1. Lecture:
Basics of Magnetism:
Magnetic reponse

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Lecture overview

1. Lecture: Basic magnetostatic properties
2. Lecture: Paramagnetism
3. Lecture: Local magnetic moments

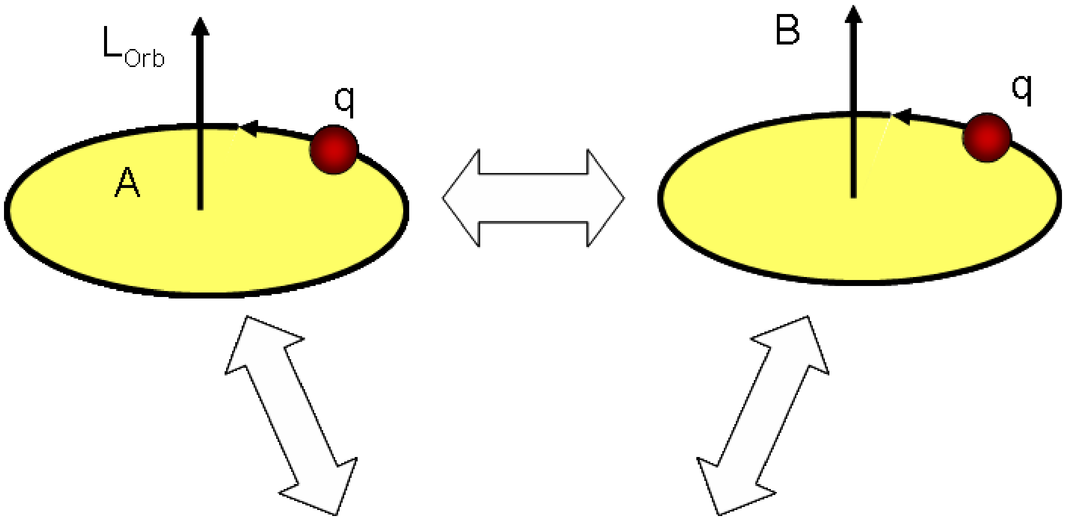
Content

1. Definitions
2. Electron in an external field
3. Diamagnetism
4. Paramagnetism: classical treatment of

1. Classical magnetic moments

Loop current has an angular momentum

Loop current generates a magnetic field



$$I = \frac{q}{T} = \frac{q\omega}{2\pi}$$

Magnetic dipole moment = current × enclosed area

$$|\vec{m}| = IA = \frac{q\omega}{2\pi} A = \frac{1}{2\pi}\frac{q}{m_e} m_e \pi r^2 \omega = \frac{1}{2}\frac{q}{m_e}\vec{L} = \gamma\,\vec{L}$$

γ = gyromagnetic ratio, m_e= electron mass

Torque and precession

Zeeman energy of magnetic moment in an external magnetic field:

$$E = -\vec{m}\cdot\vec{B}$$

Energy is minimized for m || B. B is the magnetic induction or the magnetic field density. Applying B, a torque is exerted on m:

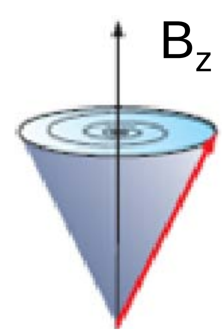
$$\vec{T} = \vec{m}\times\vec{B}$$

If m were just a dipole, such as the electric dipole, it would be turned into the field direction to minimize the energy. However, m is connected with an angular momentum, thus torque causes the dipole to precess:

$$\vec{T} = \frac{d\vec{L}}{dt} = \gamma\vec{L}\times\vec{B}$$

Assuming B = B_z, the precessional frequency is:

$$\omega_L = \gamma B_z$$



ω_L is called the *Lamor frequency*. See also EPR, FMR, MRI, etc.

Bohr magneton

An electron in the first Bohr orbit with a Bohr radius r_{Bohr} has the angular momentum:

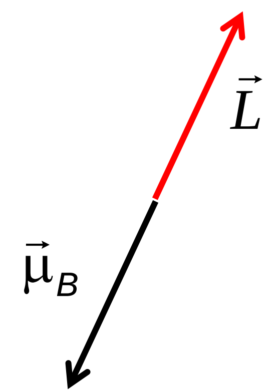
$$L = m_e r_{Bohr}^2 \omega = \hbar$$

Then magnetic moment is:

$$m_{Bohr} = \frac{1}{2}\frac{q}{m_e}L = -\frac{1}{2}\frac{e}{m_e}\hbar = -\mu_B$$

Because of negative charge, $\underline{L}$ and $\underline{m}$ are opposite.

