

Modelos de enlace

Química de Coordinación

Empezamos por lo más sencillo

La TEV se debe a Linus Pauling. Más conocida como modelo de las hibridaciones o de las orbitales híbridas, modelo muy utilizado en química orgánica en donde las discusiones se dan en términos de los híbridos sp , sp^2 o sp^3 del carbón en referencia. Linus Pauling amplía su teoría para aplicarla a los compuestos de coordinación con iones de transición, es decir con participación de las orbitales d en la hibridación, además de las s y p .

TEV

En el caso de los metales de transición en los compuestos de coordinación, deben hibridizarse tantos orbitales atómicos como se necesiten para acomodar los pares libres de los ligantes.

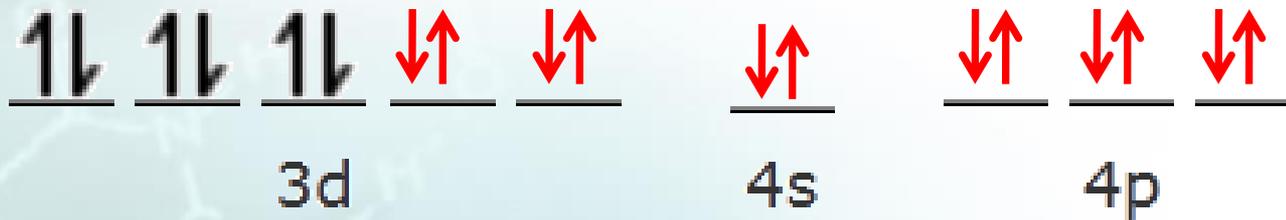
Por ejemplo, en el $[\text{Fe}(\text{CN})_6]^{4-}$:



TEV

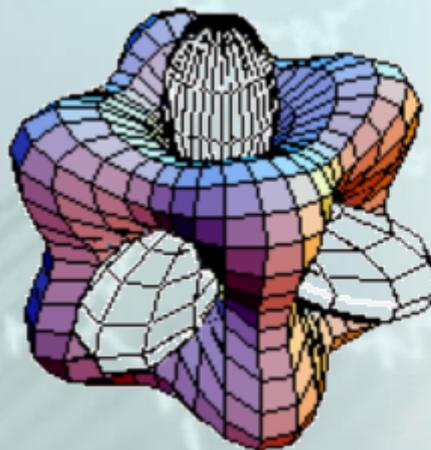


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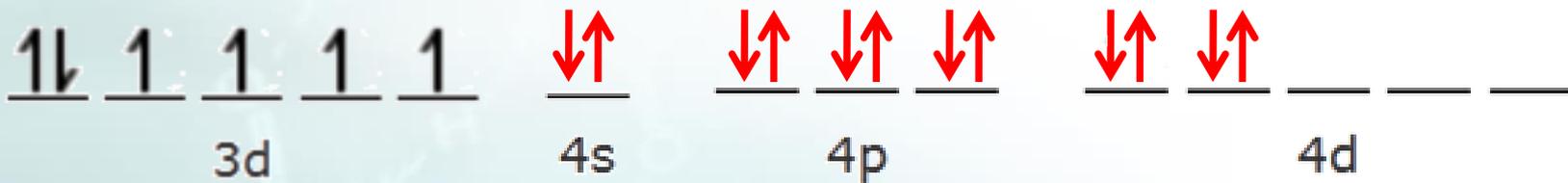


