Magnetic Resonance Spectroscopies

NMR nuclear magnetic resonance

ESR electron spin resonance

EPR electron paramagnetic resonance

Classical Physics
Newton Laws

The motion of a pointlike particle with reference to appropriate coordinates, given the initial speed (**v**) and position (**r**), is described by the Newton's Laws

I

$$\vec{v} = \frac{d\vec{r}}{dt} = \dot{r}$$

II

$$\vec{F} = \mathrm{m}\frac{d\vec{v}}{dt} = \dot{p}$$

m particle's mass

moment $\vec{p} = \mathrm{m}\vec{v}$

Corio

In some instances, the particle's motion is better described by the torque Γ (capital gamma) (moment of the force) and by the angular moment **l** (moment of the linear moment).

$$\vec{\Gamma} = \vec{r} \wedge \vec{F}$$

$$\vec{l} = \vec{r} \wedge \vec{p} = \vec{r} \wedge m\vec{v}$$

$$\vec{v} = \vec{\omega} \wedge \vec{r}$$

ω: angular frequency

$$\vec{l} = mr^2\vec{\omega}$$

$\boldsymbol{\omega}$ and **l** are collinear

In analogy with **F**, which changes the linear moment and is the time derivative of the linear moment, $\boldsymbol{\Gamma}$ is the time derivative of the angular moments and changes it, **l**.

Conservation of the angular moment

If $\boldsymbol{\Gamma}$= 0, **l** is a constant of motion, i.e. it is constant in time since its time derivative is zero.

$$\vec{\Gamma} = \frac{d\vec{l}}{dt}$$

The last equation is obtained from the previous ones as follows:

$$\frac{d\vec{l}}{dt} = \frac{d(\vec{r} \wedge m\vec{v})}{dt}$$

on the basis of the rules for the derivative of a product

$$\frac{d\vec{l}}{dt} = \vec{v} \wedge m\vec{v} + \vec{r} \wedge \vec{F}$$

since in classical physics the self-vector product is zero

$$\frac{d\vec{l}}{dt} = \vec{\Gamma}$$

- As Γ is the vector product **r** x **F**, it is perpendicular to the instantaneous plane defined by the the vectors

- analogously, **l** is perpendicular to the plane of the vectors **r** e **v**

Magnetic Field: definition

The magnetic field is defined by means of the force that acts on a moving charged particle

$$\vec{F} = q\vec{E} + q\vec{v} \wedge \vec{B}$$

Lorentz Force

F is orthogonal both to **B** and **v**. Thus a particle possessing initial speed **v** is not traveling at uniform speed in a uniform field **B**. The module, |v|, is constant and the particle experiences a force **F**, with constant modulus, and always perpendicular both to **B** and to the direction of the particle’s motion. The particle is moving in a plane perpendicular to **B**.

Magnetic Induction
Magnetic Flux Density

- are the proper names for B
- In the SI the measurement unit is Tesla
- $T = NC^{-1}m^{-1}s = NA^{-1}m^{-1} =$
- $(Kg\ m\ s^{-2}\ A^{-1}m^{-1}) = Kg\ s^{-2}\ A^{-1} =$
- $(CVm^{-1}C^{-1}m^{-1}s) = Vsm^{-2} =$
- $JA^{-1}m^{-2} = Wb\ m^{-2}$
- In the CGS system the measurement unit is Gauss

$$1\ T = 10^4\ G$$

Magnetic Flux Φ

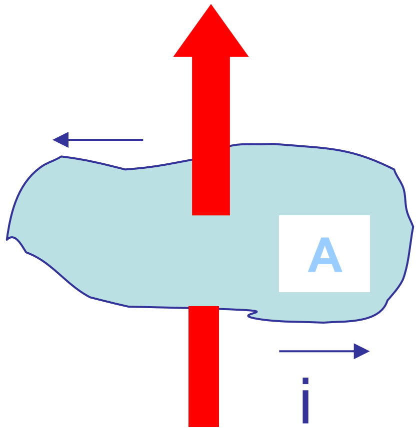
- The Weber is its SI measurement unit
- Wb= Vs= Tm^2

