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Descripción del modelo

Tema-Ib

Remembering

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An atom is classified according to its number of protons and neutrons:

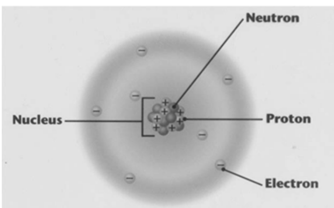
The number of protons in the nucleus of an atom determines an element's atomic number "chemical element"

All carbon atoms, and only carbon atoms, contain six protons and have an atomic number of 6

The number of neutrons determines the "isotope" of that element All atoms have a mass number, which is the sum of protons and neutrons.

The carbon atom has several isotopes. The most abundant with six neutrons and one with seven neutrons (^{12}C and ^{13}C)

The nuclei of all atoms may be characterized by:
a nuclear spin quantum number (I)



Only nuclei with ***spin number (I) ≠ 0*** *can absorb/emit electromagnetic radiation.*

NMR Active nucleus

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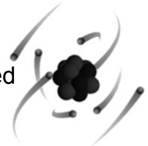
The nuclear spin quantum number **I** can either be equal to zero, or to multiples of 1/2
For atoms with there is no nuclear spin and therefore, they cannot have a nuclear magnetic resonance. These atoms are called NMR silent. All other values of **I** yield nuclear spin.



Even mass # and Even atomic # — No Nuclear spin
I=0 (^{12}C, ^{16}O, etc) — **NMR Inactive**

Odd mass# and Even atomic # — Nuclear Spin
I=1/2 (^{1}H,^{13}C, ^{15}N) — Spherical charge distribution

Odd mass# and Odd atomic#
I= n/2 (n≠1) integer I=3/2 (^{11}B, ^{23}Na); ^{53}Ca I=7/2

Even mass # and Odd atomic # — Ellipsoidal charge distribution
I=whole integer I=1 (^{2}H, ^{14}N) ; I=3 ^{10}B

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Tabla periódica

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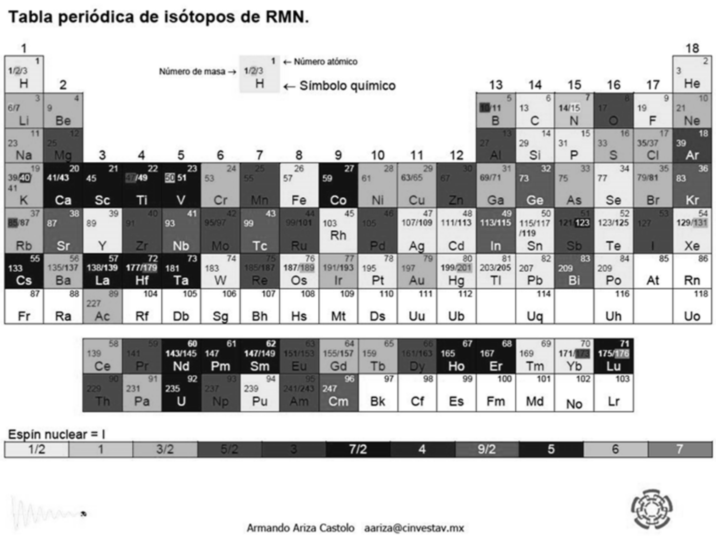

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Nuclear properties related to NMR