d^2sp^3

Octaedro

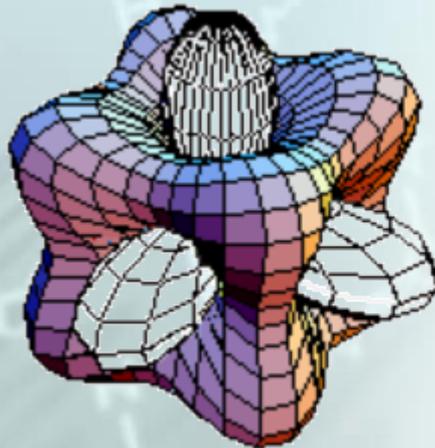


TEV



sp^3d^2

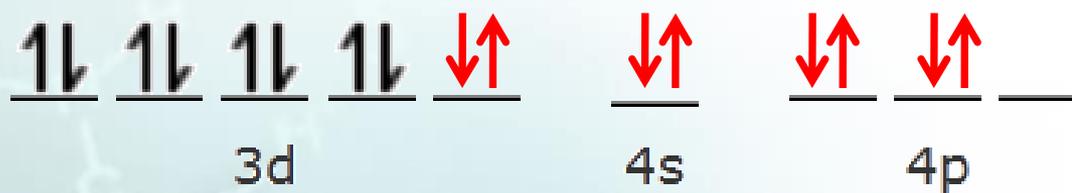
Octaedro



TEV otras geometrías

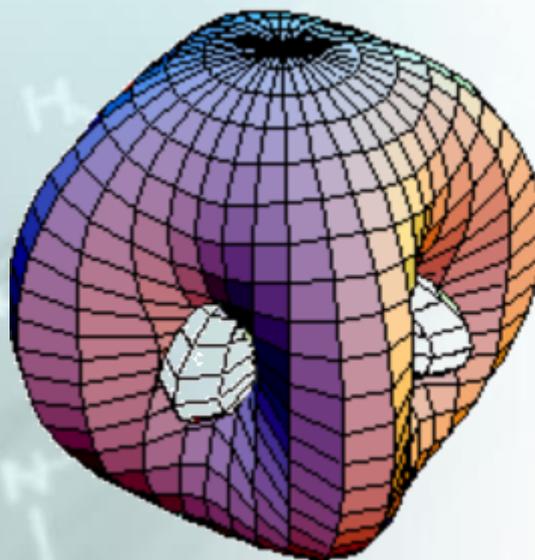


TEV



dsp^2

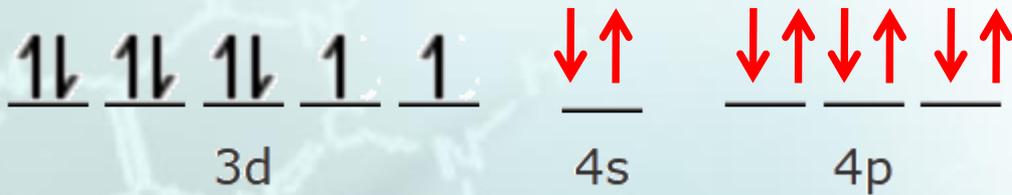
Cuadrado



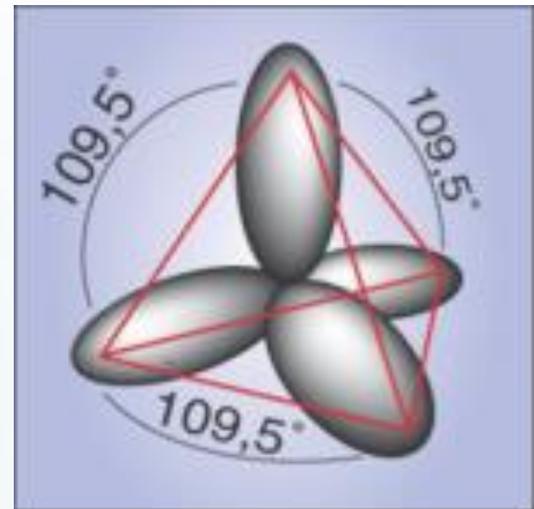
TEV



Este es paramagnético



sp^3



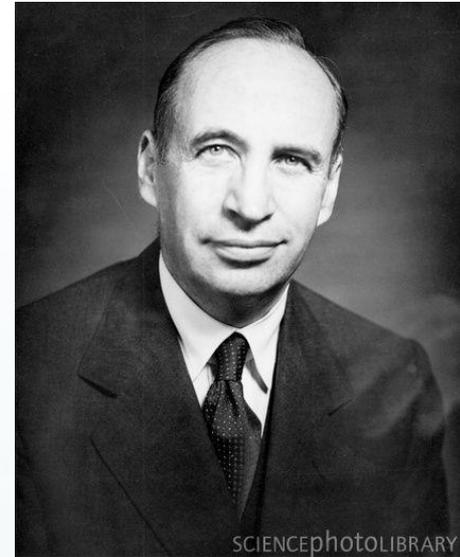
Lo mismo con todas las geometrías

Coordination number	Arrangement of donor atoms	Orbitals hybridized	Hybrid orbital description	Example
2	Linear	s, p_z	sp	$[\text{Ag}(\text{NH}_3)_2]^+$
3	Trigonal planar	s, p_x, p_y	sp^2	$[\text{HgI}_3]^-$
4	Tetrahedral	s, p_x, p_y, p_z	sp^3	$[\text{FeBr}_4]^{2-}$
4	Square planar	$s, p_x, p_y, d_{x^2-y^2}$	$sp^2 d$	$[\text{Ni}(\text{CN})_4]^{2-}$
5	Trigonal bipyramidal	$s, p_x, p_y, p_z, d_{z^2}$	$sp^3 d$	$[\text{CuCl}_5]^{3-}$
5	Square-based pyramidal	$s, p_x, p_y, p_z, d_{x^2-y^2}$	$sp^3 d$	$[\text{Ni}(\text{CN})_5]^{3-}$
6	Octahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$	$sp^3 d^2$	$[\text{Co}(\text{NH}_3)_6]^{3+}$
6	Trigonal prismatic	$s, d_{xy}, d_{yz}, d_{xz}, d_{z^2}, d_{x^2-y^2}$ or $s, p_x, p_y, p_z, d_{xz}, d_{yz}$	sd^5 or $sp^3 d^2$	$[\text{ZrMe}_6]^{2-}$
7	Pentagonal bipyramidal	$s, p_x, p_y, p_z, d_{xy}, d_{x^2-y^2}, d_{z^2}$	$sp^3 d^3$	$[\text{V}(\text{CN})_7]^{4-}$
7	Monocapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{z^2}$	$sp^3 d^3$	$[\text{NbF}_7]^{2-}$
8	Cubic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, f_{xyz}$	$sp^3 d^3 f$	$[\text{PaF}_8]^{3-}$
8	Dodecahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{xy}, d_{xz}, d_{yz}$	$sp^3 d^4$	$[\text{Mo}(\text{CN})_8]^{4-}$
8	Square antiprismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$	$sp^3 d^4$	$[\text{TaF}_8]^{3-}$
9	Tricapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{z^2}, d_{x^2-y^2}$	$sp^3 d^5$	$[\text{ReH}_9]^{2-}$

Teoría de campo cristalino TCC

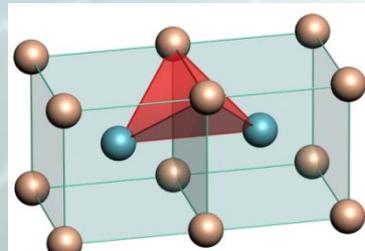
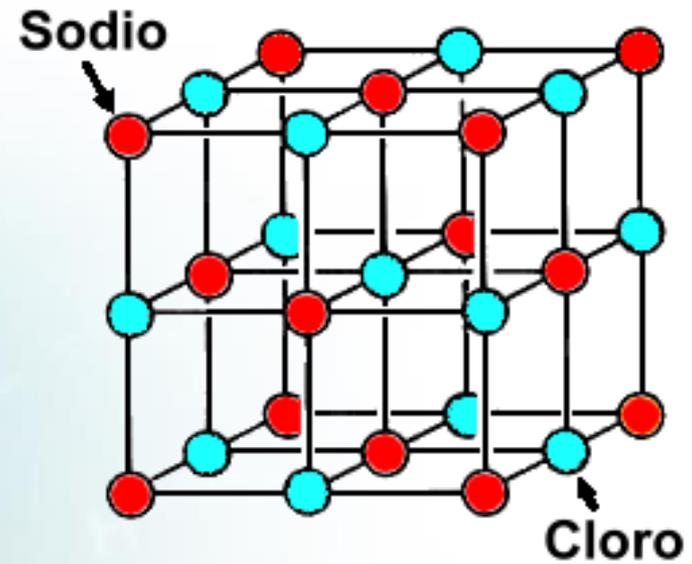
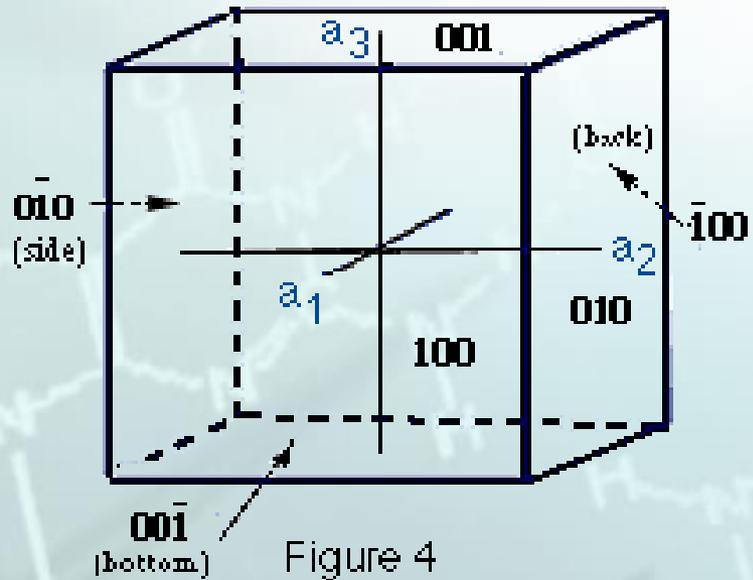
La idea principal es simple:

