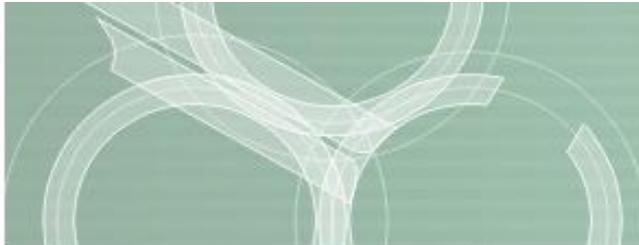




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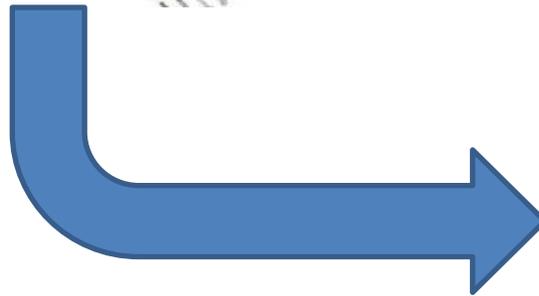
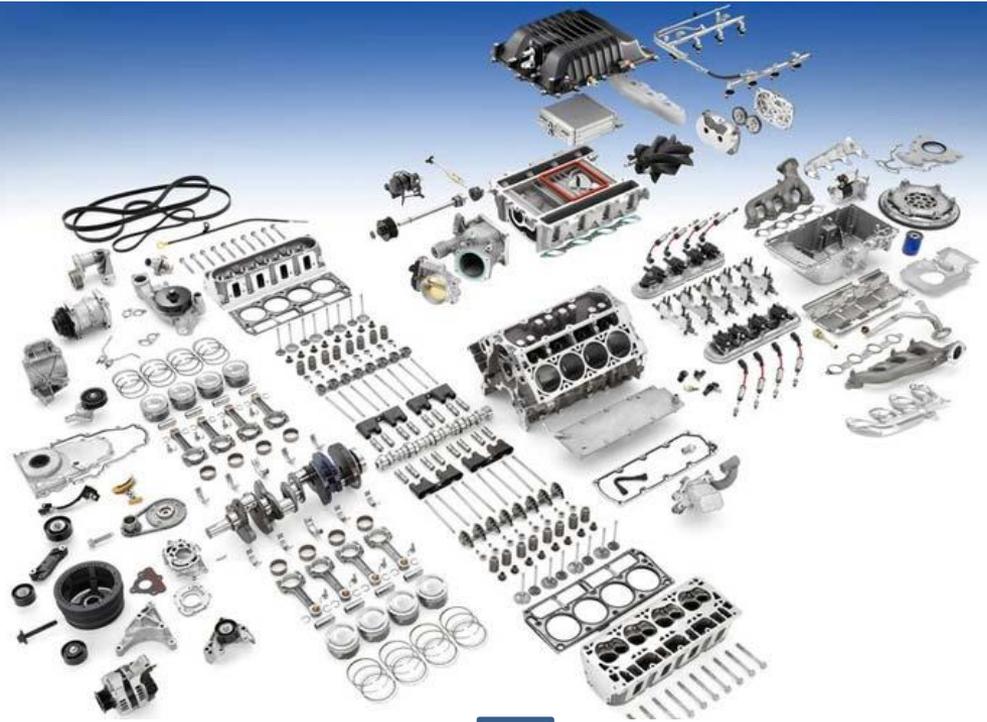


# ***Aula 06 e 07 – Teoria da ligação de valência e Teoria do campo cristalino***

**Este conjunto de slides foi usado nas aulas 06 e 07**

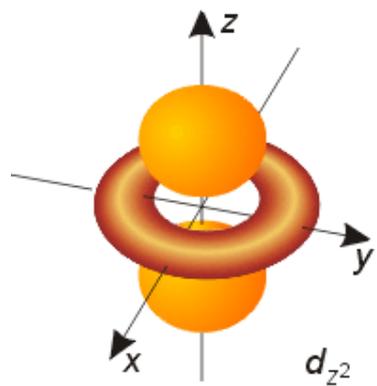
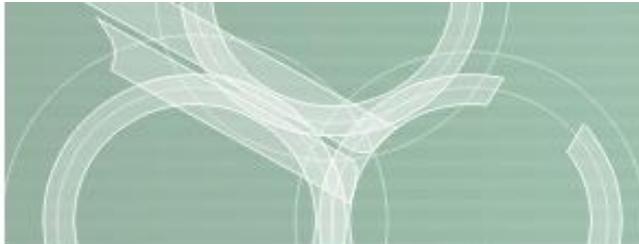


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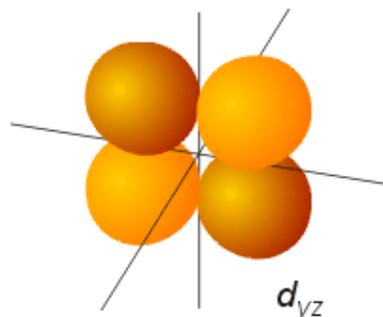




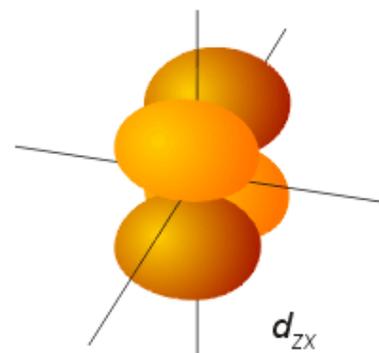
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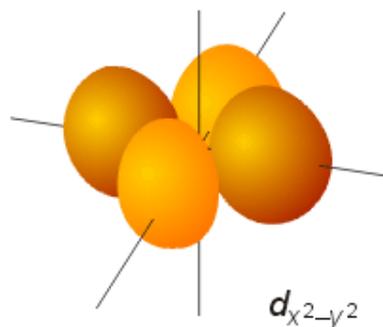
$d_{z^2}$



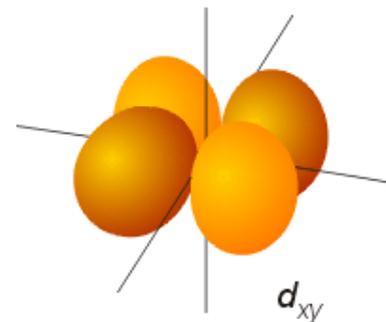
$d_{yz}$



$d_{zx}$



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



$d_{xy}$



11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn
55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb
87	88		104	105	106	107	108	109	110	111	112		



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# Teoria de ligação de valência

- Reação ácido-base de Lewis
- Regra do octeto
  - Compostos de coordenação = 18 e<sup>-</sup> na camada de valência
- Número atômico efetivo = e<sup>-</sup><sub>metal</sub> + e<sup>-</sup><sub>compartilhados ligante</sub>
  - [Fe(CN)<sub>6</sub>]<sup>4-</sup> (Z<sub>Fe</sub> = 26)
- Hibridização
  - Combinação linear do orbitais atômicos puros de maneira a formar novos orbitais híbridos

NC	Hibridização	Geometria	Exemplos
6	d <sup>2</sup> sp <sup>3</sup>	Oh	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> , [PtCl <sub>6</sub> ] <sup>2-</sup>
4	sp <sup>3</sup>	Td	[Ni(CO) <sub>4</sub> ] <sup>2+</sup> , MnO <sub>4</sub> <sup>-</sup> , [Zn(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>
4	dsp <sup>2</sup>	Quadrado planar	[Ni(CN) <sub>4</sub> ] <sup>2-</sup> [Pt(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>



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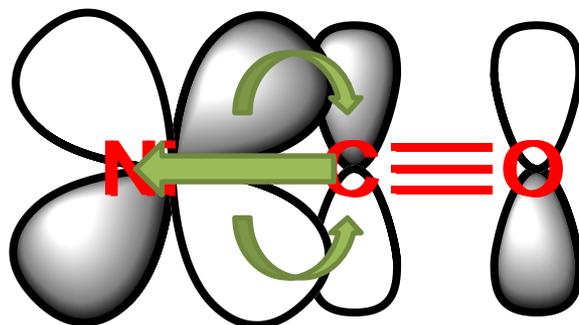
# Teoria de ligação de valência

- Estabilização de estado de oxidação e ligação  $\pi$

**Regra Geral:** Coordenação com átomos de menor eletronegatividade que o oxigênio  $\rightarrow$  estabilização no estado de oxidação imediatamente mais alto que o íon água mais estável, desconsiderando outros fatores como a ligação  $\pi$ .

