# Measurement of $T_1$, $T_2$ and $T_{1\rho}$

Inversion Recovery

Spin echo and CPMG

Spin lock

# Inversion Recovery

- $T_1$, is the inverse of the kinetic constant with which $M_z$ reaches the equilibrium value, $M_0$. It is important to have information on its magnitude in order:
- to determine the pulse length
- to perform multipulsed experiments
- to gain information on molecular motions or on the motion of molecular subunits (groups of atoms)
- to gain information on molecular structure

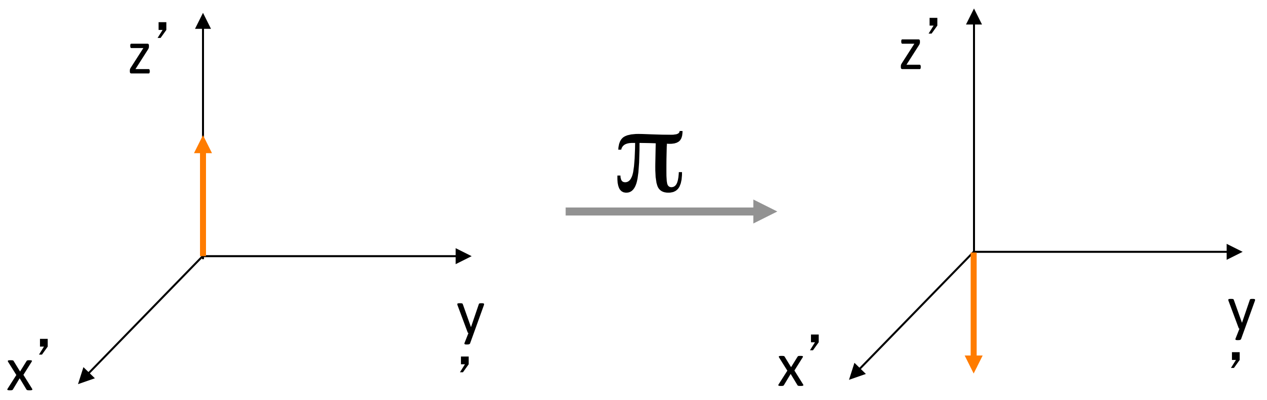
# Longitudinal relaxation

$$\frac{dM_z(t)}{dt} = -\frac{M_z(t) - M_0}{T_1}$$

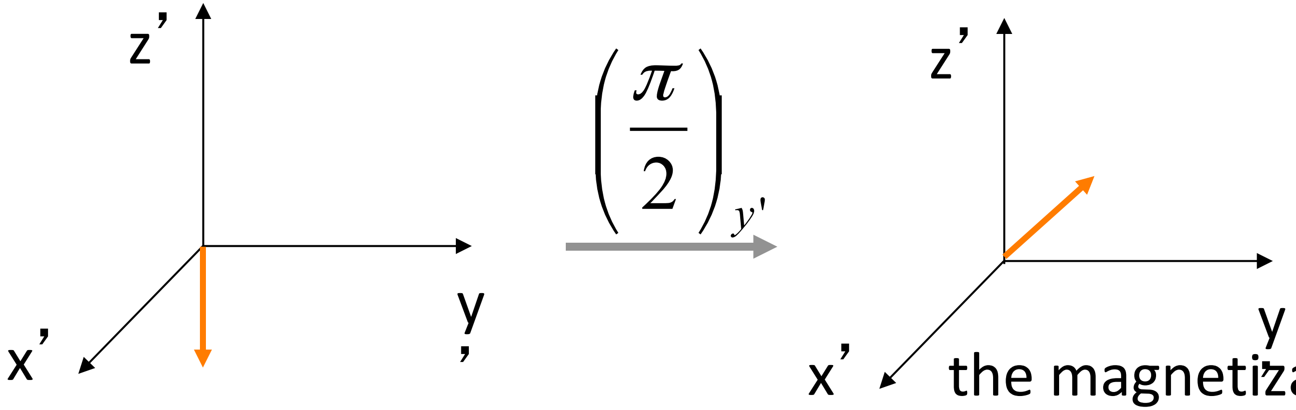
The integrated kinetic law:

$$\ln \frac{M_z(t_a) - M_0}{M_z(t = 0) - M_0} = -\frac{t_a}{T_1}$$

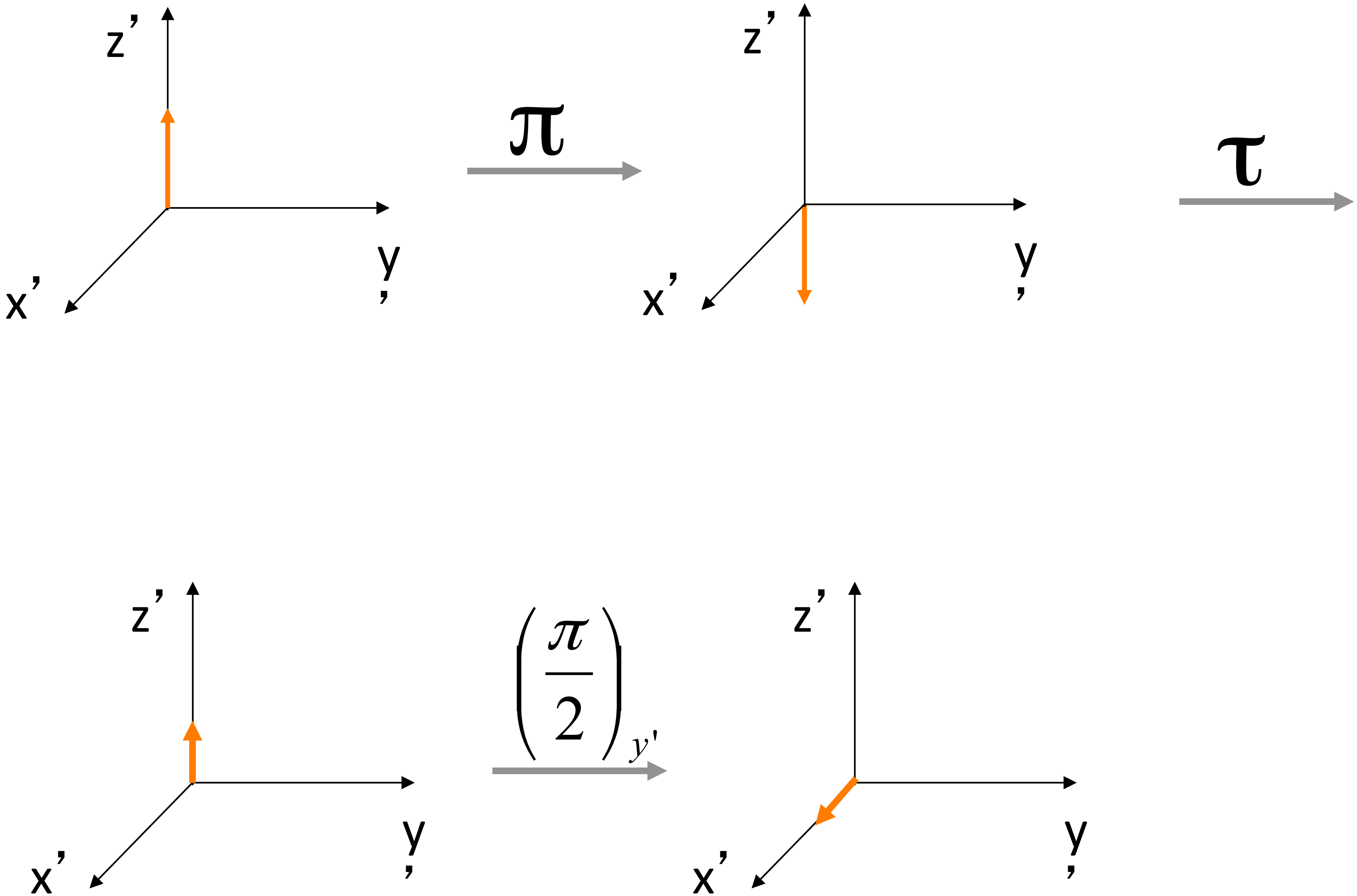
In the inversion recovery experiments the starting condition corresponds to the maximum deviation from equilibrium: the magnetization vector is brought onto the negative z axis by a $\pi$ pulse.