Earth Magnetic Field

The intensity of earth magnetic field in proximity to the surface is 0.5 G= 0.5 mT

Ampere’s Law

magnetic dipole



All loops with the same current-area product originate, at distance, equally intense magnetic dipole moments

$$\vec{\mu}=i\vec{A}$$

for a solenoid with n loops $\vec{\mu}=ni\vec{A}$

μ is a vector, the **magnetic dipole moment**

Magnetic Dipole Moment μ

- The direction of μ coincides with the coil normal, i.e. with that of the A vector, the area of the coil.
- The positive sense of μ and the one of the corrent must fulfil the right hand rule

For a charge q circulating at speed v in a round coil with radius r

$$i = \frac{qv}{2\pi r} = \frac{qp}{2\pi rm}$$

A= πr^2

$$\mu = \frac{q}{2m} pr = \frac{q}{2m} l$$

q/2m is the ratio between the magnetic and the angular moments (magnetogiric ratio)

γ

For the **electron** in the conventional electromagnetic theory

$$\gamma_e = -\frac{e}{2m_e}$$

thus, considering the z component of the orbital angular moment

$$\mu_z = -\frac{e}{2m_e} m_l \eta$$

$$\mu_z = -\mu_B m_l$$

$$\mu_B = -\frac{e\eta}{2m_e} = 9.274 \cdot 10^{-24} JT^{-1}$$

Bohr magneton

For a **spin angular moment**

$$\mu_z = g_e\left(-\frac{e}{2m_e} m_s \eta\right) = g_e \mu_B m_S$$

g_e is the g factor of the electron, from the Dirac equation

g_e= 2.0023 for the free electron

For nuclei it is more convenient to use the giromagnetic ratios, specific for each nucleus

$$\gamma_I = \frac{g_I \mu_N}{\eta}$$

γ_I and g_I depend of the specific isotopic nucleus

nuclear magneton

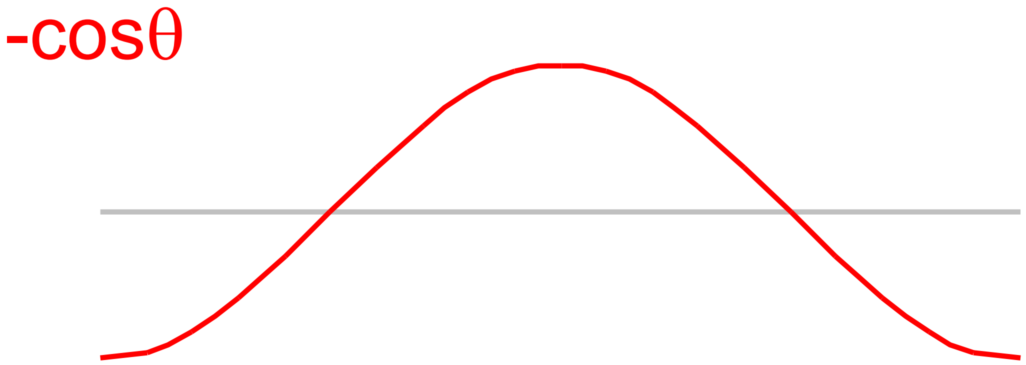
$$\mu_N = \frac{e\eta}{2m_p} = 5.051 \cdot 10^{-27} JT^{-1}$$

Magnetic Dipole Moment

- A magnetic dipole moment can be measured placing it in an external magnetic field
- B, the density of magnetic flux, can be considered as the density of magnetic field lines permeating the medium

