

SHIELDING

- WE DO NOT HAVE AN ISOLATED NUCLEUS IN AN APPLIED MAGNETIC FIELD.
- ALL NUCLEI ARE SURROUNDED BY ELECTRONS AND OTHER NEIGHBORING ATOMS
- WHEN PLACED IN A MAGNETIC FIELD THE SURROUNDING ELECTRON CLOUD TENDS TO CIRCULATE IN SUCH A DIRECTION AS TO PRODUCE A FIELD OPPOSING THE APPLIED FIELD (DIAMAGNETIC CIRCULATION)
RECALL $\vec{F} = q(\vec{v} \times \vec{B})$
- MAGNETIC FIELD EXPERIENCED BY THE NUCLEUS IS

$$B_{\text{EFF}} = B_0 - B_{\text{INDUCED}}$$

\downarrow APPLIED FIELD \downarrow OPPOSING INDUCED FIELD DUE TO DIAMAGNETIC CIRCULATION

$$B_{\text{INDUCED}} = \sigma B_0$$

\downarrow SHIELDING CONSTANT

$$B_{\text{EFF}} = B_0 (1 - \sigma)$$

- NUCLEI IN DIFFERENT CHEMICAL GROUPS HAVE DIFFERENT σ VALUES.

- THE HYDROGEN NUCLEUS IN O-H BONDS EXPERIENCES GREATER FIELD THAN THE HYDROGEN NUCLEUS IN C-H BONDS

→ OXYGEN IS A BETTER ELECTRON ACCEPTOR THAN CARBON

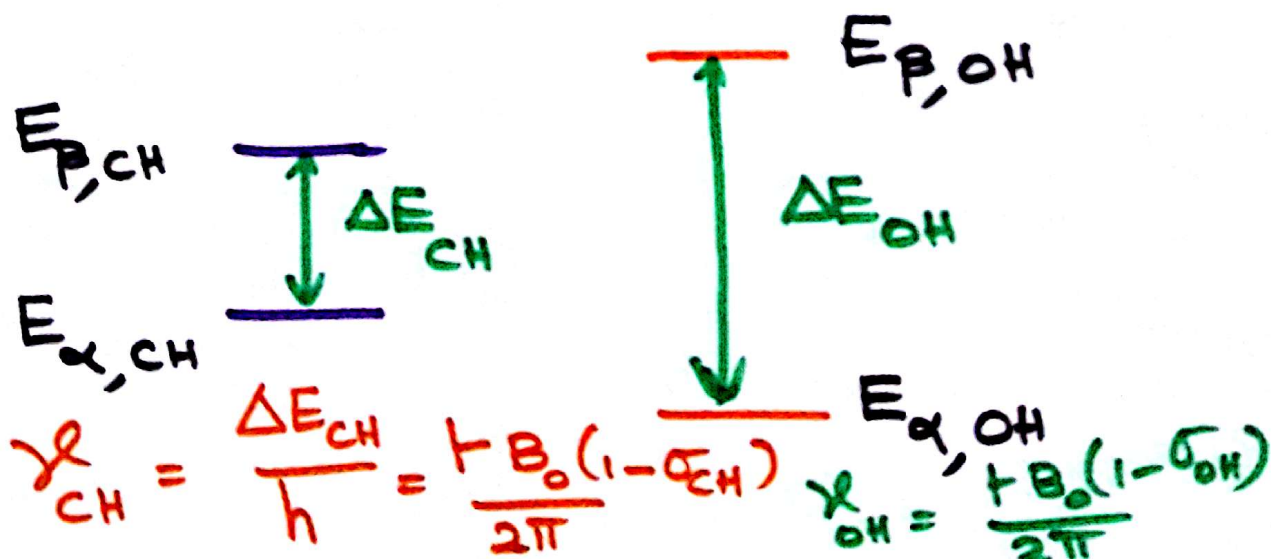
(OXYGEN HAS THE GREATER ELECTRONEGATIVITY)

→ THE ELECTRON DENSITY ABOUT THE HYDROGEN ATOM IN C-H BONDS IS HIGHER THAN IN O-H BONDS

$$\sigma_{CH} > \sigma_{OH}$$

$$B_0(1 - \sigma_{CH}) < B_0(1 - \sigma_{OH})$$

- $\Delta E_{CH} = \hbar B_0(1 - \sigma_{CH})$
 $\Delta E_{OH} = \hbar B_0(1 - \sigma_{OH})$



