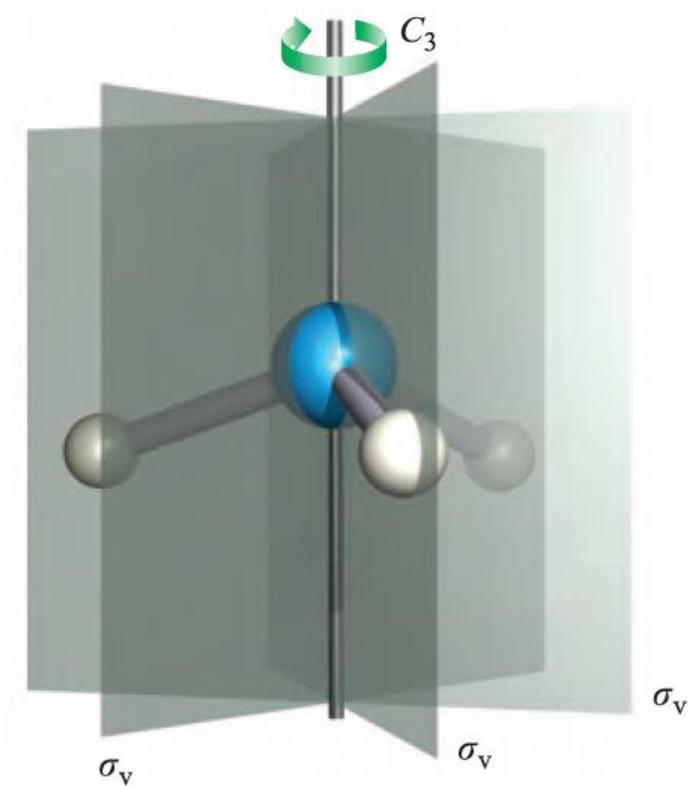
carbon

oxygen

Energy

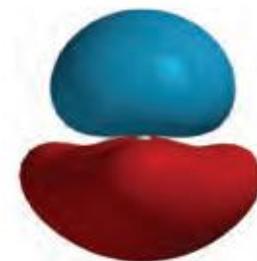
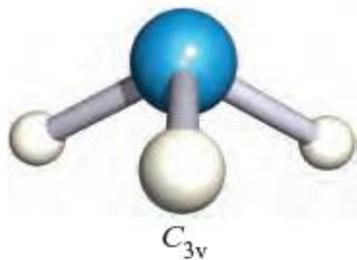
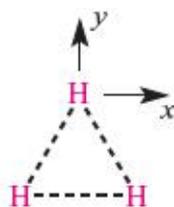
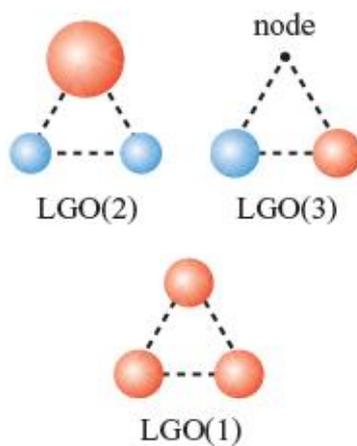
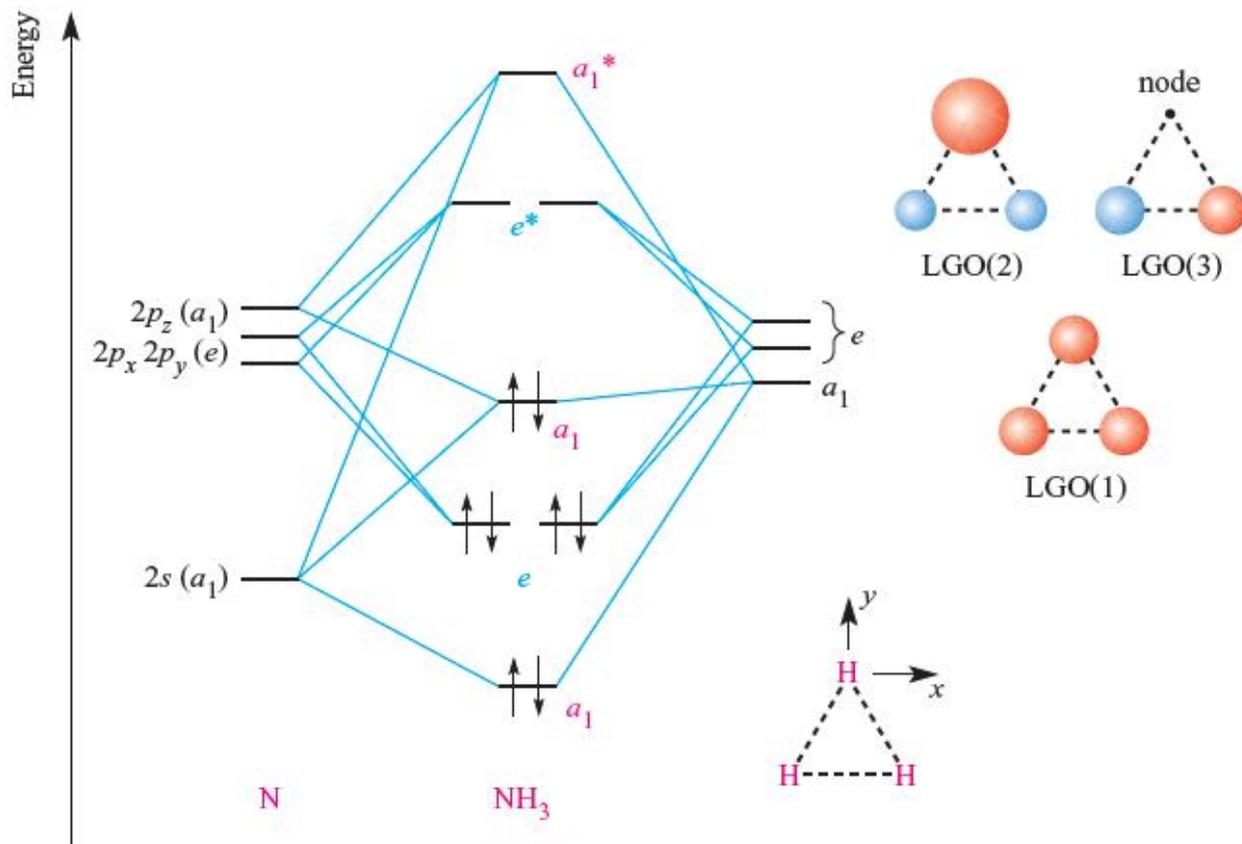


NH₃

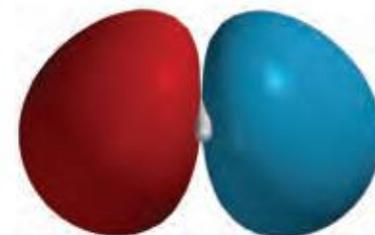


C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

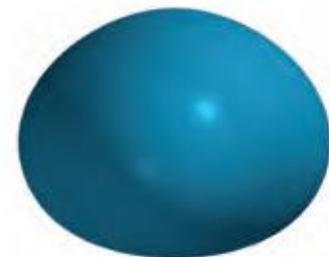
NH₃



Representation of the HOMO (a_1)



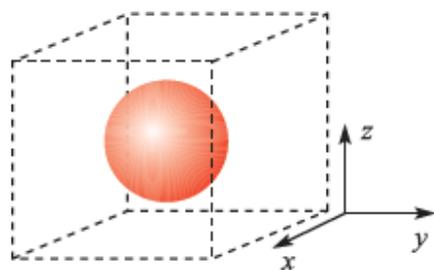
Representation of one of the e MOs



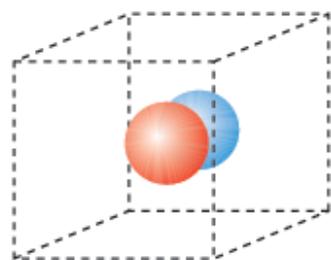
Representation of the lowest lying a_1 MO

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

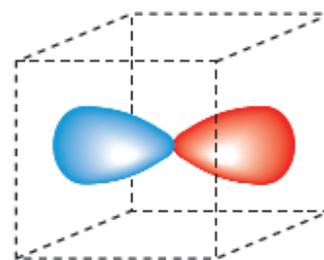
CH₄



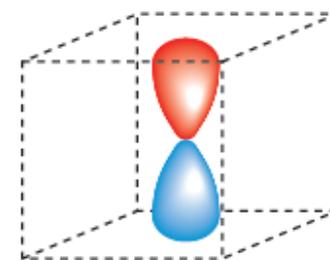
$2s (a_1)$



$2p_x (t_2)$

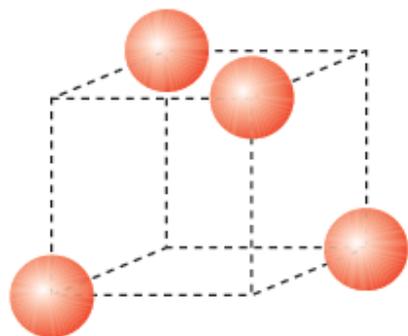


$2p_y (t_2)$

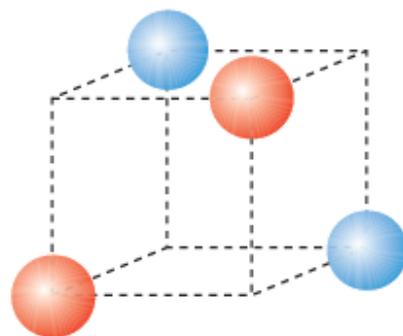


$2p_z (t_2)$

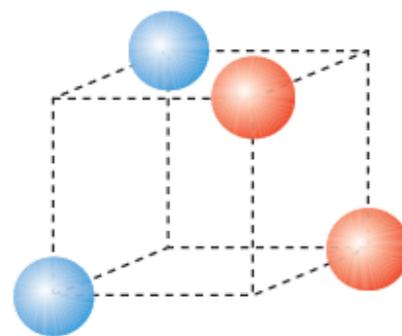
(a)



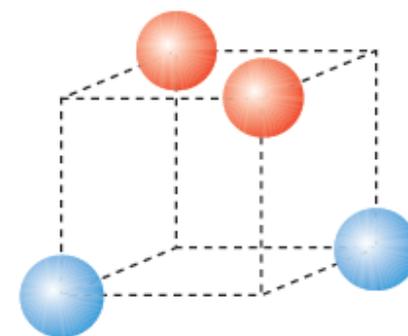
LGO(1) (a_1)



LGO(2) (t_2)

