# 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).

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

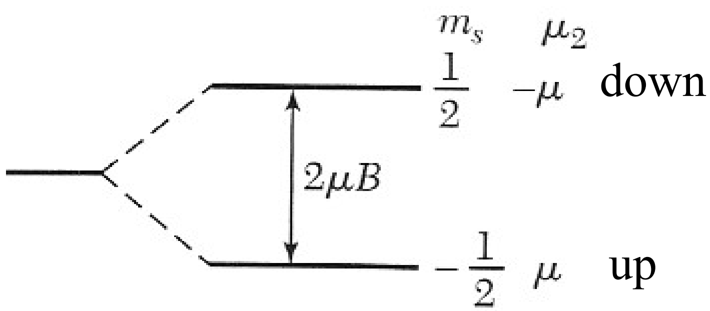
| **Paramagnetic susceptibility** | |
|---|---|
| Aluminum | $2.3\times10^{-5}$ |
| Calcium | $1.9\times10^{-5}$ |
| Magnesium | $1.2\times10^{-5}$ |
| Oxygen | $2.1\times10^{-6}$ |
| Platinum | $2.9\times10^{-4}$ |
| Tungsten | $6.8\times10^{-5}$ |

# Boltzmann factors

To take the average value of quantity *A*

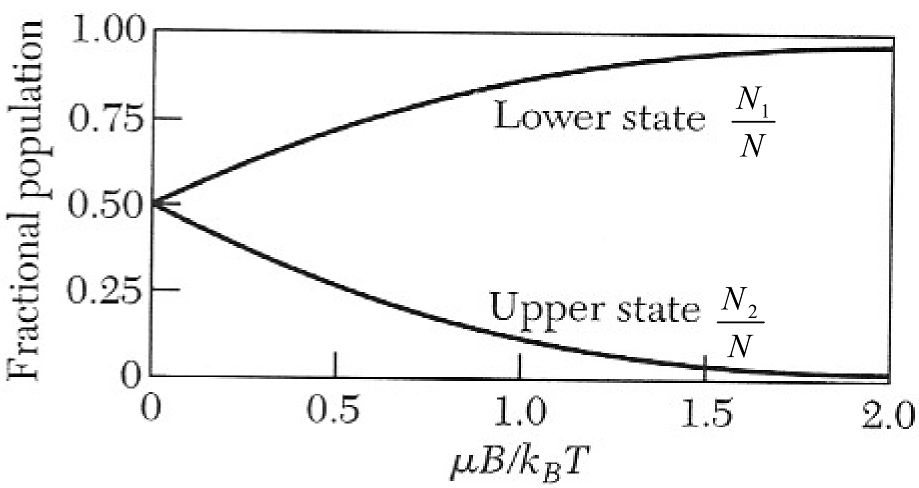
$$\langle A \rangle = \frac{\sum_i A_i e^{-E_i / k_B T}}{\sum_i e^{-E_i / k_B T}}$$