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Nuclear properties

Nuclide	Spin I	Electric quadrupole moment[a)] [eQ] [10^{-28} m^2]	Natural abundance) [%]	Relative sensitivity[b)]	Gyromagnetic ratio γ[a)] [10^7 rad T^{-1} s^{-1}]	NMR frequency [MHz][b)] (B_0 = 2.3488 T)
^{1}H	1/2	–	99.985	1.00	26.7519	100.0
^{2}H	1	2.87×10^{-3}	0.015	9.65×10^{3}	4.1066	15.351
^{3}H[c)]	1/2	–	–	1.21	28.5350	106.664
^{6}Li	1	-6.4×10^{-4}	7.42	8.5×10^{-3}	3.9371	14.716
^{10}B	3	8.5×10^{-2}	19.58	1.99×10^{-2}	2.8747	10.746
^{11}B	3/2	4.1×10^{-2}	80.42	0.17	8.5847	32.084
^{12}C	0	–	98.9	–	–	–
^{13}C	1/2	–	1.108	1.59×10^{-2}	6.7283	25.144
^{14}N	1	1.67×10^{-2}	99.63	1.01×10^{-3}	1.9338	7.224
^{15}N	1/2	–	0.37	1.04×10^{-3}	–2.7126	10.133
^{16}O	0	–	99.96	–	–	–
^{17}O	5/2	-2.6×10^{-2}	0.037	2.91×10^{-2}	–3.6280	13.557
^{19}F	1/2	–	100	0.83	25.1815	94.077
^{23}Na	3/2	0.1	100	9.25×10^{-2}	7.0704	26.451
^{25}Mg	5/2	0.22	10.13	2.67×10^{-3}	–1.6389	6.1195
^{29}Si	1/2	–	4.70	7.84×10^{-3}	–5.3190	19.865
^{31}P	1/2	–	100	6.63×10^{-2}	10.8394	40.481
^{39}K	3/2	5.5×10^{-2}	93.1	5.08×10^{-4}	1.2499	4.667
^{43}Ca	7/2	-5.0×10^{-2}	0.145	6.40×10^{-3}	–1.8028	6.728
^{57}Fe	1/2	–	2.19	3.37×10^{-5}	0.8687	3.231
^{59}Co	7/2	0.42	100	0.28	6.3015	23.614
^{119}Sn	1/2	–	8.58	5.18×10^{-2}	–10.0318	37.272
^{133}Cs	7/2	-3.0×10^{-3}	100	4.74×10^{-2}	3.5339	13.117
^{195}Pt	1/2	–	33.8	9.94×10^{-3}	5.8383	21.499

NMR Periodic Table

http://www-usr.rider.edu/~grushow/nmr/NMR_tutor/periodic_table/nmr_pt_frameset.html

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Nuclear spin and Magnetic Moment

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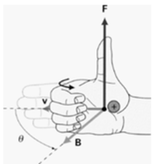
Nucleus rotates about its axis (spin)

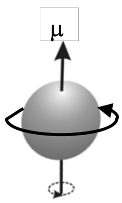
Nuclear spin results in angular momentum (**P**). $P = \hbar \times \sqrt{I(I+1)}$

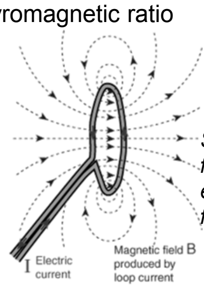
Quantized spin quantum number I
2I+1 States I, I-1, I-2, …, -I

Since the nucleus is charged, spin will produce a magnetic momentum (**u**)

$\mu = \gamma P$ Where γ is the proportionality constant called the gyromagnetic ratio







Similar to magnetic field created by electric current flowing in a coil

The magnetic moment is quantized (m)

for proton ***m*** **=+½ & -½**

m = I, I-1, I-2, …, -I

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Quantization of magnetic moment

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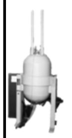


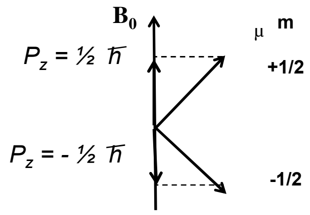
The angular momentum for a nucleus, in a static magnetic field, with will be oriented directionally

$$P_z = m\hbar$$

m is the magnetic quantum number m = I, I-1, I-2, …, -I

therefore, there are (2*I*+1) *values for m, and (2I+1) possible orientations for the* angular momentum

For a nucleus with I = 1/2 there are two possible orientations of the magnetic moment



This is the simplest case only two orientations and only one transition between them

the components of the magnetic moment along *z*

$$\mu_z = \gamma P_z = m\gamma\hbar$$

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Precession Classical description

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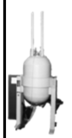
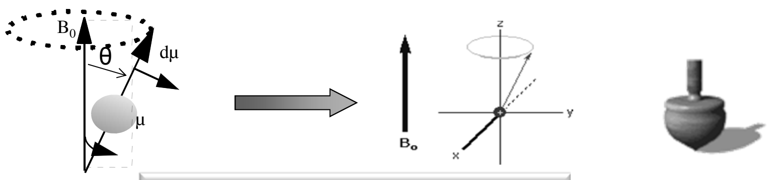


