

Paramagnetism

Paramagnetism

Materials that have a magnetic moment are paramagnetic.

An applied field aligns the magnetic moments in the material making the field in the material larger than the applied field.

The internal field is zero at zero applied field (random magnetic moments).

$$\vec{M} = \chi \vec{H}$$

Paramagnetic susceptibility

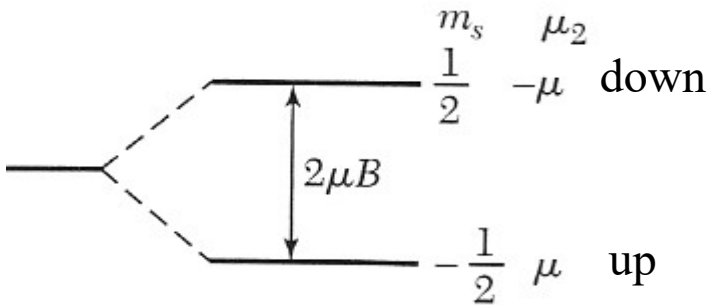
Aluminum	2.3×10^{-5}
Calcium	1.9×10^{-5}
Magnesium	1.2×10^{-5}
Oxygen	2.1×10^{-6}
Platinum	2.9×10^{-4}
Tungsten	6.8×10^{-5}

Boltzmann factors

To take the average value of quantity A

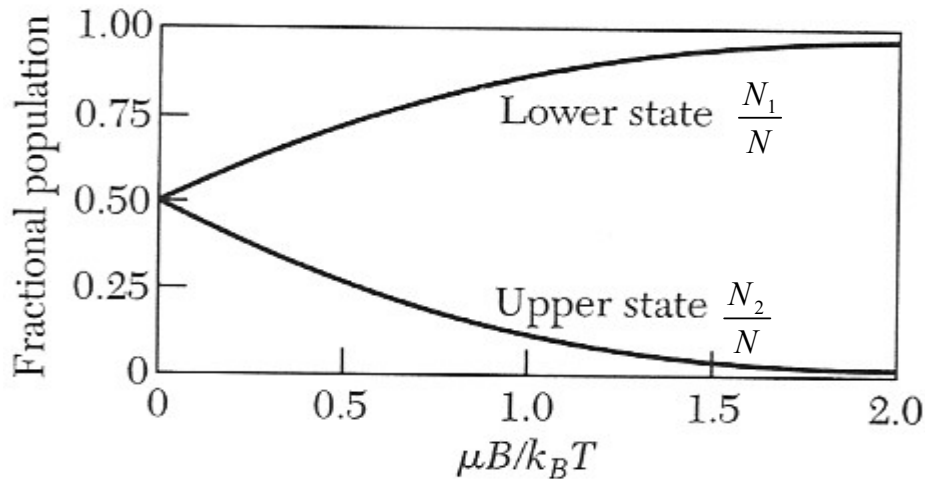
$$\langle A \rangle = \frac{\sum_i A_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

Spin populations



$$\frac{N_1}{N} = \frac{\exp(\mu B / k_B T)}{\exp(\mu B / k_B T) + \exp(-\mu B / k_B T)}$$

$$\frac{N_2}{N} = \frac{\exp(-\mu B / k_B T)}{\exp(\mu B / k_B T) + \exp(-\mu B / k_B T)}$$

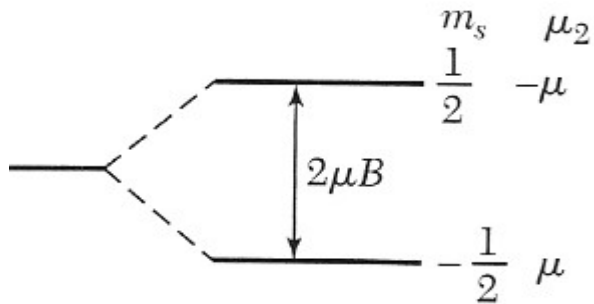


$$M = (N_1 - N_2)\mu / V$$

$$= n\mu \frac{\exp(\mu B / k_B T) - \exp(-\mu B / k_B T)}{\exp(\mu B / k_B T) + \exp(-\mu B / k_B T)}$$