“Que le pasan a los orbitales atómicos de un elemento central cuando otras especies interaccionan con este átomo en una dirección preferente”

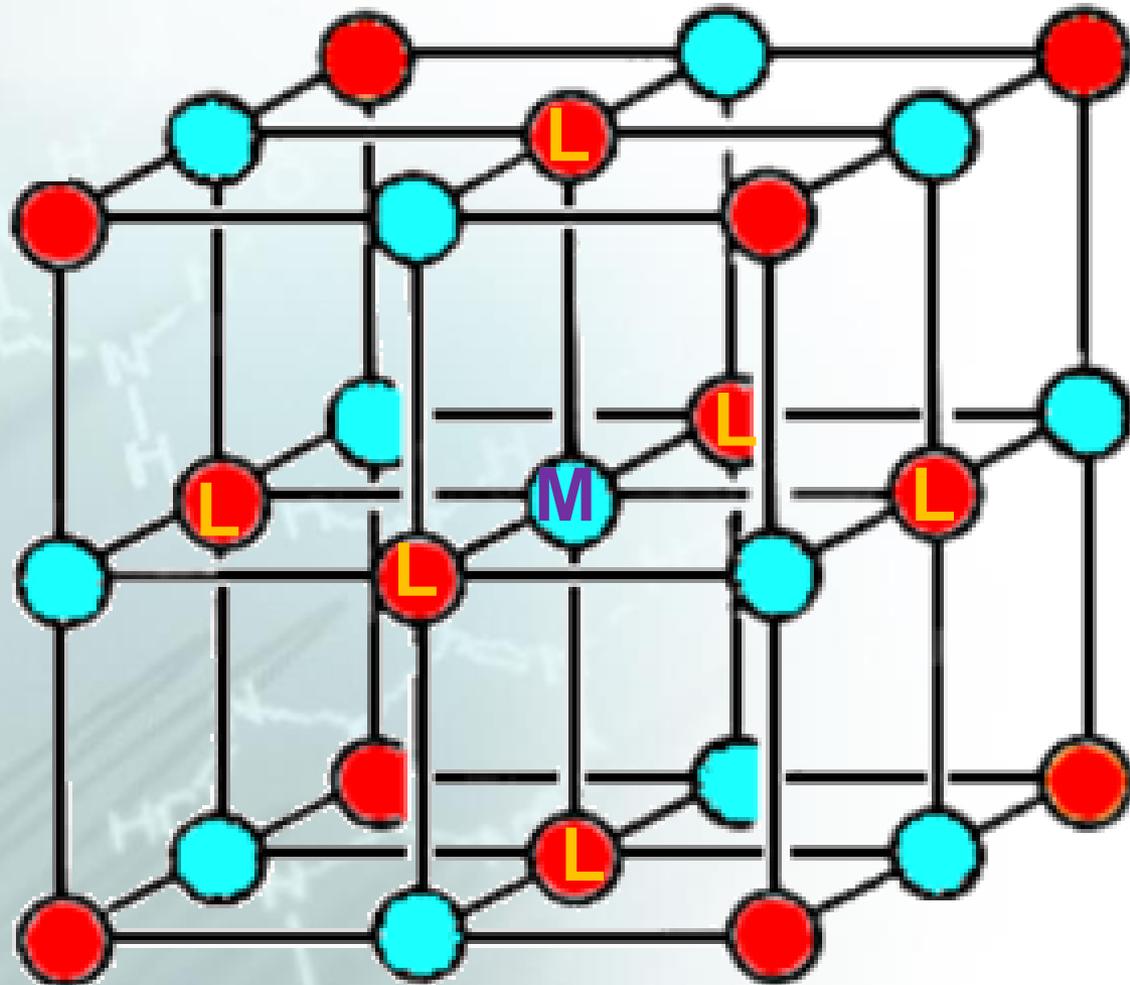


John Hasbrouck van Vleck en 1930

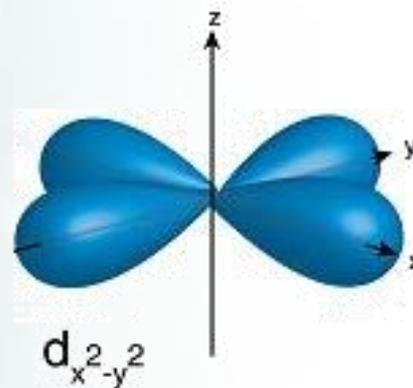
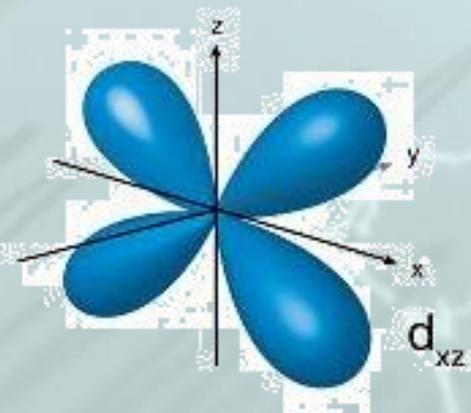
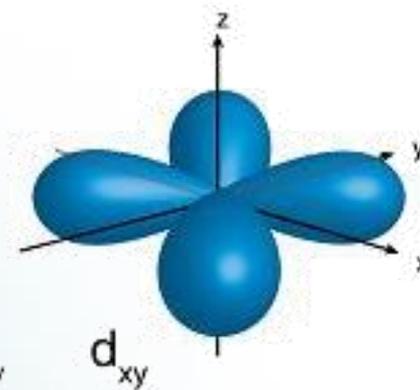
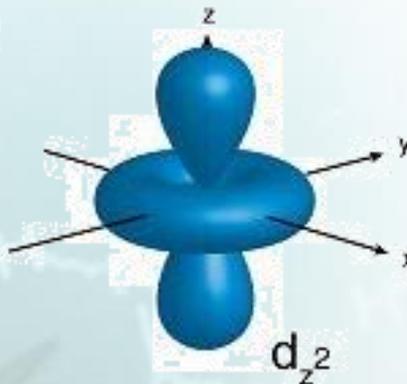
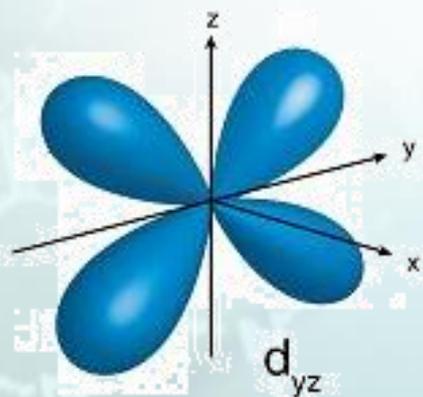
TCC



