

**Fig. 3.6** Successive  $C_3$  rotations in  $\text{NH}_3$  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  $\text{NH}_3$  in the initial configuration.

$$S_3 = C_3 \times \sigma_h$$

Point group	Characteristic symmetry elements	Comments
$C_s$	$E$ , one $\sigma$ plane	
$C_i$	$E$ , inversion centre	
$C_n$	$E$ , one (principal) $n$ -fold axis	
$C_{nv}$	$E$ , one (principal) $n$ -fold axis, $n$ $\sigma_v$ planes	
$C_{nh}$	$E$ , one (principal) $n$ -fold axis, one $\sigma_h$ 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 $\sigma_h$ 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 $\sigma_h$ plane, $n$ $\sigma_v$ planes, one $S_n$ -fold axis	The $S_n$ axis necessarily follows from the $C_n$ axis and $\sigma_h$ 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, $n$ $\sigma_v$ 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

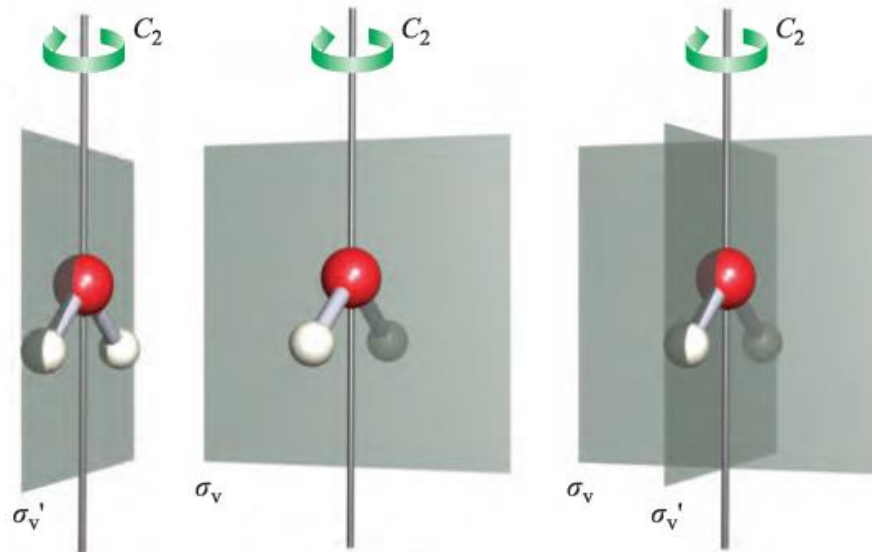
**A**, cuando la rotación alrededor del eje principal es simétrica.  
**B**, cuando la rotación alrededor del eje principal es asimétrica.  
**E** y **T** son representaciones doble y triplemente degeneradas respectivamente.

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:  $\Sigma$ ,  $\Pi$ ,  $\Delta$ .

# Tabla de caracteres

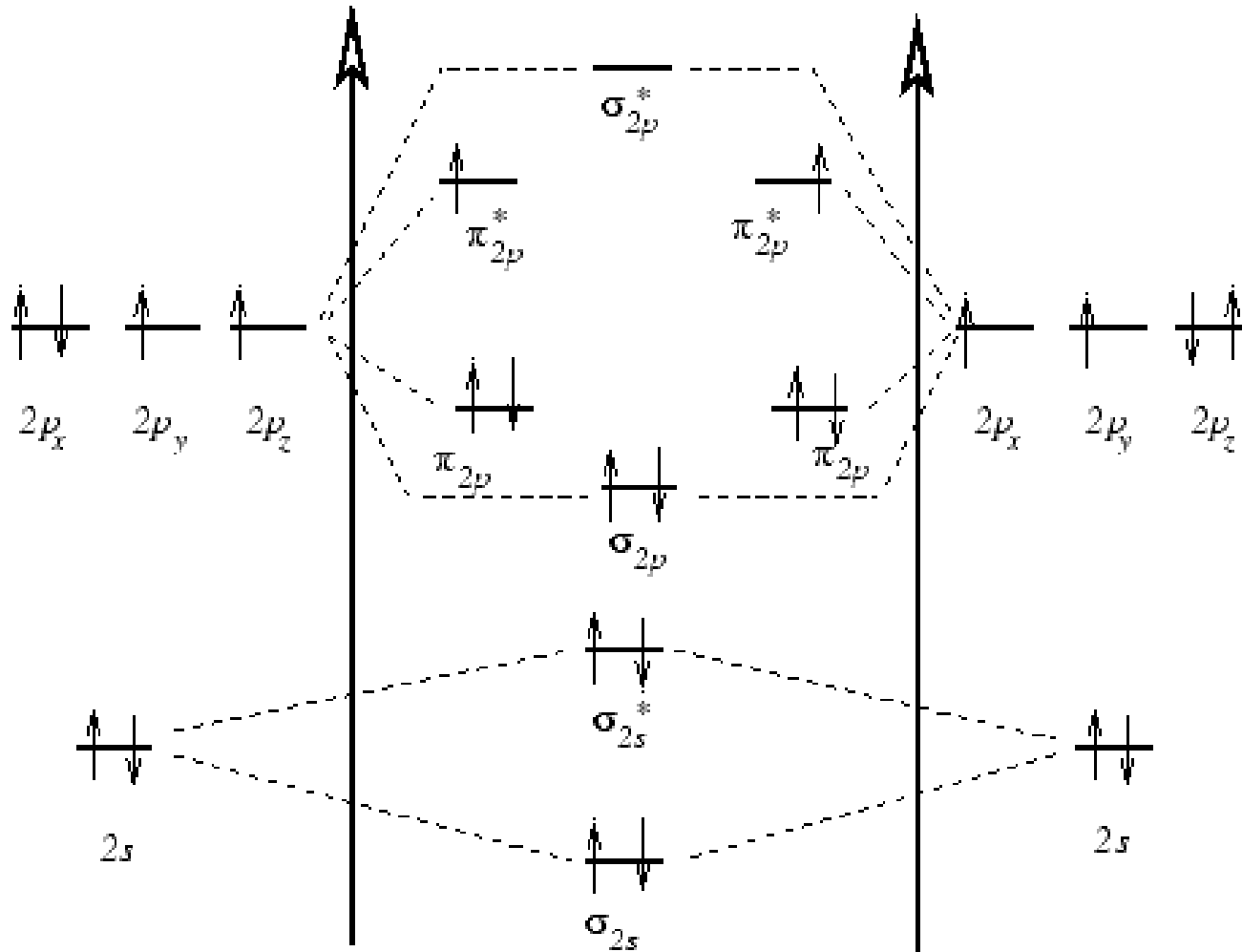
Agua



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

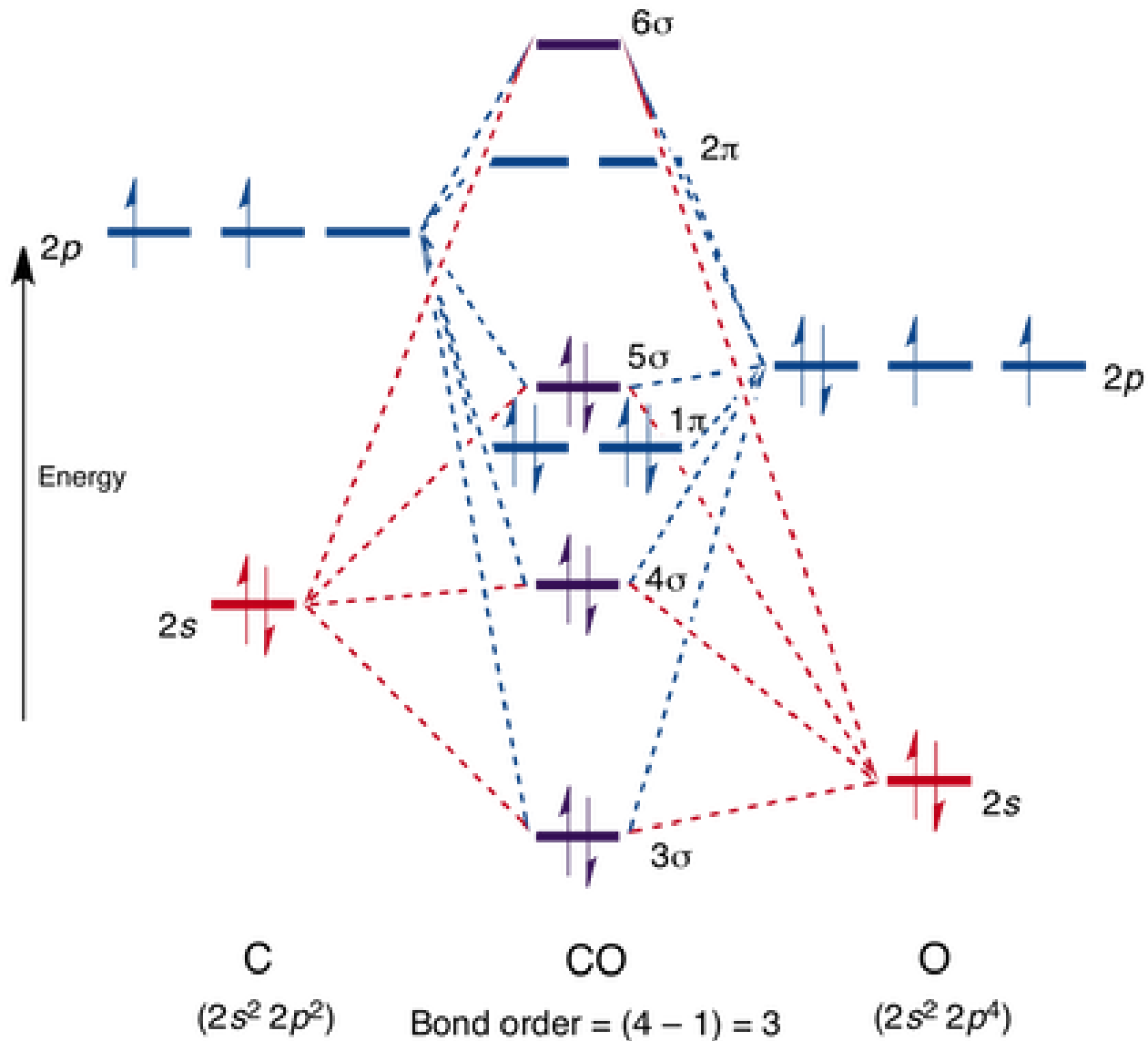
$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$x, xz$
$B_2$	1	-1	-1	1	$y, R_x$	$y, yz$

