Principles of Nuclear Magnetic Resonance

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Nuclear magnetic resonance (NMR) spectroscopy

Process: tune the spectrometer to the frequency of a particular magnetic nucleus, viz., ^{1}H, ^{13}C, ^{19}F (radio frequency), and record the absorption of energy due to transition between quantized nuclear spin energy levels

Nuclear spin quantum number (I):

Mass number	Z	I
Even	Even	0
Odd	Even or odd	1/2, 3/2, 5/2,…
Even	Odd	1, 2, 3,…

^{4}He, ^{12}C, ^{16}O, ^{18}O, ^{32}S

I=1/2 (e.g., ^{1}H, ^{13}C, ^{15}N, ^{19}F)

I=3/2, ^{11}B

I =1, ^{2}H, ^{14}N,

Angular momentum vector $S = \hbar I$

gyromagnetic ratio

nuclear g-factor

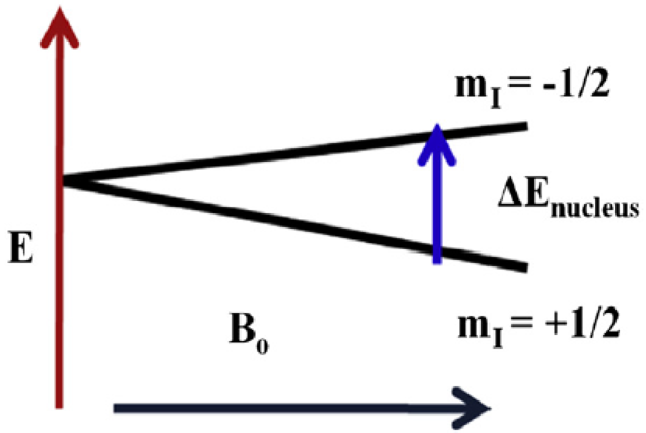
Table 1.1 Natural abundances of some common nuclear magnetic resonance–active isotopes with I = 1/2

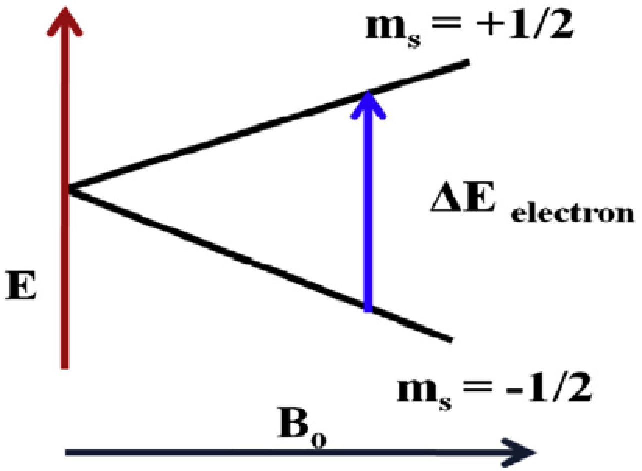
Isotope	Natural abundance (%)	μ (magnetic moment)[a]	g_N	γ [10^8 rad $T^{-1}s^{-1}$]	υ (MHz at 2.35 T)
^{1}H	100	2.7927	5.585	2.675	100
^{13}C	1.108	0.7022	1.404	0.672	25.14
^{15}N	0.365	0.4036	−0.566	−0.271	10.13
^{19}F	100	2.6273	5.255	2.516	94.07
^{31}P	100	1.1305	2.261	1.083	40.48
^{29}Si	4.71	−0.5555	−1.110	−0.532	19.87

[a] μ in units of nuclear magnetons = 5.05×10^{-27} JT^{-1}.