CHEMICAL SHIFT

ALSO

$$\left(\delta = \frac{\nu - \nu_0}{\nu_0} \right)$$

⇒

$$\delta = \nu - \nu_0$$

↓
RESONANCE
FREQUENCY
OF THE
NUCLEUS

↓
RESONANCE
FREQUENCY OF
A REFERENCE
NUCLEUS

(PROTON REFERENCE RESONANCE
IN TETRAMETHYLSILANE)



⇒ LET US CALCULATE

UNIT OF B_0 CAN BE DIFFERENT

$$\nu_{OH} - \nu_{CH} = \frac{\hbar B_0}{2\pi} (\sigma_{CH} - \sigma_{OH})$$

$$\frac{\nu_{OH} - \nu_{CH}}{\nu_{CH}} = \frac{\sigma_{CH} - \sigma_{OH}}{(1 - \sigma_{CH})}$$

UNIT IS NOT A PROBLEM ANYMORE.

⇒ IN GENERAL :

$$\sigma = \sigma_{\text{LOCAL}} + \sigma_{\text{NEIGHBOUR}} + \sigma_{\text{SOLVENT}}$$

↓
DUE TO ELECTRONS OF THE ATOM THAT CONTAINS THE NUCLEUS

↓
DUE TO NEIGHBOURING ATOMS

↓
DUE TO SOLVENT

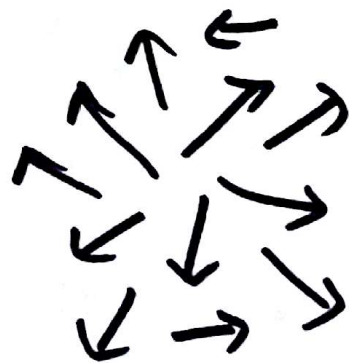
MAGNETIZATION

- CONSIDER N NUCLEAR SPINS IN A SAMPLE
- $\vec{\mu}_i$ IS THE NUCLEAR MAGNETIC MOMENT OF i TH SPIN

- MAGNETIZATION \vec{M}

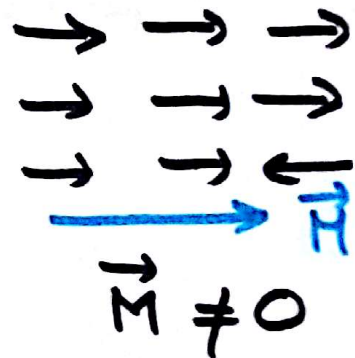
$$\vec{M} = \sum_{i=1}^N \vec{\mu}_i \quad (\text{VECTOR SUM})$$

\vec{M} IS THE NET NUCLEAR MAGNETIC MOMENT OF THE SAMPLE

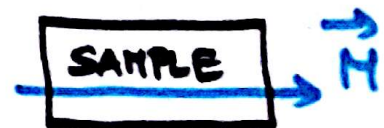
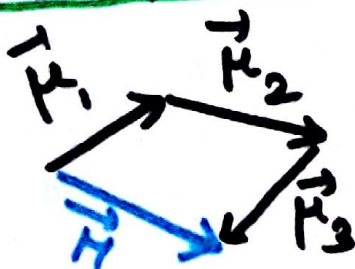