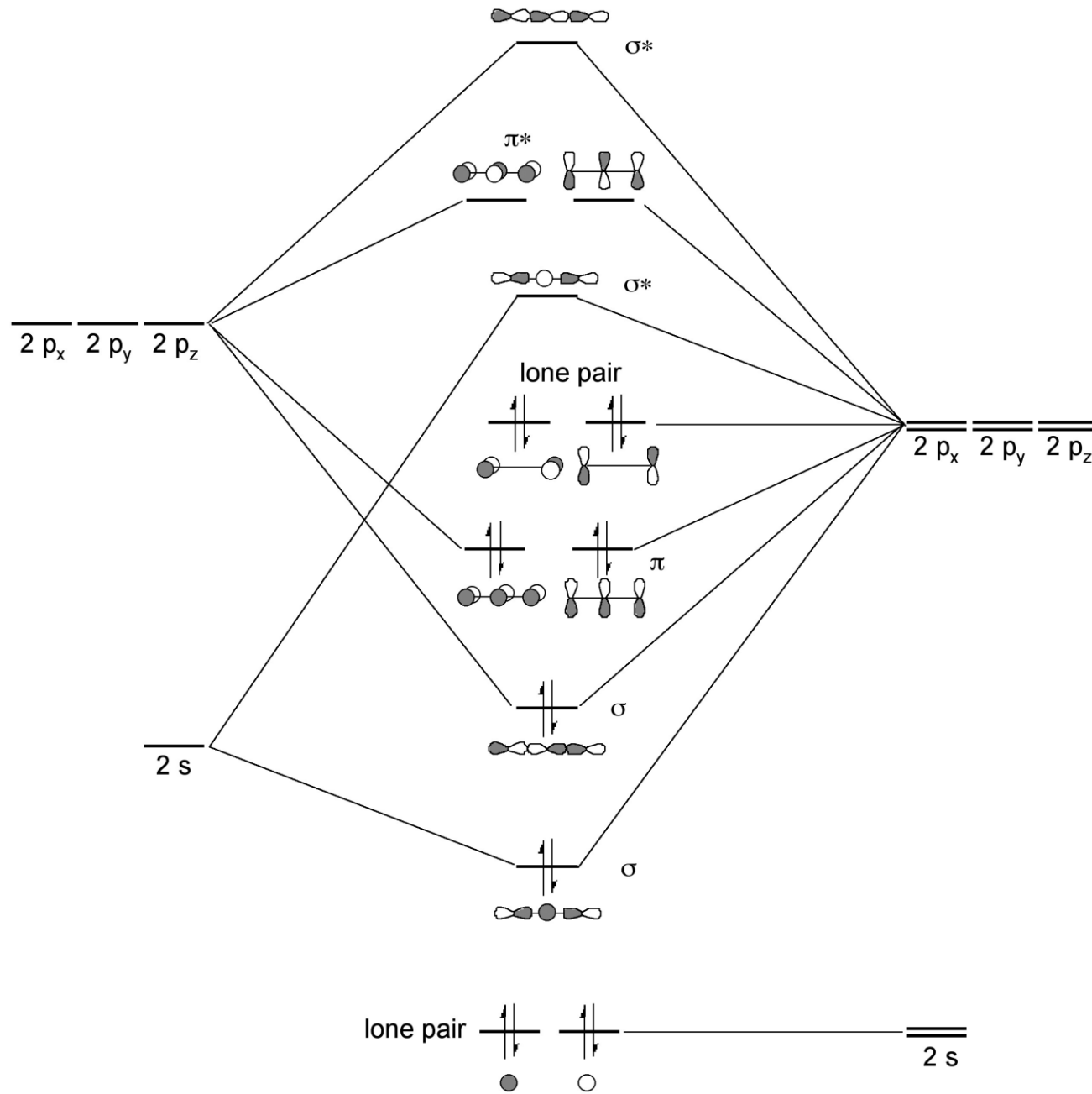
# Orbitales moleculares





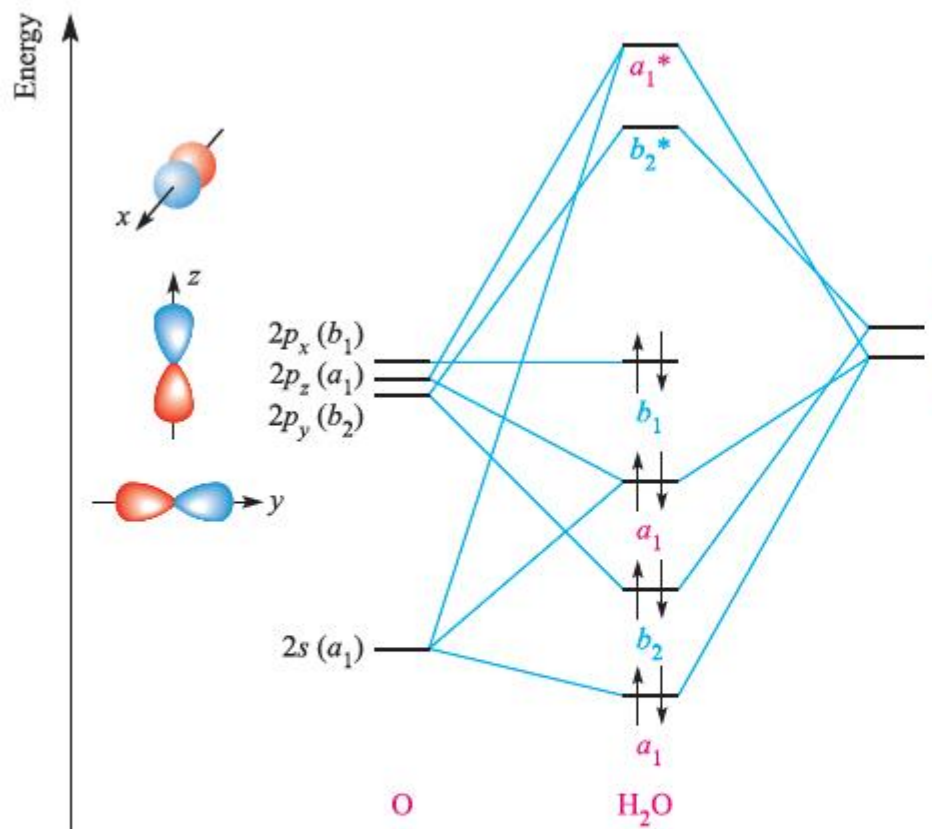
# Monóxido de carbono



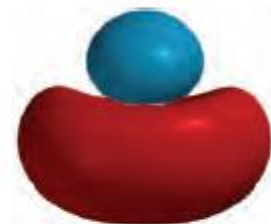


carbon

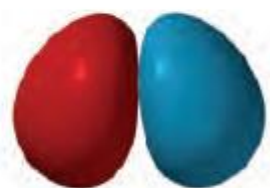
oxygen



Representation of the  $b_1$  MO



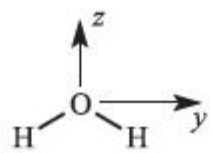
Representation of the higher energy  $a_1$  MO



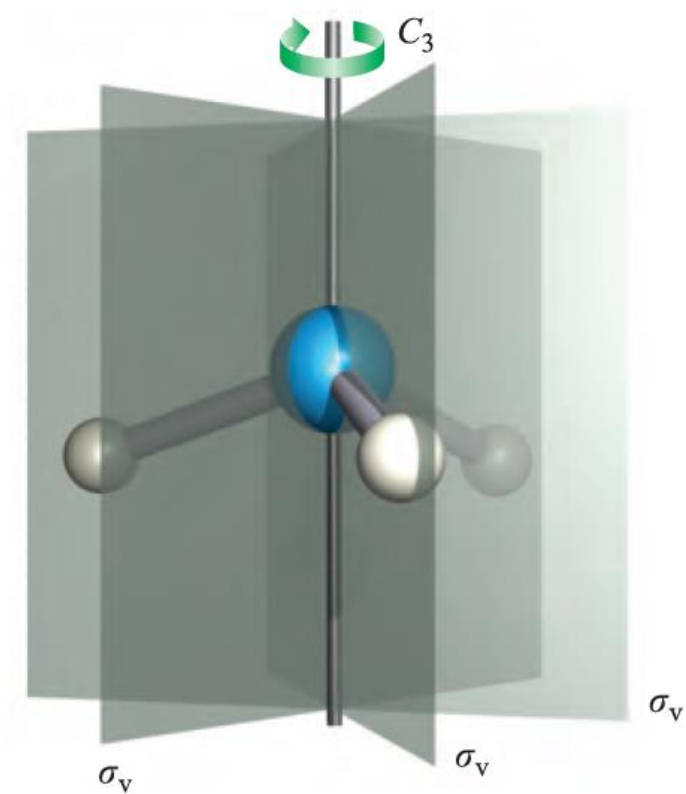
Representation of the  $b_2$  MO



Representation of the lower energy  $a_1$  MO

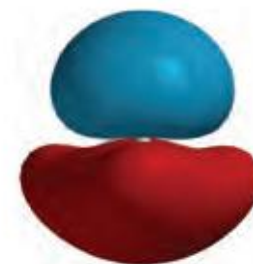
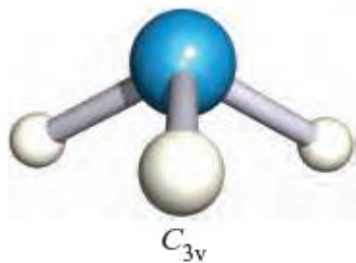
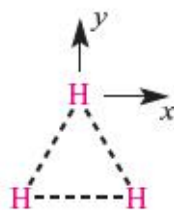
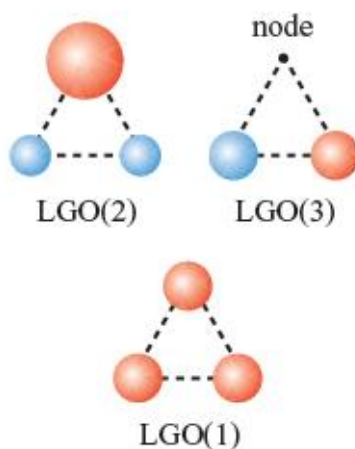
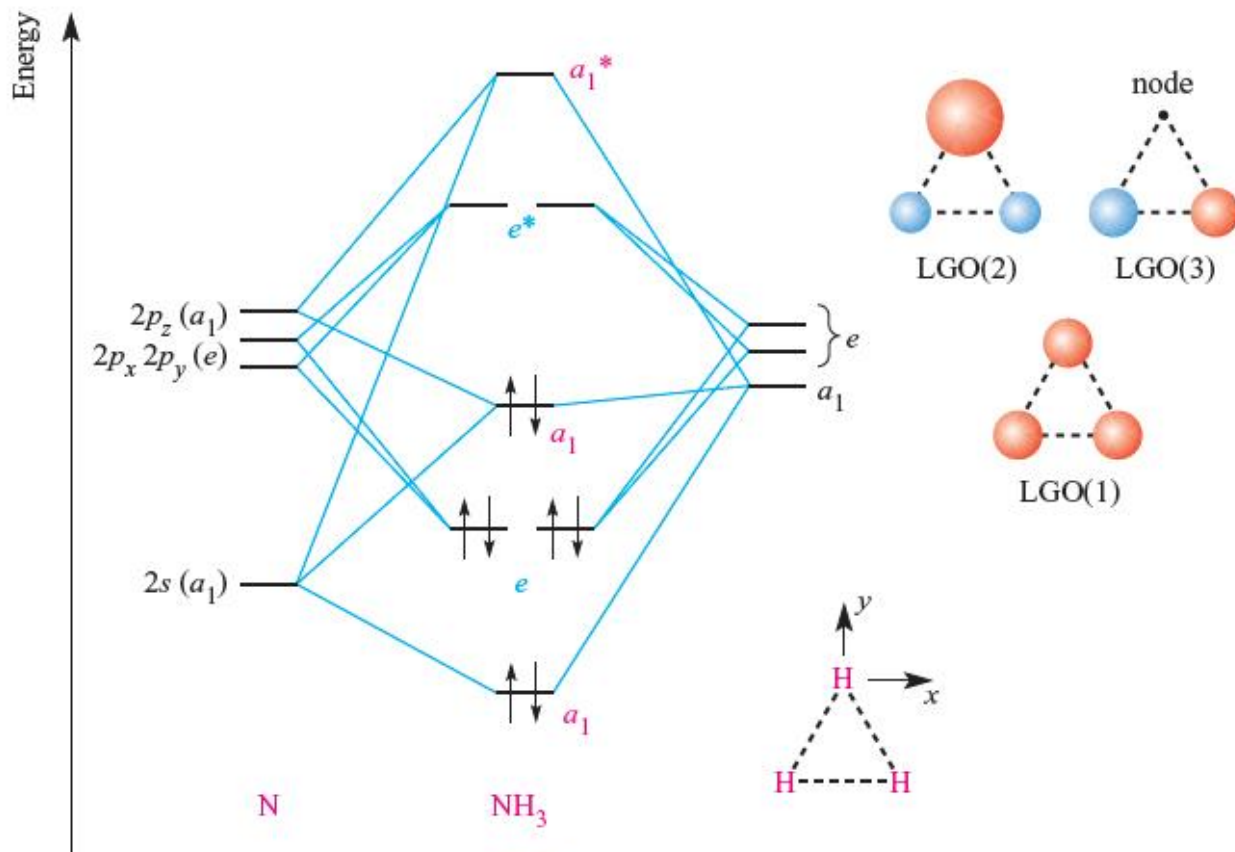


# NH<sub>3</sub>

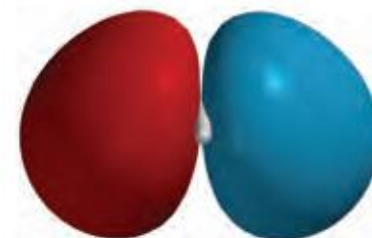


$C_{3v}$	$E$	$2C_3$	$3\sigma_v$
$A_1$	1	1	1
$A_2$	1	1	-1
$E$	2	-1	0

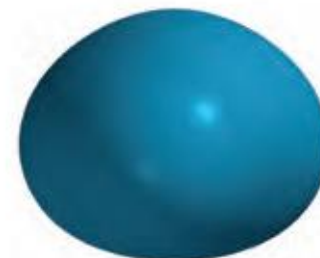
# NH<sub>3</sub>



Representation of the HOMO (a<sub>1</sub>)



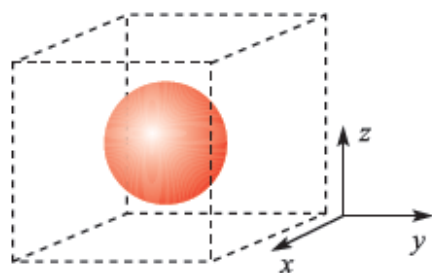
Representation of one of the e MOs



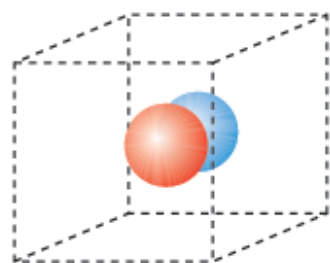
Representation of the lowest lying a<sub>1</sub> MO

$T_d$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$A_1$	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

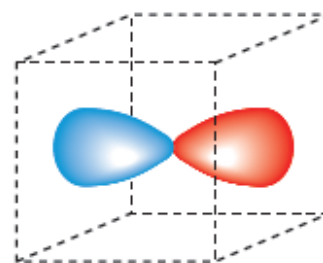
# CH<sub>4</sub>



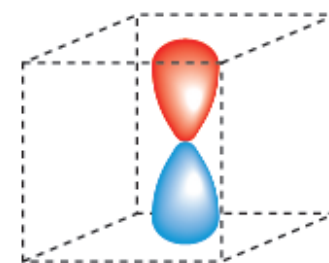
$2s (a_1)$



$2p_x (t_2)$

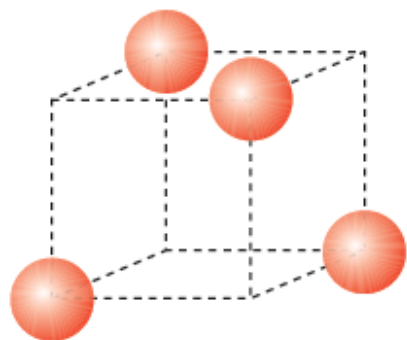


$2p_y (t_2)$

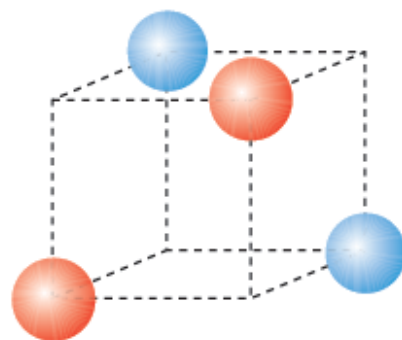


$2p_z (t_2)$

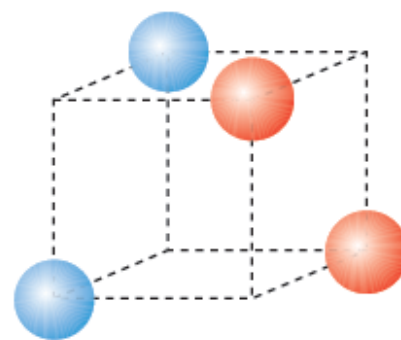
(a)



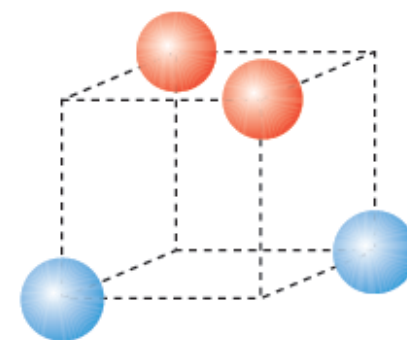
LGO(1) ( $a_1$ )



LGO(2) ( $t_2$ )

