## Chapter 2

## Principle of NMR

### Properties of Atomic Nuclei

The majority of nuclei possess angular momentum, or spin. Nuclei bear charges and have what is called a magnetic moment $\vec{\mu}$, that behave like microscopic bar magnet (Fig.2-1).(GE: 5-6)

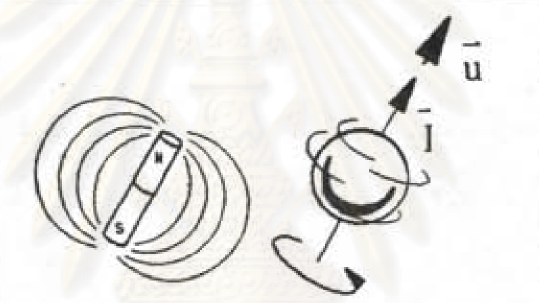


Fig.2-1 Magnetic nuclei behave like microscopic bar magnets. (GE: 5)

### Nuclei in a Magnetic Field

The randomly oriented magnetic dipoles (Fig.2-2) will interact with an applied magnetic field by trying to line up with it and have quantized energy levels in that field.

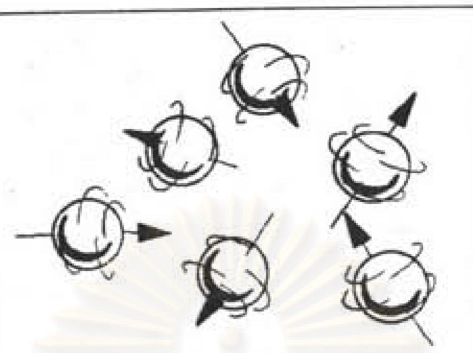

Fig.2-2 In the absence of a magnetic field, spins are randomly oriented. (GE: 5)

The theory of nuclear magnetic resonance can be derived from two differing viewpoints, quantum and semi-classical; these two methods are developed in more detail later.

The application of quantum mechanics to the case of spin quantum number **I** lead to the total spin angular momentum vector can be represented by $\hbar\vec{I}$, where the magnitude of $\vec{I}$ is $\sqrt{I(I+1)}$. The associated magnetic moment $\vec{\mu}$ is collinear with $\vec{I}$ and is related through the expression

$$\vec{\mu} = \gamma\hbar\vec{I} \tag{2.1}$$

where $\gamma$ is the magnetogyric ratio or the ratio between the magnetic and mechanical moments.

The applied magnetic field $\vec{B}_0$ (in the z-direction) will interact with magnetic moment $\vec{\mu}$, by the hamiltonian

$$H = -\vec{\mu}\cdot\vec{B}_0. \tag{2.2}$$

Substituting $\vec{\mu}$ into Eq.(2.2), we have

$$H = -\gamma\hbar B_0 I_z.$$

The eigenvalues of $I_z$ are m, where m take the (2I+1) values from +I through +(I-1) to -I, and so the possible energies of the system are

$$E_m = -\gamma \hbar B_0 m \tag{2.3}$$

These are the Zeeman energies. The energy difference between adjacent levels is $\gamma\hbar B_0$ This quantization picture is shown in Fig.2-3 for cases of I=1/2 and I=3/2.

