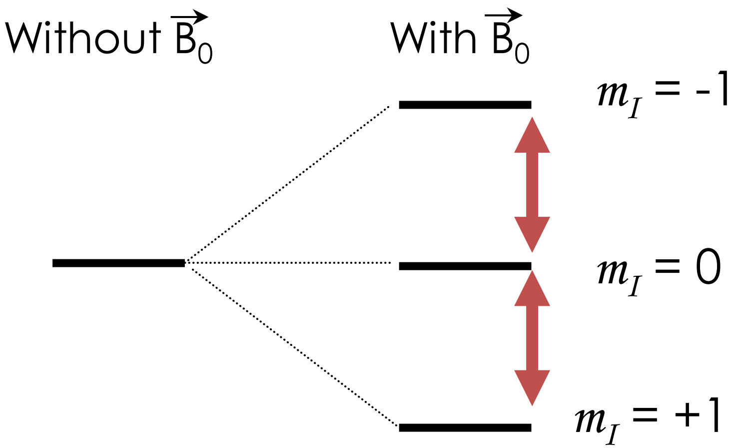
2. Zeeman effect

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

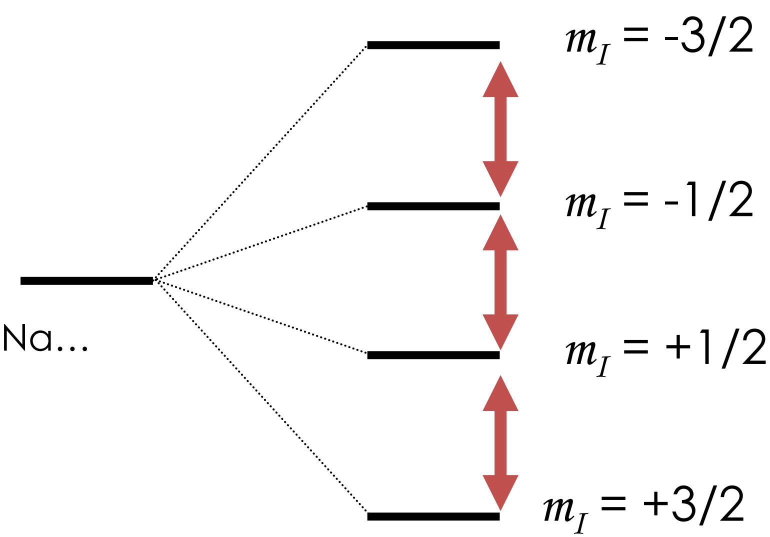


Two allowed transition: $\Delta m_I = 1$

$\Delta E = \gamma_{(I)}.\hbar.B_0$

$\nu_0 = \gamma_{(I)} B_0/2\pi$

I = 3/2
Ex : ^{7}Li, ^{11}B, ^{23}Na…

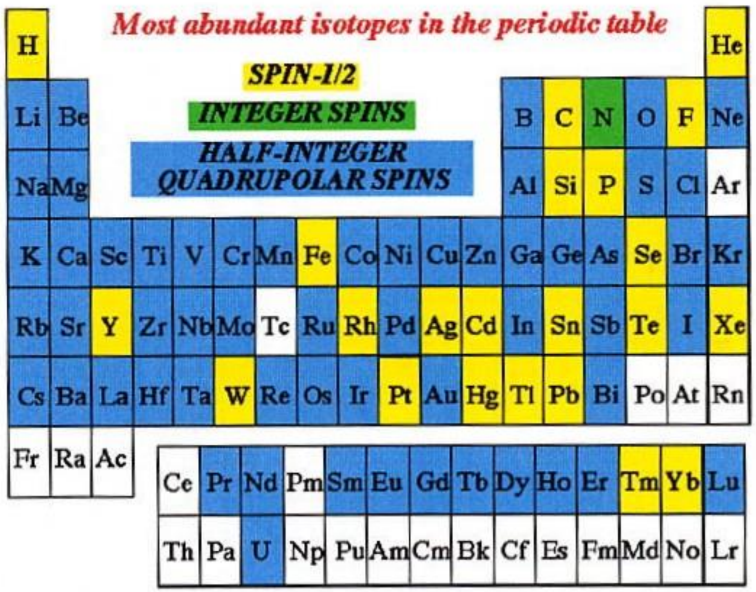


Three allowed transition: $\Delta m_I = 1$

$\Delta E = \gamma_{(I)}.\hbar.B_0$

$\nu_0 = \gamma_{(I)} B_0/2\pi$

3. Isotopes



Isotope ID card: ^{13}C

- **spin I**
- **natural abundance (%)**
- **Gyromagnetic ratio γ (rad s^{-1} T^{-1})**

I = n/2 avec n : integer

n = 0 if A et Z even
n pair if A even et Z odd