THEORY OF NUCLEAR MAGNETIC RESONANCE AND ELECTRON SPIN RESONANCE SPECTROSCOPY

Nuclear magnetic resonance	Electron spin resonance
$E = -\mu B_0 = -\mu B_0 \cos\theta$	$E = -\mu B_0 \cos\theta$ (1.1)
$\mu = g_N \mu_N I$	$\mu = -g_e \mu_B S$
g_N = nuclear g-factor	g_e = Lande g-factor (g_e is 2.0023)
μ_N = nuclear magneton	μ_B = Bohr magneton
$\mu_N = eh/4\pi m_p$	$\mu_B = eh/4\pi m_e$
e = electronic charge	e = electronic charge
m_p = mass of the proton	m_e = mass of the electron
$E = -g_N \mu_N B_0 I$	$E = g_e \mu_B B_0 S$
$Em_I = -g_N \mu_N B_0 m_I$	$Em_s = g_e \mu_B B_0 m_S$
$E_{1/2} = -g_N \mu_N B_0/2$	$E_{1/2} = g_e \mu_B B_0/2$
$E_{-1/2} = g_N \mu_N B_0/2$	$E_{-1/2} = -g_e \mu_B B_0/2$
$\Delta E = E_{-1/2} - E_{1/2} = g_N \mu_N B_0$	$\Delta E = E_{1/2} - E_{-1/2} = g_e \mu_B B_0 = h\upsilon$





For example, ^{1}H
μ = 2.7927 nuclear magnetons

g_N=5.585

Constant μ_N=5.05e-27 J/T

$$I = \frac{1}{2}$$

Assuming B_0=2.35 T,
the interaction energy
E=-33.1424e-27 J
ΔE=66.28e-27 J

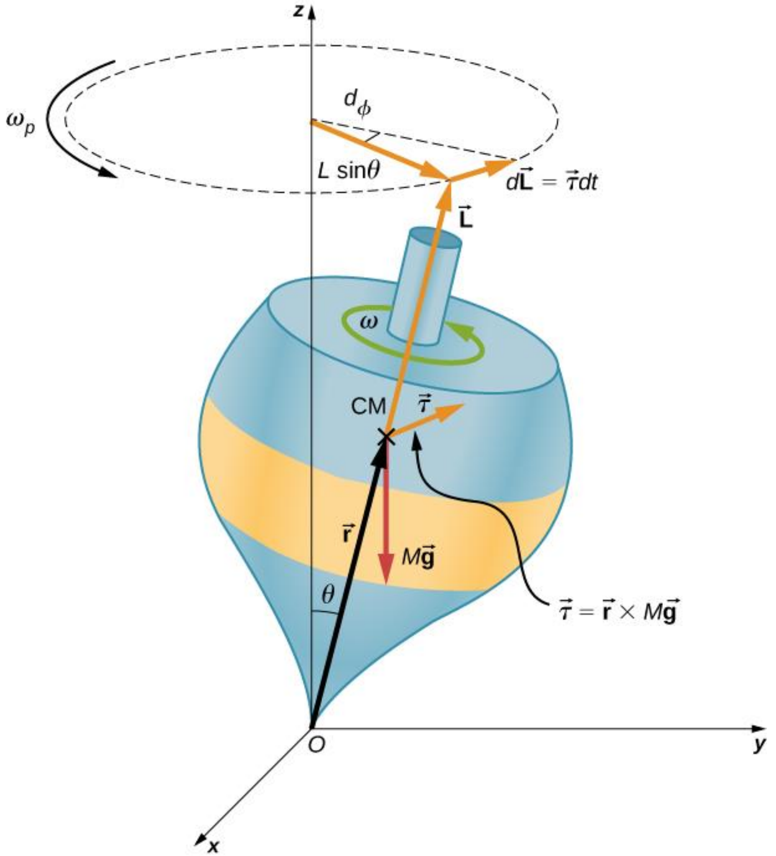
$\upsilon = \frac{\Delta E}{h}$ =66.28e-27/6.62e-34=1e8 Hz