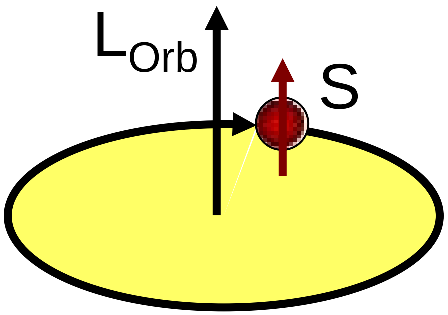
$$\mu_B = \frac{1}{2}\frac{e}{m_e}\hbar = \gamma\hbar$$



μ_B is the Bohr magneton. $[\mu_B] = 9.274 \times 10^{-24}\ \mathrm{Am}^2$.

Magnetic moment: $[m] = \mathrm{A\ m}^2$

Electron spin



Spin S of the electon contributes to the magnetic moment:

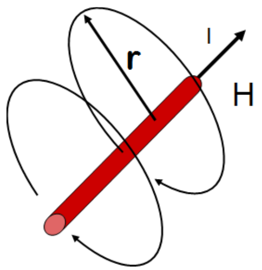
$$\vec{m}_{spin} = \frac{q}{m_e}\vec{S}$$

The missing factor ½ is of quantum mechanical origin and will be discussed later.

Including orbital and spin contributions, the magnetic moment of an electron is:

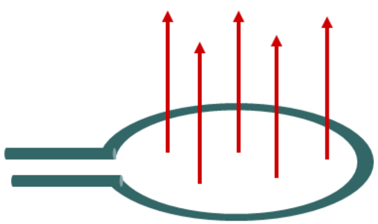
$$\vec{m} = \frac{1}{2}\frac{q}{m_e}(\vec{L} + 2\vec{S}) = -\gamma(\vec{L} + 2\vec{S})$$

Magnetic field and magnetic induction



Oersted field *H* due to *dc* current:

$$H = \frac{I}{2\pi r}$$



Any time variation of the magnetic flux $\Phi = BA$ through the loop causes an induced voltage:

$$U_{ind} = -\frac{d}{dt}\left(\vec{B}\cdot\vec{A}\right)$$

Therefore *B* is called the magnetic induction or the magnetic flux density $B = \Phi/A$.
In vacuum both quantities are connected via the permeability of the vacuum:

$$B = \mu_0 H$$

$$\boxed{\mu_0 = 4\pi\ 10^{-7}\ \frac{\mathrm{V\cdot s}}{\mathrm{A\cdot m}}}$$

$$\boxed{[B] = [\mu_0]\cdot\left[\frac{I}{2\pi r}\right] = \frac{\mathrm{V\cdot s}}{\mathrm{A\cdot m}}\times\frac{\mathrm{A}}{\mathrm{m}} = \frac{\mathrm{V\cdot s}}{\mathrm{m}^2} = \mathrm{T}}$$

$$\boxed{1\ \frac{\mathrm{V\cdot s}}{\mathrm{m}^2} = 1\ \mathrm{T} = 10^4\ \mathrm{G}}$$

Definitions

1. Magnetization is the sum over all magnetic moments in a volume element normalized by the volume element:

$$\vec{M} = \frac{1}{V}\sum_i \vec{m}_i$$

2. Thermal average of the magnetization:

$$\langle \vec{M} \rangle = \frac{N}{V}\langle \vec{m} \rangle$$

3. Magnetic susceptibility:

$$\vec{M} = \chi_{mag}\vec{H}, \quad \chi_{mag} = \frac{\partial |M|}{\partial H}$$

4. Magnetic Induction: .

$$\vec{B} = \mu_0\left(\vec{H} + \vec{M}\right) = \mu_0\vec{H}(1 + \chi_{mag}) = \mu_0\mu_r\,\vec{H} = \mu\vec{H}$$

H = magnetic field, usually externally applied by a magnet.

μ_0 = magnetic permeability of the vacuum.