# Spin populations




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

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

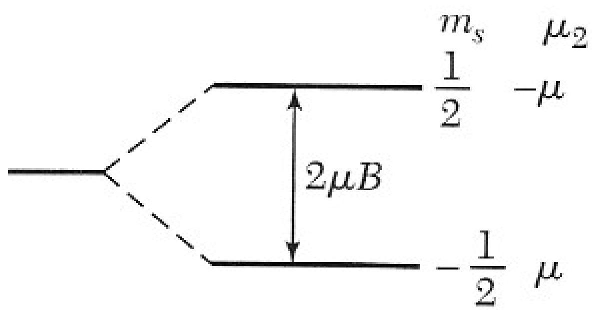



$$M = (N_1 - N_2)\mu / V$$

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

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

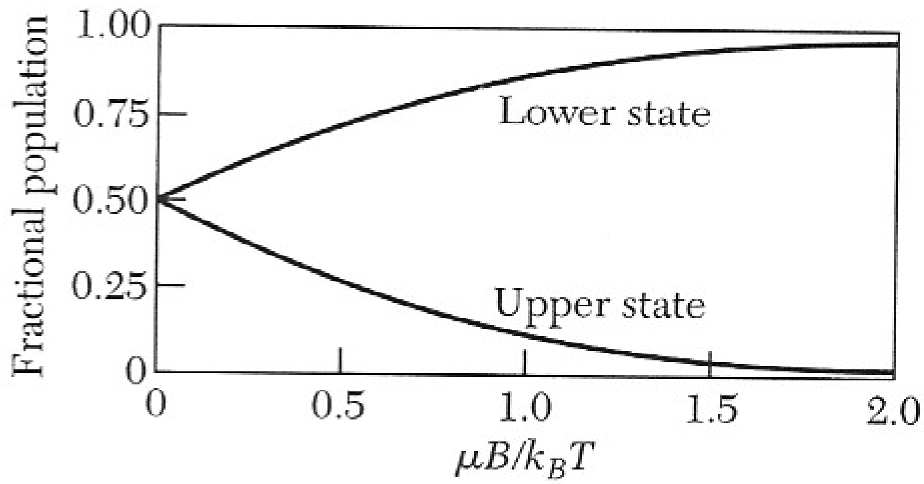
# Paramagnetism, spin 1/2

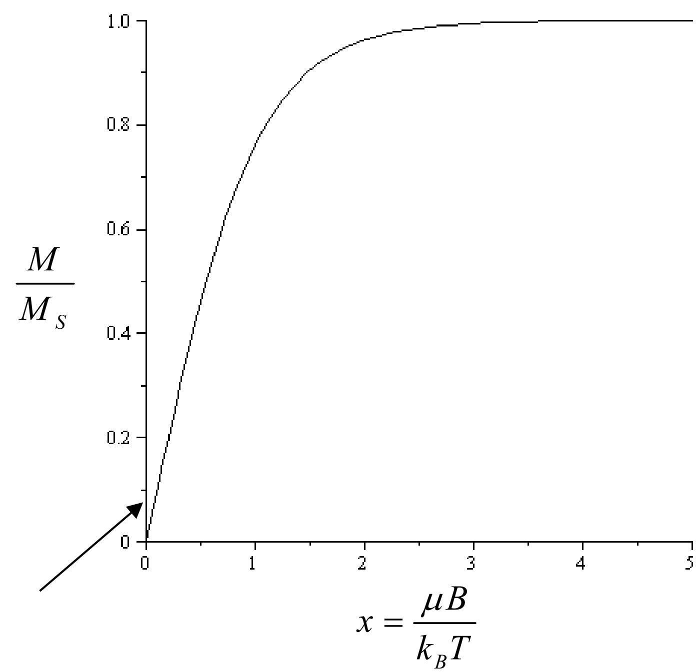



$$M = n\mu \tanh\left(\frac{\mu B}{k_B T}\right) \approx \frac{n\mu^2 B}{k_B T} = \frac{CB}{T}$$