Compostos de maior estado de oxidação são fortes oxidantes e são estáveis apenas para os ligantes mais eletronegativos; **F e O**

**Exceções: Compostos com CO, CN<sup>-</sup> e 1,10-fenantrolina**



**Retrodoação**



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# Teoria de ligação de valência

- Susceptibilidade magnética

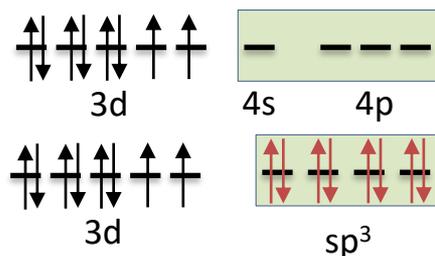
- Usada para determinar o número de elétrons desemparelhados em complexos

24	25	26	27	28
Cr	Mn	Fe	Co	Ni

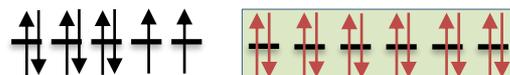
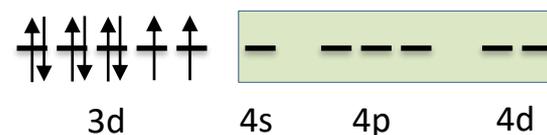
Expressão de Landé

$$\mu_M = \sqrt{n(n + 2)}$$

Compostos de Ni<sup>2+</sup> (Td)



Compostos de Ni<sup>2+</sup> (Oh)

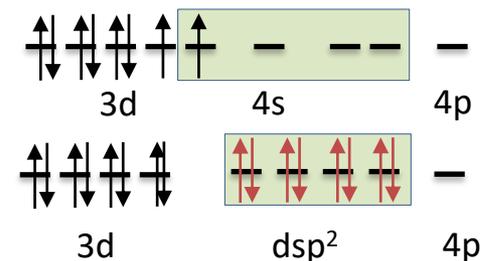


[Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> Oh μ<sub>M</sub> = 2,82 Bohr magnetons

Compostos de Ni(II):

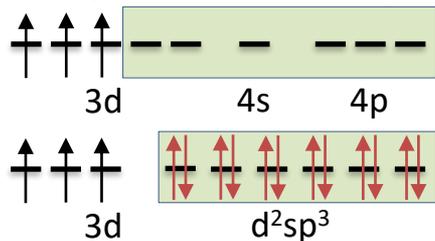
n = 2 ∴ μ<sub>M</sub> = 2,82 Bohr magnetons

Compostos de Ni<sup>2+</sup> (D<sub>4h</sub>)

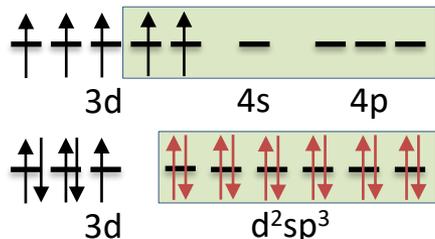


[Ni(CN)<sub>4</sub>]<sup>2-</sup> D<sub>4h</sub> μ<sub>M</sub> ≈ 0 Bohr magnetons

Compostos de Cr<sup>3+</sup> (Oh)



Compostos de Fe<sup>3+</sup> (Oh)





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# Teoria de ligação de valência

- Problemas:

Ni(II): Ni + H<sub>2</sub>O e Ni + NH<sub>3</sub> – Complexos Oh paramagnéticos

Ni + CN<sup>-</sup> – D<sub>4h</sub> – Diamagnético

Como explicar a diferença no comportamento?

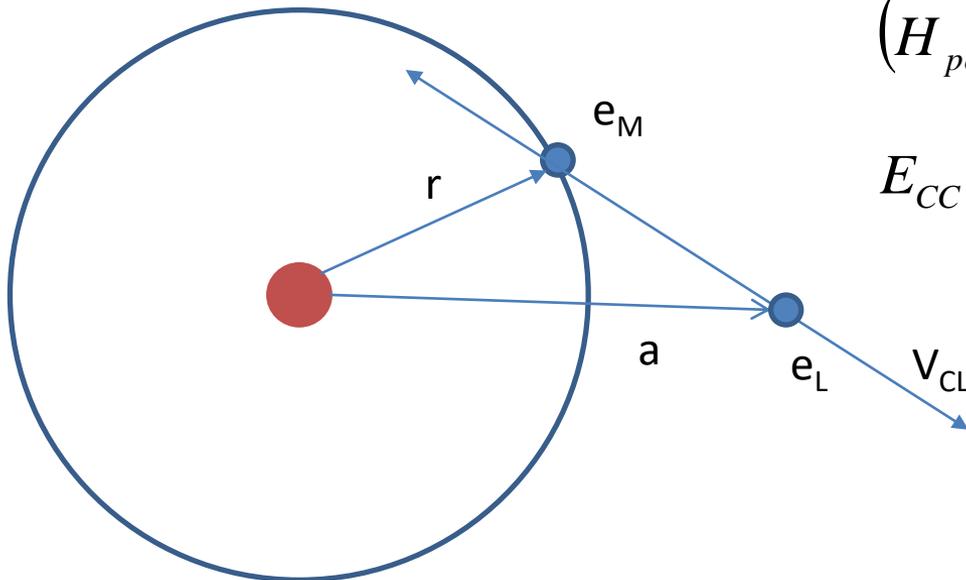
**Teoria FALHA**



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# Teoria de campo cristalino

- Teoria do campo cristalino (Bethe 1929)
  - Considera que apenas elétrons do metal ocupam os orbitais d
  - Modelo puramente eletrostático



$$V_{CC} = Z_L e^2 \left( \frac{r^4}{a^5} \right)$$

$$(H_{poli} + V_{CC})\psi = E\psi$$

$$E_{CC} = \langle \psi | V_{CC} | \psi \rangle = Dq \therefore Dq \propto \frac{r^4}{a^5}$$

**Dq = medida quantitativa da repulsão  $e^-_{\text{Ligante}} - e^-_{\text{Metal}}$**



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# Teoria de campo cristalino

- Considerações sobre Dq

$$E_{CC} = \langle \psi | V_{CC} | \psi \rangle = Dq \therefore Dq \propto \frac{r^4}{a^5}$$

**Dq = medida quantitativa da repulsão e<sup>-</sup><sub>Ligante</sub> - e<sup>-</sup><sub>Metal</sub>**

- Cresce com r<sup>4</sup>
  - Dq 5d > Dq 4d > Dq 3d

11	12											13	14
Na	Mg											Al	Si
19	20	21	22	23	24	25	26	27	28	29	30	31	32
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
37	38	39	40	41	42	43	44	45	46	47	48	49	50
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn
55	56		72	73	74	75	76	77	78	79	80	81	82
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb
87	88		104	105	106	107	108	109	110	111	112		