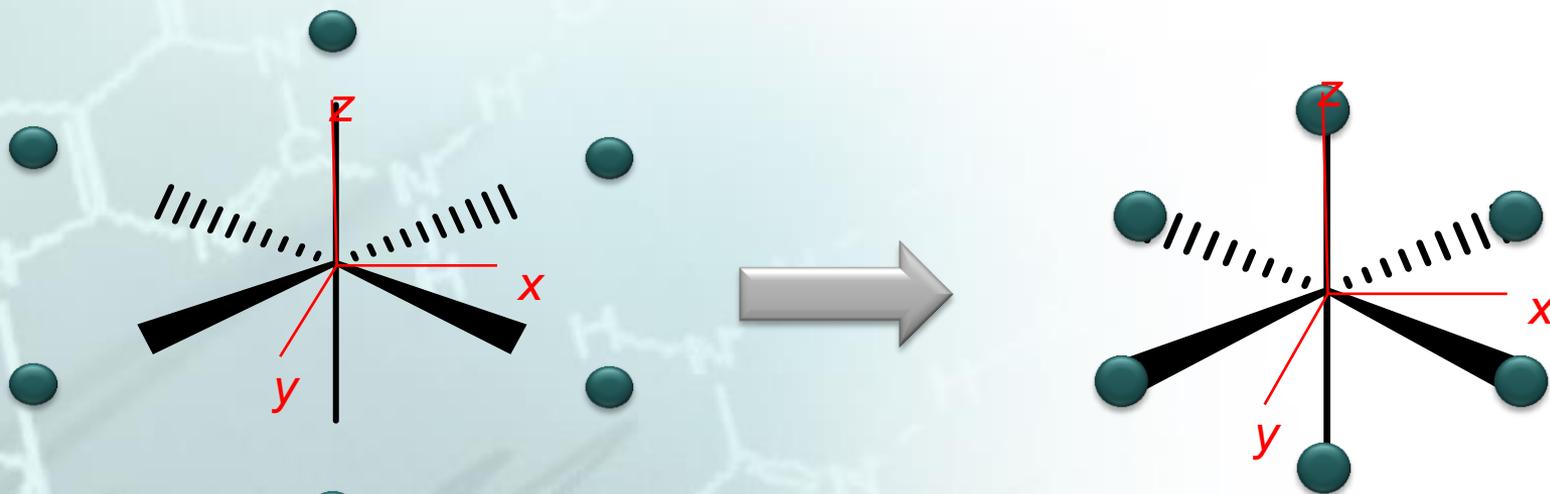
Ahora pasamos de sólidos a CC



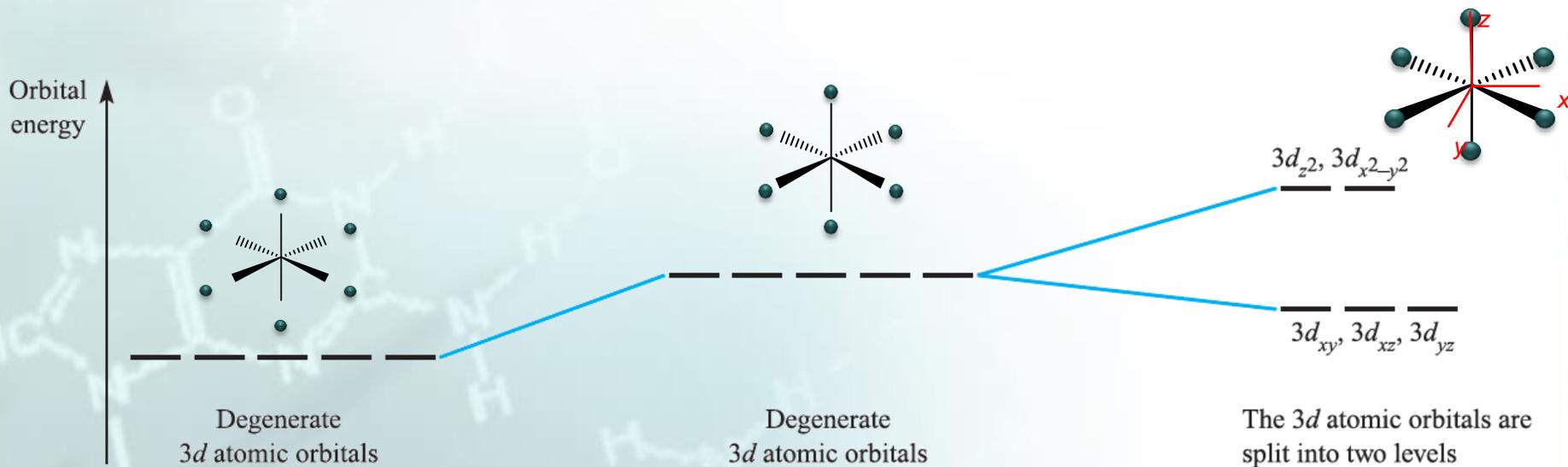
Como se orientan los orbitales «d»