In a external magnetic field the nuclear spin precesses at **Larmor frecuency**

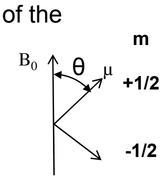
$\varpi_o = -\gamma B_0$ (rad s^{-1}) ⟶ ($\upsilon = \omega_0/2\pi$) $\upsilon_0 = \gamma B_0 /2\pi$ (Hz)



Larmor frecuency related with γ and B_0

The relative orientation of the magnetic moment (θ) is depend of value **I**

For a nucleus with I = 1/2 there are two possible orientations of the magnetic moment



(General rule: # orientations = 2I+1):

This is the simplest case, only two orientations and only one transition between them

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Magnetic alignment

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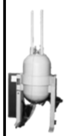
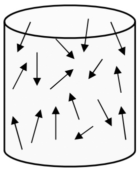
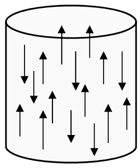
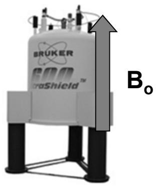


↑ = γ h / 4π







In the absence of external field,
each nuclei is energetically degenerate

Add a strong external field (B_o) and the nuclear magnetic moment: aligns with (low energy)
against (high-energy)

At equilibrium (in the magnetic field), there is excess of nuclei in the a state of low energy

The energy of a spin in a magnetic field (E) will depend on a static magnetic field called B_0, and µ. $E = -\mu_z B_0 = -m\gamma h B_0$

For I=1/2 then **m** can be +1/2 and -1/2

m=-1/2 (β) —— $E_\alpha = +1/2\gamma h B_0$

m=+1/2 (α) —— $E_\alpha = -1/2\gamma h B_0$

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Nuclear Energy levels in a Static Magnetic Field

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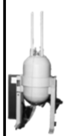

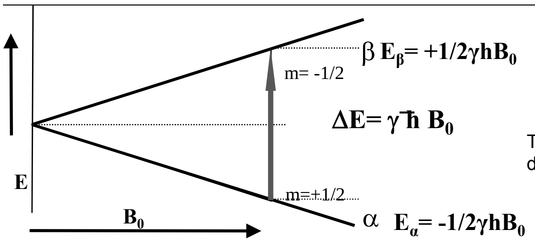

$E = -\mu_z B_0 = -m\gamma h B_0$

The energy difference is linearly dependent on **γ** and on ***B₀***

•At thermal equilibrium the energy difference between α and β states prevents these states from being equally populated

•The relative population of a particular state is given by the Boltzman distribution:

$$\frac{N_\beta}{N_\alpha} \approx 1 - \frac{\gamma \hbar B_0}{K_B T}$$

Nα = number of nuclei in the α state
Nβ = number of nuclei in the β state
K_B = Boltzman constant K_B=1.3085 x10^{-23} JK^{-1}
T = temperature (Kelvin)

B_0=1.41T (60 MHz) $\frac{N_\beta}{N_\alpha}$ = **0.9999904**

B_0=1.41T (800 MHz) $\frac{N_\beta}{N_\alpha}$ = **0.99987**

The Difference is very small (ppm)

NMR IS INSENSITIVE

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Net Magnetization

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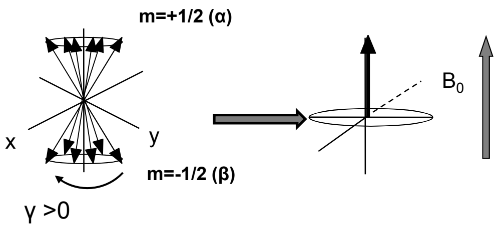
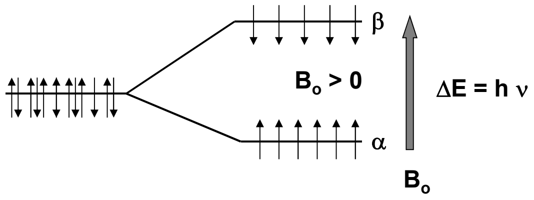
<u>Classic vectorial View:</u>