n odd if A et Z odd

Examples
I = ½ : ^{1}H, ^{13}C, ^{31}P, ^{29}Si, ^{15}N…
Integer spins : ^{2}H, ^{14}N..
Half-integer quadrupolar spins : ^{11}B, ^{27}Al, ^{17}O, ^{23}Na…

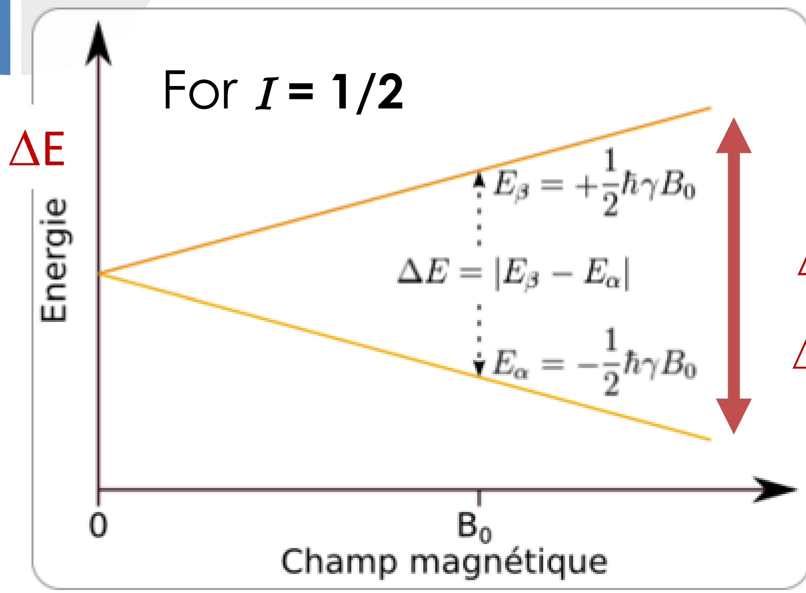
$$\Delta E = \gamma_{(I)} . \hbar . B_0$$

$$\nu_0 = \gamma_{(I)} . B_0 / 2\pi$$

ΔE does not depend on I !

Nevertheless **NMR is nucleus selective** because of the gyromagnetic ratio !

4. Sensitivity and Magnetic field



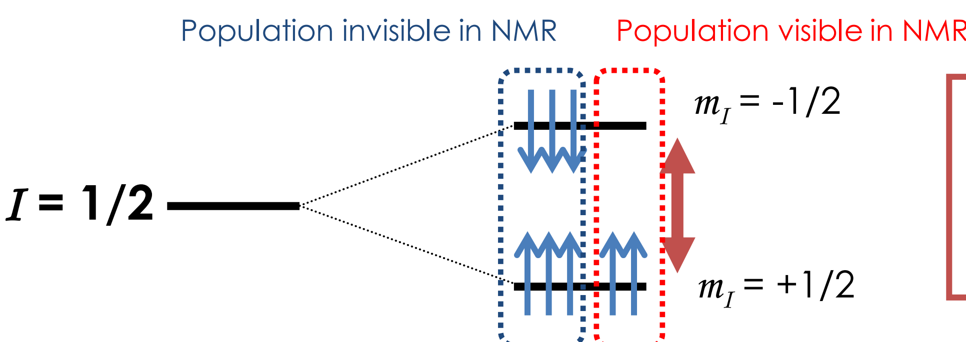
$\Delta E = \gamma_{(I)}.\hbar.B_0$

ΔE increases linearly with B_0

However ΔE is very low

→ $6{,}6.10^{-26}$ J at B_0 = 2,3 Tesla ($\nu_{0(1H)}$ = 100 MHz)