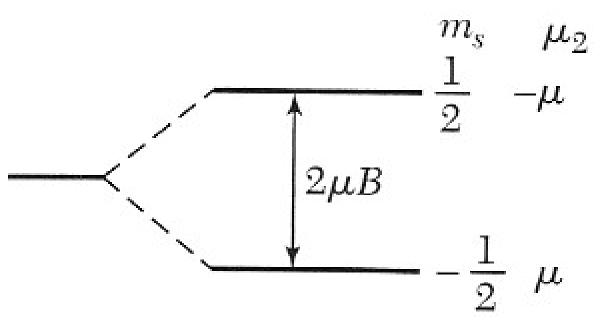
for $\mu B << k_B T$

Curie law



# Paramagnetism, spin 1/2

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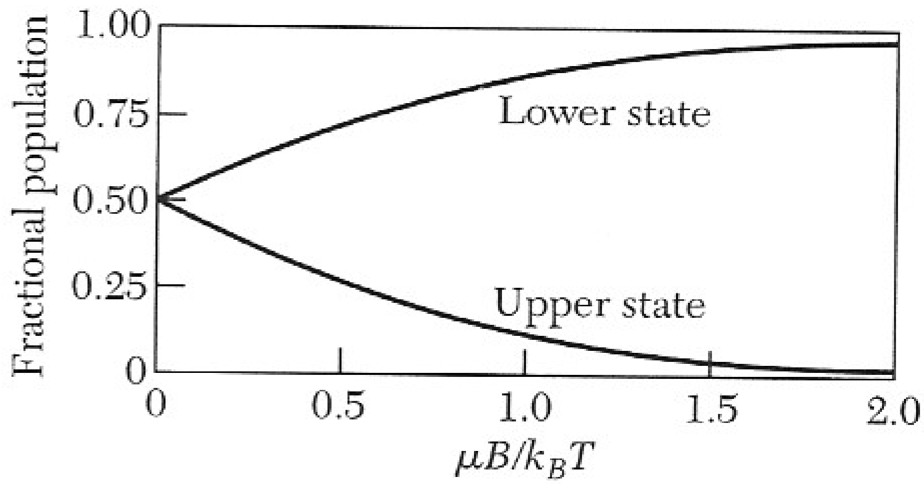
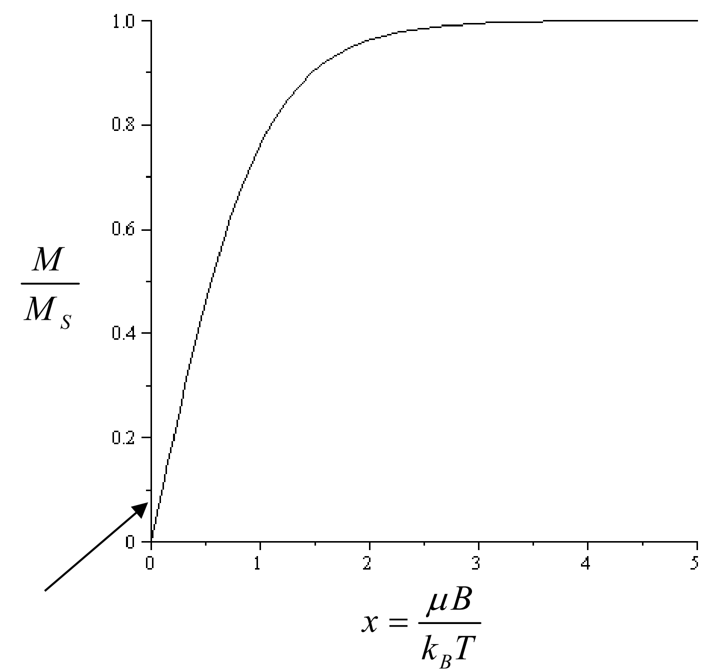