The intensity of the longitudinal magnetization, $M_z$, is measured by shifting the longitudinal magntization to the transverse plane through a $\pi/2$ pulse

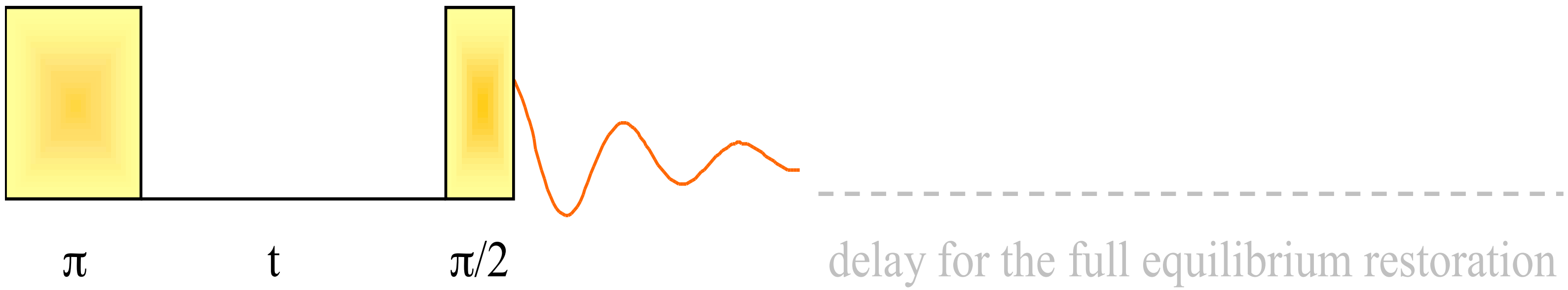



the magnetization vector is aligned with –x, the signal is negative equilibrium



The experiment is repeated about 20 times varying τ, the time interval between the inverting π pulse and the read π/2 pulse. During the time τ relaxation takes place (restoration of equilibrium).

## Scheme of the Inversion Recovery experiment



In the Inversion Recovery experiment $M_z(t=0)= -M_0$, i.e., after the $\pi$ pulse. The equation

$$\ln \frac{M_z(\tau) - M_0}{M_z(t=0) - M_0} = -\frac{\tau}{T_1}$$

becomes

$$\ln \frac{M_z(\tau) - M_0}{-2M_0} = -\frac{\tau}{T_1}$$

i.e.

$$\ln \frac{M_0 - M_z(\tau)}{2M_0} = -\frac{\tau}{T_1}$$

$$\ln[M_0 - M_z(\tau)] = \ln(2M_0) - \tau/T_1$$

Experiomental data can be fitted to a straight line, the **slope** of which corresponds to $1/T_1$

After each experiment the system must be let fully return to equiibrium waiting at least 5 $T_1$.

For $\tau$ small with respect to $T_1$ the signal is still inverted, for $\tau_{null}$= 0.693 $T_1$ the longitudinal magnetization is zero, whereas for longer $\tau$ it is positive and grows with $\tau$.

To get a quick estimate of $T_1$, to be used later to choose the best suited $\tau$ values, one determines the $\tau$ for the null signal, $M_z(\tau = \tau_{null}) = 0$

$$\ln \frac{M_z(\tau_{null}) - M_0}{-2M_0} = -\frac{\tau_{null}}{T_1} \quad \text{i.e.} \quad \ln \frac{1}{2} = -\frac{\tau_{null}}{T_1}$$

$$\tau_{null} = T_1 \ln(2) = 0.693 T_1$$

and

$T_1 = 1.44\ \tau_{null}$

A non linear fit to the experimental data can be performed as well:

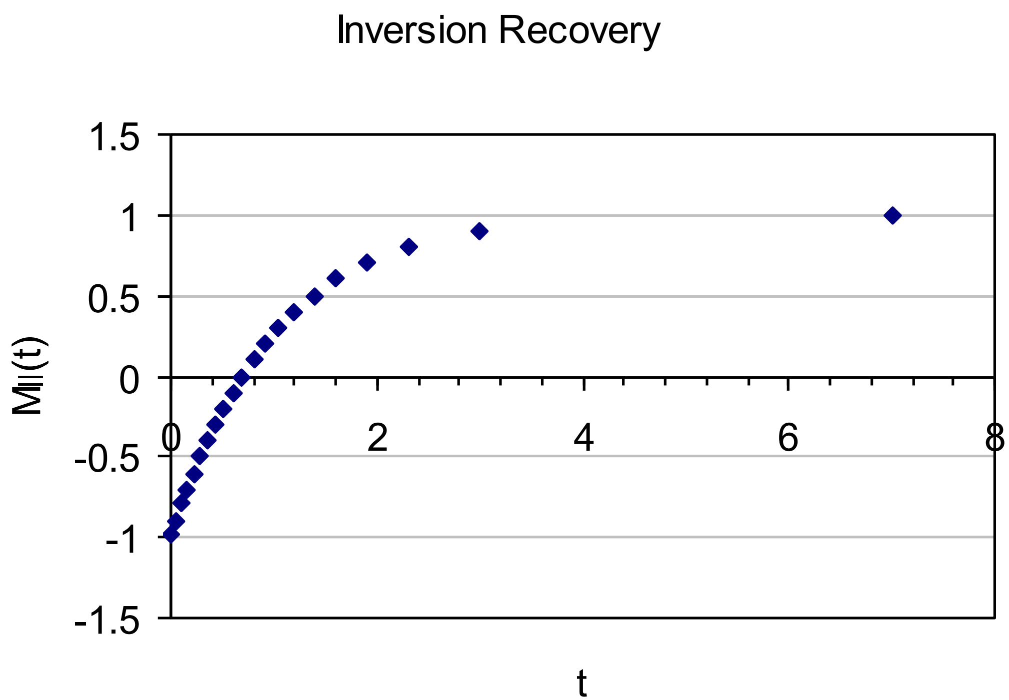
$$\frac{M_0 - M_z(\tau)}{2M_0} = \exp\left(-\frac{\tau}{T_1}\right)$$