➢ the populations of the two energy levels is controlled by the **thermal energy**



$$P_{+1/2}/P_{-1/2} = 1 + (\gamma_{(I)}\hbar B_0)/(k_B T)$$
$$= 1.000007$$

ΔP = 0.0007% for ^1H at 1Tesla and 25°C

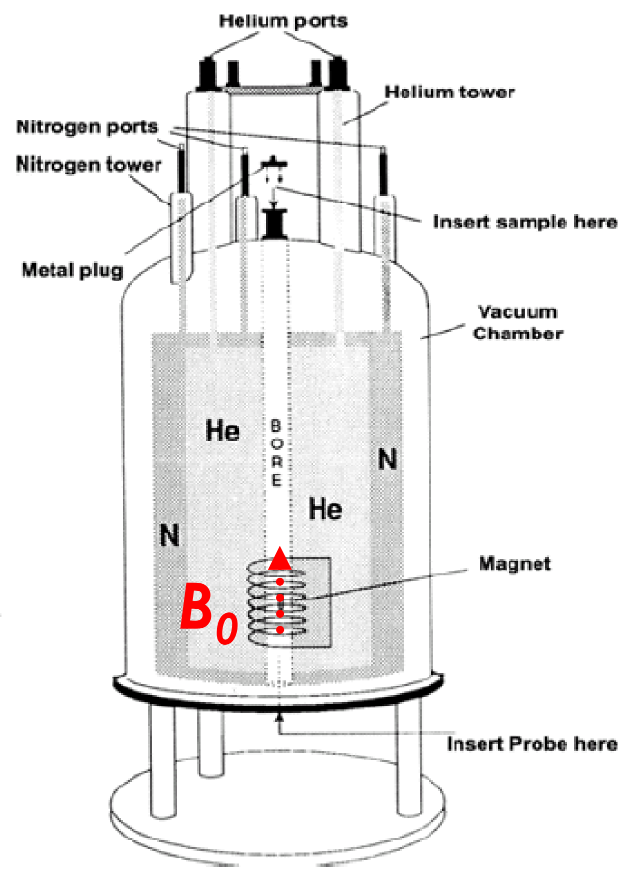
*Δ*P increases with B_0

So the sensitivity increases with B_0 !!!