Energy of the magnetic dipole moment in a magnetic field

$$E = -\vec{\mu} \cdot \vec{B} = -\mu B cos\theta$$



$$\frac{dE}{d\theta} = \mu B \sin \theta$$

The minimum energy occurs at $\theta = 0$

Magnetic fields vectors **H** and **B**

- **B** the magnetic flux density correlates with **H** the applied magnetic field (it is the true magnetic field vector) and with M, the magnetization **M** through the magnetic permittivity μ
- μ_0 is a fundamental constant known as vacuum permittivity

$$\mu_0 = 4\pi \cdot 10^{-7} JC^{-2}m^{-1}s^{2} = 4\pi \cdot 10^{-7} NA^{-2}$$

Magnetic Field Vector H

H units $Am^{-1}/(4\pi \cdot 10^{-7})$

$$\vec{B} = \bar{\bar{\mu}} \cdot \bar{\bar{H}}$$

$$\mu_0 = 4\pi \cdot 10^{-7}\ NA^{-2}$$

$$\vec{B} = \mu_0(\vec{H} + \vec{M}) = \mu_0(1 + \bar{\bar{\chi}})\vec{H}$$

M **<u>magnetization vector: magnetic moment per unit volume</u>**, same dimensions as **H**

$$\bar{\bar{\mu}} = \mu_0 \left(1 + \bar{\bar{\chi}}\right)$$

The magnetic flux density, **B**, can be considered as the field lines density permeating the medium. It increases when **M** adds to **H** (for $\chi > 0$), whereas it decreases whenever **M** is counteracting **H** (for $\chi < 0$)

Magnetic fields in a medium volume magnetic susceptibility χ

- χ has no dimensions, is a pure number

Selected χ values $\chi/10^{-6}$ at 298 K

H_2O	-90
C_6H_6	-7.2
CCl_4	-8.9
$NaCl_{(s)}$	-13.9
$Cu_{(s)}$	-96
$Hg_{(l)}$	-28.5

weakly repulsed by the magnetic field

$\chi < 0$

diamagnetic substances

Atkins

Selected values $\chi/10^{-6}$ a 298 K

$CuSO_4{\cdot}5H_2O_{(s)}$	+176
$NiSO_4{\cdot}7H_2O_{(s)}$	+416
$Pt_{(s)}$	+262
$Na_{(s)}$	+7.3

attracted by the magnetic field

$\chi > 0$

paramagnetic substances

Magnetic Subsceptibility Measuren

- Gouy’s method
- the force on the sample placed in a non uniform magnetic field is measured by a balance

http://www.sestechno.com/pro1/2l1.html

$$F_Z = \mu \cdot \frac{\partial B}{\partial z}$$

alternatively by means of a Superconducting Quantum interference Device (SQUID) magnetometer

http://www.cryogenic.co.uk/products/s700x-squid-magnetometer

https://www.youtube.com/watch?v=Km2f4yzqXmQ

Diamagnetism

- it is the result of the electronic motions induced by the magnetic field
- <u>it does not require permanent magnetic moments</u>
- it does not respond to temperature

Paramagnetism

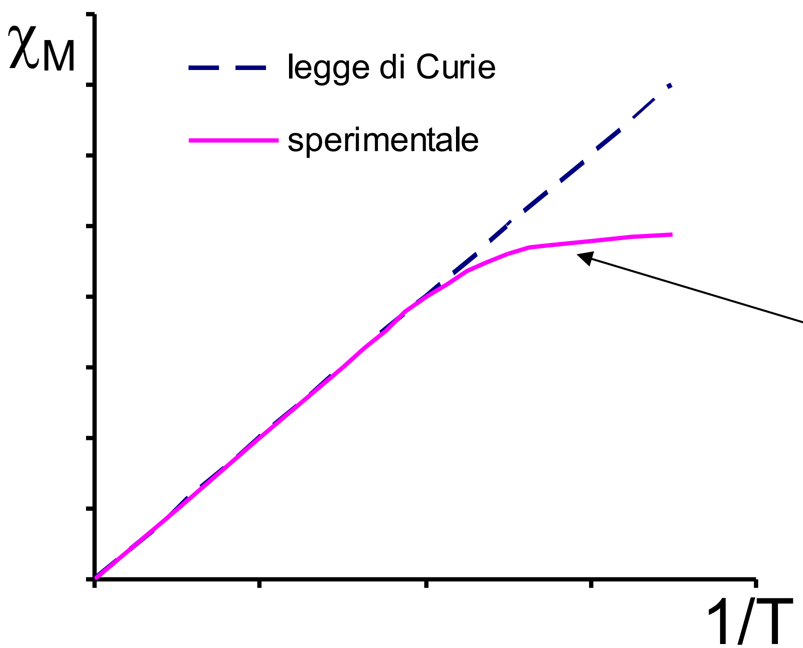
- substances made of atoms or molecules with permanent magnetic moments
- temperature dependent

