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CAPÍTULO 3: PARAMAGNETISMO

PARAMAGNETISMO DE LANGEVIN

- ✘ Momentos magnéticos idênticos permanentes que não interagem e apontam em qualquer direção (Langevin, 1905).
- ✘ Na presença de um campo magnético, a energia de cada dipolo é

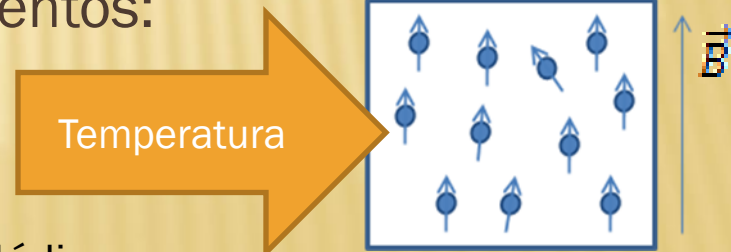
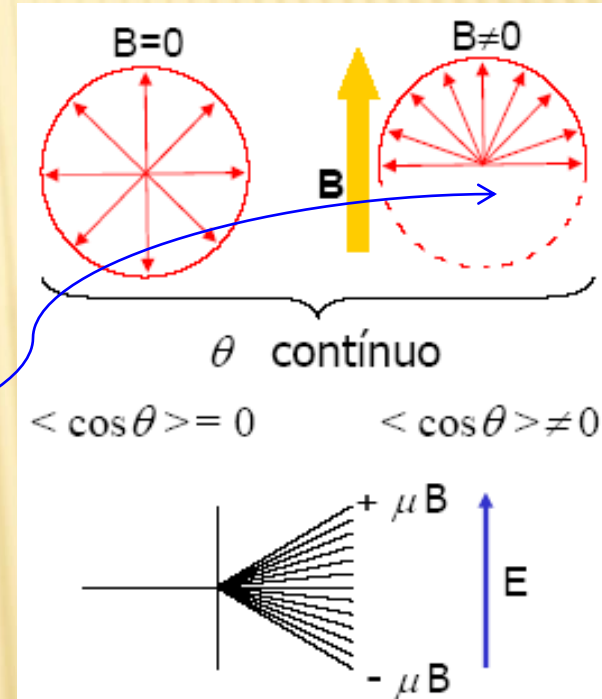
Componente ao longo de B

$$E(\theta) = -\vec{\mu} \cdot \vec{B} = -\overbrace{\mu \cos \theta}^{\text{Componente ao longo de B}} B$$

- ✘ Estado de menor energia: momentos alinhados com B
- ✘ Energia térmica se opõe a esse alinhamento
- ✘ A uma T, a resposta magnética de N momentos:

$$M = N \langle \mu_z \rangle_T = N \mu \langle \cos \theta \rangle_T$$

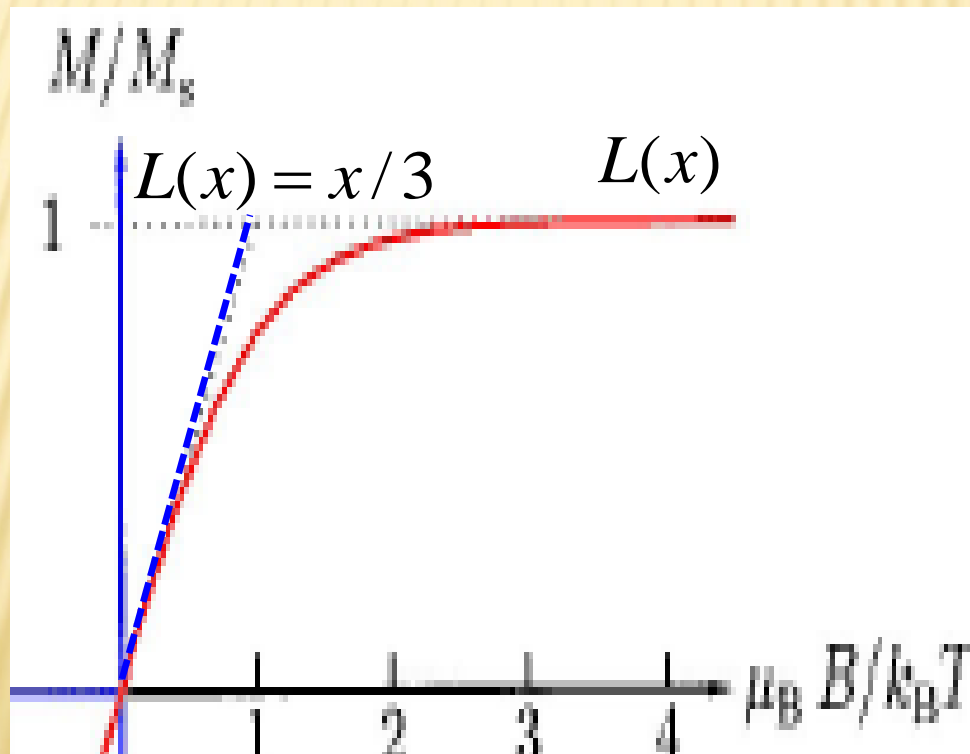
Média térmica



PARAMAGNETISMO DE LANGEVIN

✘ A solução

$$M = N \langle \mu_z \rangle_T = \underbrace{N \mu}_{M_S} \left[\coth x - \frac{1}{x} \right] = M_S L(x) \quad \text{onde} \quad x = \frac{\mu B}{kT}$$



MODELO VETORIAL DOS ÁTOMOS

- ✗ O momento angular total de um átomo

$$\vec{L} = \sum_i \vec{l}_i$$

- ✗ Camadas eletrônicas completas não contribuem.
- ✗ Camadas incompletas apresentam contribuição.
- ✗ Mesmo argumento para o momento angular de spin

$$\vec{S} = \sum_i \vec{s}_i$$

- ✗ Acoplamento spin-órbita entre L e S (Russell-Saunders)

$$\vec{J} = \vec{L} + \vec{S}$$

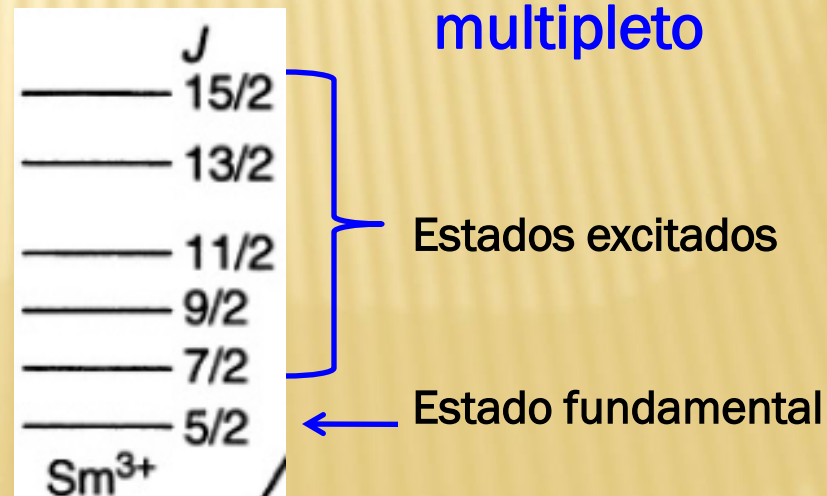
- ✗ J pode assumir os valores :
 $J = (L-S), (L-S+1), \dots, (L+S-1), (L+S)$



Part-filled d shell (Red)

Part-filled f shell (Cyan)

IA																	VIII						
H	IIA											IIIB	IVB	VB	VIB	VIB	He						
Li	Bc																	B	C	N	O	F	Ne
Na	Mg	IIIA	IVA	VA	VIA	VIIA	VIIIA	IB	IIB	Al	Si	P	S	Cl	Ar								
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
Fr	Ra	Ac																					
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu								
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es												



MODELO VETORIAL DOS ÁTOMOS

✘ Lembrado que:

$$\vec{\mu}_L = -\mu_B \vec{L} \quad \vec{\mu}_S = -g_e \mu_B \vec{S}$$

$$g_e \sim 2$$

Também precessam em torno de J .