RANDOM ORIENTATIONS

$$\vec{M} = 0$$

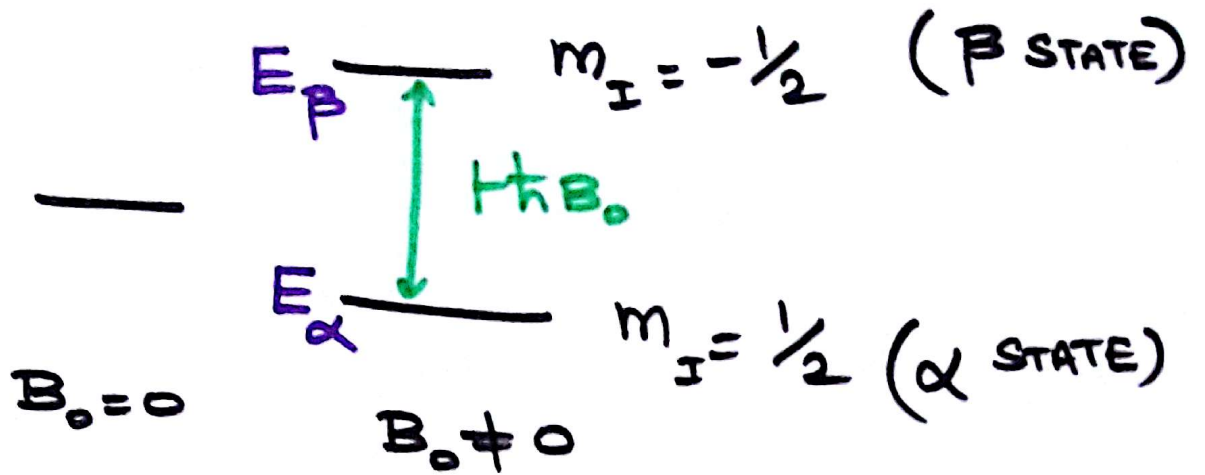


VECTOR ADDITION



- \vec{M} IS A SYSTEM PROPERTY
- CHANGE IN ANY ONE OR MORE $\vec{\mu}_i$ WILL BE REFLECTED IN \vec{M}

NUCLEAR MAGNETIC RESONANCE



$$\Delta E = E_\beta - E_\alpha$$

POPULATION OF α -STATE: $N_\alpha \propto e^{-\frac{E_\alpha}{k_B T}}$

POPULATION OF β -STATE: $N_\beta \propto e^{-\frac{E_\beta}{k_B T}}$

$$\frac{N_\beta}{N_\alpha} = e^{-\frac{1}{k_B T} (E_\beta - E_\alpha)} = e^{-\frac{\Delta E}{k_B T}}$$

$$\frac{N_\beta}{N_\alpha} = e^{-\frac{\Delta E}{k_B T}} \approx 1 - \frac{\Delta E}{k_B T} \quad (\Delta E \ll k_B T)$$

$$1 - \frac{N_\beta}{N_\alpha} \approx \frac{\Delta E}{k_B T}$$

$$\frac{N_\alpha - N_\beta}{N_\alpha} \approx \frac{\Delta E}{k_B T} = \frac{h\nu_{B_0}}{k_B T}$$

$$N_\alpha - N_\beta \propto h\nu_{B_0}$$

• WHEN $B_0 = 0$

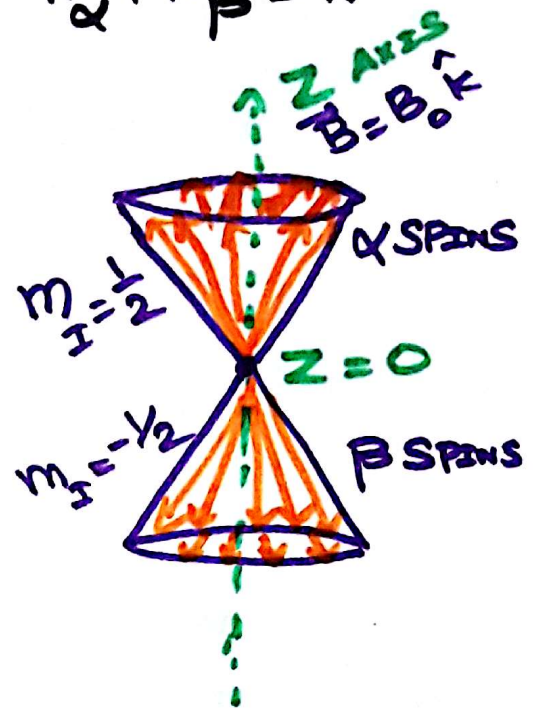
$$N_\alpha - N_\beta = 0$$

$$N_\alpha = N_\beta$$

$$\vec{M} = N_\alpha \left(g_I \mu_N \right) \hat{k} - N_\beta \left(g_I \mu_N \right) \hat{k}$$