Curie's Law

χ_M (molar magnetic susceptibility) of paramagnetic substances at T on the order of r.T. follows the Curie's law

C: Curie's constant

$$\chi_M = \frac{C}{T}$$



experimental data show the reaching of saturation

μ_{eff} depends on the number of unpaired electrons

spin only: $\mu_{eff}^2 = 4S(S+1)\hbar^2$

$g_e^2 \sim 4$

weak spin-orbit coupling:

$$C = N_A \frac{\mu_{eff}^2 \mu_B^2}{3k_B}$$

$$\mu_{eff}^2 = [4S(S+1) + L(L+1)]\hbar^2$$

- N_A Avogadro's number
- μ_{eff} efficaceous magnetic moment
- μ_B magnetone di Bohr
- k_B costante di Boltzmann

Ferromagnetism

disregarded

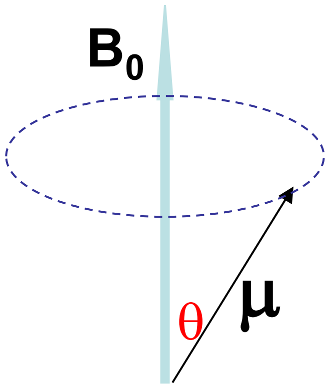
Nuclear Paramagnetism

- at r.T. nuclear paramagnetic susceptibility is on the order of 10^{-10}, therefore static nuclear magnetization in a stationary magnetic field is overwhelmed by the presence of eventual electronic paramagnetism and by the ubiquous diamagnetism of the material (on the order of 10^{-6}).
- For this reason the measurement of nuclear paramagnetism by the methods used for the measurements of materials' magnetic susceptibility is impracticable.

Larmor Precession

- For electrons in matter, the Lorentz force induces deformations in their trajectories
- It can be demonstrated that the effect of the stationary external magnetic field (at a first approximation) is to add to the electrons' motion a uniform rotation about the direction of the field: the Larmor precession
- It is equal to the creation in each molecule of a new current, running in a loop normal to the field and with such a sense to generate a magnetic field opposing to the inducing field

Precession of a magnetic moment about the magnetic field



$\mathbf{B_0}$ is constant, $|\mu|$ is constant

$E = -\mu B_0 \cos\theta =$ constant

Since B_0, $|\mu|$ and E are constant, also the angle θ is costant

thus the motion is a rotation of μ about $\mathbf{B_0}$

Larmor Frequency

$$\omega_0 = -\gamma_N B_0$$

more properly is an angular frequency

N.B. for a few nuclei γ_N is negative

Quantomechanical Introduction

- Spectroscopy is defined as the interaction between matter and an electromagnetic radiation such that it is either absorbed or emitted in agreement
- with the Bohr frequency condition **$\Delta E = h\nu$**
- where ΔE is the energy difference, commonly quantized, between end and starting states of matter
- $h = 6.626 \cdot 10^{-34}$ Js Planck constant

