BLOCH EQUATIONS

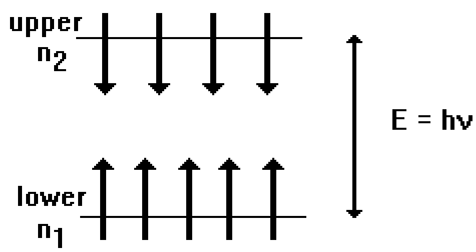
initial comment:

the phenomenological description of the macroscopic event,
valid only for isolated, non-coupled nuclei.

aim: the description of the magnetic resonance phenomenon.

initial status:

Boltzman distribution of the lower and the upper spin states at thermal equilibrium:

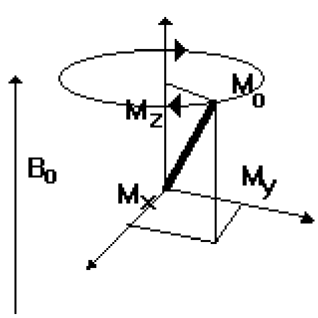


$$\frac{n_1}{n_2} = \exp\left(\frac{h\nu}{kT}\right) \approx 1 + \frac{h\nu}{kT}$$

conclusion :

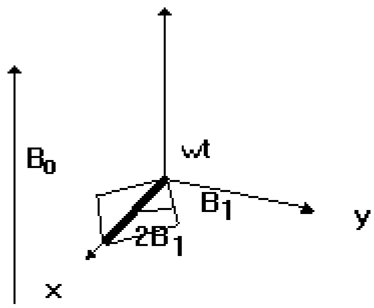
- this excess of nuclei generate a bulk magnetic moment (M_o)
- $M_o \parallel B_o$ (equilibrium Z magnetisation [M_o] is parallel to the external field [B_o]).
- NMR is very insensitive (approx. a unit excess for an ensemble of 1E+9 spins (at normal temp.)!)

A: in the absence of exciting field (no B_1).



$dM_x/dt = \gamma B_o M_y$	M_y rotates about B_o	(Larmor precession)
$dM_y/dt = -\gamma B_o M_x$	M_x rotates about B_o	(Larmor precession)
$dM_z/dt =$ const.	M_z is constant	

B: in the presence of an exciting field ($2B_1$)



$B_{1x} = B_1 \cos(\omega t)$ and $B_{1y} = -B_1 \sin(\omega t)$

$dM_x/dt = \gamma B_o M_y - \gamma B_{1y} M_z$ — M_y rotates about B_o and M_z rotates about B_1
$dM_y/dt = -\gamma B_o M_x - \gamma B_{1x} M_z$ — M_x rotates about B_o and M_z rotates about B_1
$dM_z/dt = -\gamma B_{1y} M_x + \gamma B_{1x} M_y$ — M_x rotates about B_1 and M_y rotates about B_1

$$dM_x/dt = \gamma B_o M_y + \gamma B_1 M_z \sin(\omega t)$$
$$dM_y/dt = -\gamma B_o M_x - \gamma B_{1x} M_z \cos(\omega t)$$
$$dM_z/dt = +\gamma B_1 M_x \sin(\omega t) + \gamma B_1 M_y \cos(\omega t)$$

$$dM_x/dt = \gamma(B_o M_y + B_1 M_z \sin(\omega t))$$
$$dM_y/dt = -\gamma(B_o M_x + B_1 M_z \cos(\omega t))$$
$$dM_z/dt = -\gamma(-B_1 M_x \sin(\omega t) - B_1 M_y \cos(\omega t))$$

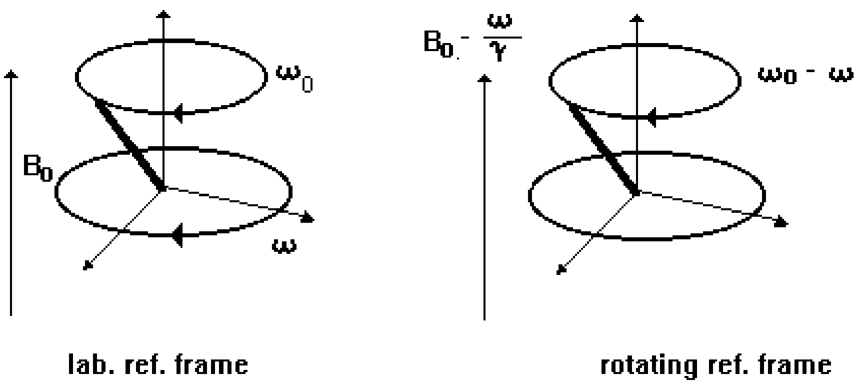
introduction of the two relaxation time constants:

- longitudinal (z) or T_1
- transverse (x, y) or T_2.

$$dM_x/dt = \gamma(B_o M_y + B_1 M_z \sin(\omega t)) - M_x/T_2$$
$$dM_y/dt = -\gamma(B_o M_x + B_1 M_z \cos(\omega t)) - M_y/T_2$$
$$dM_z/dt = -\gamma(-B_1 M_x \sin(\omega t) - B_1 M_y \cos(\omega t)) - (M_z - M_o)/T_1$$

This is the Bloch equation in an external x, y, z coordinate (in the laboratory frame).

Transformation of the Bloch equation from laboratory frame (x,y,z) to rotating frame (x',y',z').

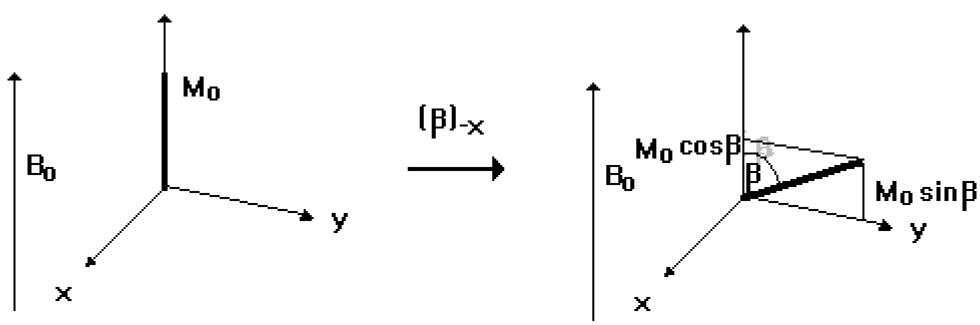


$dM_{x'}/dt = \quad (\omega_o - \omega)M_{y'} \qquad - \; M_{x'}/T_2$

$dM_{y'}/dt = - (\omega_o - \omega)M_{x'} \qquad + \omega_1 M_{z'} \qquad - M_{y'}/T_2$

$dM_{z'}/dt = - \; \omega_1 M_{y'} \qquad - \; (M_{z'} - M_o)/T_1$

FREE PRECESSION (the absence of radio-frequency field)



initial conditions after the β pulse:

$M_z(t{=}0) = M_o\cos(\beta)$	if $\beta{=}90^o$	$M_z(t{=}0) = 0$
$M_x(t{=}0) = 0$		$M_x(t{=}0) = 0$
$M_y(t{=}0) = M_o\sin(\beta)$		$M_y(t{=}0) = M_o$

A: the alteration of the Z magnetisation (β=90^o)

No B_1, ($\omega_1 = 0$), therefore $dM_{z'}/dt = -(M_{z'} - M_o)/T_1$

memo: $M_{z'}$ is toward its M_o [equil. value] with time constant T_1.

the solution of the diff. equ.: $M_{z'}(t) = M_o + \exp(-t/T_1)[M_z(t=0) - M_o]$

at t=0 (after the $90^o{}_x$) [$M_z(0) = M_o$] $M_{z'}(t) = M_o + \exp(-t/T_1)[- M_o]$

$M_{z'}(t) = M_o (1- \exp(-t/T_1)$

B: the dumped rotation in the X,Y plane (β=90^o)

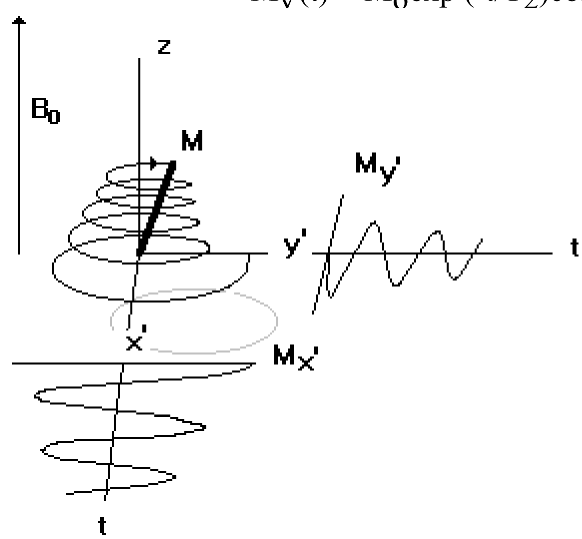
$dM_{x'}/dt = (\omega_o - \omega)M_{y'} - M_{x'}/T_2$