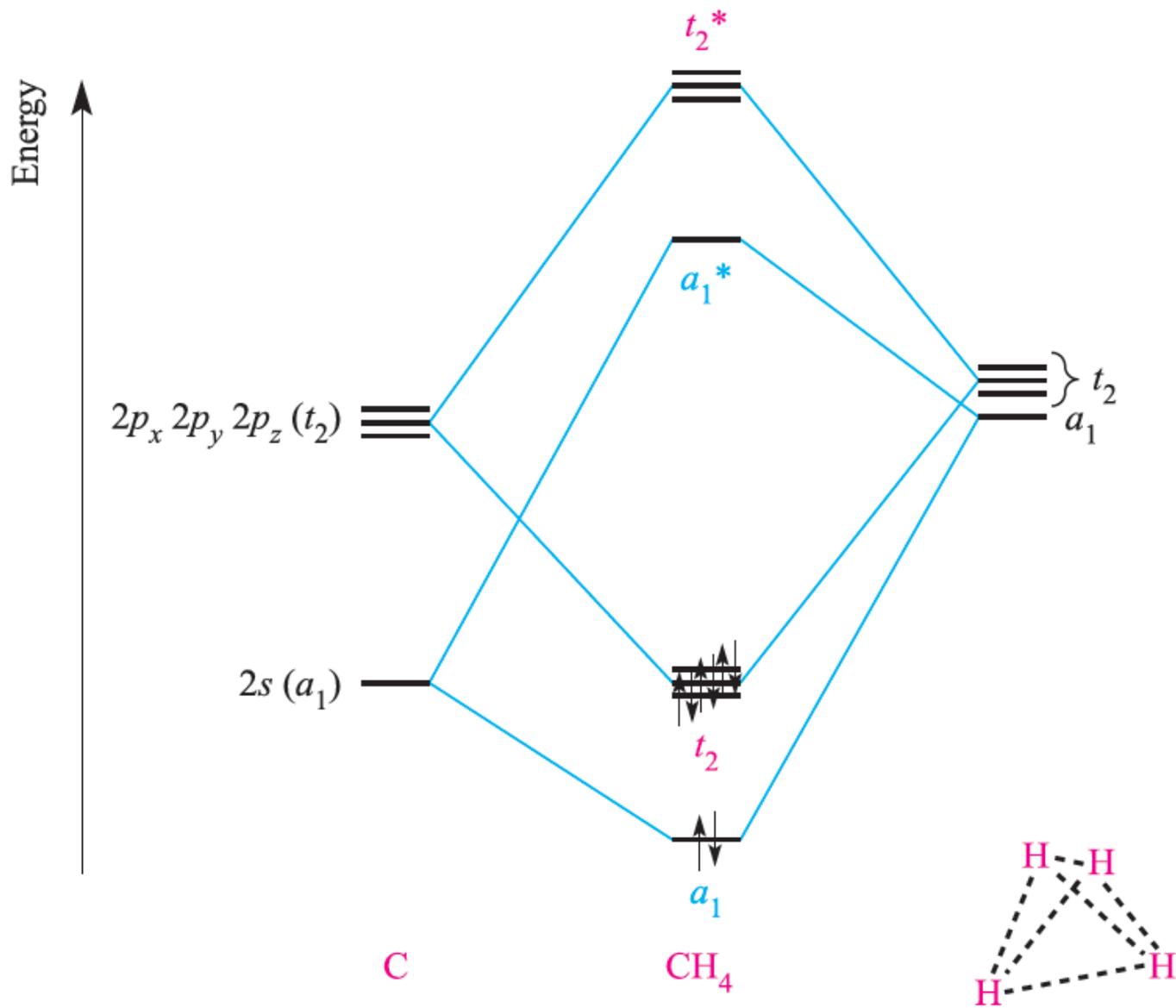


LGO(3) (t_2)

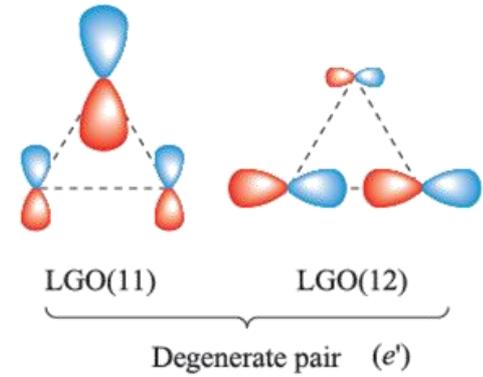
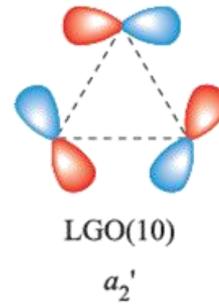
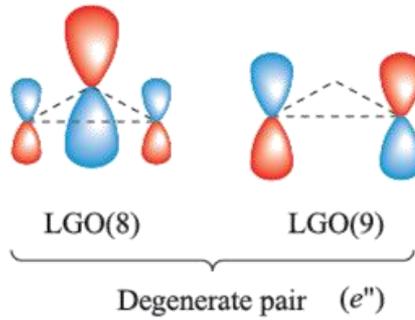
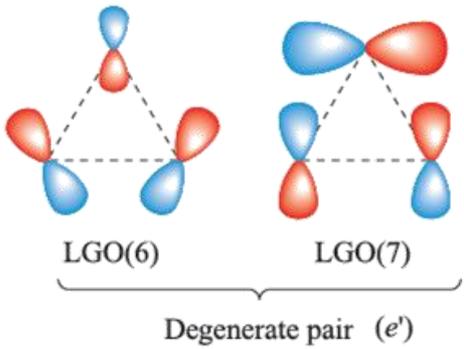
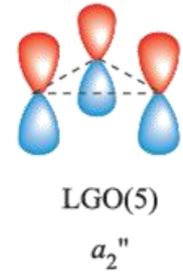
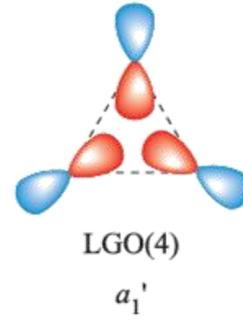
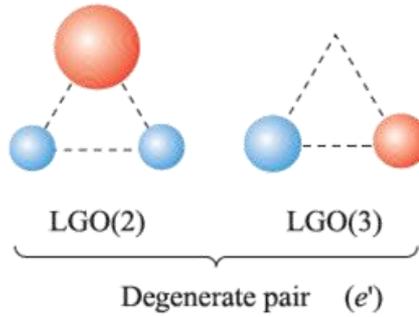
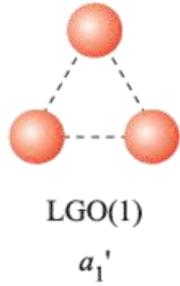
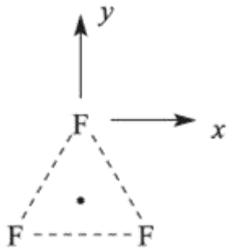


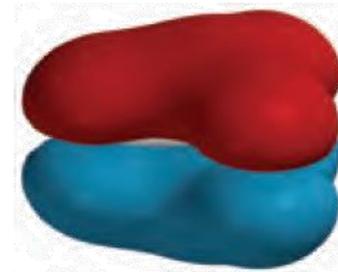
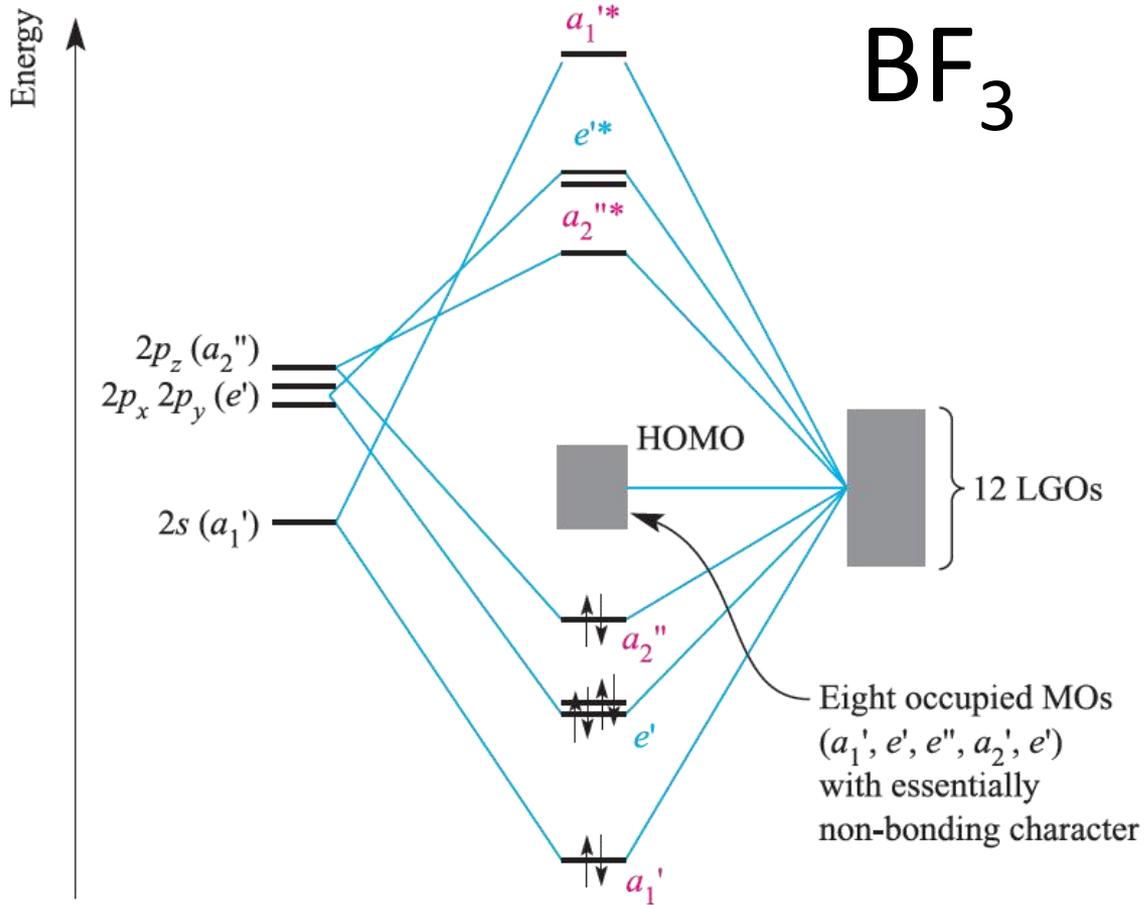
LGO(4) (t_2)

(b)

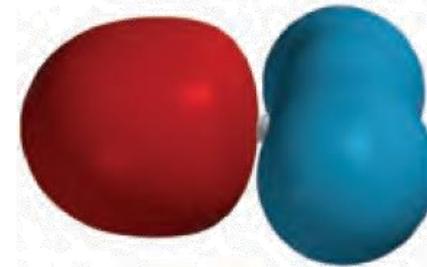


AHORA EL BF_3

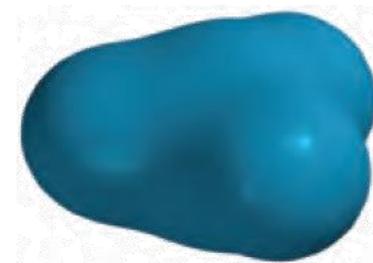




Representation of the a_2'' MO



Representation of one of the e' MOs

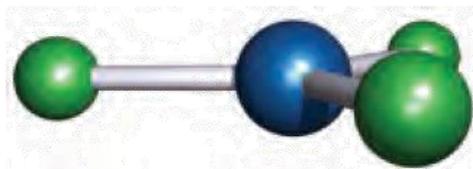


Representation of the a_1' MO

B

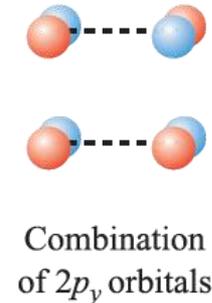
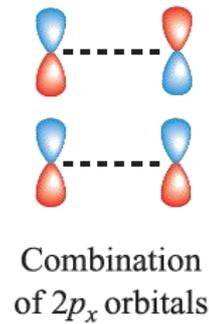
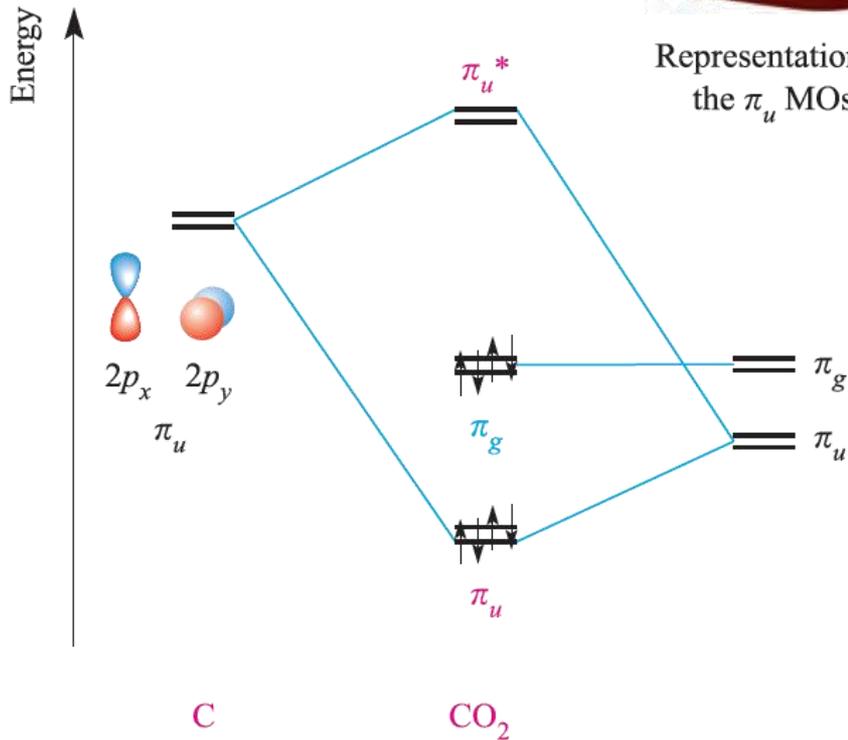
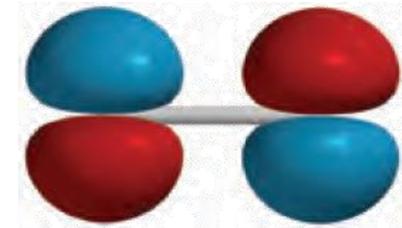
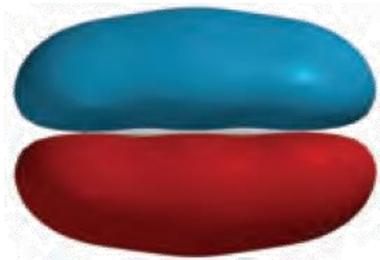
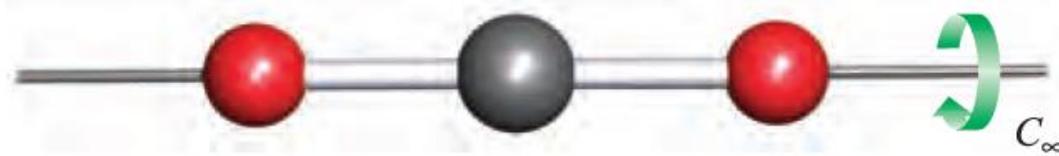
BF_3