μ_r = relative magnetic permeability $\mu_r = (1+\chi)$ (tensor, or a number for collinearity)

Potential Energy and Derivatives

Potential energy (Zeeman – term):

$$E_{Zeeman} = -\vec{m} \cdot \vec{B}$$

1. Derivative $\rightarrow$ magnetic moment:

$$|m| = -\frac{\partial E_{Zeeman}}{\partial B}$$

2. Derivative $\rightarrow$ Susceptibility:

$$\chi_{mag} = \frac{\partial |M|}{\partial H} = -\mu_0 \frac{N}{V} \frac{\partial^2 E_{Zeeman}}{\partial B^2}$$

The susceptibility is the response f

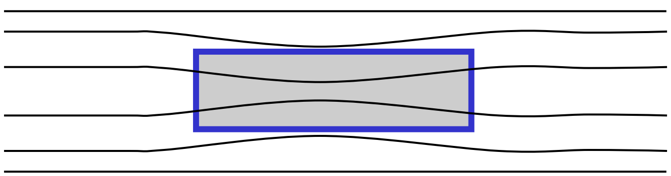
What is more fundamental, H or B?

Lorentz force:	$\vec{F} = q\left(\vec{v} \times \vec{B}\right)$	$[F] = N$
Zeeman energy:	$E = -\vec{m} \bullet \vec{B}$	$[E] = J = VAs = Ws$
Vector potential:	$\vec{B} = \nabla \times \vec{A}$	$[B] = T = Vs/m^2$
Oersted field:	$H = \dfrac{I}{2\pi r}$	$[H] = A/m$
Magnetization:	$M = \chi H$	$[M] = A/m$

Classification

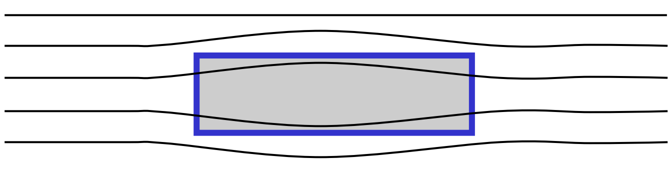
Application of an external field:

a. Paramagnetism: $\chi > 0$ und $\mu_r > 1$



Magnetic moments align parallel to external field, field lines are more dense in the material than in vacuum.

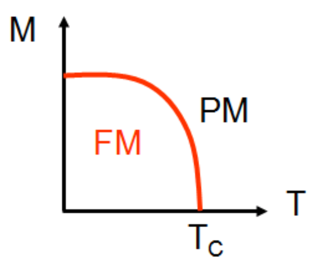
b. Diamagnetism: $\chi < 0$ und $\mu_r < 1$



External field is weakend by inducing screening currents according to Lenz rule. Field lines are less dense than in vacuum.

Ideal diagmagnetism, realized in superconductors with ***M*** and ***B*** antiparallel, for $\chi = -1$ and $\mu_r = 0$.

c. Ferromagnetism:



Spontaneous Magnetization without external field due to the interaction of magnetic moments

μ_r attaines very high values for ferromagnets, $> 10^4$-10^5

2. Electron in an external field

Consider a non-relativistic Hamilton operator for electrons in an external magnetic field:

$$\mathrm{H} = \frac{1}{2m_e}\left(\vec{p} + q\vec{A}\right)^2$$

The vector potential: $\vec{A}$ is defined by the Coulomb gauge: $\vec{B} = \nabla \times \vec{A}$
and using

$$\vec{B} = \left(0,0,B_z\right)$$

$$\mathrm{H} = \underbrace{\frac{p^2}{2m_e}}_{\substack{\text{kinetic}\\ \text{energy}}} + \underbrace{\mu_B B_z L_z}_{\substack{\text{paramagnetism}\\ \text{orbital}\\ \sim B_z}}{}^{*} + \underbrace{\frac{e^2}{12m_e} B_z^2 \left\langle a^2 \right\rangle}_{\substack{\text{diamagnetism}\\ \sim B_z^2}}$$

*L_z is here a dimensionless quantum number

Where we assumed an average over the electron orbit perpendicular to the magnetic field:

$$\left\langle x^2 \right\rangle + \left\langle y^2 \right\rangle = \frac{2}{3}\left\langle a^2 \right\rangle$$

Hamiltonian for electron with spin

Considering the electron spin in the external field with a Zeeman energy:

$$E_{Zeeman} = -\vec{m}_s \cdot \vec{B} = -g_s \mu_B \vec{S} \cdot \vec{B} = \frac{e\hbar}{m} \vec{S} \cdot \vec{B}$$

