NMR, the vector model and the relaxation

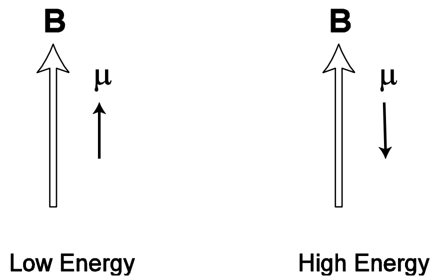
Reading/Books:

One and two dimensional NMR spectroscopy, **VCH**, *Friebolin*
Spin Dynamics, Basics of NMR, **Wiley**, *Levitt*
Molecular Quantum Mechanics, **Oxford Univ. Press**, *Atkins*.
NMR: The Toolkit, **Oxford Science Publications,** *Hore, Jones and Wimperis*
Understanding NMR Spectroscopy, **Willey**, *Keeler*

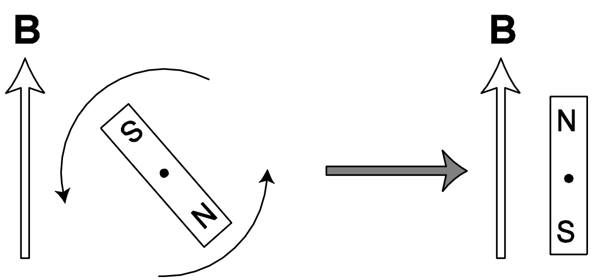
Effect of the Magnetic Field on Matter

Interaction of Magnetic Field and Matter: Macroscopic Magnetism

$$\boxed{E = -\mu \cdot B}$$



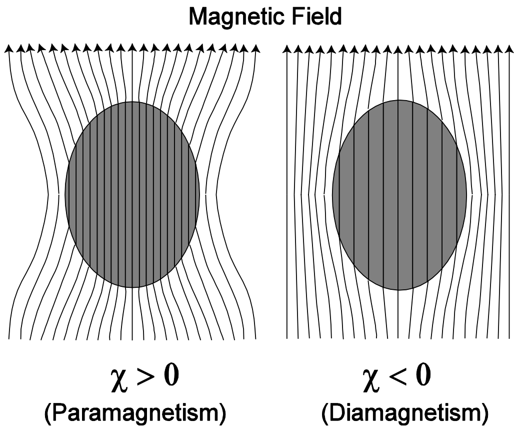
Permanent magnetic moment, *e.g.* magnets:



Induced magnetic moment

$$\boxed{\mu_{induced} = \frac{\chi}{\mu_0} \times VB}$$

V: Volume
χ: Magnetic susceptibility
B: Applied field
$\mu_0 = 4\pi \times 10^{-7}$ H/m



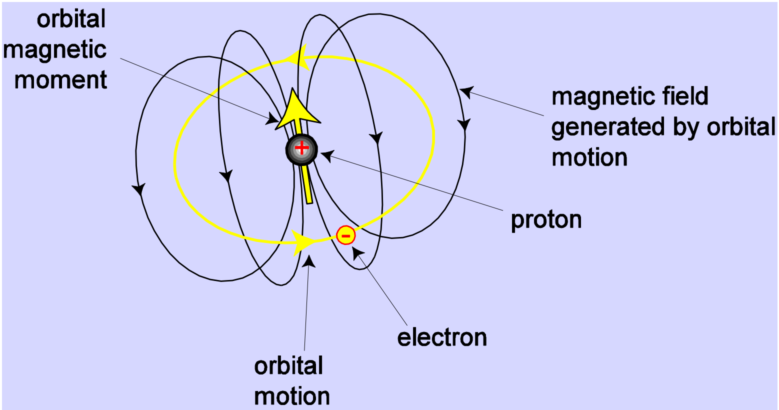
Effect of the Magnetic Field on Matter

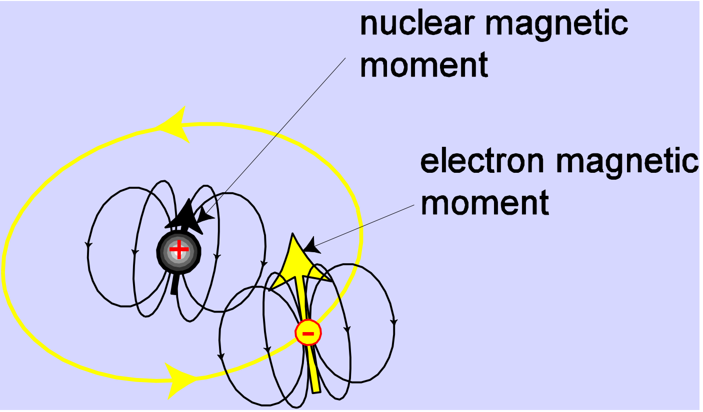
Interaction of Magnetic Field and Matter: Macroscopic Magnetism

Source of magnetism:

1) circulation of electron currents (negative contribution to susceptibility)
2) magnetic moments of electrons (positive contribution to susceptibility)
3) magnetic moments of nuclei (positive contribution to susceptibility)

with 1 and 2 > 3

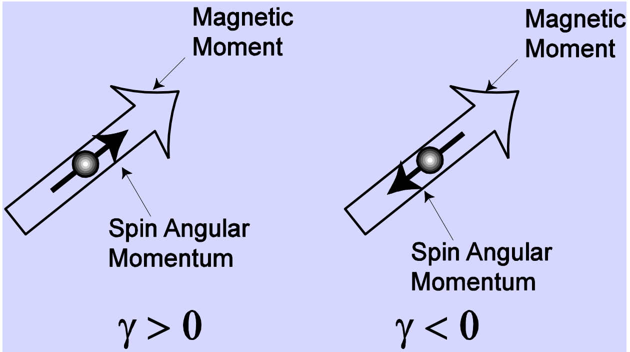




Spins and magnetism:

$$\boxed{\hat{\mu} = \gamma \hat{S}}$$

γ = gyromagnetic (or magnetogyric) ratio (positive or negative and characteristic of the nuclei).



The magnetic moment of the electron has been predicted by Dirac.

