3. Principle

(1) Quantum mechanical description of nuclear magnetic resonance

1) Magnetic resonance of a single nucleus

The projection $\vec{\mu}$ of the total magnetic moment of the nucleus in its angular momentum direction $\vec{P}$ is usually called the nuclear magnetic moment, and the relationship between them is usually written as:

$$\vec{\mu} = \gamma \cdot \vec{P} \text{ 或 } \vec{\mu} = g_N \cdot \frac{e}{2m_p} \cdot \vec{P}, \tag{2-1}$$

where, $\gamma = g_N \cdot \frac{e}{2m_p}$, is called the gyromagnetic ratio; e is the electron charge; m_p is the proton mass; g_N is the Lande factor or g-factor. For hydrogen nuclei, $g_N = 5.5851$.

According to quantum mechanics, the size of the nuclear angular momentum is determined by the following formula

$$P = \sqrt{I(I+1)}\hbar, \tag{2-2}$$

where h is the Planck's constant $\hbar = \frac{h}{2\pi}$, I is the spin quantum number for the nucleus, can be taken these values $I = 0, \frac{1}{2}, 1, \frac{3}{2}, \cdots$. For the hydrogen nucleus, $I = \frac{1}{2}$.

Put the hydrogen nucleus in the external magnetic field $\vec{B}$, the direction of $\vec{B}$ can be takes as the coordinate axis Z. The projection value of the angular momentum of the nucleus in the direction $\vec{B}$ is determined by the following formula

$$P_B = m \cdot \hbar. \tag{2-3}$$

Where m is called the magnetic quantum number and can be taken these values $m = I, I-1, \cdots, -(I-1), -I$. The projected value of the nuclear magnetic moment in the direction $\vec{B}$ is $\mu_B = g_N \frac{e}{2m_p} P_B = g_N \left(\frac{e\hbar}{2m_p} \right) m$. Write it as

$$\mu_B = g_N \mu_N m, \tag{2-4}$$

where $\mu_N = 5.050787 \times 10^{-27} JT^{-1}$, is called nuclear magneton, and it is the unit of nuclear magnetic moment.

A nucleus with a magnetic moment $\vec{\mu}$ has a potential energy E in a constant magnetic field $\vec{B}$ as: $E = -\vec{\mu} \cdot \vec{B} = -\mu_B B = -g_N \mu_N m B$. The energy difference between any two energy levels is:

$$\Delta E = E_{m1} - E_{m2} = -g_N \mu_N B(m_1 - m_2). \tag{2-5}$$

Consider the simplest case. For the hydrogen nucleus, the spin quantum number $I = \frac{1}{2}$, so the magnetic quantum number can only take two values, namely $m = \frac{1}{2}$ and $m = -\frac{1}{2}$. The projection of the magnetic moment in the direction of the external field can only take two values, as shown in Figure 2-1 (a), and the corresponding energy level is shown in (b) Figure 2-1 (b).

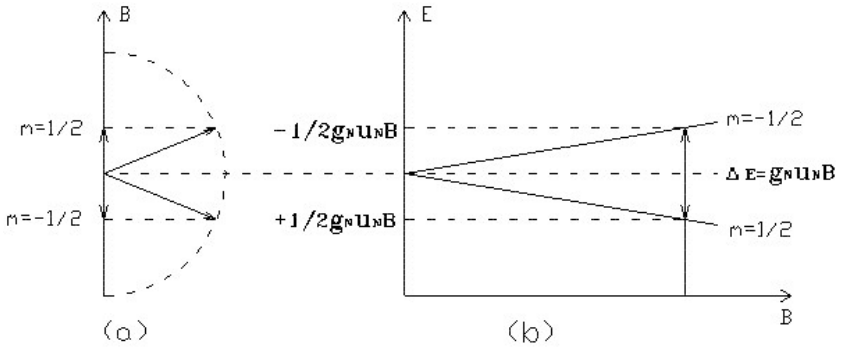

Figure 2-1 Splitting of hydrogen nuclear energy levels in a magnetic field

According to the selection rule of quantum mechanics, only the transition between two energy levels of $\Delta m = \pm 1$ can occur, and the energy difference between these two transition energy levels is

$$\Delta E = g_N \cdot \mu_N \cdot B \,. \tag{2-6}$$

From this formula, the energy difference between two adjacent energy levels is proportional to the size of the external magnetic field. The stronger the magnetic field, the greater the split between the two energy levels.

If the external magnetic field is $\vec{B}_0$, an electromagnetic field is superimposed on the hydrogen nucleus in the region of the steady magnetic field. If the energy of the electromagnetic wave is exactly equal to the energy difference between the two levels of the hydrogen nucleus

$$h\nu_0 = g_N \mu_N B_0 \,. \tag{2-7}$$

Then the hydrogen nucleus will absorb the energy of the electromagnetic wave, and jumps from energy level $m = \frac{1}{2}$ to the energy level $m = -\frac{1}{2}$, which is the phenomenon of nuclear magnetic resonance absorption. Equation (2-7) is the NMR condition. For the convenience of application, it is often written as:

$$\nu_0 = \left(\frac{g_N \cdot \mu_N}{h} \right) B_0 \,, \quad \text{i.e. } \omega_0 = \gamma \cdot B_0 \,. \tag{2-8}$$

2) Signal strength of NMR

The above discussion is the NMR theory of a single nucleus placed in an external magnetic field. But the sample used in the experiment is a large collection of similar nuclei. If there is no difference between the number of nuclei at a high energy level and the number of nuclei at a low energy level, then under the excitation of electromagnetic waves, the nuclei at the upper

and lower energy levels will all transition, and the probability of transition is equal, so the absorption energy is equal to the radiation energy. No NMR signal can be observed. Only when the number of nuclei at the low energy level is greater than the number of nuclei at the high energy level, absorbs more energy than radiation energy, so that the NMR signal can be observed. In the thermal equilibrium state, the relative distribution of the number of nuclei at two energy levels is determined by the Boltzmann factor:

$$\frac{N_2}{N_1} = \exp\left(-\frac{\Delta E}{kT}\right) = \exp\left(-\frac{g_N \mu_N B_0}{kT}\right), \tag{2-9}$$

where N_1 is the number of nuclei at the low energy level, N_2 is the number of nuclei at the high energy level, ΔE is the energy difference between the upper and lower energy levels, k is the Boltzmann constant, and T is the absolute temperature. When $g_N \mu_N B_0 << kT$, the above formula can be approximated as

$$\frac{N_2}{N_1} = 1 - \frac{g_N \mu_N B_0}{kT}, \tag{2-10}$$

The above formula shows that the number of nuclei at the low energy level is slightly more than the number at the high energy level. For hydrogen nuclei, if the experimental temperature is $T = 300K$ and external magnetic field is $B_0 = 1T$, we have $\frac{N_2}{N_1} = 1 - 6.75 \times 10^{-6}$ or $\frac{N_1 - N_2}{N_1} \approx 7 \times 10^{-6}$.