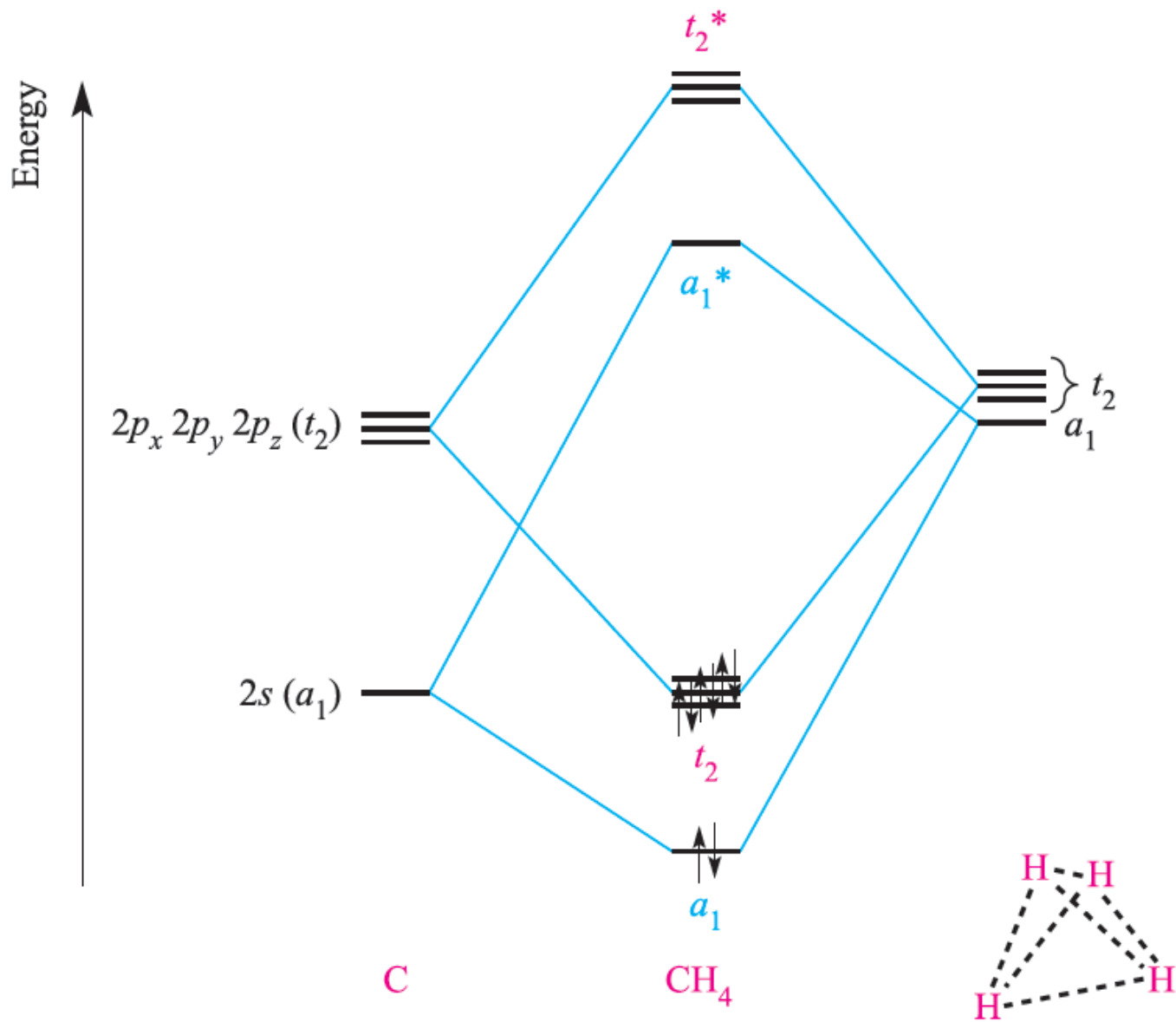


LGO(3) ( $t_2$ )



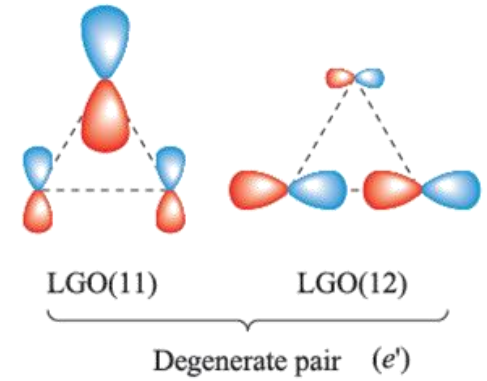
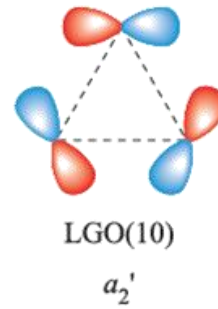
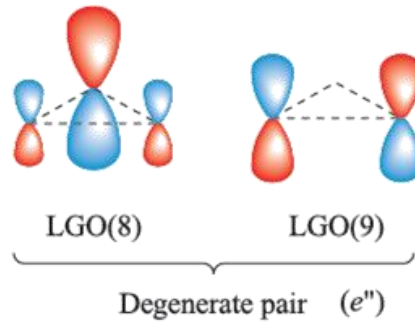
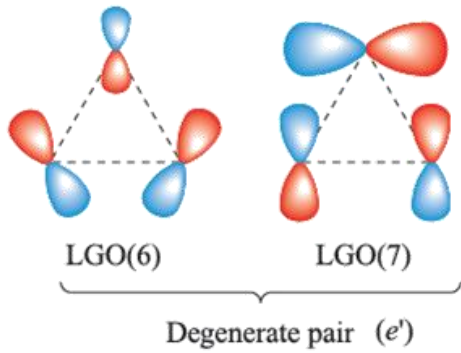
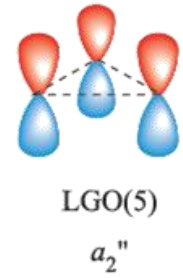
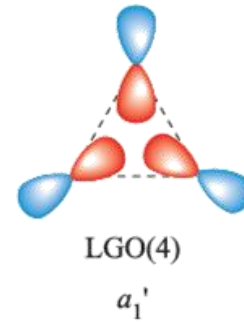
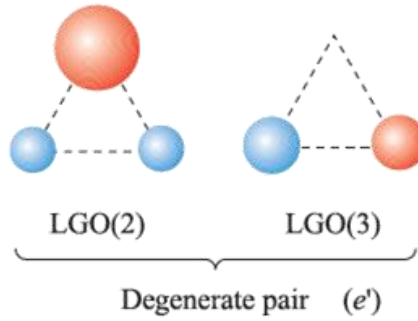
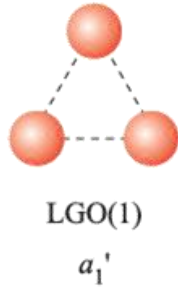
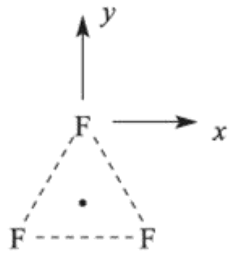
LGO(4) ( $t_2$ )

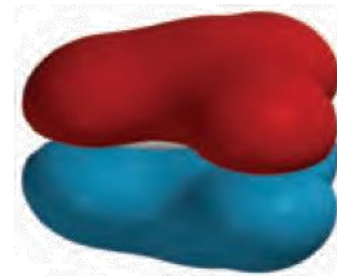
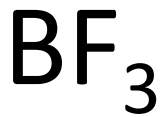
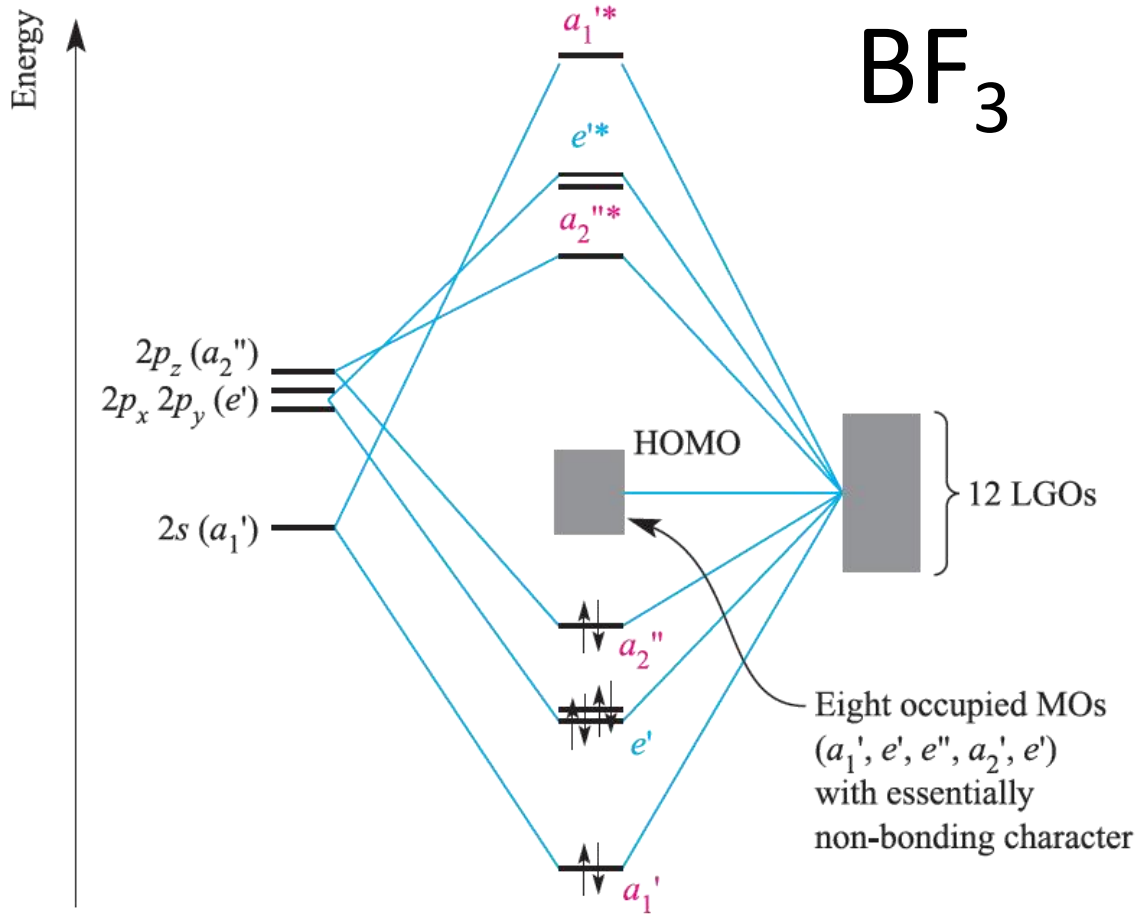
(b)



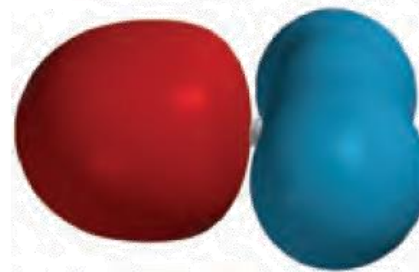


# AHORA EL $\text{BF}_3$

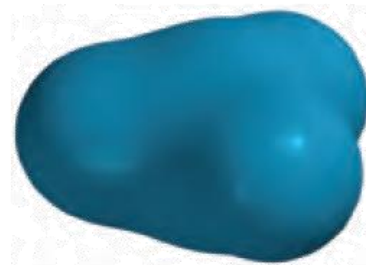




Representation of the  $a_2''$  MO



Representation of one of the  $e'$  MOs

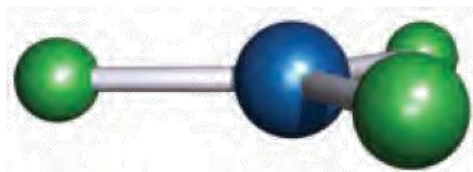


Representation of the  $a_1'$  MO

B

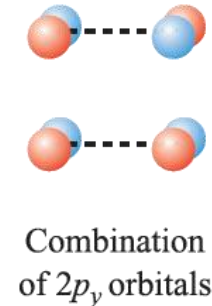
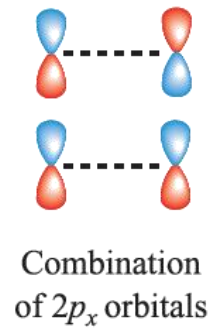
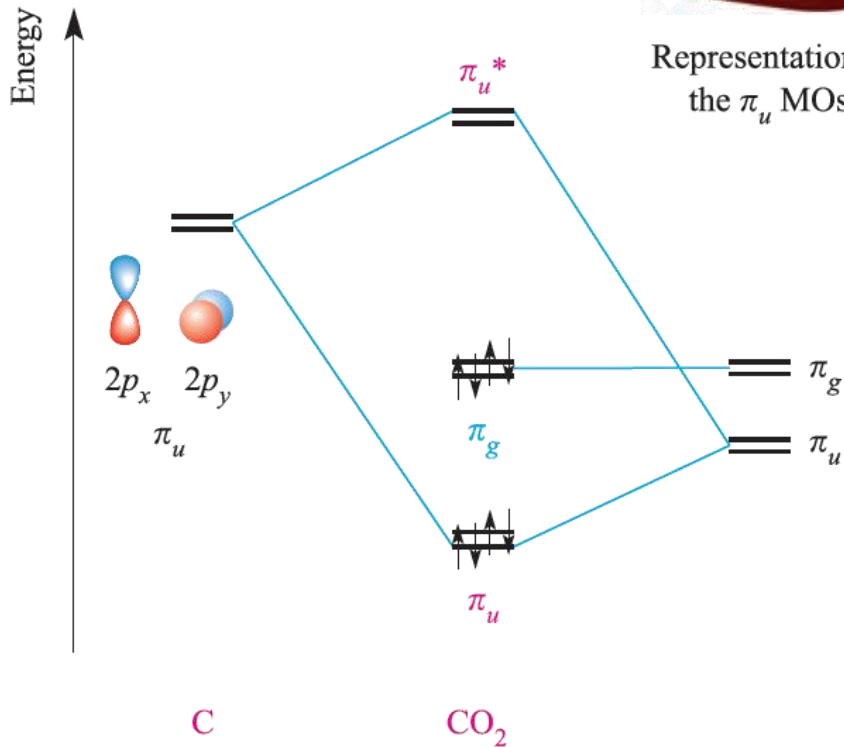
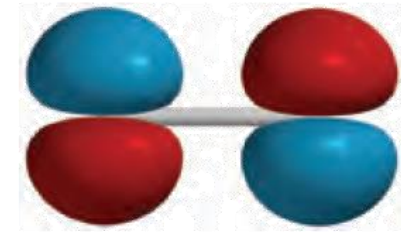
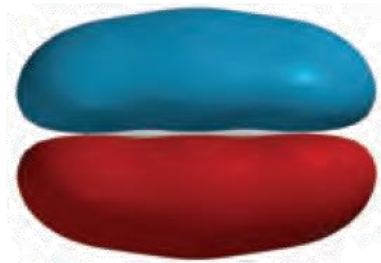
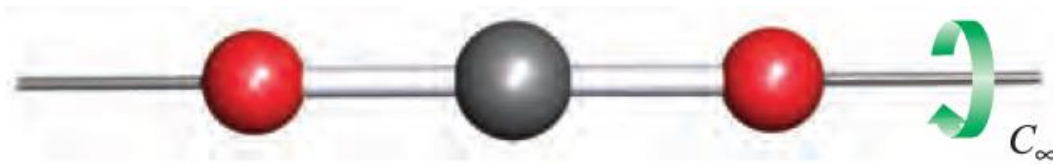
$\text{BF}_3$