- **Nuclei either align with or against external magnetic field along the z-axis.**
- **Since more nuclei align with field, net magnetization (M_o) exists parallel to external magnetic field**



<u>Quantum Description:</u>

- **Nuclei either populate low energy (α, aligned with field) or high energy (β, aligned against field)**
- **Net population in a lower energy level.**
- **Absorption of radio-frequency promotes nuclear spins from α → β.**



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Resonance

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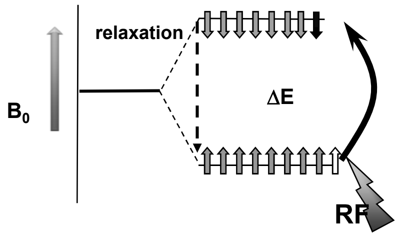
The relationship between the Larmor frequency and Δ*E is as follows:*

ΔE= ħν_i $\Delta E = \gamma\hbar B_0$ *and* $v_L = (\gamma/2\pi) B_0$, $\Delta E = hv_L$

Transitions between energy levels (between α and β spin states for spin 1/2 nuclei) are quantized, and can only be promoted by an energy Δ*E*
In NMR the transitions are promoted by an applied electromagnetic field, ***B_1* with** a frequency, v_1 (radiofrequency) matching the Larmor frequency of the nucleus

$\nu_L = \nu_i = (\gamma/2\pi) B_0$ $\Delta E = hv_1$

This is known as ***resonance ($v_1 = v_L$),*** when the frequency of our externally applied electromagnetic field (B_1) are coincident with the Larmor frequency of the nucleus of interest



$N_\alpha > N_\beta$ —($\nu_i = \nu_L$)→ signal

$N_\alpha = N_\beta$ → Saturation

http://ochem.jsd.claremont.edu/movies.dir/nmr.htm

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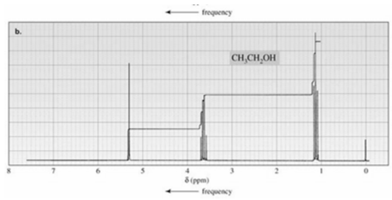
Continous Wave (CW)

NMR can be performed like other spectroscopy's (UV/vis, IR) by simply slowly varying the frequency of monochromatic incident radiation and monitoring for absorption

The first spectrometers using a frequency sweep, a constant magnetic field, to obtain the spectra.

One alternative was to sweep the magnetic field while maintaining a constant frequency.



The scan rate determines the resolution and the possibility of saturation of the signals. The average duration of a sweep might be between 2 and 10 minutes.

The system is very inefficient because much of the time was recorded only noise in the spectrum.

Most spectrometers could not add different sweeps

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Fourier Transform

How to efficiently detect a range (spectrum) of NMR frequencies

4.3 SENSITIVITY OF FOURIER SPECTROSCOPY 157

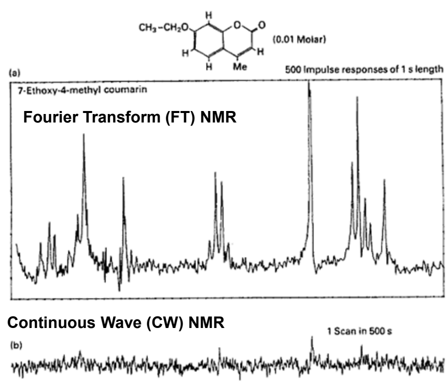

FIG. 4.3.4. 60-MHz proton magnetic resonance spectra of 7-ethoxy-4-methyl coumarin. (a) Fourier transform of 500 free induction signals recorded in 500 s. (b) Single scan recorded in 500 s by slow passage on the same instrument. (Reproduced from Ref. 4.130.)