$$\vec{M} = 0$$

$$N_\alpha + N_\beta = N$$

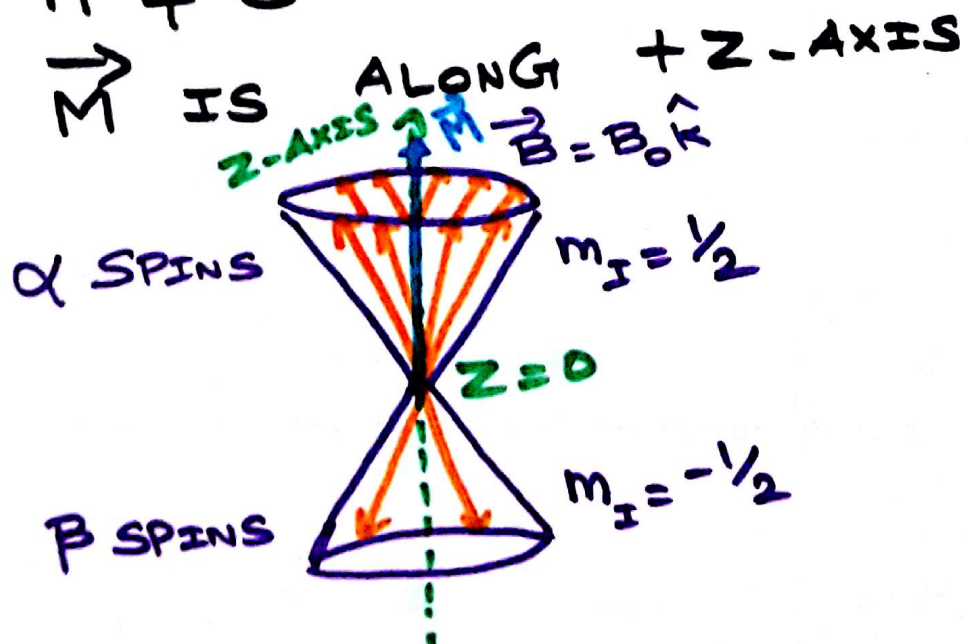


• WHEN $B_0 \neq 0$

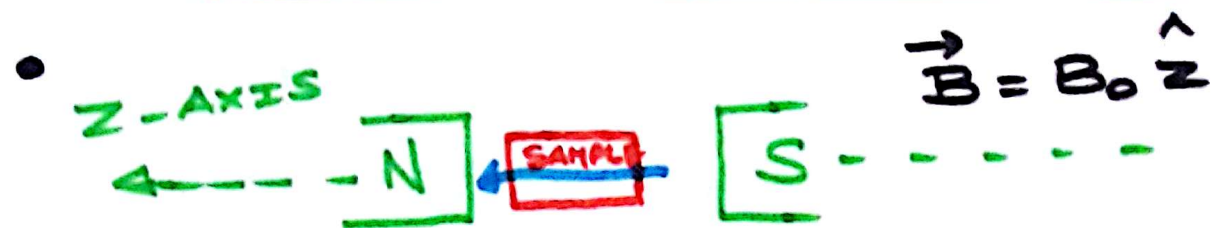
$$N_\alpha > N_\beta$$

$$\vec{M} = \frac{g_I \mu_N}{2} \hat{k} (N_\alpha - N_\beta)$$

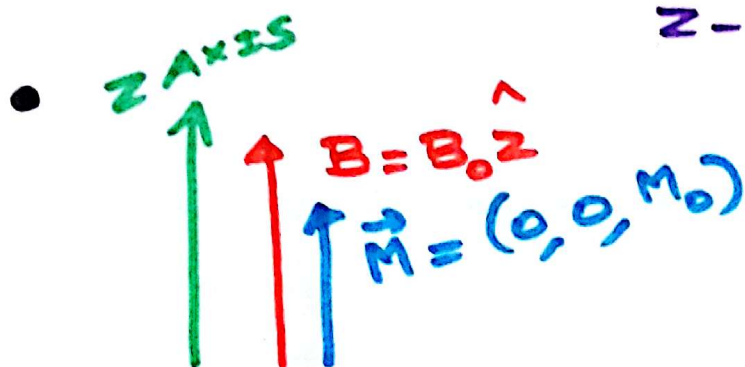
$$\vec{M} \neq 0$$



PULSE TECHNIQUES IN NMR



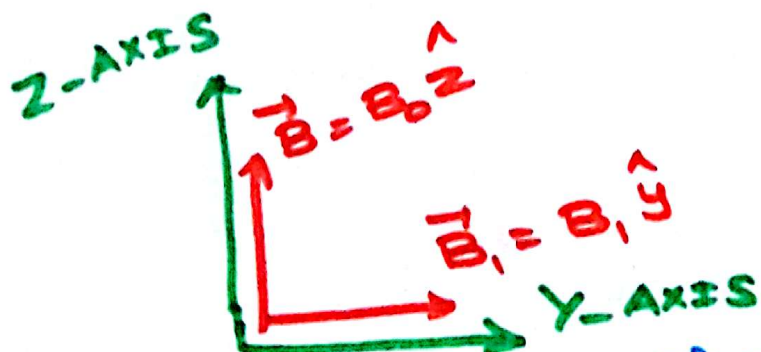
RF FIELD
(MAGNETIC FIELD \vec{B}_1 OF THIS RF FIELD IS PERPENDICULAR TO Z-AXIS)