$\text{F}_3$  fragment



$D_{3h}$

# Con orbitales $\pi$



OM en compuestos de coordinación

**El caso más general es el Oh**



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

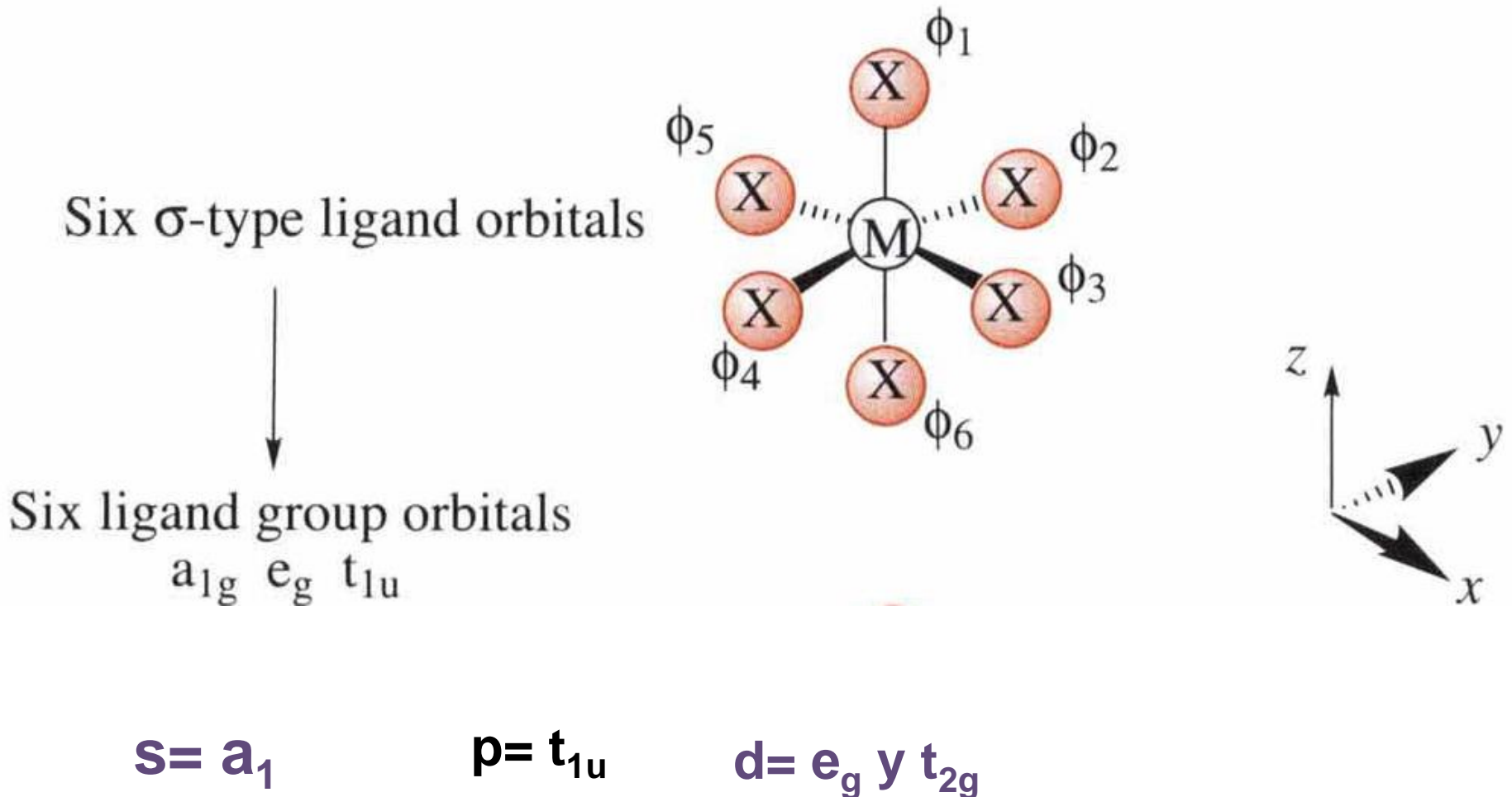
**Si consideramos la simetría**

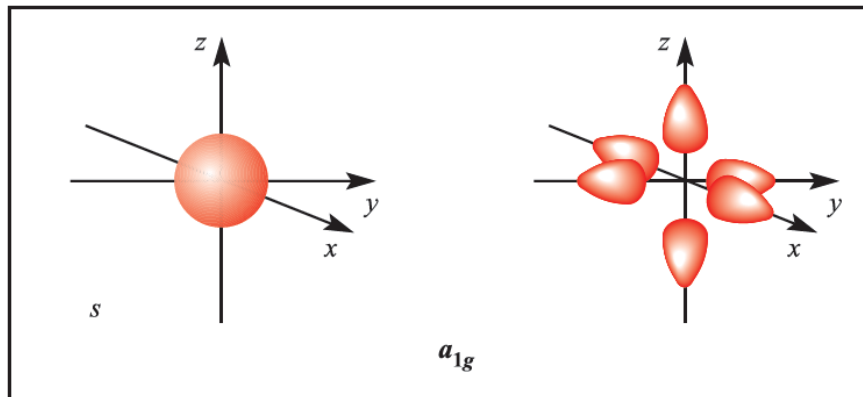
**s =  $a_1$**

**p son degenerados y son =  $t_{1u}$**

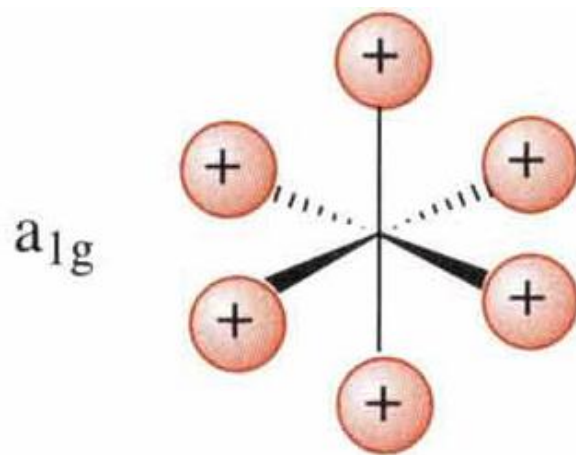
**d =  $e_g$  y  $t_{2g}$**

Consideraremos ahora un centro metálico y ligantes que únicamente mostrarán interacciones  $\sigma$



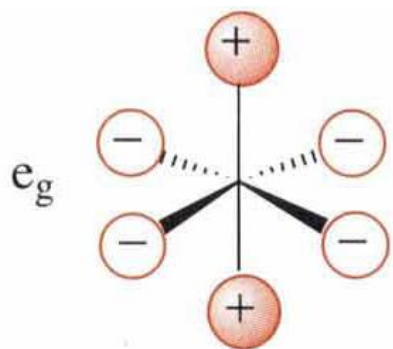
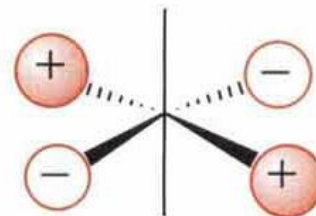


**Ligantes**

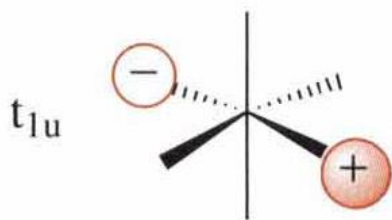


$$\psi(a_{1g})$$

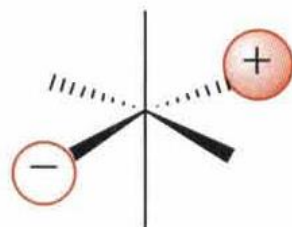
$$\psi(a_{1g}) = 1/\sqrt{6}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$


 $\psi_1(e_g)$ 

 $\psi_2(e_g)$ 

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


 $\psi_1(t_{1u})$ 

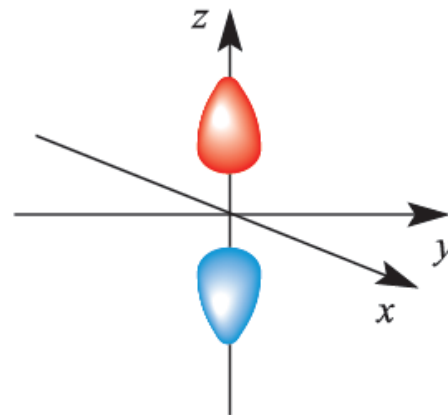
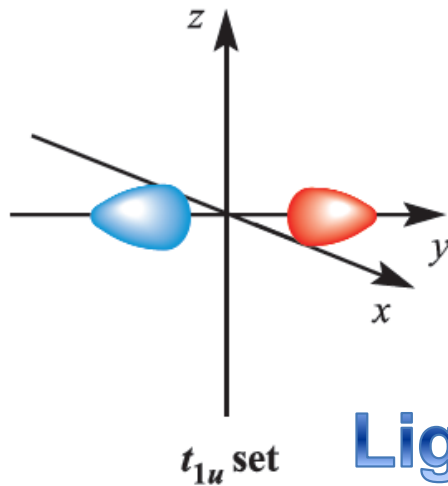
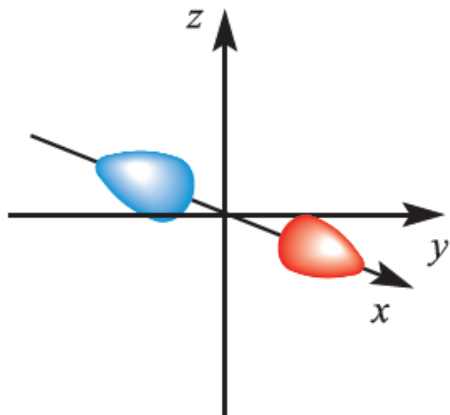
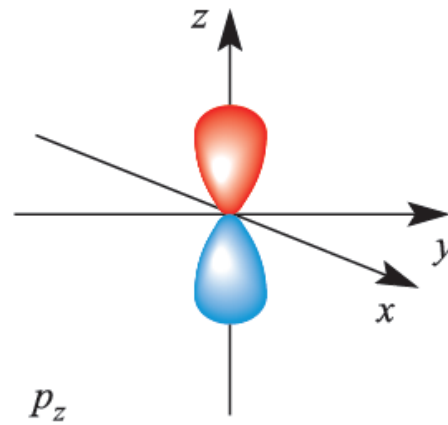
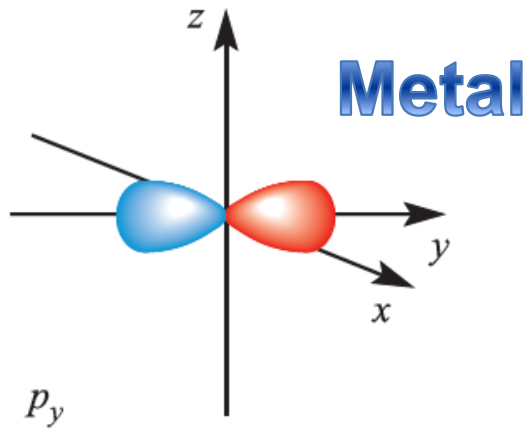
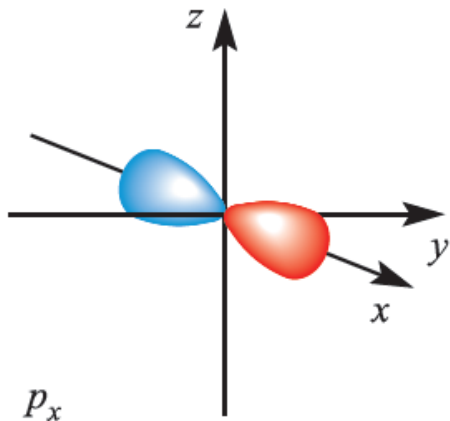
$$\psi_1(t_{1u}) = 1/\sqrt{2}(\phi_3 - \phi_5)$$


 $\psi_2(t_{1u})$ 

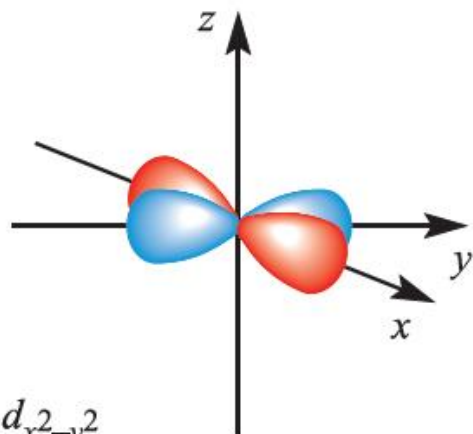
$$\psi_2(t_{1u}) = 1/\sqrt{2}(\phi_2 - \phi_4)$$