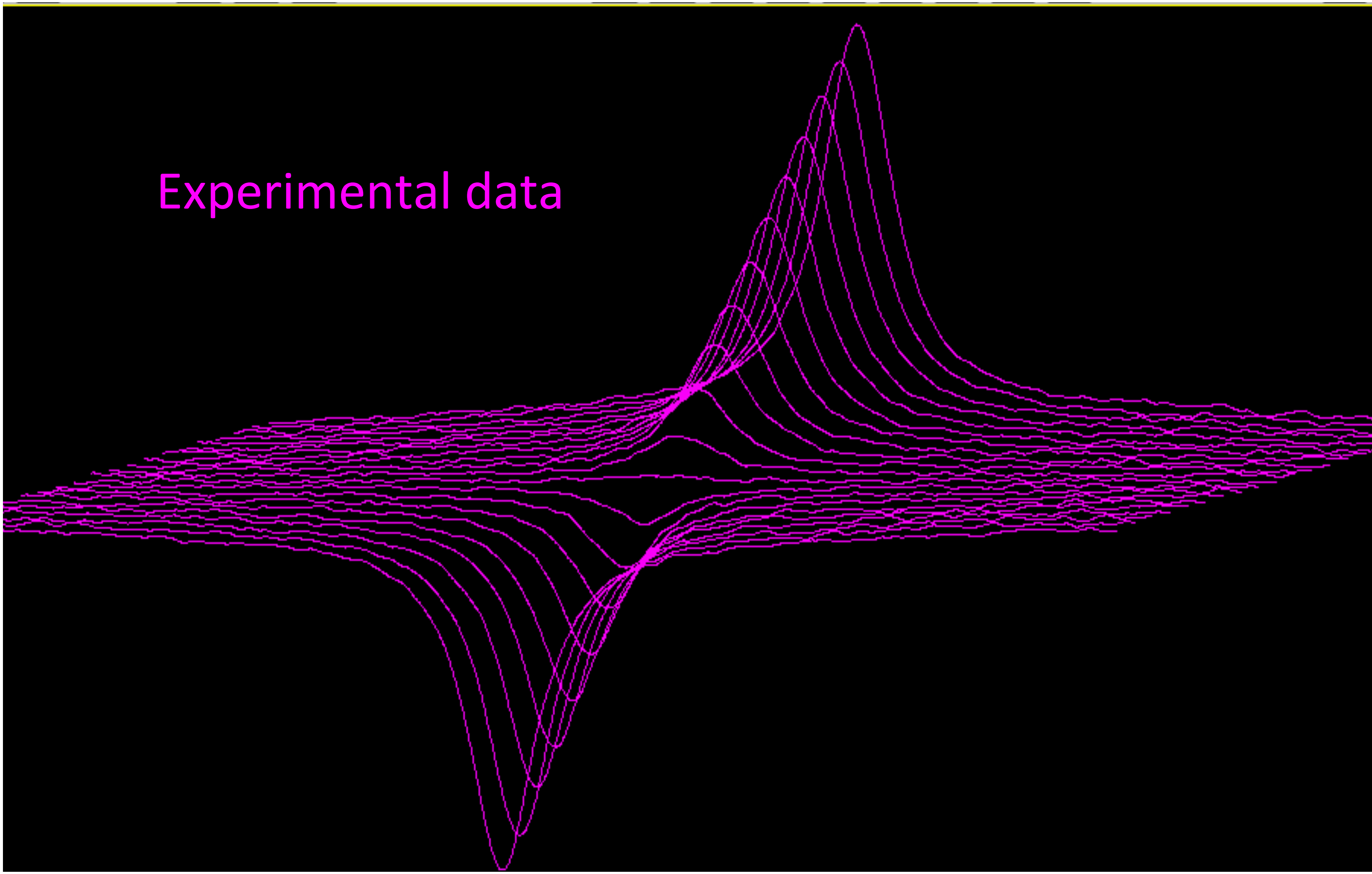
$$M_z(\tau) = M_0\left[1 - 2\exp\left(-\frac{\tau}{T_1}\right)\right]$$

Here $M_0$ and 2 can be optimized in order to minimize the errors between calculated and experimental data. The departure from the value of 2 suggest a deviation for the $\pi$ pulse, usually due to $B_1$ inhomogeneity.

Owing to the non linear dependence of $M_z(\tau)$ on $\tau$ it is convenient to to use not linearly increasing $\tau$ that reflect such dependence

| | | | |
|---|---|---|---|
| $\tau/T_1$ | 0.01 | 0.05 | 0.11 |
| 0.16 | 0.22 | 0.29 | 0.36 |
| 0.43 | 0.51 | 0.6 | 0.69 |
| 0.8 | 0.92 | 1.05 | 1.2 |
| 1.39 | 1.61 | 1.9 | 2.3 |
| 3 | 7 | | |

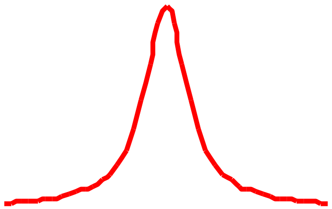



Experimental data

# Experimental cautions *(usefuls also in the determination of the $\pi/2$ pulse)*

- accurate probe syntonization
- adequate receiver gain (use the autogain option for a spectrum recorded by a $\pi/2$ pulse which give the maximum signal, then decrease the gain by 2 units, deselect the autogain option)
- delay betwee two experiments long enough
- check the $\pi/2$ pulse on the sample of interest

# NMR Signal



- The NMR signal has a Lorentzian shape

$$S(\nu) = \frac{T_2}{1+\left[2\pi(\nu-\nu_0)T_2\right]^2}$$

- The line-width at half height is

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2}$$

- in the absence of $B_0$ inhomogeneity
- actually they are constantly present
- are expressed as $\delta B_0$

$$\Delta\nu_{1/2} = \frac{1}{\pi T^*_2}$$

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{\gamma \delta B_0}{2\pi}$$

# Lorentzian Lineshape

$$h = \frac{H_{MAX}}{1 + 4\pi^2 \Delta\nu_h^2 T_2^2}$$

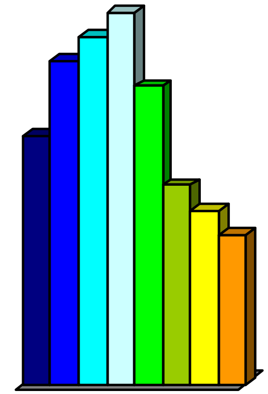
$$1 + 4\pi^2 \Delta\nu_h^2 T_2^2 = \frac{H_{MAX}}{h}$$

$$\Delta\nu_h = \pm \frac{1}{2\pi T_2} \sqrt{\frac{H_{MAX}}{h} - 1}$$

| $h/H_{MAX}$ | $2\Delta\nu_h$ |
|---|---|
| 0.5 | $\frac{1}{\pi T_2}$ |
| 0.55 % | 13.4 $\frac{1}{\pi T_2}$ |
| 0.11 % | 30.1 $\frac{1}{\pi T_2}$ |