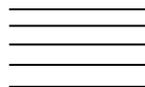
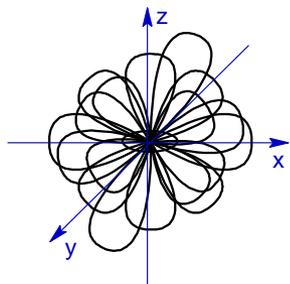
Aumenta r

- Aumenta com a contração da distância M-L (a<sup>5</sup>)



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# Teoria de campo cristalino

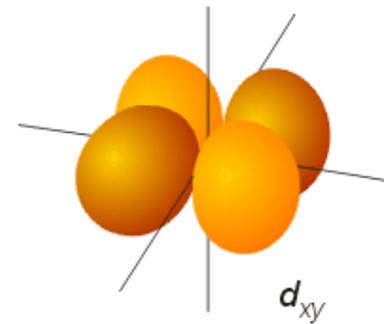
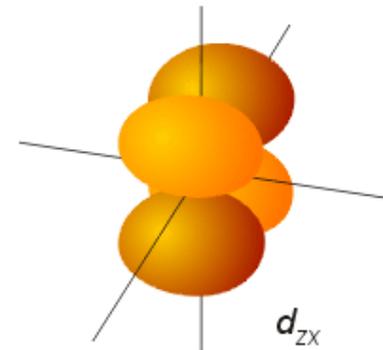
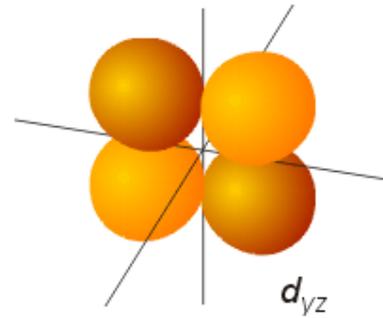
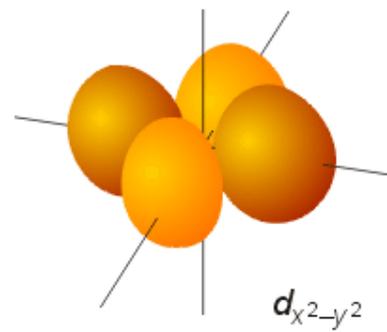
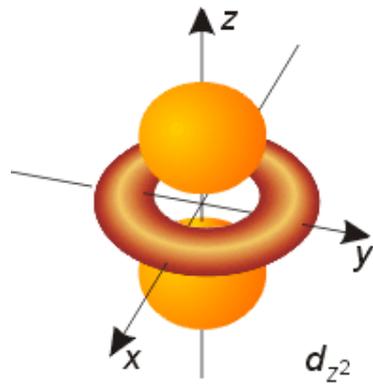
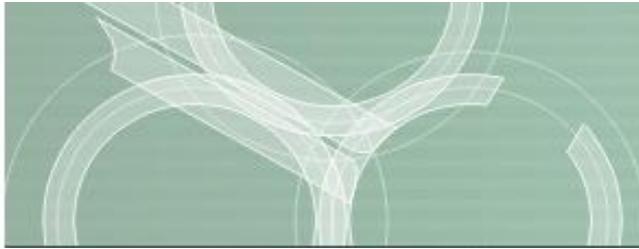


Complexo octaédrico





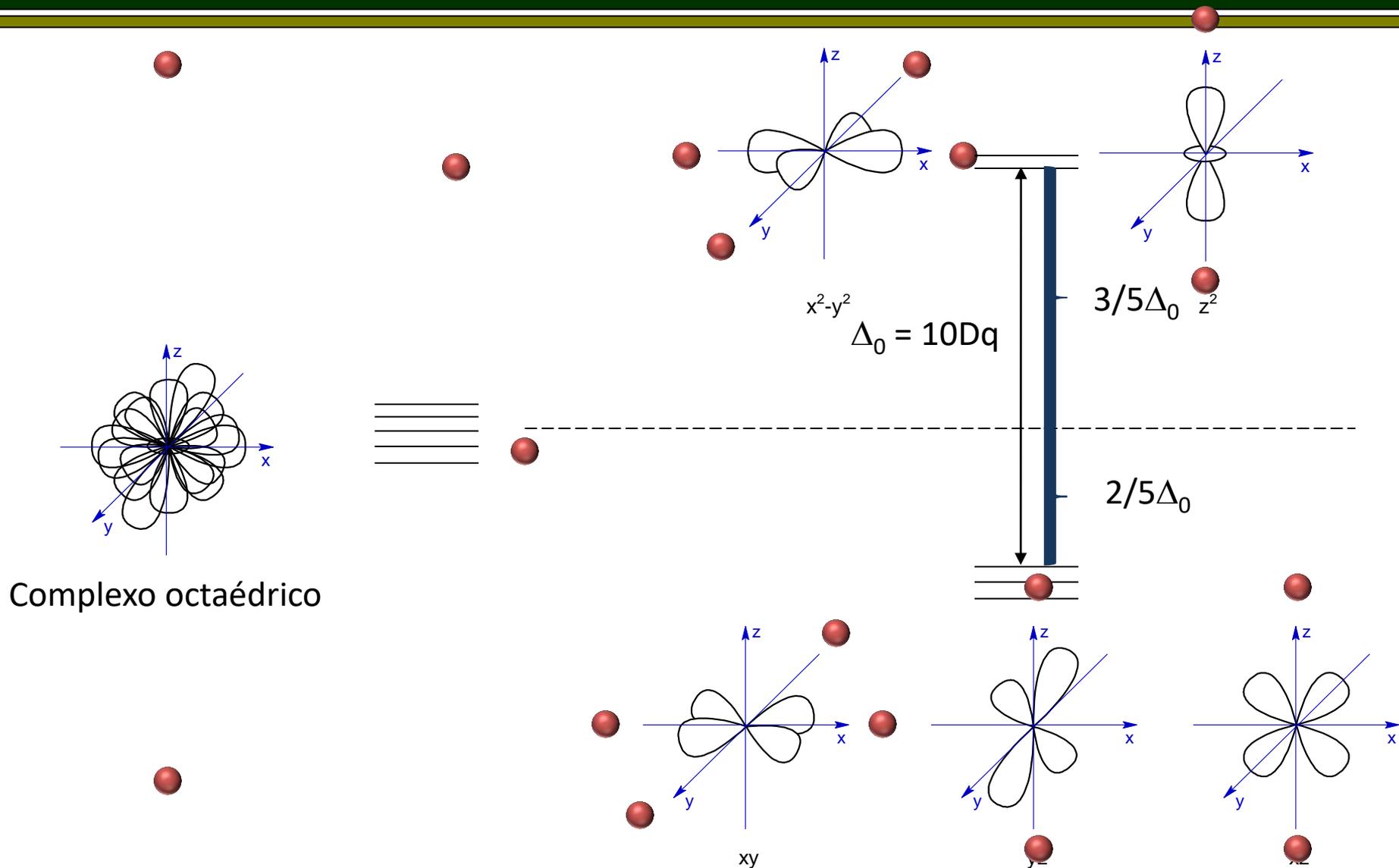
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# Teoria de campo cristalino