$dM_{y'}/dt = - (\omega_o - \omega)M_{x'} - M_{y'}/T_2$

If precession starts at t=0 (after $90^o{}_{-x}$), then $M_{x'}=0$ and $M_{y'} = M_o$

the solution of the diff. equ. $M_{x'}(t) = M_o\exp(-t/T_2)\sin(\omega_o - \omega)$

$M_{y'}(t) = M_o\exp(-t/T_2)\cos(\omega_o - \omega)$



the damped rotation of **M** in the x',y' plane induces the oscillation of the $\mathbf{M_{y'}}$ and $\mathbf{M_{x'}}$.

memo : The two components are 90^o out of phase.

If $M_{x'}$ is the real and $M_{y'}$ is the imaginary part of the complex magnetisation, then :

$$M^+ = M_{x'} + i\, M_{y'}$$

therefore:

$$dM_{x'} /dt = (\omega_o - \omega)M_{y'} - M_{x'}/T_2$$

$$+ d(iM_{y'})/dt = - i(\omega_o - \omega)M_{x'} - iM_{y'}/T_2$$

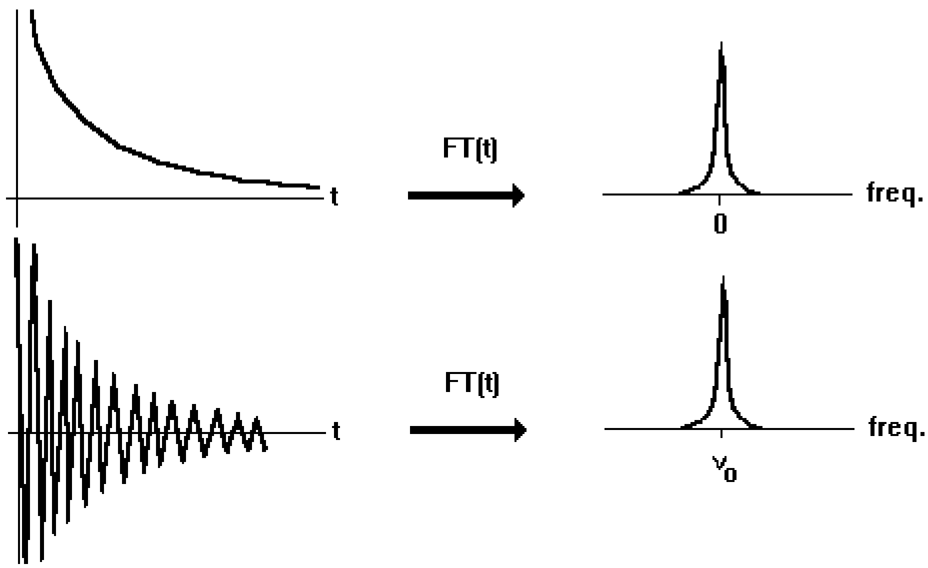
$$dM^+ /dt = (\omega_o - \omega)(M_{y'} - iM_{x'}) - M^+/T_2$$

$dM^+ /dt = (\omega_o - \omega)(M_{y'} - iM_{x'}) - M^+/T_2$ $\quad /(1 = - i^2)$
$dM^+ /dt = (\omega_o - \omega)(-i^2 M_{y'} - iM_{x'}) - M^+/T_2$
$dM^+ /dt = -i(\omega_o - \omega)(iM_{y'} + M_{x'}) - M^+/T_2$
$dM^+ /dt = -i(\omega_o - \omega)(M^+) - M^+/T_2$
$dM^+ /dt = -\{i(\omega_o - \omega) + 1/T_2\}(M^+)$

the solution of the diff. equ. ---> $M^+(t) = M^+_o \exp \{-[i(\omega_o - \omega)+1/T_2]t\} M^+(0)$