 $\psi_3(t_{1u})$ 

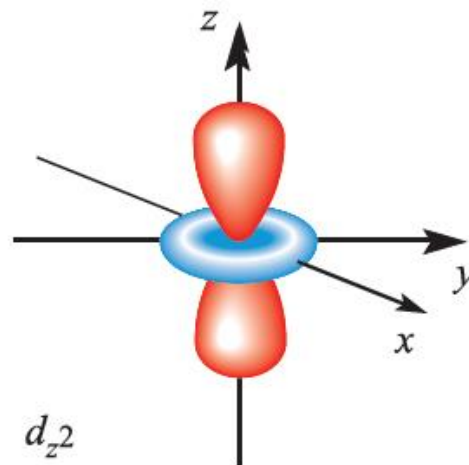
$$\psi_3(t_{1u}) = 1/\sqrt{2}(\phi_1 - \phi_6)$$



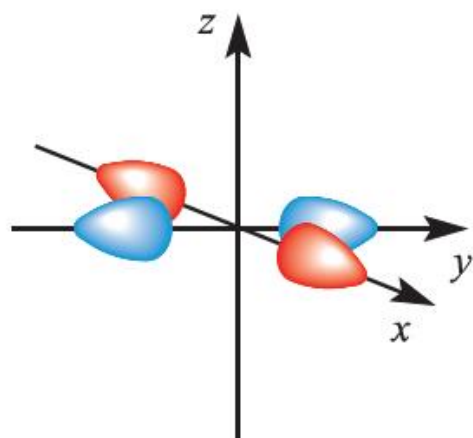




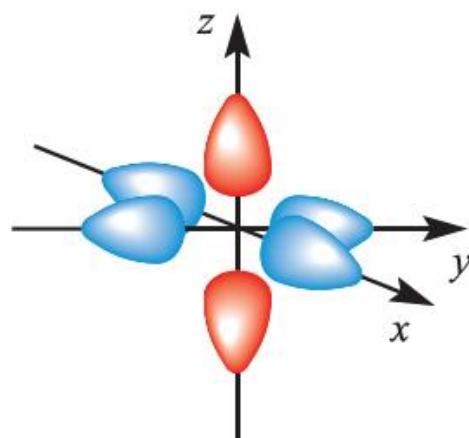
$d_{x^2-y^2}$



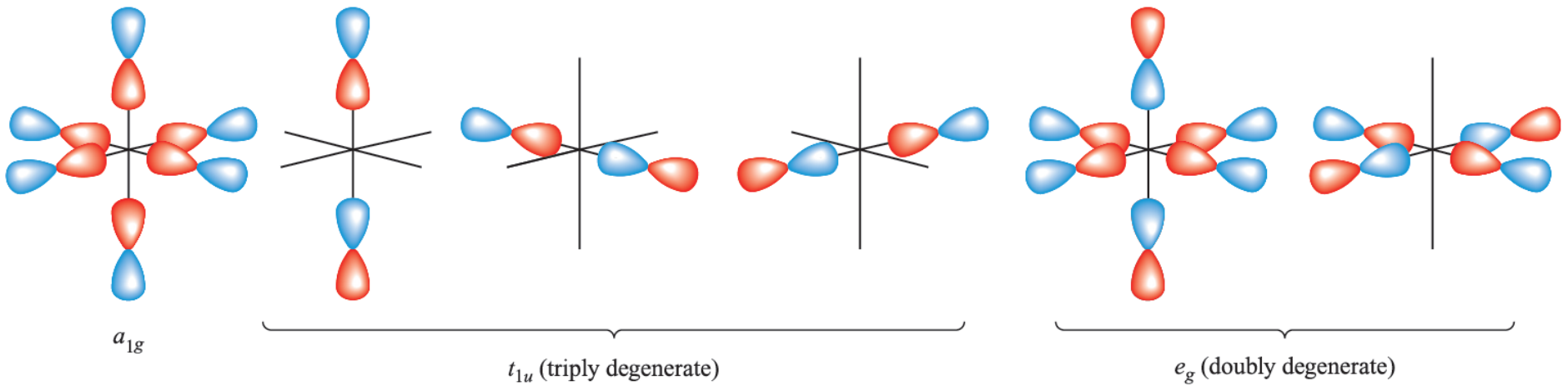
$d_{z^2}$



$e_g$  set

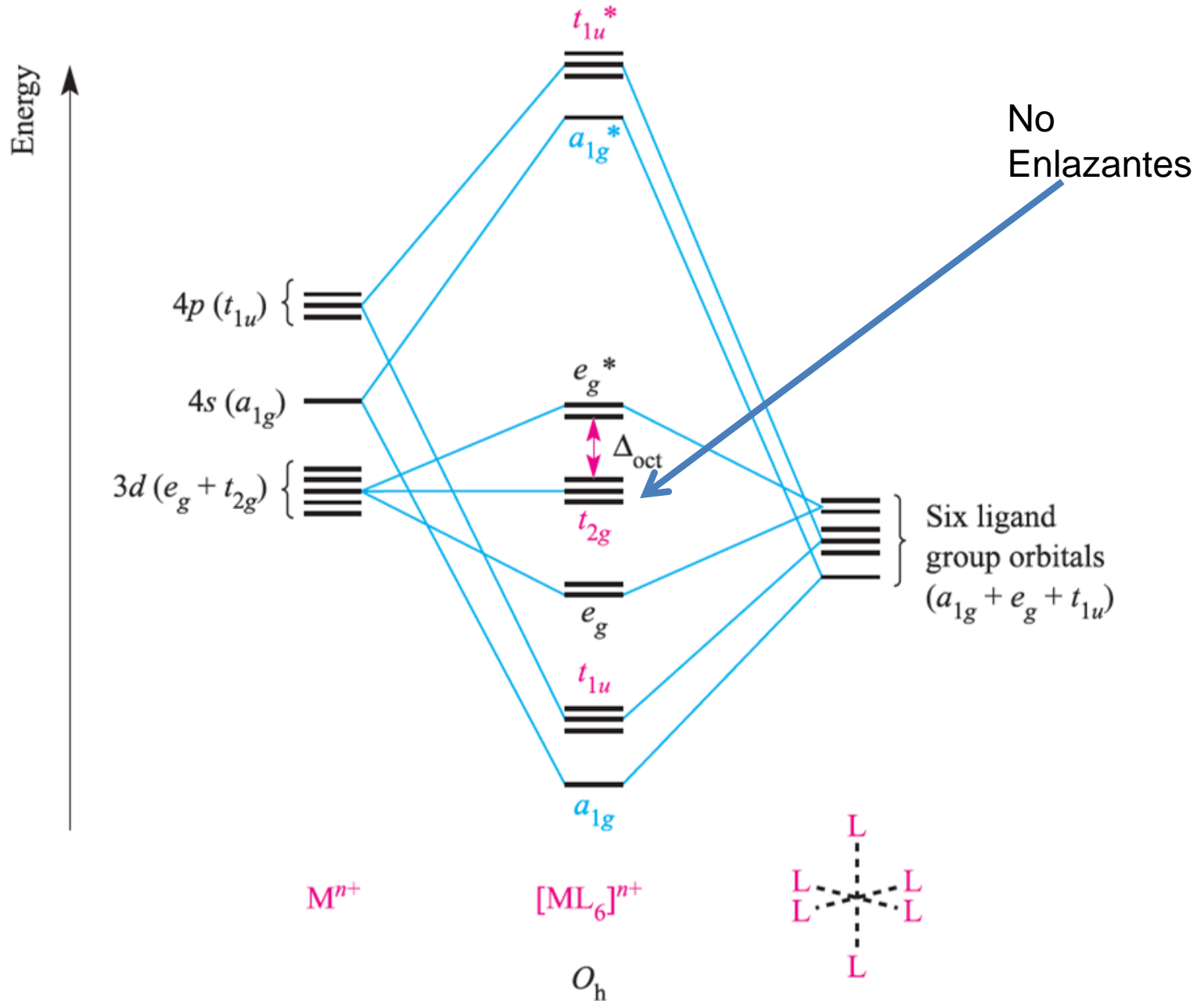


# Los 6 ligantes

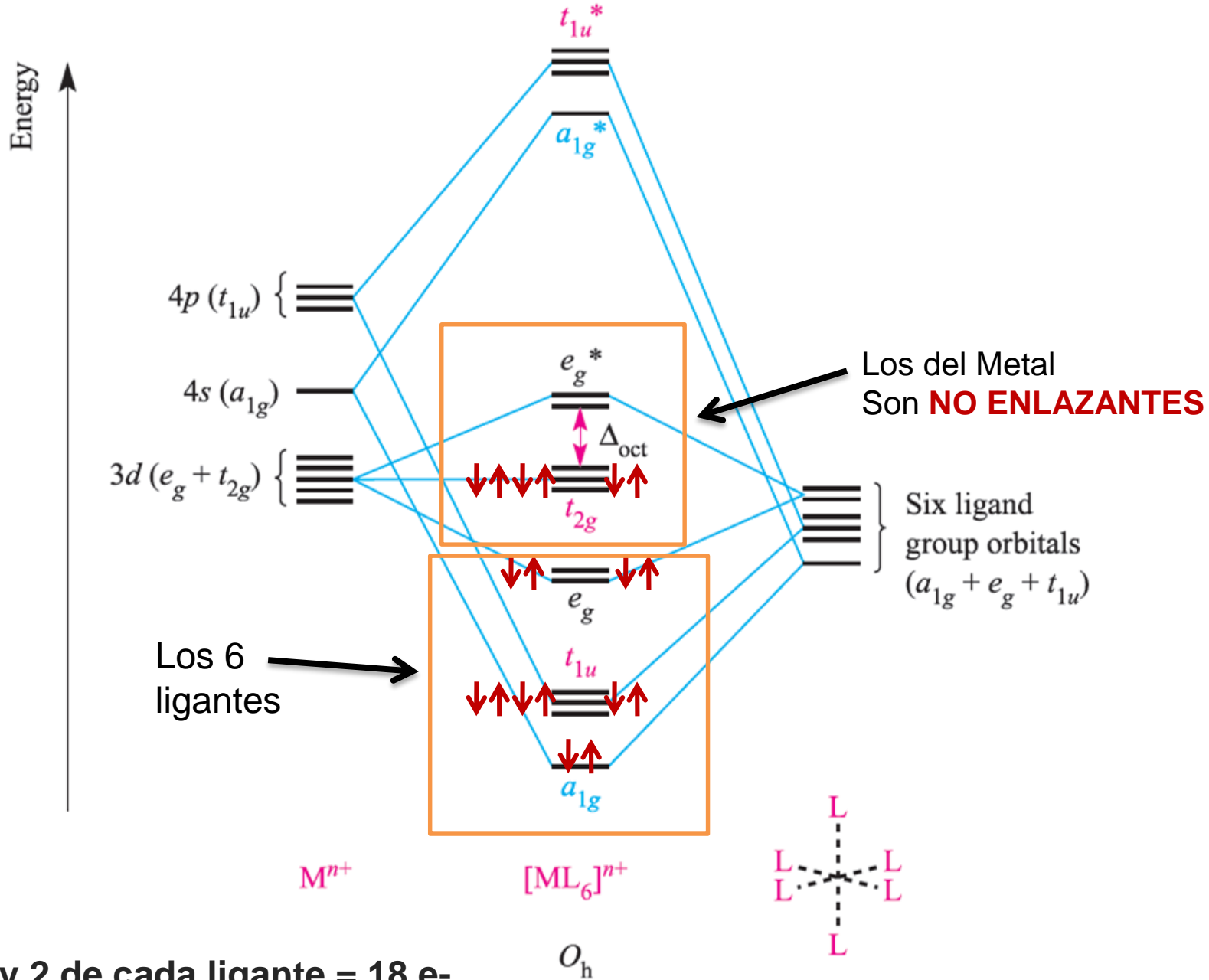


Los Goles  
Grupo orbital de los ligantes

# 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



# 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  $e_g^*$

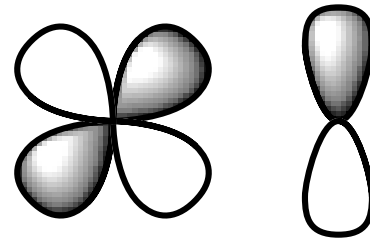
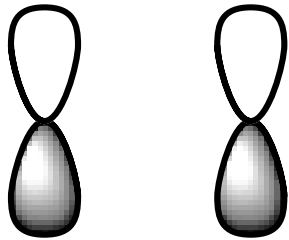
Es decir se repite lo que había salido en campo cristalino la misma degeneración y por lo tanto se explican las propiedades magnéticas de la misma forma. Sin embargo.....

# ¿Y si los ligantes tienen electrones en sistema $\pi$ ?

- Hay que clasificarlos
- Los  $\pi$  dadores
- y los  $\pi$  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  $\sigma$  y pueden superponerse con los orbitales de los ligantes de simetría adecuada para dar interacciones  $\pi$ .



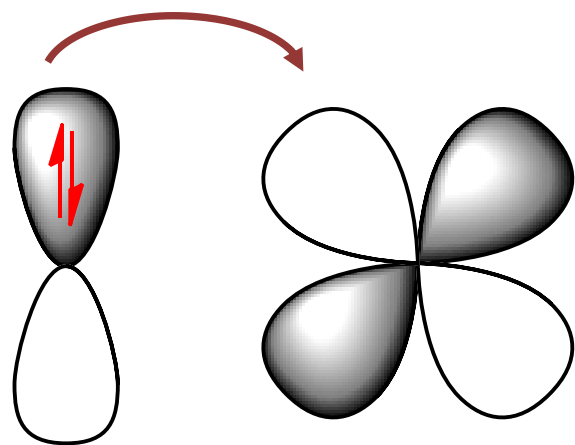
# Con interacción $\pi$

Un ligante  $\pi$  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.