5. Sensitivity and Macroscopic magnetization

Needs of intense B_0 magnetic fields to increase the sensitivity

Superconducting magnet

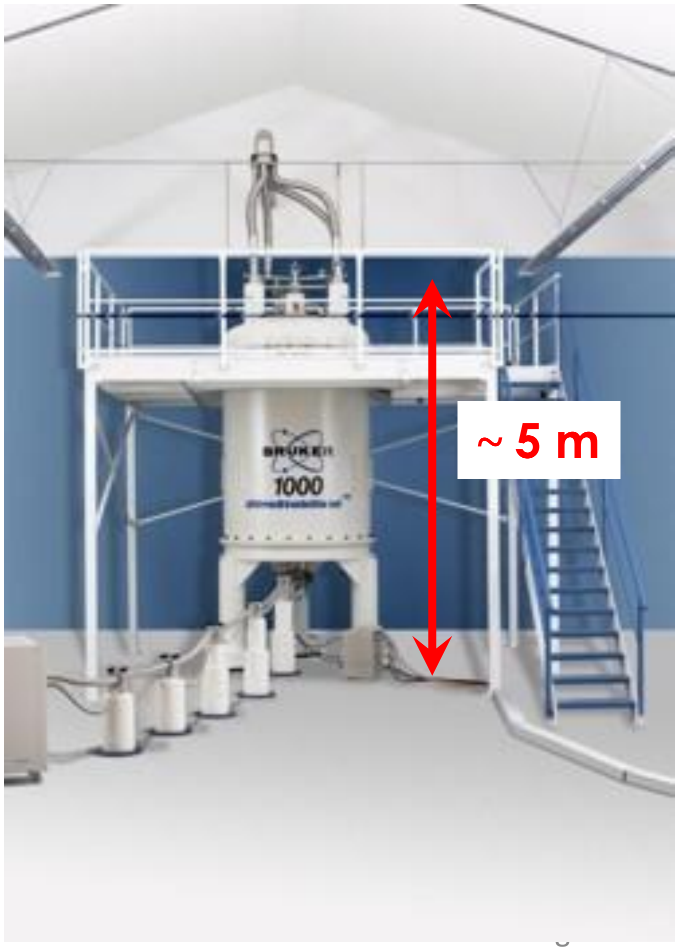


$$\nu_0 = \gamma B_0 / 2\pi$$

$\gamma(^1H)$ = 26,7519.10^7 rad T^{-1} s^{-1}

B_0 (T)	ν_0 (^{1}H) (MHz)
7	300
14	600
21	900
23.5	1000

Earth's magnetic field = 5.10^{-6} T



At the right center of the coil B_0 is static, vertical and homogeneous

NMR principles

5. Sensitivity

Sensitivity : value relative to the proton considering 100% natural abundance.

$$S = (\gamma_X/\gamma_{1H})^3 \frac{(I_X+1)I_X}{(I_{1H}+1)I_{1H}}$$

Example

^1H : I=1/2, γ = 26,7519.10^7 rad T^{-1} s^{-1} → S = 1

^3H : I=1/2, γ = 28.535.10^7 rad T^{-1} s^{-1} → S = 1.21

^{19}F : I=1/2, γ = 25.181.10^7 rad T^{-1} s^{-1} → S = 0.83

^{31}P : I=1/2, γ = 10,841.10^7 rad T^{-1} s^{-1} → S = 0.066

^{13}C : I=1/2, γ = 6,7283.10^7 rad T^{-1} s^{-1} → S = 0.016

^{29}Si : I=1/2, γ = -5.3188.10^7 rad T^{-1} s^{-1} → S = 7,86.10^{-3}

The proton is the most NMR sensitive nucleus

Sensitivity decreases quickly as soon as γ decreases because of $(1/\gamma)^3$

NMR principles

5. Receptivity

$$D = (\gamma_X/\gamma_{1H})^3 \frac{(ab.nat.)_X(I_X+1)I_X}{(ab.nat.)_{1H}(I_{1H}+1)I_{1H}}$$

Takes into account the natural abundance !