The Fourier transform of the solution

memo 1: Fourier pairs

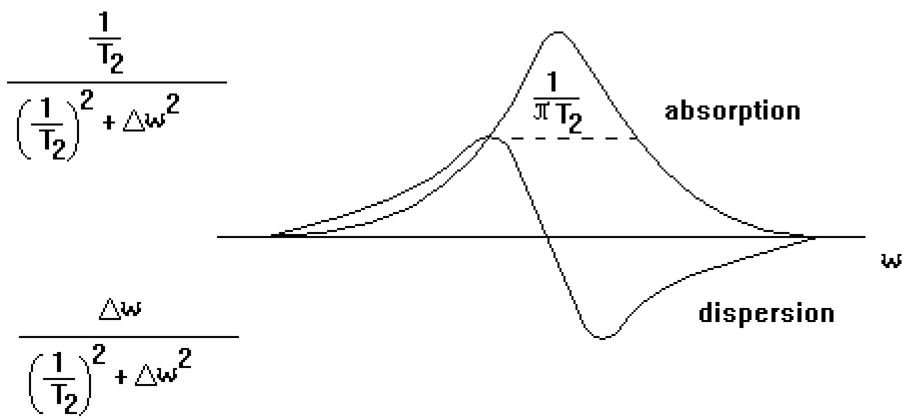


comment : decaying exp. ---> a Lorentzian at zero frequency
exponentially decaying cosinusoid ---> a Lorentzian offset from zero frequ. by the amount of the frequ. of oscillation.

memo 2: $S(\omega) = \int S^+(t) \exp(-i\omega t)\, dt$

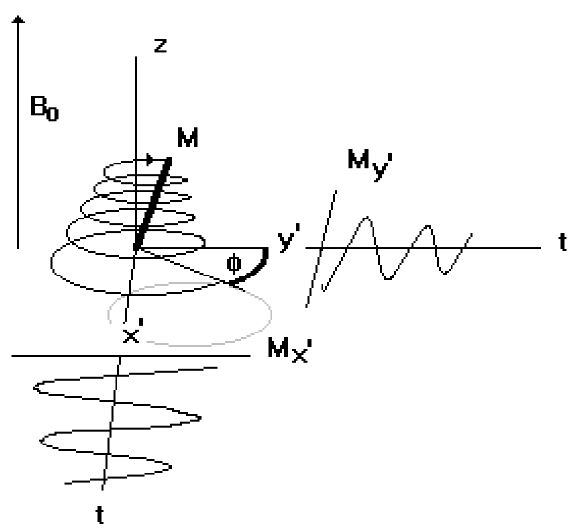
If the signal $\{M^+(t)\}$ is Fourier transformed, then the result (the spectrum) has the following form:

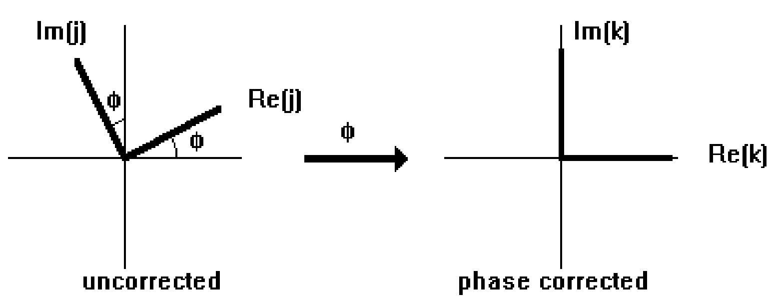
$S(\omega) = M_o a(\Delta\omega) - i\, M_o d(\Delta\omega)$
where $a(\Delta\omega)$ is the absorptive signal (Lorentzian)
$d(\Delta\omega)$ is the dispersive signal (Lorentzian)



The phasing of the solution

Since there is a time delay between the r.f. pulse and the t=0 of the acquisition (instrumental reason) a phase correction (ϕ) is needed.





THE STEADY-STATE AND THE TRANSIENT SOLUTION OF THE BLOCH EQUATIONS

$M_{x'} = M_o(2\pi[\omega_o - \omega]\gamma B_1 T_2^2)/\{1 + (2\pi[\omega_o - \omega]T_2^2) + \gamma^2 B_1^2 T_1 T_2\}$
$M_{y'} = M_o(\gamma B_1 T_2) \quad /\{1 + (2\pi[\omega_o - \omega]T_2^2) + \gamma^2 B_1^2 T_1 T_2\}$
$M_{z'} = M_o(4\pi^2[\omega_o - \omega]^2 T_2^2) \quad /\{1 + (2\pi[\omega_o - \omega]T_2^2) + \gamma^2 B_1^2 T_1 T_2\}$

if $T_1 = T_2$
$a = 2\pi[\omega_o - \omega]T_2$
$b^2 = \gamma^2 B_1^2 T_1 T_2$

then
$M_{x'} = M_o\, a\, b \quad /(1+a^2+b^2)$ dispersive spec.
$M_{y'} = M_o\, b \quad /(1+a^2+b^2)$ absorptive spec.
$M_{z'} = M_o(1+a^2)/(1+a^2+b^2)$ population diff.