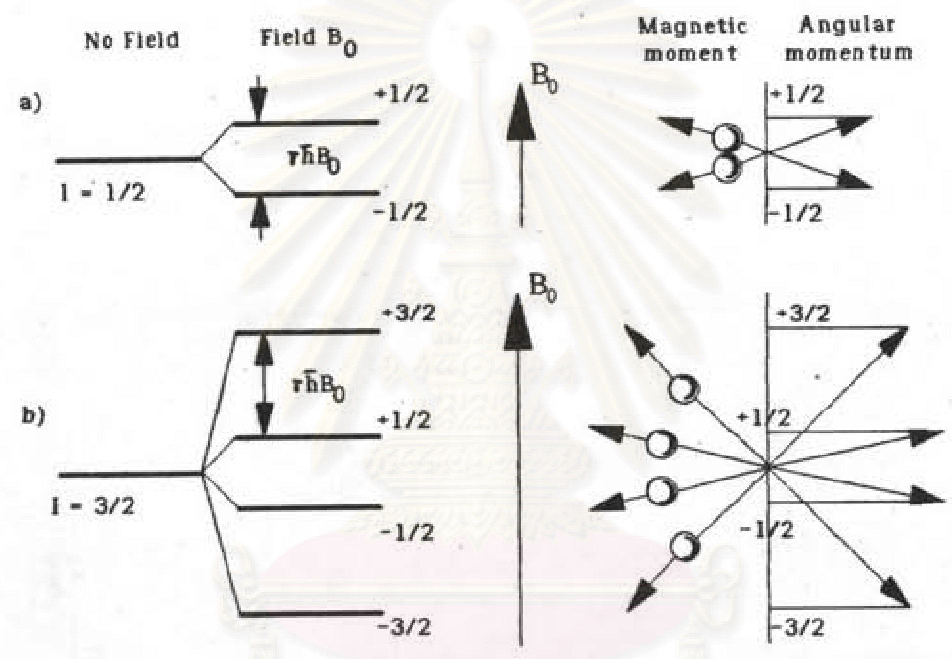


Fig.2-3 Energy levels and space quantization picture for nuclei with (a) I = 1/2 and (b) I = 3/2, both with positive $\gamma$, in a magnetic field $B_0$ The angular momentum vecters are in units of $\hbar$; these vectors could also represent (for positive $\gamma$) the associated magnetic moment vectors in units of $\gamma\hbar$. Note that for positive $\gamma$, the lowest energy levels occur for maximum positive m.(Rushworth, Tunstall 1973: 3)

The transitions between neighbouring energy levels ($\Delta m = \pm 1$) will be expressed as

$$E = \hbar w = \gamma \hbar B_0,$$

and hence

$$w = \gamma B_0. \tag{2.4}$$

This equation is the so-called Larmor relationship, which state that angular frequency or Larmor frequency $\omega$ of the precession is the product of the magnetic field $B_0$ and magnetogyric ratio $\gamma$. The magnetic dipoles precess about the direction of the field in a manner which is an analogous to the wobbling of a top as it spins and tries to orient itself in the earth's gravitational field (Fig.2-4).

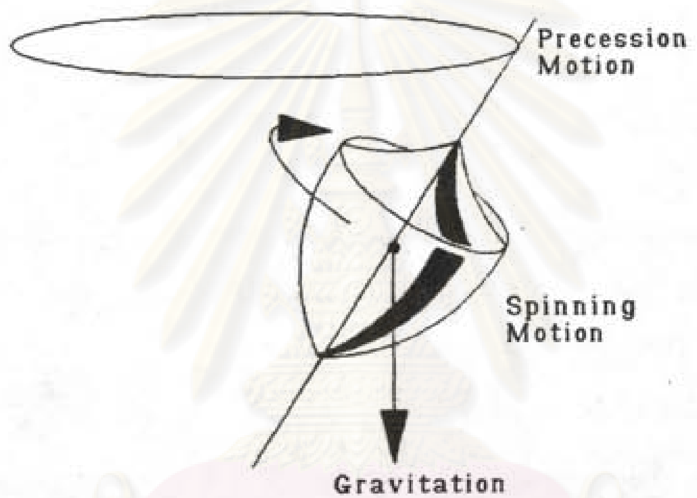


Fig.2-4 Spinning top. Gravitation exerts a torque and thus forces the top into a precessional motion. For magnetic nuclei, the torque is created by the interaction of the magnetic moments with the external magnetic field.

A much simpler approach to the field magnetism is to consider the bulk or macroscopic magnetic properties of the material (Poole, Farach 1971: 5). Instead of focusing attention on an individual magnetic moment $\vec{\mu}$, we can study the bulk magnetization $\vec{M}$ which is the magnetic moment per unit volume.

$$\vec{M} = \sum_i \vec{\mu}_{ni} \tag{2.5}$$

Because of the very large number ($\sim 10^{23}$) of nuclei in a unit volume, small irregularities will usually average out to give a spatially uniform bulk magnetization.

## Resonance

There exists a dynamics balance between the two basic energy states, determined by magnetic field and temperature (GE: 6). In thermal equilibrium, the number of transitions from the lower to the upper state are equal to those from the upper to the lower state.