$\text{Cl}^-$   $\text{Br}^-$  y  $\text{I}^-$

Configuración  $s^2p^5$



ligante

metal

También el metal debe tener pocos electrones en *d*

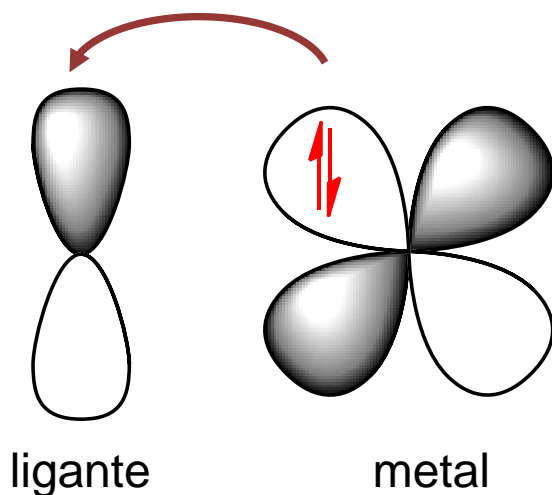


**Un ligante  $\pi$  aceptor acepta electrones del centro metálico en una interacción en la que interviene un orbital del metal lleno y un orbital del ligante vacío.**

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

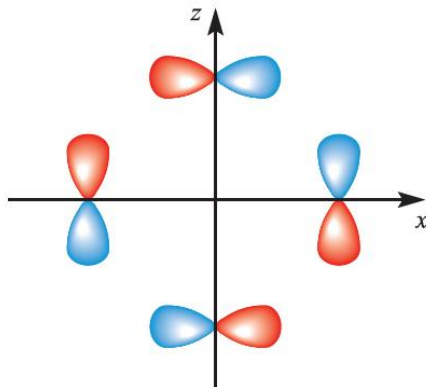
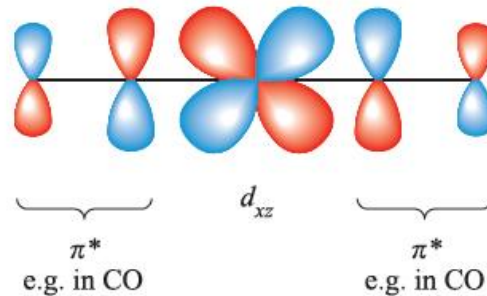
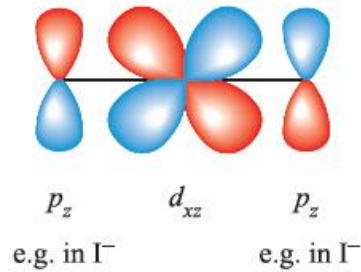
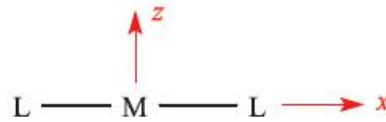
**Configuración  $s^2p^2, 3$**

**CO, NO,  $N_2$**

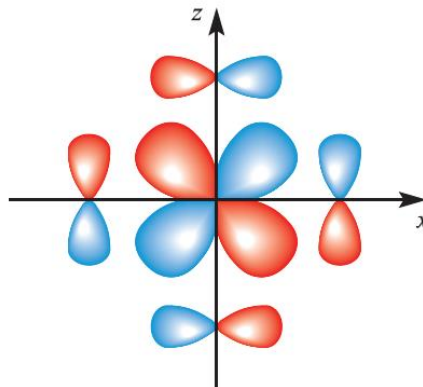


# Con interacción $\pi$

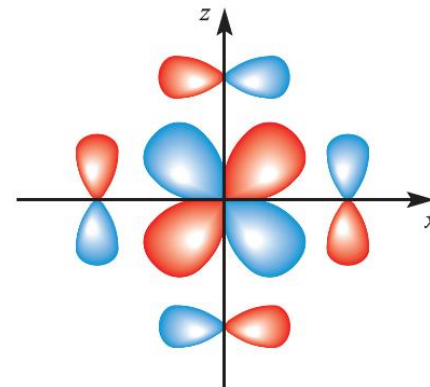
- Los ligantes  $\pi$  aceptores pueden estabilizar complejos metálicos de bajos estados de oxidación



(a)

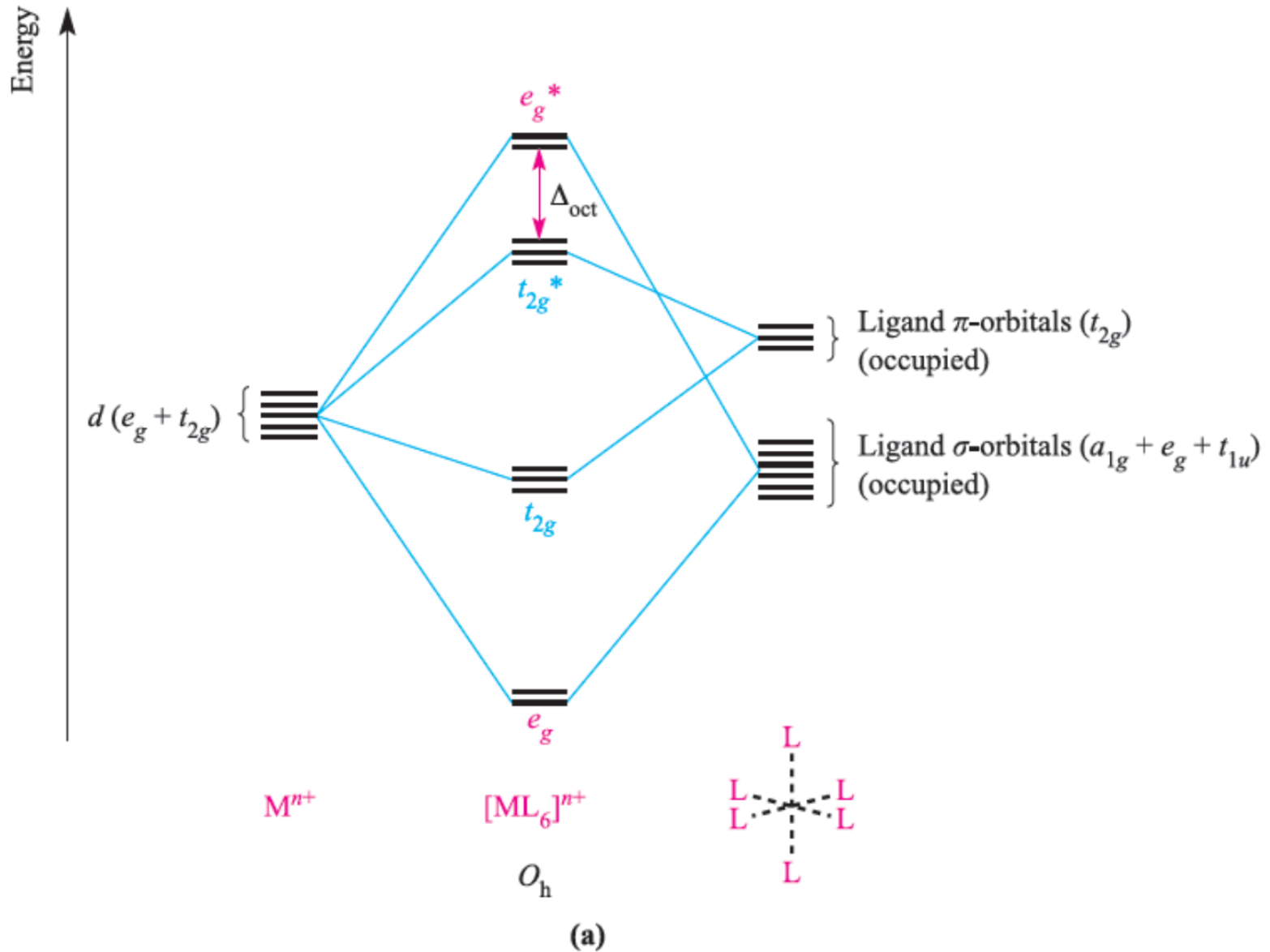


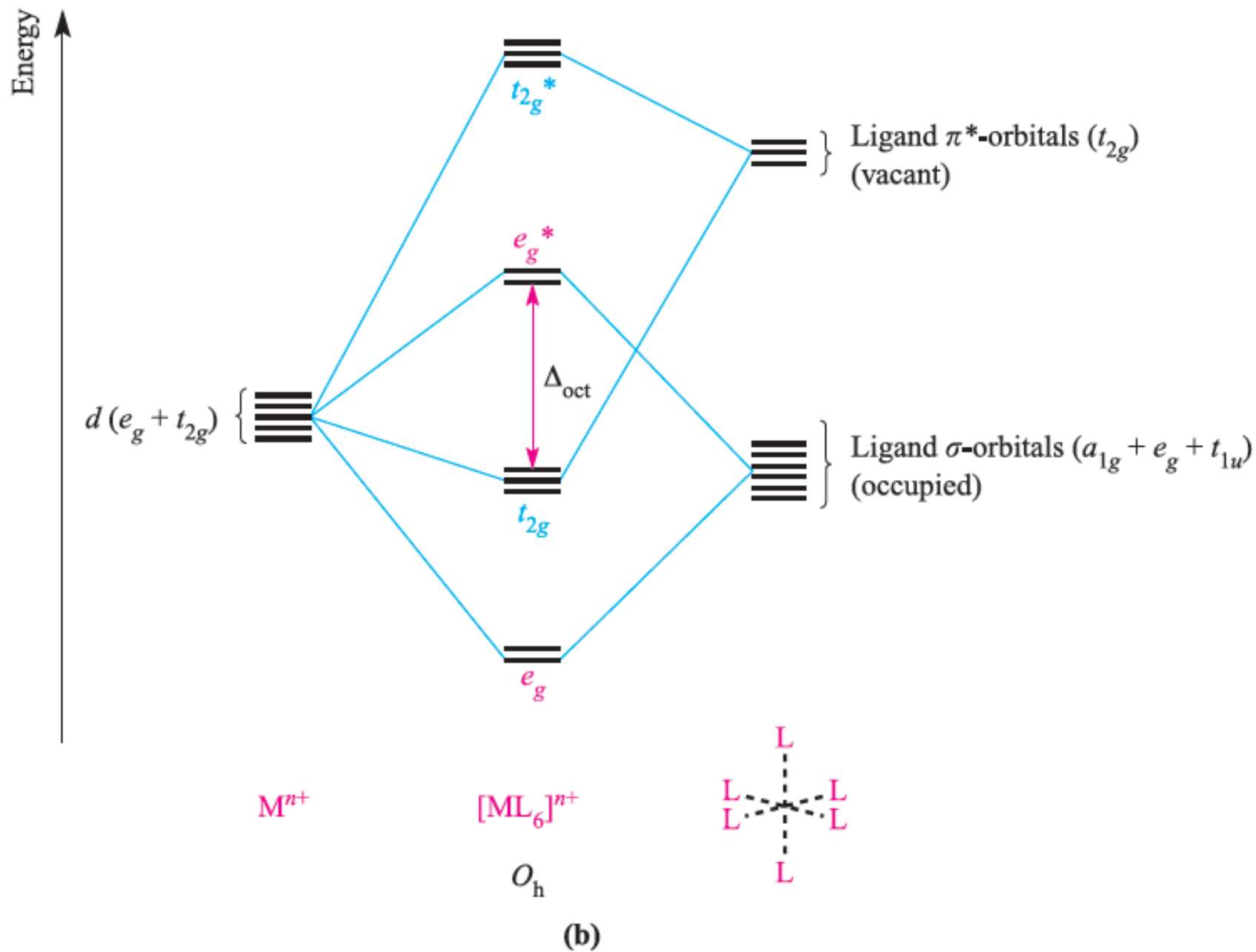
(b)



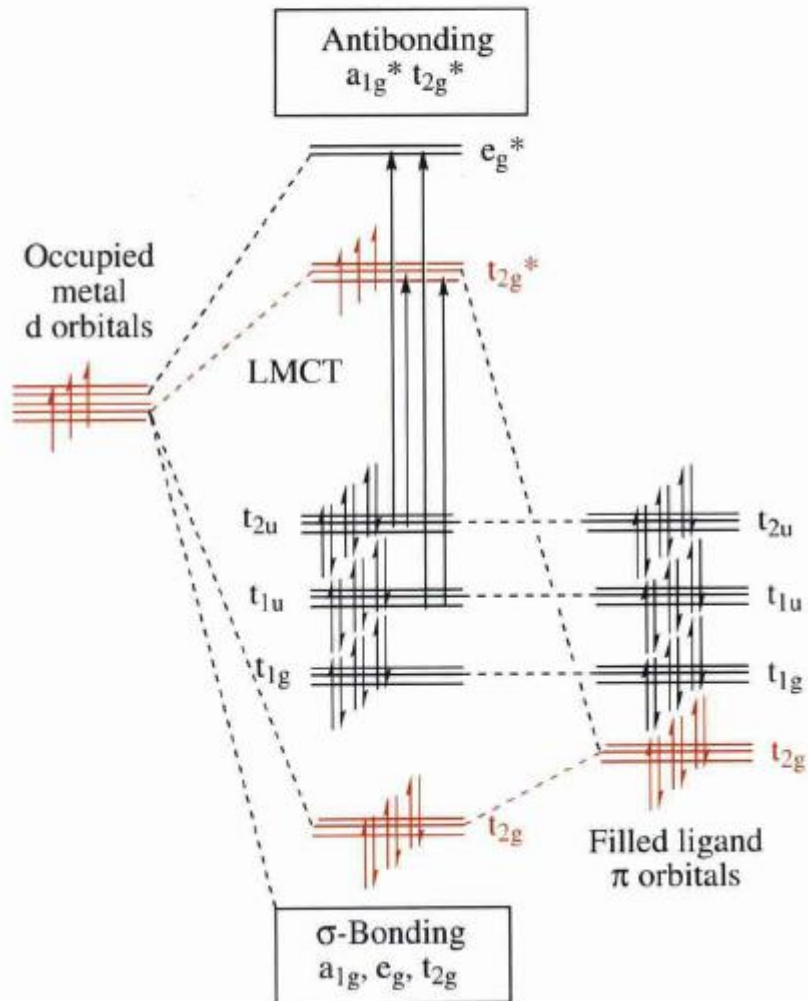
(c)