This shows that at room temperature, there are only about 7 nuclei per million at low-level more than high-level. This means that only 7 out of every 1 million nuclei involved in NMR absorption at low energy levels are not canceled by resonance radiation. Therefore, the MRI signal is very weak, and detecting such a weak signal requires a high-quality receiver.

It can be seen from equation (2-10) that the higher the temperature, the smaller the nuclei number difference, and the more unfavorable to observe the nuclear magnetic resonance signal. The stronger the external magnetic field B_0 and the larger the nuclei number difference, the more benefits to observing the NMR signal. So, the general magnetic resonance experiment requires a stronger magnetic field.

In addition, to observe the NMR signal, it is not enough to have a strong magnetic field. The magnetic field should be highly uniform within the sample range, otherwise the NMR signal cannot be observed even if the magnetic field is strong. One of the reasons is that the NMR signal is determined by formula (2-7). If the magnetic field is not uniform, the resonance frequency of each part in the sample is different. For a certain frequency of electromagnetic waves, only a few nuclei will participate in the resonance, and as a result the signal is overwhelmed by noise, making it difficult to observe the nuclear magnetic resonance signal.

(2) Classical mechanical description of nuclear magnetic resonance

The following discusses on nuclear magnetic resonance is from a classical theoretical point of view. It is not strict to apply the classical theoretical nuclear vector model to microscopic particles, but it can explain certain questions. The value is not necessarily correct, but it can give a clear physical picture to help us understand the essence of the question.

1) Larmor precession of a single nucleus

We know that if the gyro does not rotate, when its axis deviates from the vertical direction, it will fall under the action of gravity. However, if the gyro itself rotates, it will not fall down and move forward around the direction of gravity, as shown in Figure 2-2.

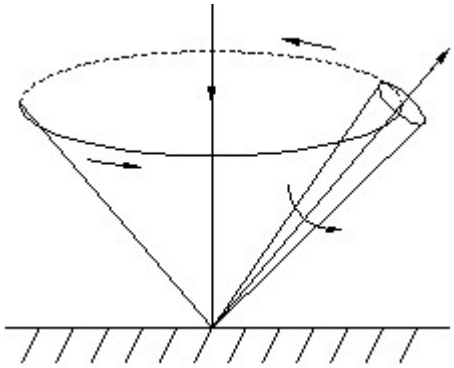

Figure 2-2 Larmor precession of a gyro

Because the atomic nucleus has spin and magnetic moment, its behavior in the external magnetic field is exactly the same as that of the gyro in the gravity field. Suppose the angular momentum of the nucleus is $\vec{P}$, the magnetic moment is $\vec{\mu}$, and the external magnetic field is $\vec{B}$, from the classical theory , it can be seen

$$\frac{d\vec{P}}{dt} = \vec{\mu} \times \vec{B} \ . \tag{2-11}$$

Because of $\vec{\mu} = \gamma \cdot \vec{P}$, so

$$\frac{d\vec{\mu}}{dt} = \lambda \cdot \vec{\mu} \times \vec{B} \ . \tag{2-12}$$

The components in x, y, z are:

$$\begin{cases} \dfrac{d\mu_x}{dt} = \gamma \cdot (\mu_y B_z - \mu_z B_y) \\ \dfrac{d\mu_y}{dt} = \gamma \cdot (\mu_z B_x - \mu_x B_z) \\ \dfrac{d\mu_z}{dt} = \gamma \cdot (\mu_x B_y - \mu_y B_x) \end{cases} . \tag{2-13}$$

Assume the steady magnetic field is $\vec{B}_0$ with direction in z axis, i.e. $B_x = B_y = 0$ and $B_z = B_0$, then the above formula will become

$$\begin{cases} \dfrac{d\mu_x}{dt} = \gamma \cdot \mu_y B_0 \\ \dfrac{d\mu_y}{dt} = -\gamma \cdot \mu_x B_0 \\ \dfrac{d\mu_z}{dt} = 0 \end{cases} . \tag{2-14}$$

It can be seen that the magnetic moment component μ_z is a constant, that is, the projection of the magnetic moment $\vec{\mu}$ in the direction $\vec{B}_0$ will remain unchanged. Differentiate the first formula of formula (2-14) and substitute the second formula into it, we have:

$$\frac{d^2\mu_x}{dt^2} = \gamma \cdot B_0 \frac{d\mu_y}{dt} = -\gamma^2 {B_0}^2 \mu_x .$$

or

$$\frac{d^2\mu_x}{dt^2} + \gamma^2 {B_0}^2 \mu_x = 0 \ . \tag{2-15}$$

This is a simple harmonic motion equation whose solution is $\mu_x = A\cos(\gamma \cdot B_0 t + \varphi)$. From the first formula of (2-14) we obtain:

$$\mu_y = \frac{1}{\gamma \cdot B_0}\frac{d\mu_x}{dt} = -\frac{1}{\gamma \cdot B_0}\gamma \cdot B_0 A\sin(\gamma \cdot B_0 t + \varphi) = -A\sin(\gamma \cdot B_0 t + \varphi)$$

Substitute $\omega_0 = \gamma \cdot B_0$ into above expression, we have

$$\begin{cases} \mu_x = A\cos(\omega_0 t + \varphi) \\ \mu_y = -A\sin(\omega_0 t + \varphi) \\ \mu_L = \sqrt{(\mu_x + \mu_y)^2} = A = \text{Constant} \end{cases} \tag{2-16}$$

It can be seen that the characteristics of the nuclear magnetic moment $\vec{\mu}$ in a steady magnetic field are:

a) It precesses around the external magnetic field $\vec{B}_0$, the angular frequency of the precession is $\omega_0 = \gamma \cdot B_0$, and has no relation with the angle θ between $\vec{\mu}$ and $\vec{B}_0$;

b) Its projection μ_L on the plane xy is constant;

c) Its projection μ_z in the direction $\vec{B}_0$ of the external magnetic field is constant.