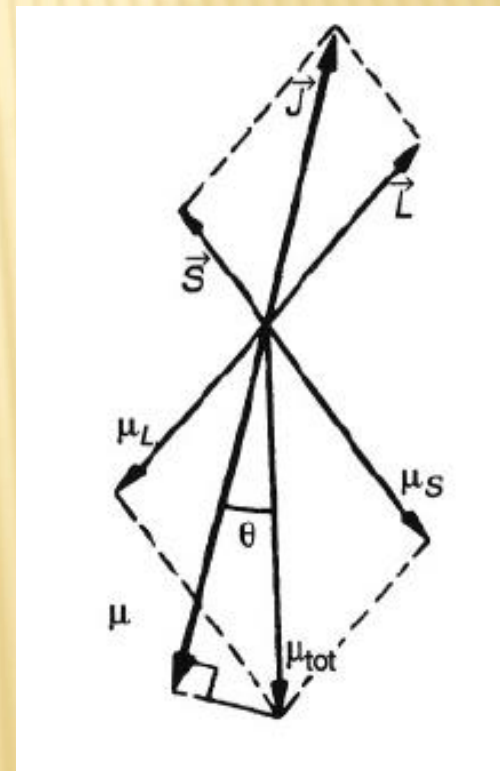
✘ $\vec{\mu}_{tot} = \vec{\mu}_L + \vec{\mu}_S$ faz um ângulo θ com J .

✘ As propriedades magnéticas são determinadas por:

$$\vec{\mu} = \vec{\mu}_{tot} \cos \theta = -g_J \mu_B J$$

g_J é o fator de Landé.

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

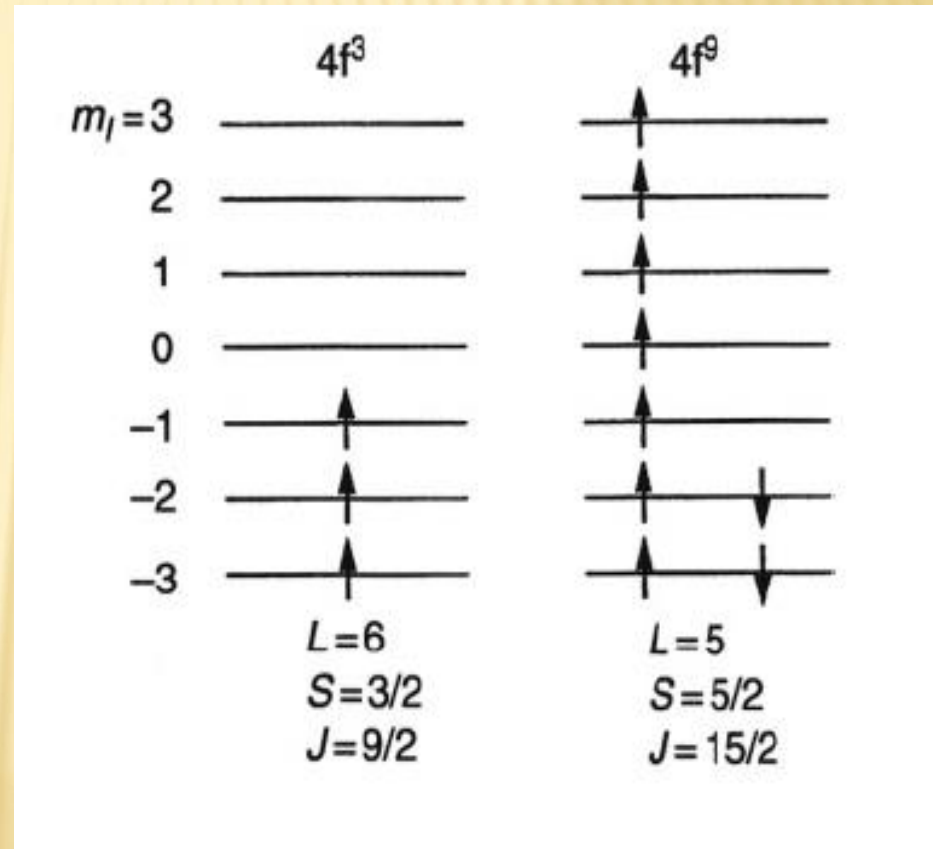


REGRAS DE HUND

- ✗ Regras de Hund para achar os valores de L, S e J para um átomo livre no seu estado fundamental.

Os elétrons ocuparão orbitais de modo que o estado fundamental fique caracterizado por:

- 1) O valor máximo de S permitido pelo princípio de exclusão de Pauli.
- 2) O valor máximo de L permitido pela regra 1.
- 3) Se o orbital está menos que a metade cheio, o estado fundamental do multiplete tem $J=L-S$, mas se este está mais que a metade cheio, o estado fundamental tem $J=L+S$.



REGRAS DE HUND

- ✘ O momento angular orbital L é representado da seguinte forma:

$$L = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6$$

$$X = S \ P \ D \ F \ G \ H \ I$$

- ✘ O multiplete J é descrito por:

$$(2S+1)X_J$$

Table 31.2

GROUND STATES OF IONS WITH PARTIALLY FILLED d - OR f -SHELLS, AS CONSTRUCTED FROM HUND'S RULES^a

d -shell ($l = 2$)						S	$L = \Sigma l_z $	J	SYMBOL	
n	$l_z = 2,$	$1,$	$0,$	$-1,$	-2					
1	↓					1/2	2	3/2	$J = L - S $	${}^2D_{3/2}$
2	↓	↓				1	3	2		3F_2
3	↓	↓	↓			3/2	3	3/2		${}^4F_{3/2}$
4	↓	↓	↓	↓		2	2	0		5D_0
5	↓	↓	↓	↓	↓	5/2	0	5/2		${}^6S_{5/2}$
6	↑↓	↑	↑	↑	↑	2	2	4	$J = L + S$	5D_4
7	↑↓	↑↓	↑	↑	↑	3/2	3	9/2		${}^4F_{9/2}$
8	↑↓	↑↓	↑↓	↑	↑	1	3	4		3F_4
9	↑↓	↑↓	↑↓	↑↓	↑	1/2	2	5/2		${}^2D_{5/2}$
10	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0		1S_0
f -shell ($l = 3$)						S	$L = \Sigma l_z $	J	SYMBOL	
n	$l_z = 3,$	$2,$	$1,$	$0,-1,-2,-3$						
1	↓					1/2	3	5/2	$J = L - S $	${}^2F_{5/2}$
2	↓	↓				1	5	4		3H_4
3	↓	↓	↓			3/2	6	9/2		${}^4I_{9/2}$
4	↓	↓	↓	↓		2	6	4		5I_4
5	↓	↓	↓	↓	↓	5/2	5	5/2		${}^6H_{5/2}$
6	↓	↓	↓	↓	↓	3	3	0	7F_0	
7	↓	↓	↓	↓	↓	7/2	0	7/2	${}^8S_{7/2}$	
8	↑↓	↑	↑	↑	↑	3	3	6	$J = L + S$	7F_6
9	↑↓	↑↓	↑	↑	↑	5/2	5	15/2		${}^6H_{15/2}$
10	↑↓	↑↓	↑↓	↑	↑	2	6	8		5I_8
11	↑↓	↑↓	↑↓	↑↓	↑	3/2	6	15/2		${}^4I_{15/2}$
12	↑↓	↑↓	↑↓	↑↓	↑	1	5	6		3H_6
13	↑↓	↑↓	↑↓	↑↓	↑↓	1/2	3	7/2	${}^2F_{7/2}$	
14	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0	1S_0	

^a↑ = spin $\frac{1}{2}$; ↓ = spin $-\frac{1}{2}$.