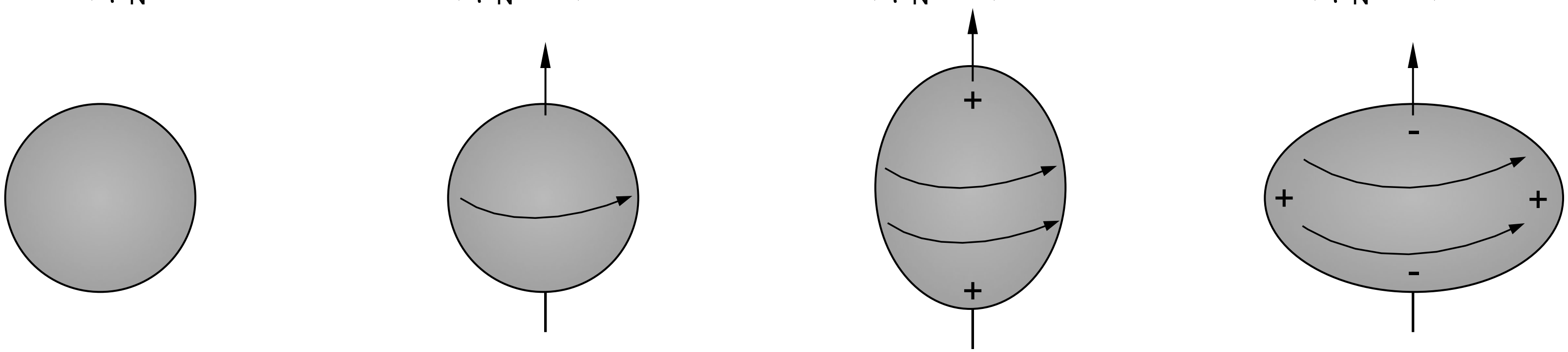
However, today the magnetic moments of quarks and nucleons, and thereby nuclei, are not year understood.

Effect of the Magnetic Field on Nuclei

Properties at the atomic level: *Nuclear Spin Quantum Number, I*

For protons and neutrons: I = ½
For atoms: I depends on how spin are paired or unpaired:

$I = 0$, $\mu_N = 0$ | $I = ½$, $\mu_N \neq 0$, $eQ = 0$ | $I \geq 1$, $\mu_N \neq 0$, $eQ > 0$ | $I \geq 1$, $\mu_N \neq 0$, $eQ < 0$



No nuclear spin
Nuclei with even numbers of both protons and neutrons (A and Z are even)
e.g. ^{12}C, ^{16}O, ^{32}S…

Distribution of positive charge in the nucleus is spherical (spinning sphere)
e.g. ^{1}H, ^{13}C, ^{19}F, ^{31}P…
as well as ^{195}Pt…

Non-spherical distribution of charges (electric dipole, eQ)
eQ = 0 in spherical environment
e.g. ^{2}D, ^{14}N, ^{17}O…

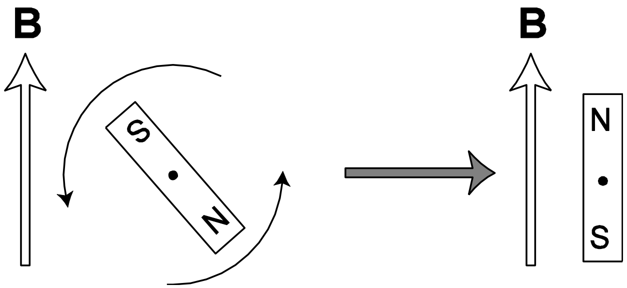
A = even, Z = odd, I = integer
A = odd, I = half integer

Unpaired nuclear spins ($I \neq 0$) → nuclear magnetic moment (μ_N).
Spinning charges → angular momentum (*I*).
The allowed orientation of m are indicated by *nuclear spin angular momentum quantum number, m_I with m_I = I, I-1, …, -I+1 and I, a total of $2m_I$+1 states*

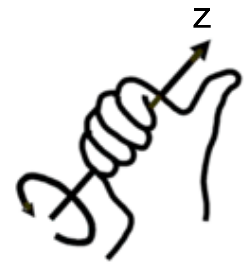
This is associated with a magnetic moment μ, a characteristic of the nuclei: $\boxed{\vec{\mu}_N = \gamma \hbar \vec{I}}$

Effect of the Magnetic Field on one Nucleus

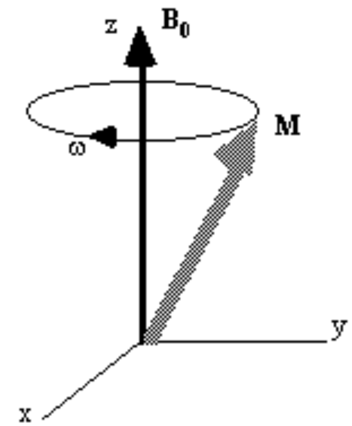
Macroscopic Magnetism



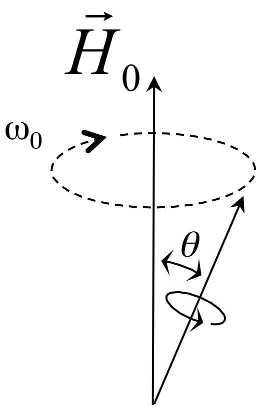
Microscopic Magnetism



In such an axis system, a positive rotation is defined by the curl of the fingers



For $\gamma > 0$



$$\vec{\mu}_N = -\gamma\hbar\vec{I}$$

H_0 exerts a force (torque) on μ_N, causing a precession, perpendicular to μ_N and *H_0, with a frequency ω_0 (Larmor frequency):*

$$\boxed{\vec{\tau} = \vec{\mu} \times \vec{H}_0} \qquad \boxed{\omega_0 = -\gamma H_0}$$

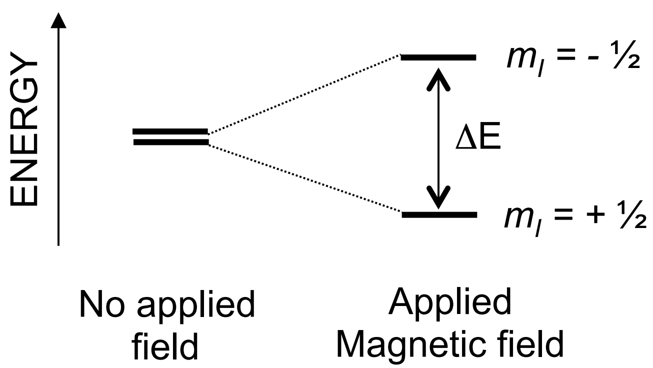
γ = gyromagnetic (or magnetogyric) ratio, associated with the angular momentum *I and a characteristic of the nucleus*

^{1}H, I =½; γ = 267.522×10^6 rad/s/T (-500 MHz at 11.74 T)
^{2}H, I =1; γ = 41.066×10^6 rad/s/T (-76.75 MHz at 11.74 T)
^{13}C, I =½; γ = 67.283×10^6 rad/s/T (-125 MHz at 11.74 T)
^{29}Si, I =½; γ = - 53.190×10^6 rad/s/T (99.34 MHz at 11.74 T)

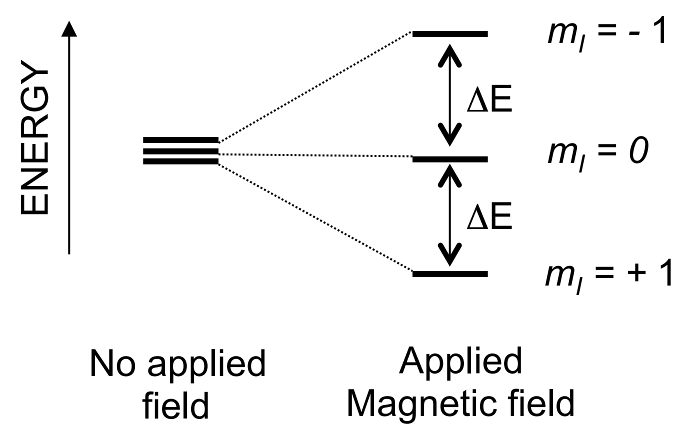
Effect of the Magnetic Field on one Nucleus

