MAGNETIC RESONANCE

WE HAVE DISCUSSED THE MOTION OF AN ISOLATED SPIN IN THE PRESENSE OF STATIC AND TIME DEPENDENT FIELDS. THE MOST IMPORTANT (AND INTERESTING) CASE IS THAT WHERE: $|\vec{H}_0| >> |\vec{H}_1(t)|$

$\vec{H}_1(t) \perp \vec{H}_0$

IF $\vec{H}_1(t)$ OSCILLATES AT FREQ ω THE MOTION OF THE SPIN IN ω ROTATING FRAME IS

$$\frac{\delta \vec{\mu}}{\delta t} = \vec{\mu} \times \gamma \vec{H}_{eff}$$

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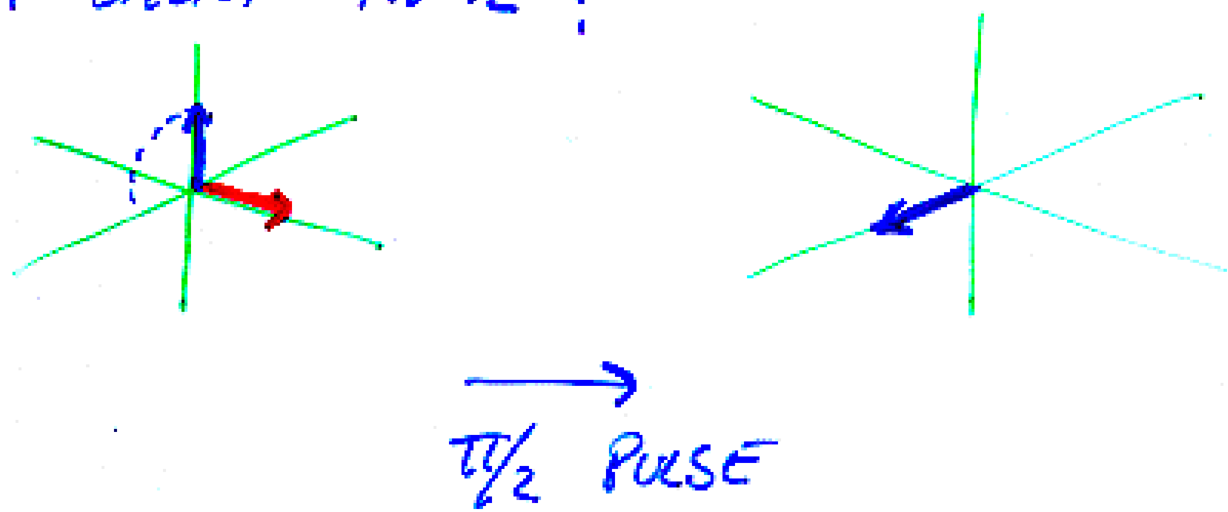
$$H_{eff} = \hat{k}\left(H_0 - \frac{\omega}{\gamma}\right) + H_1 \hat{i}$$

RESONANCE OCCURS AT $\omega = \gamma H_0$

SUPPOSE WE TURN $\vec{H}_1(t)$ OFF AFTER A SHORT TIME?



THE ANGLE THAT THE SPIN IS DRIVEN THROUGH DURING THE PULSED $\vec{H}_1$ EXCITATION:

$$\theta = \gamma H_1 \tau$$

τ IS THE TEMPORAL LENGTH OF THE PULSE

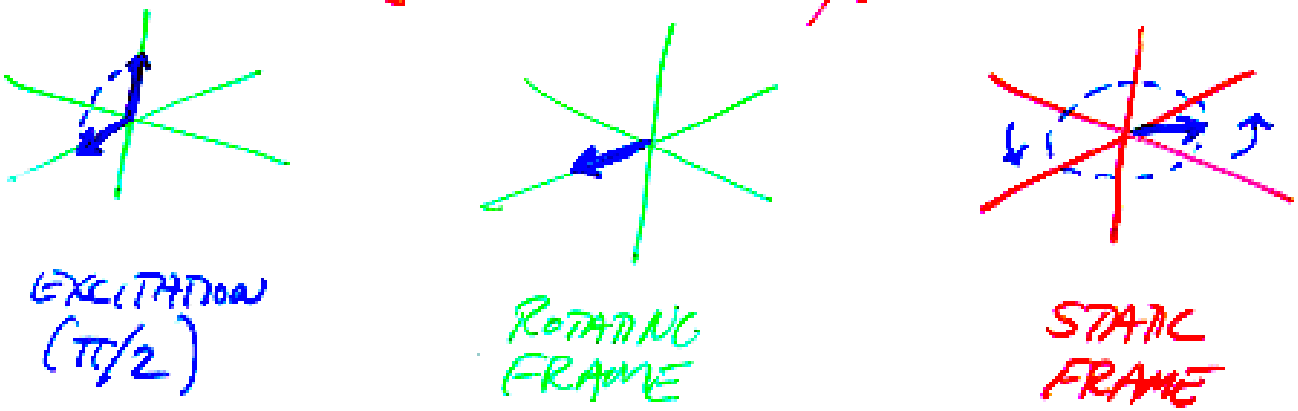
WHAT WOULD HAPPEN WITH A π PULSE?

$\frac{3\pi}{2}$ PULSE?

2π PULSE?

NOTE: AFTER A SINGLE $\pi/2$ PULSE THE SPIN IS LEFT IN THE $\hat{x}, \hat{y}$ PLANE AND PRECESSES AT FREQUENCY γH_0

THIS MUST LEAD TO THE EMISSION OF RADIATION (RADIO WAVES).

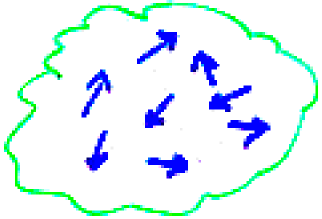


BUT ISN'T IT HARD TO DETECT A SINGLE MAGNETIC MOMENT? HARD --- ALMOST IMPOSSIBLE

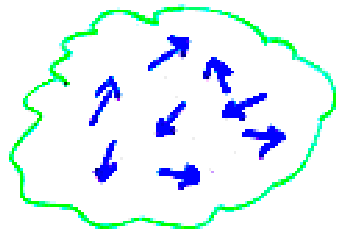
TYPICAL NMR SAMPLES MUST CONTAIN $> 10^{16}$ SPINS FOR ADEQUATE SIGNAL

WHAT HAPPENS WHEN A COLLECTION OF SPINS IS IN THE SAMPLE?

AT $H_0 = 0$ (IN THE LAB) THE SPINS MUST BE DIRECTED RANDOMLY



$$\vec{M} = \sum_i \vec{\mu_i} = 0$$



$$\vec{M} = \sum_i \vec{\mu}_i = 0$$

THE NET MAGNETIZATION OF THE SAMPLE IS ZERO !!

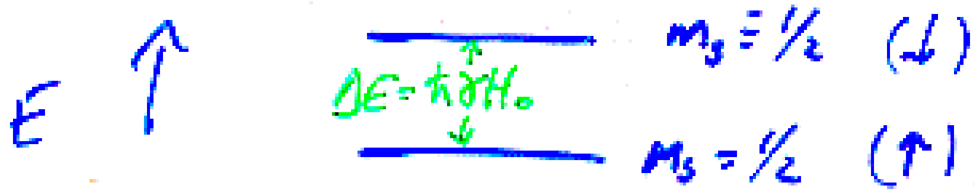
IF H_0 IS BROUGHT TO SOME LARGE VALUE (LIKE IN THE NMR MACHINE), ALL THE SPINS SHOULD PRECESS AROUND $\vec{H}_0$ AND $\vec{M}$ SHOULD STILL BE ZERO

NOT IF THERE IS RELAXATION!

MORE SPINS SHOULD POINT UP THAN DOWN

BECAUSE THEY HAVE LOWER ENERGY!