Resonance is the induction of transitions between two different energy states, it produce a signal that can be detectable. In NMR, resonance occurs when the magnetic moments is flipped from their lower to their upper states by applying radio frequency energy at the Larmor frequency. (GE: 7)

### Effect of alternating magnetic field

In the previous section, referring to radio frequency at Larmor frequency that can cause resonance. This section will explain how the resonance occurs. Consider alternating magnetic field (or radio frequency) $B_x(t) = B_{x0}\cos wt$ composing two components, each of amplitude $B_1$, one rotating clockwise and the other counterclockwise. (Slichter 1963: 18-20)

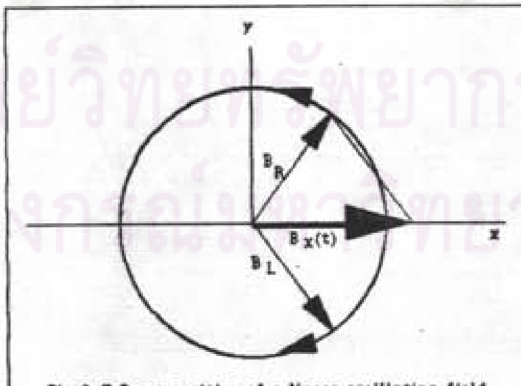


Fig.2-5 Decomposition of a linear oscillating field into two rotating elements. (Slichter 1963: 18)

We denote the rotating fields by $B_R$ and $B_L$:

$$\overline{B}_R = B_1[\hat{i}\cos(wt) + \hat{j}\sin(wt)], \qquad (2.6)$$

$$\vec{B}_L = B_1[\hat{i}\cos(wt) - \hat{j}\sin(wt)] = B_1[\hat{i}\cos(-wt) + \hat{j}\sin(-wt)].$$

Assuming we have only the field $B_R$, because the using of a negative $w$ will convert it to $B_L$. We shall introduce the symbol $w_z$, the component of $w$ along the z-axis that may be positive or negative. We may, therefore, change Eq.(2.6) to

$$\vec{B}_1 = B_1[\hat{i}\cos(w_z t) + \hat{j}\sin(w_z t)] \tag{2.7}$$

which will give us either sense of rotation, depending on the sign of $w_z$.

In presence of the alternating field $\vec{B}_1(t)$, the equation of motion of a spin including the effects both of $B_1(t)$ and of the static field $\vec{B}_0 = \hat{k}B_0$ becomes

$$\frac{d\vec{\mu}}{dt} = \vec{\mu} \times \gamma[\vec{B}_0 + \vec{B}_1(t)]. \tag{2.8}$$

In rotating frame that rotates about the z-direction at frequency $w_z$, $\vec{B}_1$ will be static. Since the axis of rotation coincides with the direction of $B_0$, $B_0$ will also be static. Let us take the x-axis in the rotating frame along $B_1$. Then Eq.(2.8) becomes

$$\frac{\delta\vec{\mu}}{\delta t} = \vec{\mu} \times [\hat{k}(w_z + \gamma B_0) + \hat{i}\gamma B_1] \tag{2.9}$$

where $\frac{\delta\vec{\mu}}{\delta t} = \hat{i}\frac{d\mu_x}{dt} + \hat{j}\frac{d\mu_y}{dt} + \hat{k}\frac{d\mu_z}{dt}$

= the time rate of change of $\vec{\mu}$ about the coordinate system $\hat{i}$, $\hat{j}$ and $\hat{k}$

Notice that we have encountered two effects in making the transformation of Eq.(2.8) to Eq.(2.9) by using

$$\frac{d\vec{\mu}}{dt} = \frac{\delta\vec{\mu}}{\delta t} + \vec{\Omega} \times \vec{\mu} \tag{2.10}$$

where $\vec{\Omega}$ is angular velocity. The first is associated with the derivative of the rotating unit vectors $\vec{B}_0$ and $\vec{B}_1$ in terms of their components in the rotating system and gives rise to the conversion of $B_1$ from a rotating to a static field. Eq.(2.9) may be rewritten to emphasize that near resonance $w_r + \gamma B_0 \cong 0$, by setting $w_r = -w$, where $w$ is now positive (we assume here that $\gamma$ is positive). Then

$$\frac{\delta \vec{\mu}}{\delta t} = \vec{\mu} \times \gamma \left[ \left( B_0 - \frac{w}{\gamma} \right) \hat{k} + B_1 \hat{i} \right]$$
$$= \vec{\mu} \times \gamma \vec{B}_{eff},$$

where $\vec{B}_{eff} = \hat{k}\left( B_0 - \frac{w}{\gamma} \right) + B_1 \hat{i}$.