Energies of spin states

For I = ½, $m_I = \pm ½$



For I = 1, $m_I = -1, 0, 1$

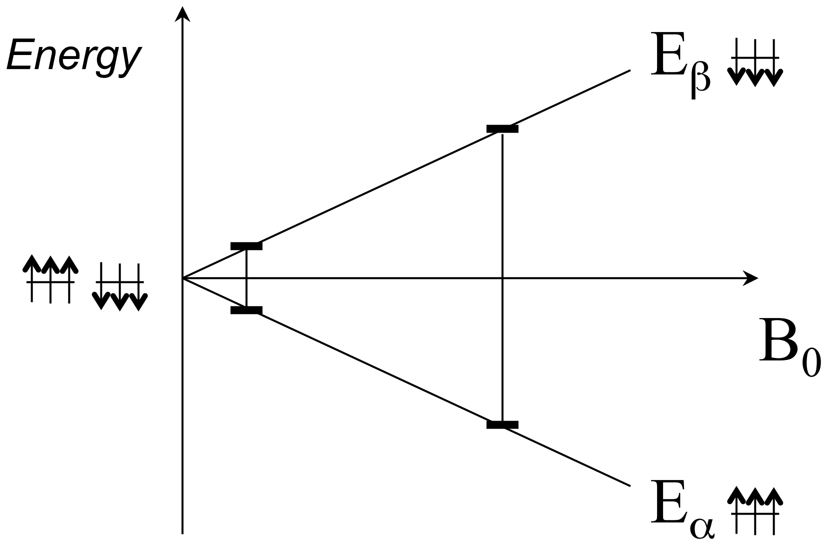


μ_N in the direction of the applied field for $m_I > 0$
μ_N opposed to the applied field for $m_I < 0$
μ_N perpendicular to the applied field for $m_I = 0$

ΔE: Energy difference between two states,
it is associated with a radio frequency ν.
This is what will be detected in the NMR experiment.

$$\boxed{\Delta E = \gamma \hbar H_0 \Delta m_I = \hbar \omega_0}$$

Nuclear spins in B_0



From quantum mechanics:

$$\hat{H} = -\vec{\mu} \cdot \vec{H}_0 = -\gamma_N \hbar H_0 \hat{I}_z$$

$$E = -\gamma \hbar m_I H_0$$

$$\Delta E = \gamma \hbar H_0 \Delta m_I = \hbar \omega_0$$

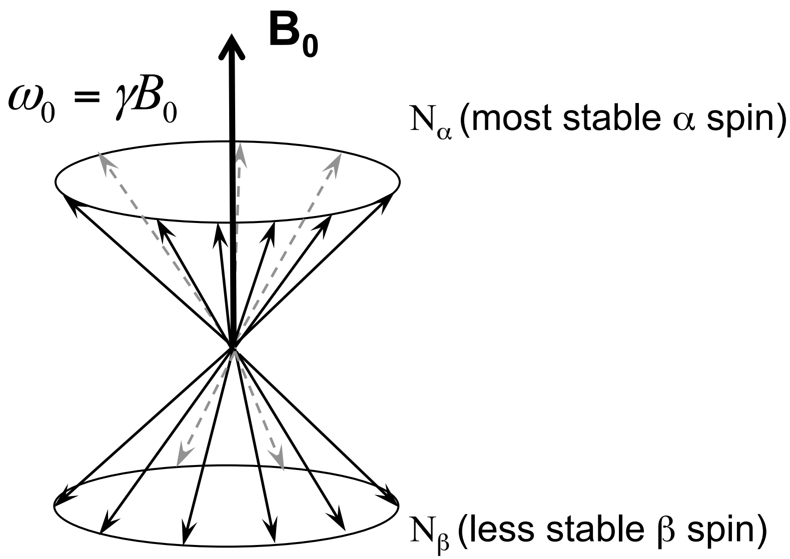
Boltzman Distribution:

$$\boxed{\frac{N_\beta}{N_\alpha} = e^{\frac{-(E_\beta - E_\alpha)}{kT}} = e^{\frac{-\gamma \hbar B_0}{kT}} \cong 1 - \frac{\gamma \hbar B_0}{kT}}$$

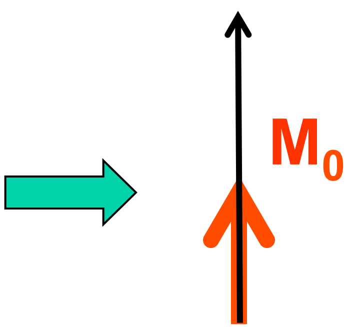
For ω = 60 MHz B_0 = 1.4092 Tesla
For ω = 500 MHz B_0 = 11.740 Tesla
Note that B_{Earth} = 50 μT

At room temperature, the ratio $\frac{N_\alpha}{N_\beta} = 1.0000066$

Nuclear spins in B_0



$$\boxed{\frac{N_\alpha}{N_\beta} = 1.0000066}$$



Net magnetization
aligned with B_0 (not the spins !)
No net magnization perpendicular to B_0

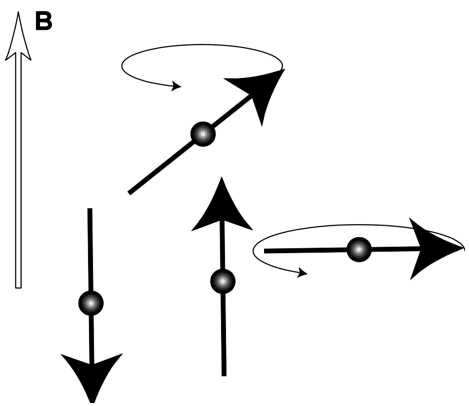
Note that:

- $M_0 << B_0$ and cannot be easily detected directly!
- Low sensitivity of NMR (sensibility is proportional to $B_0^{3/2}$, hence the development of high field NMR spectrometer).

Nuclear spins in B_0

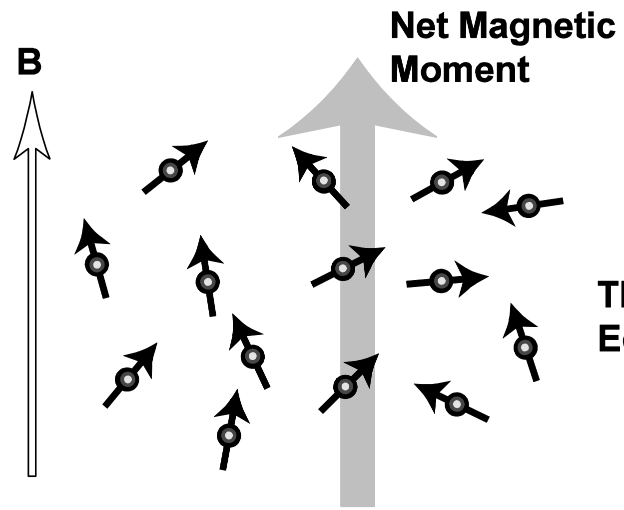
A more real model:

Effect of B_0 on of sum of spins



However, due to the isotropic distribution of spins, there is no contribution to the magnetism of the material.