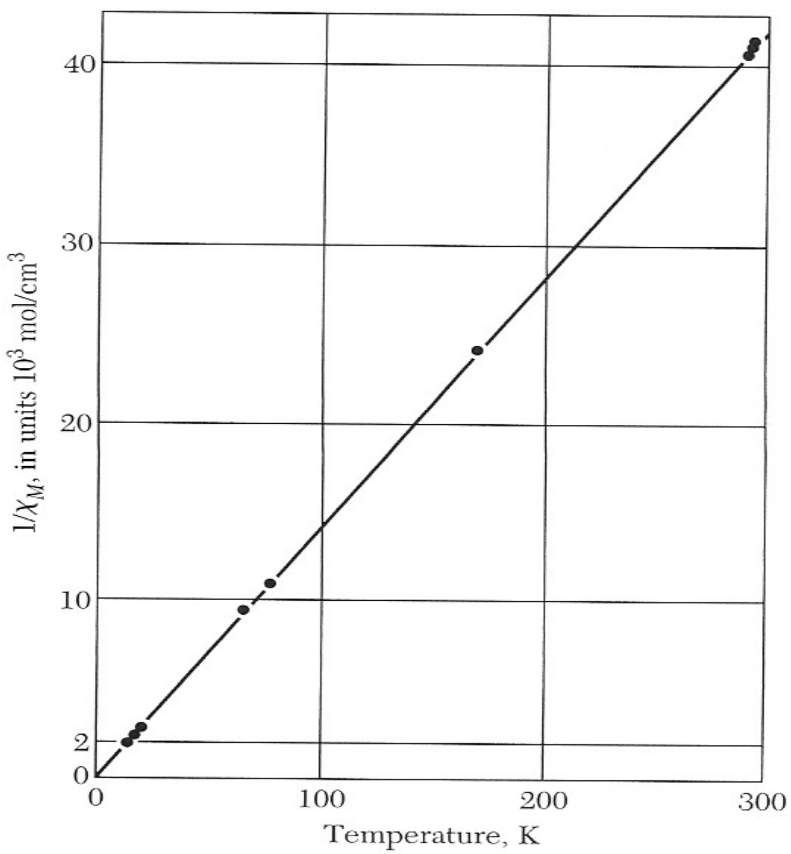
# Curie law

for $\mu B << k_B T \quad M = CB/T$

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

$C$ is the Curie constant

$Gd(C_2H_3SO_4)_3 9H_2O$



# 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

$J = L + S$ Orbital $L$ + spin $S$ angular momentum

Magnetic quantum number

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

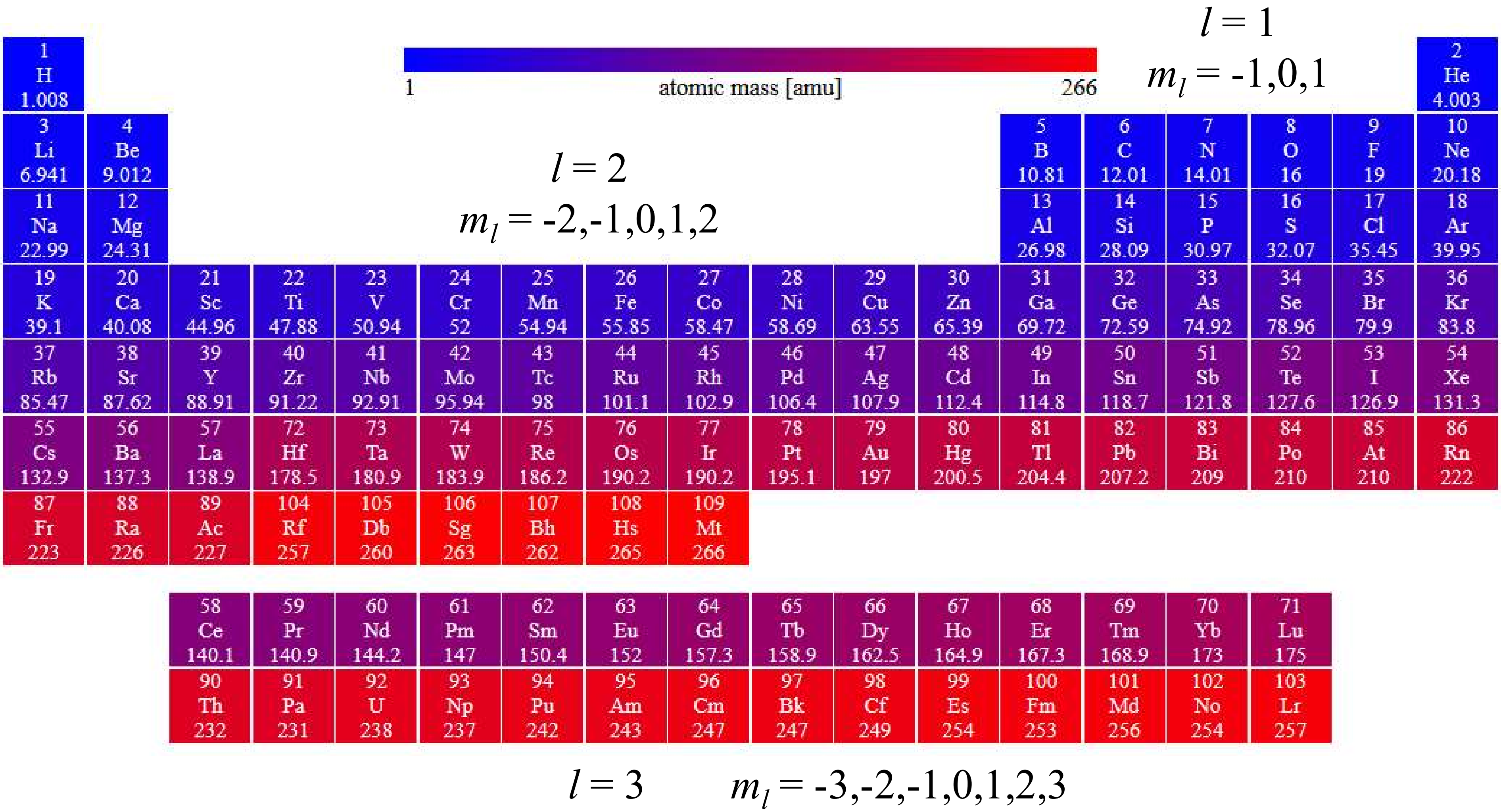
Allowed values of the magnetic moment in the z direction