Landé factor $\quad g_s = 2$

Bohr magneton $\quad \mu_B = -\frac{e\hbar}{2m} = 9.27 \times 10^{-24}\, Am^2$

Hamilton operator for spin and orbital contributions of a single bond electron then is:

$$\mathrm{H} = \underbrace{\frac{p^2}{2m_e}}_{\substack{\text{kinetic}\\ \text{energy}}} + \underbrace{\mu_B B_z \left(L_z + 2S_z\right)}_{\substack{\text{paramagnetism}\\ \text{spin} + \text{orbital}\\ \sim B_z}} + \underbrace{\frac{e^2}{12m_e} B_z^2 \left\langle a^2 \right\rangle}_{\substack{\text{diamagnetism}\\ \sim B_z^2}}$$

The g_S=2 for the electron is put into the Schrödinger equation by „hand“ but would occur naturally using the Dirac equation. The exact value of 2.0023 is determined by QED.

Response functions

	1. derivative	2. derivative
	$\left\lvert \vec{m} \right\rvert = -\dfrac{\partial\, \mathrm{H}}{\partial\, B_z}$	$\chi_{mag} = -\mu_0 \dfrac{N}{V} \dfrac{\partial^{\,2}\mathrm{H}}{\partial\, B_z^2}$
Diamagnetic response for Z electrons	$\dfrac{Ze^2}{6m_e}\left\langle a^2 \right\rangle B_z$	$-\mu_0 \dfrac{Ze^2}{6m_e}\left\langle a^2 \right\rangle$
Paramagnetic response	$\mu_B \left(L_z + 2S_z \right) > 0$	$0*$

*For single atom we can not define a paramagnetic susceptibility. This is only possible for an ensemble of atoms.

3. Properties of the Langevin diamagnetism

With *Z* electrons in an atom and an effective radius of <a>

$$\boxed{\chi_{Langevin} = -\mu_0 \frac{N}{V}\frac{e^2}{6m_e}\sum_i \left\langle r_i^2 \right\rangle = -\mu_0 \frac{N}{V}\frac{Ze^2}{6m_e}\left\langle a^2 \right\rangle}$$

- $\chi_{Langevin}$ is constant, independent of field strength;
- $\chi_{Langevin}$ is induced by external field;
- $\chi_{Langevin}$ < 0, according to Lenz‘ rule;
- $\chi_{Langevin}$ is alway present, but mostly covered by bigger and positive paramagnetic contribution;
- $\chi_{Langevin}$ the only contribution to magnetism for empty or filled electron orbits;
- $\chi_{Langevin}$ yiels $\langle a \rangle$ and the symmetry of the electron distribution;
- $\chi_{Langevin}$ is proportional to the area of an atom perpendicular to the field direction, important for chemistry;
- $\chi_{Langevin}$ is temperature independent.