LETS TRY A QM TREATMENT OF WHAT HAPPENS



$H_0 \neq 0$

DEFINE N_+, N_- THE # OF SPINS IN ↑, ↓

IF $\Delta E = 0$ AT EQUILIBRIUM $N_+^\circ = N_-^\circ$

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IF $\Delta E \neq 0$ AT EQUILIBRIUM

$$\frac{N_-^\circ}{N_+^\circ} = e^{-\Delta E/kT} = e^{-\gamma \hbar H_0/kT}$$

FOR 100 MHz NMR @ 300 K

$$\frac{N_-^\circ}{N_+^\circ} = 0.999983 \equiv \Delta$$

$$\frac{N_+^\circ - N_-^\circ}{N_+^\circ + N_-^\circ} = \frac{1-\Delta}{1+\Delta} = 1.67 \times 10^{-5} \equiv \text{NORMALIZED POPULATION DIFFERENCE}$$

* NET MAGNETIZATION, $\vec{M}$, COMES FROM $N_+ - N_-$!!

Consequence: NMR is not very sensitive!!

Contrast NMR (proton) and EPR (electron) sensitivity

Proton freq 42.6 MHz / Tesla 1T = 10000 Gauss

Electron freq 28.0 GHz / Tesla

Some numbers;

at 12T (500MHz proton NMR spectrometer)

energy sep'n = 0.017 cm^{-1}

$\exp(-0.017/200) = 0.9999148 = \Delta$

$(1-\Delta)/(1+\Delta) = 4.3 \times 10^{-5}$

at 0.3T (X Band EPR spectrometer)

energy sep'n = 0.28 cm^{-1}

$\exp(-0.28/200) = 0.998601$

$(1-\Delta)/(1+\Delta) = 7.0\times10^{-4}$

Relaxation in Magnetic Resonance

Without interaction of the spins with their environment, or each other, there would be no signal (no net magnetization) and no information in the signal (no chemical shift).

The rate at which the spins exchange energy with their surroundings is characterized by a relaxation rate, k, or its inverse, a characteristic relaxation time t = 1/k.

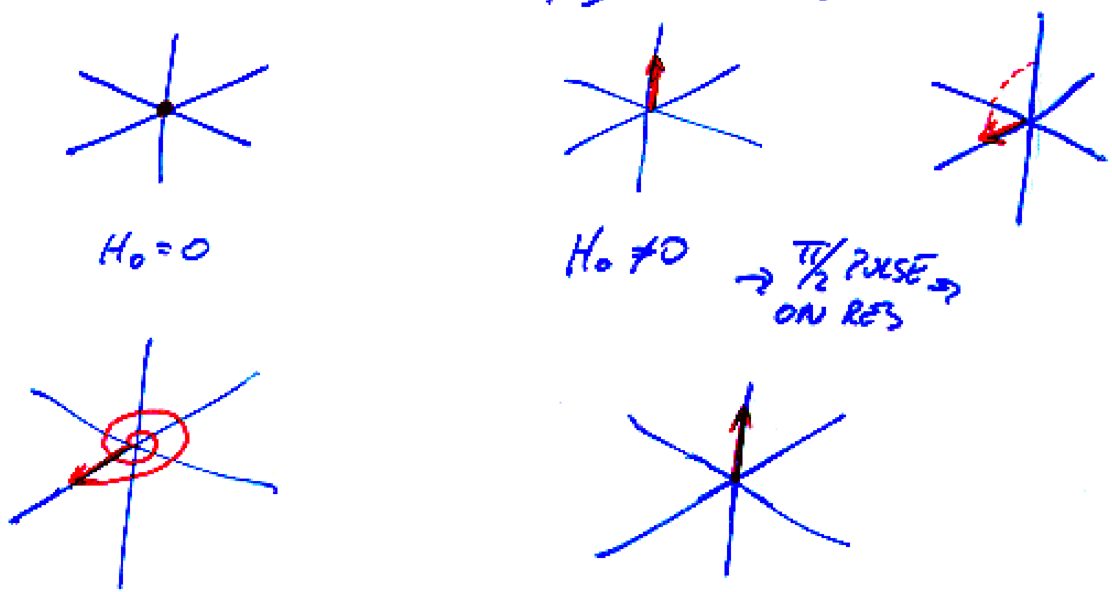
The process for relaxation of the magnetization along **z** (H_0) requires energy exchange, whereas changing the magnetization along **x** or **y** does not. The mechanism for relaxation is therefore different and the rates are too.