The movement scenery is shown in Figure 2-3.

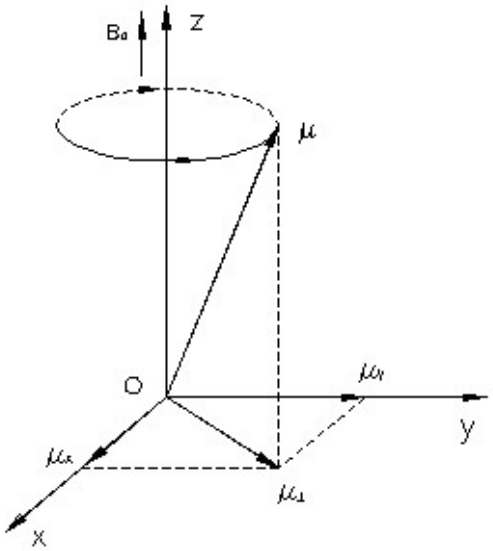

Figure 2-3 Movement of magnetic moment is external magnetic field.

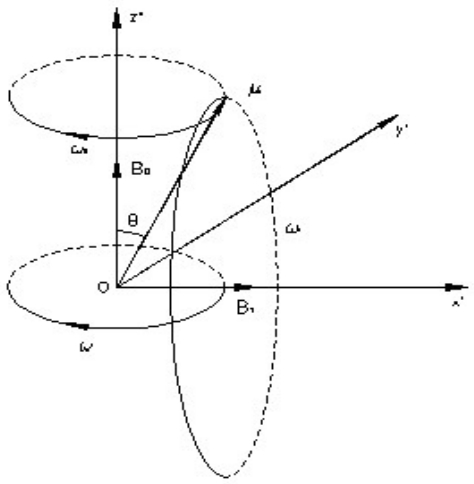

Figure 2-4 Rotating magnetic field $\vec{B}_1$ applied to $\vec{B}_0$ in perpendicular direction

If a rotating magnetic field $\vec{B}_1$ is applied in the direction perpendicular to $\vec{B}_0$ and $B_1 << B_0$. The angular frequency and direction of rotation of $\vec{B}_1$ are the same as those of the magnetic moment $\vec{\mu}$, as shown in Figure (2-4). At this time, in addition to the effect of external magnetic field $\vec{B}_0$, the nuclear magnetic moment $\vec{\mu}$ is also affected by the rotating magnetic field $\vec{B}_1$. In other words, in addition to the precession around $\vec{B}_0$, also the precesse around $\vec{B}_1$, So the angle θ between μ and $\vec{B}_0$ will change. The potential energy of nuclear magnetic moment is:

$$E = -\vec{\mu} \cdot \vec{B} = -\mu \cdot B_0 \cos\theta \ . \tag{2-17}$$

It can be seen that the change of θ means the change of nucleus energy state. As the θ value increases, the nucleus absorbs energy from the rotating magnetic field $\vec{B}_1$. This is nuclear magnetic resonance. The condition for resonance is

$$\omega = \omega_0 = \gamma \cdot B_0 \, . \tag{2-18}$$

This conclusion is completely consistent with the conclusion derived by quantum mechanics.

If the rotation angular frequency ω of the rotating magnetic field $\vec{B}_1$ is not equal to the precession angular frequency ω_0 of the nuclear magnetic moment μ, i.e. $\omega \neq \omega_0$, then the angle change is not significant. On average, the change in angle θ is zero. The nucleus does not absorb the energy of the magnetic field, so no nuclear magnetic resonance signal can be observed.

2) Bloch equation

Discussed above is the NMR of a single nucleus. The sample is not a single nuclear magnetic moment. The magnetization vector $\vec{M}$ is the vector sum of the nuclear moments $\vec{\mu}$ per unit volume, there is

$$\frac{d\vec{M}}{dt} = \gamma \cdot (\vec{M} \times \vec{B}). \tag{2-19}$$

It shows that the magnetization intensity vector $\vec{M}$ precesses around the external magnetic field $\vec{B}_0$, the angular frequency of the precession is $\omega = \gamma \cdot B$. Assume that the external magnetic field $\vec{B}_0$ is along the z-axis direction, and then add a radio frequency field along the x-axis direction:

$$\vec{B}_1 = 2B_1 \cos(\omega \cdot t)\vec{e}_x, \tag{2-20}$$

where $\vec{e}_x$ is the unit vector on the x-axis and $2B_1$ is the amplitude.

This linearly polarized field can be regarded as the superposition of a left-handed circularly polarized field and a right-handed circularly polarized field. In the two circularly polarized fields, it only has effect when the direction of rotation of the circularly polarized field is the same as the direction of precession. So for a system with positive γ, the effect is a clockwise circular polarization field, that is $M_z = M_0 = \chi_0 H_0 = \chi_0 B_0 / \mu_0$, χ_0 is the static magnetic susceptibility, μ_0 is the magnetic permeability in vacuum, and M_0 is the magnetization intensity of the spin system when the spin system and the lattice reach thermal equilibrium.

After the nuclear system absorbs the energy of the *RF* field, the number of particles in a high-energy state increases, which also causes $M_z < M_0$. The system deviates from the thermal equilibrium state. Due to the interaction between the spin and the lattice, the lattice will absorb the energy of the nucleus, causing the atomic nucleus to transition to a low energy state and transition to thermal equilibrium. The characteristic time representing this transition is called the longitudinal relaxation time and is represented by T_1 (it reflects the amount of time required for the magnetization intensity vector M_z to recover to the equilibrium value M_0 in the direction of the external magnetic field). After considering the longitudinal relaxation effect, it is assumed that the speed of transition from M_z to the equilibrium value M_0 is proportional to the degree of deviation $(M_0 - M_z)$, i.e.