Origin of net magnetization:
Molecular motions
→ Induction of overall fluctuating fields (time scale = nanosecond), and a biased magnetic moment aligned with B_0 (longitudinal magnetic moment).
→ Stable anisotropic distribution of nuclear spin polarization, also named ***thermal equilibrium***

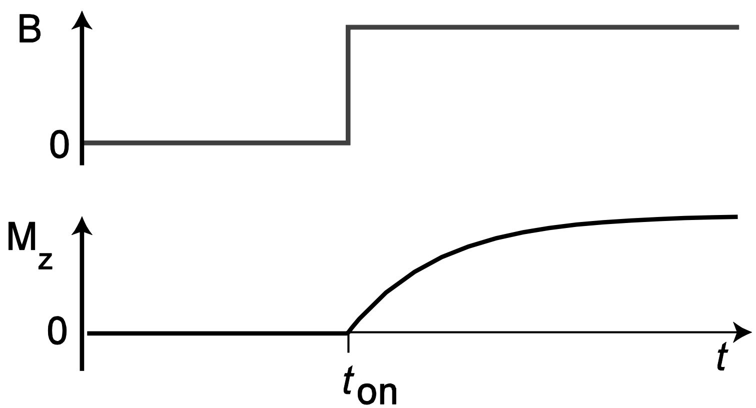


$$\boxed{\Delta E = \gamma\hbar H_0 = \hbar\omega_0}$$

Nuclear spins in B_0

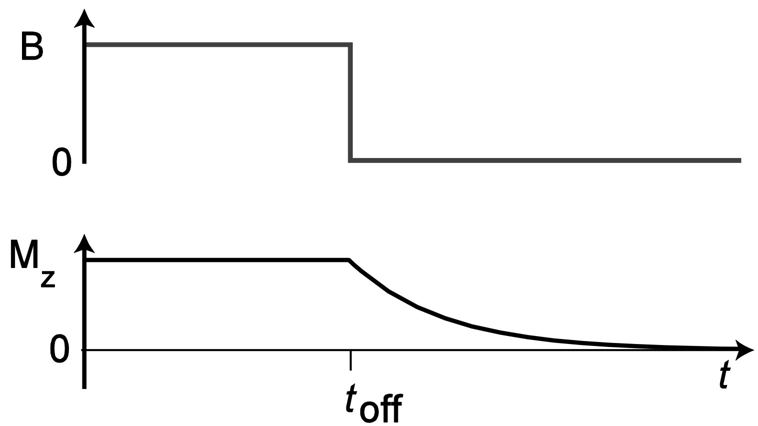
A more real model:

Build-up of Longitudinal magnetization (sudden introduction of a sample in B_0)



$$M_z(t) = M_0(1 - \exp[-\frac{(t - t_{on})}{T_1}])$$

Loss of Longitudinal magnetization (sudden removal of a sample from B_0)



$$M_z(t) = M_0 \exp[-\frac{(t - t_{off})}{T_1}]$$

Longitudinal relaxation (see Section on relaxation)

Observation of the NMR phenomenon
Sequences RMN and magnetization

What happens when M_0, aligned with the z axis, is moved away from its equilibrium position (effect of B_1) ?
It will vary under the control of two factors:

1) Torque $\vec{\tau} = \vec{\mu} \times \vec{B} = \gamma \vec{I} \times \vec{B}$

2) Relaxation (physical phenomena, which will bring back the system to equilibrium)

The resulting motion will be a precession around the magnetic field at the Larmor frequency ω_0 (it is like a gyroscope in a gravitational field) with a dissipation of the energy to return to the equilibrium position

$$\omega_0 = 2\pi\nu_0 = -\gamma B_0$$

How does the magnetization is moved away from its equilibrium position?

Application of a B_1 field perpendicular to B_0

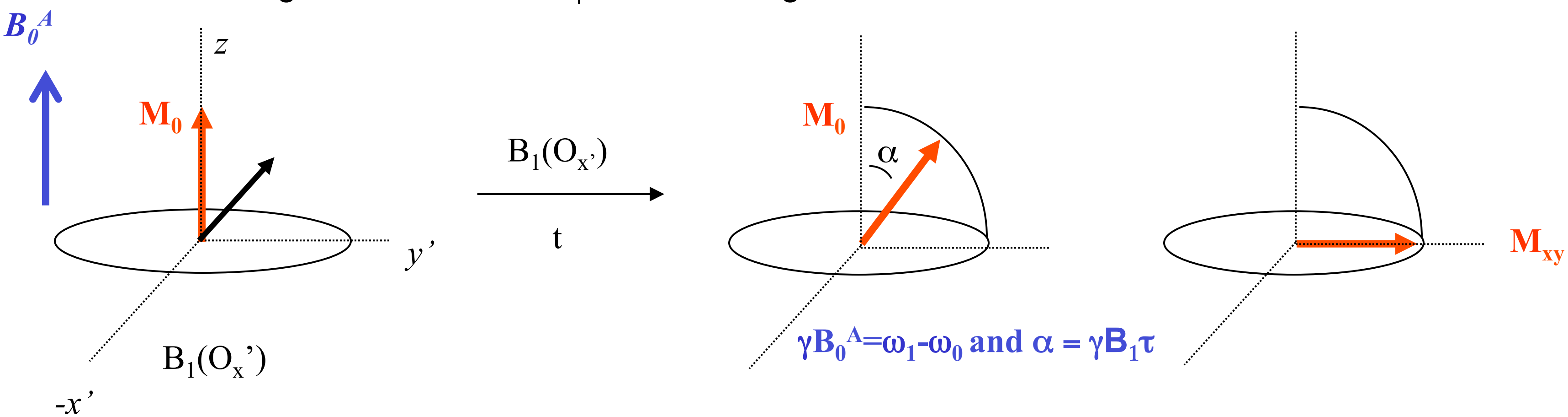
- Effect of B_1 field perpendicular to B_0:
Magnetization will be precessing around B_0+B_1. However, because $B_1 << B_0$ the effect will be only very small.
- Effect of a B_1 field perpendicular to B_0 but rotating in the O_{xy} plane at ω close to ω_0
→ Resonance effect, which corresponds to a adsorption of a continuous wave at ω_0 and which is like having a B_0+B_1 field (very effective to tip the magnetization in the xy plane).