Physically Eq.(2.10) states that in the rotating frame. The moment acts as through it experienced effectively a static magnetic field $\vec{B}_{eff}$. The moment therefore precesses in a cone of fixed angle about the direction of $\vec{B}_{eff}$ at angular frequency $\gamma B_{eff}$. The situation is illustrated in Fig.2-6 for a magnetic moment which, at t=0, was oriented along the z-direction.

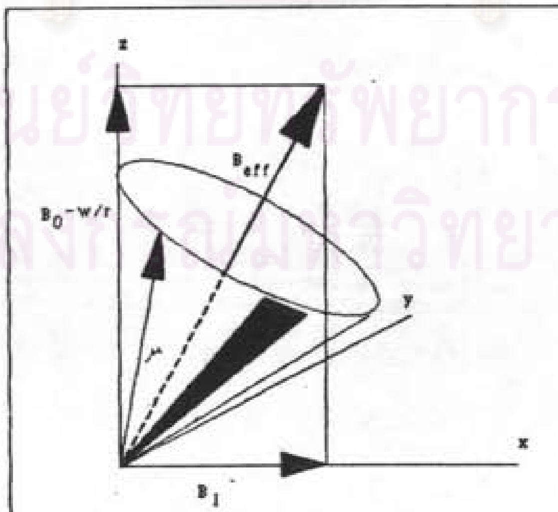


Fig.2-6 The effective field and motion of the moment $\mu$ in the rotation coordinate system. (Slichter 1963: 19)

All the energy it takes to tilt $\vec{\mu}$ away from $\vec{B}_0$ is returned in a complete cycle of $\vec{\mu}$ around the cone. There is no net absorption of energy from the alternating field but rather alternately receiving and returning of energy.

If the resonance condition is fulfilled exactly ($\omega = \gamma B_0$), the effective field is then simply $\hat{i}B_1$. A magnetic moment that is, it will precess but remaining always perpendicular to $\vec{B}_1$. If we were to turn on $B_1$ for a short time (that is, apply a wave train of duration $t_w$), the moment would precess an angle $\theta = \gamma B_1 t_w$. If $t_w$ were chosen such that $\theta = \pi$, the pulse would simply invert the moment. Such a pulse is referred to in the literature as a "180 degree pulse". If $\theta = \pi/2$ (90 degree pulse), the magnetic moment is turned from the z-direction to the y-direction.

**<u>Relaxation times</u>**

This section is a brief discussion of spin-spin and spin-lattice relaxation times.

**Spin-spin relaxation**

These simple method of observing magnetic resonance, illustrated in Fig.2-7 and Fig.2-9 (GE: 8). The detectable signal can be received from a coil, an axis of which is oriented perpendicular to $\vec{B}_0$.

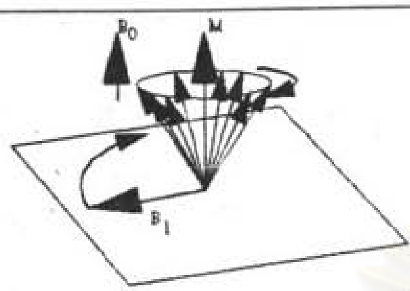


Fig.2-7 Transverse magnetization is produced by a radio frequency field $B_1$ rotating synchronously with the precessing spins. (GE: 8)

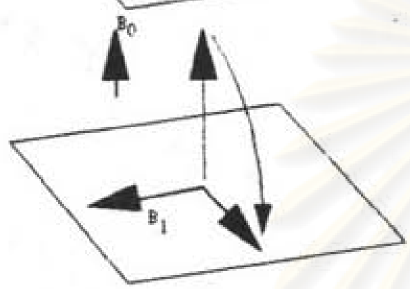


Fig.2-8 If we were to turn on B for a short time, that were chosen such that 0 = 90 degree (90 degree pulse). (GE: 8)

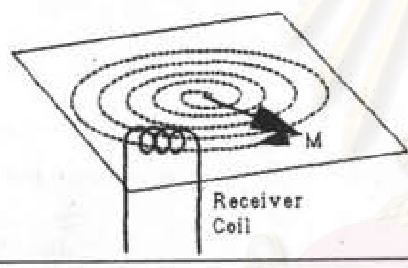


Fig.2-9 Following the RF pulse, the transverse magnetization $M_{xy}$ precesses around the axis of the external field, thereby inducing an a.c. signal in the receiver coil situated in the transverse plane. (GE: 8)