$$\mu_Z = m_j g_J \mu_B$$

Lande $g$ factor → $g_J$

Bohr magneton → $\mu_B$

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




$$\frac{\left\langle \psi_{Cu3d^{10}4s^{1}} \middle| H \middle| \psi_{Cu3d^{10}4s^{1}} \right\rangle}{\left\langle \psi_{Cu3d^{10}4s^{1}} \middle| \psi_{Cu3d^{10}4s^{1}} \right\rangle} < \frac{\left\langle \psi_{Cu3d^{9}4s^{2}} \middle| H \middle| \psi_{Cu3d^{9}4s^{2}} \right\rangle}{\left\langle \psi_{Cu3d^{9}4s^{2}} \middle| \psi_{Cu3d^{9}4s^{2}} \right\rangle}$$

# Hund's rules (f - shell)

| $n$ | $l_z = 3$, | 2, | 1, | 0, | $-1$, | $-2$, | $-3$ | $S$ | $L = \lvert \Sigma l_z \rvert$ | $J$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ↓ | | | | | | | 1/2 | 3 | 5/2 | |
| 2 | ↓ | ↓ | | | | | | 1 | 5 | 4 | |
| 3 | ↓ | ↓ | ↓ | | | | | 3/2 | 6 | 9/2 | |
| 4 | ↓ | ↓ | ↓ | ↓ | | | | 2 | 6 | 4 | $J = \lvert L - S \rvert$ |
| 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 | $J = L + S$ |
| 12 | ⇵ | ⇵ | ⇵ | ⇵ | ⇵ | ↑ | ↑ | 1 | 5 | 6 | |
| 13 | ⇵ | ⇵ | ⇵ | ⇵ | ⇵ | ⇵ | ↑ | 1/2 | 3 | 7/2 | |
| 14 | ⇵ | ⇵ | ⇵ | ⇵ | ⇵ | ⇵ | ⇵ | 0 | 0 | 0 | |