F_3 fragment



D_{3h}

Con orbitales π



OM en compuestos de coordinación

El caso más general es el Oh



Orbitales de valencia son 3d, 4s, 4p

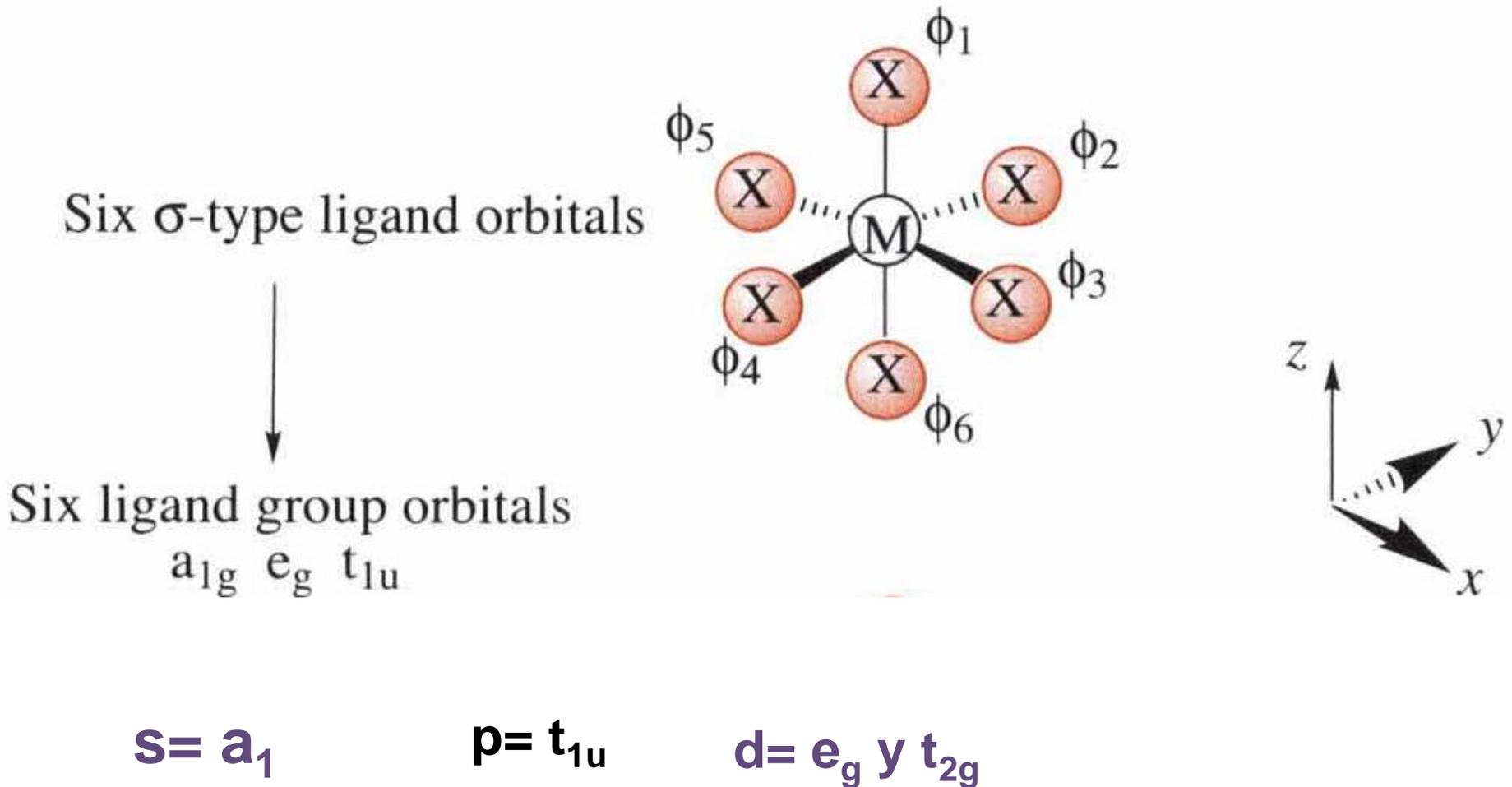
Si consideramos la simetría

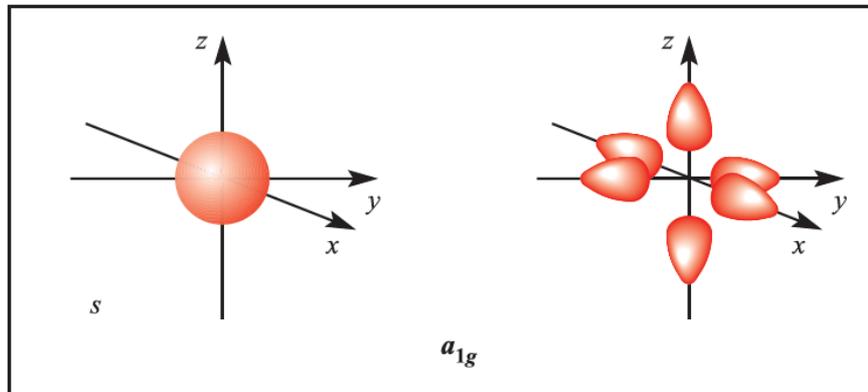
s = a_1

p son degenerados y son = t_{1u}

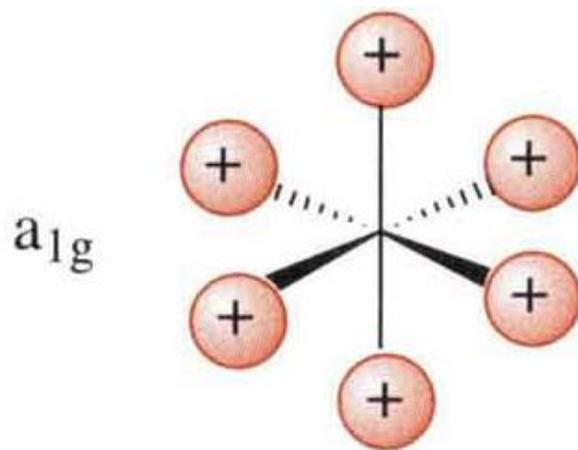
d = e_g y t_{2g}

Consideraremos ahora un centro metálico y ligantes que únicamente mostrarán interacciones σ



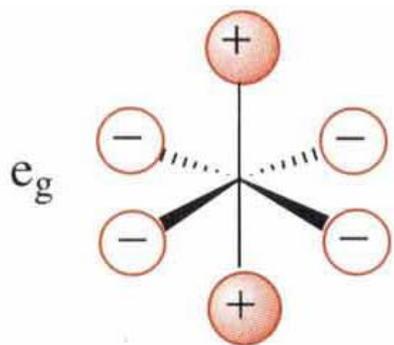
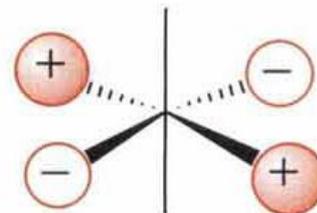


Ligantes

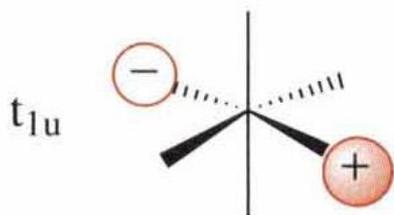


$$\psi(a_{1g})$$

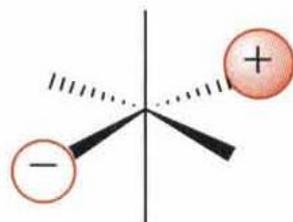
$$\psi(a_{1g}) = 1/\sqrt{6}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$


 $\psi_1(e_g)$

 $\psi_2(e_g)$

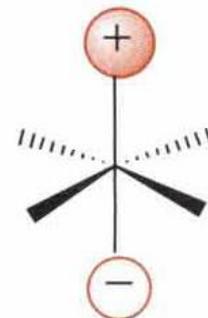
$$\psi_1(e_g) = 1/\sqrt{12}(2\phi_1 - \phi_2 - \phi_3 - \phi_4 - \phi_5 + 2\phi_6) \quad \psi_2(e_g) = 1/2(\phi_3 - \phi_2 - \phi_4 + \phi_5)$$