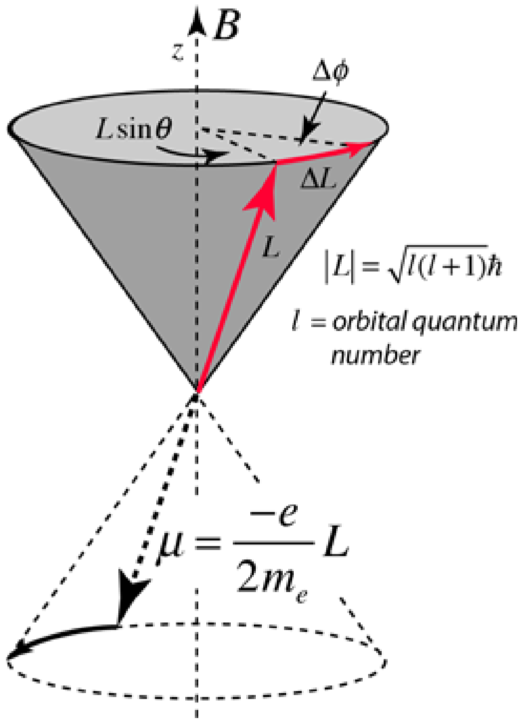
For **ESR**, μ_B=9.274e-24 J/T

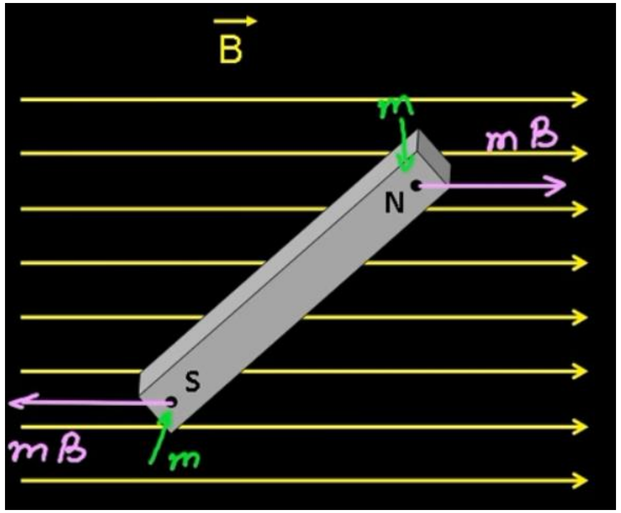
$\upsilon = \frac{\Delta E}{h}$ = 6.59e10 Hz, microwave

Resonance frequency

Larmor precession







$$\tau = rMg\sin\theta.$$

$$dL = rMg\sin\theta\, dt.$$

$$\omega_P = \frac{rMg}{L} = \frac{rMg}{I\omega}$$

$$\vec{\tau} = \vec{\mu} \times \vec{B} = \gamma \vec{L} \times \vec{B}$$

$$dL = \gamma L B \sin\theta\, dt$$
$$dL = L\sin\theta\, d\phi$$
$$\omega_0 = \frac{d\phi}{dt} = \gamma B$$