Peculiarities of Magnetic Resonance Spectroscopies

- The transition is due to the magnetic oscillating field of the radiation, not to the electric field.
- ΔE is very low, even at the highest magnetic fields, so that the relevant frequencies lie in the radiofrequency range for NMR and in the microwave range for ESR

Nuclear Spin

- A great number of isotopes possess nuclei with spin quantum number $I \neq 0$
- I may be integer as well half-integer
- the **nuclear spin angular moment I**
- is a quantum angular moment vector
- the modulus of which is $|\mathbf{I}| = [I(I+1)]^{1/2}\hbar$
- and the component along the z axis is $m_I\hbar$

- m_I has one of the possible 2I+1 values in the range $-I \leq m_I \leq I$

- to the nuclear angular quantum moment is associated the spin nuclear magnetic moment, which has the properties of a magnetic moment, and is a quantum vector

$$\vec{\mu} = \gamma_N \vec{I}$$

γ_N: **magnetogyric ratio** is a scalar and can be also negative

Table γ_N

nucleus	I	nat. ab.	ν/MHz at 9.4 T	γ/rad s^{-1} T^{-1}
^{1}H	1/2	99.98%	400	$26.75 \cdot 10^{7}$
^{13}C	1/2	1.108%	100.577	$6.73 \cdot 10^{7}$
^{15}N	1/2	0.368%	40.531	$-2.71 \cdot 10^{7}$
^{19}F	1/2	100%	376.3	$25.16 \cdot 10^{7}$
^{23}Na	3/2	100%	105.805	$7.08 \cdot 10^{7}$
^{29}Si	1/2	4.683%	79.46	$-5.32 \cdot 10^{7}$

- In the magnetic field the nuclear magnetic moment has one of the (2I+1) allowed orientations
- $\mathbf{B_0}$ direction is conventionally taken as the z axis of the laboratory coordinates
- The magnetic energy (**Zeeman energy**) of a magnetic moment in a magnetic field is:

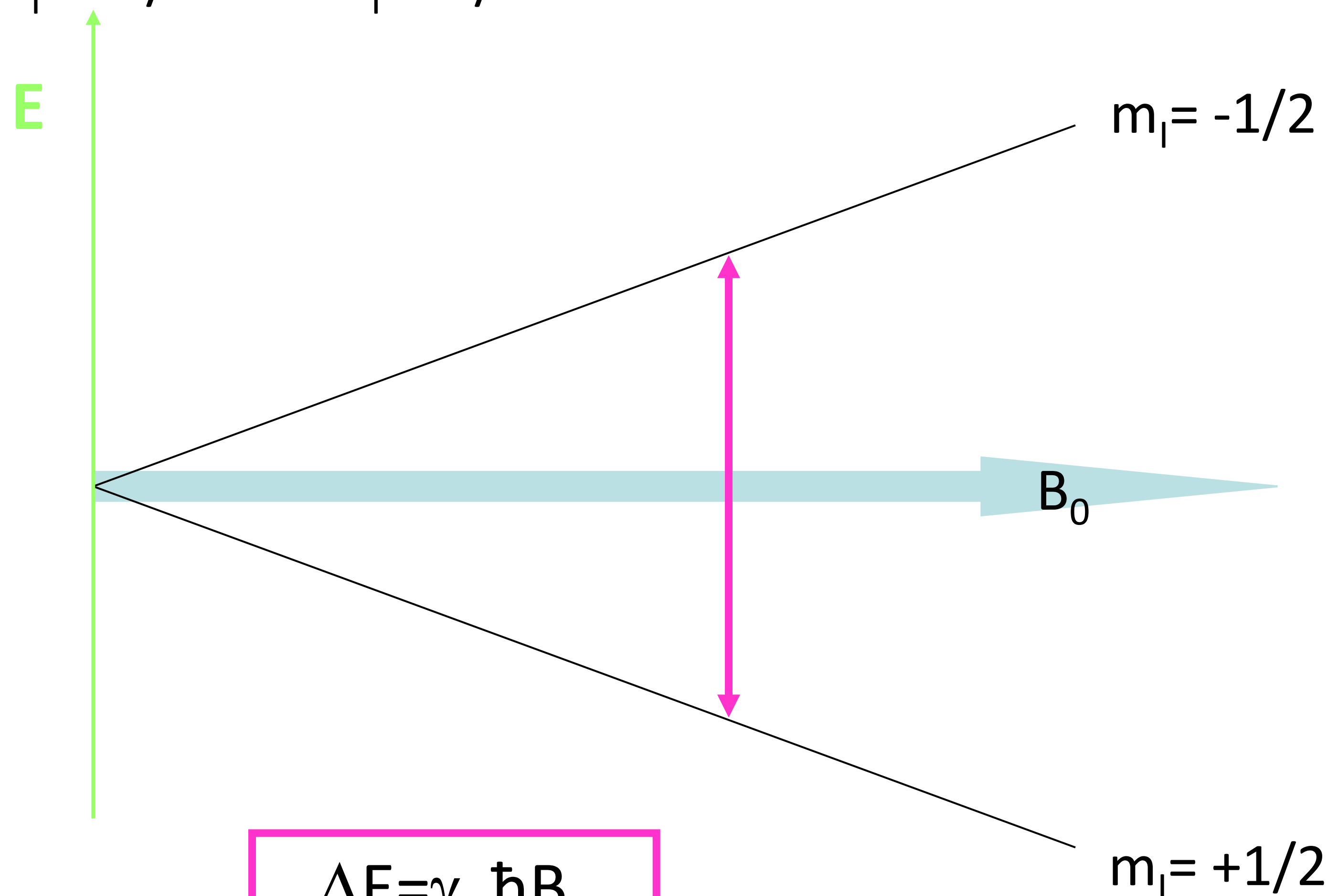
$$E = -\vec{\mu} \cdot \overrightarrow{B_0}$$