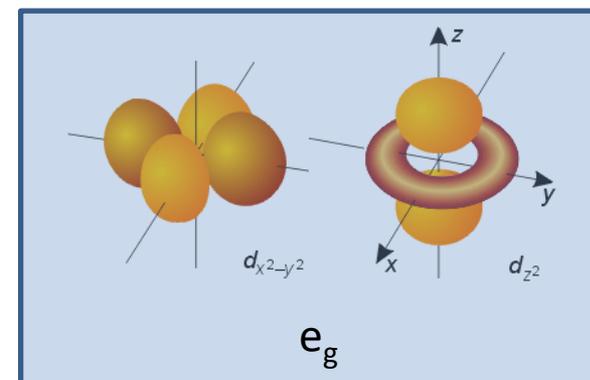
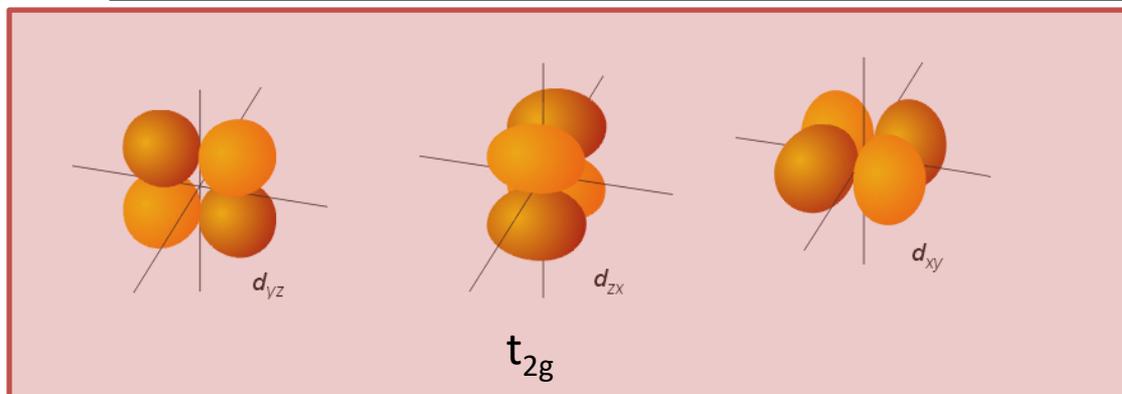




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# Utilizando a tabela de caracteres

$O_h$ ( $m3m$ )	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ( $= C_4^2$ )	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
$A_{2g}$	1	1	-1	-1	1	1	-1	1	1	-1	
$E_g$	2	-1	0	0	2	2	0	-1	2	0	$(2z^2 - x^2 - y^2, \sqrt{3}(x^2 - y^2))$
$T_{1g}$	3	0	-1	1	-1	3	1	0	-1	-1	$(R_x, R_y, R_z)$
$T_{2g}$	3	0	1	-1	-1	3	-1	0	-1	1	$(xy, xz, yz)$
$A_{1u}$	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	$(x, y, z)$
$T_{2u}$	3	0	1	-1	-1	-3	1	0	1	-1	





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# Complexos Oh

• Caso  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

$t_{2g}^1 e_g^0$

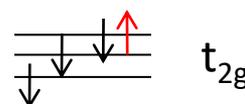


- $t_{2g}^1 e_g^0 = -0,4 \Delta_0 = -4 \text{ Dq}$
- $t_{2g}^2 e_g^0 = -0,8 \Delta_0 = -8 \text{ Dq}$
- $t_{2g}^3 e_g^0 = -1,2 \Delta_0 = -12 \text{ Dq}$

• Adição de mais um elétron???

– Energia de emparelhamento (P)

- Se  $\Delta_0 < P$ ; spin alto (não ocorre emparelhamento)
- Se  $\Delta_0 > P$ ; spin baixo (ocorre emparelhamento)



$d^n$	Weak field			Strong field		
	Configuration	Unpaired electrons	CFSE	Configuration	Unpaired electrons	CFSE
$d^1$	$t_{2g}^1$	1	$0.4\Delta_0$	$t_{2g}^1$	1	$0.4\Delta_0$
$d^2$	$t_{2g}^2$	2	$0.8\Delta_0$	$t_{2g}^2$	2	$0.8\Delta_0$
$d^3$	$t_{2g}^3$	3	$1.2\Delta_0$	$t_{2g}^3$	3	$1.2\Delta_0$
$d^4$	$t_{2g}^3 e_g^1$	4	$0.6\Delta_0$	$t_{2g}^4$	2	$1.6\Delta_0$
$d^5$	$t_{2g}^3 e_g^2$	5	$0.0\Delta_0$	$t_{2g}^5$	1	$2.0\Delta_0$
$d^6$	$t_{2g}^4 e_g^2$	4	$0.4\Delta_0$	$t_{2g}^6$	0	$2.4\Delta_0$
$d^7$	$t_{2g}^5 e_g^2$	3	$0.8\Delta_0$	$t_{2g}^6 e_g^1$	1	$1.8\Delta_0$
$d^8$	$t_{2g}^6 e_g^2$	2	$1.2\Delta_0$	$t_{2g}^6 e_g^2$	2	$1.2\Delta_0$
$d^9$	$t_{2g}^6 e_g^3$	1	$0.6\Delta_0$	$t_{2g}^6 e_g^3$	1	$0.6\Delta_0$
$d^{10}$	$t_{2g}^6 e_g^4$	0	$0.0\Delta_0$	$t_{2g}^6 e_g^4$	0	$0.0\Delta_0$

<sup>a</sup> This table is somewhat simplified because pairing energies and electron-electron effects have been neglected.



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# Teoria do campo ligante

- Teoria do campo ligante
  - Basicamente a mesma abordagem da teoria de campo cristalino, mas com **interações covalentes sendo consideradas quando necessário.**

• Caso  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

$t_{2g}^1 e_g^0$



•  $t_{2g}^1 e_g^0 = -0,4 \Delta_0$

•  $t_{2g}^2 e_g^0 = -0,8 \Delta_0$

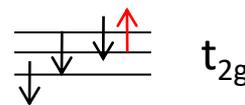
•  $t_{2g}^3 e_g^0 = -1,2 \Delta_0$

• **Adição de mais um elétron???**

- Energia de emparelhamento (P)
- Se  $\Delta_0 < P$ ; campo fraco ou spin alto
- Se  $\Delta_0 > P$ ; campo forte ou spin baixo

$d^n$	Weak field			Strong field		
	Configuration	Unpaired electrons	CFSE	Configuration	Unpaired electrons	CFSE
$d^1$	$t_{2g}^1$	1	$0.4\Delta_0$	$t_{2g}^1$	1	$0.4\Delta_0$
$d^2$	$t_{2g}^2$	2	$0.8\Delta_0$	$t_{2g}^2$	2	$0.8\Delta_0$
$d^3$	$t_{2g}^3$	3	$1.2\Delta_0$	$t_{2g}^3$	3	$1.2\Delta_0$
$d^4$	$t_{2g}^3 e_g^1$	4	$0.6\Delta_0$	$t_{2g}^4$	2	$1.6\Delta_0$
$d^5$	$t_{2g}^3 e_g^2$	5	$0.0\Delta_0$	$t_{2g}^5$	1	$2.0\Delta_0$
$d^6$	$t_{2g}^4 e_g^2$	4	$0.4\Delta_0$	$t_{2g}^6$	0	$2.4\Delta_0$
$d^7$	$t_{2g}^5 e_g^2$	3	$0.8\Delta_0$	$t_{2g}^6 e_g^1$	1	$1.8\Delta_0$
$d^8$	$t_{2g}^6 e_g^2$	2	$1.2\Delta_0$	$t_{2g}^6 e_g^2$	2	$1.2\Delta_0$
$d^9$	$t_{2g}^6 e_g^3$	1	$0.6\Delta_0$	$t_{2g}^6 e_g^3$	1	$0.6\Delta_0$
$d^{10}$	$t_{2g}^6 e_g^4$	0	$0.0\Delta_0$	$t_{2g}^6 e_g^4$	0	$0.0\Delta_0$