For ^{1}H, γ = 2.675e+08 rad $s^{-1}T^{-1}$

= 4.2574e+07 Hz/T

Assume, B_0=2.35 T

Then, υ =1e8 Hz

Larmor frequency = resonance frequency

= RF field frequency

Larmor precession

Larmor frequency = resonance frequency = RF field frequency

1. Due to Zeeman effect and magnetic resonance

$$\Delta E = \gamma\ h\ B_o$$

$$E = h\ f_o = \gamma\ h\ B_o$$

or

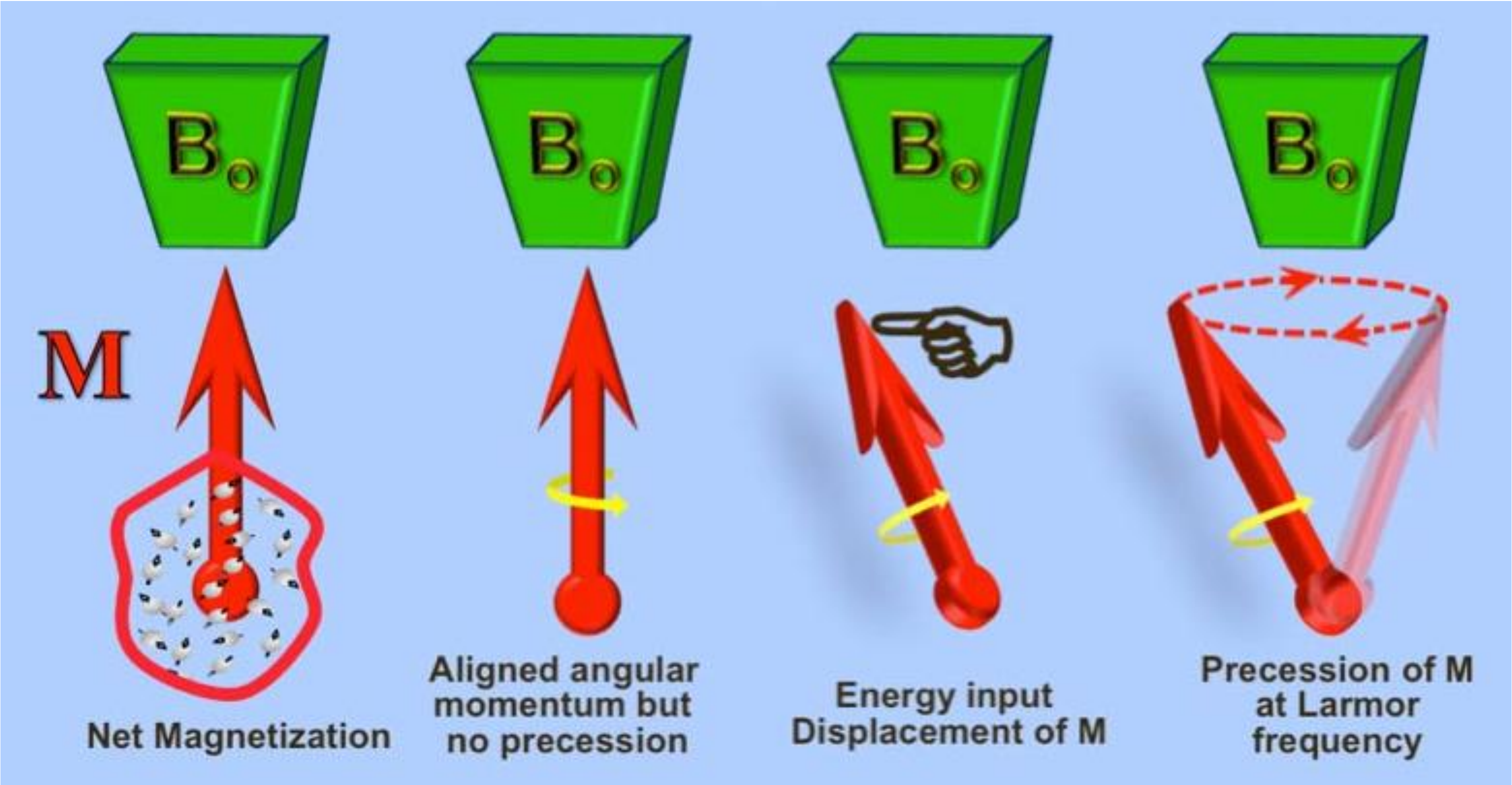
$$f_o = \gamma\ B_o$$

2. **Magnetic resonance and radio-frequency pulses**

Only when υ_{rf} matches υ_L, precession will occur.