B_1 is the high frequency alternative field, which is generated by a solenoid oriented perpendicular to the z axis. The intensity and the duration of the radiofrequency wave are controlled. This corresponds to two rotating fields in opposite direction

Sequences RMN and magnetization

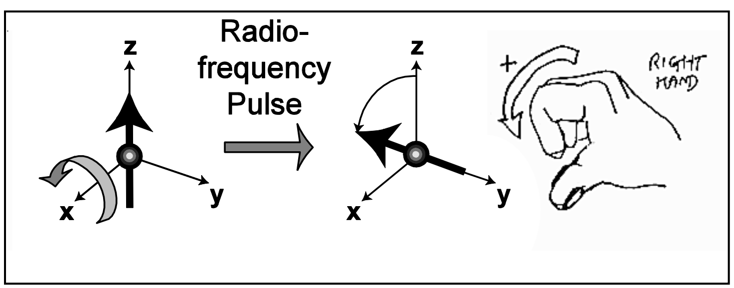
http://www.drcmr.dk/BlochSimulator/

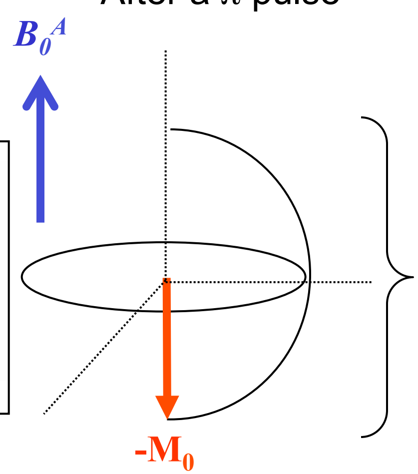
Influence of magnetization under B_1 in the rotating frame



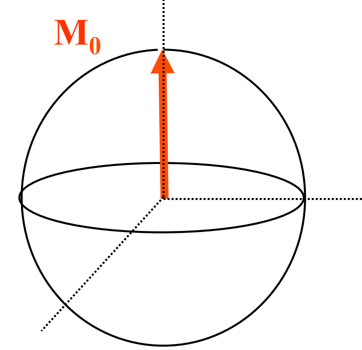
After a π pulse

After relaxation, back to equilibrium !

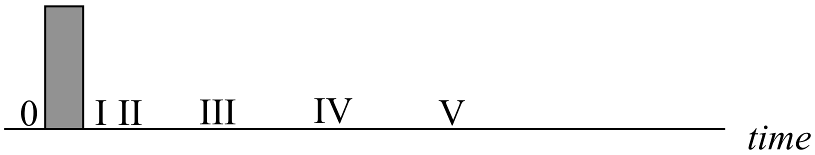




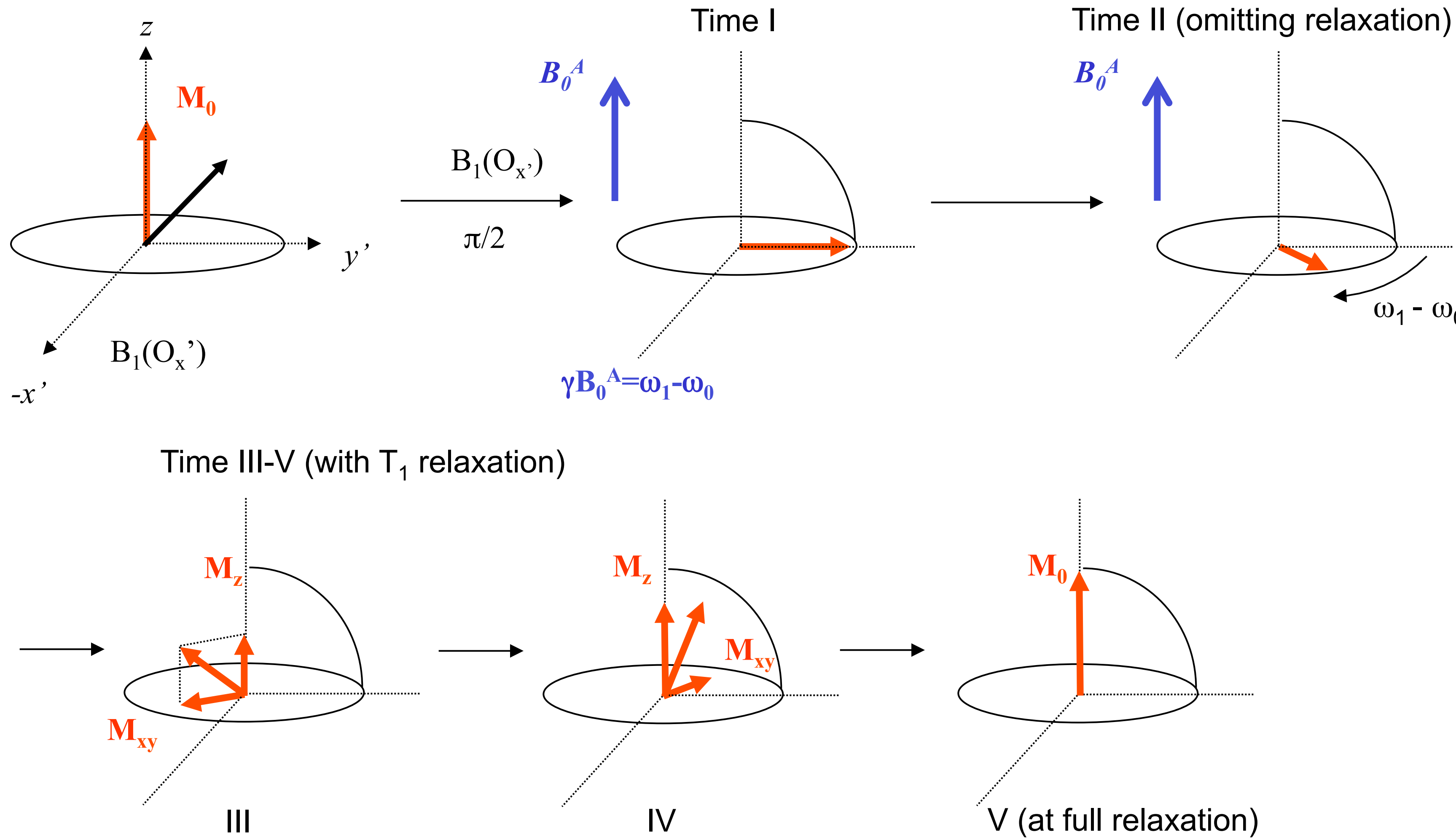
Consequence of π-pulse: inversion of population