R.R Ernst et al Principles NMR

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Pulse NMR

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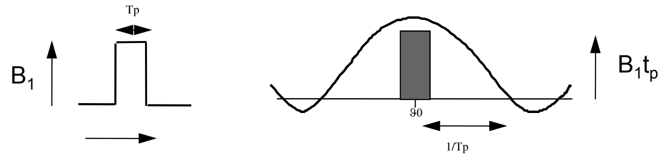
In pulsed Fourier transform NMR, for a given nucleus (1H for example), all frequencies are excited simultaneously by a short, high power radiofrequency pulse (***B_1 field)***



The pulse is applied at a particular frequency, ν_1, but a short pulse excites a large continuous band of frequencies (the **bandwidth)** centered around ν_1.

The useful or effective bandwidth is proportional to **1/τp** (τ**p is the pulse length,** also called the **pulse width or pulse duration).**

The **pulse amplitude** is a measure of the power with which the pulse is applied, and determines the strength of the *B_1 field*

τp is usually very short, i.e. µs

For all frequencies can be excited in a homogeneous mode must be satisfied that **$\gamma B_1 = 2\pi SW$**, (SW equal to spectral window), **Pw_{90} << 1/4sw**

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Rotating Frame

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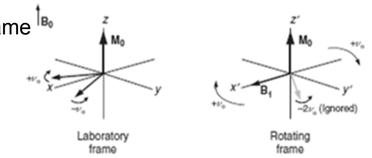
The RF pulse provides an oscillating magnetic field B1 (at Lamor Frequency) in transverse plane (is equivalent to two counter-rotating vectors)

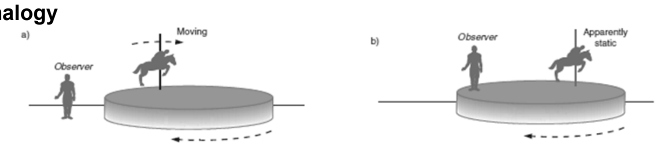
__Simplification__: Laboratory frame to Rotating Frame



The system rotate to the equal RF frecuency v_0

The -2v_0 is far to the resonance frequency and may be ignored

Analogy



Laboratory frame   Rotating frame

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RMN Experiment

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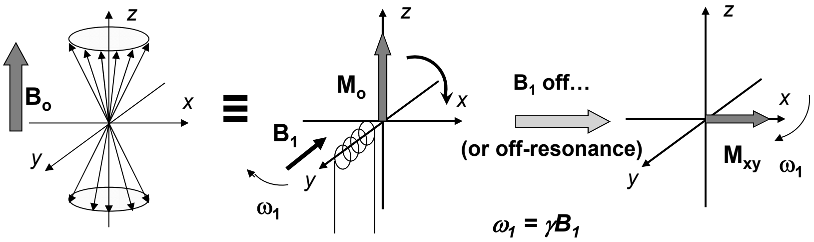
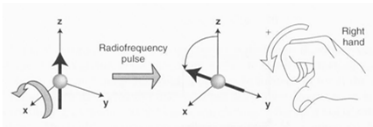
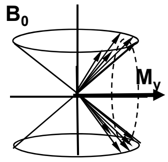
Resonant condition: frequency (ω_1) of B_1 matches *Larmor* frequency (ω_o) energy is absorbed and population of α and β states are perturbed.



M_o now precesses about B_1 for as long as the B_1 field is applied.



Right-hand rule



Phase coherence

Pulse effect

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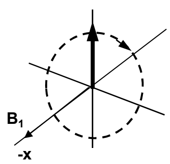
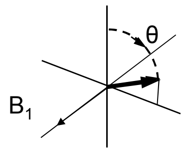
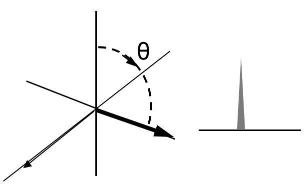
The pulse generates Mxy transverse magnetization

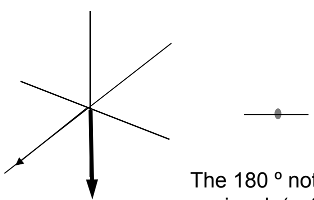
The flip angle is: $\alpha = 360\ \gamma B_1 t_p$ degrees







The 90º pulse correspond to maximum signal



The 180 º not produce signal (saturation)