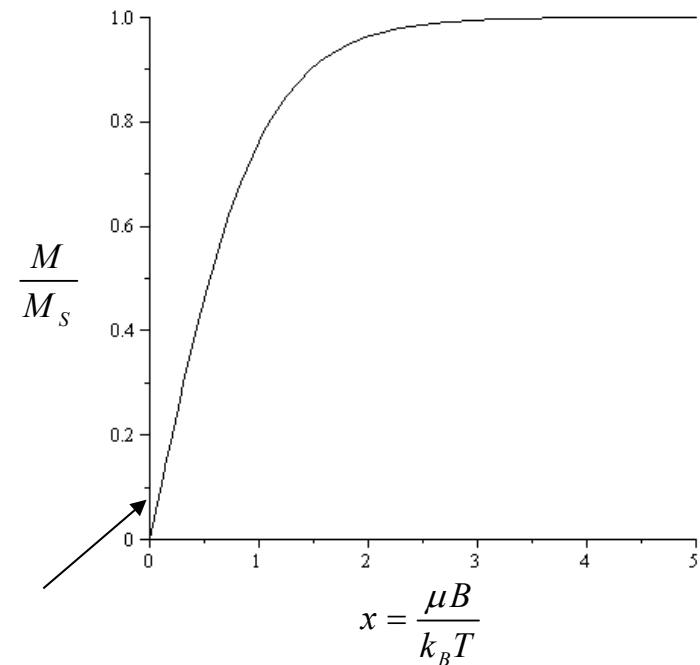
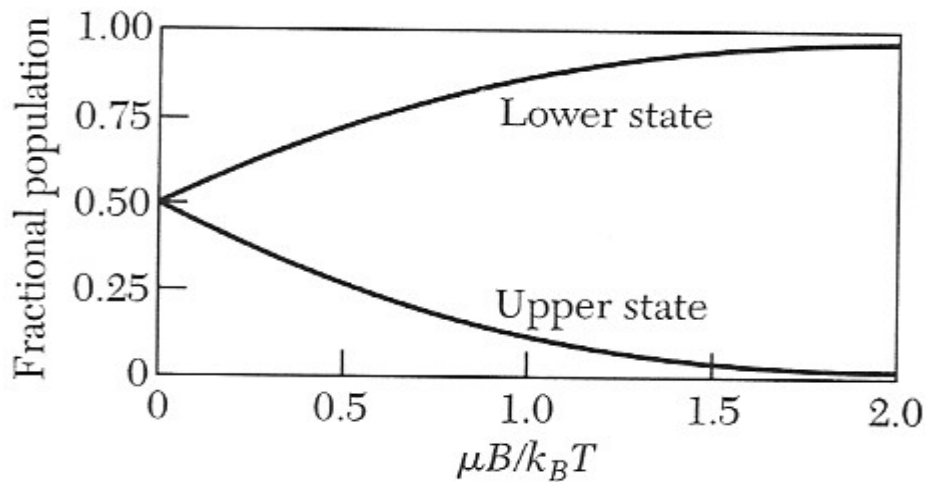
$$= n\mu \tanh\left(\frac{\mu B}{k_B T}\right)$$

Paramagnetism, spin 1/2

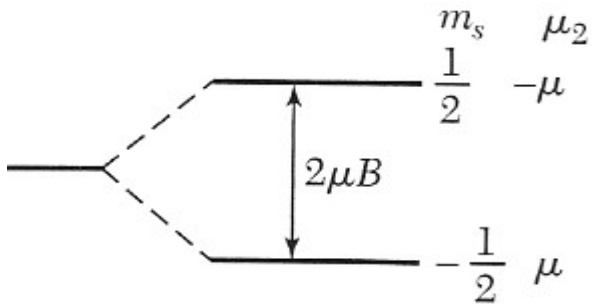


$$M = n\mu \tanh\left(\frac{\mu B}{k_B T}\right) \approx \frac{n\mu^2 B}{k_B T} = \frac{CB}{T}$$