Simple NMR experiment (sequence) and magnetization

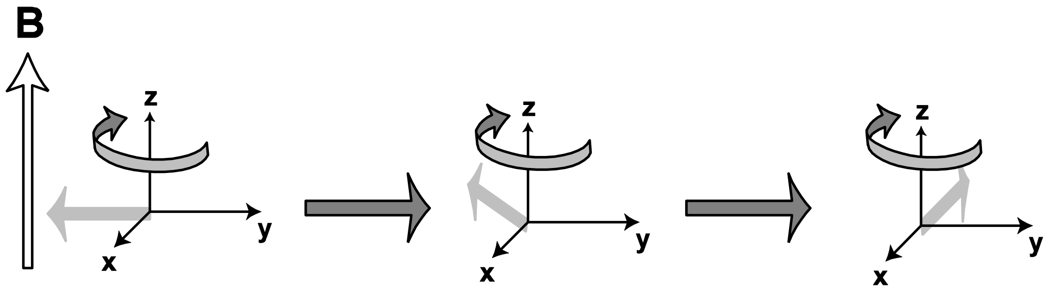


Influence of magnetization under B_1



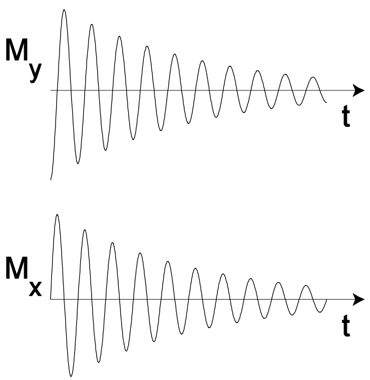
Sequences RMN and magnetization

M_{xy} in the laboratory frame

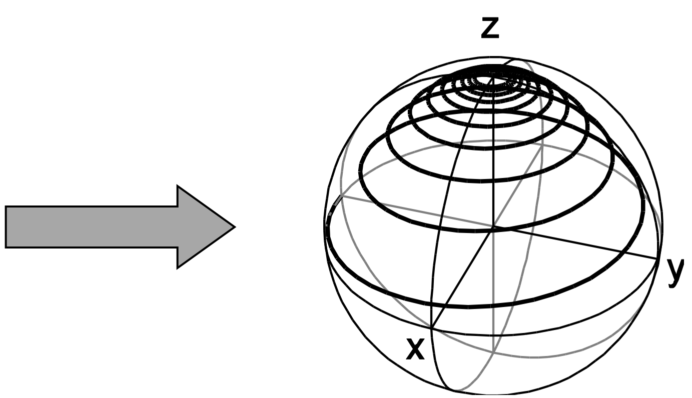


$$M_y(t) = M_0 \sin(\omega_0 t) \exp\{-t/T_2\}$$

$$M_x(t) = -M_0 \cos(\omega_0 t) \exp\{-t/T_2\}$$



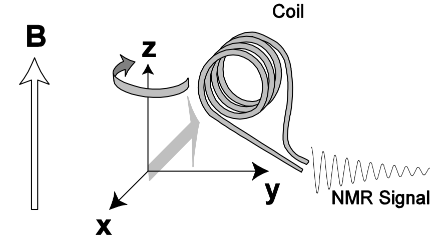
M_{xy} magnetization (transverse magnetization) decays slowly, because of the inhomogeneous field leading to a return to equilibrium (net magnetization along B_0). This is called transverse magnetization (T_2).
For small molecules, $T_2 \sim T_1$
i.e. nuclear spins precess millions of Larmor precession cycles before losing their synchrony.

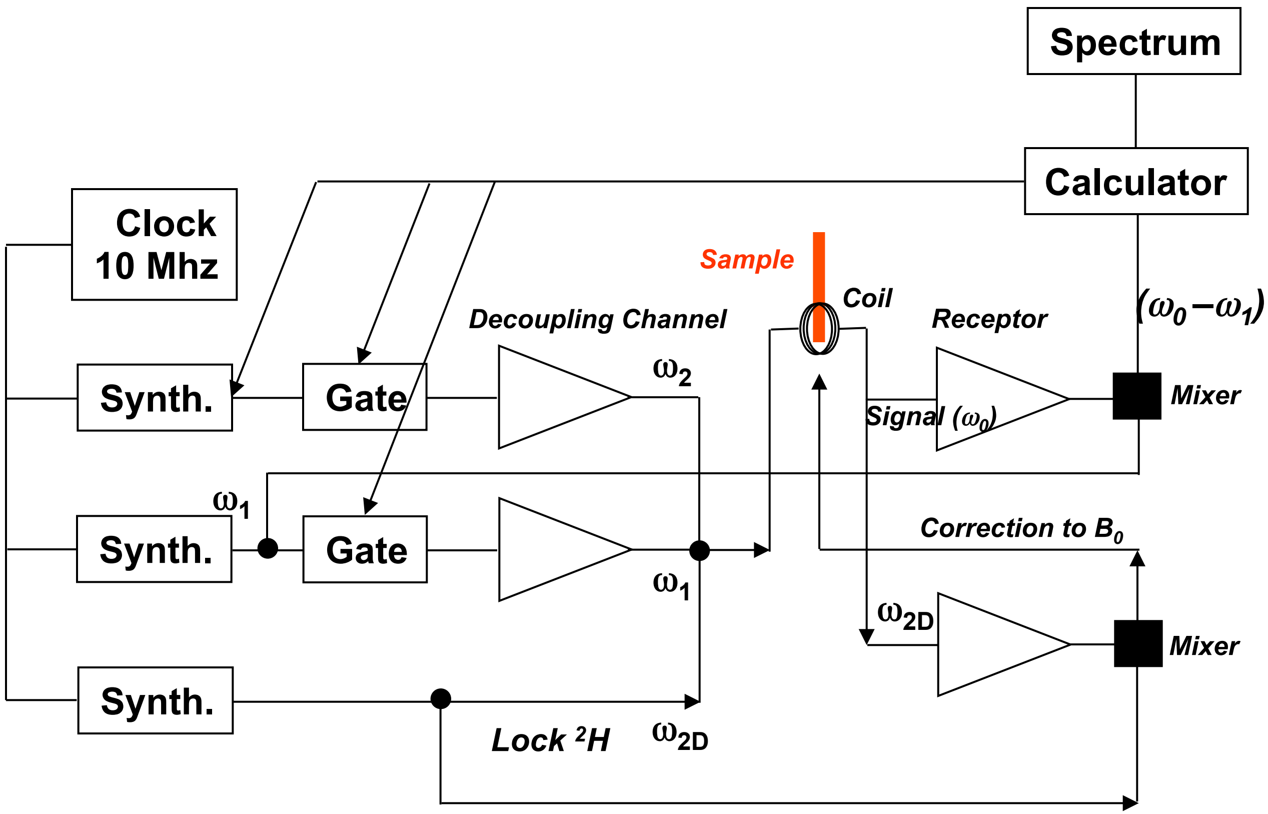


Observation of the NMR phenomenon
Spectrometer

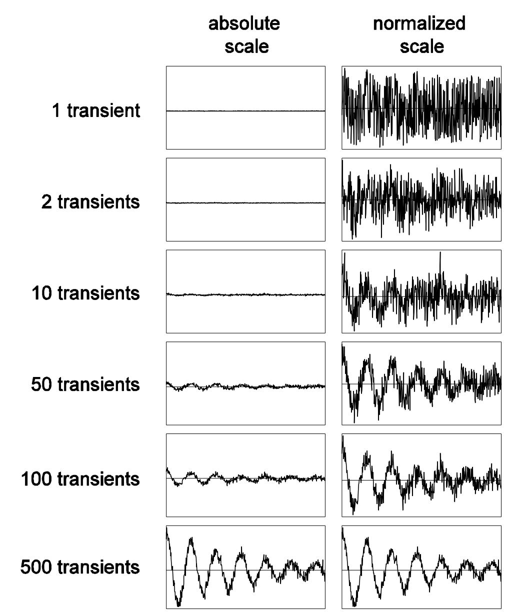
NMR probe: A coil oriented perpendicular to B_0 is used to generate B_1 and to detect the signal.
The signal of frequency ω_0 close to ω_1 is amplified and compared to ω_1 giving $(\omega_0 - \omega_1)$, which is the chemical shift.
A second coil provide a second field B_2, generation of highly precise frequencies (ω_n) using a clock (Quartz, 10 MHz temperature regulated):