Developing the scalar product, one gets an energy value for each m_I $E_{mI} = -g_N m_I \hbar B_0$

as an overall there are 2I+1 energy level

For I= ½ there are two states, in the correspondence of

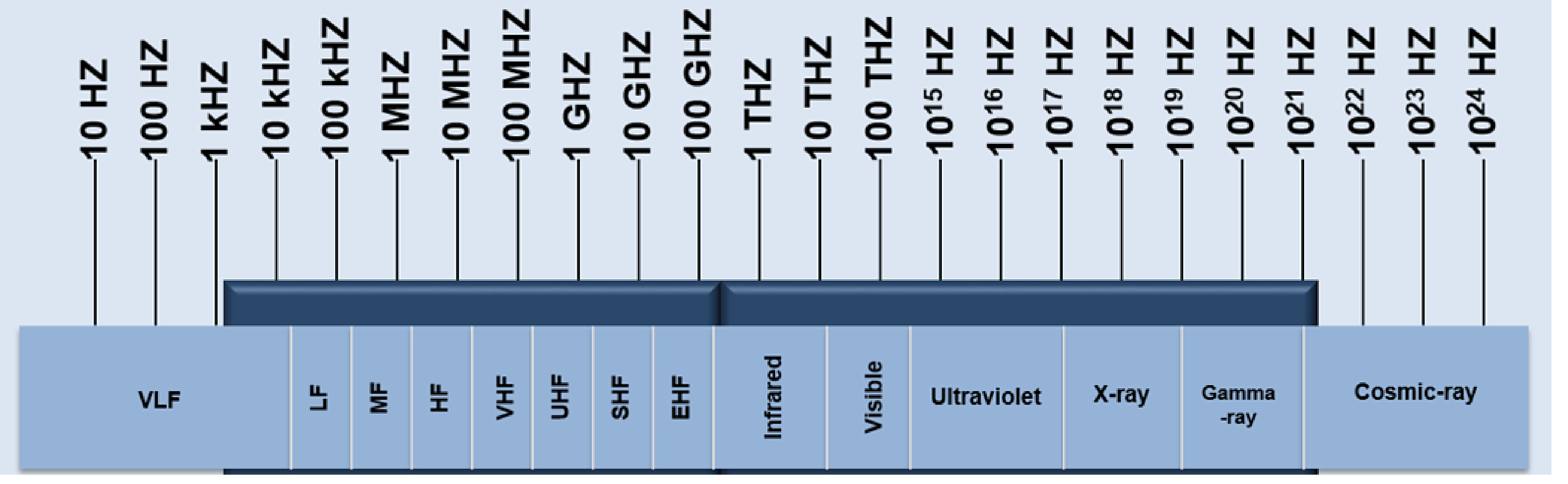
m_I= +1/2 and m_I= -1/2



$$\Delta E = \gamma_N \hbar B_0$$

ΔE depends on γ_N and increases with B_0

Electromagnetic spectrum



https://www.nasa.gov/directorates/heo/scan/spectrum/txt_electromagnetic_spectrum.html

- We use the term resonance instead of absorption or emission
- owing to the detection mode. It was devised to overcome the very low sensitivity impied by the tiny energy differences between energy levels (low signal intensity, low detector sensitivity at the low frequencies)

Rabi Nobel Prize in1944

- The Nobel Prize in Physics 1944 was awarded to Isidor Isaac Rabi *"for his resonance method for recording the magnetic properties of atomic nuclei"*.
- It allows the determination of nuclear magnetic moments in molecular beams
- In a static magnetic field, transitions between energy levels, corresponding to different orientations of the nuclear spins, are induced

Nobel 1952: Bloch and Purcell

- The Nobel Prize in Physics 1952 was awarded jointly to Felix Bloch and Edward Mills Purcell "for their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith“