# Lineshape test

Actually the NMR signal is the hystogram of $B_0$ inhomogeneities



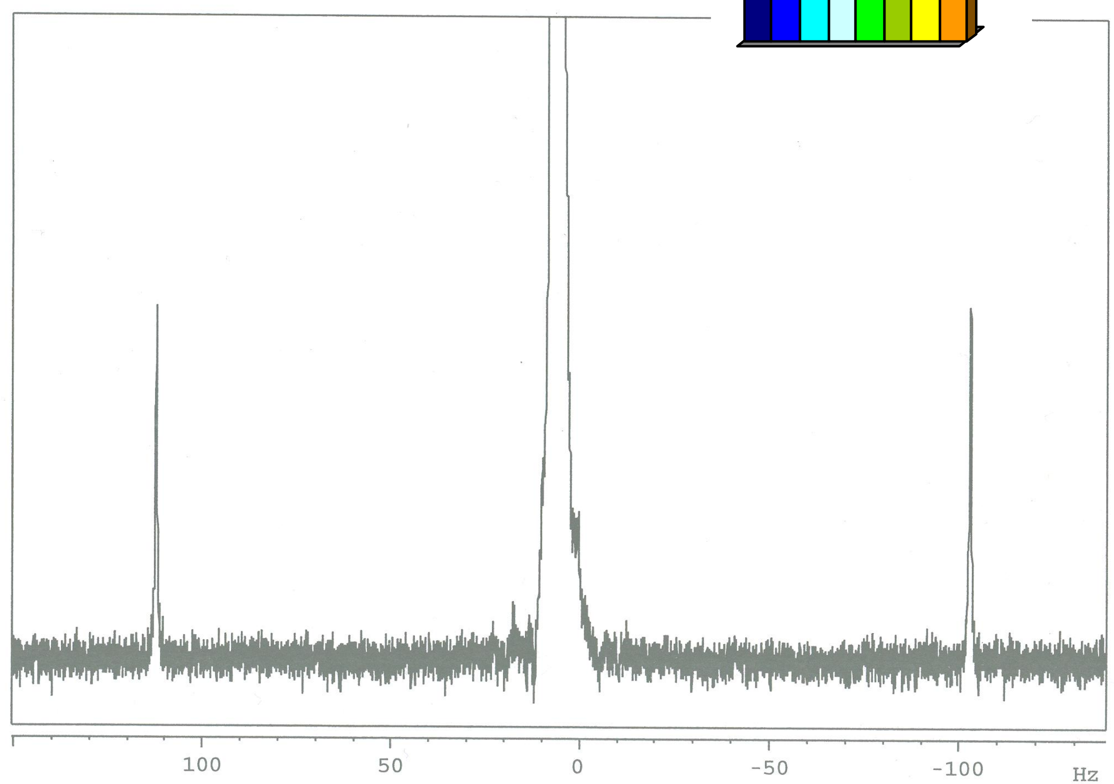
**Line shape:**

**6/12**

**Chloroform**

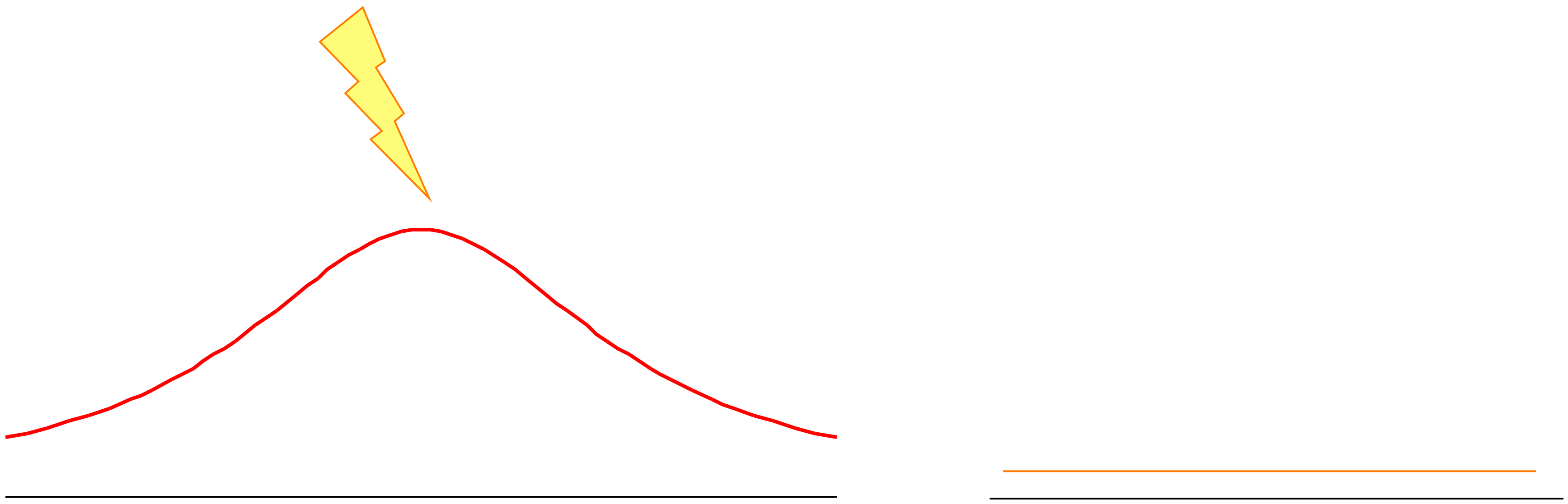
**non spinning**

**500 MHz**

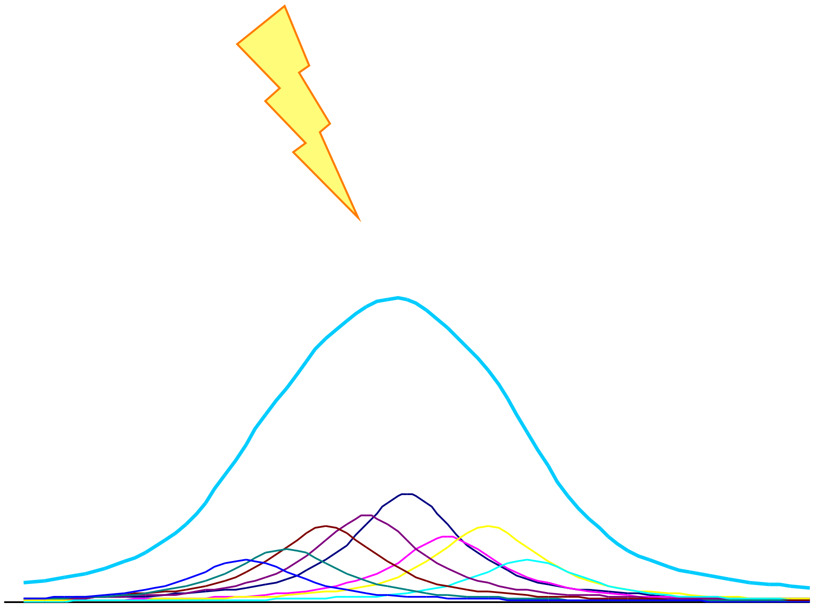


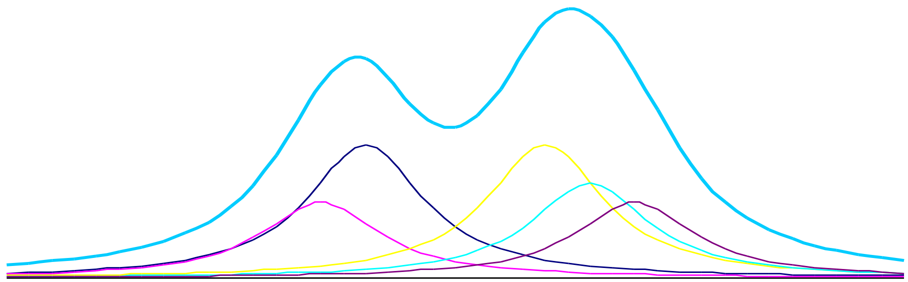
How to tell whether a broad signal is either the sum of many Lorentian lines centrered at slightly diffeent frequencies or an inherently broad signal?