 $\psi_1(t_{1u})$

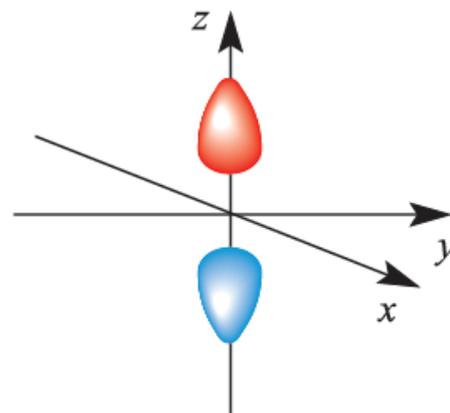
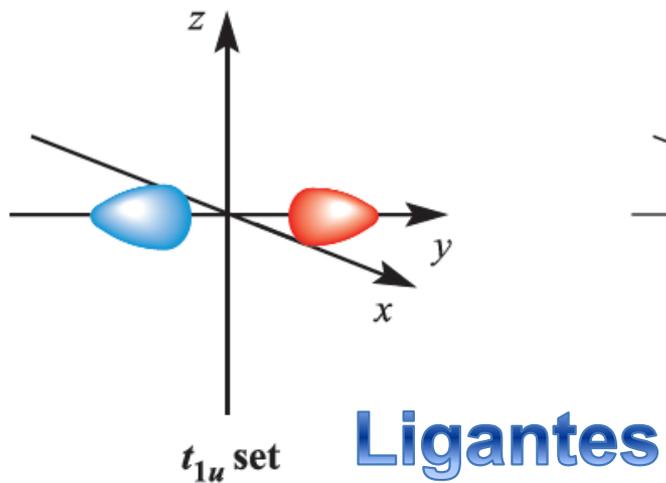
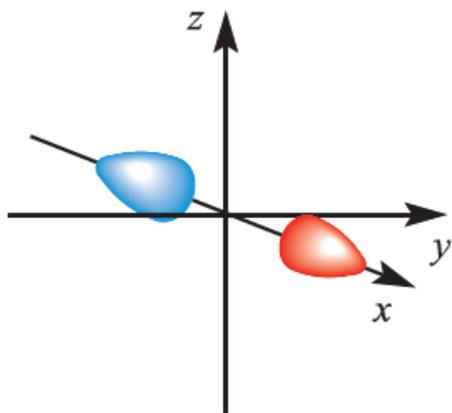
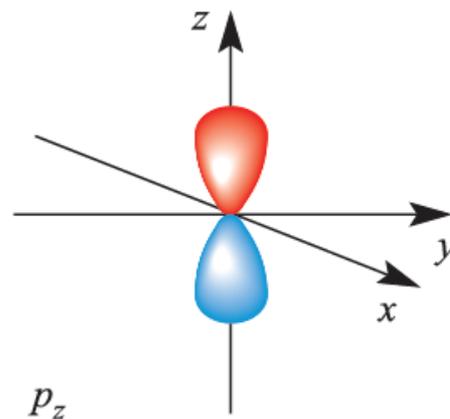
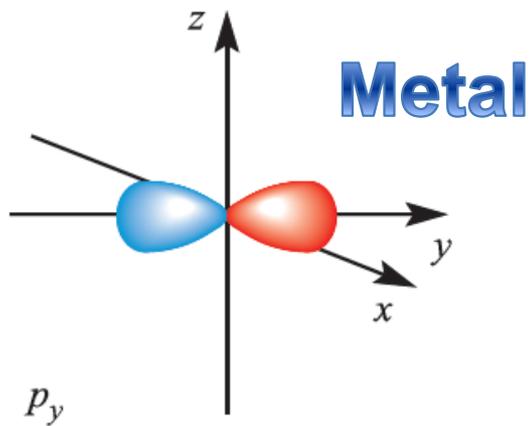
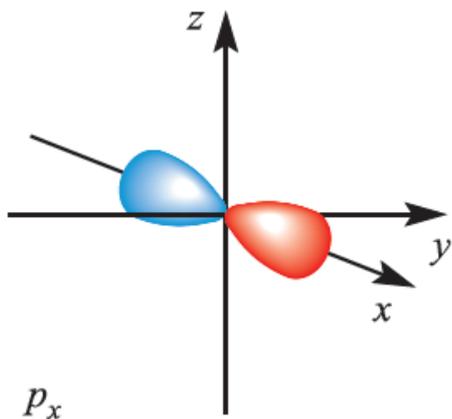
$$\psi_1(t_{1u}) = 1/\sqrt{2}(\phi_3 - \phi_5)$$