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 → $g_J$

Bohr magneton → $\mu_B$

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

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

# Brillouin functions

Average value of the magnetic quantum number

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

Lande $g$ factor → $g_J$

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

Bohr magneton → $\mu_B$

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

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

# Brillouin functions

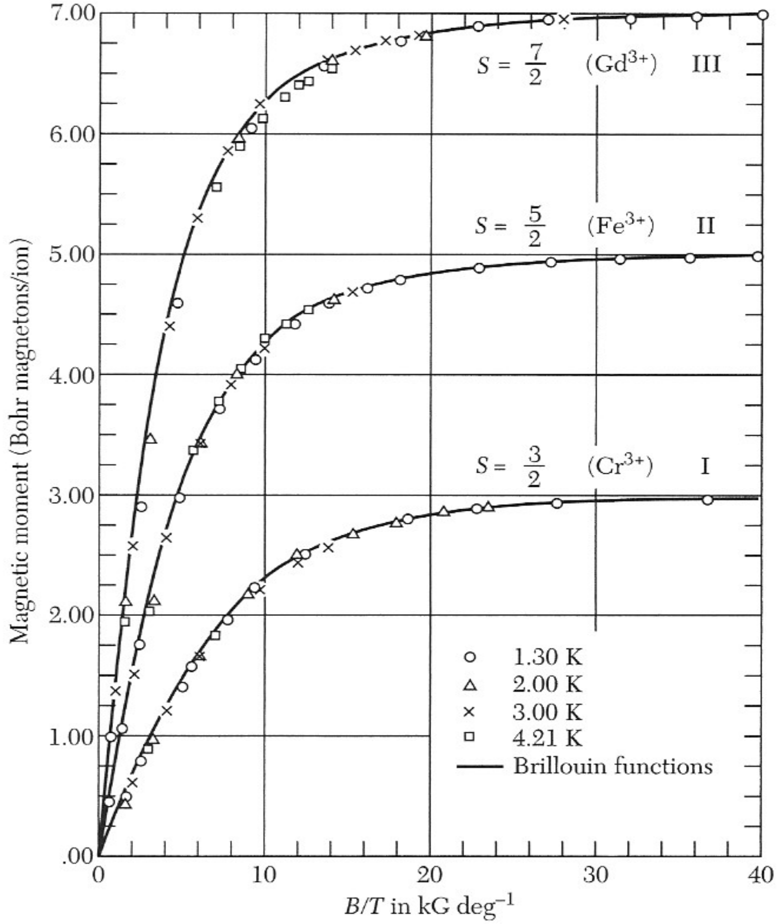
$$Z = \sum_{-J}^{J} e^{-m_J x} = \frac{\sinh\left(\left(2J+1\right)\frac{x}{2}\right)}{\sinh\left(\frac{x}{2}\right)}$$

$$M = n g_J \mu_B \left\langle m_J \right\rangle = n g_J \mu_B \frac{1}{Z}\frac{dZ}{dx}$$

Brillouin function

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

# Paramagnetism

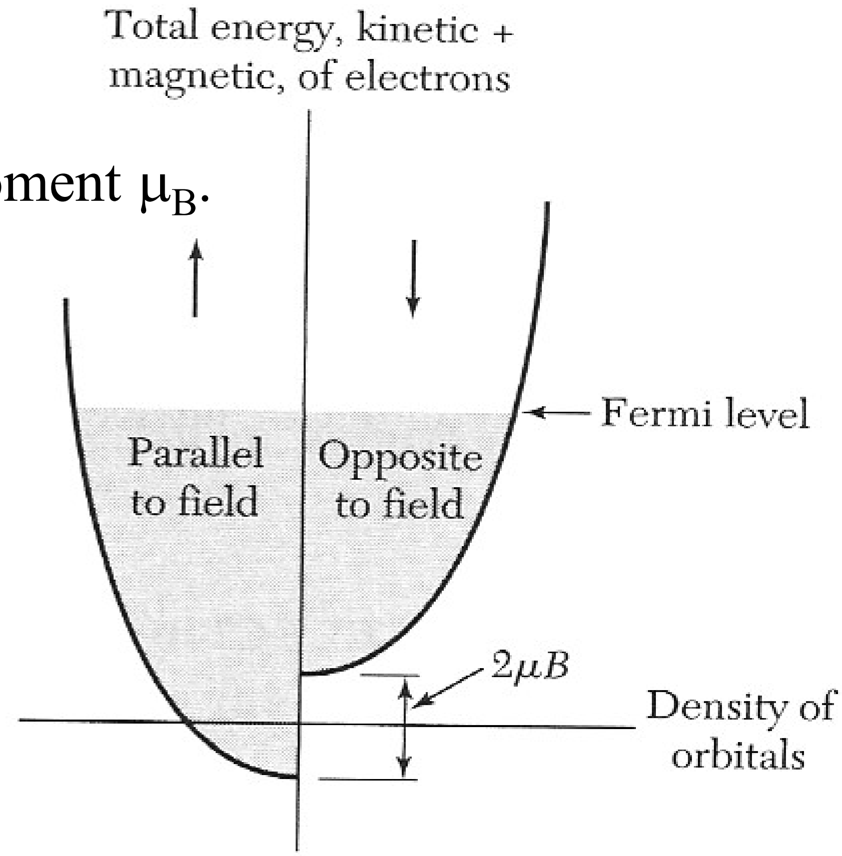



$$M = Ng\mu_B J\left(\frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}\frac{g\mu_B JB}{k_B T}\right)-\frac{1}{2J}\coth\left(\frac{1}{2J}\frac{g\mu_B JB}{k_B T}\right)\right)$$

# Pauli paramagnetism

Paramagnetic contribution due to free electrons.