Irradiating a single, broad signal, it disappears because of saturation: the populations of the two level are equalized



# Hole burning





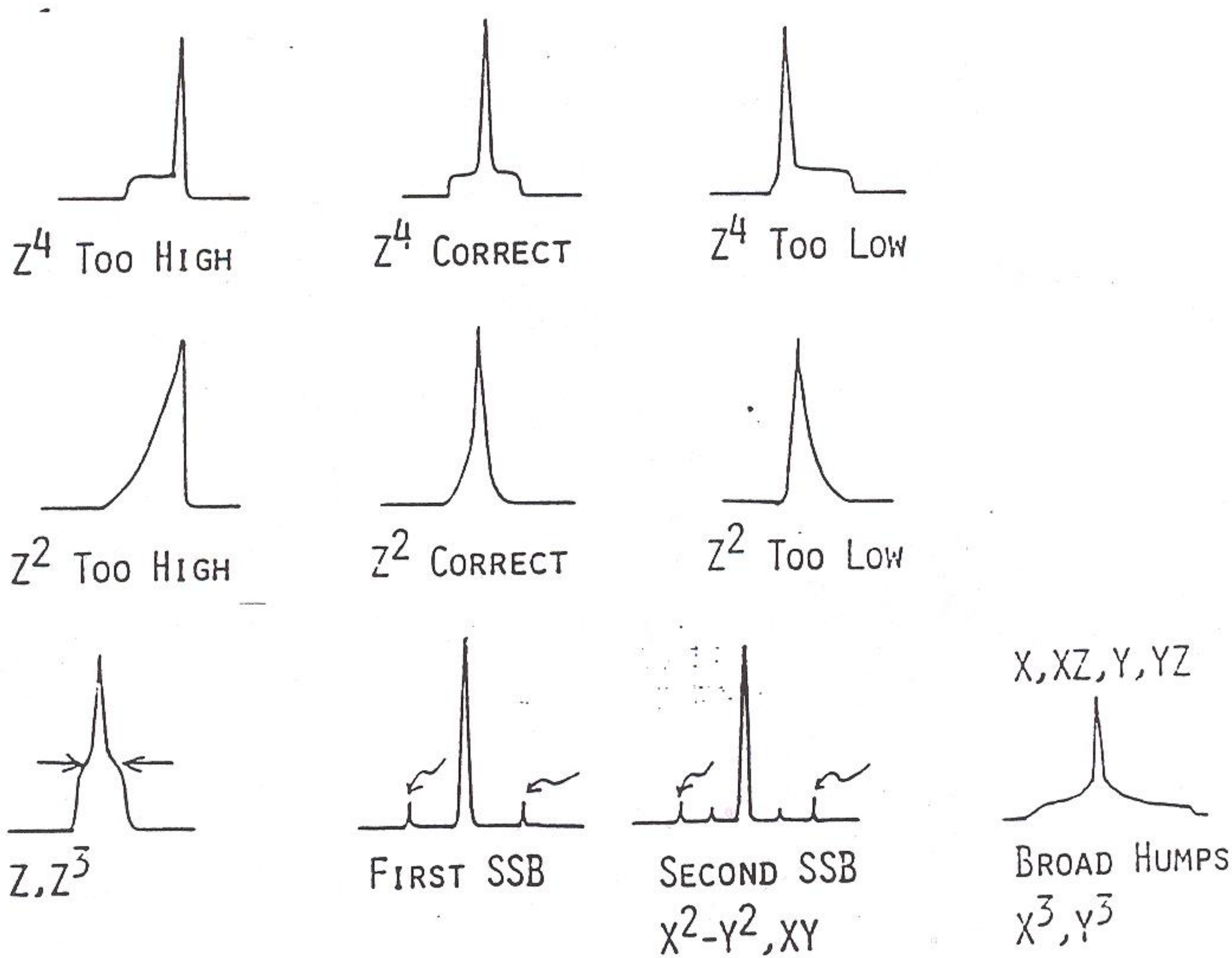
In the presence of many signals, unless high power levels are employed, only the signals closest to the irradiation frequency are saturated

**NB** solvent signal presaturation

# Shims

- The shims for field homogenity are coils projected to be carry tunable direct currents
- they originate small magnetic field in the sample region
- with the appropriate current are established these magnetic field counteract the deviations of the static magnetic field making $B_0$ highly homogeneous across the whole sample
- The were introduced (1957) by Marcel Golay (1902-1987), a mathematician of *Perkin Elmer Corporation*.
- **He stopped by ... and gave us High Resolution**

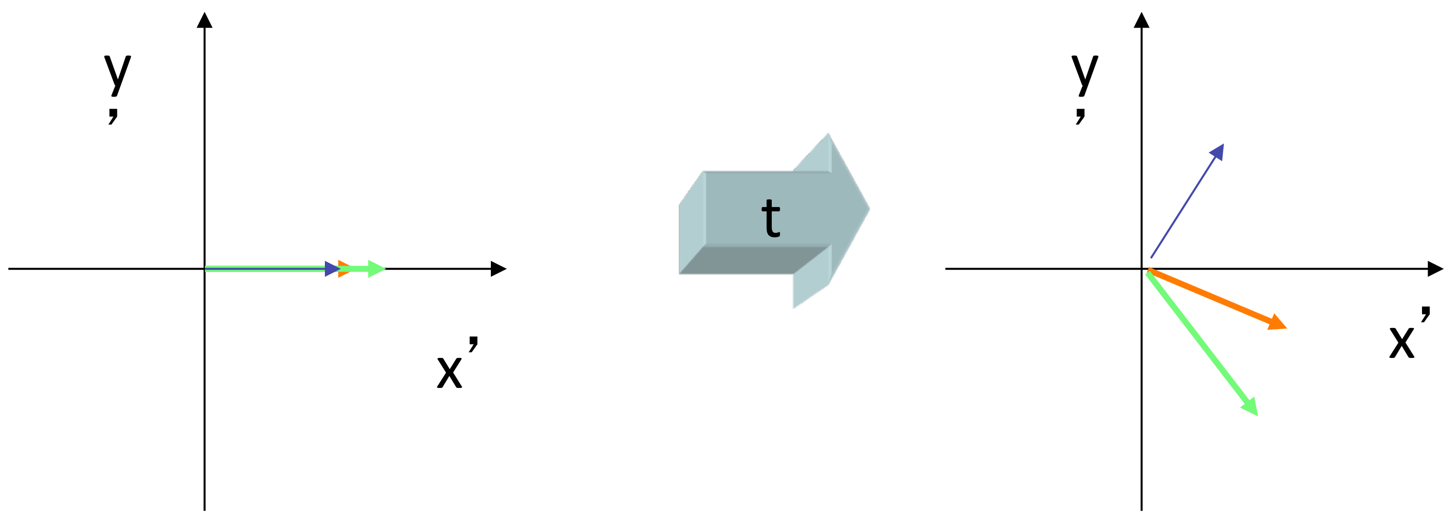
# Shim Circuits: Real Spherical Harmonics