PROPRIEDADES MAGNÉTICAS DOS ÍONS PARAMAGNÉTICOS

Elementos 4f

Table 2.2.1. Selected ionic properties of the rare-earth elements. The quantity G^* represents the De Gennes factor $G = (gJ - 1)^2 J(J + 1)$, normalized to the value for Gd^{3+}

Ion	$4f^n$ n	Ground term	S	L	J	g	$g\sqrt{J(J+1)}$	gJ	G^*
La ³⁺	0	¹ S ₀	0	0	—	0	0	0	0
Ce ³⁺	1	² F _{5/2}	1/2	3	5/2	6/7	2.54	2.14	0.011
Pr ³⁺	2	³ H ₄	1	5	4	4/5	3.58	3.20	0.051
Nd ³⁺	3	⁴ I _{9/2}	3/2	6	9/2	8/11	3.62	3.28	0.116
Pm ³⁺	4	⁵ I ₄	2	6	4	3/5	2.68	2.40	0.217
Sm ³⁺	5	⁶ H _{5/2}	5/2	5	5/2	2/7	0.84	0.72	0.283
Eu ³⁺	6	⁷ F ₀	3	3	0	0	0	0	0
Gd ³⁺	7	⁸ S _{7/2}	7/2	0	7/2	2	7.94	7	1
Tb ³⁺	8	⁷ F ₆	3	3	6	3/2	9.72	9	0.667
Dy ³⁺	9	⁶ H _{15/2}	5/2	5	15/2	4/3	10.63	10	0.450
Ho ³⁺	10	⁵ I ₈	2	6	8	5/4	10.60	10	0.286
Er ³⁺	11	⁴ I _{15/2}	3/2	6	15/2	6/5	9.59	9	0.162
Tm ³⁺	12	³ H ₆	1	5	6	7/6	7.57	7	0.074
Yb ³⁺	13	² F _{7/2}	1/2	3	7/2	8/7	4.54	4	0.020
Lu ³⁺	14	¹ S ₀	0	0	0	—	0	0	0

Table 2.2.2. Selected ionic properties of iron-group elements containing Z electrons

Z	Ion	Ground term	L	S	J	$M_{\text{eff,exp}}$	$g\sqrt{J(J+1)}$	$2\sqrt{S(S+1)}$	$g\sqrt{L(L+1)+4S(S+1)}$
18	K ⁺ , V ⁵⁺	¹ S ₀	0	0	0	diam.	0	0	0
19	Sc ²⁺ , Ti ³⁺ , V ⁴⁺	² D _{3/2}	2	1/2	3/2	1.73	1.55	3.01	1.78
20	Ti ²⁺ , V ³⁺	³ F ₂	3	1	2	2.83	1.63	4.49	2.83
21	V ²⁺ , Cr ³⁺ , Mn ⁴⁺	⁴ F _{3/2}	3	3/2	3/2	3.82	0.70	5.21	3.87
22	Cr ²⁺ , Mn ³⁺	⁵ D ₀	2	2	0	4.81	0	5.50	4.91
23	Mn ²⁺ , Fe ³⁺	⁶ S _{5/2}	0	5/2	5/2	5.85	5.92	5.92	5.92
24	Fe ²⁺	⁵ D ₄	2	2	4	5.52 – 5.22	6.71	5.50	4.91
25	Co ²⁺	⁴ F _{9/2}	3	3/2	9/2	5.20 – 4.43	6.63	5.21	3.87
26	Ni ²⁺	³ F ₄	3	1	4	3.23	5.59	4.49	2.83
27	Cu ²⁺	² D _{5/2}	2	1/2	5/2	2.02 – 1.81	3.55	3.01	1.73

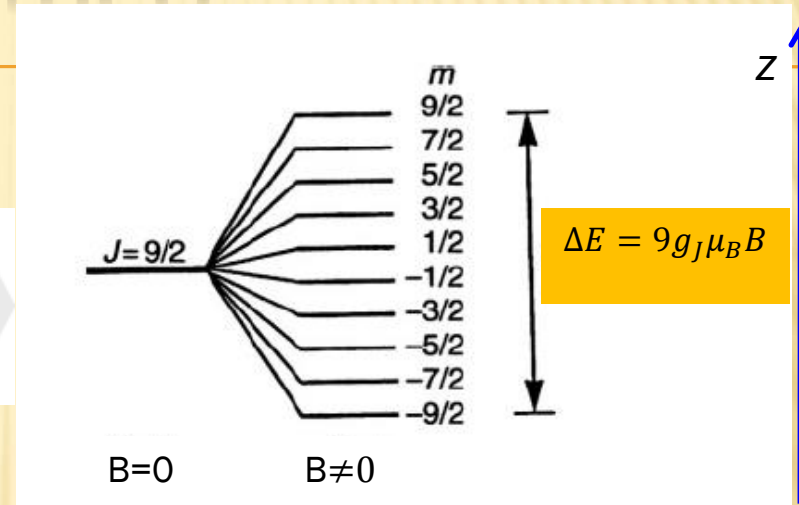
Elementos 3d

PARAMAGNETISMO QUÂNTICO

N átomos sob a influência de B
(efeito Zeeman)
 $m = \pm J, \pm(J-1), \dots$

Campo Magnético
 \times
Temperatura

$$\mu_z = -g_J m \mu_B$$



- ✗ Distribuição de Boltzmann: A probabilidade P_i de achar um átomo com energia E_i :
- ✗ A média térmica da magnetização é dada por:

$$P_i = \frac{\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}$$

$$M = N \langle \mu_z \rangle = N \frac{\sum_{m=-J}^J -g_J m \mu_B \exp\left(-\frac{g_J m \mu_B B}{kT}\right)}{\sum_{m=-J}^J \exp\left(-\frac{g_J m \mu_B B}{kT}\right)}$$