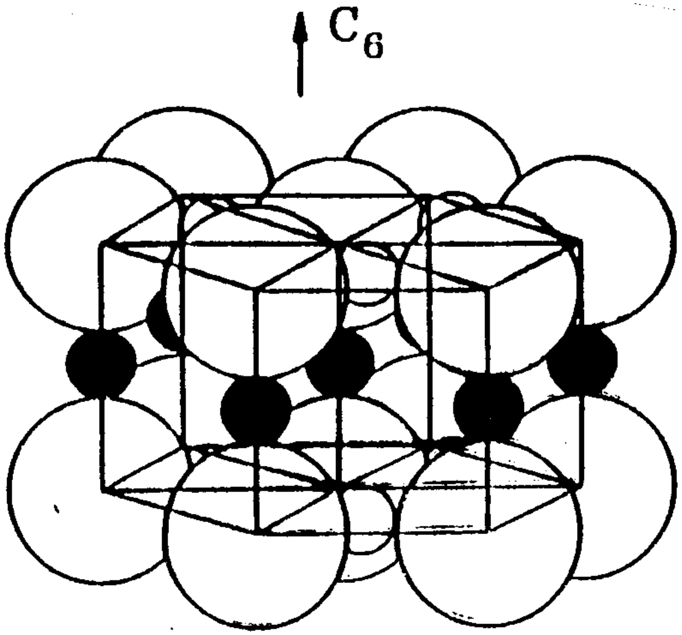
Examples for Diamagnetism

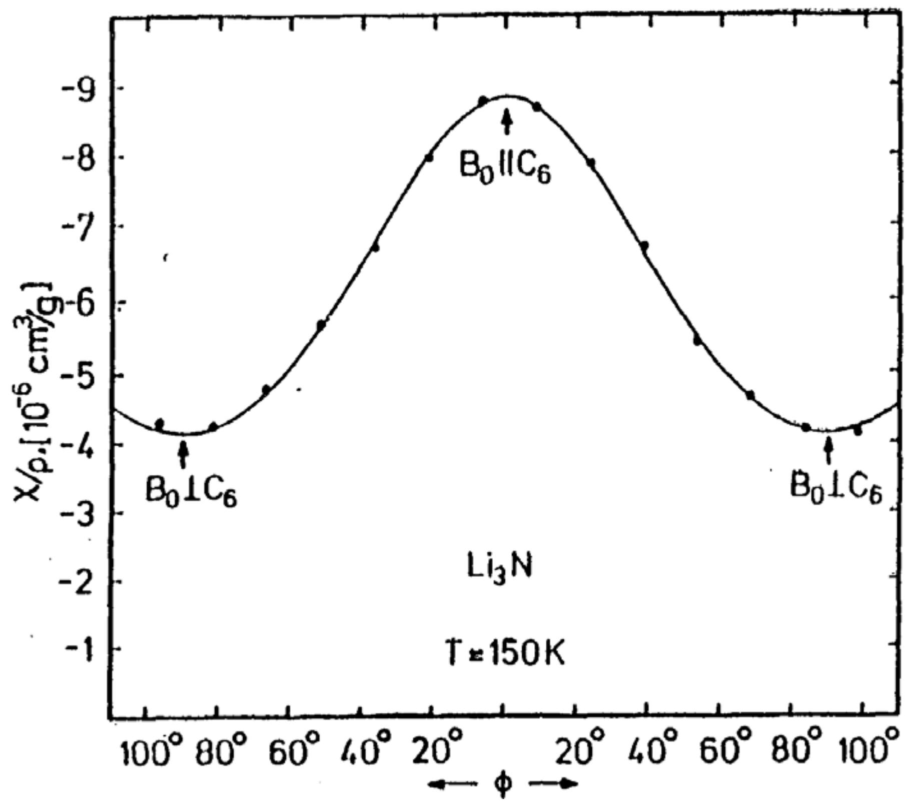
Material	χ_{Langevin} **at RT**
He	$-1.9 \cdot 10^{-6} cm^3/mol$
Xe	$-43 \cdot 10^{-6} cm^3/mol$
Bi	$-16 \cdot 10^{-6} cm^3/g$
Cu	$-1.06 \cdot 10^{-6} cm^3/g$
Ag	$-2.2 \cdot 10^{-6} cm^3/g$
Au	$-1.8 \cdot 10^{-6} cm^3/g$

(χ is normalized to the magnetization of 1 cm^3 containing one 1 Mol of gas at 1 Oe)

- All noble metals and noble gases are diamagnetic. In case of the nobel metals Ag, Au, Cu mainly the d-electrons contribute to the diamagnetism.
- In 3d transition metals the diamagnetismus is usually exceeded by the much bigger paramagnetic response.

Anisotropy of diamagnetismus for Li_3N



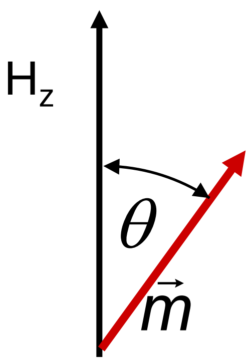


Levitation of diamagnetic materials

4. Paramagnetism of free local moments: classical treatment

(free = without interactions)

Orientation of permanent and isolated magentic moments in an external field $B_z = \mu_0 H_z$ parallel to the z-axis (orientational polarization)