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}. \tag{2-21}$$

In addition, there is also an interaction between spin and spin, and the lateral component M_x and M_y of M must also be transitioned from the non-equilibrium state to the equilibrium state, $M_x = M_y = 0$. The characteristic time that characterizes this process is the lateral relaxation time, expressed by T_2. Similar to M_z, it can be assumed that:

$$\begin{cases} \dfrac{dM_x}{dt} = -\dfrac{M_x}{T_2} \\ \dfrac{dM_y}{dt} = -\dfrac{M_y}{T_2} \end{cases} \tag{2-22}$$

When the above two effects exist at the same time, the basic motion equation describing the NMR phenomenon is:

$$\frac{d\vec{M}}{dt} = \gamma \cdot (\vec{M} \times \vec{B}) - \frac{1}{T_2}(M_x\vec{i} + M_y\vec{j}) - \frac{M_z - M_0}{T_1}\vec{k} \quad . \tag{2-23}$$

This equation is called Bloch equation. In the formula, $\vec{i}$, $\vec{j}$ and $\vec{k}$ are unit vectors in the direction of x ,y and z, respectively.

It is worth noting that in the formula $\vec{B}$ is the superposition of the external magnetic field $\vec{B}_0$ and the linear polarization field $\vec{B}_1$. Among them, $\vec{B}_0 = B_0\vec{k}$, $\vec{B}_1 = B_1\cos(\omega \cdot t)\vec{i} - B_1\sin(\omega \cdot t)\vec{j}$. The three components of $\vec{M} \times \vec{B}$ are:

$$\begin{cases} (M_y B_0 + M_z B_1 \sin\omega \cdot t)\vec{i} \\ (M_z B_1 \cos\omega \cdot t - M_x B_0)\vec{j} \\ (-M_x B_1 \sin\omega \cdot t - M_y B_1 \cos\omega \cdot t)\vec{k} \end{cases} \quad . \tag{2-24}$$

In this way, the component form of Bloch equation is written as:

$$\begin{cases} \dfrac{dM_x}{dt} = \gamma \cdot (M_y B_0 + M_z B_1 \sin\omega \cdot t) - \dfrac{M_x}{T_2} \\ \dfrac{dM_y}{dt} = \gamma \cdot (M_z B_1 \cos\omega \cdot t - M_x B_0) - \dfrac{M_y}{T_2} \\ \dfrac{dM_z}{dt} = -\gamma \cdot (M_x B_1 \sin\omega \cdot t + M_y B_1 \cos\omega \cdot t) - \dfrac{M_z - M_0}{T_1} \end{cases} \quad . \tag{2-25}$$

Solving Bloch equations under various conditions can explain various nuclear magnetic resonance phenomena. Generally speaking, the Bloch equation contains high-frequency oscillation terms $\cos\omega \cdot t$ and $\sin\omega \cdot t$, which are troublesome to solve. If we can do a coordinate transformation on it and transform it into a rotating coordinate system, it will be much easier to solve.

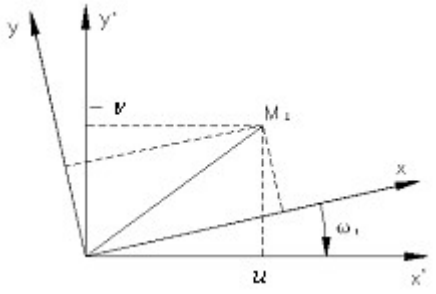

Figure 2-5 Rotating coordinate system

As shown in (2-5), in the new coordinate system $x'y'z'$, z' is taken to coincide with the original laboratory coordinate system z , and the rotating magnetic field $\vec{B}_1$ coincides with x' . Obviously, the new coordinate system is a rotating coordinate system that rotates at the same frequency ω as the rotating magnetic field. In the figure, $\vec{M}_\perp$ is the component of $\vec{M}$ in the direction perpendicular to the constant magnetic field, that is, the component of $\vec{M}$ in the plane xy , let u and v be the component in the x' and y' direction, then

$$\begin{cases} M_x = u\cos\omega\cdot t - v\sin\omega\cdot t \\ M_y = -v\cos\omega\cdot t - u\sin\omega\cdot t \end{cases}.$$

Substitute them into the formula (2-25), we get:

$$\begin{cases} \dfrac{du}{dt} = -(\omega_0 - \omega)v - \dfrac{u}{T_2} \\ \dfrac{dv}{dt} = (\omega_0 - \omega)u - \dfrac{v}{T_2} - \gamma\cdot B_1 M_z \\ \dfrac{dM_z}{dt} = \dfrac{M_0 - M_z}{T_1} + \gamma\cdot B_1 v \end{cases}. \tag{2-27}$$

In the formula (2-27), $\omega_0 = \gamma\cdot B_0$. This formula shows that the change of M_z is a function of v rather than a function of u. Since the change of energy represents the energy change of the nuclear magnetization vector M_z, the change of v reflects the energy change of the system.

It can be seen from equation (2-27) that they no longer include these high-frequency oscillation terms $\cos\omega\cdot t$ and $\sin\omega\cdot t$. But it is still quite difficult to solve strictly. It is usually simplified according to experimental conditions. If the change of the magnetic field or frequency is very slow, it can be considered that u, v and M_z does not change with time, i.e. $\dfrac{du}{dt} = 0$, $\dfrac{dv}{dt} = 0$ and $\dfrac{dM_z}{dt} = 0$. The system reaches a stable state. At this time, the solution of the above formula is called the steady state solution:

$$\begin{cases} u = \dfrac{\gamma\cdot B_1 T_2{}^2(\omega_0 - \omega)M_0}{1 + T_2{}^2(\omega_0 - \omega)^2 + \gamma^2 B_1{}^2 T_1 T_2} \\ v = \dfrac{\gamma\cdot B_1 M_0 T_2}{1 + T_2{}^2(\omega_0 - \omega)^2 + \gamma^2 B_1{}^2 T_1 T_2} \\ M_z = \dfrac{\left[1 + T_2{}^2(\omega_0 - \omega)\right]M_0}{1 + T_2{}^2(\omega_0 - \omega)^2 + \gamma^2 B_1{}^2 T_1 T_2} \end{cases}. \tag{2-28}$$

According to equation (2-28), the changes of u and v with the change of ω can be drawn as curves by using the first two terms. Based on the curves, when the angular frequency ω of the applied rotating magnetic field $\vec{B}_1$ is equal to the precession angular frequency ω_0 in the magnetic field $\vec{B}_0$, the absorption signal is the strongest, that is, the resonance absorption phenomenon occurs.