for $\mu B \ll k_B T$ Curie law

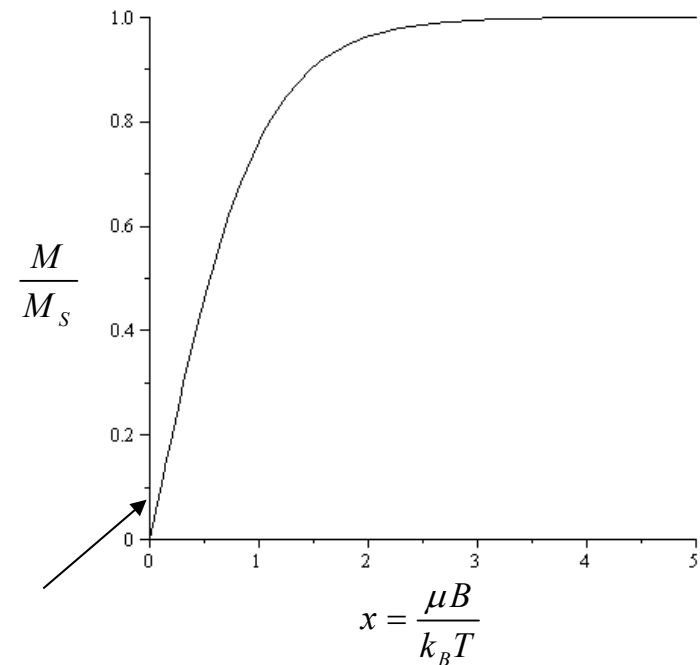
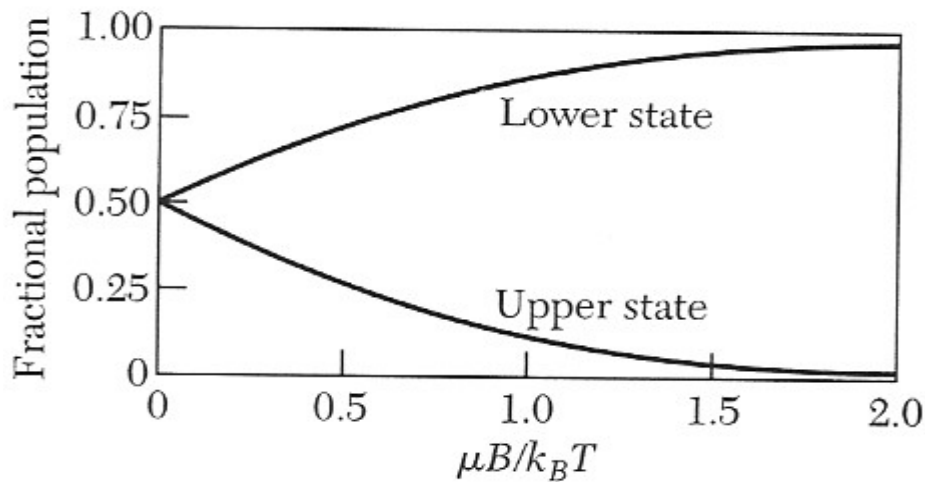


Paramagnetism, spin 1/2



$$M = n\mu \tanh\left(\frac{\mu B}{k_B T}\right) \approx \frac{n\mu^2 B}{k_B T} = \frac{CB}{T}$$