The magnetic moment induce a voltage in the receiver coil, situated in the transverse plane (Fig.2-9)(GE: 9). Since precession occurs at the Larmor frequency, the voltage induced in the coil circuit is of the same frequency. However, the transverse magnetization $M_{xy}$ does not persist. It decays to zero with a characteristic time constant and so does the amplitude of the detected voltage. For this reason, the signal is denoted *free induction decay* (FID), manifesting itself as a damped oscillation (Fig.2-10). If the field is perfectly homogeneous, this characteristic time is the spin-spin relaxation time ($T_2$) or the transverse relaxation time. In practice, it is not quite the spin-spin relaxation, but it has the another effects, such as loose phase coherence because of the inhomogeneity of the static magnetic field and the diffusion of the magnetization.

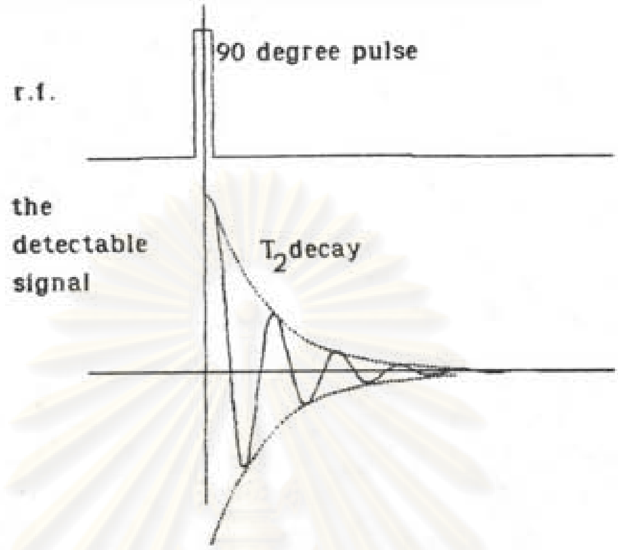


Fig.2-10 The method for measuring spin-spin relaxation time ($T_2$).

Measurement of spin-spin relaxation times (Morris 1986: 49-50) can be simply done by sending two rf pulses to the sample as illustrated in Fig.2-11. Following the initial 90° pulse applied along the x-direction (Fig.2-11(a)), the spins begin to dephase. This process is allowed continue for a time TE/2 (Fig.2-11(b)) at which point a 180° is applied, again along the x-direction (Fig.2-11(c)), spins continue to move in their original sense and so rephase along the negative y-axis after a further time TE/2 (Fig.2-11(d)). The echo will be formed at time TE (Fig.2-11(e)). From analysis the reduction of echo amplitudes will depend solely on the natural $T_2$, that is on those processes which are not coherent and cannot therefore be refocused.

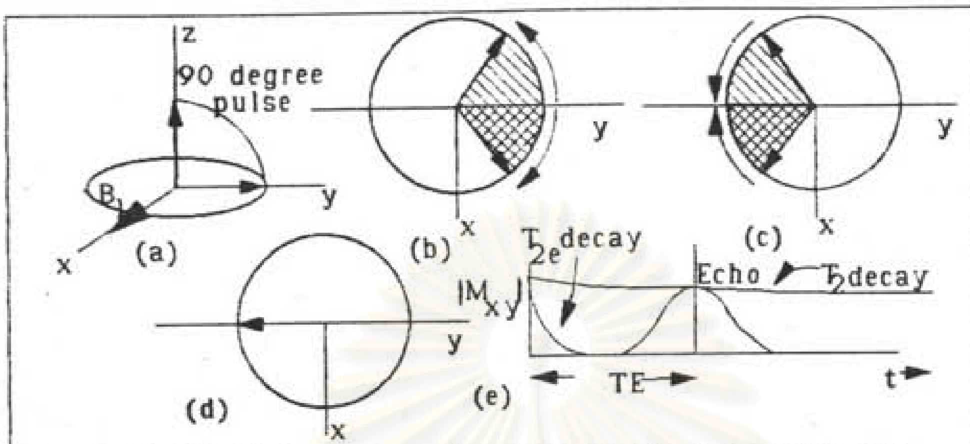


Fig.2-11 The Hahn spin-echo experiment. (a) Application of 90 degree pulse. (b) Dephasing of spins during period TE/2. (c) Position of spin isochromats following 180 degree pulse. (d) Negatively-refocused magnetization after further period TE/2. (e) Evolution of magnetization in xy-plane of rotating frame. Note the sign reversal following the 180 degree pulse has been removed for clarity. (Morris 1986: 49)