Pulse phase

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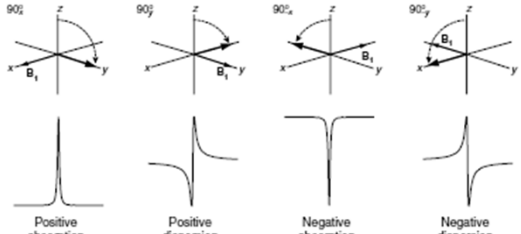
Detection in -y



Some sequences use a different phase pulse: Phase Cycling
Selecting the some signals in NMR experiment and rejecting the those that are not required

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NMR Signal Detection
FID: Free Induction Decay

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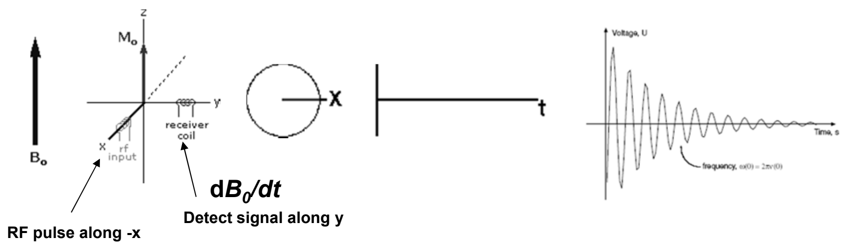
The pulse generates M_{xy} transverse magnetization that precesses around the z axis at precession frequency w_o

The FID reflects the change in the magnitude of M_{xy} as the signal is changing relative to the receiver along the y-axis



Again, the signal is precessing about B_o at its Larmor Frequency (ω_o).

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Events after the pulse:
Evolution of the magnetization

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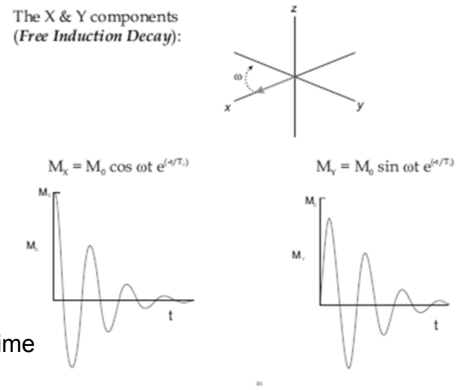
The magnetic moment (*M) precessing about a static magnetic field (B_0) results in* a local magnetic field (*B') varying in time (dM/dt ∞dB'/dt)*



$M_y(t)=-M_0 \cos(w_o t)\, e^{(-t/T_2)}$

$M_x(t)=M_0\, sen(w_o t)\, e^{(-t/T_2)}$

T_2 transverse relaxation time

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NMR Sensitivity in NMR

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The sensitivity of a nucleus depends of :
- Gyromagnetic constant
- External magnetic field
- Natural abundance isotope to observe

$dM/dt \propto \gamma B_0 M \propto N \gamma^3 B_0^2 h^2 I(I+1)/(3k_B T)$

Isotope	I	γ (10^7 rad T^{-1} s^{-1})	Abundancia N(%)	Resonance Frec. B=2.3488T	relative* sensitivity
1H	1/2	26.7519	99.98	100.0	1
19F	1/2	25.1815	100	94.077	0.83
31P	1/2	10.8394	100	40.481	$6.63x10^{-2}$
13C	1/2	6.7283	1.10	25.144	$1.56x10^{-2}$
2H	1	4.1066	0.015	15.351	$9.65x10^{-3}$
15N	1/2	-2.7126	0.37	10.133	$1.04x10^{-3}$

$\gamma\ ^1H$ = 26,753 rad/G

$\gamma\ ^{13}C$ = 6,728 rad/G

Ratio ($\gamma\ ^1H/ \gamma\ ^{13}C)^3 \approx 64$

If we consider the term A (Natural abundance) $^1H \approx 100\%$; $^{13}C \approx 1\%$

<u>^1H is 6400 times more sensible than 13C</u>

Nuclei with larger **γ** will absorb/emit more energy, and will therefore be more sensitive.