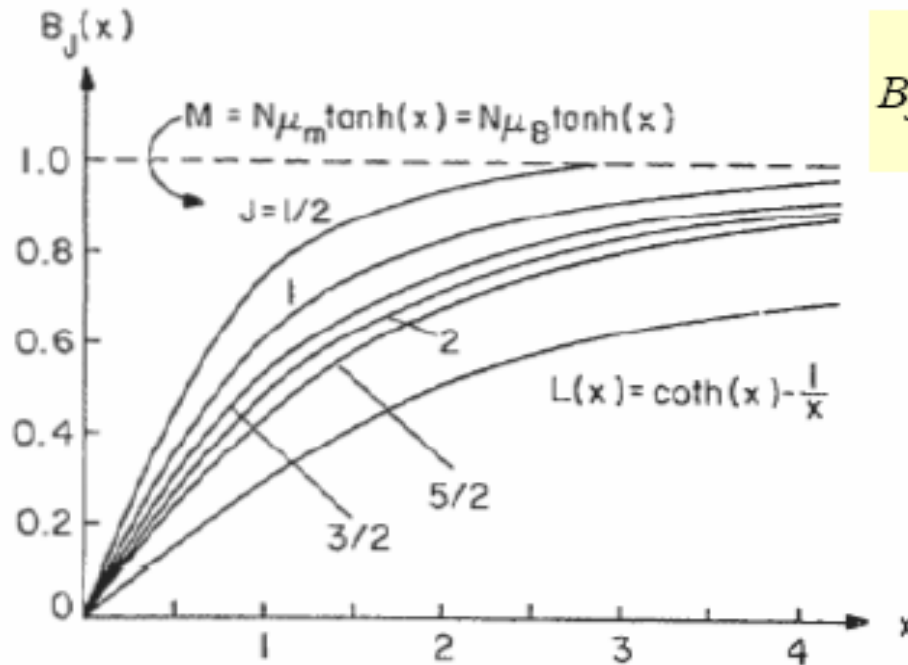
- ✗ Ou

$$M = N g_J \mu_B J \mathcal{B}_J(x), \quad x = g_J \mu_B B / kT$$

Função de Brillouin

$$\mathcal{B}_J(x) = \frac{2J+1}{2J} \coth \frac{(2J+1)x}{2J} - \frac{1}{2J} \coth \frac{x}{2J}$$

PARAMAGNETISMO QUÂNTICO



■ No limite de J muito grande:

$$B_J(x) \xrightarrow{J \rightarrow \infty} L(x)$$

Limite Clássico!!

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$$

■ Para $x = \frac{\mu B}{kT} \ll 1$ temos:

$$\coth x = \frac{1}{x} + \frac{x}{3} \dots$$

$$B_J(x) \xrightarrow{x \ll 1} \frac{J(J+1)}{3J^2} x$$

■ Logo:

$$M = \frac{N g_J^2 \mu_B^2 J(J+1)}{3kT} B = \frac{C}{T} B$$

$$\chi = \frac{M}{H} = \mu_0 \frac{N g_J^2 \mu_B^2 J(J+1)}{3kT}$$

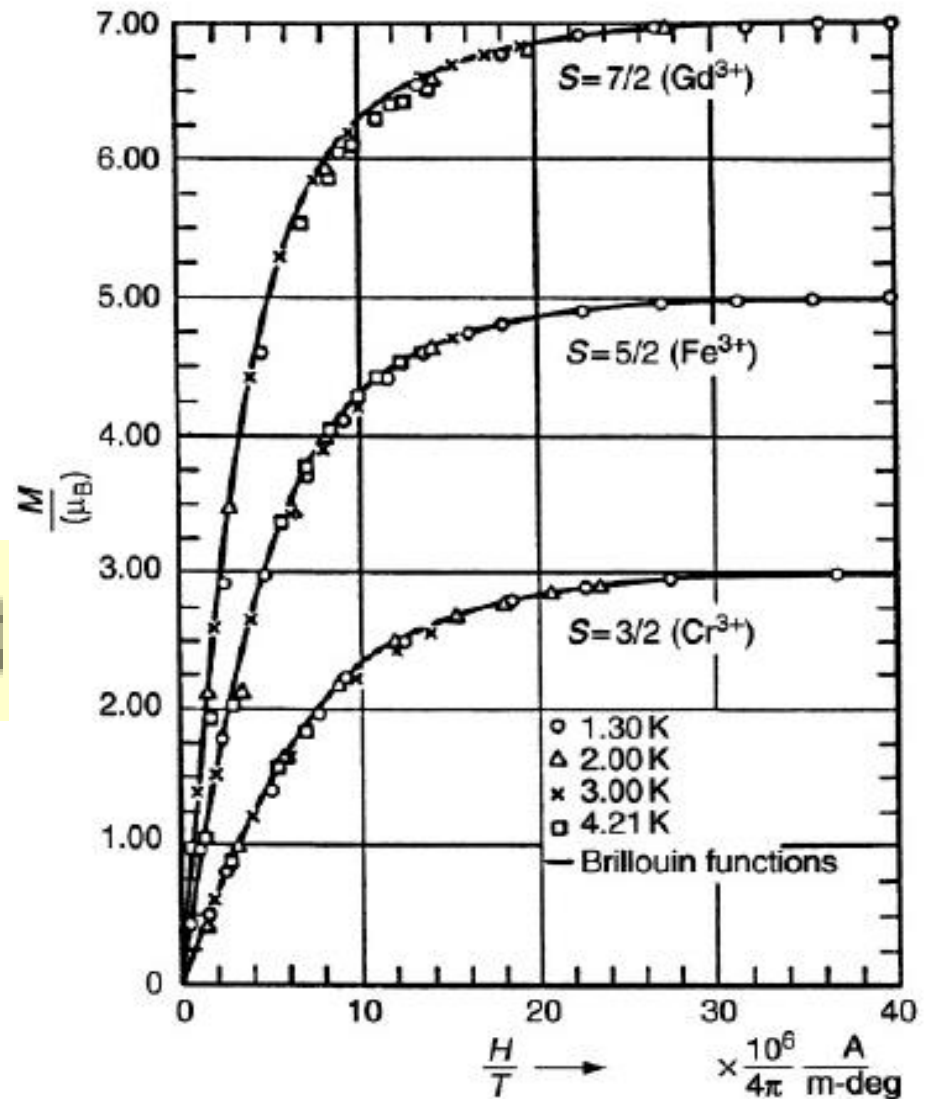
PARAMAGNETISMO QUÂNTICO

- Para um átomo com momento angular J :
- $2J+1$ níveis de energia

$$M = g \mu_B J N B_J(x)$$

Função de Brillouin

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$$



PARAMAGNETISMO QUÂNTICO

Número efetivo de magnetons de Bohr

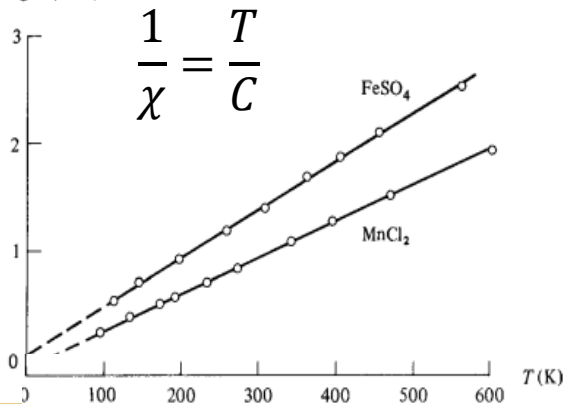
$$M = \frac{NJ(J+1)g^2\mu_B^2B}{3kT} = \frac{C}{T}B$$

$$p \equiv g[J(J+1)]^{1/2}$$

$$\langle \mu_z \rangle = p\mu_B$$

$$\chi = \frac{M}{H} = \mu_0 \frac{Ng^2\mu_B^2J(J+1)}{3J^2kT}$$

$1/\chi$ (10^4 g-Oe/emu)



(Near room temperature)