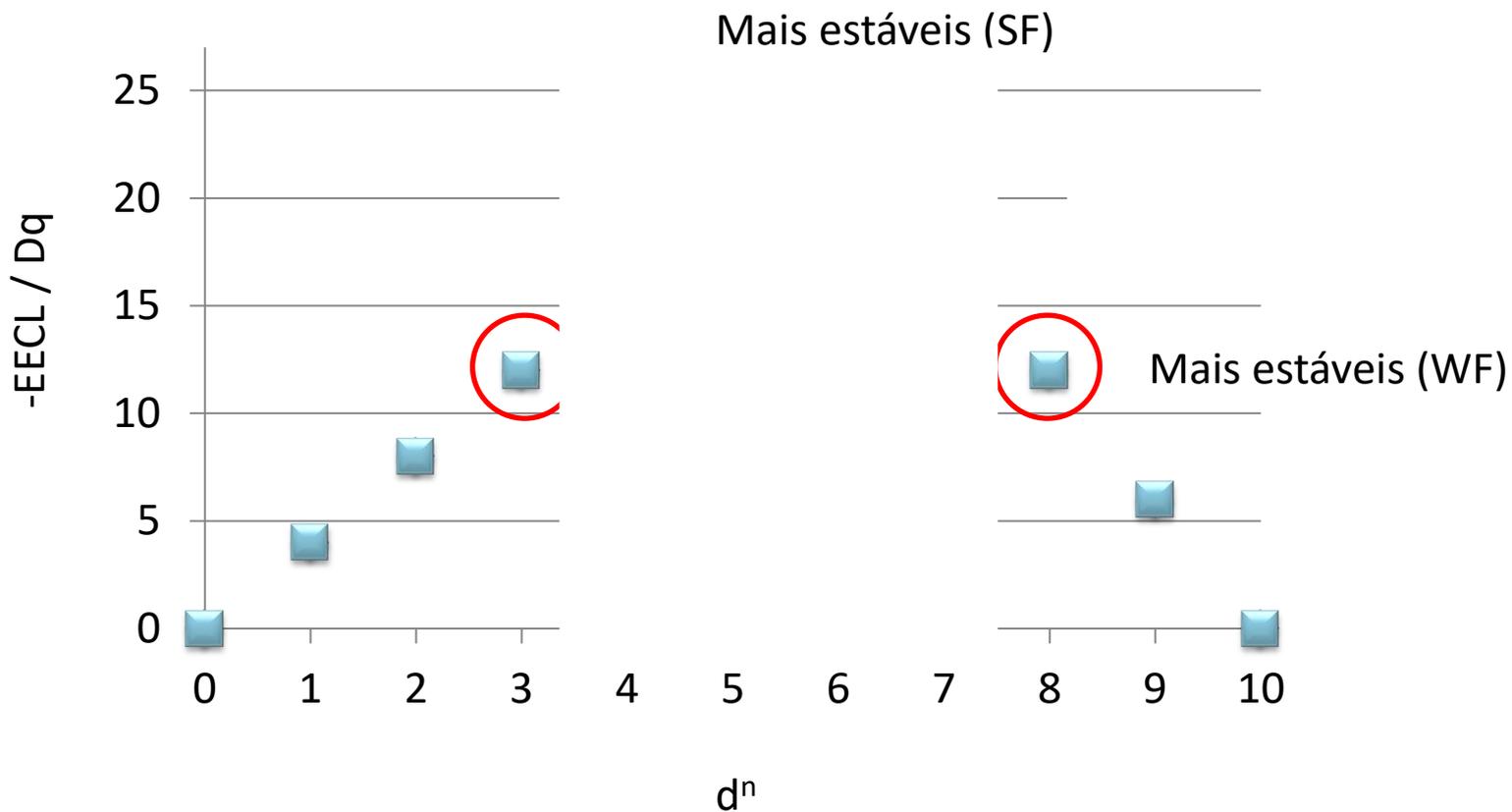
<sup>a</sup> This table is somewhat simplified because pairing energies and electron-electron effects have been neglected.





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# Energia de estabilização de campo ligante (EECL)



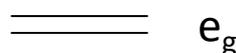
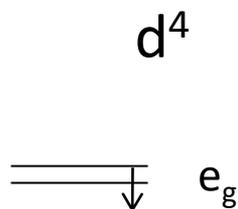


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# Teoria de campo ligante

## Campo forte

Complexos  $d^4$ ,  $d^5$ ,  $d^6$ ,  $d^7$  e  $d^8$



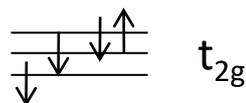
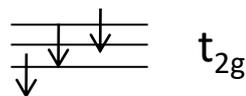
No equilíbrio:

$$6Dq = 16Dq - P$$

$$10Dq = P$$

**Campo fraco:  $10Dq < P$**

**Campo forte:  $10Dq > P$**



$$EECL = 6Dq$$

$$EECL = 16Dq - P$$

$P$  = energia de emparelhamento em função de  $B$



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# Teoria de campo ligante

B = Parâmetro de Racah

Cresce

**B**

	3	4	5	6	7	8	9	10	11	12
21	22	23	24	25	26	27	28	29	30	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
39	40	41	42	43	44	45	46	47	48	
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
*	72	73	74	75	76	77	78	79	80	
	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	

P = energia de emparelhamento em função de B

**Dq**

Cresce

$r \sim \text{cte}; a - \text{diminui}$

a varia menos que r

	3	4	5	6	7	8	9	10	11	12
21	22	23	24	25	26	27	28	29	30	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
39	40	41	42	43	44	45	46	47	48	
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
*	72	73	74	75	76	77	78	79	80	
	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	



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# Teoria de campo ligante

## Dependência de $Dq$ em função do ligante

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  paramagnético  $k_{(\text{H}_2\text{O})} = 10^7 \text{ s}^{-1}$

$[\text{Fe}(\text{CN})_6]^{4-}$  diamagnético  $k_{(\text{CN})} = 10^{-9} \text{ s}^{-1}$

## Série espectroquímica

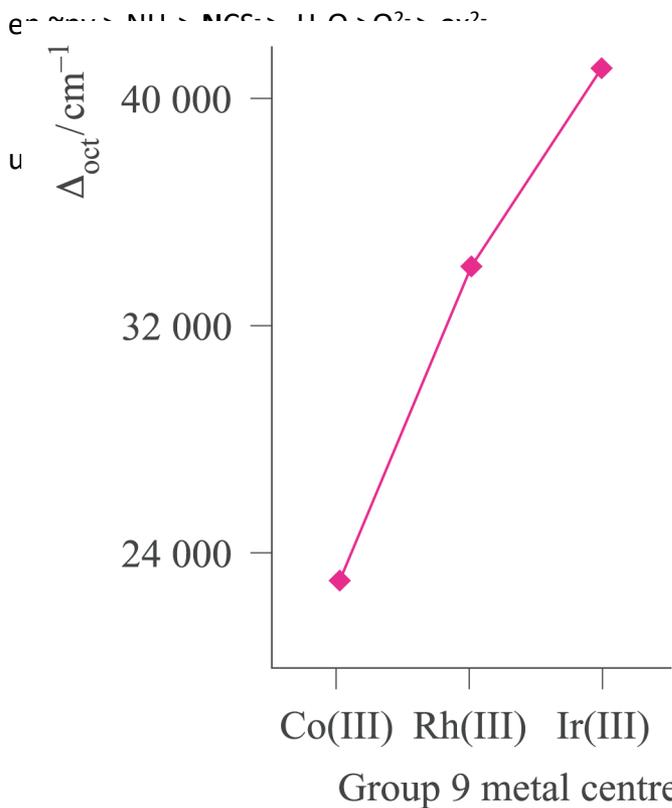
$\text{NO}^+ > \text{CO} > \text{CN}^- > \text{C}_6\text{H}_5^- > \text{CH}_3^- > \text{NO}_2^- > \text{bpy, phen}$  Campo forte