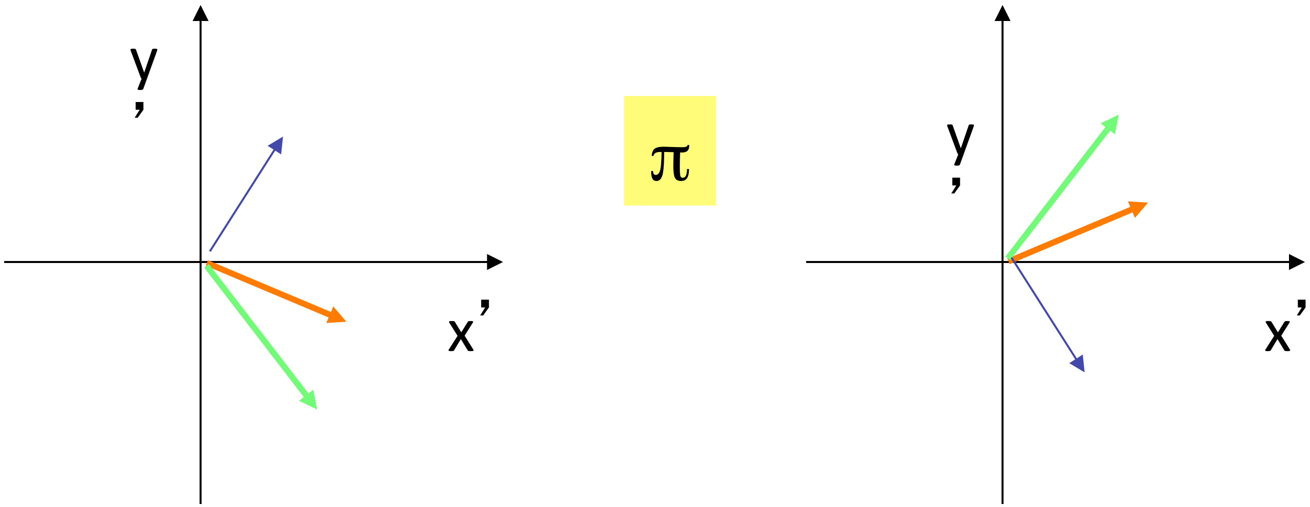
# Spin Echo

Soon after a $\pi/2$ pulse along y' : all isochromats lie on the x' axis

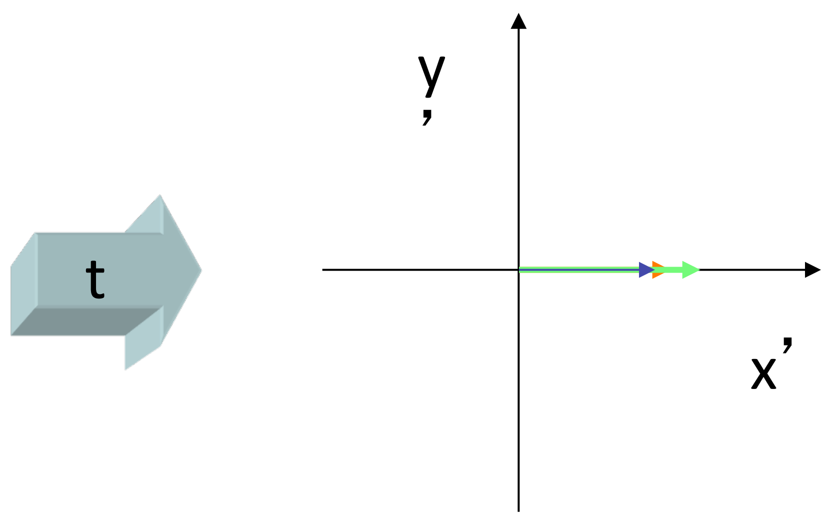
After a certain time t they are defocussed because they precess in the rotating frame with different $\Omega$, owing to different $\delta B_0$



π pulse along x’ : the position of each isochromat is inverted




Magically, after a time t equal to the previous one, the system reverted to the starting situation except for the decay due to realtransverse relaxation



# Hahn echo



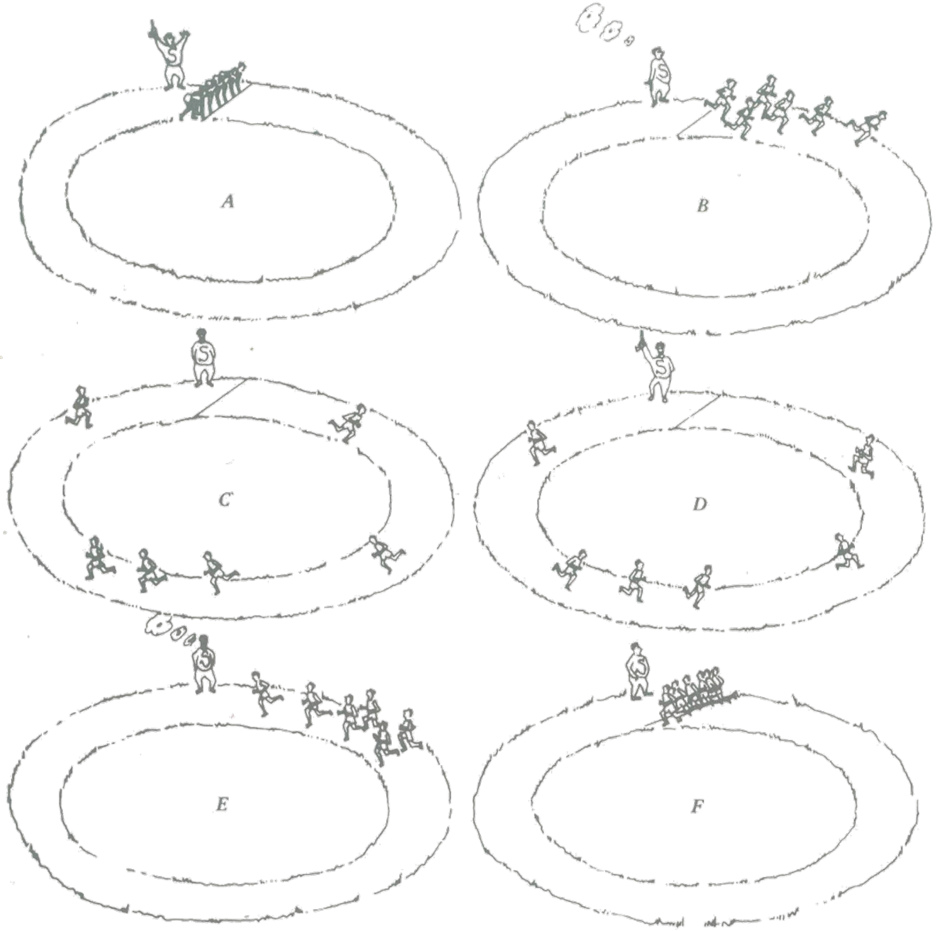
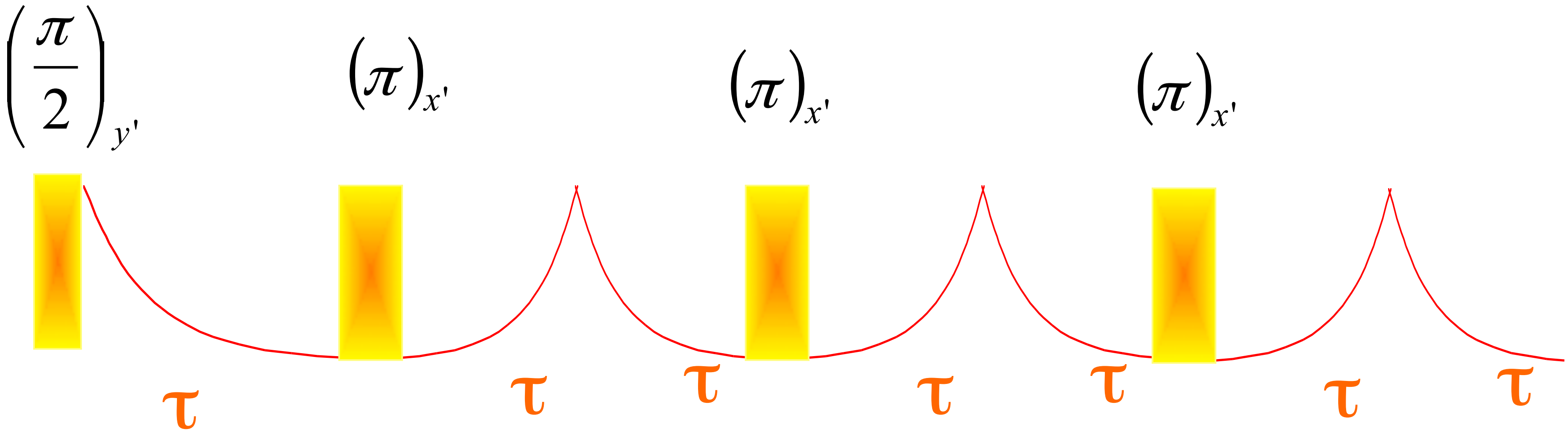
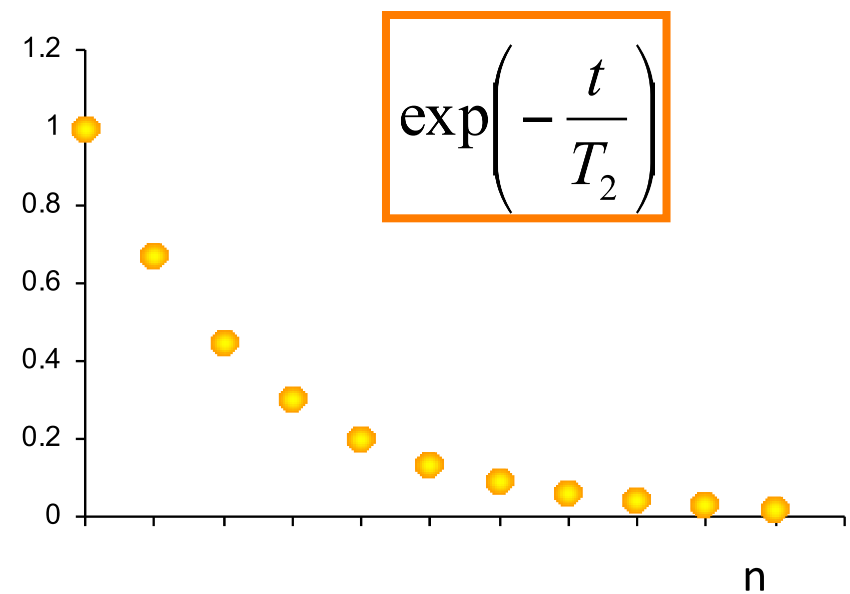