$$\gamma_n = \frac{e}{2m_p} g_n = g_n \frac{\mu_N}{\hbar}$$

Precession of M



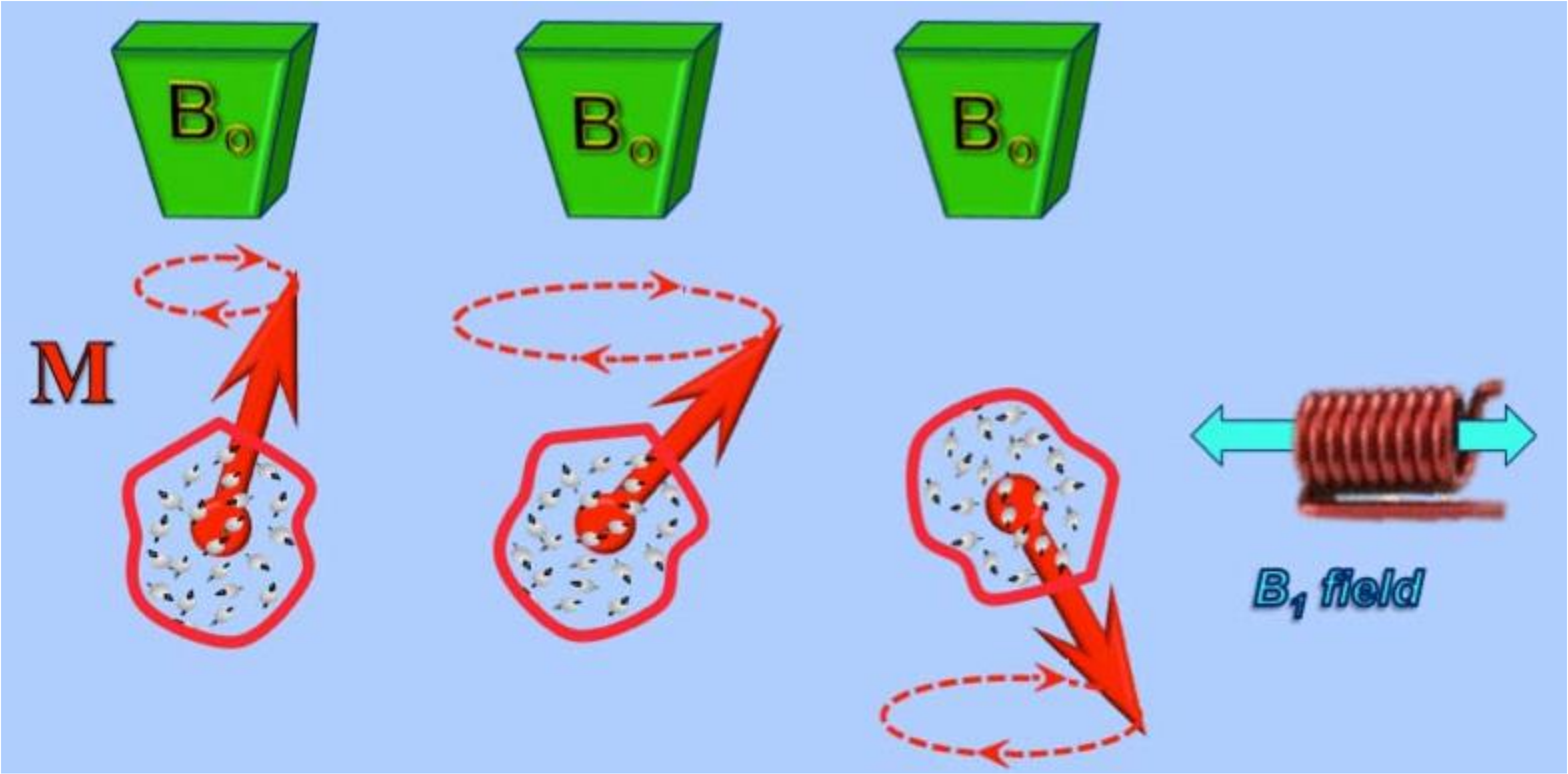
1. M can be tipped out of its initial alignment with B_0 by a perpendicular RF-field (B_1) rotating at Larmor frequency

2. Once tipped out of alignment, **M** will precess in the transverse plane also at the Larmor frequency.

3. This onset of **M**'s precession coincides with the start of an oscillating energy exchange between $\mathbf{B_1}$, the spins, and their environments.

Precession of M

1. Nuclear precession is not the same as NMR
2. Precession of **M** is NMR
3. Every magnetically receptive nucleus is precessing in the earth's magnetic field (50 µT)
4. Precession of the net magnetization (**M**) *is* a manifestation of resonance.