$\text{en} \sim \text{py} > \text{NH}_3 > \text{NCS}^- > \text{H}_2\text{O} > \text{O}^{2-} > \text{ox}^{2-}$  Campo intermediário

$\text{ureia, OH}^- > \text{F}^-, \text{N}_3^- > \text{Cl}^- > \text{SCN}^- > \text{S}^{2-} > \text{Br}^- > \text{I}^-$  Campo fraco



NO<sup>+</sup> > CO > CN<sup>-</sup> > C<sub>6</sub>H<sub>5</sub><sup>-</sup> > CH<sub>3</sub><sup>-</sup> > NO<sub>2</sub><sup>-</sup> > bpy, phen  
 Campo forte



es of  $\Delta_{\text{oct}}$  for some *d*-block metal complexes.

Complex	$\Delta / \text{cm}^{-1}$	Complex	$\Delta / \text{cm}^{-1}$
[TiF <sub>6</sub> ] <sup>3-</sup>	17 000	[Fe(ox) <sub>3</sub> ] <sup>3-</sup>	14 100
[Ti(OH <sub>2</sub> ) <sub>6</sub> ] <sup>3+</sup>	20 300	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	35 000
[V(OH <sub>2</sub> ) <sub>6</sub> ] <sup>3+</sup>	17 850	[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	33 800
[V(OH <sub>2</sub> ) <sub>6</sub> ] <sup>2+</sup>	12 400	[CoF <sub>6</sub> ] <sup>3-</sup>	13 100
[CrF <sub>6</sub> ] <sup>3-</sup>	15 000	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	22 900
[Cr(OH <sub>2</sub> ) <sub>6</sub> ] <sup>3+</sup>	17 400	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	10 200
[Cr(OH <sub>2</sub> ) <sub>6</sub> ] <sup>2+</sup>	14 100	[Co(en) <sub>3</sub> ] <sup>3+</sup>	24 000
[Cr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	21 600	[Co(OH <sub>2</sub> ) <sub>6</sub> ] <sup>3+</sup>	18 200
[Cr(CN) <sub>6</sub> ] <sup>3-</sup>	26 600	[Co(OH <sub>2</sub> ) <sub>6</sub> ] <sup>2+</sup>	9 300
[MnF <sub>6</sub> ] <sup>2-</sup>	21 800	[Ni(OH <sub>2</sub> ) <sub>6</sub> ] <sup>2+</sup>	8 500
[Fe(OH <sub>2</sub> ) <sub>6</sub> ] <sup>3+</sup>	13 700	[Ni(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	10 800
[Fe(OH <sub>2</sub> ) <sub>6</sub> ] <sup>2+</sup>	9 400	[Ni(en) <sub>3</sub> ] <sup>2+</sup>	11 500



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# Teoria de campo ligante

## Efeito da natureza do metal

Metais  $3d^n$ : Existência de campo forte ou fraco, dependendo de L ( $10 Dq \sim P$ )

Metais  $4d^n$  e  $5d^n$ :

$$10 Dq \gg P$$

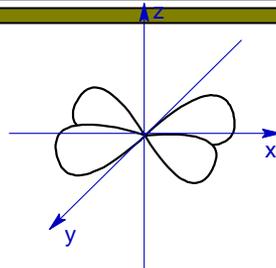
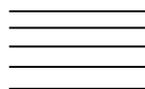
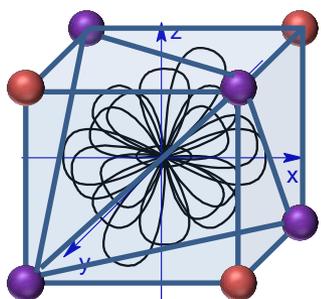
	Dq										P
	3	4	5	6	7	8	9	10	11	12	
Cresce ↓	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	Diminui ↓
	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	
	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	

Logo os metais 4d e 5d sempre possuem campo forte (spin baixo), independente de L

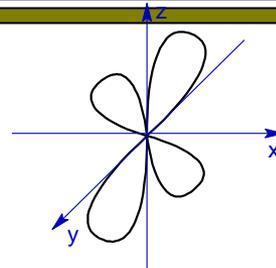


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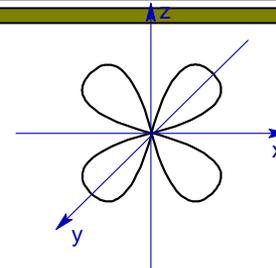
# Complexos Td



$xy$



$yz$

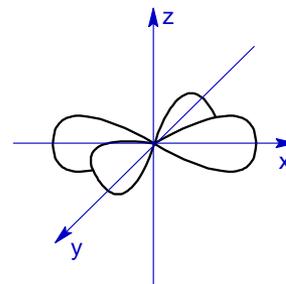


$xz$



$2/5\Delta_t$

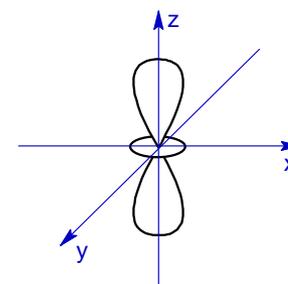
$3/5\Delta_t$



$x^2-y^2$



$e$



$z^2$



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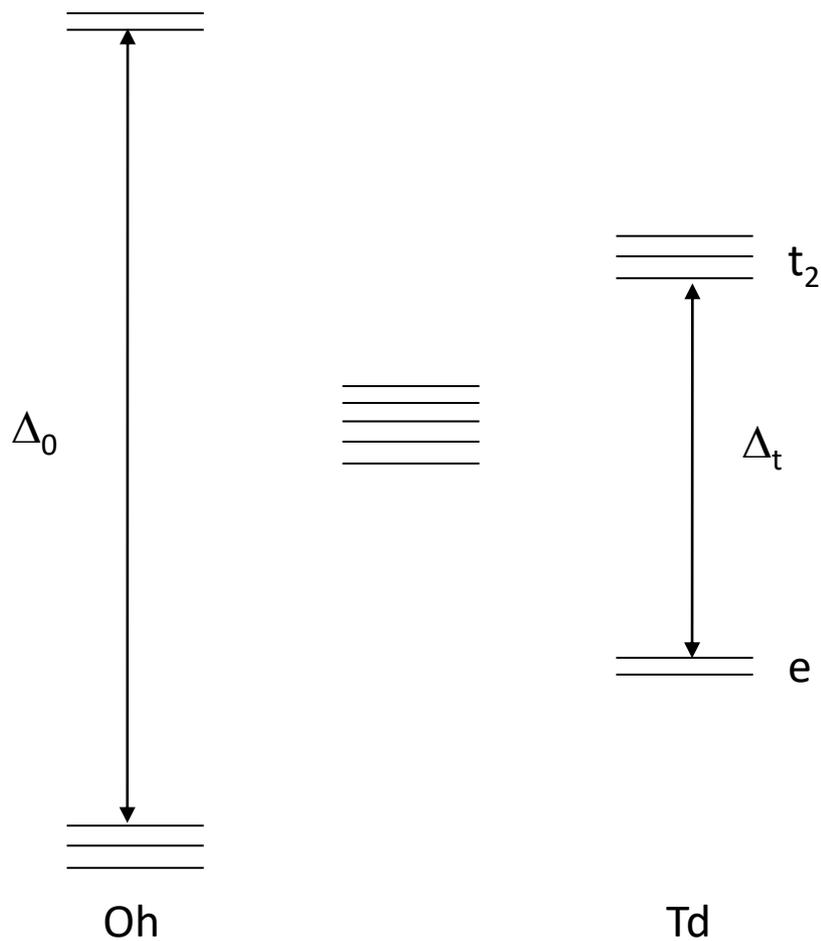
# Complexos Td