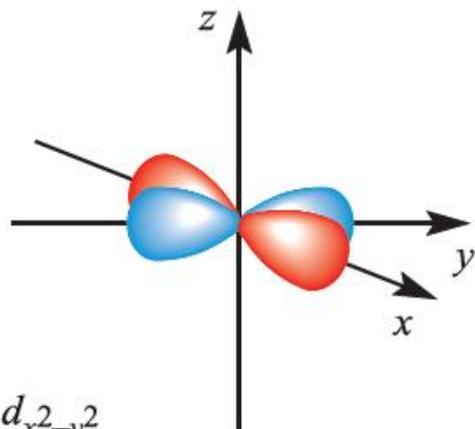

 $\psi_2(t_{1u})$

$$\psi_2(t_{1u}) = 1/\sqrt{2}(\phi_2 - \phi_4)$$

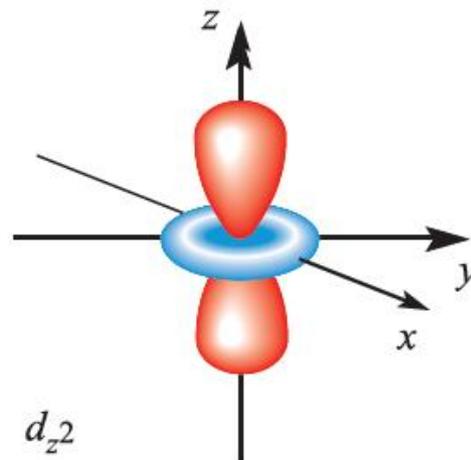

 $\psi_3(t_{1u})$

$$\psi_3(t_{1u}) = 1/\sqrt{2}(\phi_1 - \phi_6)$$

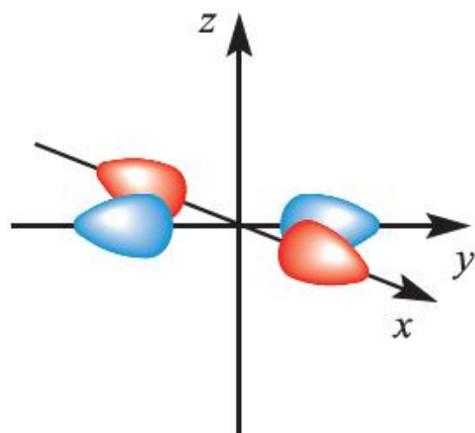




$d_{x^2-y^2}$

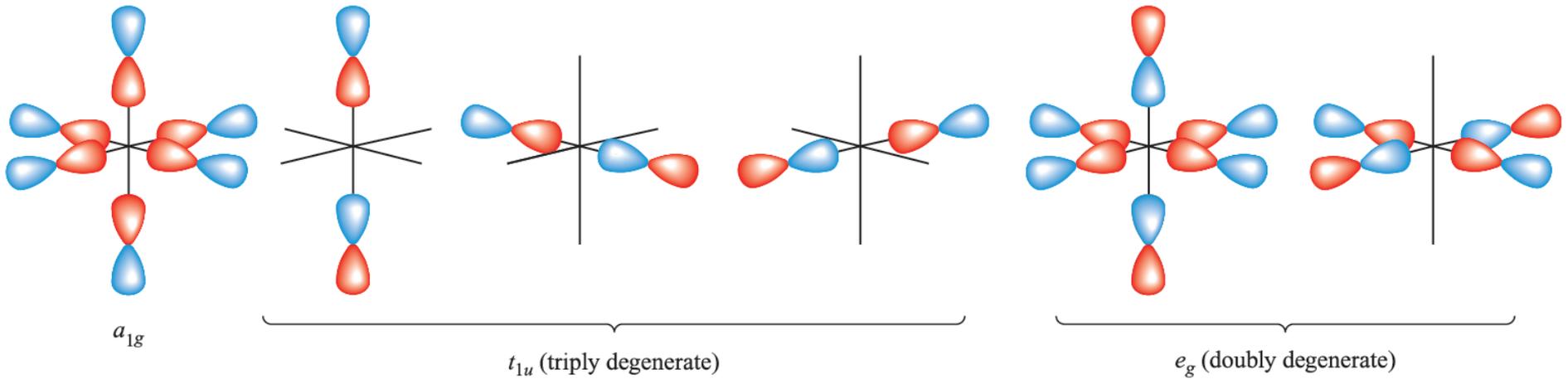


d_{z^2}



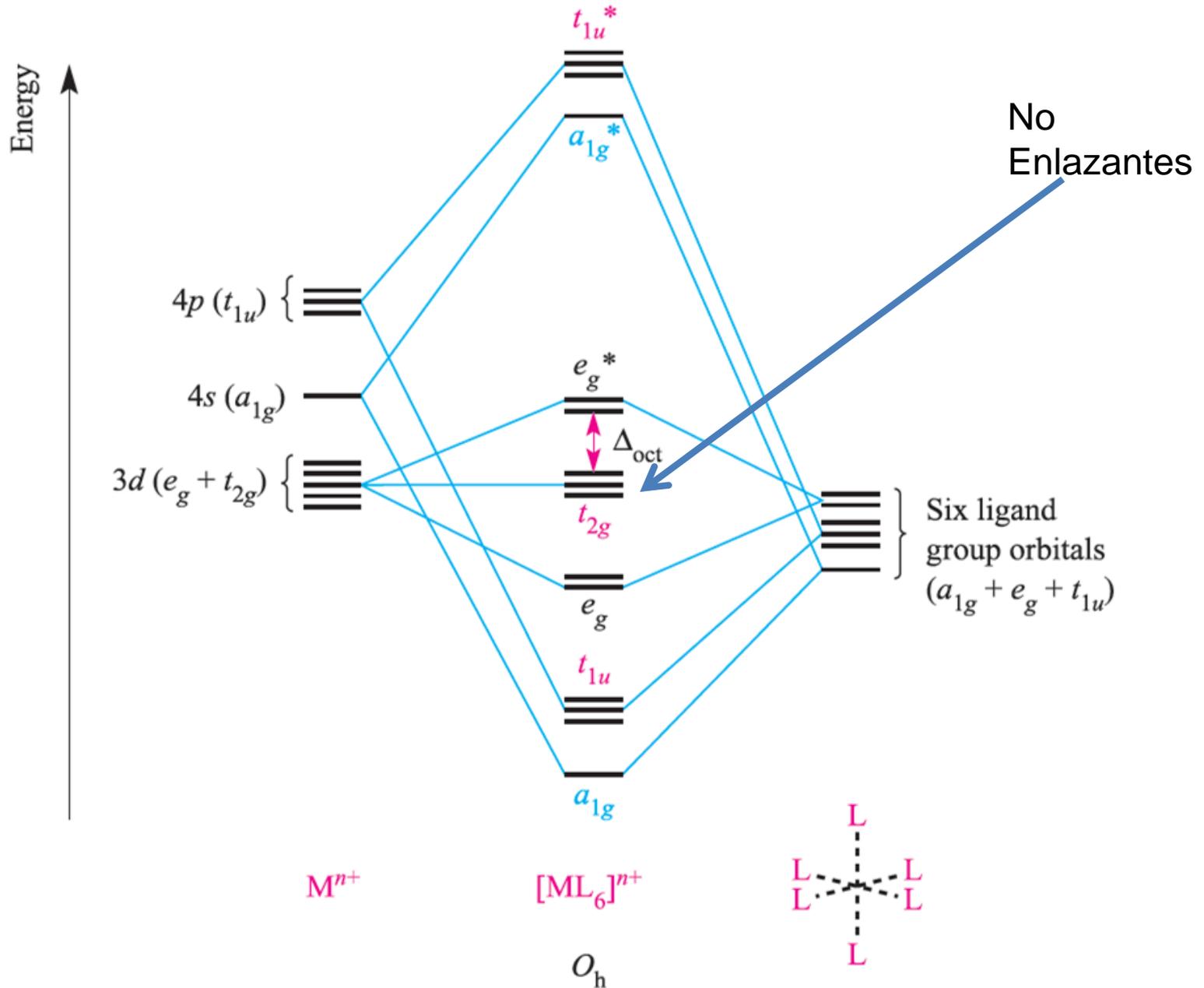
e_g set

Los 6 ligantes

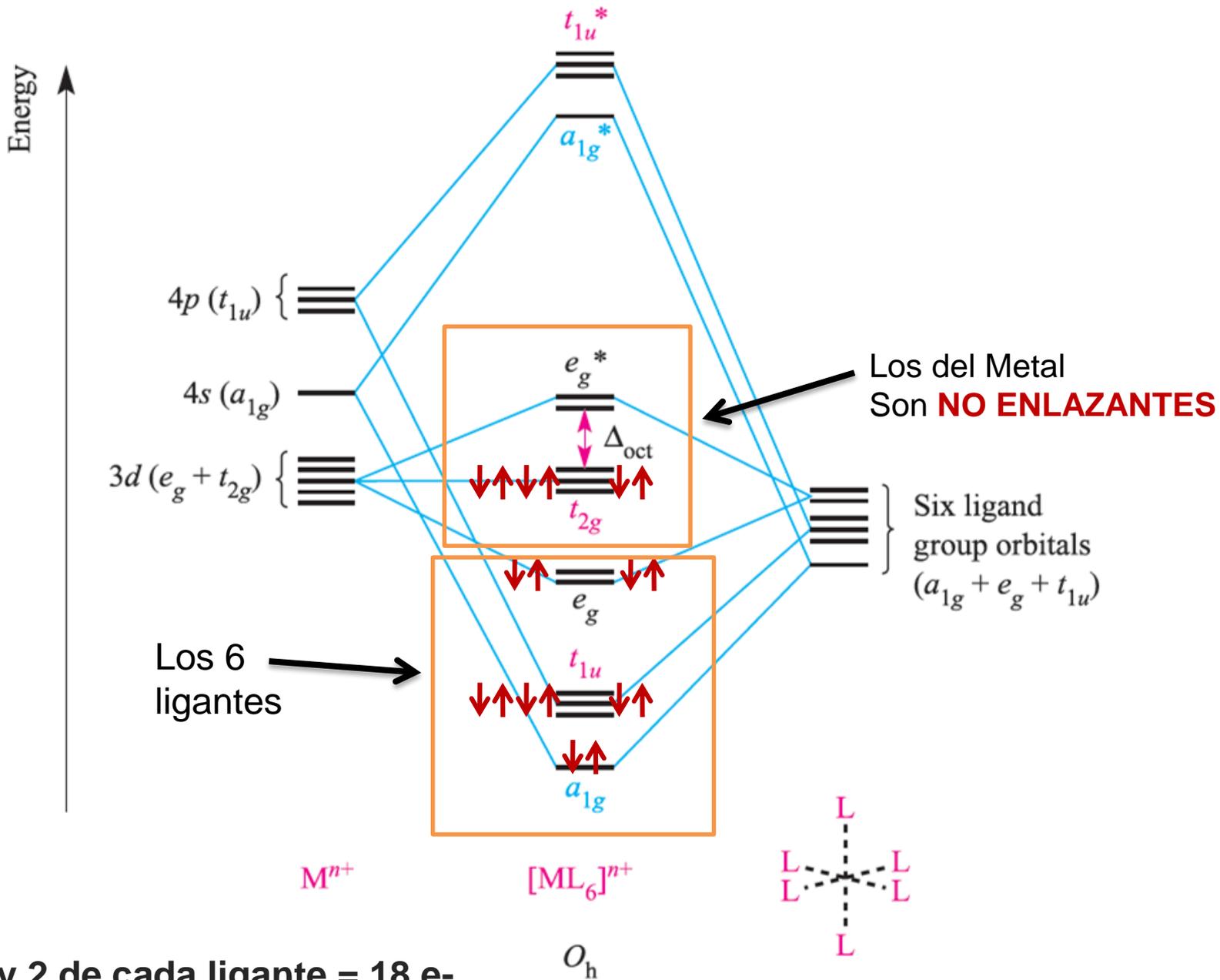


Los Goles
Grupo orbital de los ligantes

Si se combina todo se forman



La superposición de los orbitales de los ligantes con los s y p del metal es mayor que la de los d



$[\text{Co}(\text{NH}_3)_6]^{3+}$
 6 e- del metal y 2 de cada ligante = 18 e-

A donde van los electrones

En principio los electrones de los ligantes entran en los a_{1g} , t_{1g} y e_g

Los del metal entrarán a t_{2g} y e_g^*

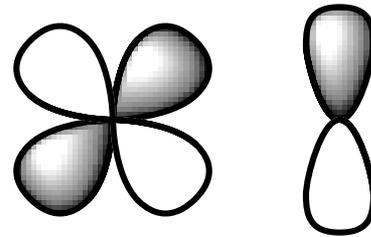
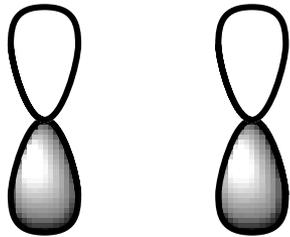
Es decir se repite lo que había salido en campo cristalino la misma degeneración y por lo tanto se explican las propiedades magnéticas de la misma forma. Sin embargo.....

¿Y si los ligantes tienen electrones en sistema π ?

- Hay que clasificarlos
- Los π dadores
- y los π aceptores

Seguimos con el caso ML_6

- Los orbitales d_{xy} , d_{yz} , y d_{xz} (los t_{2g}) son no enlazantes en un complejo con enlace σ y pueden superponerse con los orbitales de los ligantes de simetría adecuada para dar interacciones π .



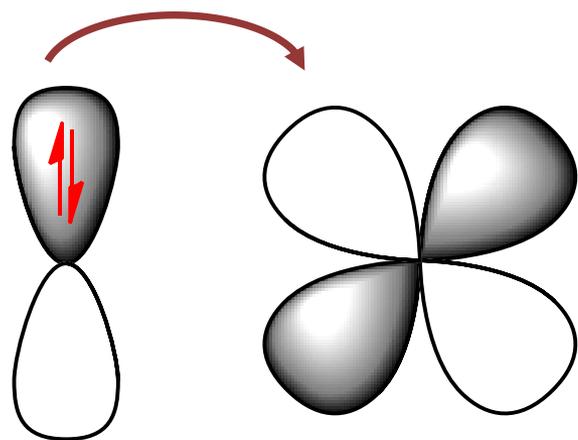
Con interacción π

Un ligante π dador cede electrones al centro metálico en una interacción en la que interviene un orbital del ligante lleno y un orbital del metal vacío.

Los elementos con muchos electrones en la cv como los halógenos son este caso.

Cl^- Br^- y I^-

Configuración s^2p^5



ligante

metal

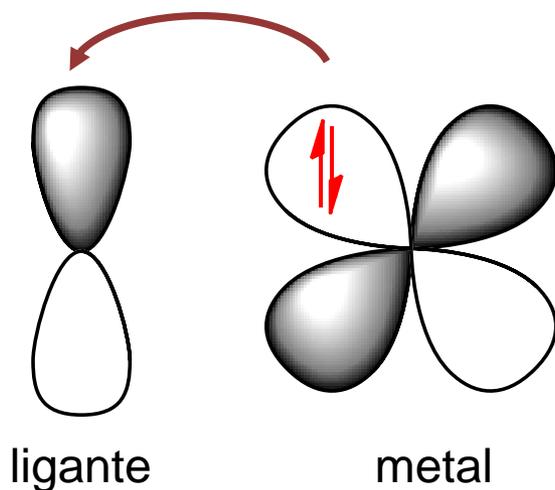
También el metal debe tener pocos electrones en d

Un ligante π aceptor acepta electrones del centro metálico en una interacción en la que interviene un orbital del metal lleno y un orbital del ligante vacío.

Los elementos con pocos electrones en la cv son este caso.

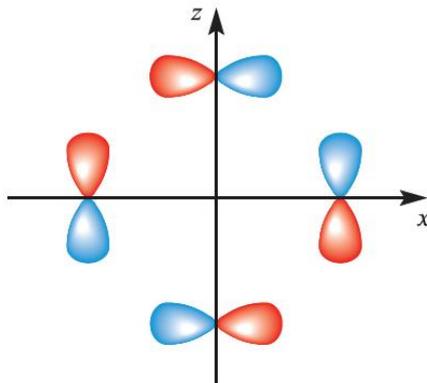
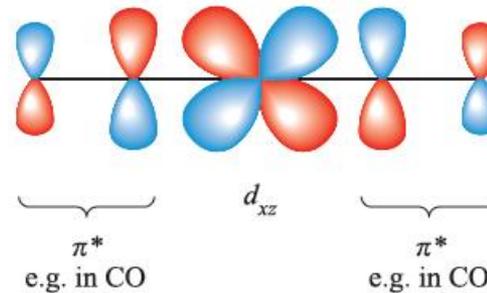
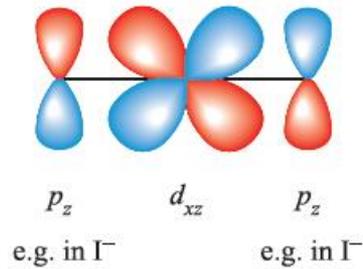
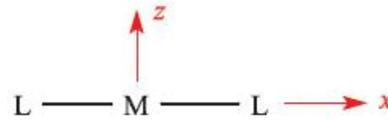
Configuración $s^2p^2, 3$

CO, NO, N_2

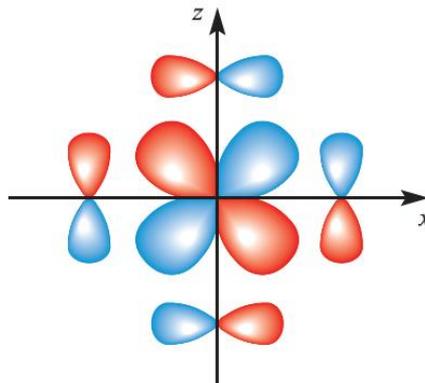


Con interacción π

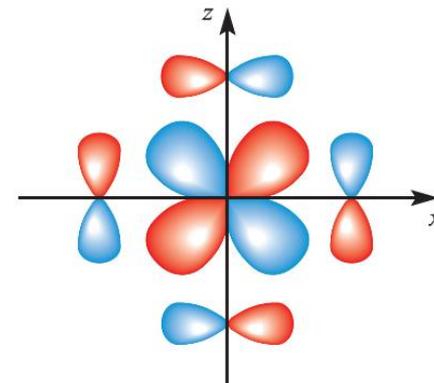
- Los ligantes π aceptores pueden estabilizar complejos metálicos de bajos estados de oxidación



(a)