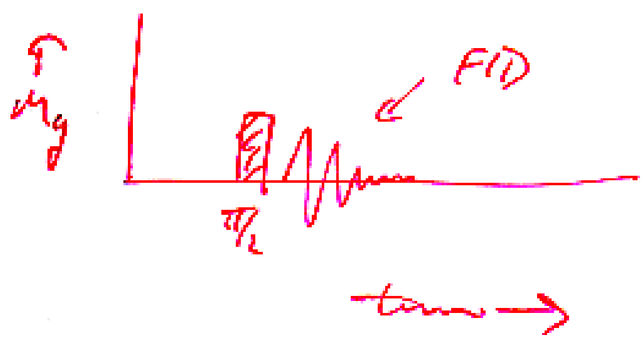
Longitudinal relaxation rate = $1/T_1$

Transverse relaxation rate = $1/T_2$ (> $1/T_1$)

The basic NMR experiment (modern era)

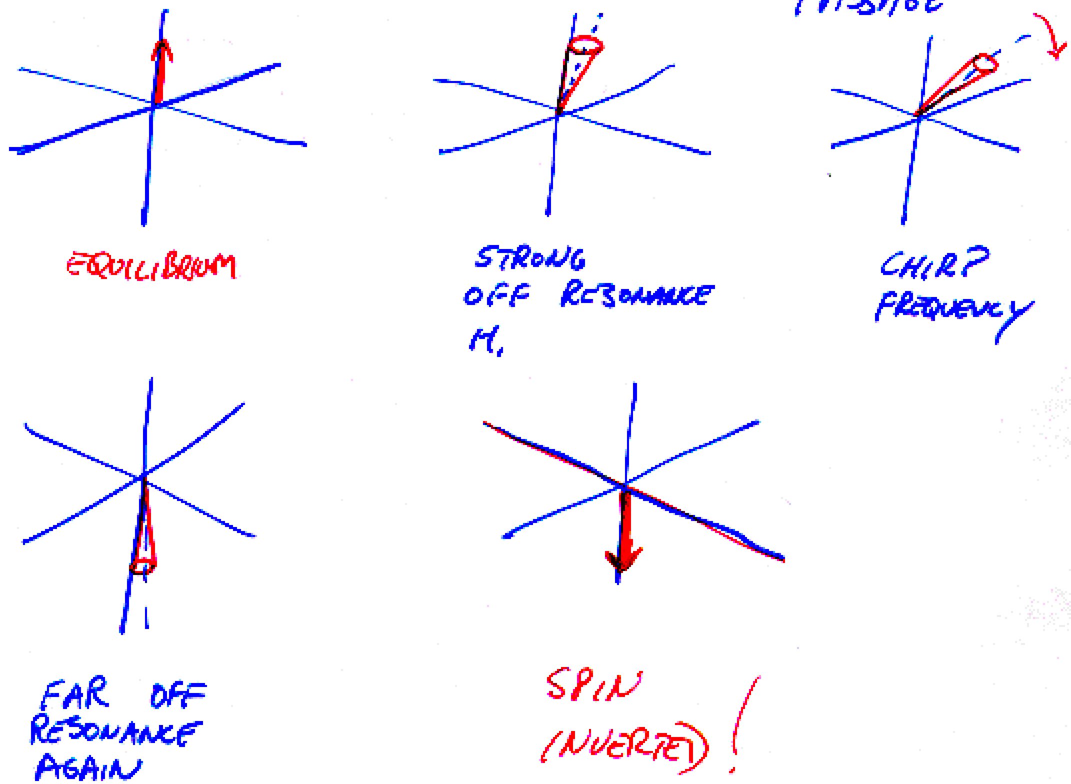
SOME NMR CONCEPTS : FID



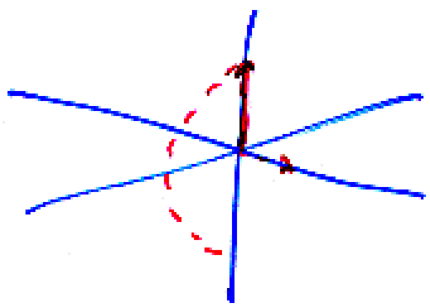


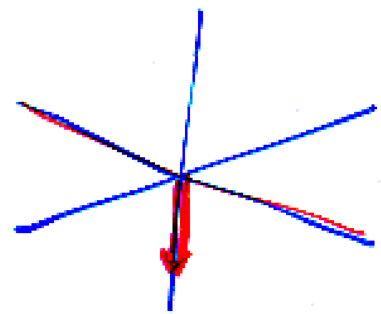
SPIN INVERSION BY ARP

ADIABATIC RAPID PASSAGE