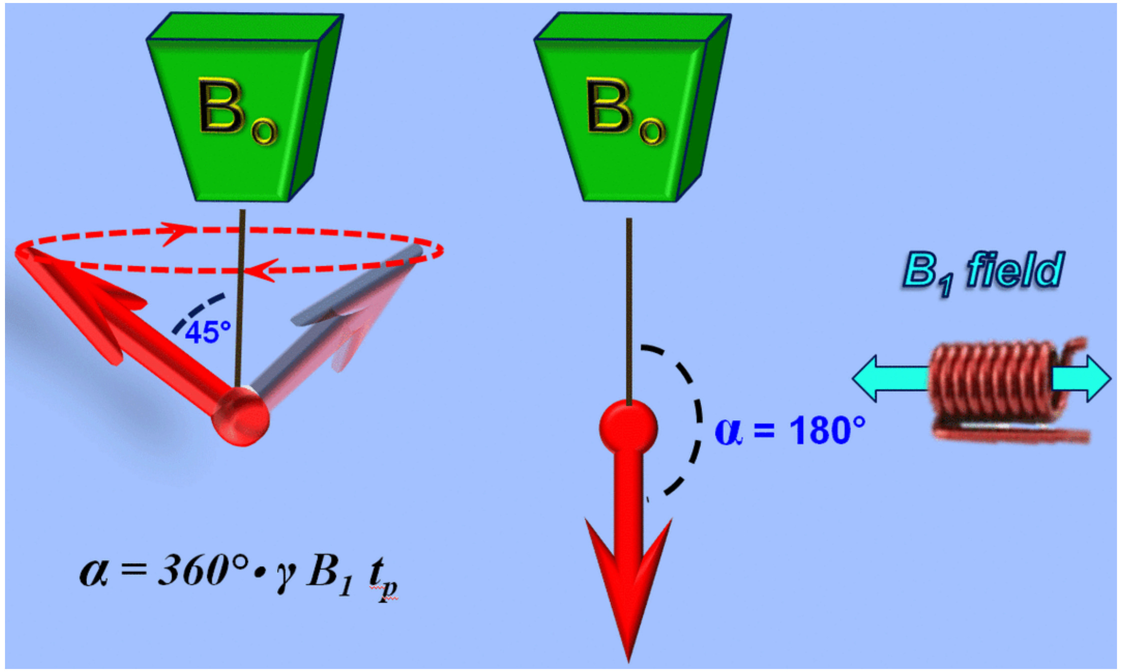


Continued application of the rotating/oscillating $\mathbf{B_1}$ field results in progressive tipping
Any angle by B_1
No change of magnitude of M

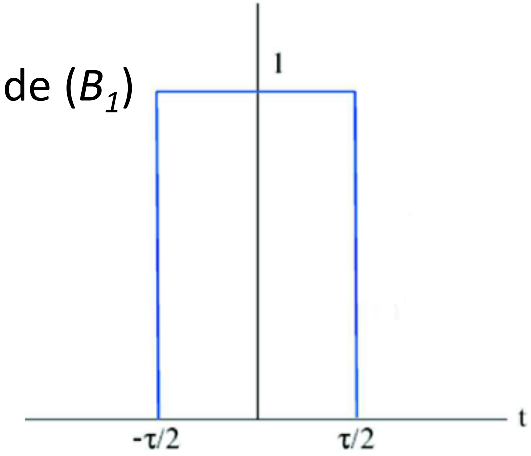
Flip (or Tip) Angle

Flip angle, also called ***tip angle (α)***, is the amount of rotation the net magnetization (**M**) experiences during application of a radiofrequency (RF) pulse.