**Fig. 9.2** Dephasing and reversal on a race track, leading to coherent rephasing and an "echo" of the starting configuration. [From *Phys. Today*, front cover, November 1953. Reproduced by permission.]

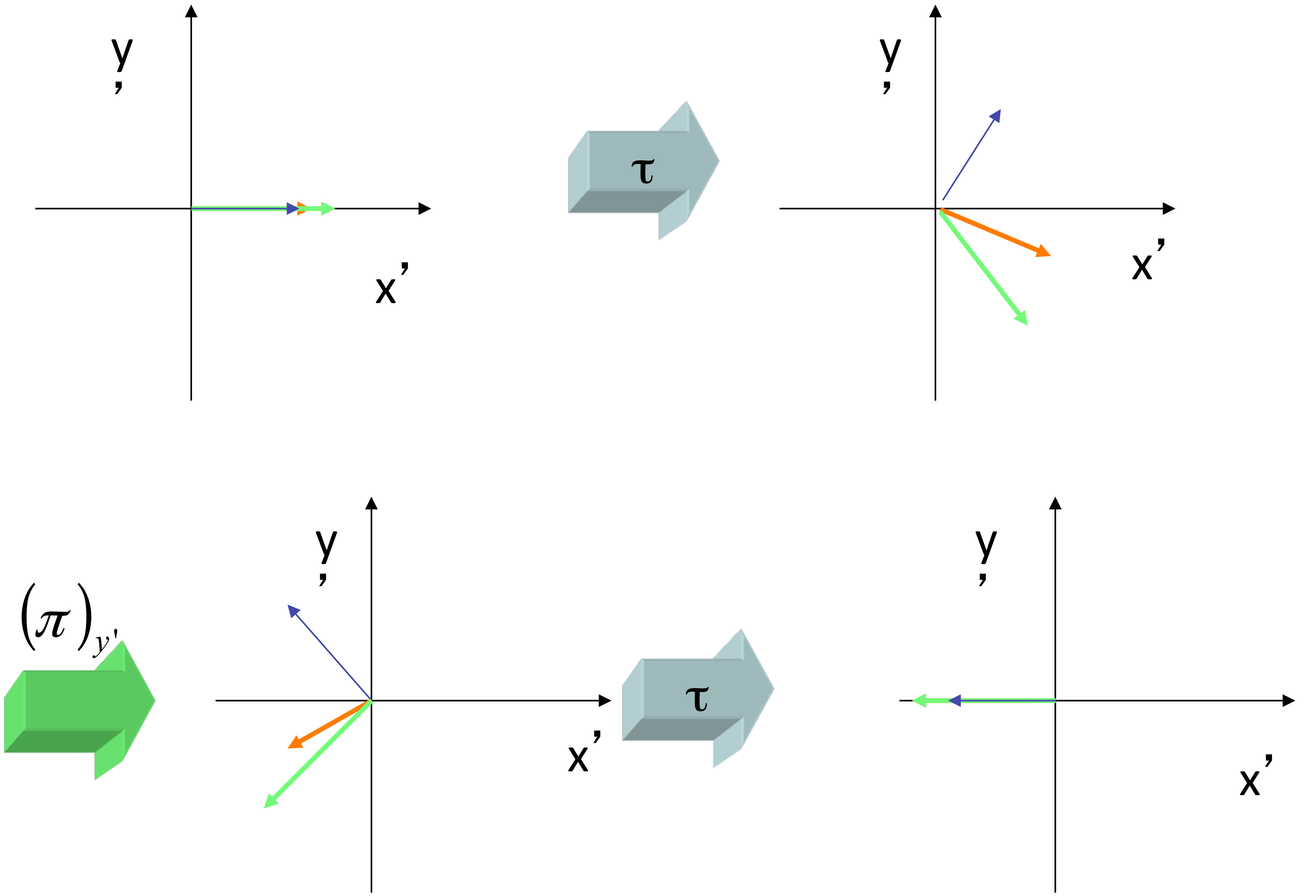


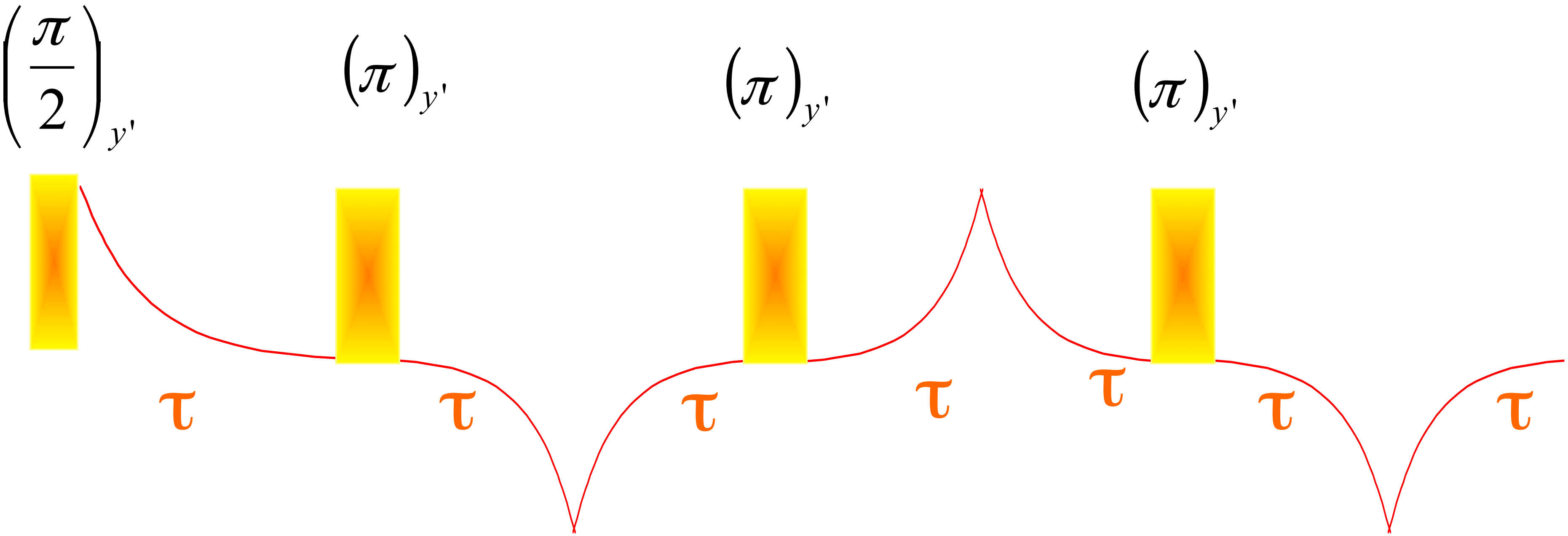

Per determinare il $T_2$ di solito non si fanno esperimenti a τ via via crescenti, ma si aumenta via via il numero di echi. Si danno impulsi di π a τ dispari e si campiona l'intensità del segnale a τ pari



# Carr Purcell Meiboom Gill

- to compensate for the effects of imperfect $\pi$ pulses $\pi$ pulses with the same phase of the first $\pi/2$ pulse are used
- The deviations compensate every second pulse
- Every second echo is sampled because of the alternating signs of echo signals


y’
x’
τ
y’
x’
$(\pi)_{y'}$
y’
x’
τ
y’
x’

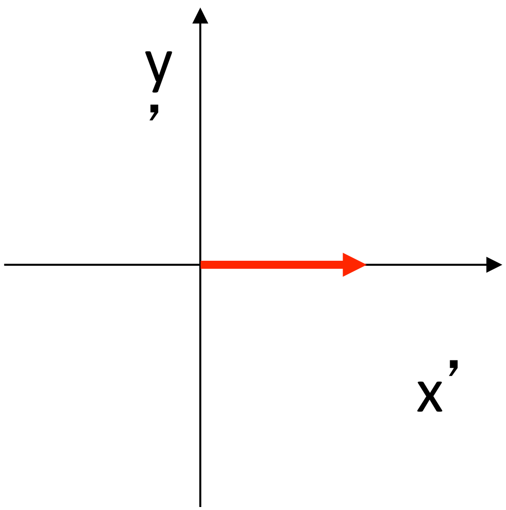


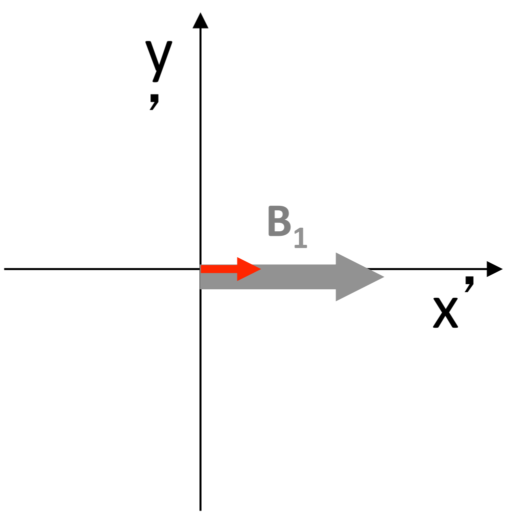

Thus the data are collected at every 4 n τ

The π pulses refocus the magnetic field inhomogeneities and the chemical shift, but not homonuclear J coupling.