Electrons have an intrinsic magnetic moment $\mu_B$.




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

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

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

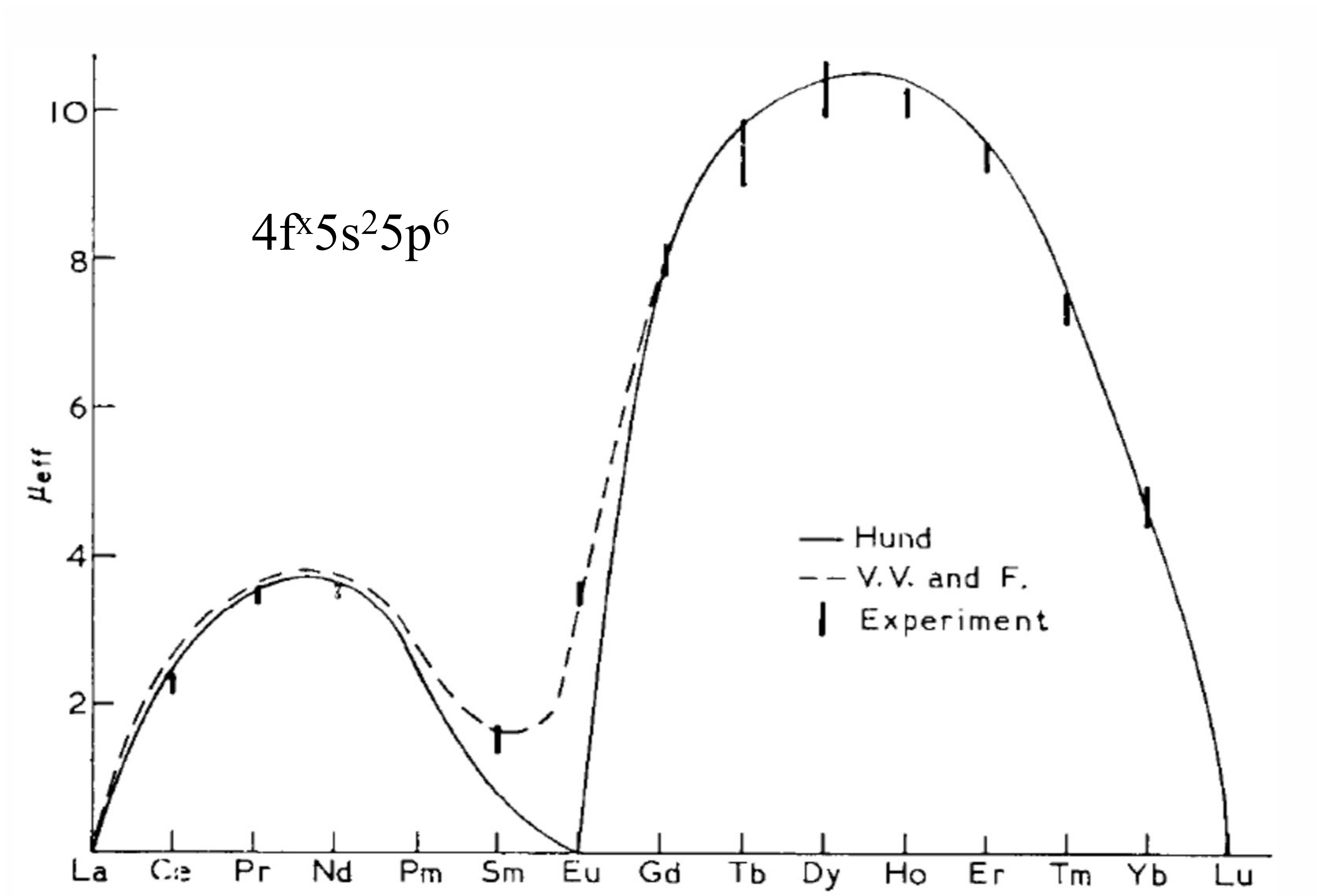
$$M = \mu_B^2 D(E_F) B = \mu_0 \mu_B^2 D(E_F) H$$

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

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

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