$T_d$ ( $\bar{4}3m$ )	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
$A_1$	1	1	1	1	1	$x^2 + y^2 + z^2$
$A_2$	1	1	1	-1	-1	
$E$	2	-1	2	0	0	$(2z^2 - x^2 - y^2, \sqrt{3} (x^2 - y^2))$
$T_1$	3	0	-1	1	-1	$(R_x, R_y, R_z)$
$T_2$	3	0	-1	-1	1	$(x, y, z)$ $(xy, xz, yz)$



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# Complexos Td



Não tem centro de inversão  
Aumento de  $a \rightarrow$  Diminui  $Dq$

$$\Delta_t = \frac{4}{9} \Delta_0$$

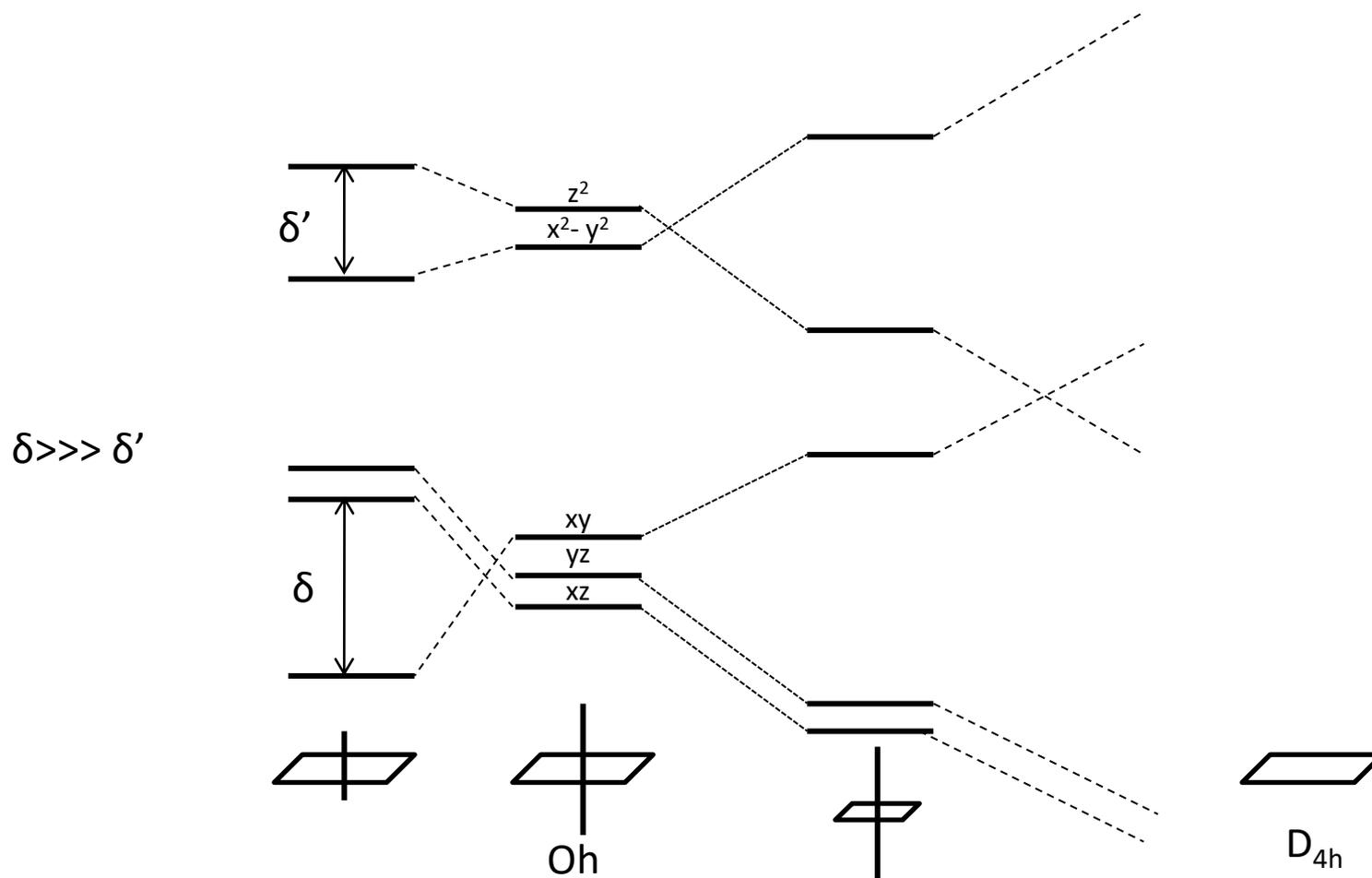
O fator determinante para geometria é o **efeito estérico**



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# Complexos QP

**Teorema de Jahn-Teller:** Para moléculas não lineares em um estado eletronicamente degenerado, tende a perder a degenerescência mediante abaixamento de simetria





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# Teoria de ligação de valência

- Problemas:

Ni(II): Ni + H<sub>2</sub>O e Ni + NH<sub>3</sub> – Complexos Oh paramagnéticos

Ni + CN<sup>-</sup> – D<sub>4h</sub> – Diamagnético

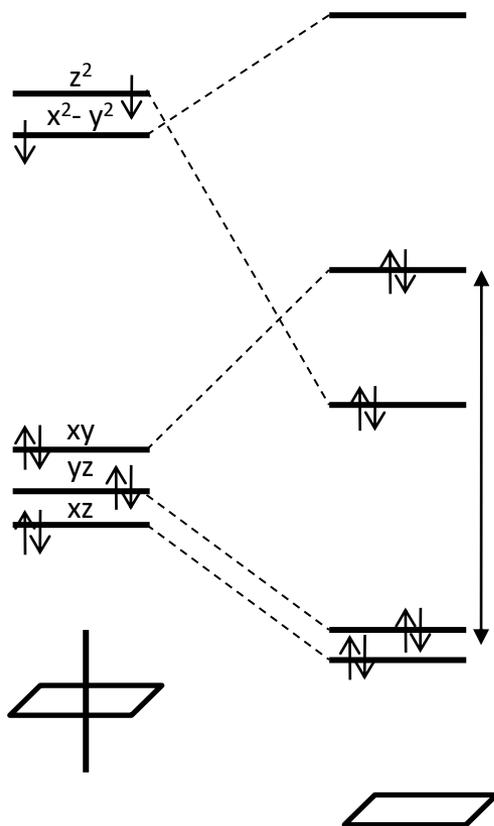
## Teoria FALHA

- Por que os compostos de Pt e Pd sempre são quadrados planares?