$$\alpha = \gamma \cdot B_1 \cdot t_p$$

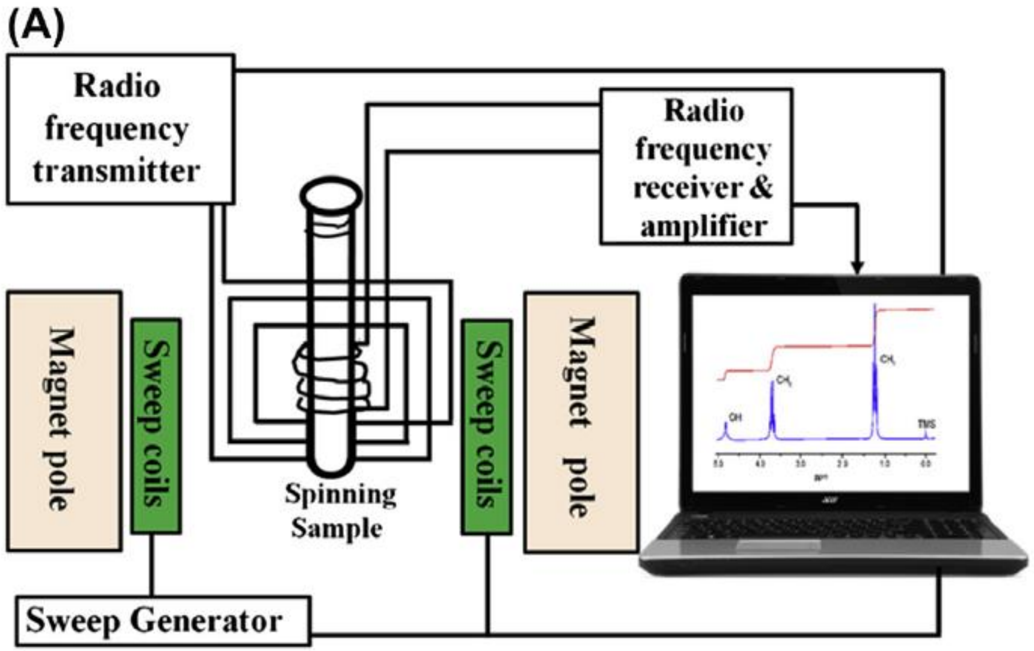


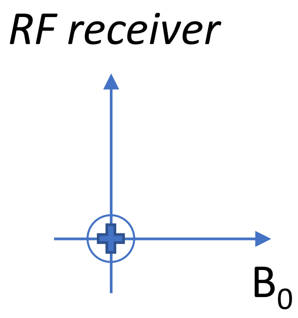
constant amplitude (B_1)

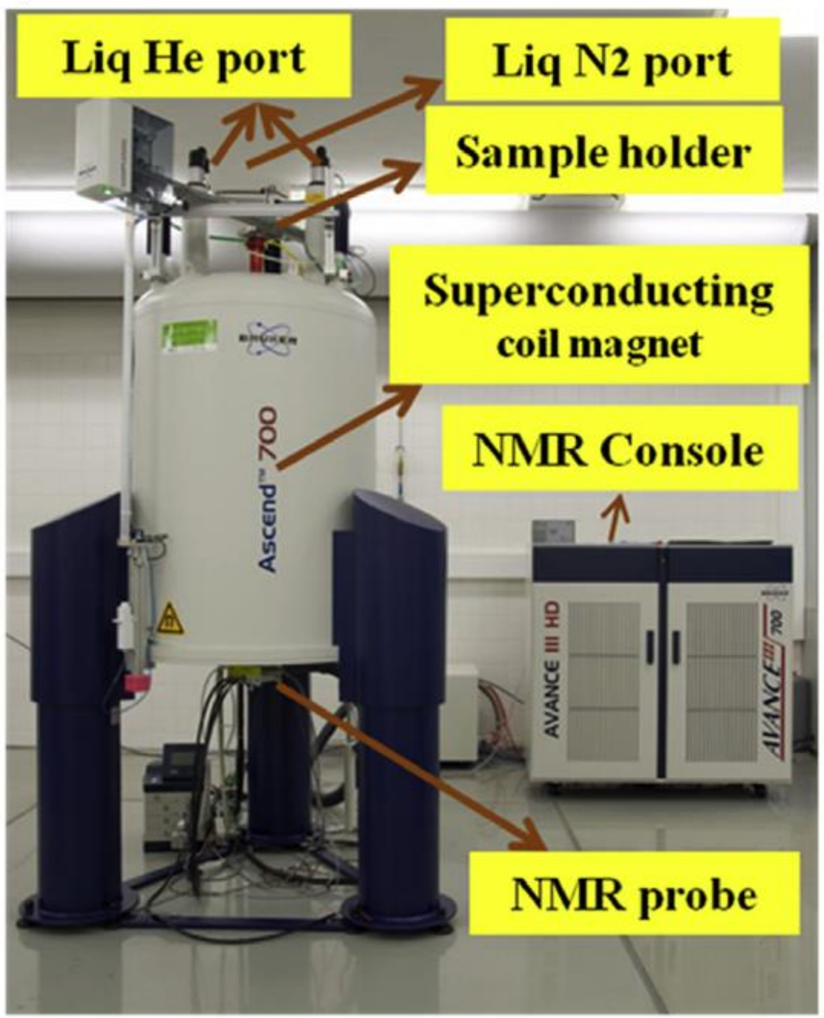


duration (t_p)

NUCLEAR MAGNETIC RESONANCE INSTRUMENTATION







1. *Electromagnet*
2. *Sweep coil generator*: vary applied magnetic field in a small range
3. *Sample holder*: spinning of the sample.
4. *RF transmitter*: The axis of the coil has to be perpendicular to the magnetic field, i.e., the RF is applied perpendicular to B_0.
5. *RF receiver*: Its axis has to be perpendicular to both the magnetic field and the axis of the transmitter coil.
6. *Read out system*

Thank you

“To be continued…”