spins 1/2

^{1}H : 100% NA → D = 1

^{3}H : 0% NA → D = 0

^{19}F : 100% NA → D = 0,834

^{31}P : 100% NA → D = 0,0665

^{13}C : 1,1% NA → D = 1,76.10^{-4}

^{29}Si : 4,7% NA → D = 3,69.10^{-4}

^{57}Fe : 2,2% NA γ = 0,87.10^{7} rad T^{-1} s^{-1} → D = 7,43.10^{-7} …

Difficult…

Low γ nucleus

Quadrupolar spins

^{27}Al : I = 5/2; 100% NA → D = 0.207

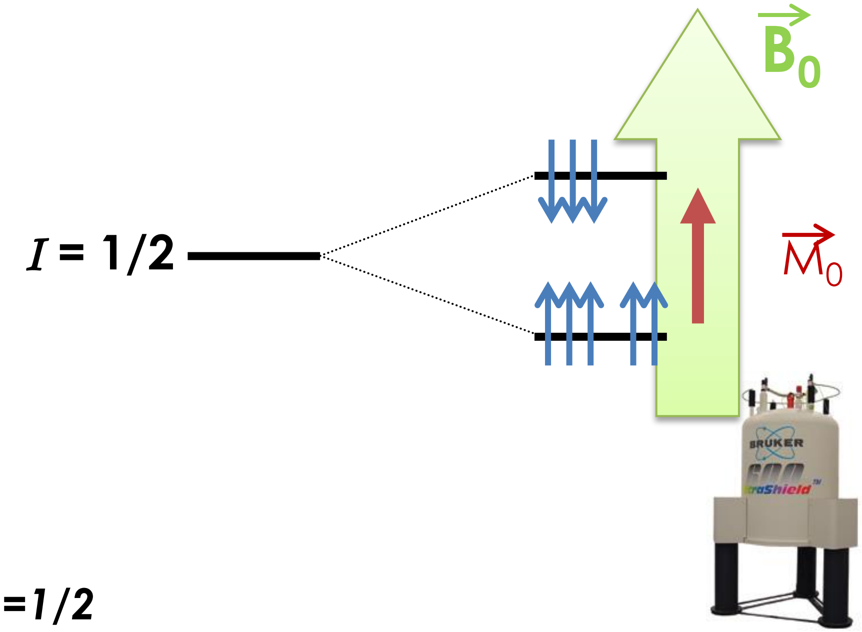
^{17}O : I = 5/2; 0,037% NA → D = 1,08.10^{-5}

^{43}Ca : I = 7/2; 0,145% NA → D = 8,67.10^{-6}

Difficult…

6. Macroscopic magnetization

Creation of a macroscopic magnetization $\vec{M}_0$



For a spin I=1/2

$$M_0 = \frac{N\gamma^2\hbar^2 B_0}{4k_B T}$$

N : number of spins

Problem : M_0 is hidden in the static magnetic field B_0 (~10^{-6} of B_0)

Impossible to measure directly !!!

How to measure it ???

7. Concept of precession

Interaction of two magnetic moments :
What happens to the magnetization $\vec{M}_0$ in the presence of a static magnetic field $\vec{B}_0$?

From the theorem of angular momentum, we know that there is a **time dependence** as follow :

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \wedge \vec{B}$$

For two ordinary vectors

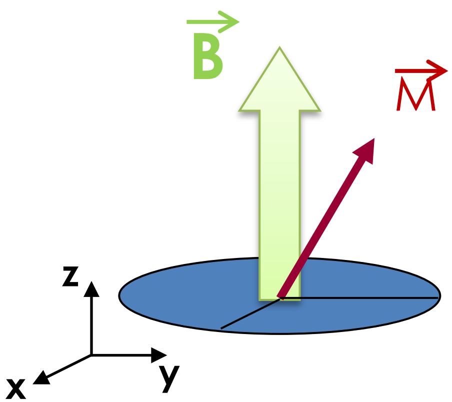
$$\vec{U}\begin{pmatrix} Ux \\ Uy \\ Uz \end{pmatrix} \qquad \vec{V}\begin{pmatrix} Vx \\ Vy \\ Vz \end{pmatrix}$$

The vector product is

$$\vec{U} \wedge \vec{V} \begin{pmatrix} UyVz - UzVy \\ UzVx - UxVz \\ UxVy - UyVx \end{pmatrix}$$

$\vec{B}$ static and collinear to the z axis :

$$\vec{M}\begin{pmatrix} Mx \\ My \\ Mz \end{pmatrix} \qquad \vec{B}\begin{pmatrix} Bx \\ By \\ Bz \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix}$$