Como entran



TCC



Degenerate
3d atomic orbitals

Degenerate
3d atomic orbitals

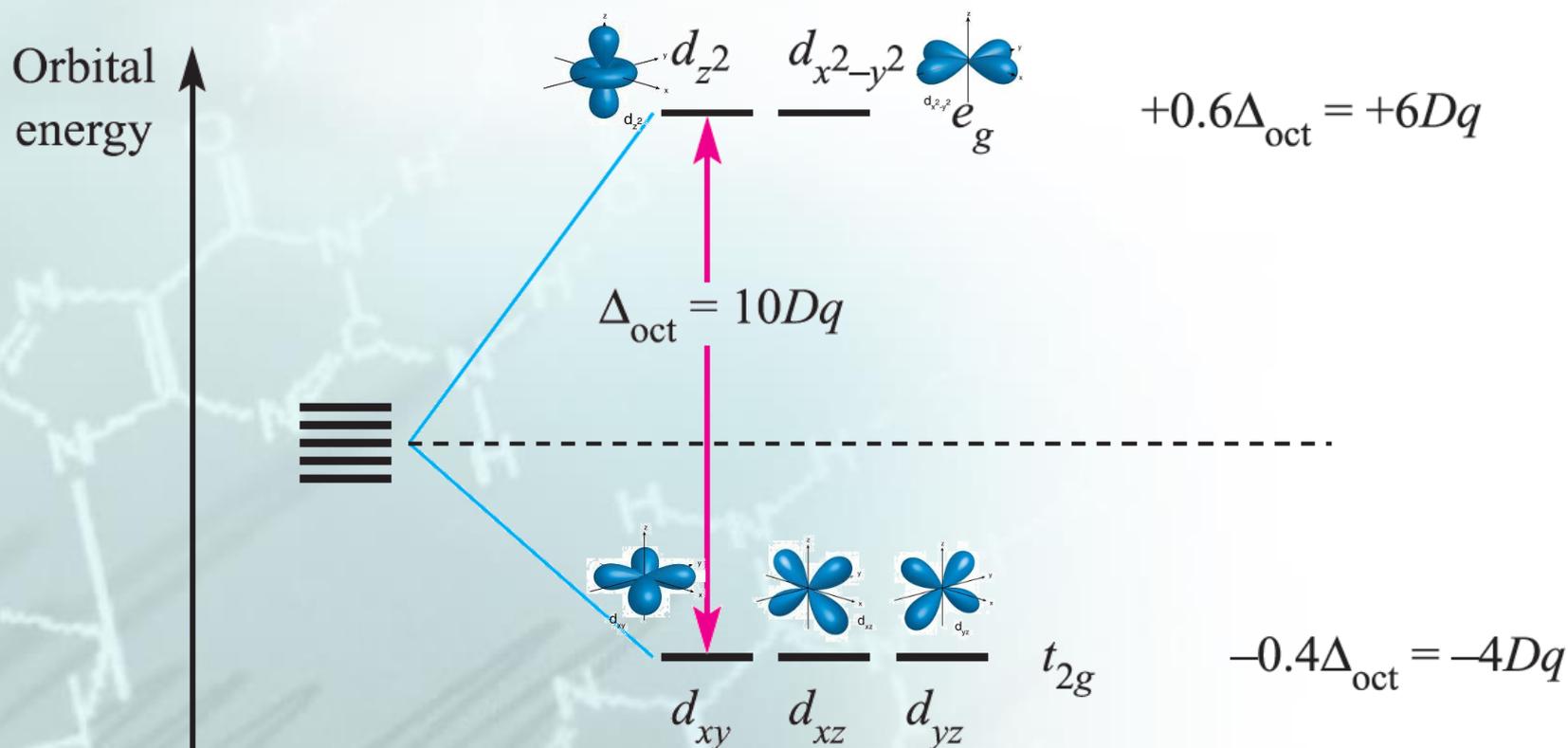
The 3d atomic orbitals are
split into two levels

Metal aislado

**Se acercan
los ligantes**

**Ya se nota
cuantos son y
de donde
vienen**

TCC



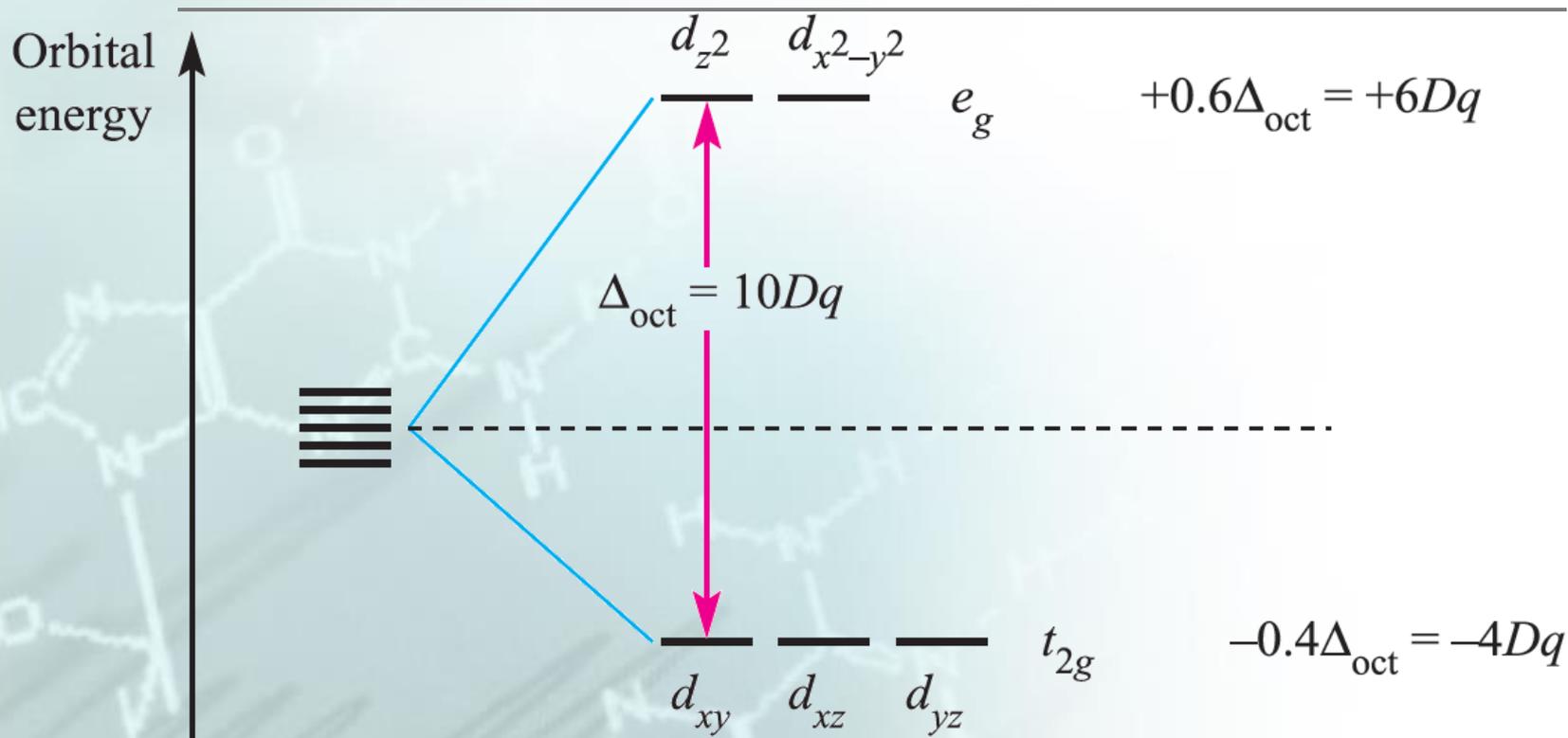
$\text{I}^- < \text{Br}^- < [\text{NCS}]^- < \text{Cl}^- < \text{F}^- < [\text{OH}]^- < [\text{ox}]^{2-}$