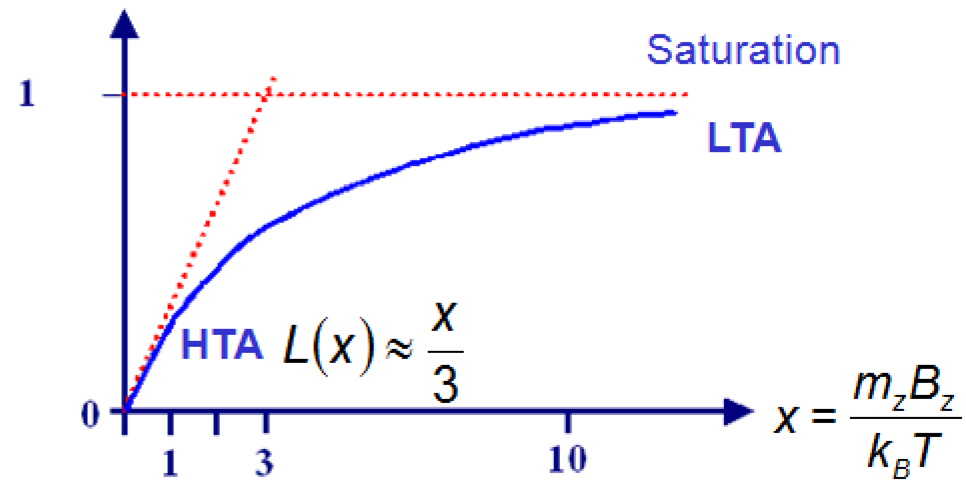


$$\langle M \rangle = \frac{N}{V} m \, \langle \cos(\theta) \rangle$$

$$= \frac{N}{V} m_z L\left(\frac{m_z H_z}{k_B T}\right)$$

$$\underbrace{\approx}_{Hohe-T} \frac{N}{V} \frac{m_z^2 H_z}{3 k_B T}$$

$$L(x) = L\left(\frac{m_z B_z}{k_B T}\right)$$



$$L(x) = coth(x) - \frac{1}{x}$$

Langevin function

Langevin function

$$\langle \cos\theta \rangle = \frac{\int \cos\theta e^{\frac{E_{pot}(\theta)}{k_B T}} d\Omega}{\int e^{\frac{E_{pot}(\theta)}{k_B T}} d\Omega} = \frac{\int_0^{\pi} 2\pi \sin\theta \cos\theta\, e^{\frac{mB\cos\theta}{k_B T}} d\theta}{\int_0^{\pi} 2\pi \sin\theta\, e^{\frac{mB\cos\theta}{k_B T}} d\theta}$$

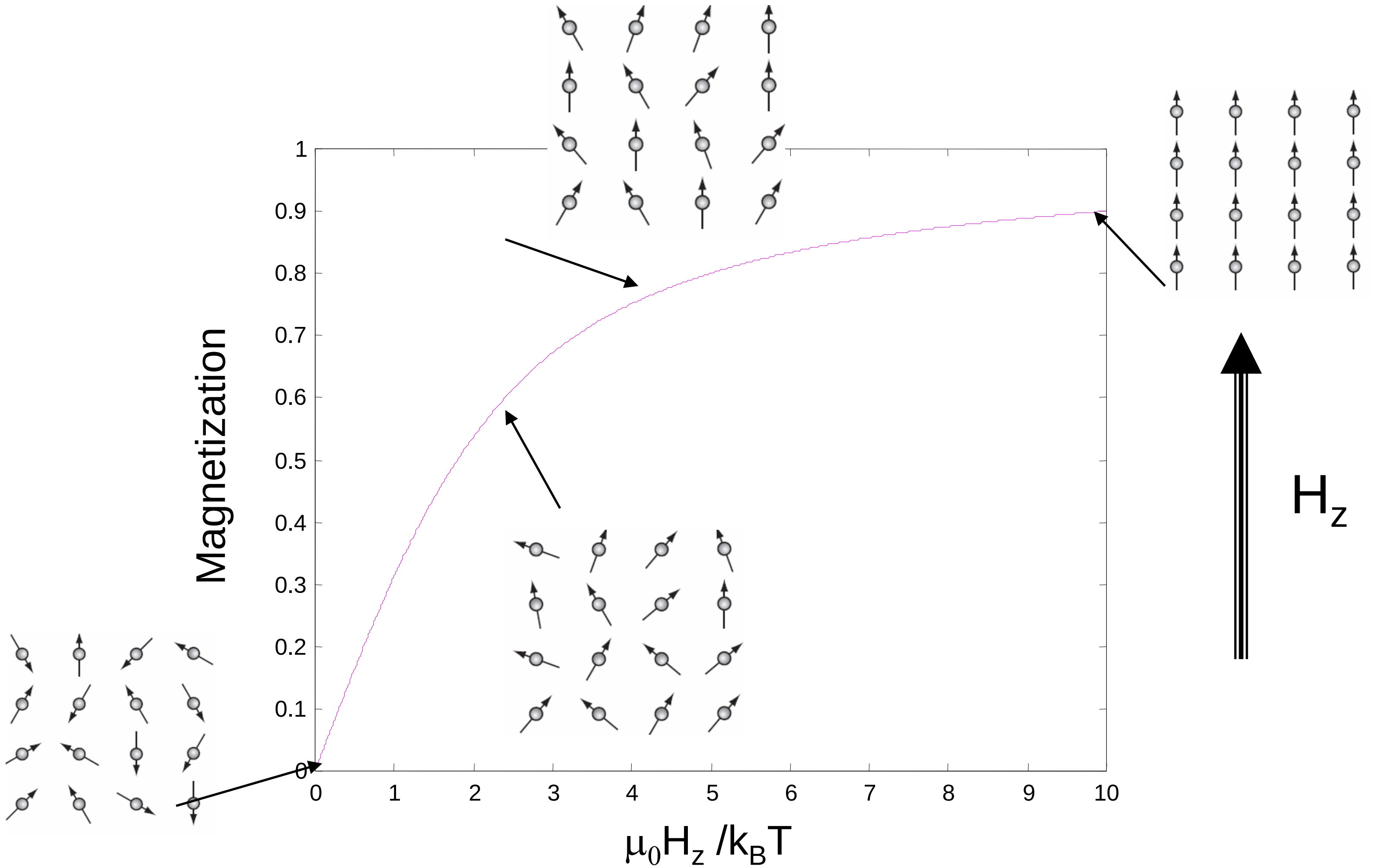
using $d\Omega = \sin\theta d\theta d\phi = 2\pi \sin\theta d\theta$ $\quad s = \cos\theta$ $\quad x = \frac{\mu B_0}{k_B T}$