3) Result analysis

From the steady-state solution of the Bloch equation obtained above, it can be seen that the steady-state resonance absorption signal has several important characteristics:

When $\omega = \omega_0$, the value v is extremely large, which can be expressed as $v_{\max} = \frac{\gamma \cdot B_1 T_2 M_0}{1 + \gamma^2 B_1^{\ 2} T_1 T_2}$. It can be seen that when $B_1 = \frac{1}{\gamma \cdot (T_1 T_2)^{1/2}}$, v reaches the maximum value $v_{\max} = \frac{1}{2}\sqrt{\frac{T_2}{T_1}} M_0$, which shows that the maximum value of the absorbed signal does not require B_1 infinite weakness, but requires it to have a certain size.

At resonance $\Delta\omega = \omega_o - \omega = 0$, the expression of the absorption signal contains a term $S = \frac{1}{1 + \gamma \cdot B_1^{\ 2} T_1 T_2}$, that is, the value S decreases when B_1 increases, which means that the energy absorbed by the spin system decreases, which is equivalent to the high energy level being partially saturated, so *S* are called saturation factor.

The actual NMR absorption does not only occur at a single frequency determined by formula (2-7), but occurs within a certain frequency range. That is, the spectrum line has a certain width. The frequency interval corresponding to the half-height width of the absorption curve is usually called the resonance line width. The line width due to the relaxation process is called the intrinsic line width. The uneven external magnetic field $\vec{B}_0$ also widens the absorption line. It can be seen from equation (2-28) that the half width of the absorption curve is

$$\omega_0 - \omega = \frac{1}{T_2 (1 - \gamma^2 B_1^{\ 2} T_1 T_2^{\ 1/2})} \ . \tag{2-29}$$

It can be seen that the line width is mainly determined by the value T_2, so the lateral relaxation time is the main parameter of the line width.

(3) Pulse nuclear magnetic resonance

1) RF pulse magnetic field transient effect

The conditions for achieving nuclear magnetic resonance:

Under the action of a constant external magnetic field B_0, another rotating magnetic field B_1 is added in the plane perpendicular to B_0 the (i.e. x-y plane), the direction of rotation is the same as the Larmor precession, see Figure 3-1. If the rotation frequency ω of B_1 and the Larmor precession frequency ω_0 are equal, the vector μ will be precessed around the combined vector of B_0 and B_1, which makes the angle θ increase, and the absorbed energy increases the system potential energy. If the frequency ω of rotation is not equal to ω_0, the spin system will absorb and release energy alternately without net energy absorption. Therefore, energy absorption is a resonance phenomenon, and resonance can only occur when the rotation frequency ω equals to ω_0.

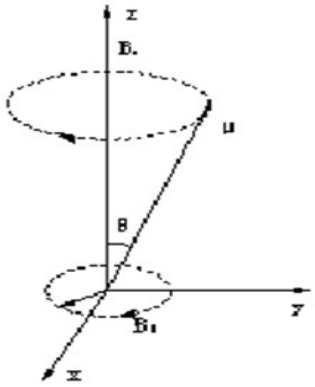

Figure 3-1 Larmor precession and rotating magnetic field

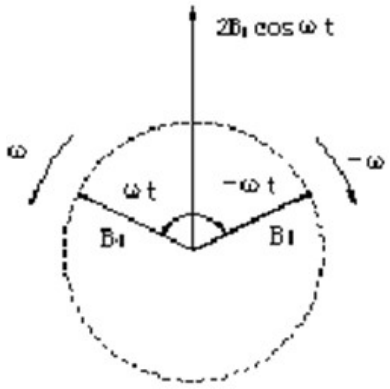

Figure 3-2 Line magnetic field

The rotating magnetic field B_1 can be easily obtained from the linear oscillating magnetic field generated in the coil of the oscillating circuit. Because a linear magnetic field can be seen as the synthesis of two magnetic fields rotating in opposite directions, see Figure 3-2. One is in the same direction as Larmor's precession and the other is in the opposite direction. The effect of the magnetic field in the opposite direction on $\vec{\mu}$ can be ignored. The action method of the rotating magnetic field may be a continuous wave method or a pulse method.

Because the object of magnetic resonance cannot be a single nucleus, but a system containing a large number of equivalent nucleuses. It is described in terms of bulk magnetization $\vec{M}$. The relationship between the nuclear system $\vec{M}$ and a single nucleus $\vec{\mu}_i$ is

$$\vec{M} = \sum_{i=1}^{N} \vec{\mu}_i \,. \tag{3-1}$$

$\vec{M}$ reflects the degree to which the nuclear system is magnetized. In a nuclear system with a magnetic moment, under the action of a constant magnetic field $\vec{B}_0$, the bulk magnetization vector $\vec{M}$ will make Larmor precession around $\vec{B}_0$, the precession angular frequency

$$\omega_0 = \gamma B_0 \,. \tag{3-2}$$

If a rotating coordinate system (x', y', z) is introduced, the direction z coincides with the direction $\vec{B}_0$, and the coordinate rotation angle frequency $\omega = \omega_0$, $\vec{M}$ is still in the new coordinate system. If at a certain moment, an RF pulse is applied perpendicular to the direction $\vec{B}_0$, and its pulse width t_p satisfies $t_p << T_1$ and $t_p << T_2$ (T_1 and T_2 are the relaxation time of the nuclear system), it can usually be decomposed into two directions of circularly polarized pulsed RF field, in which the magnetic field B_1 applied on the axis has effect. The action time t_p is the pulse width. It is in thermal equilibrium before the RF pulse is applied. The direction coincides with the z-axis (z' axis). When the RF pulse is applied, $\vec{M}$ will precess around x' axis at the frequency γB_1 .