for $\mu B \ll k_B T$ Curie law

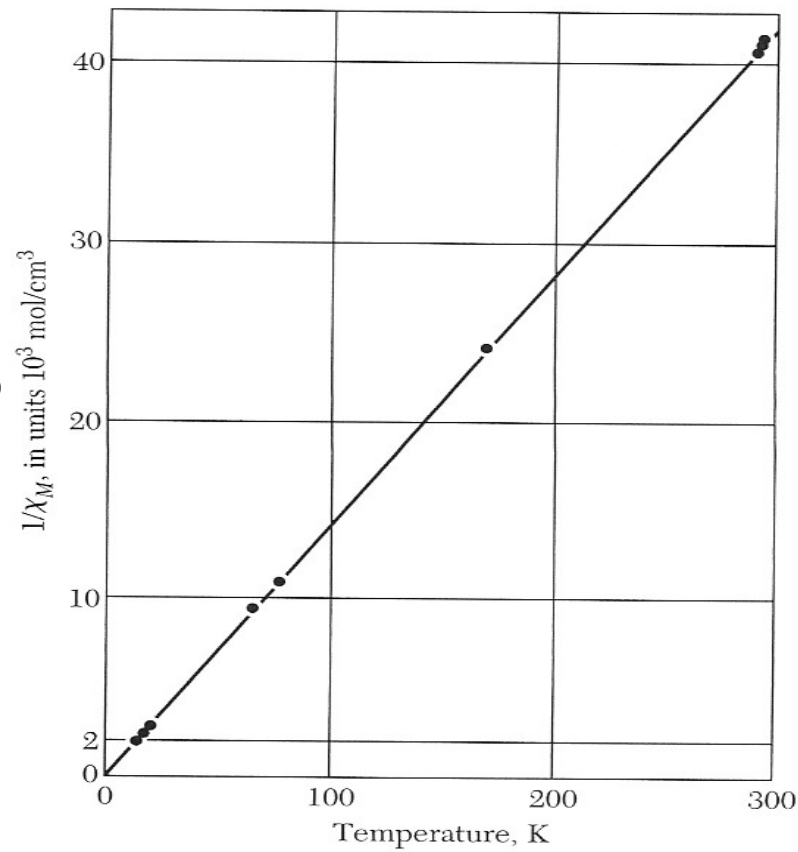


Curie law

for $\mu B \ll k_B T$ $M = CB / T$

$$\chi \propto \left. \frac{dM}{dB} \right|_{B=0} = \frac{C}{T}$$

C is the Curie constant



Atomic physics

In atomic physics, the possible values of the magnetic moment of an atom in the direction of the applied field can only take on certain values.

Total angular momentum

$$J = L + S \quad \text{Orbital } L + \text{ spin } S \text{ angular momentum}$$

Magnetic quantum number

$$m_J = -J, -J + 1, \dots, J - 1, J$$

Allowed values of the magnetic moment in the z direction

$$\mu_z = m_j g_J \mu_B$$

Lande g factor \swarrow \nwarrow Bohr magneton

$$g_J \approx \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)}$$

1 H 1.008																	2 He 4.003																		
3 Li 6.941	4 Be 9.012	$l = 2$ $m_l = -2, -1, 0, 1, 2$										5 B 10.81	6 C 12.01	7 N 14.01	8 O 16	9 F 19	10 Ne 20.18																		
11 Na 22.99	12 Mg 24.31	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95	19 K 39.1	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52	25 Mn 54.94	26 Fe 55.85	27 Co 58.47	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.9	36 Kr 83.8										
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 190.2	78 Pt 195.1	79 Au 197	80 Hg 200.5	81 Tl 204.4	82 Pb 207.2	83 Bi 209	84 Po 210	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226	89 Ac 227	104 Rf 257	105 Db 260	106 Sg 263	107 Bh 262	108 Hs 265	109 Mt 266																											

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 147	62 Sm 150.4	63 Eu 152	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173	71 Lu 175
90 Th 232	91 Pa 231	92 U 238	93 Np 237	94 Pu 242	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 249	99 Es 254	100 Fm 253	101 Md 256	102 No 254	103 Lr 257

$$l = 3 \quad m_l = -3, -2, -1, 0, 1, 2, 3$$

$$\frac{\langle \psi_{Cu3d^{10}4s^1} | H | \psi_{Cu3d^{10}4s^1} \rangle}{\langle \psi_{Cu3d^{10}4s^1} | \psi_{Cu3d^{10}4s^1} \rangle} < \frac{\langle \psi_{Cu3d^94s^2} | H | \psi_{Cu3d^94s^2} \rangle}{\langle \psi_{Cu3d^94s^2} | \psi_{Cu3d^94s^2} \rangle}$$

Hund's rules (f - shell)

n	$l_z = 3, 2, 1, 0, -1, -2, -3$	S	$L = \sum l_z $	J
1	↓	1/2	3	5/2
2	↓ ↓	1	5	4
3	↓ ↓ ↓	3/2	6	9/2
4	↓ ↓ ↓ ↓	2	6	4
5	↓ ↓ ↓ ↓ ↓	5/2	5	5/2
6	↓ ↓ ↓ ↓ ↓ ↓	3	3	0
7	↓ ↓ ↓ ↓ ↓ ↓ ↓	7/2	0	7/2
8	↑↑ ↑ ↑ ↑ ↑ ↑	3	3	6
9	↑↑ ↑↑ ↑ ↑ ↑ ↑ ↑	5/2	5	15/2
10	↑↑ ↑↑ ↑↑ ↑ ↑ ↑ ↑ ↑	2	6	8
11	↑↑ ↑↑ ↑↑ ↓↓ ↑ ↑ ↑	3/2	6	15/2
12	↑↑ ↑↑ ↓↓ ↓↓ ↓↓ ↑ ↑	1	5	6
13	↑↑ ↓↓ ↓↓ ↓↓ ↓↓ ↓↓ ↑	1/2	3	7/2
14	↑↑ ↓↓ ↓↓ ↓↓ ↓↓ ↓↓ ↓↓ ↓	0	0	0

$J = |L - S|$

$J = L + S$

The half filled shell and completely filled shell have zero total angular mo.