Ion	Configuration	Basic Level	$p(\text{calc}) = g[J(J+1)]^{1/2}$	$p(\text{exp})$ approx.
Ce ³⁺	4f ¹ 5s ² 6p ⁶	² F _{5/2}	2.54	2.4
Pr ³⁺	4f ² 5s ² 6p ⁶	³ H ₄	3.58	3.5
Nd ³⁺	4f ³ 5s ² 6p ⁶	⁴ I _{9/2}	3.62	3.5
Pm ³⁺	4f ⁴ 5s ² 6p ⁶	⁵ I ₄	2.68	...
Sm ³⁺	4f ⁵ 5s ² 6p ⁶	⁶ H _{5/2}	0.84	1.5
Eu ³⁺	4f ⁶ 5s ² 6p ⁶	⁷ F ₀	0	3.4
Gd ³⁺	4f ⁷ 5s ² 6p ⁶	⁸ S _{7/2}	7.94	8.0
Tb ³⁺	4f ⁸ 5s ² 6p ⁶	⁷ F ₈	9.72	9.5
Dy ³⁺	4f ⁹ 5s ² 6p ⁶	⁸ H _{15/2}	10.63	10.6
Ho ³⁺	4f ¹⁰ 5s ² 6p ⁶	⁵ I ₈	10.60	10.4
Er ³⁺	4f ¹¹ 5s ² 6p ⁶	⁴ I _{15/2}	9.59	9.5
Tm ³⁺	4f ¹² 5s ² 6p ⁶	³ H ₆	7.57	7.3
Yb ³⁺	4f ¹³ 5s ² 6p ⁶	² F _{7/2}	4.54	4.5

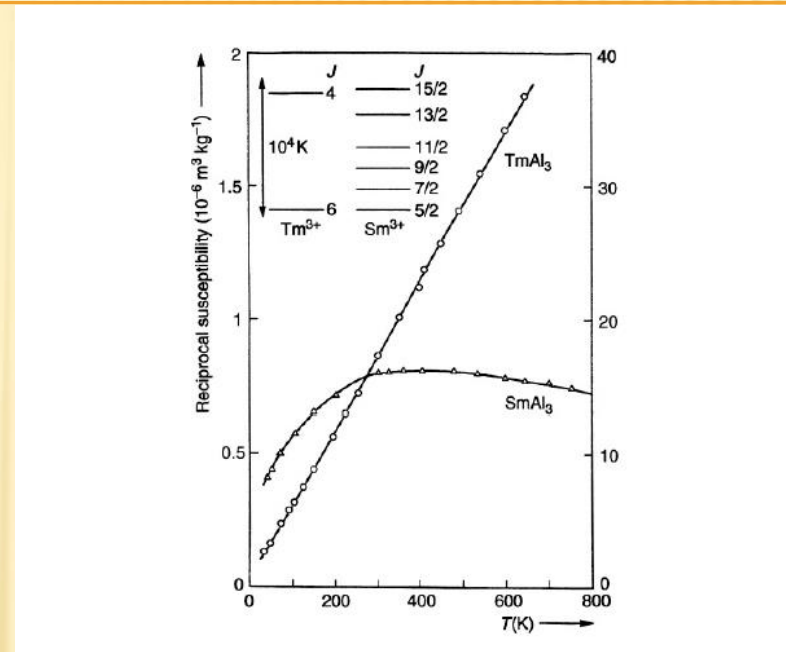
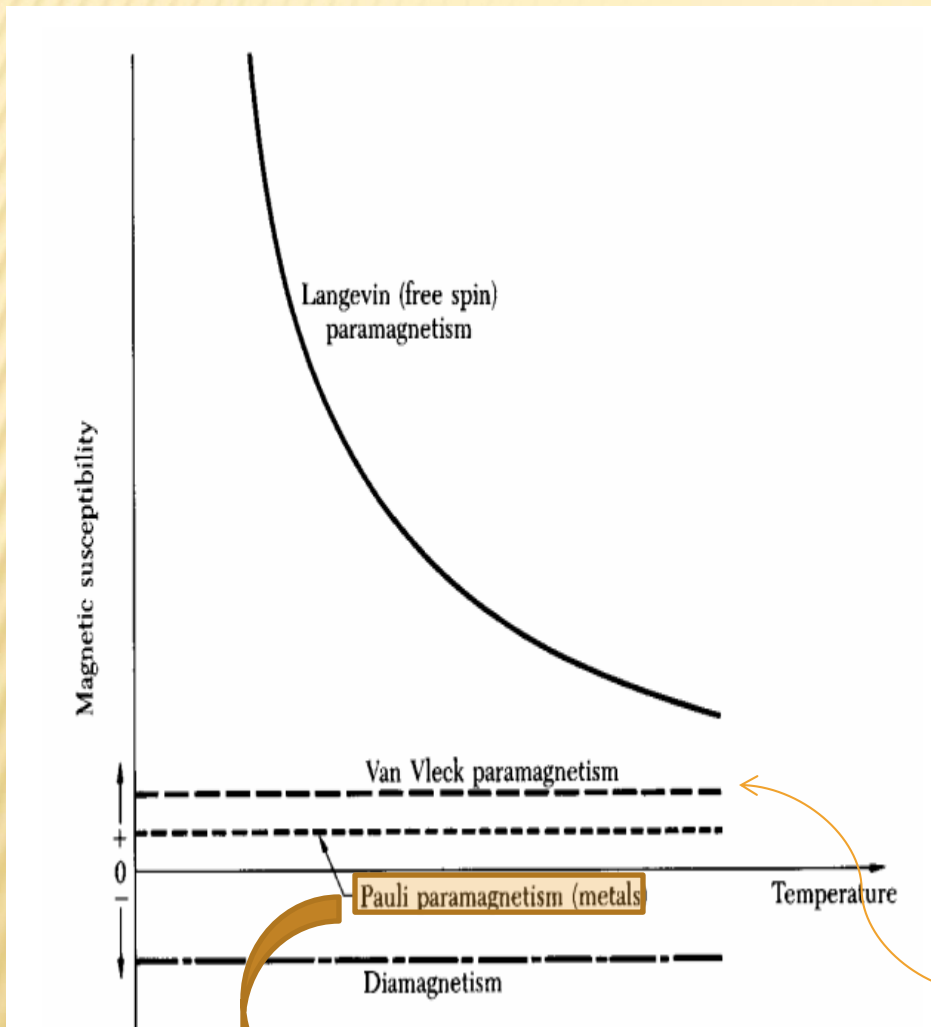
Ion	Config-uration	Basic Level	$p(\text{calc}) = g[J(J+1)]^{1/2}$	$p(\text{calc}) = 2[S(S+1)]^{1/2}$	$p(\text{exp})$ †	$g(\text{exp})$ ‡
Ti ³⁺ , V ⁴⁺	3d ¹	² D _{3/2}	1.55	1.73	1.8
V ³⁺	3d ²	³ F ₂	1.63	2.83	2.8	(1.98)
Cr ³⁺ , V ²⁺	3d ³	⁴ F _{3/2}	0.77	3.87	3.8	(1.97)
Mn ³⁺ , Cr ²⁺	3d ⁴	⁵ D ₀	0	4.90	4.9	2.0
Fe ³⁺ , Mn ²⁺	3d ⁵	⁶ S _{5/2}	5.92	5.92	5.9	2.0
Fe ²⁺	3d ⁶	⁵ D ₄	6.70	4.90	5.4	2.2
Co ²⁺	3d ⁷	⁴ F _{3/2}	6.54	3.87	4.8	2.5
Ni ²⁺	3d ⁸	³ F ₄	5.59	2.83	3.2	2.3
Cu ²⁺	3d ⁹	² D _{5/2}	3.55	1.73	1.9	2.2

† Representative values.

‡ In this column $g = p(\text{exp})/[S(S+1)]^{1/2}$.

Por quê o momento angular total não explica os resultados experimentais ?