# Diagrama con ligantes $\pi$ dadores

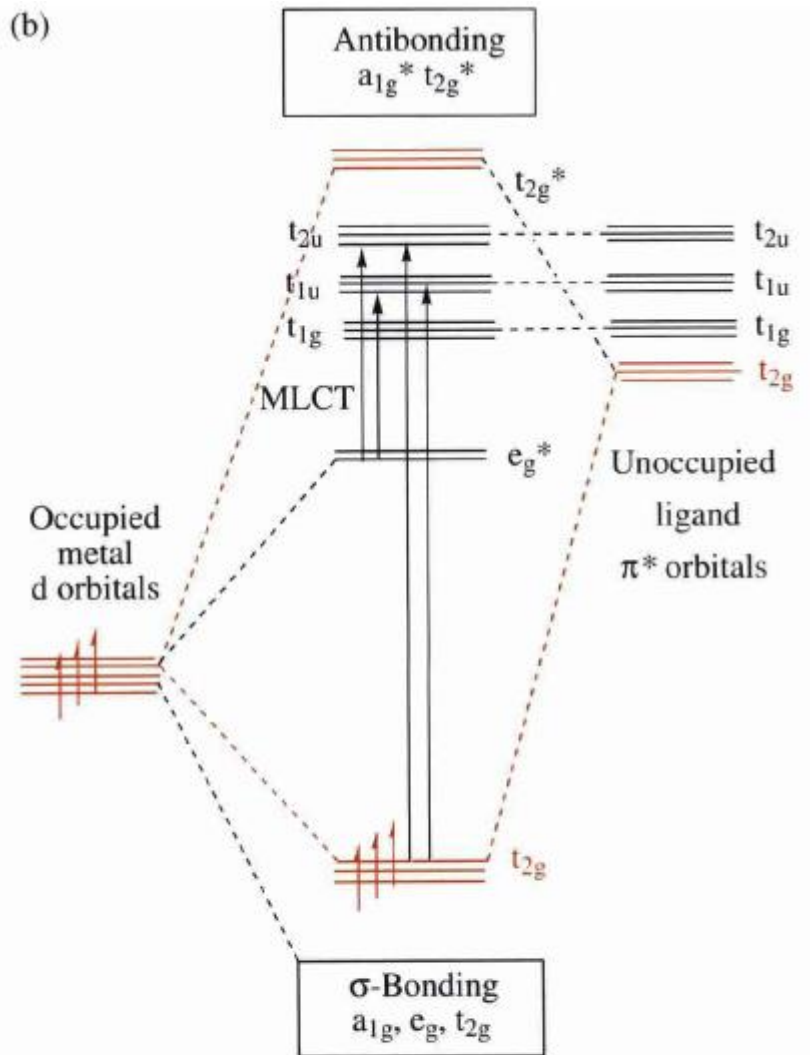




(a)



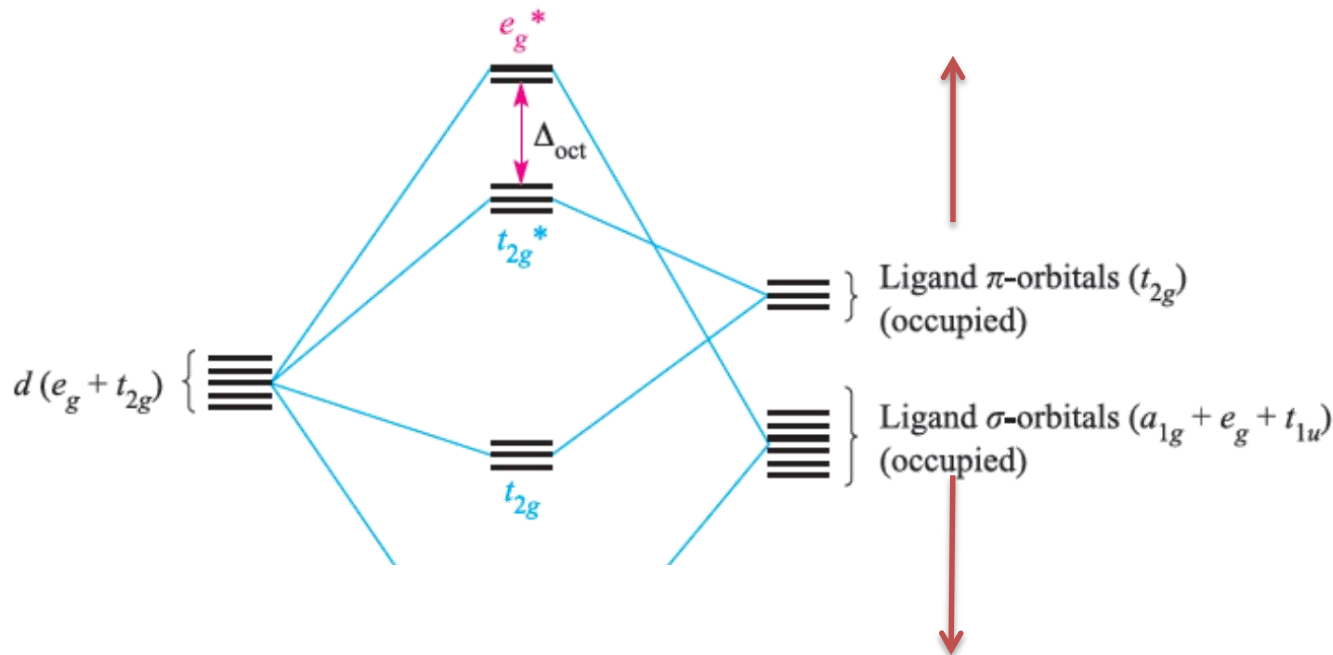
(b)



# Los cambios entre $\sigma$ y $\pi$

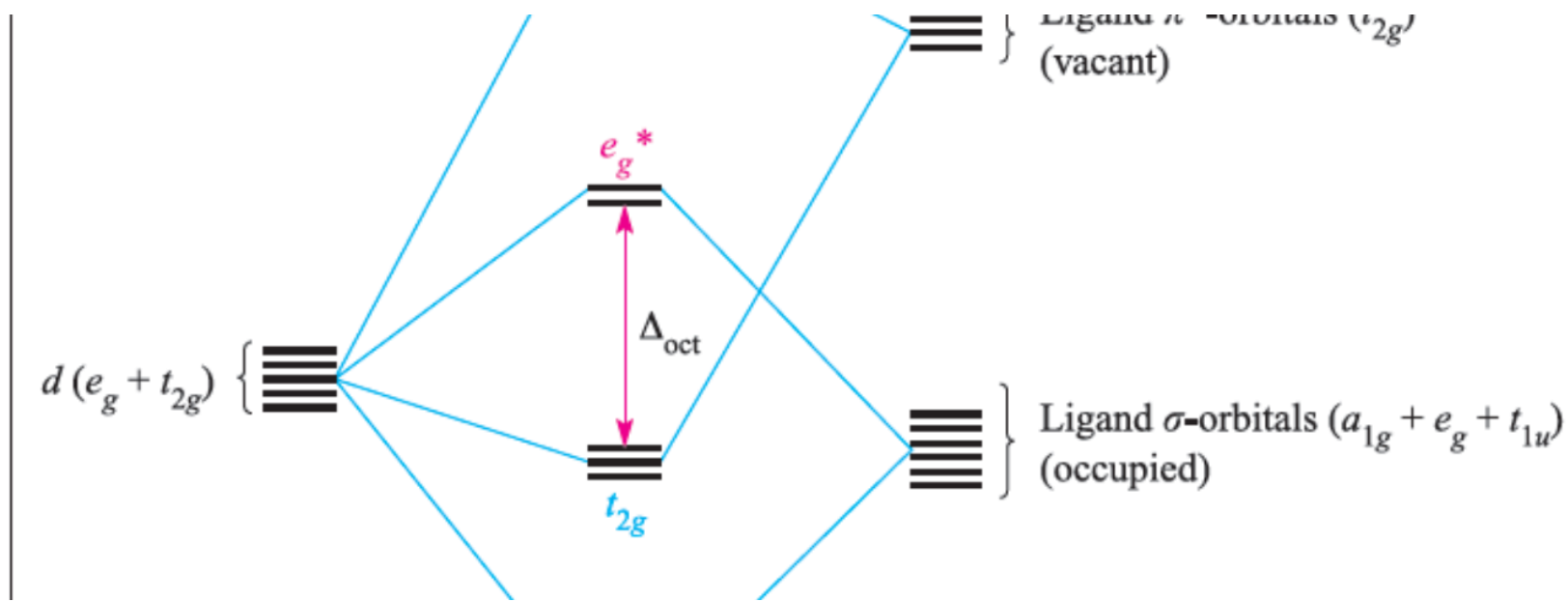
- $\Delta_0$  disminuye al pasar de un complejo  $\sigma$  a uno que contiene ligandos  $\pi$  donadores
- Para un complejo con ligandos  $\pi$  donadores, la cesión p creciente estabiliza el nivel  $t_{2g}$  y desestabiliza  $t_{2g}^*$  disminuyendo de esta manera  $\Delta_0$ .

Ene



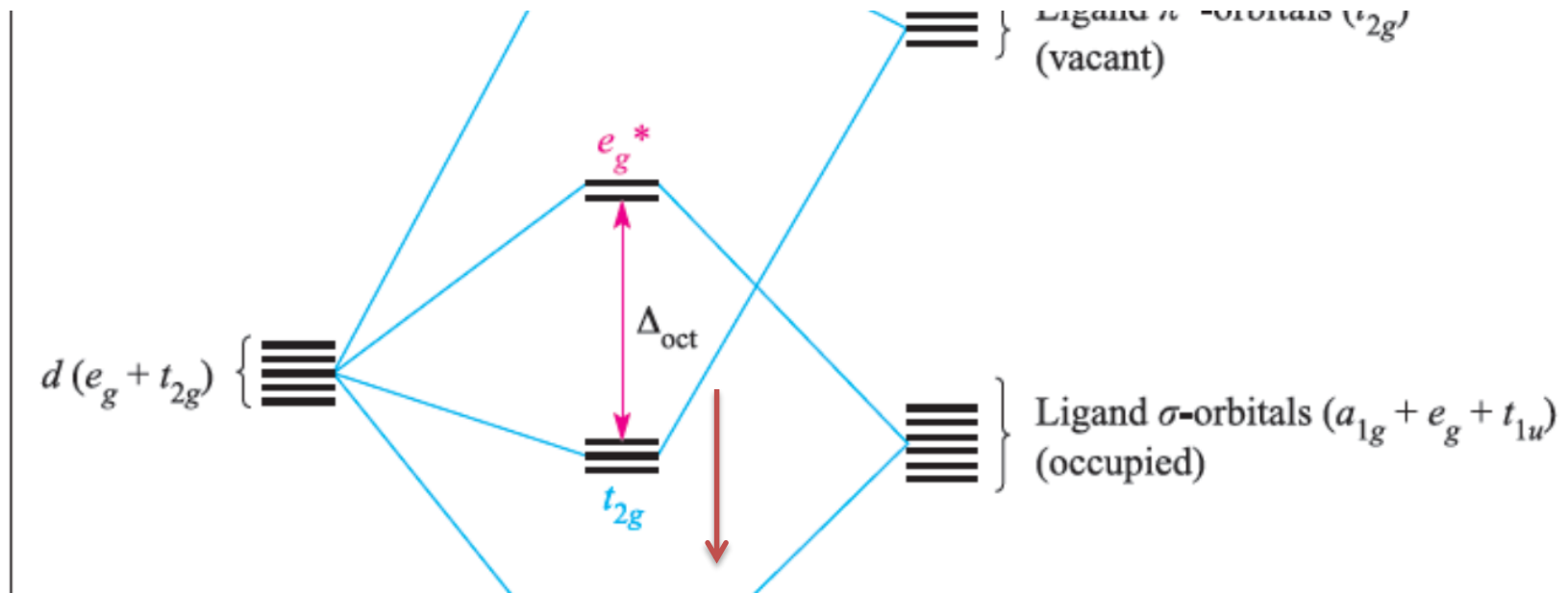
# Los cambios entre $\sigma$ y $\pi$

- Los valores de  $\Delta_0$  son relativamente grandes para los complejos que contienen ligantes  $\pi$  aceptores y es probable que estos complejos sean de bajo espín.



# Los cambios entre $\sigma$ y $\pi$

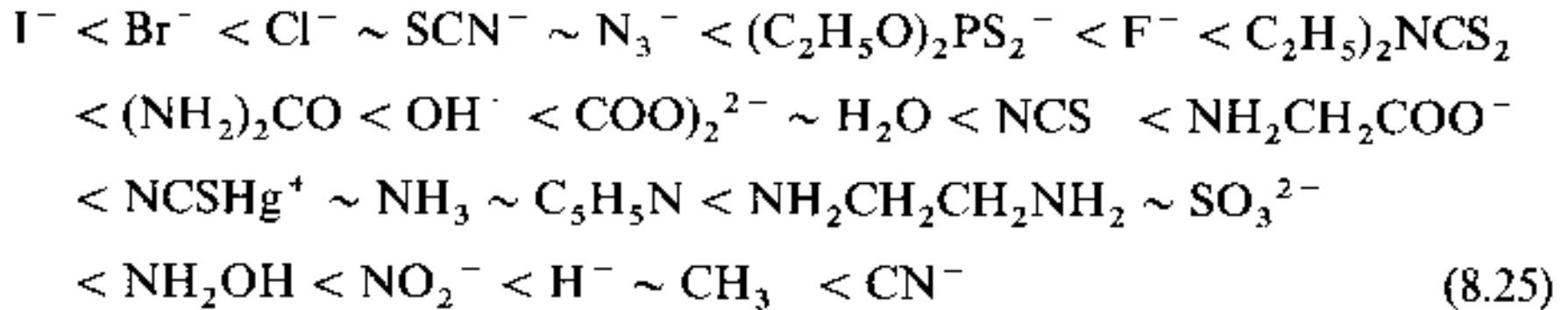
- Para un complejo con ligantes  $\pi$  aceptores la aceptación  $\pi$  creciente estabiliza el nivel  $t_{2g}$  aumentando de esta forma  $\Delta_0$