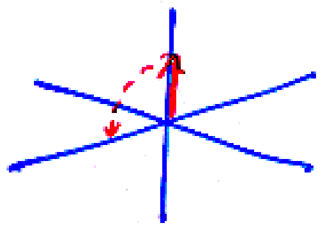
OR WE COULD USE A π-PULSE



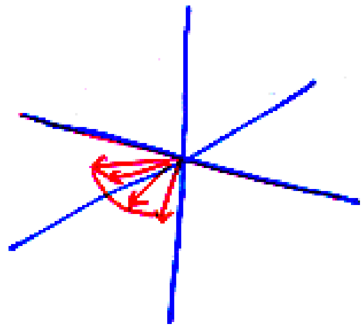


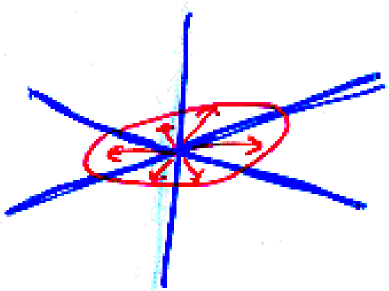
INHOMOGENEOUS BROADENING

IF ALL THE MOLECULES ARE NOT IN EXACTLY THE SAME ENVIRONMENT THEY WILL PRECESS AT SLIGHTLY DIFFERENT FREQUENCIES AND DEPHASE GIVING A SHORTER FID THAN WOULD BE PREDICTED FROM T_2!