$$\langle \cos\theta \rangle = \frac{\int_{-1}^{1} s e^{sx} ds}{\int_{-1}^{1} e^{sx} ds} = \frac{d}{dx} \ln \int_{-1}^{1} e^{sx} ds = \coth(x) - \frac{1}{x} \equiv L(x)$$

$$\boxed{M = N_0\, \mu\, L\left(\frac{m_z B_0}{k_B T}\right)}$$

L(x): Langevin-Funktion

Magnetization of paramagnetic moments in an external field



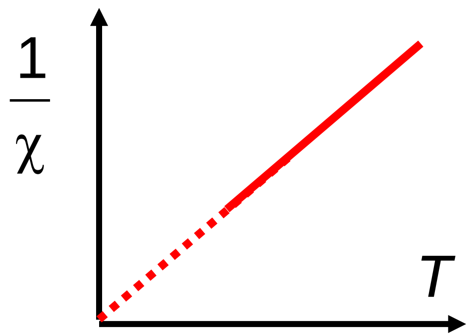
Paramagnetic Susceptibility

Curie-Suszeptibilität χ_{Curie} in HTA with the Curie-constant C:

$$\chi_{Curie} = \frac{\partial \langle M \rangle}{\partial H_z} = \frac{N}{V}\frac{\mu_0 m_z^2}{3k_B T} = \frac{C}{T}$$