PARAMAGNETISMO



Para SmAl_3 , devemos considerar também os multipletos superiores (estados excitados).

$$\chi = N\mu_0 \frac{\sum_J \left(g^2 \mu_B^2 \frac{J(J+1)}{3kT} + \alpha_J \right) (2J+1) \exp\left(-\frac{E_J}{kT}\right)}{\sum_J (2J+1) \exp\left(-\frac{E_J}{kT}\right)}$$

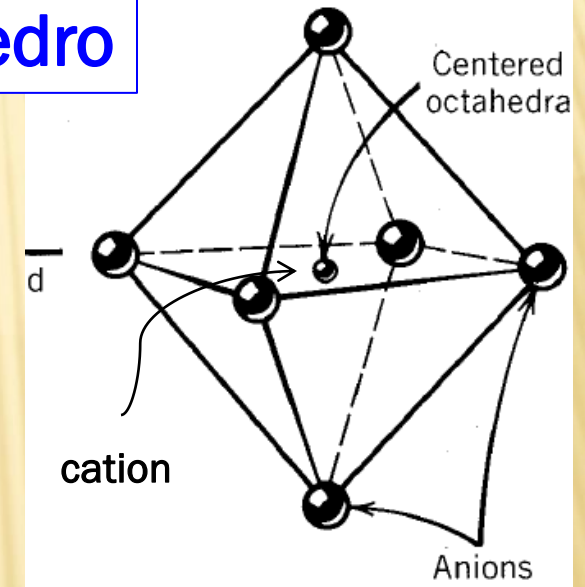
α_J termo de van Vleck

Átomo ou molécula que não possui momento magnético no estado fundamental.

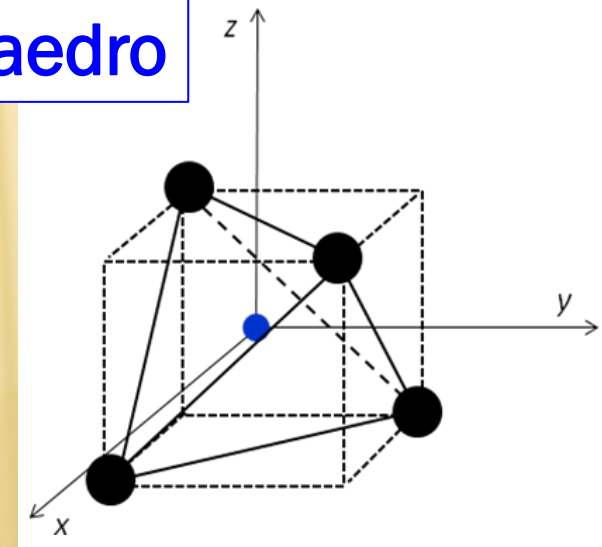
CAMPO CRISTALINO

- ✘ Sitios cristalinos mais comuns ocupados pelos ions magneticos.
- ✘ Ion central ou ion magnetico
- ✘ Os ions ligantes tem carga negativa.

octaedro

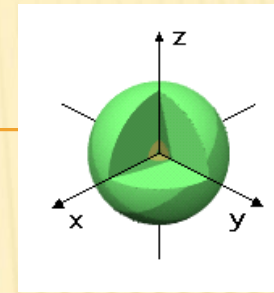


tetraedro

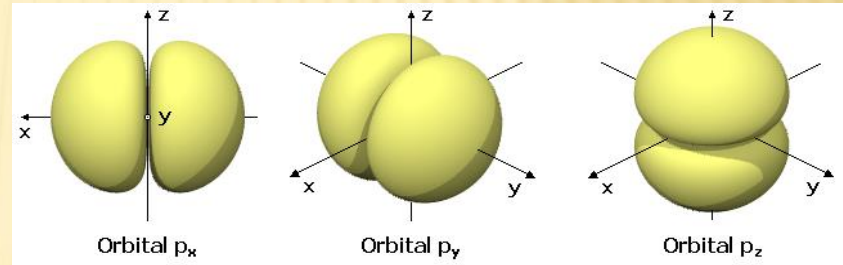


CAMPO CRISTALINO

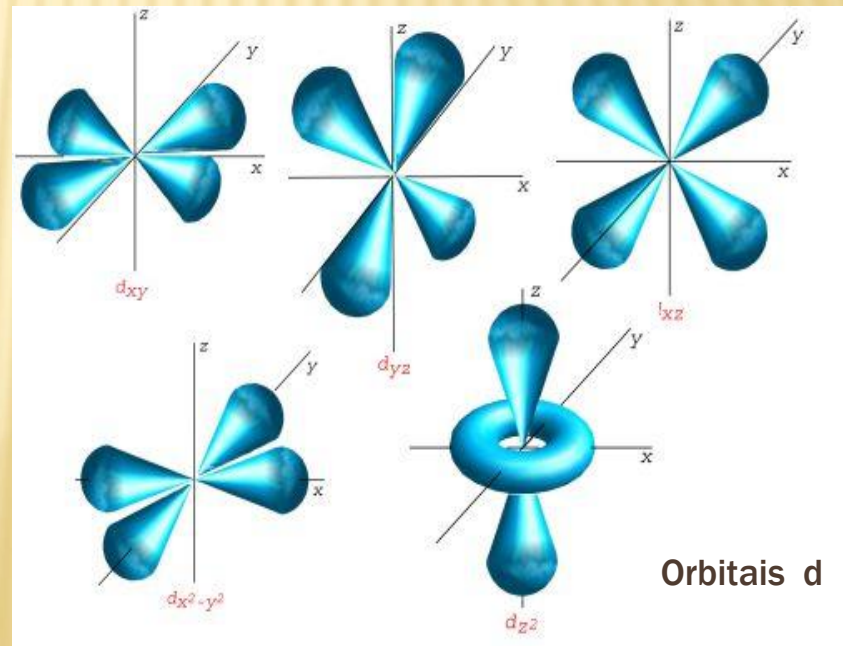
- ✘ Orbitais eletronicos dos atomos.
- ✘ Os orbitais d parcialmente ocupados proporcionam as propriedades magneticas para os ions $3d^n$.
- ✘ Exemplo: o ion Fe^{2+} tem uma configuracao electronica $[Ne]3s^23p^63d^6$



Orbitais s



Orbitais p



Orbitais d

CAMPO CRISTALINO

TABLE 9.2. EFFECTIVE MAGNETON NUMBERS FOR IRON GROUP IONS

Ion	Config-uration	Basic Level	$p(\text{calc}) = g[J(J+1)]^{1/2}$	$p(\text{calc}) = 2[S(S+1)]^{1/2}$	$p(\text{exp})^\dagger$	$g(\text{exp})^\ddagger$
Ti ³⁺ , V ⁴⁺	3d ¹	² D _{3/2}	1.55	1.73	1.8
V ³⁺	3d ²	³ F ₂	1.63	2.83	2.8	(1.98)
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Fe ²⁺	3d ⁶	⁵ D ₄	6.70	4.90	5.4	2.2
Co ²⁺	3d ⁷	⁴ F _{3/2}	6.54	3.87	4.8	2.5
Ni ²⁺	3d ⁸	³ F ₄	5.59	2.83	3.2	2.3
Cu ²⁺	3d ⁹	² D _{5/2}	3.55	1.73	1.9	2.2

† Representative values.