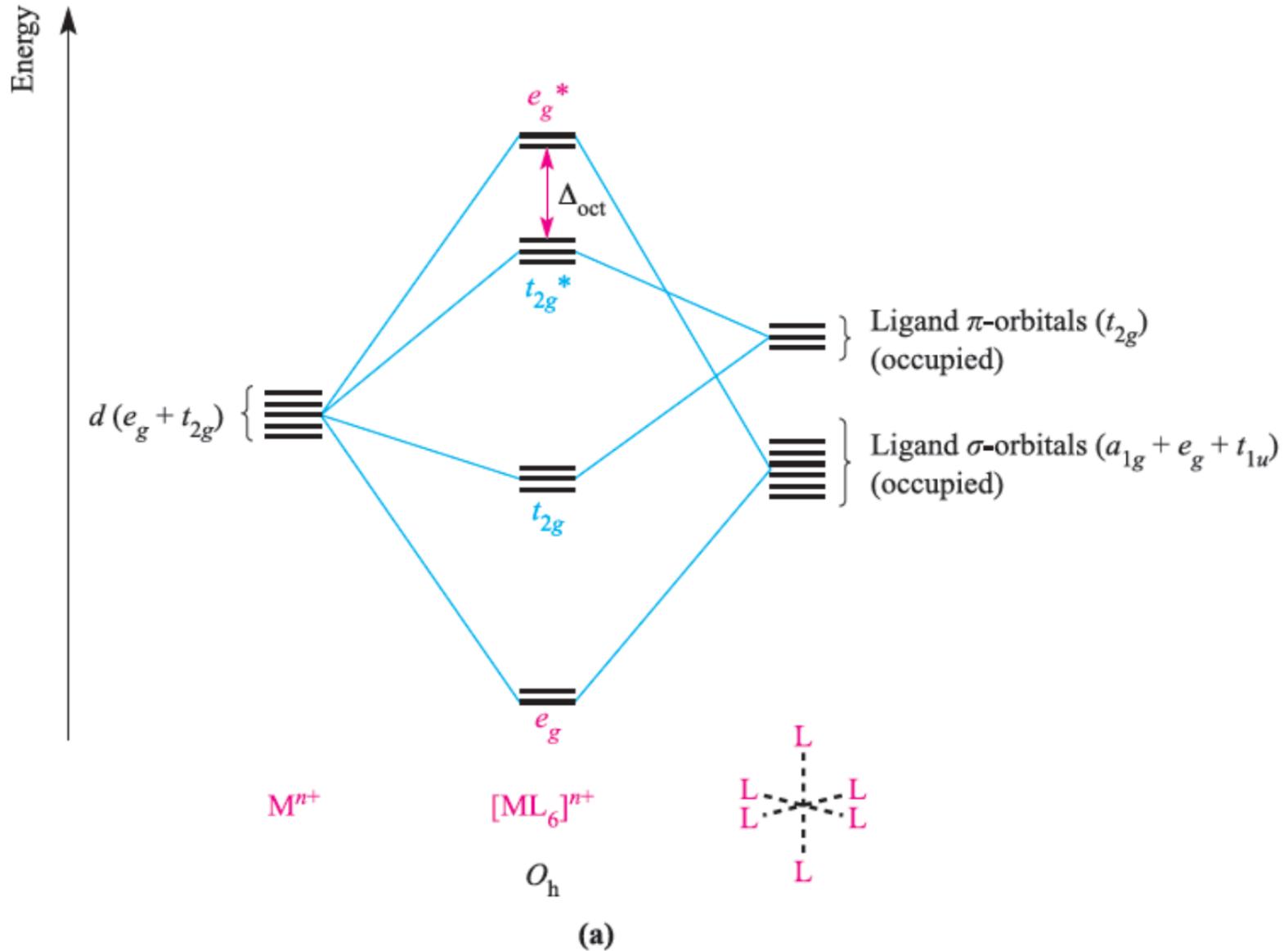


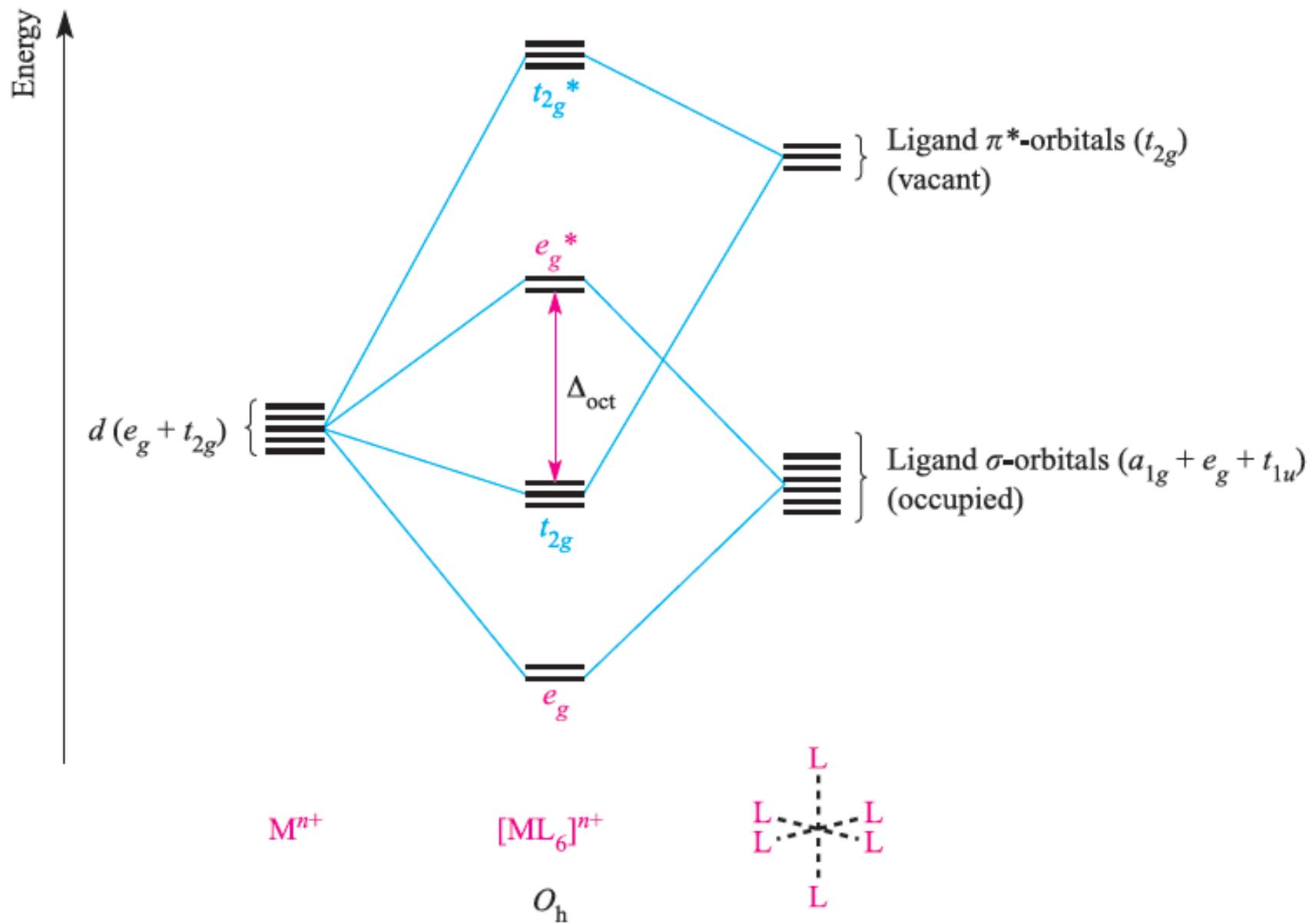
(b)



(c)

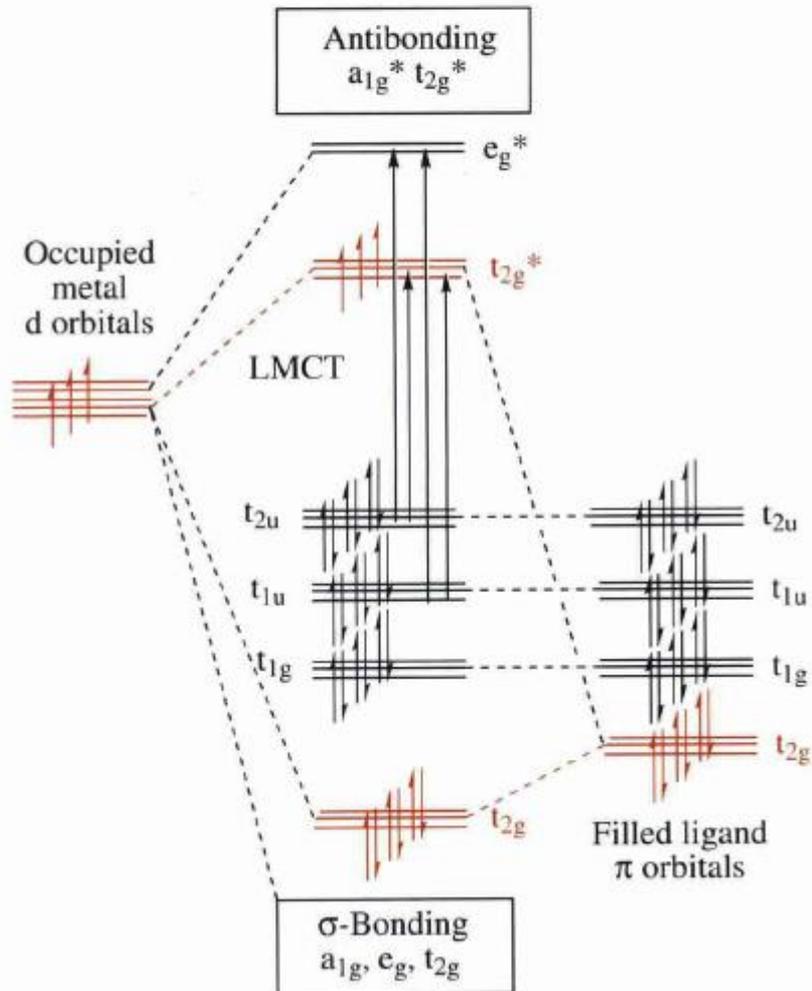
Diagrama con ligantes π dadores



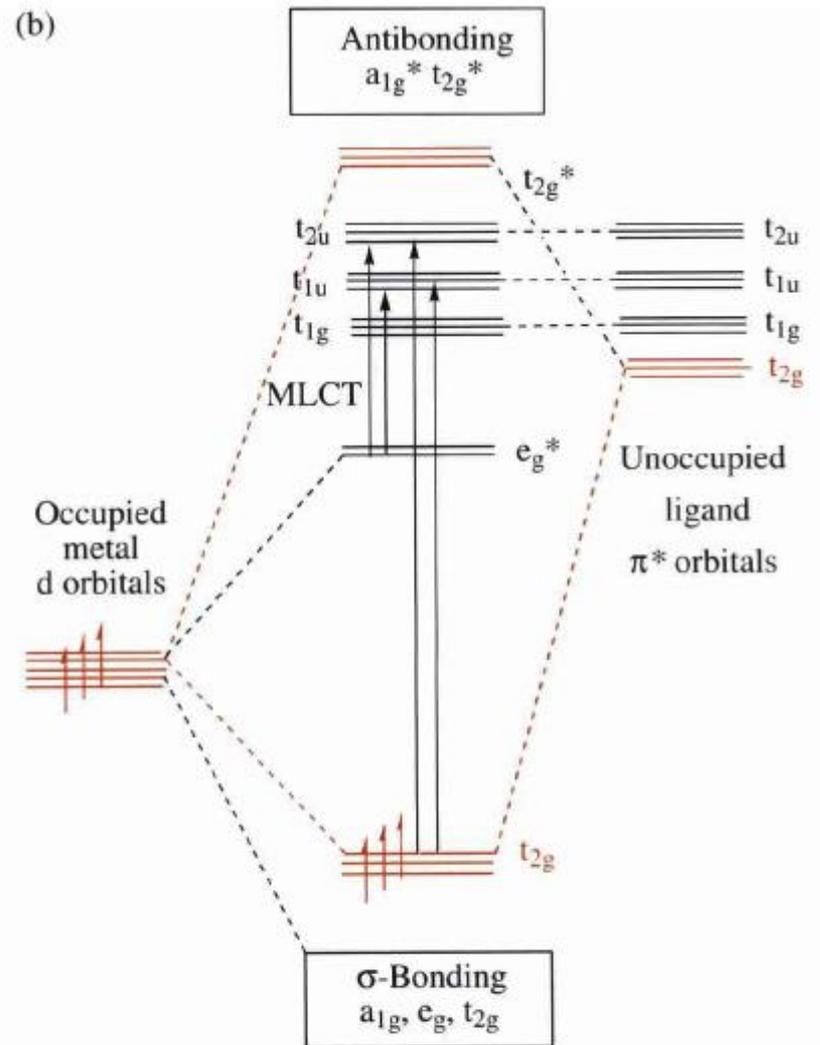


(b)

(a)

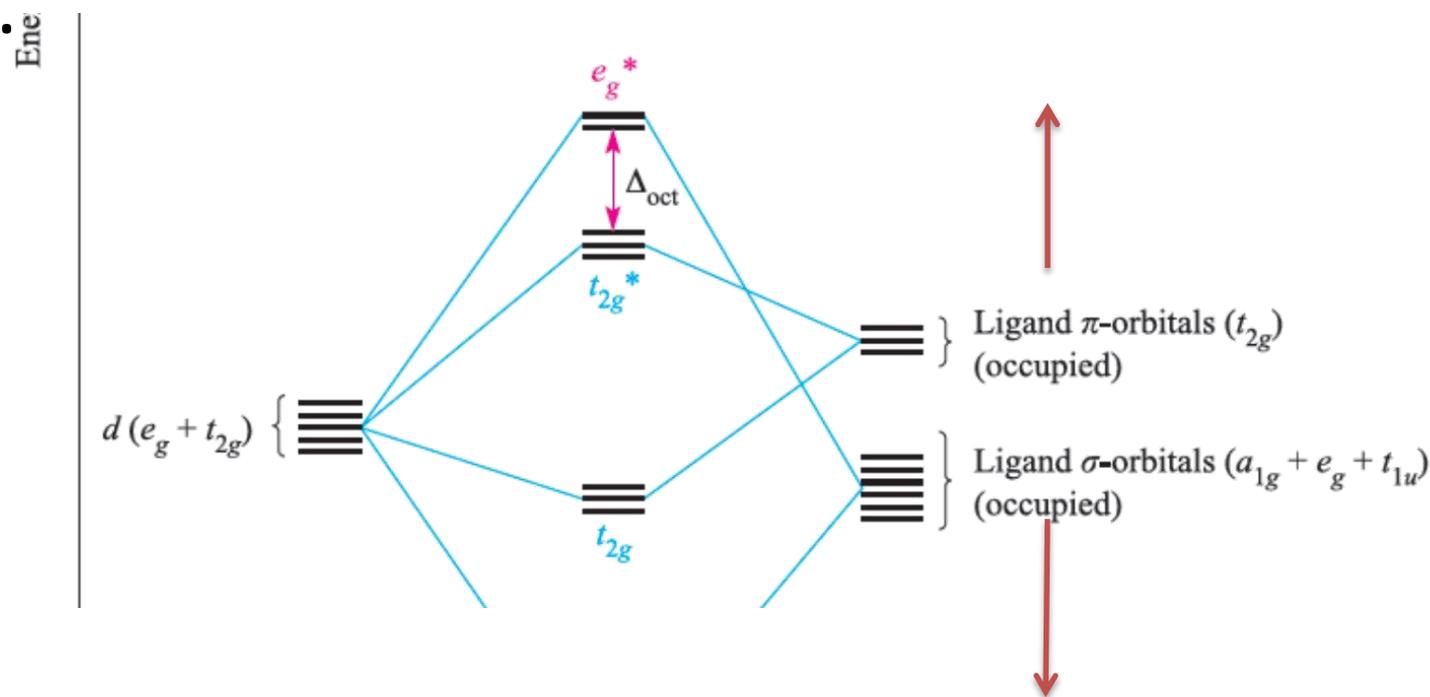


(b)