$\pi/2$ PULSE



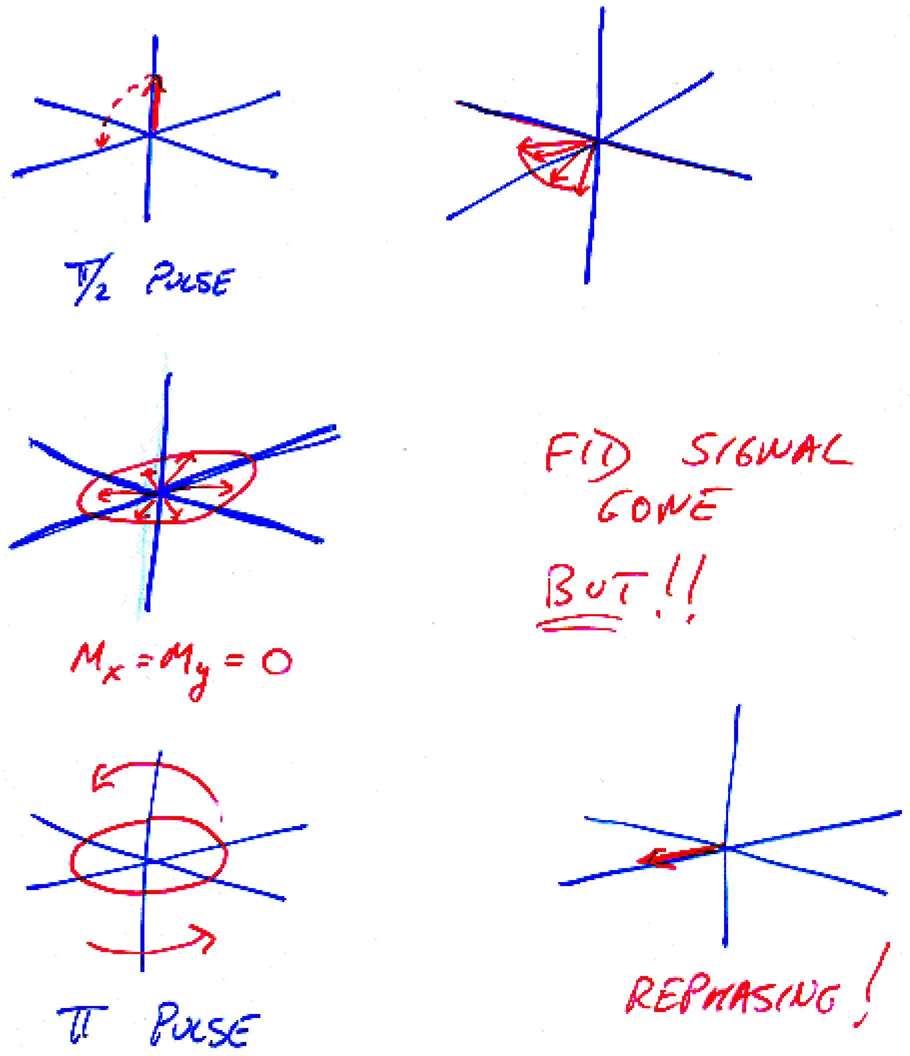


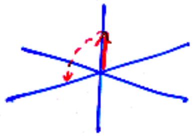
$M_x = M_y = 0$

FID SIGNAL GONE

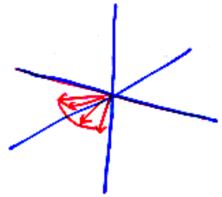
BUT!!

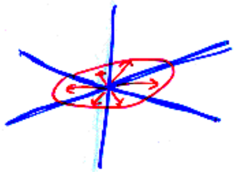
The Hahn Spin Echo





π/2 PULSE

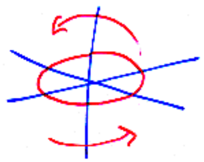




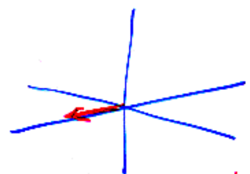
$M_x = M_y = 0$

FID SIGNAL GONE

BUT!!