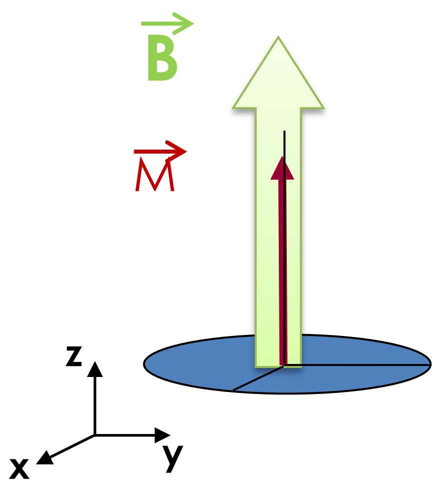
$$\begin{cases} \dfrac{dMx}{dt} = \gamma B_0.My \\[2ex] \dfrac{dMy}{dt} = -\gamma B_0.Mx \\[2ex] \dfrac{dMz}{dt} = 0 \end{cases}$$

Movement equations

Only the x and y components have a time dependence

7. Concept of precession

At the thermodynamic equilibrium, B and M are collinear to the z axis



$$\vec{B}\begin{pmatrix} Bx \\ By \\ Bz \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} \qquad \vec{M}\begin{pmatrix} Mx \\ My \\ Mz \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ M_0 \end{pmatrix}$$

then

$$\begin{cases} \dfrac{dMx}{dt} = 0 \\ \dfrac{dMy}{dt} = 0 \\ \dfrac{dMz}{dt} = 0 \end{cases}$$

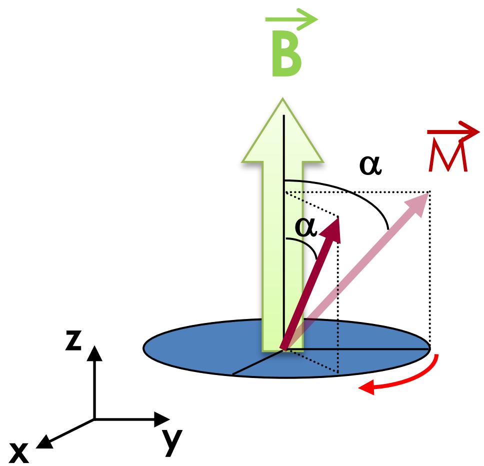
Nothing happens

7. Concept of precession

Out of the thermodynamic equilibrium : $\vec{M}$ is tilted from $\vec{B}$ by an angle α

Then the initial conditions are

$$\begin{cases} M_x(0) = 0 \\ M_y(0) = M_0 \sin\alpha \\ M_z(0) = M_0 \cos\alpha \end{cases}$$



If we solve the differential equations

$$\begin{cases} \dfrac{dM_x}{dt} = \gamma B_0 . M_y \\ \dfrac{dM_y}{dt} = -\gamma B_0 . M_x \\ \dfrac{dM_z}{dt} = 0 \end{cases} \Leftrightarrow \begin{cases} M_x(t) = M_0 \sin\alpha \sin(\gamma B_0 t) \\ M_y(t) = M_0 \sin\alpha \cos(\gamma B_0 t) \\ M_z(t) = M_0 \cos\alpha \end{cases}$$

The movement equations describe a **rotation of $\vec{M}$**

in the (xy) plane at the **angular rate $\omega_0 = \gamma B_0$**

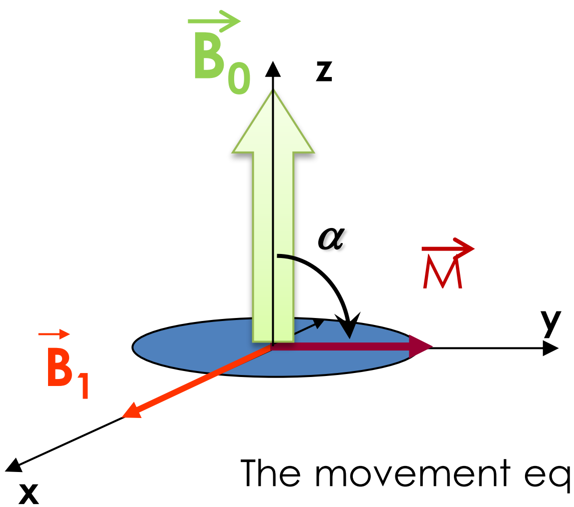
The associated angular frequency is then $\nu_0 = \gamma B_0 / 2\pi$

i.e. the **Larmor frequency !**

7. Concept of precession

Goal of the NMR experiment : put $\vec{M}$ out of the equilibrium

Best efficiency if $\alpha = 90°$



If we apply a **strong B_1 radio-frequency field** perpendicular to B_0 along the x axis then we induce a **rotation of M around the x axis**