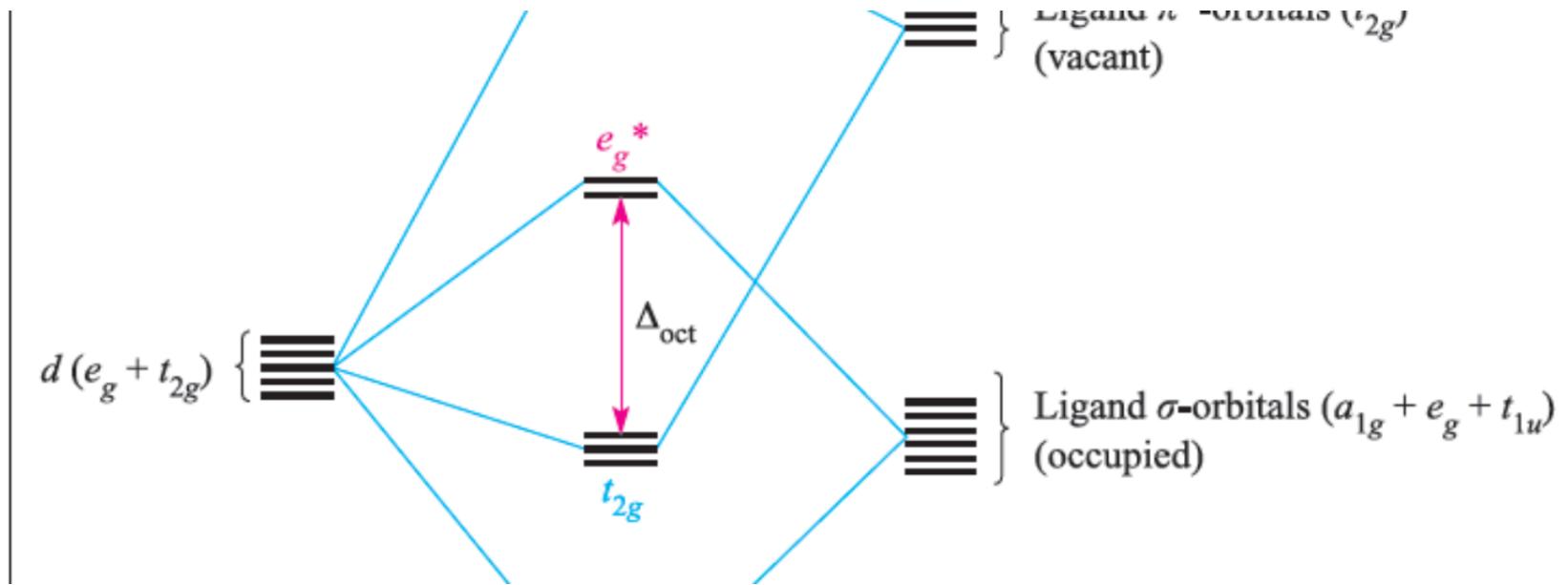
Los cambios entre σ y π

- Δ_0 disminuye al pasar de un complejo σ a uno que contiene ligandos π donadores
- Para un complejo con ligandos π donadores, la cesión p creciente estabiliza el nivel t_{2g} y desestabiliza t_{2g}^* disminuyendo de esta manera Δ_0 .



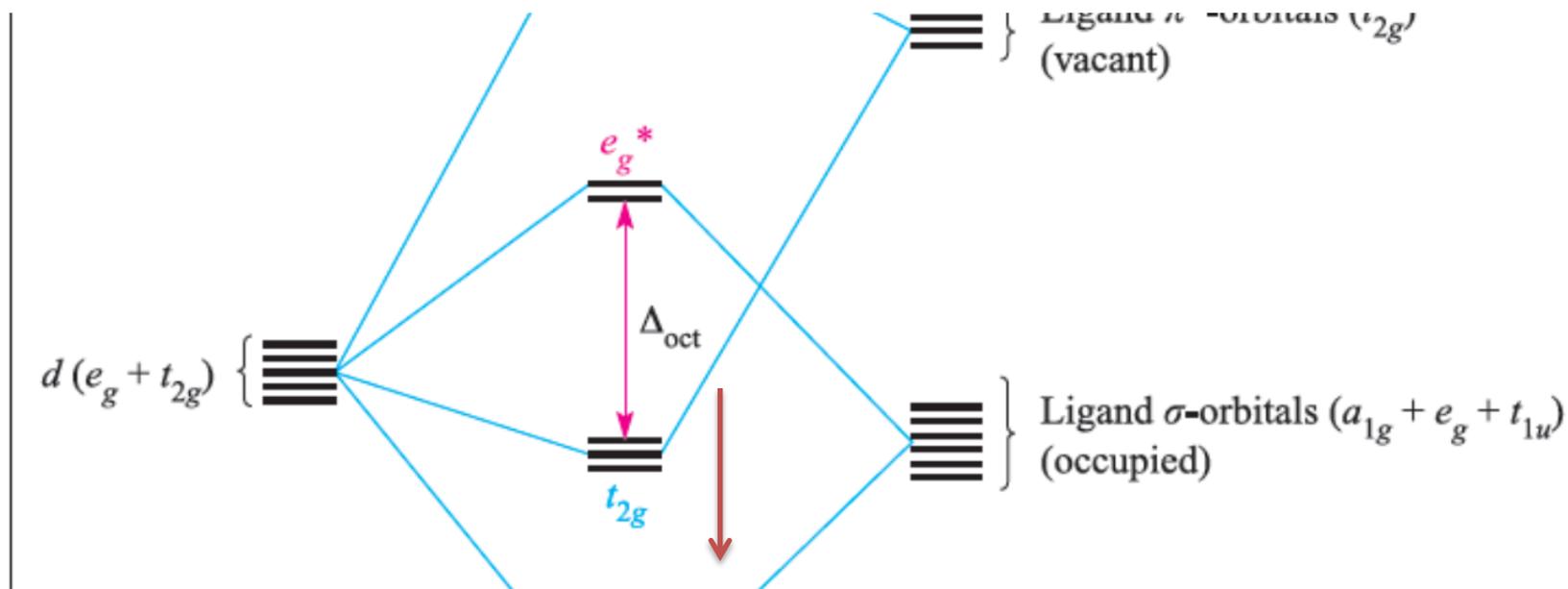
Los cambios entre σ y π

- Los valores de Δ_0 son relativamente grandes para los complejos que contienen ligantes π aceptores y es probable que estos complejos sean de bajo espín.



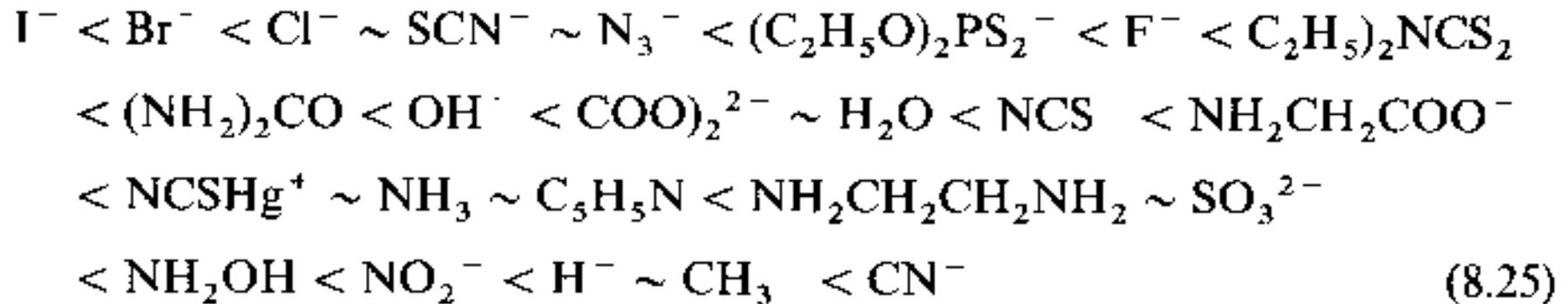
Los cambios entre σ y π

- Para un complejo con ligantes π aceptores la aceptación π creciente estabiliza el nivel t_{2g} aumentando de esta forma Δ_0