This basic experiment which is called the Hahn spin-echo experiment can be improved, as suggested by Carr and Purcell. Through the addition of further 180° pulses at intervals of TE giving a sequence 90°-TE/2-180°-TE-180°-TE... . This produces a series of echoes of alternating sign at intervals of TE and allow $T_2$ to be determined in a single experiment. It also has the virtue of reducing errors due to the effects of diffusion.

**Spin-lattice relaxation**

Spin lattice relaxation (Morris 1986: 41) is the process by which the spin population returns to its equilibrium Boltzmann distribution following the absorption of rf energy.

The main feature of the spin lattice relaxation process is an exchange of spin (Zeeman) energy with the thermal motions of the molecules (the 'lattice') of which the nuclear spin are part. Spin lattice relaxation time ($T_1$) is referred as longitudinal relaxation time since it depend on the magnetization along z-axis.

Measurements of spin lattice relaxation times ($T_1$) can be determined by conventional pulsed nmr methods in a number of ways (Morris 1986: 43-44). Of these, the 180°-TI-90° or inversion recovery sequence is generally the method of choice since it is both simple and reliable. It is illustrated in Fig.2-12 and consist of a 180° pulse to invert the magnetization follow by a variable time delay TI during which recovery take place with a time constant, equal to the spin lattice relaxation time $T_1$. The extent of the recovery is determined by applying a 90° inspection pulse to nutate the magnetization from the z-axis into the xy-plane, where the signal is detected. The initial amplitude of this FID, depends on TI as

$$M_{xy}(0) = M_z(\tau) = M_0\{1 - 2\exp(-TI/T_1)\}$$

If TI is varied over a suitable range, the spin lattice relaxation time can be found by computer fitting the exponential recovery or, more simply (but less reliably), from the gradient of a logarithmic plot. It must wait for a period > $4T_1$ between repetitions of the inversion recovery sequence to be sure that magnetization returns to its equilibrium value.

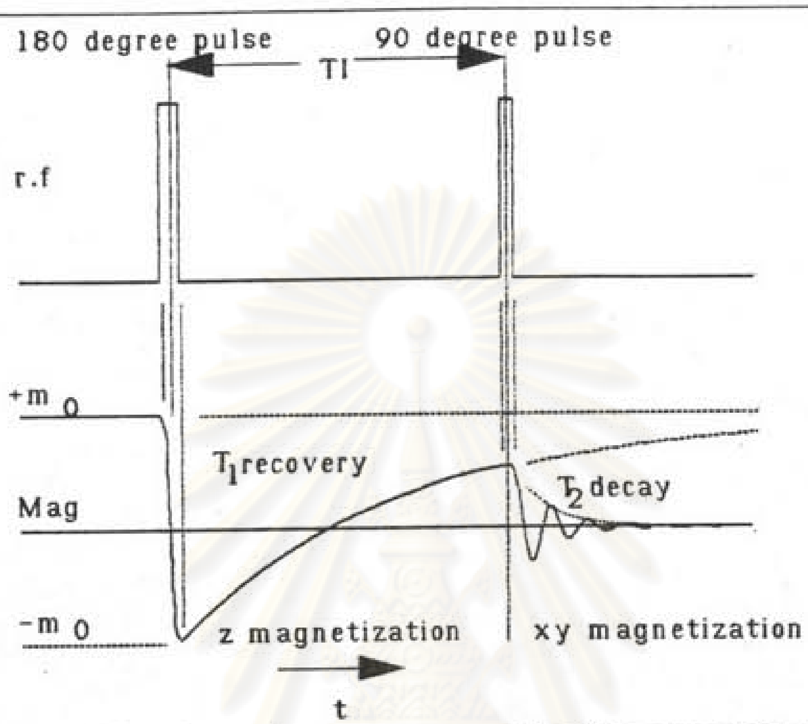


Fig.2-12 The inversion recovery method for measuring $T_1$. The width of the r.f. pulses has been increased relative to the interpulse spacing TI for clarity. (Morris 1986: 44)