$$\boxed{C = \frac{N}{V}\frac{\mu_0 m_z^2}{3k_B}}$$

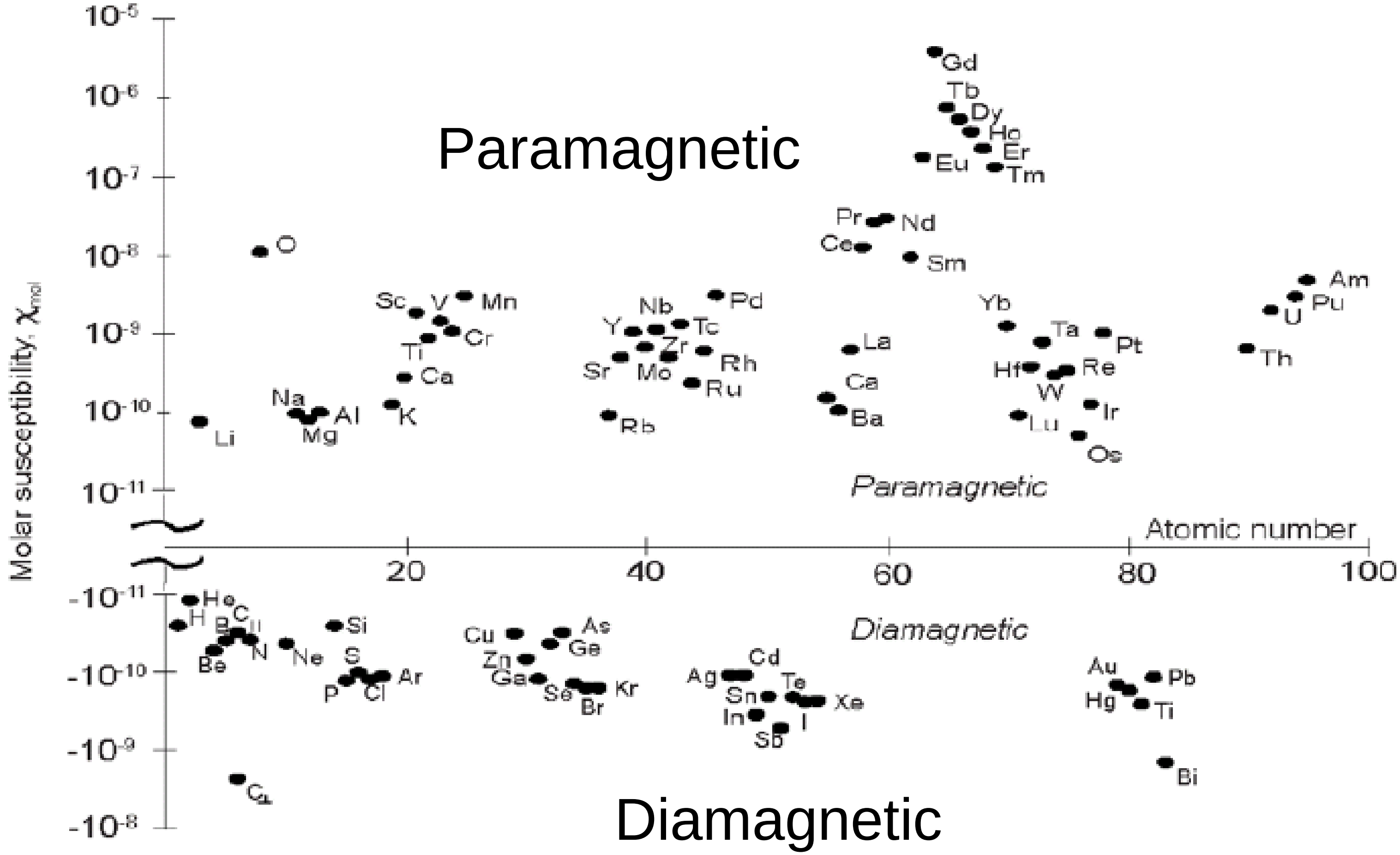
Magnetic moment: $m_z = \mu_B (L_z + 2S_z)$



Linear dependence fullfilled at high temperatures. At low T often deviations observed due to interactions.

But: However, magnetism is not a classical problem, thus Langevin function is only a rough approximation. As quantum mechanics allows only discrete values for the z-component of the magnetic moments, a different approach has to be chosen $\Rightarrow$ **Brillouin function** replaces the Langevin function. –
The susceptibility of **superparamagnetic particles** containing a macrospin can be treated classically as the spin orientation of nanoparticles in the field is continuous.

Susceptibility of the Elements



From J.M.D. Coey

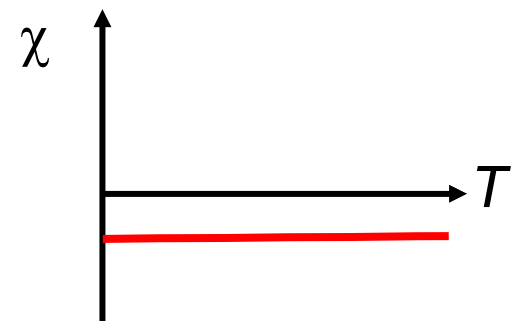
Summary

1. Hamilton operator for an electron in an external field:

$$\mathrm{H} = \underbrace{\frac{p^2}{2m_e}}_{\substack{\text{kinetic}\\ \text{energy}}} + \underbrace{\mu_B B_z\left(L_z + 2S_z\right)}_{\substack{\text{paramagnetism}\\ \text{spin + orbital}\\ \sim B_z}} + \underbrace{\frac{e^2}{12m_e} B_z^2 \left\langle a^2 \right\rangle}_{\substack{\text{diamagnetism}\\ \sim B_z^2}}$$

2. Diamagnetic response:

$$\boxed{\chi_{Langevin}^{diamagnetic} = -\mu_0 \frac{N}{V} \frac{Ze^2}{6m_e} \left\langle a^2 \right\rangle}$$



3. Paramagnetic response (HTA):

$$\boxed{\chi_{Curie}^{paramagnetic} = \frac{N}{V} \frac{\mu_0 m_z^2}{3k_B T}}$$