Brillouin functions

Average value of the magnetic quantum number

$$\langle m_J \rangle = \frac{\sum_{-J}^J m_J e^{-E(m_J)/k_B T}}{\sum_{-J}^J e^{-E(m_J)/k_B T}} = \frac{\sum_{-J}^J m_J e^{m_J g_J \mu_B B / k_B T}}{\sum_{-J}^J e^{m_J g_J \mu_B B / k_B T}} = \frac{1}{Z} \frac{dZ}{dx}$$

Lande g factor

$$x = g_J \mu_B B / k_B T$$

Bohr magneton

$$Z = \sum_{-J}^J e^{m_J x} = \frac{\sinh\left(\left(2J+1\right)\frac{x}{2}\right)}{\sinh\left(\frac{x}{2}\right)}$$

Brillouin functions

Average value of the magnetic quantum number

$$\langle m_J \rangle = \frac{\sum_{-J}^J m_J e^{-E(m_J)/k_B T}}{\sum_{-J}^J e^{-E(m_J)/k_B T}} = \frac{\sum_{-J}^J m_J e^{m_J g_J \mu_B B / k_B T}}{\sum_{-J}^J e^{m_J g_J \mu_B B / k_B T}} = \frac{1}{Z} \frac{dZ}{dx}$$

Lande g factor

$$x = g_J \mu_B B / k_B T$$

Bohr magneton

$$Z = \sum_{-J}^J e^{m_J x} = e^{Jx} (1 + e^{-x} + e^{-2x} + \dots) - e^{-(J+1)x} (1 + e^{-x} + e^{-2x} + \dots)$$

$$= \frac{e^{Jx} - e^{-(J+1)x}}{1 - e^{-x}} = \frac{e^{-\frac{x}{2}} e^{(J+\frac{1}{2})x} - e^{-(J+\frac{1}{2})x}}{e^{-\frac{x}{2}} (e^{\frac{x}{2}} - e^{-\frac{x}{2}})} = \frac{\sinh\left(\left(2J + 1\right)\frac{x}{2}\right)}{\sinh\left(\frac{x}{2}\right)}$$

Brillouin functions

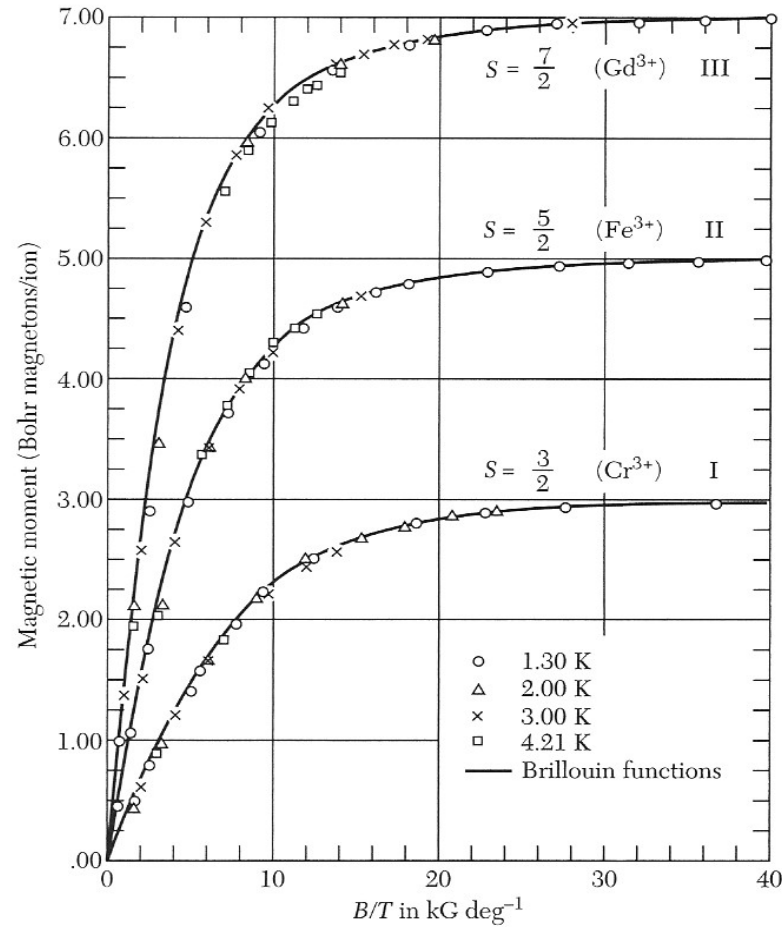
$$Z = \sum_{-J}^J e^{-m_J x} = \frac{\sinh\left(\left(2J+1\right)\frac{x}{2}\right)}{\sinh\left(\frac{x}{2}\right)}$$