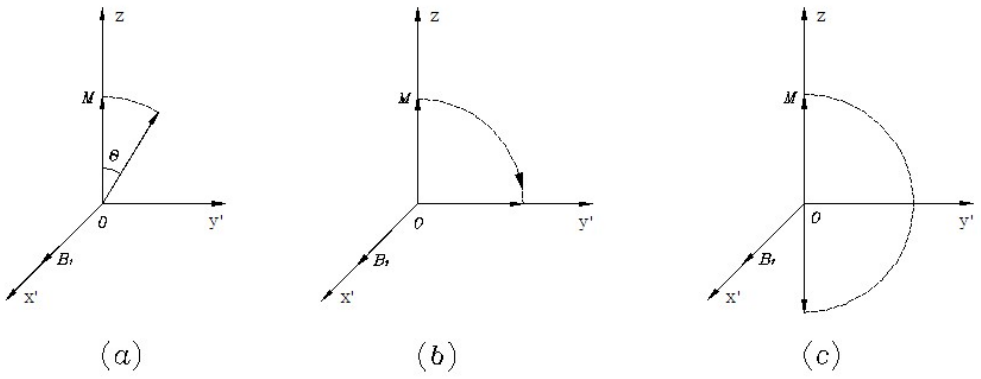

Figure 3-3 Tilt angles

The rotation angle $\theta = \gamma B_1 t_p$ of $\bar{M}$ (shown in Figure 3-3 (a)) is called the tilt angle. If the pulse width enables to obtain exactly $\theta = \pi/2$ or $\theta = \pi$, the pulse is called 90^0 or 180^0 pulse. Under the 90^0 pulse, $\bar{M}$ will fall down to y' axis, and under the 180^0 pulse, $\bar{M}$ will fall in the -z direction. From $\theta = \gamma B_1 t_p$, we know that as long as the RF field is strong enough, the value t_p can be made small enough to satisfy $t_p << T_1, T_2$, which means that the relaxation effect during the RF pulse can be ignored. (in theory the width of 180° pulse is twice of the 90° pulse.)

2) The behavior of body magnetization $\bar{M}$ after pulse action-Free Induction Decay (FID) signal

Suppose the RF field B_1 is added at the time t=0, till $t = t_p$, $\bar{M}$ rotate 90^0 around B_1 and fall on the y′ axis. At this time, the RF field B_1 disappears and the nuclear magnetic moment system will return to the thermal equilibrium state from the relaxation process. The transition speed from M_z to M_0 depends on T_1. $M_x \to 0$ and $M_y \to 0$ depend on T_2. In the view of rotating coordinate system, $\bar{M}$ is no precession, and the process of returning to the equilibrium position is shown in Figure 3-4 (a). From the view of the laboratory coordinate system, the precession around the z-axis returns to the equilibrium position in a spiral form, as shown in (b) in Figure 3-4 (b).

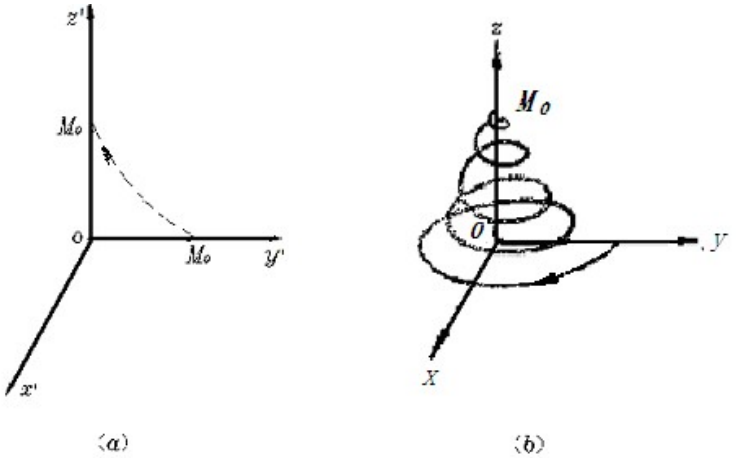

Figure 3-4 The relaxation process after the 90^0 pulse

In this relaxation process, if a receiving coil is placed perpendicular to the z axis, a radio frequency signal can be induced with the same frequency as the precession frequency ω_0, and its amplitude (i.e. envelope) decays exponentially. It is called free induction decay (FID) signal. After detecting and filtering out the radio frequency, the observed FID signal is an exponentially decaying envelope, as shown in Figure 3-5 (a). The FID signal is related to the magnitude of the lateral component of $\vec{M}$ on the plane xy, so the amplitude of the 90° pulse FID signal is the largest, and the amplitude of the 180° pulse is set to zero.

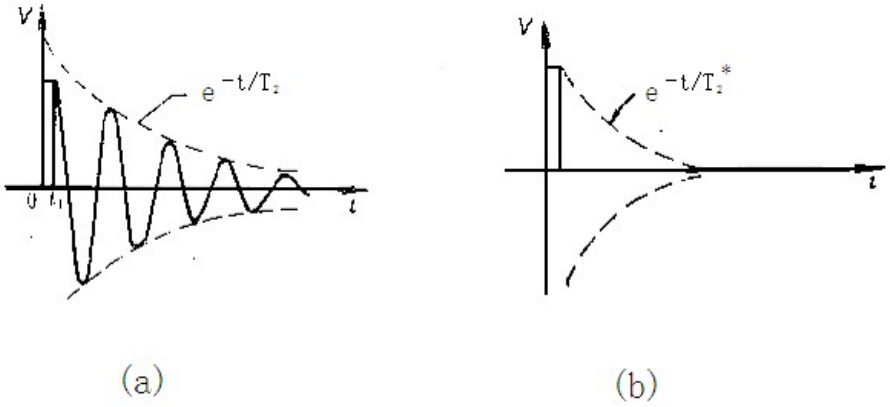

Figure 3-5 Free induction decay signal

In the experiment, because the constant magnetic field B_0 cannot be absolutely uniform, the external field of the nuclear magnetic moment at different positions in the sample is different, and its precession frequency is different. The actual observed FID signal is the superposition of the exponential attenuation signal of each precession frequency, as shown in Figure 3-5 (b). Assume $T_2^{'}$ is the equivalent lateral relaxation time of the non-uniform magnetic field, then the total FID signal decay rate is determined by T_2 and $T_2^{'}$, can be equivalent to an appearance lateral relaxation time T_2^*:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2^{'}} . \tag{3-3}$$

If the magnetic field is not uniform, $T_2^{'}$ is reduced, and therefore T_2^* is reduced, the faster the FID signal will decay.