The frequency of the B_1 field must be $\nu_1 = \nu_0$ (Larmor frequency)

If α = 90° it is called a "90° pulse" or "π pulse"

The time to reach the (xy) plane is called $t_{90°}$

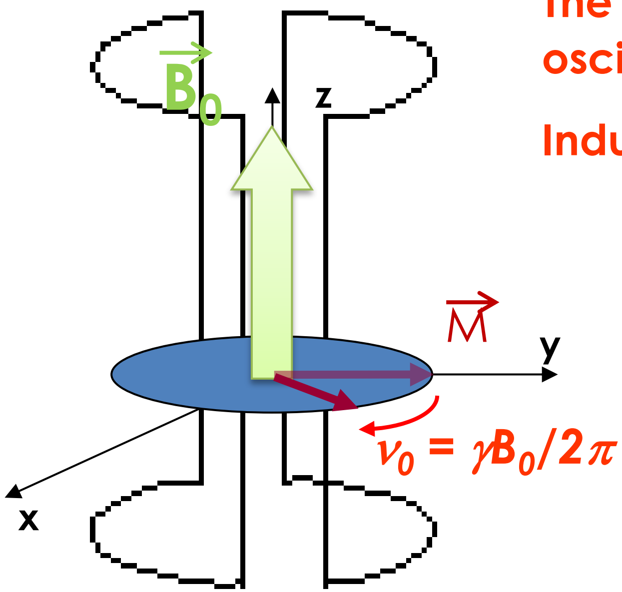
Usually, $t_{90°}$ = from 1 to 10 µs

The movement equations are becoming :

$$\begin{cases} Mx(t) = M_0 \sin\alpha \sin(\gamma B_0 t) \\ My(t) = M_0 \sin\alpha \cos(\gamma B_0 t) \\ Mz(t) = M_0 \cos\alpha \end{cases} \Leftrightarrow \begin{cases} Mx(t) = M_0 \sin(\gamma B_0 t) \\ My(t) = M_0 \cos(\gamma B_0 t) \\ Mz(t) = 0 \end{cases}$$

7. Concept of precession

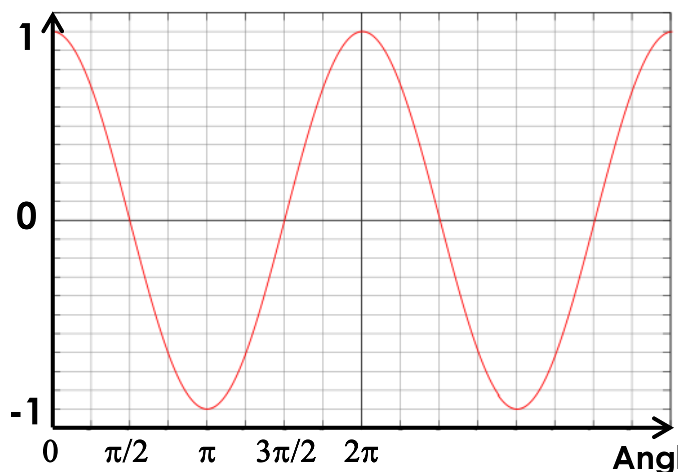
If we switch off $\vec{B_1}$, $\vec{M}$ start rotating in the (xy) plane at the ν_0 frequency (Larmor frequency).



The macroscopic magnetization M is now measurable !

The variation of M inside a coil gives rise to an oscillating electric field !

Induction phenomenon !



Beware : the coil generating B_1 is different from the one generating B_0

The coil generating B_1 is the same as the coil allowing the recording of the NMR signal.