$$M = ng_J \mu_B \langle m_J \rangle = ng_J \mu_B \frac{1}{Z} \frac{dZ}{dx}$$

Brillouin function

$$M = ng \mu_B J \left(\frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} \frac{g \mu_B JB}{k_B T}\right) - \frac{1}{2J} \coth\left(\frac{1}{2J} \frac{g \mu_B JB}{k_B T}\right) \right)$$

Paramagnetism



$$M = Ng\mu_B J \left(\frac{2J+1}{2J} \coth \left(\frac{2J+1}{2J} \frac{g\mu_B JB}{k_B T} \right) - \frac{1}{2J} \coth \left(\frac{1}{2J} \frac{g\mu_B JB}{k_B T} \right) \right)$$

Pauli paramagnetism

Paramagnetic contribution due to free electrons.

Electrons have an intrinsic magnetic moment μ_B .

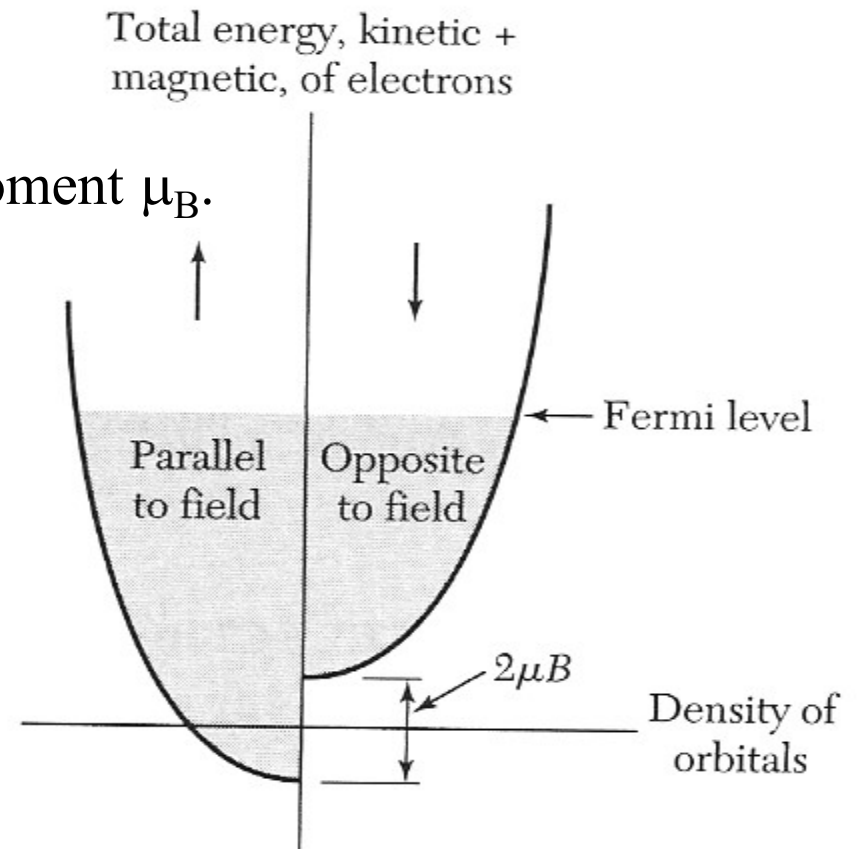
$$n_+ \approx \frac{1}{2}n + \frac{1}{2}\mu_B BD(E_F)$$

$$n_- \approx \frac{1}{2}n - \frac{1}{2}\mu_B BD(E_F)$$

$$M = \mu_B(n_+ - n_-)$$

$$M = \mu_B^2 D(E_F) B = \mu_0 \mu_B^2 D(E_F) H$$

$$\chi = \frac{dM}{dH} = \mu_0 \mu_B^2 D(E_F)$$



If E_F is 1 eV, a field of $B = 17000$ T is needed to align all of the spins.

Pauli paramagnetism is much smaller than the paramagnetism due to atomic moments and almost temperature independent because $D(E_F)$ doesn't change very much with temperature.

Quantum Mechanics: The Key to Understanding Magnetism

John H. van Vleck