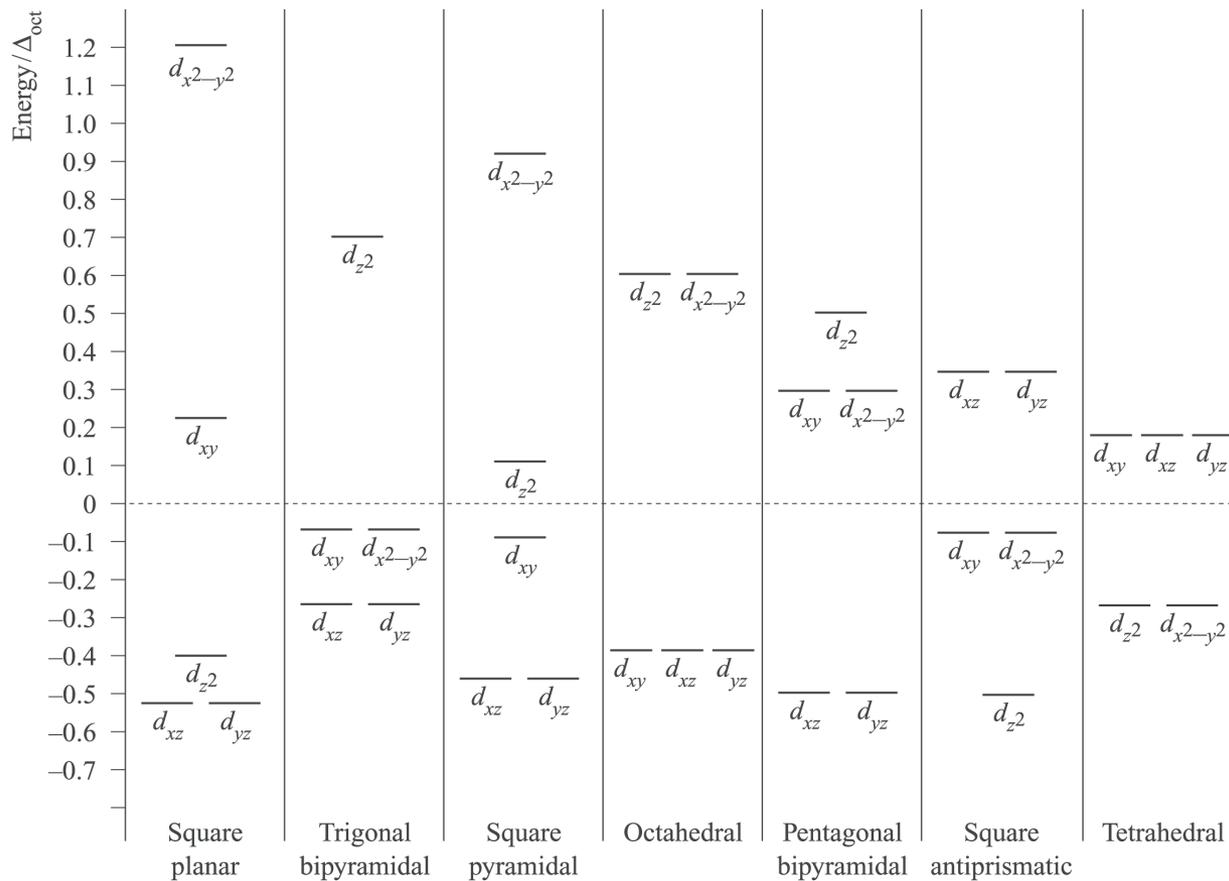
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# Caso $d^8$ spin baixo





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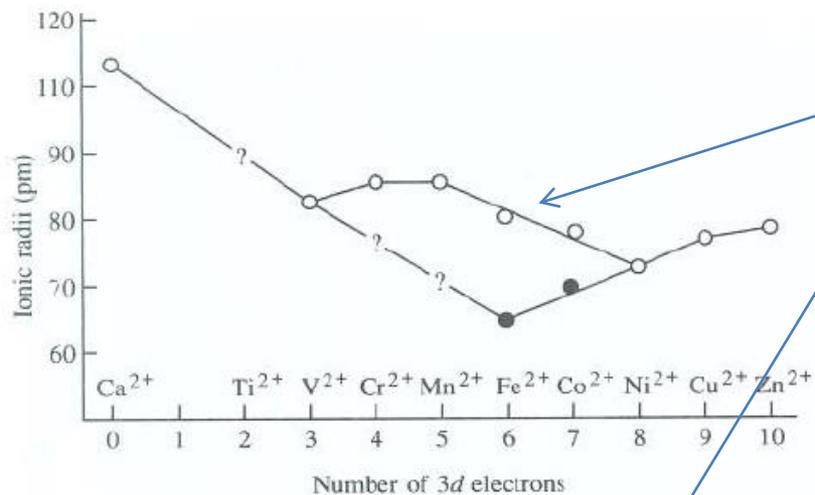
**Fig. 21.11** Crystal field splitting diagrams for some common fields referred to a common barycentre; splittings are given with respect to  $\Delta_{\text{oct}}$ .



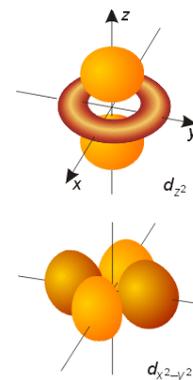
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# Raio iônico

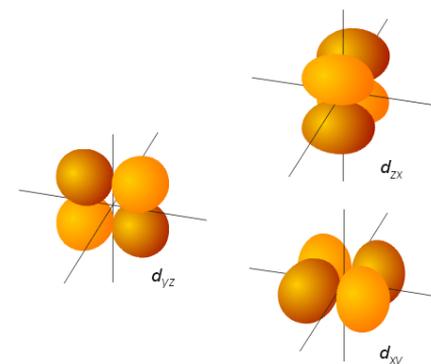
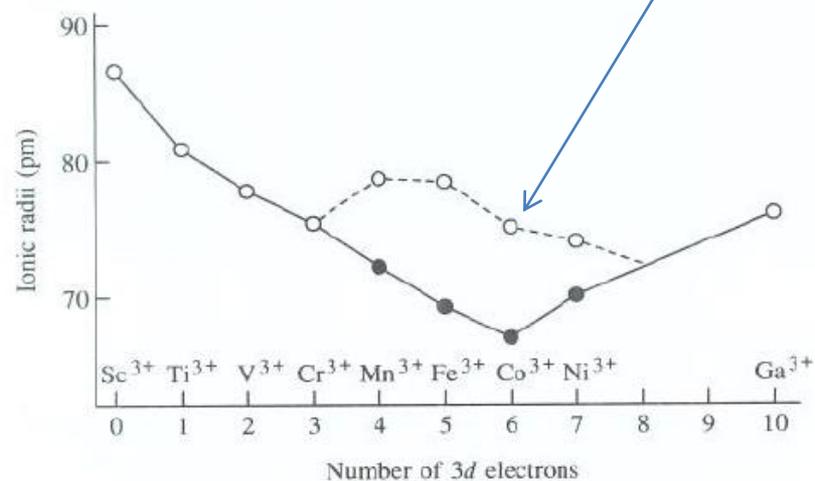
Íons  $M^{2+}$



Spin alto



Íons  $M^{3+}$





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# Estado de oxidação

$\text{Co}^{3+}$  é muito instável em relação a sua reação com água

			$E_0 / \text{V}$
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ $\Delta_0 = 9300 \text{ cm}^{-1}$	→	$[\text{Co}(\text{H}_2\text{O})_6]^{3+} + \text{e}^-$ $\Delta_0 = 18200 \text{ cm}^{-1}$	-1,83
$[\text{Co}(\text{NH}_3)_6]^{2+}$ $\Delta_0 = 10200 \text{ cm}^{-1}$	→	$[\text{Co}(\text{NH}_3)_6]^{3+} + \text{e}^-$ $\Delta_0 = 22900 \text{ cm}^{-1}$	-0,11
$[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{3-} + \text{CN}^-$	→	$[\text{Co}(\text{CN})_6]^{3-} + \text{H}_2\text{O} + \text{e}^-$	+0,83