Channel 1 with a frequency ω_1, used for the observation
Channel 2 with a frequency ω_2, typically used for decoupling or a second type of spins (^{13}C, ^{129}Sn…).
Channel 3 with a frequency ω_3, Lock, stabilization of the field by a reference nucleus usually ^{2}H



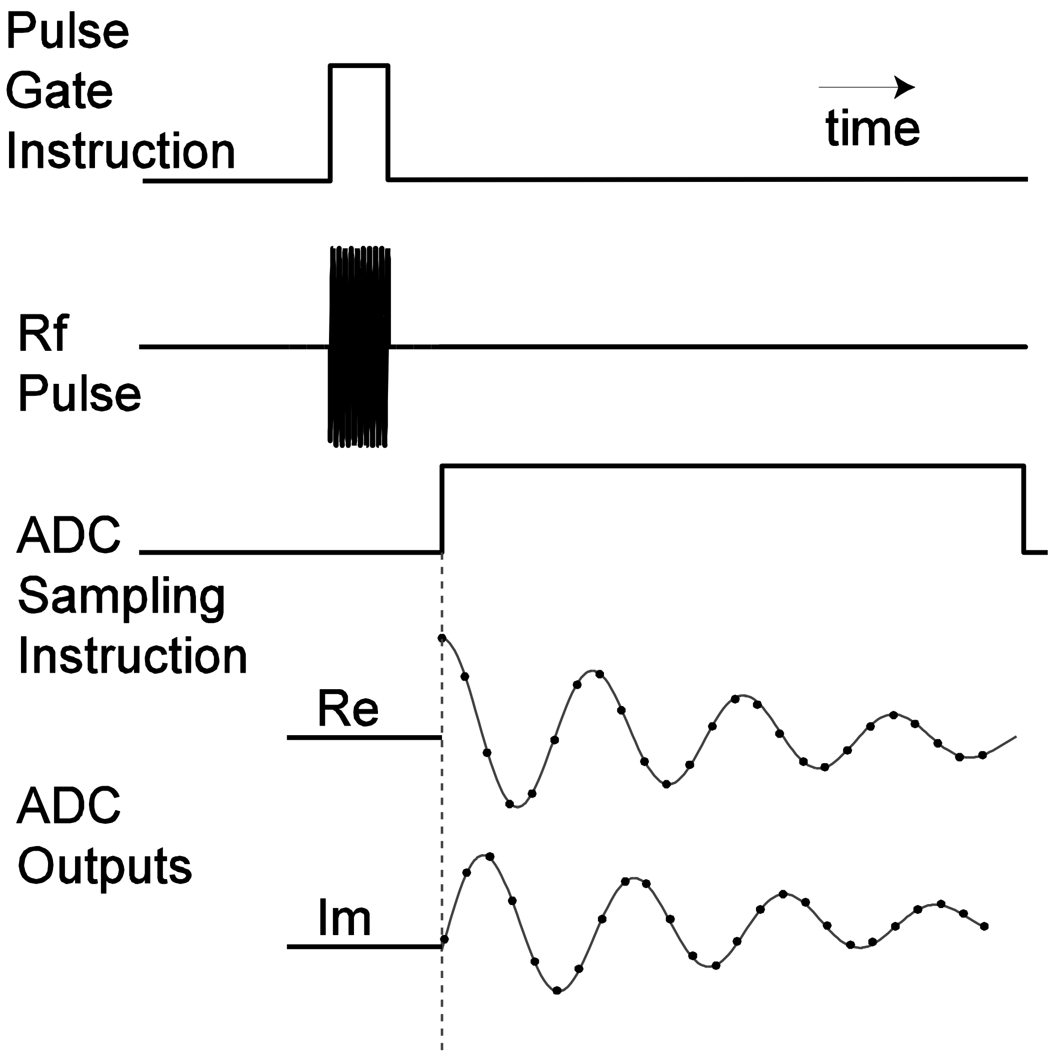


Signal: $s(t) = -\dfrac{d\Phi}{dt}$



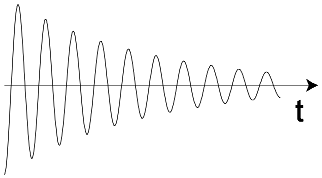
$$S/N = \sqrt{n}$$

Observation of the NMR phenomenon
Rf pulse and signal



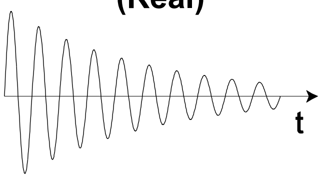
NMR Signals

(Imaginary)



$$s_B(t) \approx \sin(\omega_0 t)\exp\{-\lambda t\}$$

(Real)



$$s_A(t) \approx \cos(\omega_0 t)\exp\{-\lambda t\}$$

For a one-line spectrum:

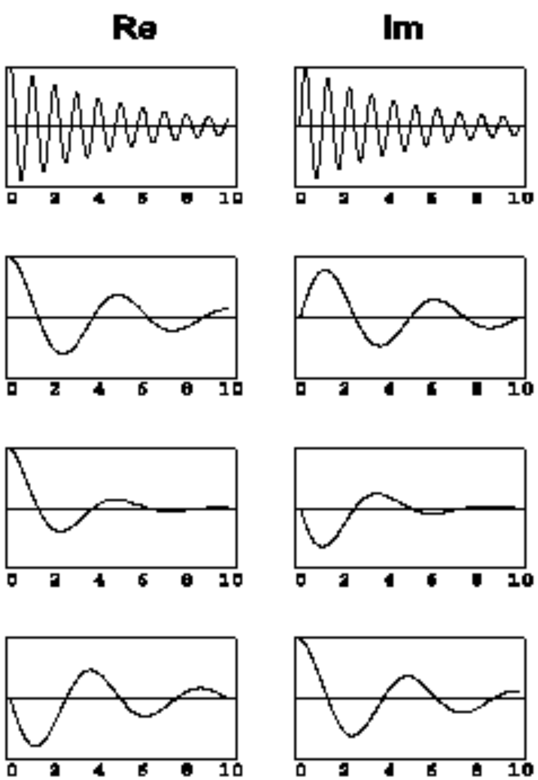
$$s(t) = \cos[(\omega_1 - \omega_0)t]\exp\{-\lambda t\} + i\sin[(\omega_1 - \omega_0)t]\exp\{-\lambda t\}$$

$$s(t) = a\exp\{[i(\omega_1 - \omega_0) - \lambda]t\}$$

For a spectrum containing ℓ lines:

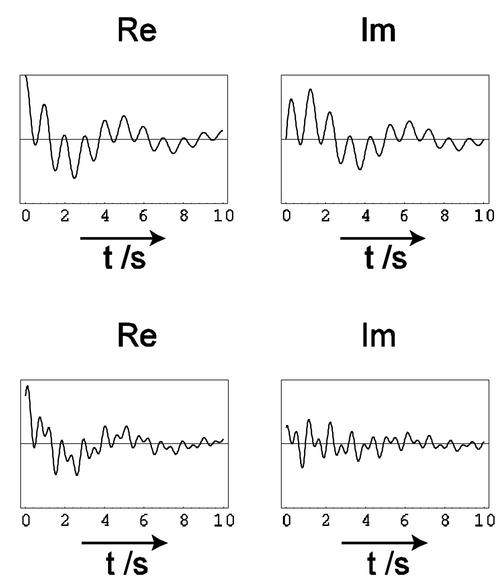
$$s(t) = \sum_\ell a_\ell \exp\{(i\omega_\ell^0 - \lambda_\ell)t\}$$

For a each lines:
One frequency ω_ℓ,
One damping rates λ_ℓ,
One amplitude (a_ℓ).



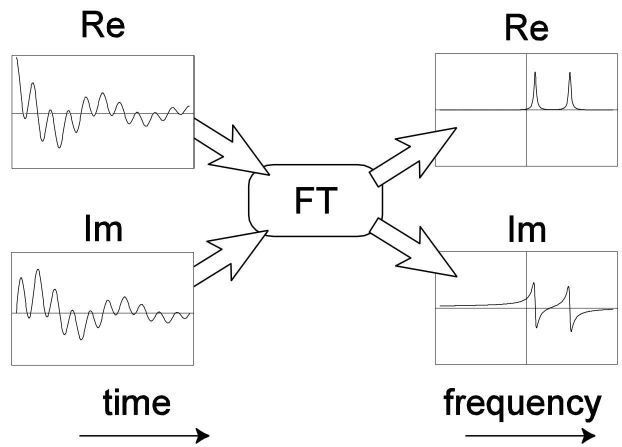
a_ℓ	$\omega_\ell/2\pi$ (Hz)	λ_ℓ (s^{-1})
1.0	1.0	0.2
1.0	0.2	0.2
1.0	- 0.2	0.2
1.0	0.2	- 0.2

***e.g.* 2 vs. 4 lines of different frequencies**



NMR Signals and Fourier Transformation

$$S(\omega) = \int_{-\infty}^{+\infty} e^{-i\omega t} s(t)\,dt$$



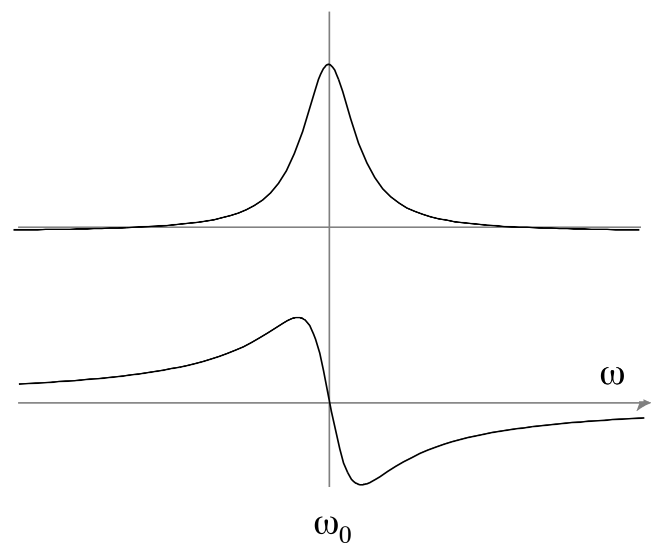
Line shapes (Lorenztian)

Adsorption line

$$\cos\{(\omega_0 - \omega)t\}\exp\{-\lambda t\} \rightarrow \frac{\lambda}{\lambda^2 + (\omega_0 - \omega)^2}$$

Dispersion line

$$\sin\{(\omega_0 - \omega)t\}\exp\{-\lambda t\} \rightarrow \frac{(\omega_0 - \omega)}{\lambda^2 + (\omega_0 - \omega)^2}$$



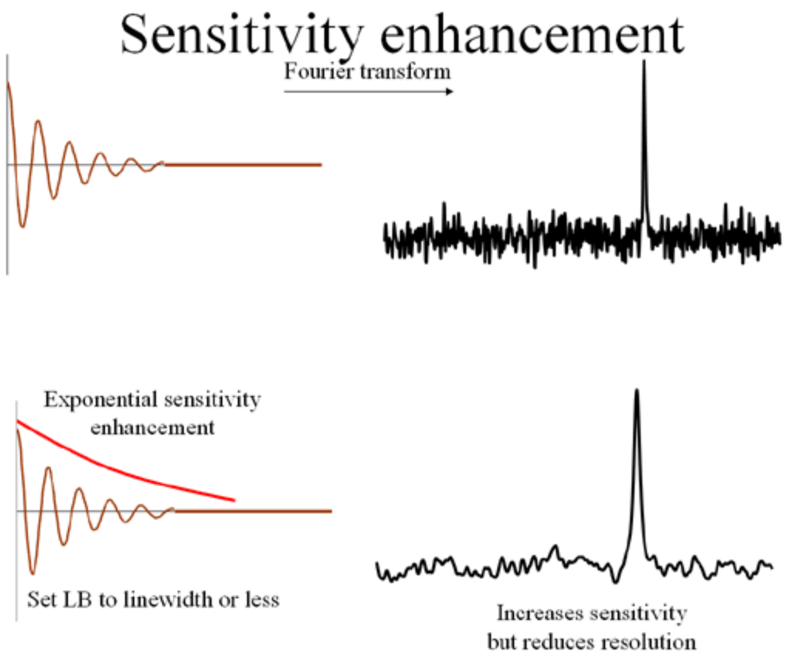
$\lambda = 1/T_2$

$$\frac{T_2^2}{1 + T_2^2(\omega_0 - \omega)^2}$$

$$\frac{T_2^2(\omega_0 - \omega)}{1 + T_2^2(\omega_0 - \omega)^2}$$

NMR Signals, Fourier Transformation and Apodization Functions

Apodization function (A): FID*A before FT. Multiplying FID by an apodization function allows the improvement of signal to noise ratio or line width.
Typically exponential decay, exp(-at), is used in order to obtain an increased S/N at the expense of line broadening.



Note that a truncated FID (experimental/acquisition time shorter than FID) corresponds to multiplying the FID by a step function, whose FT corresponds to sin(ax)/x. This will induced wiggles at each peak of the spectrum.