$\approx \text{H}_2\text{O} < [\text{NCS}]^- < \text{NH}_3 < \text{en} < \text{bpy} < \text{phen} < [\text{CN}]^- \approx \text{CO}$

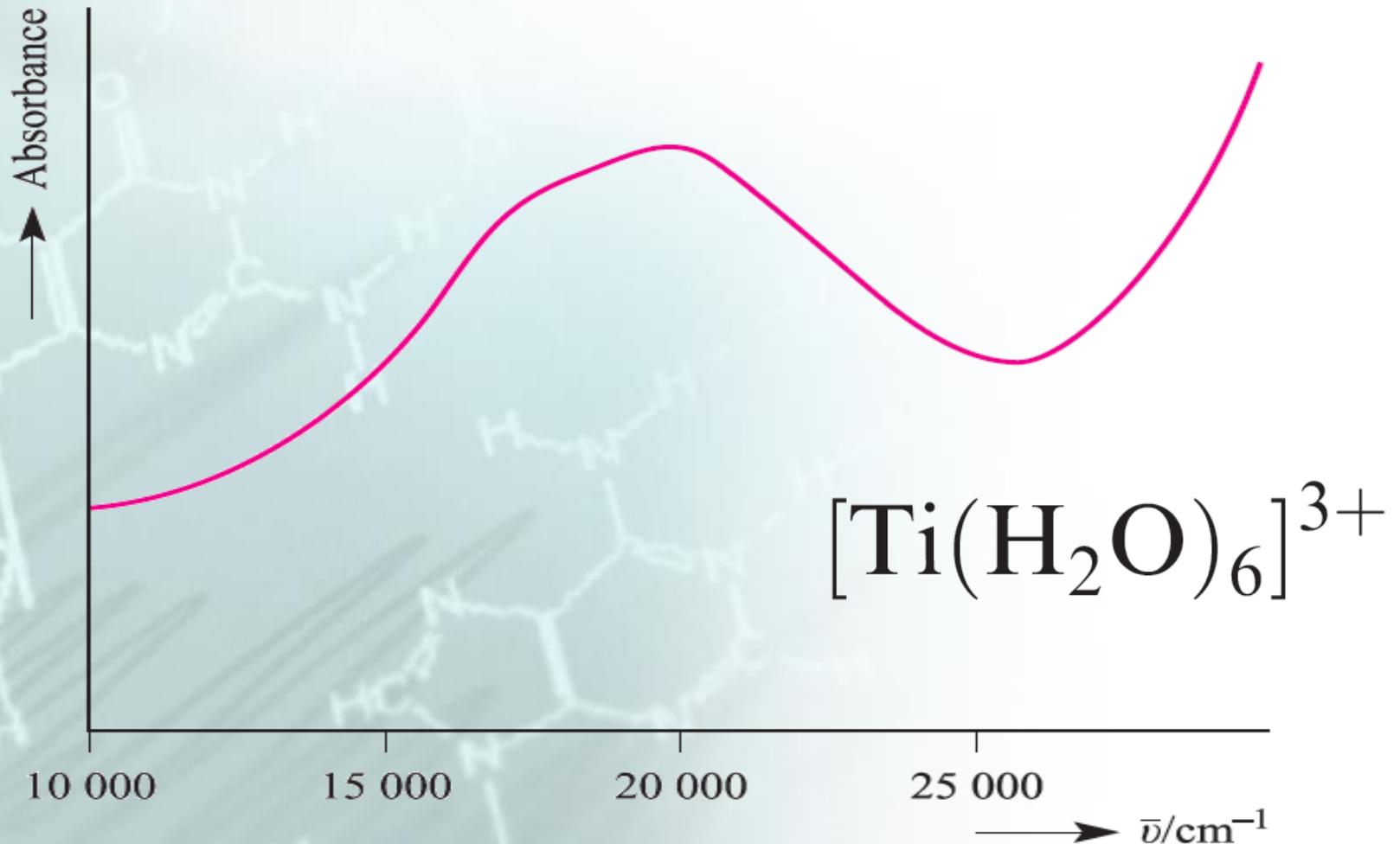
weak field ligands \longrightarrow strong field ligands

increasing Δ_{oct}

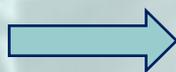
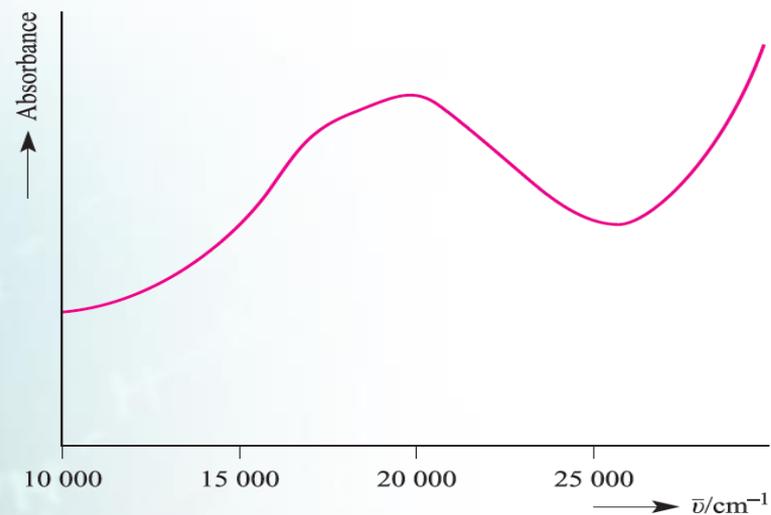
Energía de estabilización del campo cristalino



¿Como sacamos la energía?