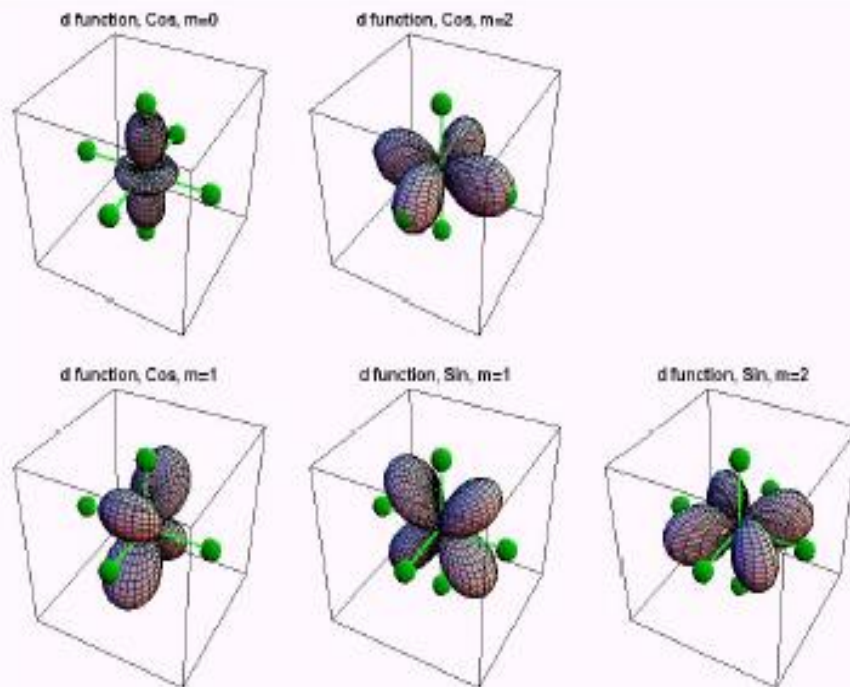
‡ In this column $g = p(\text{exp})/[S(S+1)]^{1/2}$.

- Os valores experimentais do momento magnético são diferentes dos teóricos.
- a razão é campo cristalino.
- Dois estado eletrônicos apontam para os íons vizinhos, e três apontam entre os vizinhos.
- Diferentes energias eletrostáticas.
- No cristal, os orbitais d ($l = 2$) deixam de ser degenerados.
- Isto leva a

$$\langle L_z \rangle = 0 \quad (\text{Quenching orbital})$$

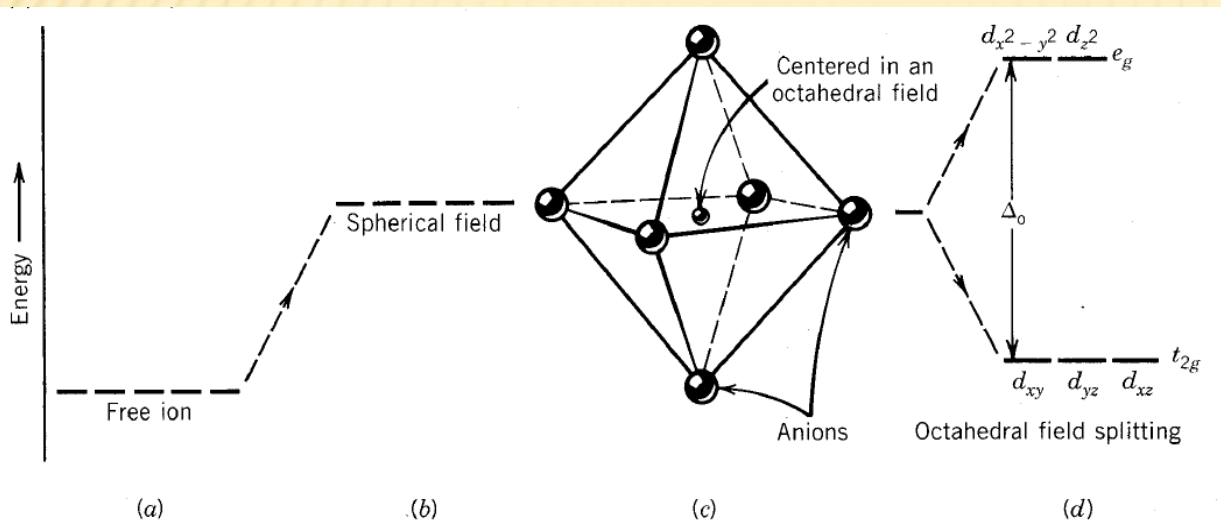
resultando

$$\langle \mu_z \rangle = \langle L_z + 2S_z \rangle = 2\langle S_z \rangle \mu_B$$



CAMPO CRISTALINO

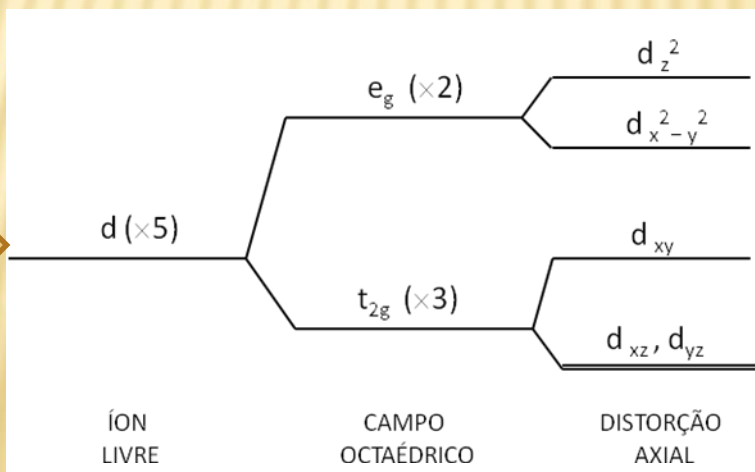
- Representação esquemática dos níveis de energia dos orbitais 3d dum metal de transição



Consequências

- Susceptibilidade anisotrópica.
- Desvios à lei de Curie em baixas T (ZFS=zero-field splitting).
- Em combinação com a interação spin-órbita, elimina parcialmente o “Quenching” orbital.

Efeito das distorções



PARAMAGNETISMO DE PAULI

Elétrons de condução

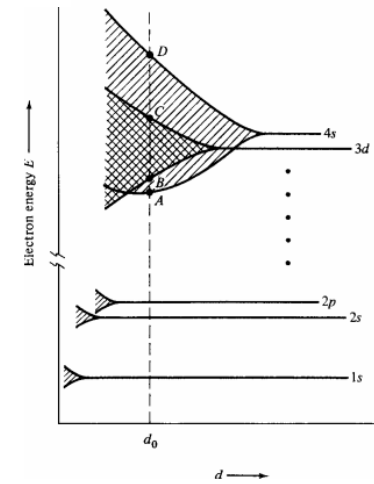
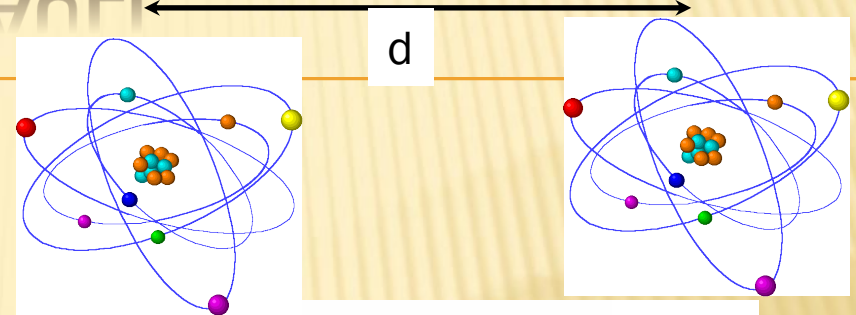
- ✘ Teoria clássica:
prevê paramagnetismo de Curie