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Time Domain to Frecuency Domain
Fourier Transform

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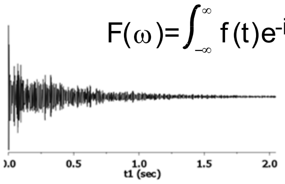
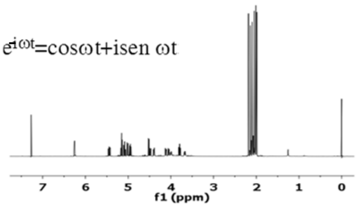
Time domain signals are converted into frequency domain signals using **the Fourier Transform**

$$F(\omega)=\int_{-\infty}^{\infty} f(t)e^{-i\omega t}dt \qquad e^{i\omega t}=\cos\omega t+i\,\mathrm{sen}\ \omega t$$

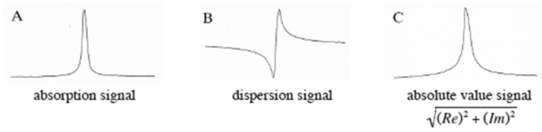




f(t)corresponds to the time domain, and F(ω) corresponds to the frequency domain

F(ω) is a complex function that has a real (Re) and an imaginary part (Im)

Re	Absortion
Im	Dispersion



line shape is Lorentzian (Fourier transform of a decaying exponential function)

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Frequency Domain

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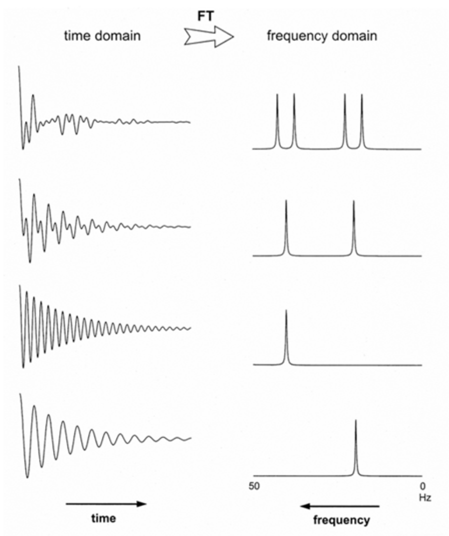

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Spectra

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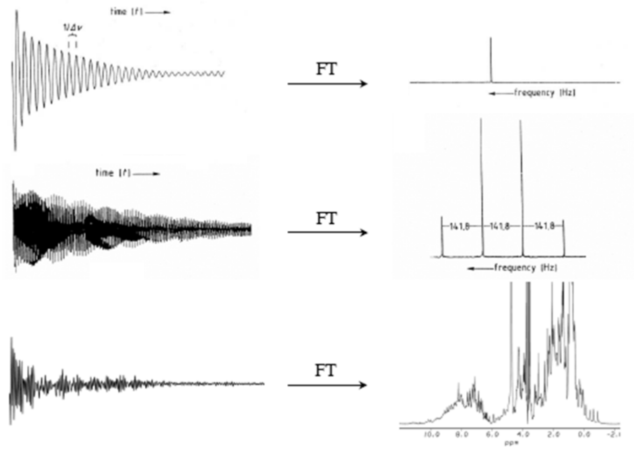
In the frequency domain (spectrum) is easier to determine the chemical shifts and couplings for individual spins



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The NMR Spectrum

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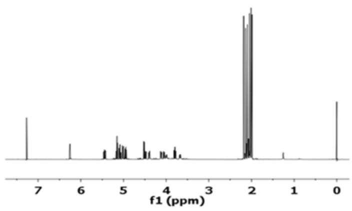
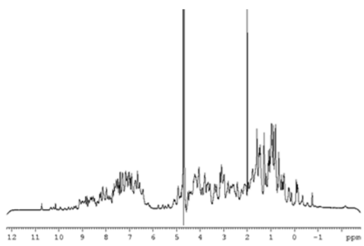
The spectrum contains the following observable

- signal position or **chemical shift**
- intensity which is proportional to @ of nuclei
- **width** which depends on the dynamics and size of the molecule
- splitting or **couplings** which is sensitive to # of bounded nuclei

The peaks in an NMR spectrum depend on the environment (structure) and the dynamics of the molecule



1H NMR spectrum of an organic molecule (acetyl-cellobiose)



1H NMR spectrum of a protein (lysozyme)

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