$$B_0 \neq 0$$

$$B_1 = 0$$

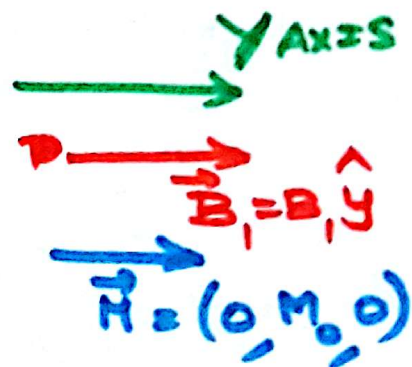
CASE I



ORIENTATION OF \vec{M} ?

\vec{M} WILL HAVE NON-ZERO Y-COMPONENT!

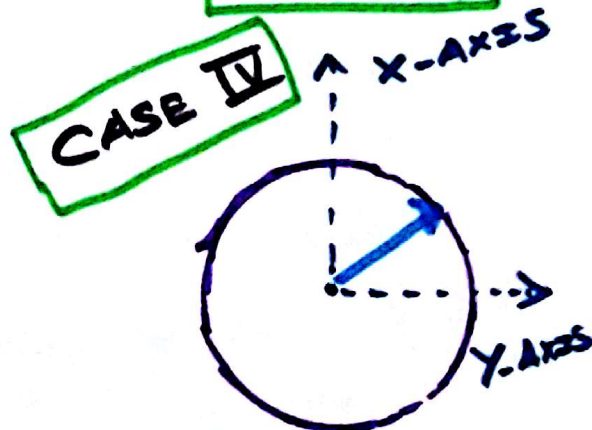
CASE III



$$B_0 = 0$$

$$B_1 \neq 0$$

CASE-II



CIRCULARLY POLARIZED RF FIELD (\vec{B}_1 ROTATES ON XY PLANE)

- 90° RF PULSE

⇒ APPLY \vec{B} AND \vec{B}_1 SUCH THAT \vec{M} IS ROTATED TO THE XY PLANE

EXCITED STATE $\vec{M} = (M_x, M_y, 0)$ (FINAL STATE)

IN THE ABSENCE OF \vec{B}_1

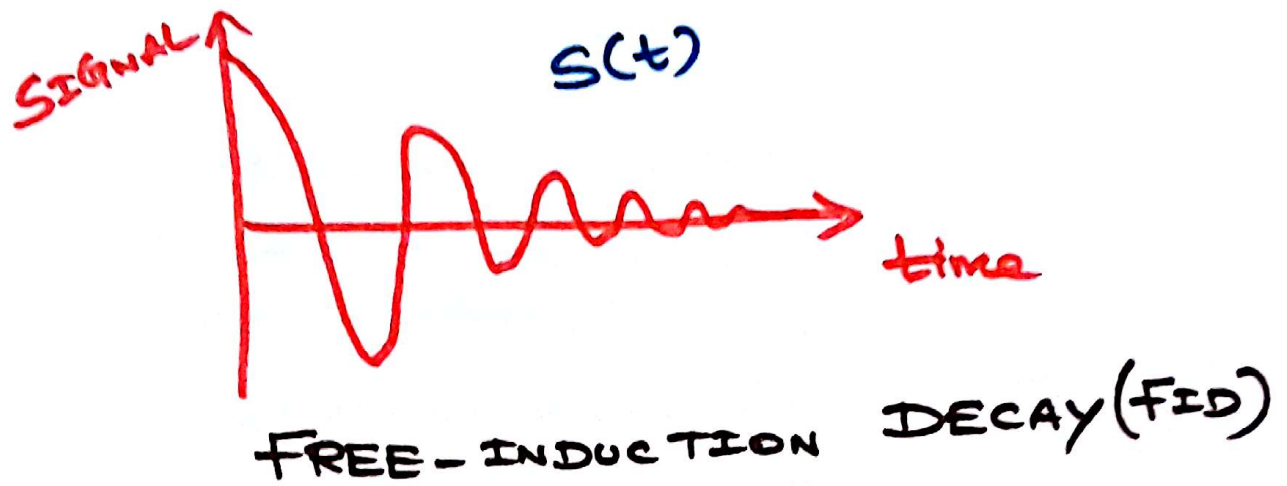
EQUILIBRIUM STATE $\vec{M} = (0, 0, M_z)$ (INITIAL STATE)

- \vec{M} ROTATES IN XY PLANE ;
ROTATING \vec{M} INDUCES CURRENT IN A COIL AROUND IT
(THIS CURRENT CAN BE MEASURED AND AMPLIFIED)
- TURN ON \vec{B} AND \vec{B}_1 AND MAKE \vec{M} TO ROTATE IN XY PLANE FOR SOME TIME. NOW, TURN OFF \vec{B}_1 .
WHAT WOULD HAPPEN?