El espectro

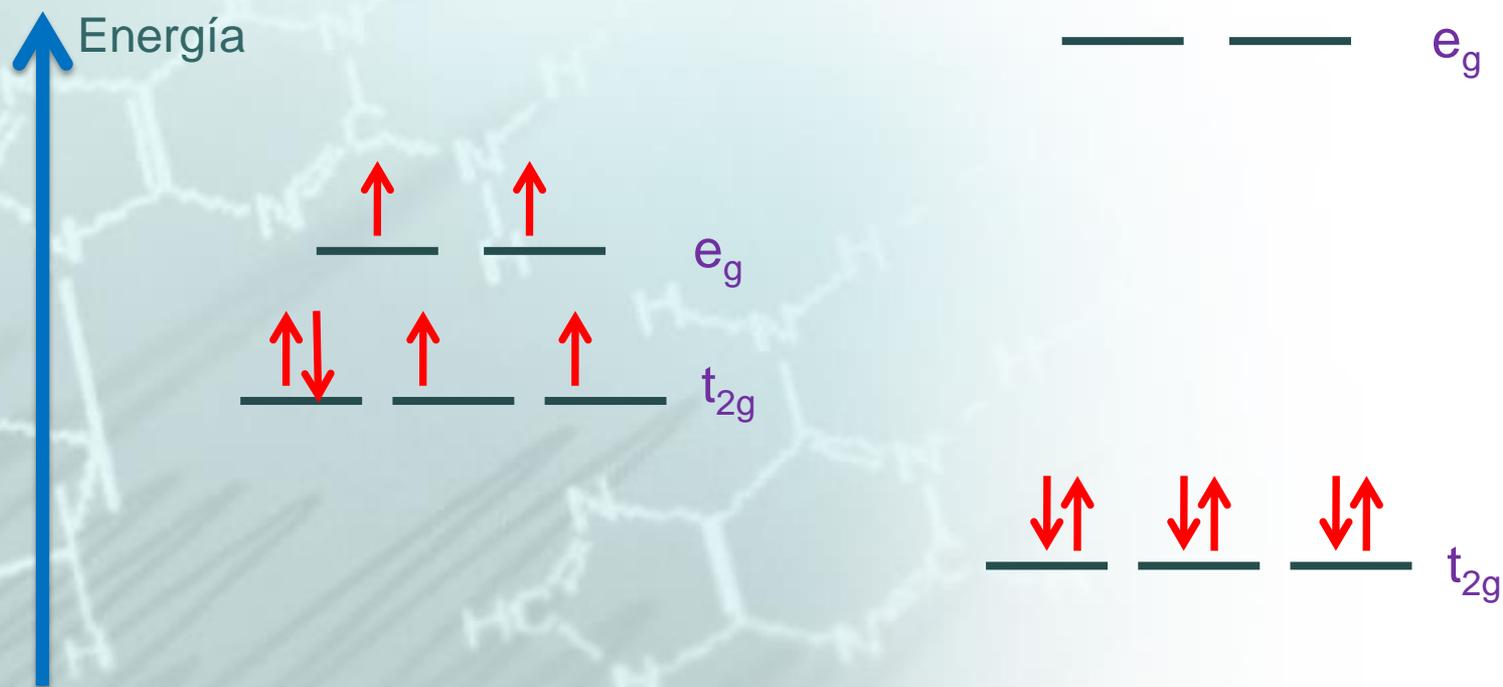


Energía de estabilización del campo cristalino

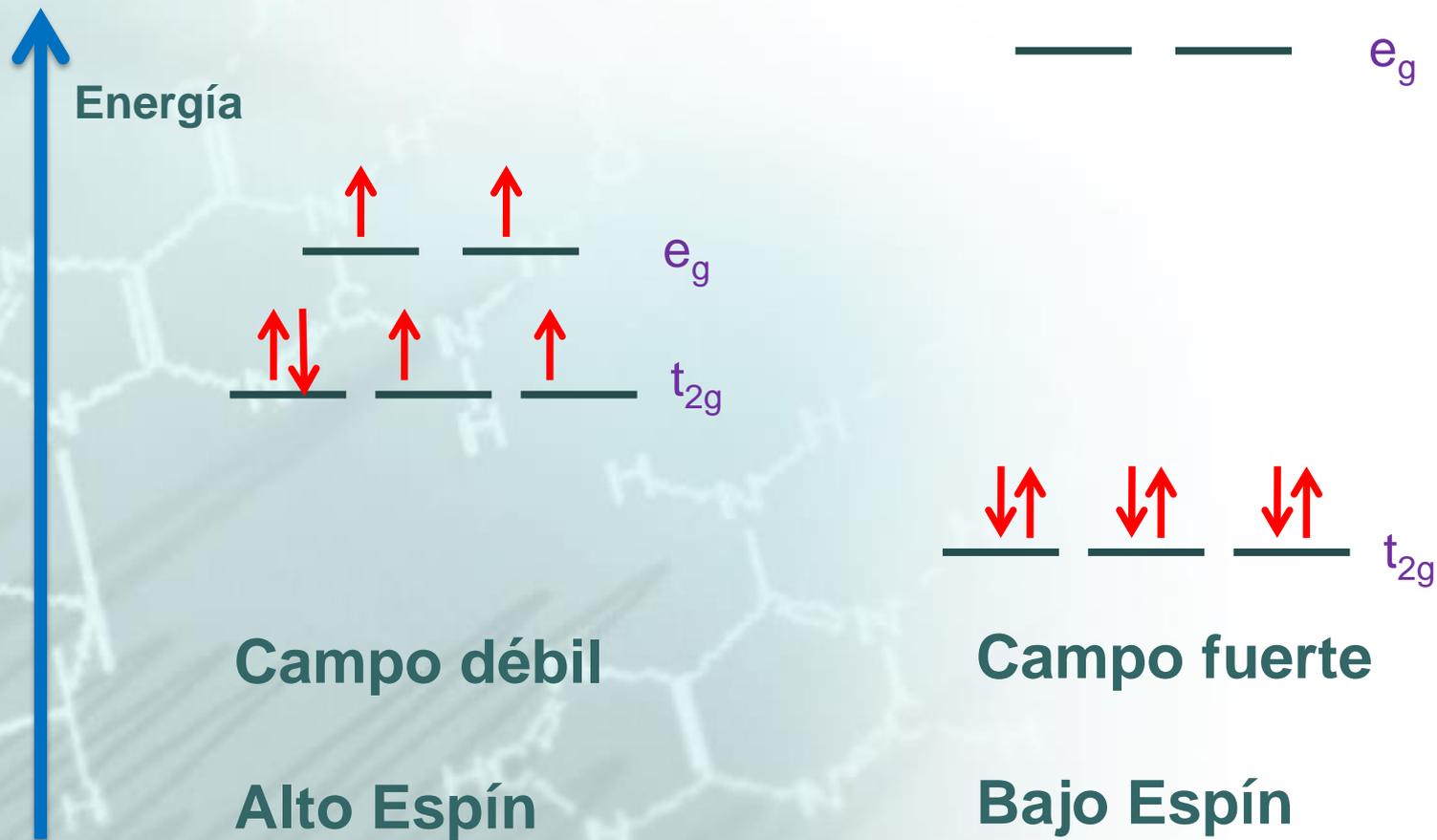
Complex	Δ / cm^{-1}	Complex	Δ / cm^{-1}
$[\text{TiF}_6]^{3-}$	17 000	$[\text{Fe}(\text{ox})_3]^{3-}$	14 100
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	20 300	$[\text{Fe}(\text{CN})_6]^{3-}$	35 000
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	17 850	$[\text{Fe}(\text{CN})_6]^{4-}$	33 800
$[\text{V}(\text{H}_2\text{O})_6]^{2+}$	12 400	$[\text{CoF}_6]^{3-}$	13 100
$[\text{CrF}_6]^{3-}$	15 000	$[\text{Co}(\text{NH}_3)_6]^{3+}$	22 900
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	17 400	$[\text{Co}(\text{NH}_3)_6]^{2+}$	10 200
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	14 100	$[\text{Co}(\text{en})_3]^{3+}$	24 000
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	21 600	$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	18 200
$[\text{Cr}(\text{CN})_6]^{3-}$	26 600	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	9 300
$[\text{MnF}_6]^{2-}$	21 800	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	8 500