$$M = \frac{N\mu_B^2 B}{k_B T}$$

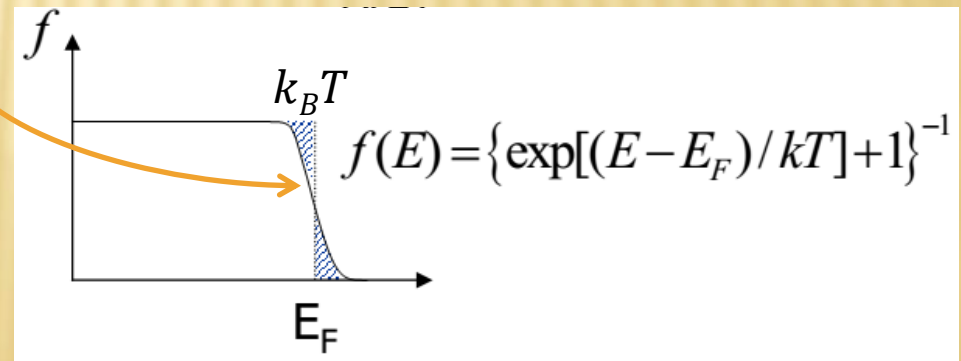
- ✘ Estatística de Fermi-Dirac:
Prevê independente de T (Pauli)

$$M = \frac{N\mu_B^2}{k_B T} B \times \frac{T}{T_F} = \frac{N\mu_B^2}{k_B T_F} B$$

T_F é a temperatura de Fermi do metal ($E_F = k_B T_F$)



Splitting of electron energy levels as the interatomic distance decreases.



PARAMAGNETISMO DE GÁS DE ELÉTRONS LIVRES

Elétrons itinerantes num metal.

Cálculo da susceptibilidade para $T \ll T_F$.

- ✘ Desdobramentos da banda de condução sob a ação de B .
- ✘ Elétrons com menor energia com spin \uparrow .

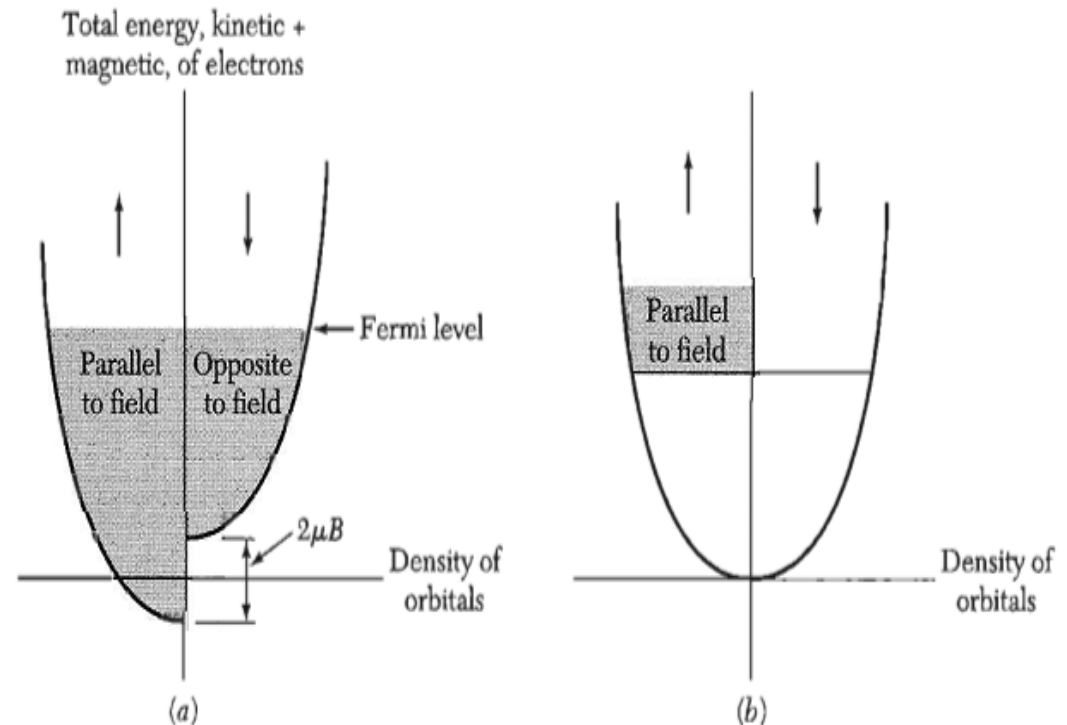


Figure 10 Pauli paramagnetism at absolute zero; the orbitals in the shaded regions in (a) are occupied. The numbers of electrons in the “up” and “down” band will adjust to make the energies equal at the Fermi level. The chemical potential (Fermi level) of the moment up electrons is equal to that of the moment down electrons. In (b) we show the excess of moment up electrons in the magnetic field.

PARAMAGNETISMO DE GÁS DE ELÉTRONS LIVRES

Cálculo da susceptibilidade para $T \ll T_F$

Concentração de elétrons com momentos magnéticos paralelos a B

$$N_+ = \frac{1}{2} \int_{-\mu_B}^{\epsilon_F} d\epsilon D(\epsilon + \mu_B) \cong \frac{1}{2} \int_0^{\epsilon_F} d\epsilon D(\epsilon) + \frac{1}{2} \mu_B D(\epsilon_F)$$

Concentração de elétrons com momentos magnéticos antiparalelos a B

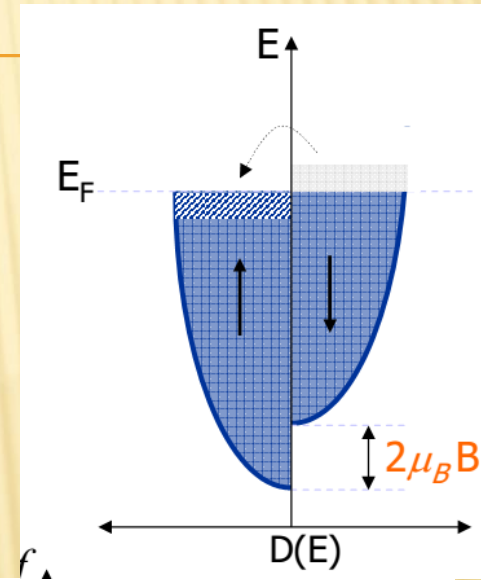
$$N_- = \frac{1}{2} \int_{\mu_B}^{\epsilon_F} d\epsilon D(\epsilon - \mu_B) \cong \frac{1}{2} \int_0^{\epsilon_F} d\epsilon D(\epsilon) - \frac{1}{2} \mu_B D(\epsilon_F)$$

A magnetização de Pauli é dado por:

$$M = N\mu(N_+ - N_-)$$

Temos que:

$$M = \mu_B^2 D(E_F) B = \frac{3N\mu_B^2 B}{2k_B T_F}$$



logo:

$$\chi_{\text{Pauli}} = \mu_0 \mu_B^2 D(E_F)$$

onde $D(E_F) = 3N / 2k_B T_F$

$$\chi_{\text{Pauli}} = \frac{3\mu_0 \mu_B^2 N}{2k_B T_F}$$

- Independe de T
- 2 fatores opostos:
 - $\uparrow T \Rightarrow \uparrow$ spins promovidos
 - $\uparrow T \Rightarrow \uparrow$ desordem térmica