3) Relaxation process

Relaxation and RF-induced excitation are two opposite processes. When the effects of the two reach dynamic equilibrium, a stable resonance signal can be observed experimentally. When in thermal equilibrium, the bulk magnetization intensity $\vec{M}$ is along the Z direction and is written as $\vec{M}_0$.

Relaxation is divided into longitudinal relaxation and lateral relaxation because it involves changes in the longitudinal and transverse components of bulk magnetization intensity.

Longitudinal relaxation is also called *spin-lattice relaxation*. The macro sample is composed of a large number of spin systems with small magnetic moments and the lattice system to which they are attached. Interactions and energy transformations occur continuously between systems. Longitudinal relaxation refers to the spin system delivering energy absorbed from the RF magnetic field to the surrounding environment and transforming it into thermal energy of the lattice. The spin nucleus returns from the high-energy state to the low-energy state without radiation, and the number of particles in the energy state varies according to the following law

$$n = n_0 \exp(-t / T_1), \tag{3-4}$$

where n_0 is the energy particle difference at time $t = 0$. T_1 is called the longitudinal relaxation time. It is a measure of the speed when the spin system interacts with the environment.

Lateral relaxation is also called *spin-spin relaxation*. Energy exchanges occur inside the spin system, does not exchange energy with the outside, so the total energy of the process system remains unchanged. In the spin-spin relaxation process, the lateral component $M_\perp$ of the bulk magnetization intensity $\vec{M}$ decrease form $M_\perp \neq 0$ to $M_\perp$=0, the required characteristic time is recorded as T_2. Since it is related to the relaxation time of the lateral component $M_\perp$ of the bulk magnetization, it is also called the lateral relaxation time.

4) Spin echo method to measure lateral relaxation time T_2 (90°-delay-180° pulse sequence method)

Spin echo is a method of observing nuclear magnetic resonance signals with double pulses or multiple pulses. It is particularly suitable for measuring the transverse relaxation time T_2. The natural line width of the spectral line is determined by the spin-spin interaction. But in many cases, the spectral line becomes wider because the external magnetic field is not uniform enough. The lateral relaxation time corresponding to this width is the appearance lateral relaxation time T_2* discussed above, but not T_2. Using spin-echo method, the lateral relaxation time T_2 can still be measured.

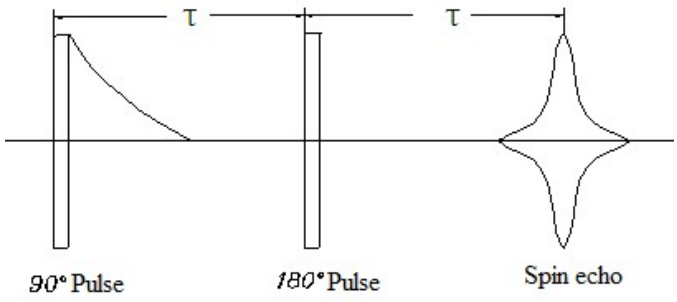

Figure 3-6 Spin echo signal

In practical applications, two or more radio frequency pulses are often used to form a pulse sequence, which periodically acts on the nuclear magnetic moment system. For example, after the 90^0 RF pulse is applied, another 180^0 RF pulse is applied after time τ to form a pulse sequence $90^0 - \tau - 180^0$. The pulse width t_p and pulse distance τ of these pulse sequences should meet the following conditions:

$$t_p << T_1, T_2, \tau . \tag{3-5}$$

$$T_2^* < \tau < T_1, T_2 . \tag{3-6}$$

The effect of the pulse sequence $90^0 - \tau - 180^0$ is shown in Figure 3-6. The FID signal is observed after the 90^0 RF pulse; an "echo" signal can be observed after the 180^0 RF pulse at the initial time 2τ. This echo signal is caused by the motion of the nuclear spin system under the action of a pulse sequence, so it is called a spin echo.

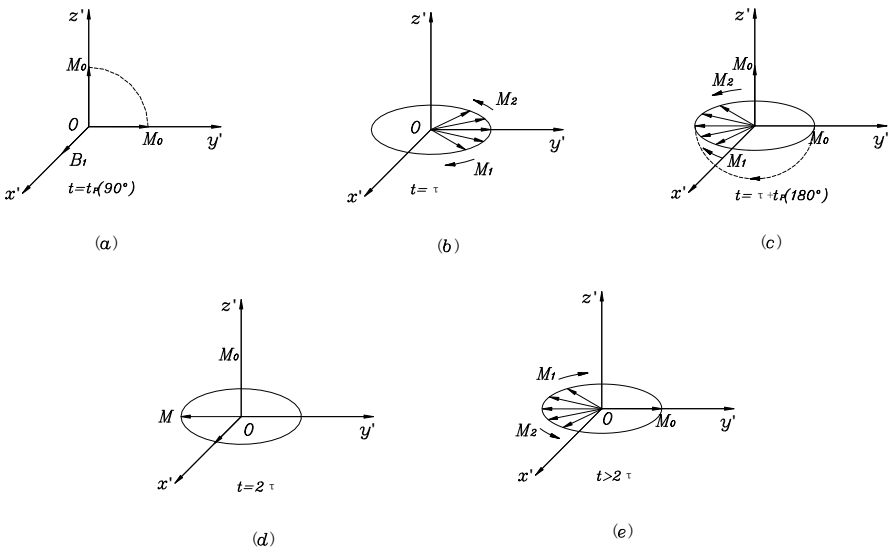

Figure 3-7 Vector illustration of $90^0 - \tau - 180^0$ spin echo

The spin echo is closely related to the FID signal. If there is no lateral relaxation, the spin echo amplitude should be the same as the initial FID signal, but the lateral relaxation effect cannot be ignored in time 2τ. The lateral component of the bulk magnetization intensity decreases accordingly, making the amplitude of the spin echo signal smaller than the initial amplitude of the FID signal, and the larger the pulse distance τ, the smaller the spin echo amplitude U. The echo amplitude U has the following relationship with the pulse distance τ:

$$U = U_0 e^{-t/T_2}, \tag{3-7}$$

where $t = 2\tau$, U_0 is the initial amplitude of the FID signal at the end of the 90^0 RF pulse. As long as the pulse distance τ is changed, the peak value of the echo will change accordingly. Sequentially increase τ, the envelope of all the peaks is obtained. Take the logarithm of both sides of formula (3-7), we can get the straight line equation.

$$\ln U = \ln U_0 - 2\tau / T_2 . \tag{3-8}$$

Use 2τ as the independent variable in the formula (3-8), the reciprocal of the slope of the straight line is T_2.