- In1946 they demonstrated the magnetic resonance of proton in a condensed phase
- Bloch from a water sample
- Purcell from solid paraffin

- Since the observation is done on a macroscopic sample, for which the laws of classical physics hold, we can cope with this issue also by them.
- The relationship between quantum mechanics and classical mechanics is achieved by means of statistical mechanics.

Unit Volume Macroscopic Magnetization Vector **M**

- A macroscopic samples possesses a huge number of nuclear spins
- In the magnetic field the 2I+1 allowed energy levels are populated at thermal equilibrium in agreement with the **Boltzmann** distribution

$$p_{mI} = \frac{\exp\left(-\frac{E_{mI}}{k_B T}\right)}{\sum_{mI=-I}^{+I} \exp\left(-\frac{E_{mI}}{k_B T}\right)}$$

Magnetization VectorM for I= 1/2

- 2 levels corresponding to m_I= +1/2 (α) e m_I= -1/2 (β)
- if γ_N> 0 α corresponds to a spin up ↑ and β to a spin down ↓
- N_0 spin density per unit volume
- since NMR experiments are usually carried out at high T compared to 0 K
- and the relevant energies are low

the exponents' values are small enough to allow the approximation of the eponentials by the first two terms of the series expansion

$$\exp\left(-\frac{E_{mI}}{k_B T}\right) \approx 1 - \frac{E_{mI}}{k_B T}$$

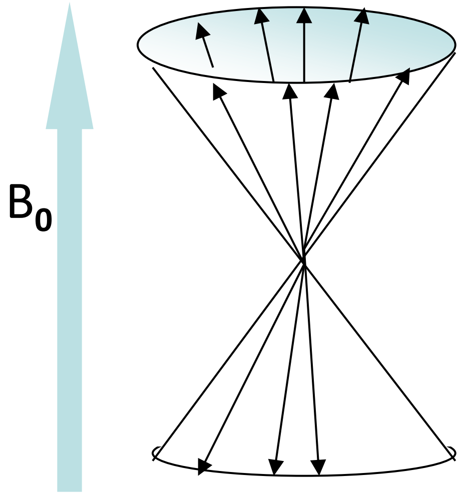
In this way the populations are:

$$p_{-\frac{1}{2}} = \frac{1 - \frac{1}{2}\frac{\gamma_N \hbar B_0}{k_B T}}{1 + \frac{1}{2}\frac{\gamma_N \hbar B_0}{k_B T} + 1 - \frac{1}{2}\frac{\gamma_N \hbar B_0}{k_B T}} = \frac{1 - \frac{1}{2}\frac{\gamma_N \hbar B_0}{k_B T}}{2} = \frac{1}{2} - \frac{1}{4}\frac{\gamma_N \hbar B_0}{k_B T}$$

$$p_{+\frac{1}{2}} = \frac{1}{2} + \frac{1}{4}\frac{\gamma_N \hbar B_0}{k_B T}$$

$$p_{-\frac{1}{2}} = \frac{1}{2} - \frac{1}{4}\frac{\gamma_N \hbar B_0}{k_B T}$$

The macroscopic magnetization vector per unit volume is given by the sum over all microscopic magnetization vector



Sometimes the spin ensamble is represented with the α and β states as vectors on the surfaces of two opposite cones (to signify the impossibility of knowing the other two components beside modulus and z component)

The number of vectors on the upper cone (situation with lower energy) slightly exceeds that of the vectors on the lower cone

- In the case of proton ^{1}H: $\gamma_H = 26.75 \cdot 10^{7}$ $radT^{-1}s^{-1}$
- with $B_0 = 9.4$ T and T= 298 K
- $\hbar = 1.054 \cdot 10^{-34}$ J s rad^{-1}
- $k_B = 1.381 \cdot 10^{-23}$ JK^{-1}
- $p_{+1/2}$ population of α nuclei
- $p_{-1/2}$ population of β nuclei
- it ensues $p_{+1/2} = 0.500161$
- $p_{-1/2} = 0.4999389$
- and $p_{+1/2} - p_{-1/2} = 3.22 \cdot 10^{-5}$

$$M_0=N_0(p_{+1/2}\mu_{z+1/2}+p_{-1/2}\mu_{z-1/2})$$

$$M_0 = N_0\frac{1}{2}\left[\left(1+\frac{1}{2}\frac{\gamma_N\hbar B_0}{k_BT}\right)\left(+\frac{1}{2}\gamma_N\hbar\right)+\left(1-\frac{1}{2}\frac{\gamma_N\hbar B_0}{k_BT}\right)\left(-\frac{1}{2}\gamma_N\hbar\right)\right]=$$

$$N_0\frac{1}{4}\gamma_N\hbar\left[1+\frac{1}{2}\frac{\gamma_N\hbar B_0}{k_BT}-1+\frac{1}{2}\frac{\gamma_N\hbar B_0}{k_BT}\right]=N_0\frac{1}{4}\gamma_N\hbar\frac{\gamma_N\hbar B_0}{k_BT}$$

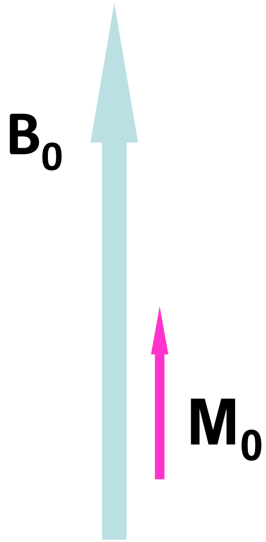
I= 1/2

any I

$$M_0 = N_0\frac{\gamma_N^2\hbar^2 B_0}{k_BT}\frac{1}{4}$$

$$M_0 = N_0\frac{\gamma_N^2\hbar^2 B_0}{k_BT}\frac{I(I+1)}{3}$$

Macroscopic magnetization vector at at thermal equilibrium M_0



At the thermal equilibrium the sample possesses a macroscopic magnetization vector that is aligned with the inducing magnetic field.