Thus in scalar coupled systems the J echo modulation is observed

# T1ρ




After getting the magnetization to the x' axis of the rotating frame by a $(\pi/2)_y$ pulse

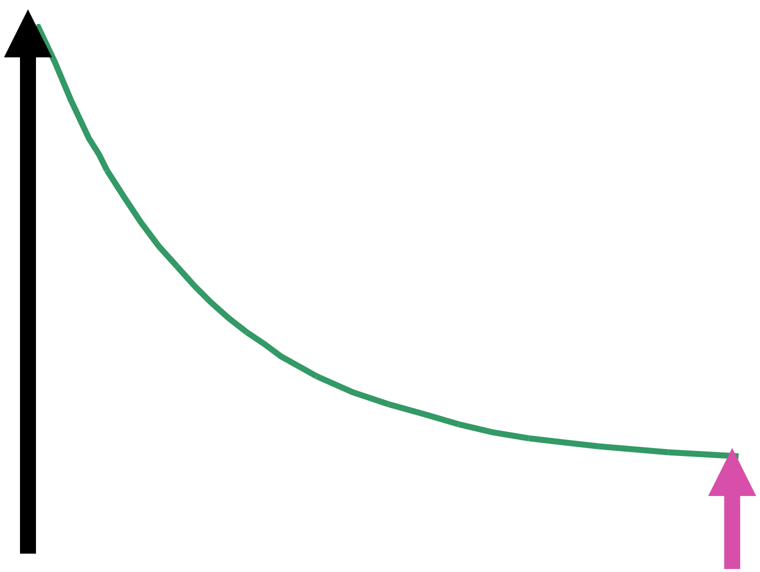
a magnetic r.f. field $B_1$ is applied along x' (it is termed **spin lock**)

in the rotating frame the magnetization feels exclusivelythe magnetic field $B_1$ (the only one component of $B^r_{eff}$) and it becomes the quantization axis

it is very weak, therefore the populatin difference among the levels is very small and the related equilibrium magnetization is tiny

A strong decrease of transverse magnetization intensity occurs. Its module decays from $M_0$ (which is due to the population difference induced by $B_0$) to the value corresponding to the population difference coherent with$B_1$

The decay is ecponential with rate constant $1/T_1\rho$



In the case of fast (compared to the Larmor frequency), isotropic motion

$T_1 = T_2 = T_{1\rho}$