5) Reverse recovery method to measure longitudinal relaxation time T_1 (180°-delay-90° pulse sequence)

When the system is added 180^0 pulse, the bulk magnetization intensity $\bar{M}$ is reversed from the +z axis to the direction –z. The amplitude of the bulk magnetization intensity in the z axis direction M_z gradually decreases along the –z-axis direction due to the longitudinal relaxation effect, and even becomes zero, and then increases in the z-axis direction until recovery to the equilibrium state M_0. The change of M_z with time is growing in exponential, as shown in Figure 3-8.

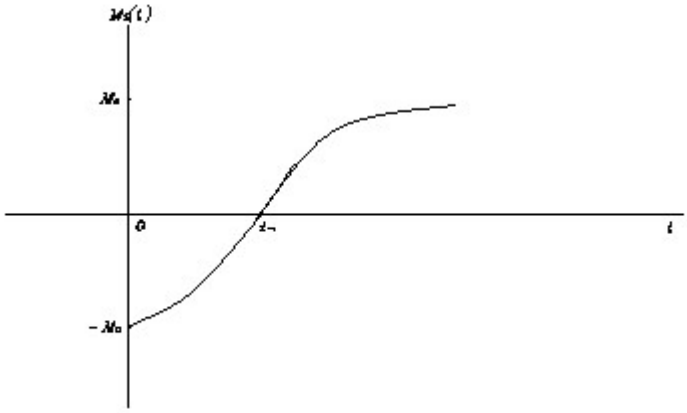

Figure 3-8 Change curve of M_Z with time t

It is expressed as

$$M_z(t) = M_0(1 - 2e^{-t/T_1}). \tag{3-9}$$

In order to detect the instantaneous value $M_z(t)$, after the 180 ° pulse, another 90^0 pulse is added at an interval t. It makes M_z lay down on x'-y' plane to generate a free decay signal. The initial amplitude of this signal must be equal to $M_Z(t)$. If the waiting time t is much longer than T_1, the sample will completely return to equilibrium. Repeat the process of the pulse sequence $180^0 - 90^0$ with another different time interval t to obtain another initial amplitude of the FID signal. In this way, by plotting the relationship between the initial amplitude and the pulse interval t, Figure 3-8 can be obtained.

From the measured curve, the longitudinal relaxation time T_1 (spin-lattice relaxation time) can be calculated. The simplest way is to find where $M_Z(t) = 0$, finally get $T_1 = t_n / \ln 2 = 1.44 t_n$.

6) Pulse NMR capture range

In order to realize nuclear magnetic resonance, continuous nuclear magnetic resonance usually uses the "swept field method" or "swept frequency method", but the efficiency is not high, because this method only captures a point on the frequency spectrum. Pulsed NMR uses short-time and high-power pulses. According to the Fourier transform, it has a wide frequency spectrum. An infinitely narrow pulse corresponds to a frequency spectrum with all frequency components and equal amplitudes. With such an ideal pulse acting on the nuclear system, all components are excited to obtain a spectrum. In actual work, a square pulse with a certain

width is used. It is a radio frequency oscillation modulated by a square pulse. The frequency spectrum can be obtained by Fourier transform. It is a continuous spectrum, but the amplitude of each frequency is not the same. The component f_0 is the strongest, and the amplitude gradually decays on both sides and negative values appear. At the time $f = \frac{1}{2T_0}$, the amplitude is zero for the first time. But as long as $2T_0$ is small enough, there is a wide enough spectrum area with substantially equal amplitude nearby, so that the nuclear system can be excited well.

The amplitude of corresponding frequency range is as follows:

$$I(f) = 2AT_0 \frac{Sin(T_0 \cdot 2\pi \cdot (f - f_0))}{T_0 \cdot 2\pi \cdot (f - f_0)}, \tag{3-10}$$

where T_0 is the half width of the rectangular pulse, U is the pulse amplitude, and f is the RF pulse frequency. It can be seen that the shorter $2T_0$, the wider the coverage range $\frac{1}{2T_0}$. So as long as there is a short enough pulse, it has a large range of capturing resonance frequency, and has no effect on the measurement. This is not achieved by continuous nuclear magnetic resonance, and it is also the reason why pulsed nuclear magnetic resonance is widely used.

7) Chemical shift

Chemical shift is the mainstay of nuclear magnetic resonance applications in chemistry. It originates from the magnetic shield produced by electrons. The nuclei in atoms and molecules are not naked nuclei. They are surrounded by electrons. Therefore, in addition to the magnetic field B_0, atoms and molecules also have a shielding effect caused by electrons around the nucleus. The electron is also a magnetic body, and its movement is also affected by the external magnetic field. The external magnetic field causes the additional movement of the electron and induces a magnetic field. The direction is opposite to the external magnetic field, and the magnitude is proportional to the external magnetic field. Therefore, the actual magnetic field at the nucleus is

$$B = B_0 - \sigma B_0 = B_0(1 - \sigma), \tag{3-11}$$

where σ is the shielding factor, which is a small quantity and its value $< 10^{-3}$.

For a different nuclear chemical environment, the shielding constant σ is also different, which causes their resonance frequencies to be different.

$$\omega_0 = \gamma(1 - \sigma)B_0. \tag{3-12}$$

The chemical shift can be measured by frequency. The resonance frequency changes with the external field B_0, which brings inconvenience to represent σ. So, the actual chemical shift is expressed in dimensionless, the unit is *ppm*.

$$\delta = \frac{\sigma_R - \sigma_S}{1 - \sigma_S} \times 10^6 \approx (\sigma_R - \sigma_S) \times 10^6 \ . \tag{3-13}$$

where σ_R and σ_S are the shielding constants of the reference object and the sample respectively. Use δ to express the chemical shift, which depends only on the difference between the shielding constants of the sample and the reference.