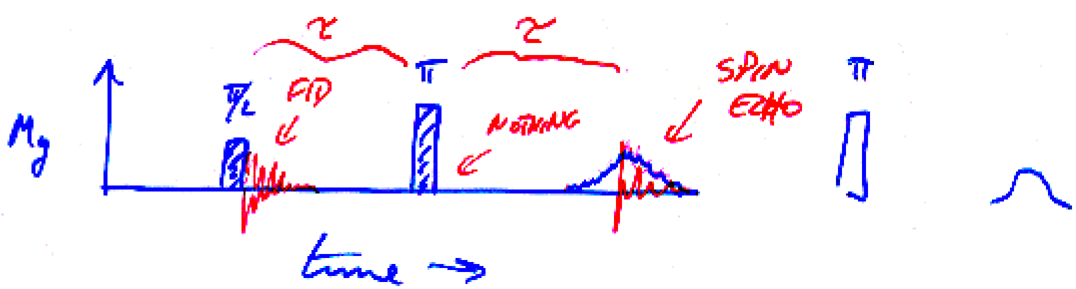


π PULSE

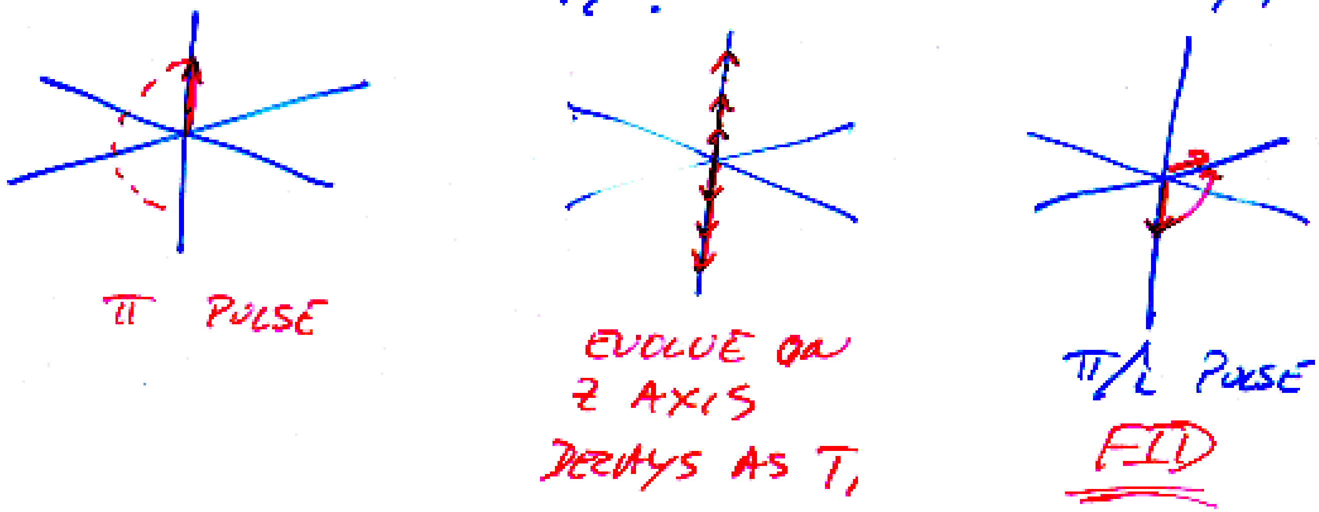


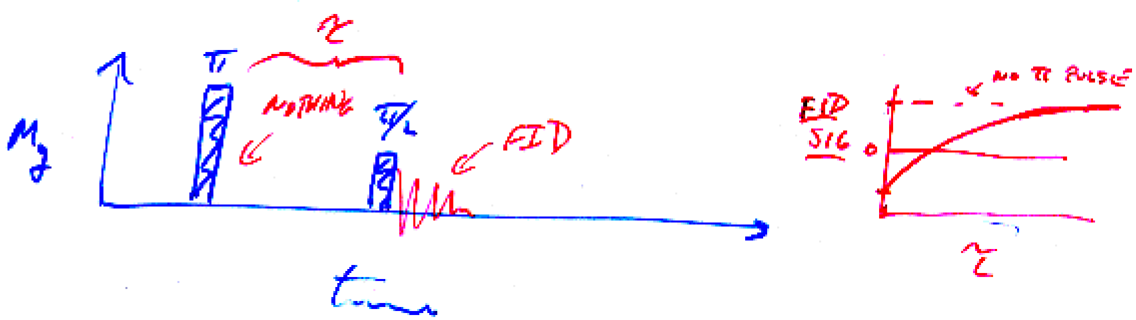
REPHASING!

BY FOLLOWING THE ECHO SIGNAL MAGNITUDE AS A FUNCTION OF τ, ONE CAN DETERMINE T_2 EVEN IN THE PRESENCE OF INHOMOGENEOUS BROADENING



WHAT ABOUT T_1? (INVERSION RECOVERY)





Fin