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	13 700	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	10 800
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	9 400	$[\text{Ni}(\text{en})_3]^{2+}$	11 500

Ahora ya podemos empezar a llenar

El caso Fe^{2+} octaédrico



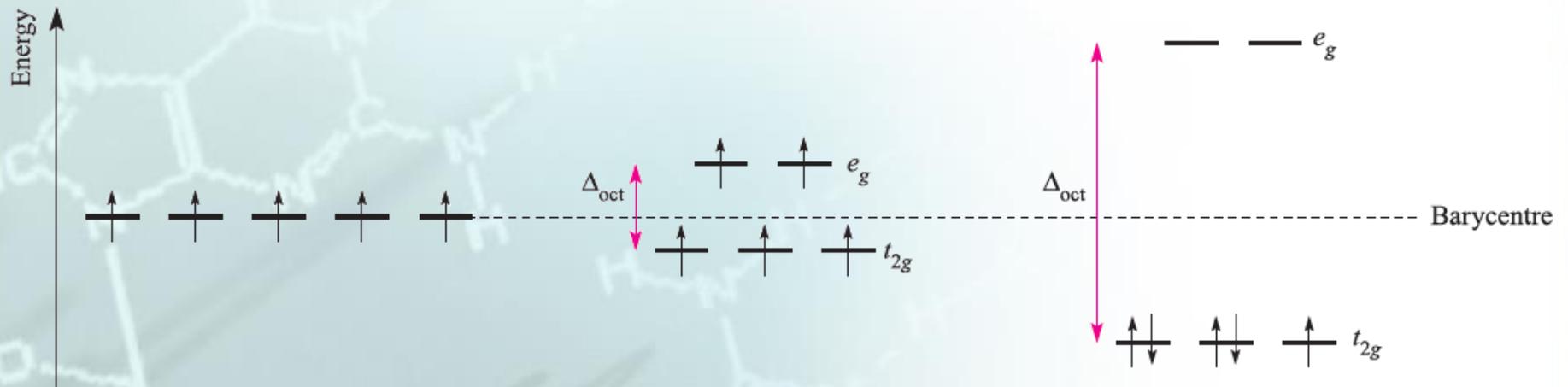
TCC



TCC

d^n	High-spin = weak field		Low-spin = strong field	
	Electronic configuration	CFSE	Electronic configuration	CFSE
d^1	$t_{2g}^1 e_g^0$	$-0.4\Delta_{\text{oct}}$		
d^2	$t_{2g}^2 e_g^0$	$-0.8\Delta_{\text{oct}}$		
d^3	$t_{2g}^3 e_g^0$	$-1.2\Delta_{\text{oct}}$		
d^4	$t_{2g}^3 e_g^1$	$-0.6\Delta_{\text{oct}}$	$t_{2g}^4 e_g^0$	$-1.6\Delta_{\text{oct}} + P$
d^5	$t_{2g}^3 e_g^2$	0	$t_{2g}^5 e_g^0$	$-2.0\Delta_{\text{oct}} + 2P$
d^6	$t_{2g}^4 e_g^2$	$-0.4\Delta_{\text{oct}}$	$t_{2g}^6 e_g^0$	$-2.4\Delta_{\text{oct}} + 2P$
d^7	$t_{2g}^5 e_g^2$	$-0.8\Delta_{\text{oct}}$	$t_{2g}^6 e_g^1$	$-1.8\Delta_{\text{oct}} + P$
d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_{\text{oct}}$		
d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_{\text{oct}}$		
d^{10}	$t_{2g}^6 e_g^4$	0		

TCC



Si ahora son cuatro ligantes y es tetraédrico el complejo



Y los cuadrados