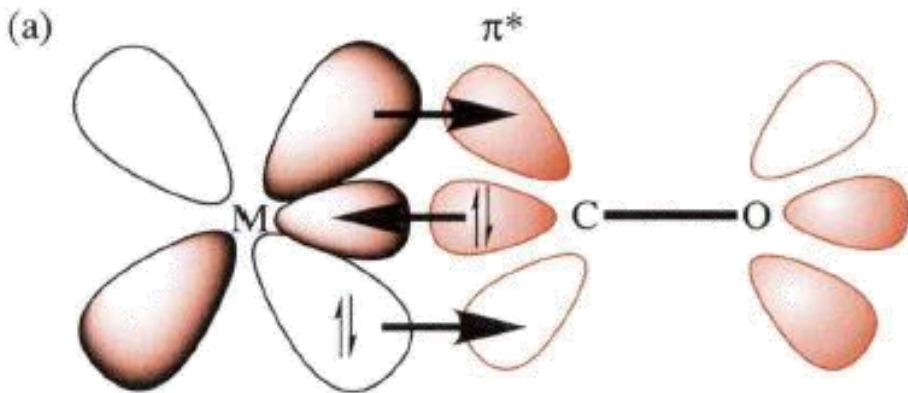
# Serie espectroquímica

## $\pi$ dadores



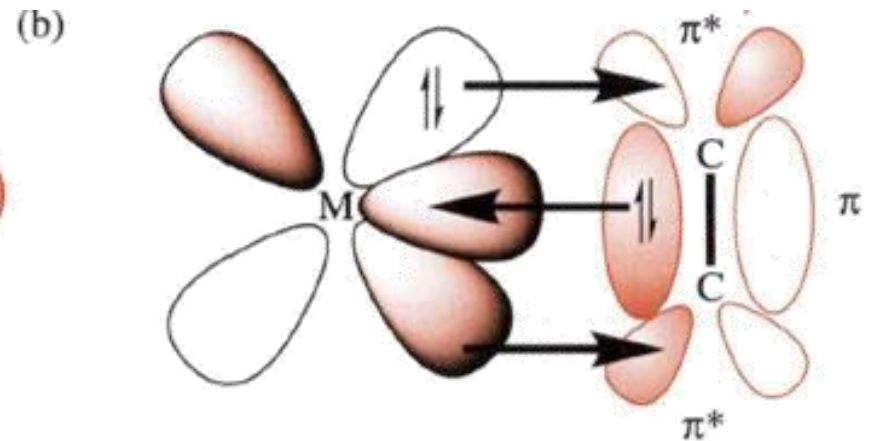
## $\pi$ aceptores

# Retrodonación



## Synergic bonding

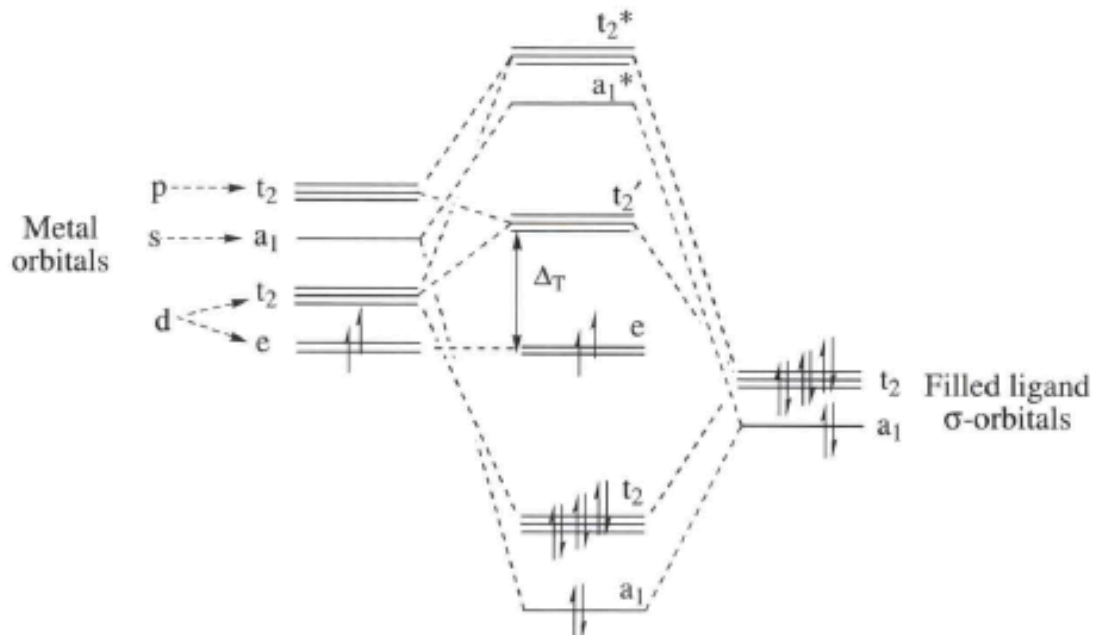
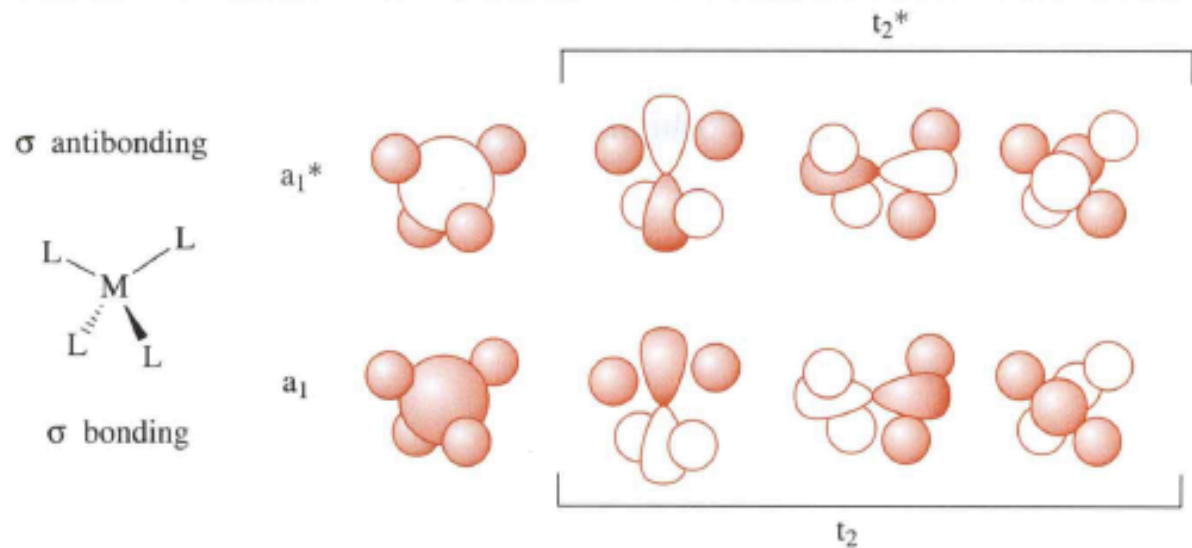
filled CO to empty M  $\sigma$  donation  
filled M d to empty CO  $\pi^*$  back-donation  
(for clarity the second out-of-plane  
 $\pi$  interaction is not shown)



## Synergic bonding

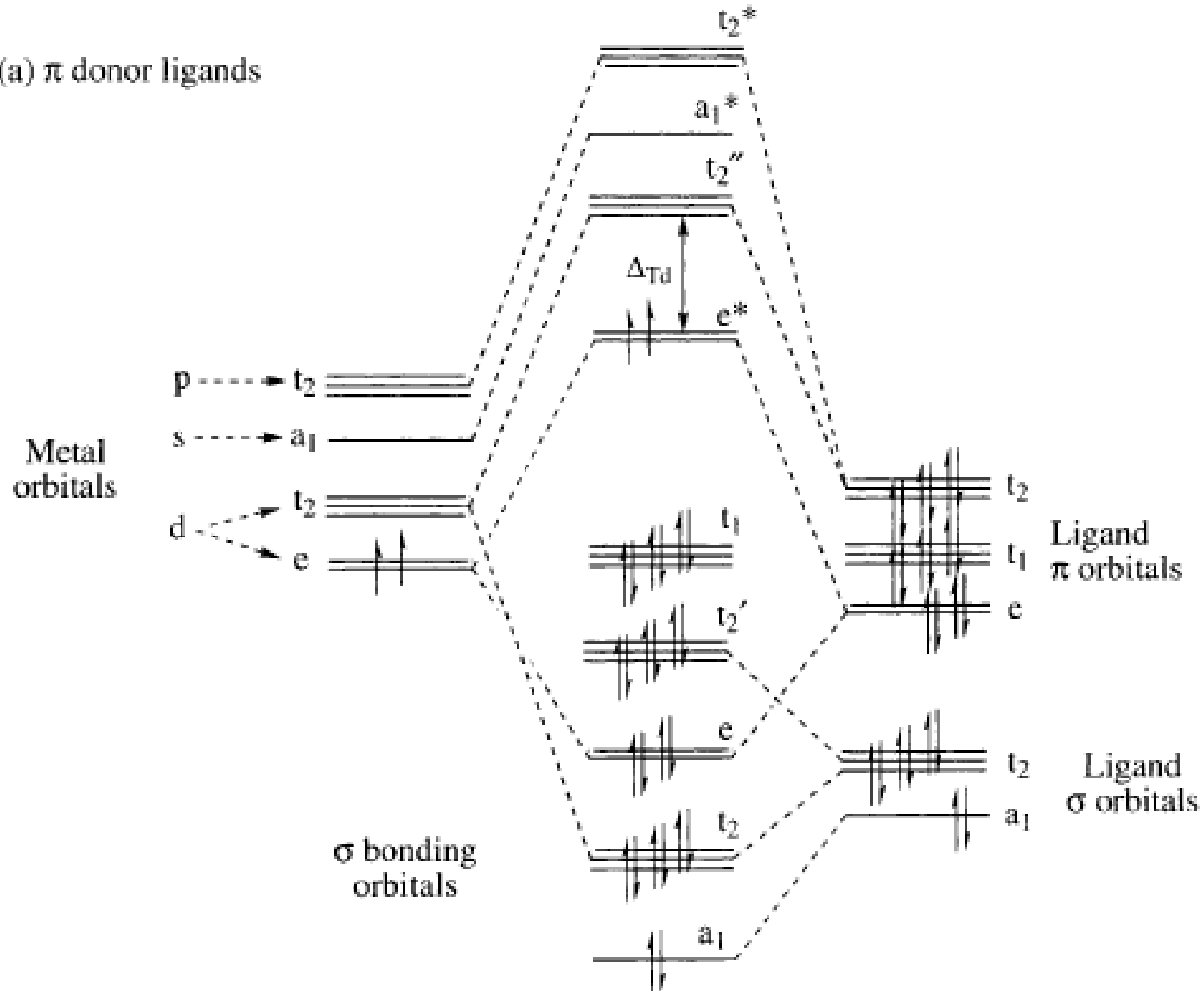
$C_2H_4$  filled  $\pi$  to empty M  $\sigma$  donation  
filled M d to empty  $C_2H_4$   $\pi^*$  back-donation

# Tetraedros solo $\sigma$



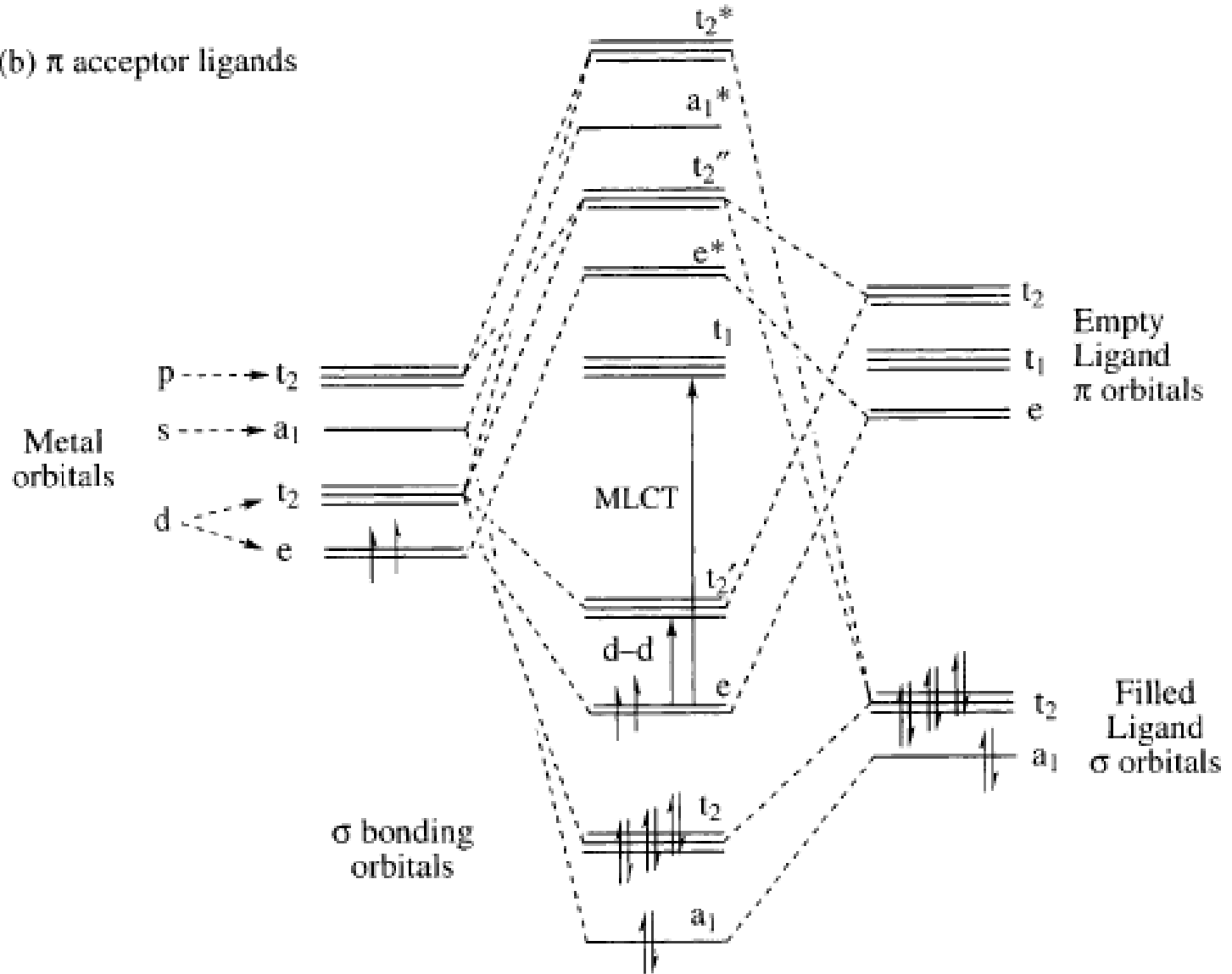
# Tetraedros con $\pi$

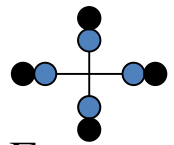
(a)  $\pi$  donor ligands



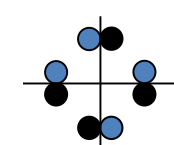
# Tetraedros con $\pi$

(b)  $\pi$  acceptor ligands

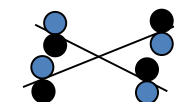




$$\Gamma_{\sigma} = A_{1g} + E_u + B_{1g}$$



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



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