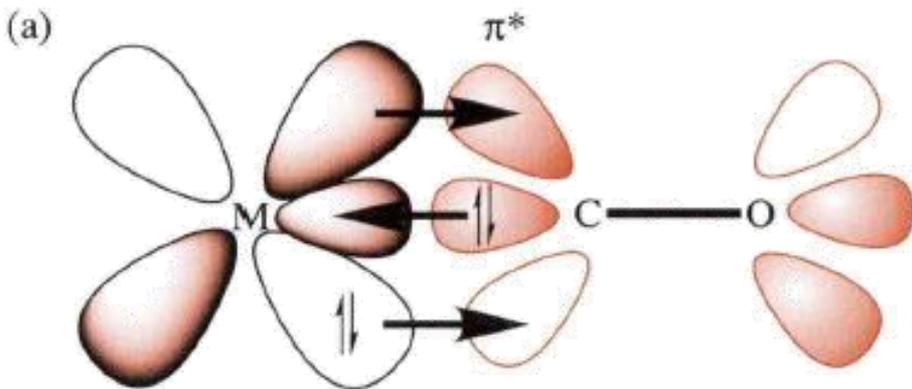
Serie espectroquímica

π dadores



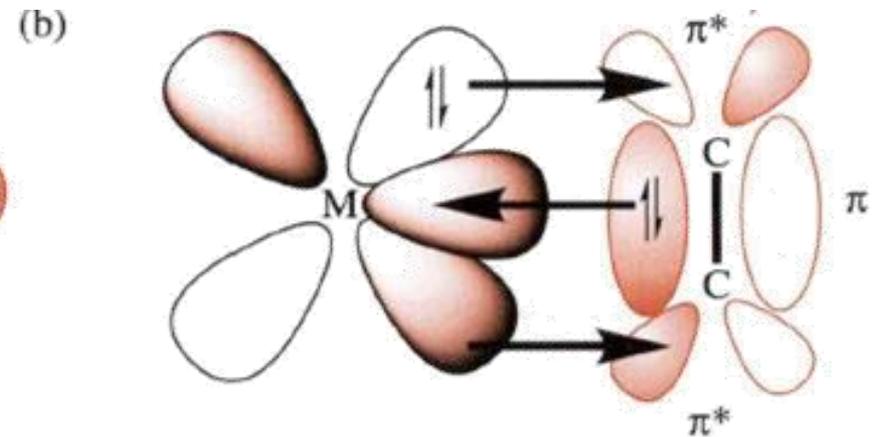
π aceptores

Retrodonación



Synergic bonding

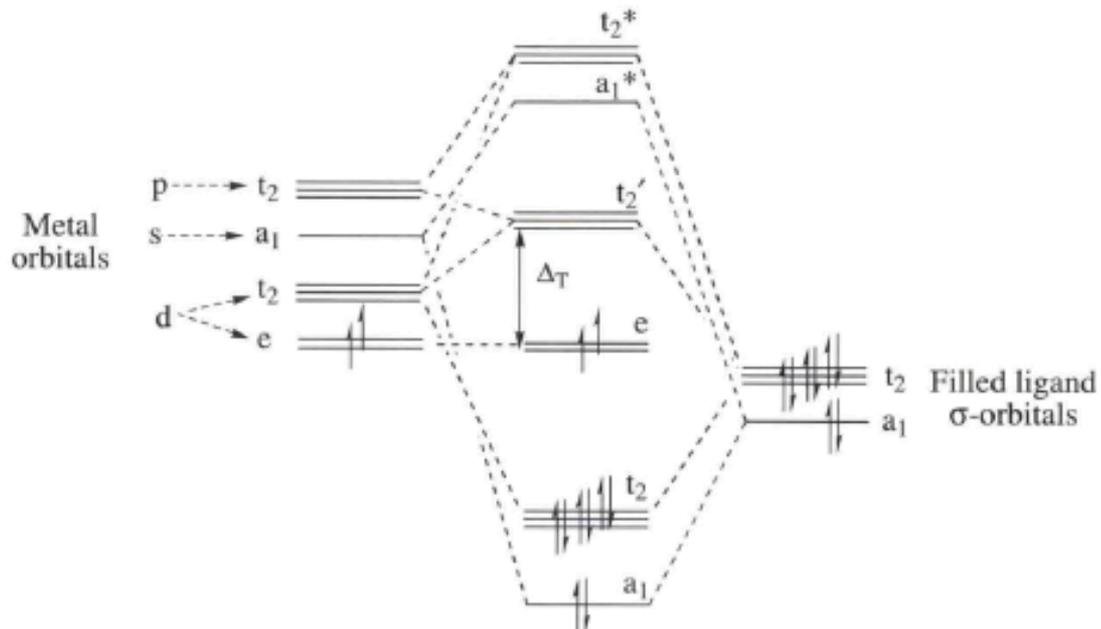
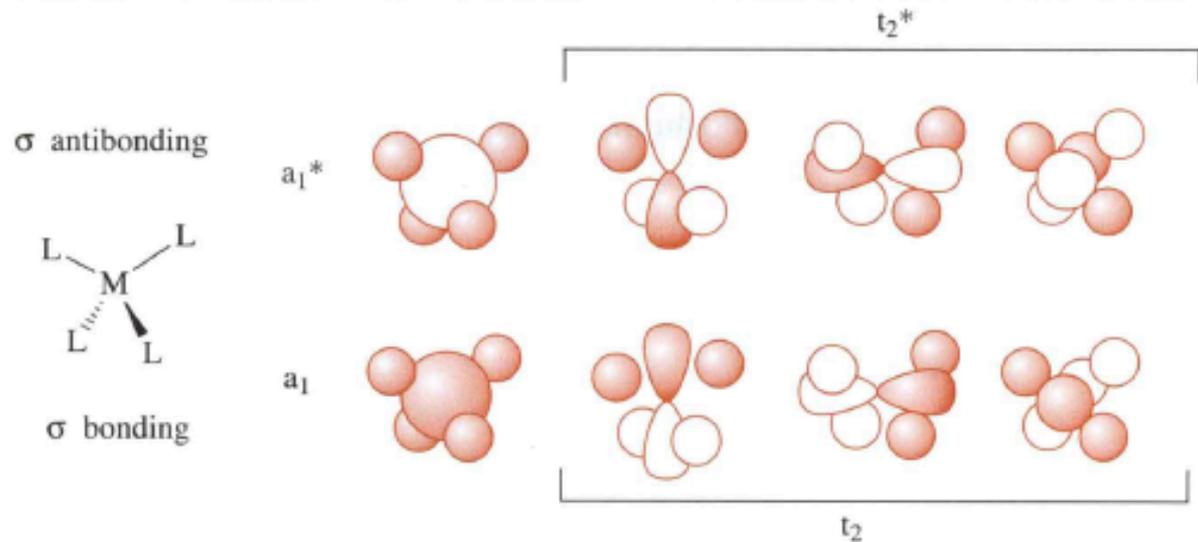
filled CO to empty M σ donation
filled M d to empty CO π^* back-donation
(for clarity the second out-of-plane
 π interaction is not shown)



Synergic bonding

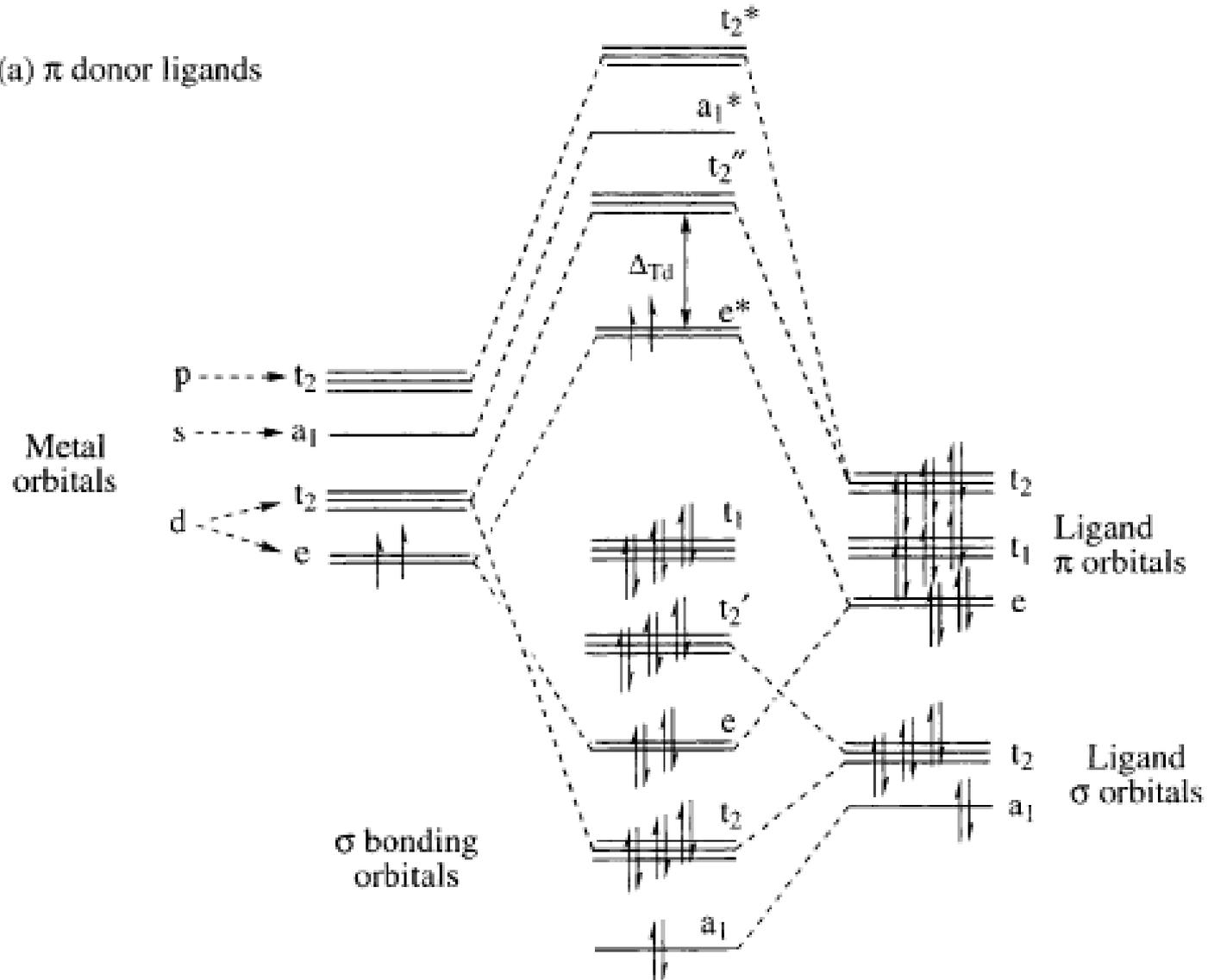
C_2H_4 filled π to empty M σ donation
filled M d to empty C_2H_4 π^* back-donation

Tetraedros solo σ



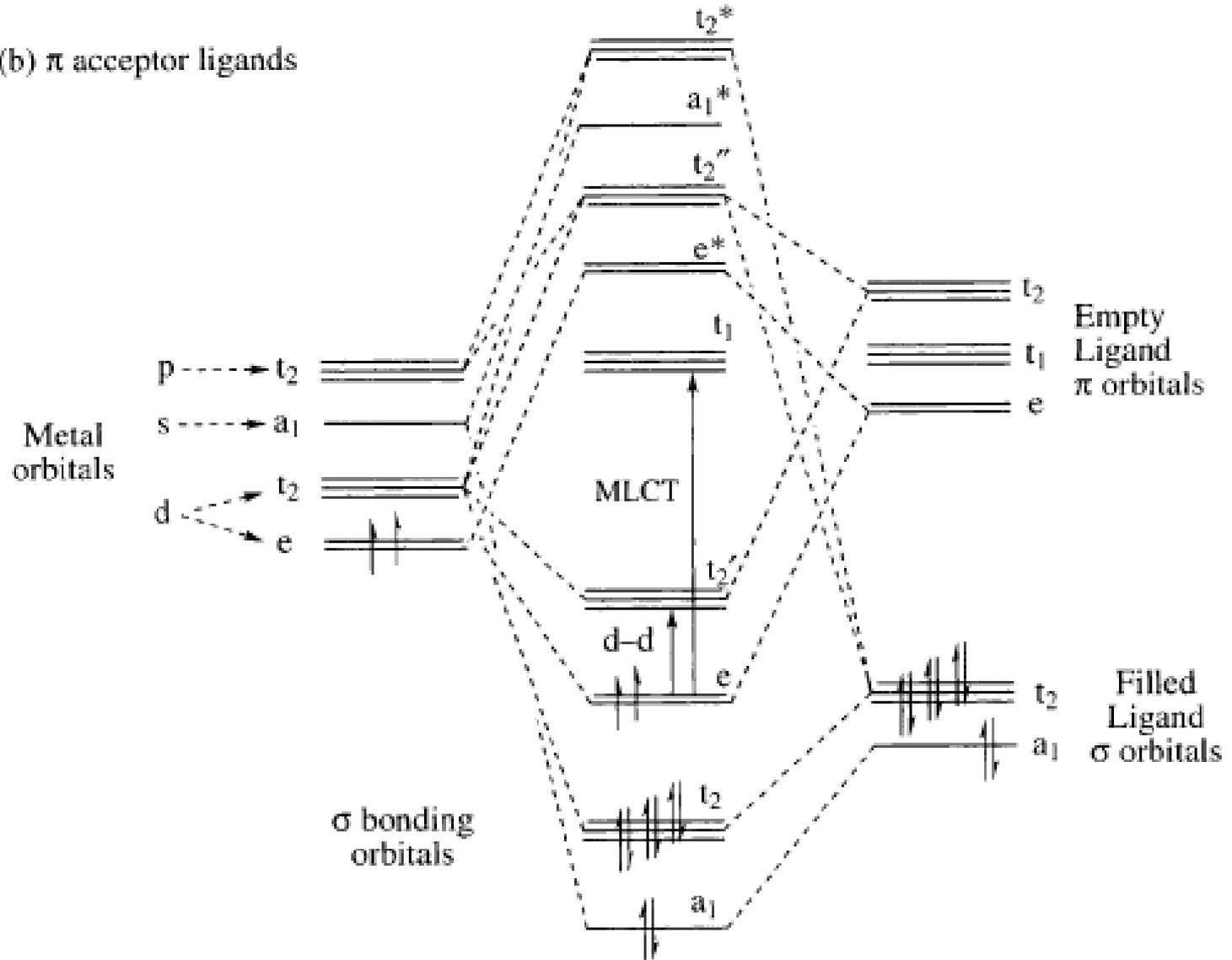
Tetraedros con π

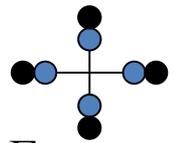
(a) π donor ligands



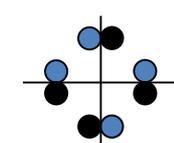
Tetraedros con π

(b) π acceptor ligands

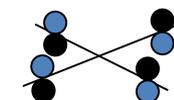




$$\Gamma_{\sigma} = A_{1g} + E_u + B_{1g}$$



$$\Gamma_{\pi^1} = A_{2g} + E_u + B_{2g}$$



$$\Gamma_{\pi} = A_{2u} + E_g + B_{2u}$$