A: the transient solution : $b^2 \ll 1$ (B1is sufficiently low to prevent saturation)

The absorptive spec. $M_{y'} = M_o\, b \quad /(1+a^2)$ a pure Lorentzian.
max. value: $\omega_o - \omega = 0 \rightarrow a = 0$
$M_{y'}(max.) = M_o\, b \quad /(1+b^2)$
if $b \ll 1$ then $M_{y'}(max.) = M_o\, b$

half-width: $1/2 M_o\, b = M_o\, b \quad /(1+a^2)$
$2 = (1+a^2)$
$1 = a^2 = (2\pi[\omega_o - \omega_{1/2}]T_2)^2$
$[\omega_o - \omega_{1/2}] = \pm 1/(2\pi T_2)$

the width at half-height (half-width): $\Delta\omega_{1/2} = 1/(\pi T_2)$

B: $b^2=1$ (B_1 has a higher power)

The absorptive spec. $M_{y'} = M_o\, 1 \quad /(1+a^2+1)$.
max. value: $\omega_o - \omega = 0 \rightarrow a = 0$
$M_{y'}(max.) = M_o \quad /(1+1)$
$M_{y'}(max.) = M_o /2$

half-width: $1/2(M_o/2) = M_o\, 1 \quad /(1+a^2+1)$
$4 = (1+a^2+1)$
$2 = a^2 = (2\pi[\omega_o - \omega_{1/2}]T_2)^2$
$[\omega_o - \omega_{1/2}] = \pm\sqrt{2}/(2\pi T_2)$

the width at half-height (half-width): $\Delta\omega_{1/2} = \sqrt{2}/(\pi T_2)$

conclusion : the signal is more intensive, but with a larger half-width.

C: the steady-state solution : $b^2 \gg 1$ (B_1 has a high power)

The absorptive spec. $M_{y'} = M_o b \quad /(1+a^2+b^2)$.

max. value: $\omega_o - \omega = 0 \rightarrow a = 0$

$M_{y'}(\text{max.}) = M_o b \ /(1+b^2)$

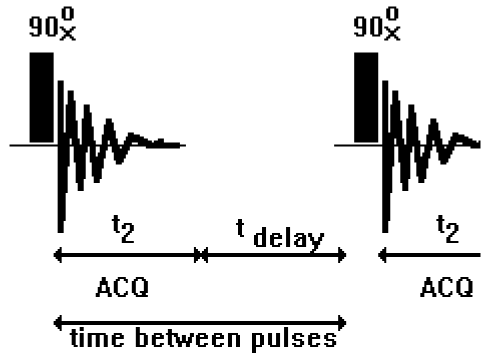
half-width:

$$1/2\{ M_o b \ /(1+b^2)\} = M_o b \ /(1+a^2+b^2)$$
$$1/2\{ 1 /(1+b^2)\} = 1/(1+a^2+b^2)$$
$$2 + 2b^2 = 1+a^2+b^2$$
$$1 + b^2 = a^2$$
$$1 + b^2 = a^2 = (2\pi[\omega_o - \omega_{1/2}]T_2)^2$$
$$[\omega_o - \omega_{1/2}] = \pm\sqrt{(1 + b^2)}/(2\pi T_2)$$

the width at half-height (half-width): $\Delta\omega_{1/2} = \sqrt{(1 + b^2)}/(\pi T_2)$

conclusion : the signal is more intensive, but with a larger half-width.

FT- and CW -NMR



If the "time between pulses" is short, then the Boltzman distribution is not restored between pulses and saturation is reached (this is the steady-state situation).

FT-NMR (the transient solution)

(half-width): $\Delta\omega_{1/2} = 1/(\pi T_2)$

sampling time ---> n T_2

measurement time ---> n T_2

CW-NMR (the steady-state solution)

(half-width): $\Delta\omega_{1/2} = \sqrt{(1 + \gamma^2 B_1{}^2 T_1 T_2)}/(\pi T_2)$

slow passage ---> n T_2 where n =2, 3

F n T_2/Δ
where F/ Δ is the number of lines in the total sweep width

comment :

$$F\, n\, T_2/\Delta = N\, n\, T_2$$

During the measurement time of a CW-NMR spectrum N FT-NMR transient can be recorded.

If F = 10 kHz and
Δ = 1 Hz
then 10^4 transient could be recorded.

If so, then sensitivity (signal to noise) improves ($\sqrt{N} = 100$)

memo : piano playing ---> CW-NMR (individual notes are presented)
---> FT-NMR (all accords are played at the same time)