RETURN OF \vec{M} FROM THE EXCITED STATE TO THE EQUILIBRIUM STATE IS CALLED SPIN RELAXATION

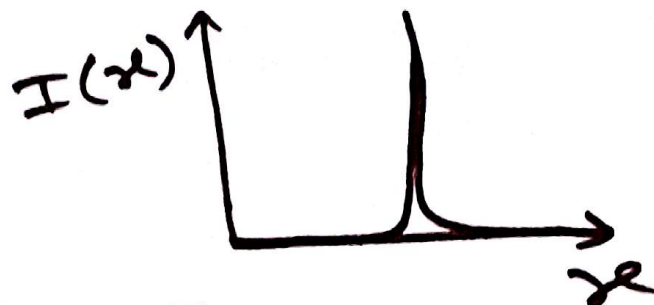
(ENERGY EXCHANGE HAPPENS WITH THE SURROUNDINGS)

- WHEN THE ~~SPIN~~ \vec{M} VECTOR RELAXES FROM THE EXCITED STATE TO THE GROUND STATE, THE PROJECTION OF \vec{M} ON XY PLANE DECREASES.
 \Rightarrow DETECTED CURRENT SIGNAL WOULD DECREASE WITH TIME.



\Rightarrow FOURIER TRANSFORM OF $S(t)$

$$I(\nu) = 2 \text{ REAL} \left[\int_0^{\infty} S(t) e^{2\pi i \nu t} dt \right]$$



\Rightarrow FID FREQUENCY IS DIFFERENT FOR DIFFERENT NUCLEI AND IT DEPENDS ON THE LOCAL ENVIRONMENT OF THE NUCLEI.

- 180° PULSE

EQUILIBRIUM STATE $\vec{M} = (0, 0, M_z)$

EXCITED STATE $\vec{M} = (0, 0, -M_z)$

POPULATION INVERSION
(MORE SPINS IN THE
B STATE THAN IN THE
 α STATE)

THIS IS POSSIBLE WHEN $B_1 \neq 0$;
(WHEN $B_1 = 0$, THIS WOULD BE A
HIGHER ENERGY STATE)

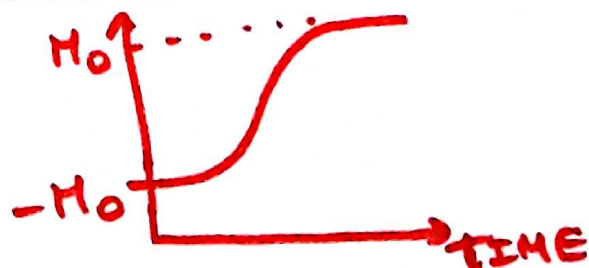
- TWO TYPES OF SPIN RELAXATION

$\Rightarrow T_1$ RELAXATION OR
LONGITUDINAL RELAXATION
OR
SPIN-LATTICE RELAXATION

$\Rightarrow T_2$ RELAXATION OR
TRANSVERSE RELAXATION
OR
SPIN-SPIN RELAXATION

- T_1 RELAXATION: APPLY 180° PULSE
 \Rightarrow INVESTIGATE HOW M_z
VARIES WITH TIME

TIME CONSTANT
 T_1



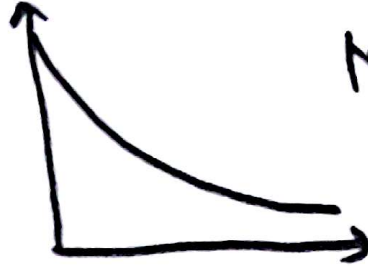
- T_2 RELAXATION

⇒ APPLY 90° PULSE

⇒ INVESTIGATE HOW

M_y VARIES WITH TIME

$M_y(t)$



$$M_y(t) \propto e^{-t/T_2}$$