Pulsed Nuclear Magnetic Resonance Experiment

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Introduction

1. Simple Resonance Theory

Magnetic resonance is a phenomenon found in magnetic systems that possess both magnetic moments and angular momentum. The term resonance implies that we are in tune with a natural frequency of magnetic system, here corresponding to the frequency of gyroscopic precession of the magnetic moment in an external static magnetic field. Nuclear Magnetic Resonance (NMR) is one among them, where the magnetic system is a nucleus. Since the nuclear magnetic resonance frequencies fall typically in the radio frequency region, we use the term radio frequency. Through studying the nuclear magnetic resonance of a nucleus, we will get enough information about processes at the atomic and nuclear level, so NMR is also a very significant tool to explore the tiny internal structure of macromolecule with high resolution in modern science.

Generally, we consider a nucleus that consists of many particles coupled together so that in any given state, the nucleus possesses a total magnetic momentum $\vec{\mu}$ and a total angular momentum $\vec{J}$. In fact, the two vectors may be taken as parallel, so that we can write $\vec{\mu} = \gamma \cdot \vec{J}$, where $\gamma$ is called the “gyromagnetic ratio”. For any given state of a nucleus, knowledge of the wave function would in principle enable us to compute both $\vec{\mu}$ and $\vec{J}$. In quantum mechanics, both $\vec{\mu}$ and $\vec{J}$ are treated as operators, and we can define $\vec{J} = \hbar \cdot \vec{I}$, where $\vec{I}$ is a dimensionless angular momentum operator, which has eigenvalues of either integer or half-integer. As we know, any component of $\vec{I}$ (for example $I_z$) commutes with $I^2$, so we can specify simultaneous eigenvalues of both $I^2$ and $I_z$. Let us call the eigenvalues $I$ and $m$ respectively. Of course, $m$ may be any of the $2I+1$ values, $I, I-1, \ldots, -I$. So we can get any component of the operator $\vec{\mu}$ and $\vec{I}$ along an arbitrary $z'$ direction, which is:

$$<\text{Im} | \mu_{z'} | \text{Im'} >= \gamma \hbar <\text{Im} | I_{z'} | \text{Im'} >$$
Now if we introduce an external magnetic field \( \vec{B} \), which will produce interaction energy \(-\vec{\mu} \cdot \vec{B}\). Taking the field to be along the z-direction, we have a very simple Hamiltonian: \( \mathbf{H} = -\gamma \hbar \cdot B \cdot \vec{I}_z \) with the allowed Eigen energy \( E = -\gamma \hbar B \cdot m \), \( m = I, I-1, \ldots, -I \). So the interaction between the magnetic field and the nucleus will result in transitions between different energy levels as spectral absorption. Most commonly coupling used to produce nuclear magnetic resonance is an altering transverse magnetic field applied perpendicular to the static field \( B_z \) at z-direction. If the amplitude of the altering field is \( B_z' \), we get an additional perturbation term in the previous Hamiltonian of

\[
\mathbf{H}_{\text{per}} = -\gamma \hbar B_z' I_x \cdot \cos(\omega \cdot t).
\]

The operator \( I_x \) has matrix elements between states \( m \) and \( m' \), as \( \langle \text{Im} | I_x | \text{Im'} \rangle \) will vanish unless \( m' = m \pm 1 \). Consequently, we will get that the allowed transitions are only between the adjacent levels and give the absorption frequency \( \omega_0 \):

\[
\hbar \cdot \omega_0 = \Delta E = \gamma \cdot \hbar \cdot B_z, \text{ or } \omega_0 = \gamma \cdot B_z.
\]

2. Motion of Single Spin System

Now we start our discussion with the motion of a spin in an external magnetic field \( \vec{B} \), and \( \vec{B} \) will produce a torque on the magnetic momentum \( \vec{\mu} \) of amount \( \vec{\mu} \times \vec{B} \). So the angular momentum \( \vec{J} \) will satisfy the following equation:

\[
\frac{d \vec{J}}{dt} = \vec{\mu} \times \vec{B}
\]

Since \( \vec{\mu} = \gamma \cdot \vec{J} \), we have \( \frac{d \vec{\mu}}{dt} = \vec{\mu} \times \gamma \cdot \vec{B} \).

This equation will hold no matter whether or not \( \vec{B} \) is time dependent, it tells us that at any instant, the changes in \( \vec{\mu} \) are perpendicular both \( \vec{\mu} \) and \( \vec{B} \). If \( \vec{B} \) is time independent, the angle between \( \vec{\mu} \) and \( \vec{B} \) does not change, the vector \( \vec{\mu} \) therefore generates a cone (please refer to Figure 1).
Consider a general vector time function $\vec{F}(t) = \vec{i} F_x(t) + \vec{j} F_y(t) + \vec{k} F_z(t)$, $\vec{i}, \vec{j}, \vec{k}$ here are corresponding to the unit axes vectors. Originally, they should be constant, but now we think they can change with time. As their lengths are fixed, they can at most rotate. We assume that they rotate with an instantaneous angular velocity $\Omega$, then we have $\frac{d}{dt} \vec{i} = \Omega \times \vec{i}$, same with the unit vector $\vec{j}$ and $\vec{k}$.

So the total time derivative of $\vec{F}(t)$ is therefore

$$\frac{d}{dt} \vec{F}(t) = \vec{i} \frac{dF_x}{dt} + \vec{j} \frac{dF_y}{dt} + \vec{k} \frac{dF_z}{dt} + \vec{i} \frac{d}{dt} \vec{i} + \vec{j} \frac{d}{dt} \vec{j} + \vec{k} \frac{d}{dt} \vec{k}$$

$$= \vec{i} \frac{dF_x}{dt} + \vec{j} \frac{dF_y}{dt} + \vec{k} \frac{dF_z}{dt} + \vec{\Omega} \times (\vec{i} F_x + \vec{j} F_y + \vec{k} F_z)$$

$$= \frac{\delta \vec{F}}{\delta t} + \vec{\Omega} \times \vec{F}$$

Where the $\frac{\delta \vec{F}}{\delta t}$ represents the time rate of change of $\vec{F}$ with respect to the coordinate system $\vec{i}, \vec{j}, \vec{k}$. By using this formula, we can rewrite the equation of motion for $\vec{\mu}$ in terms of a coordinate system rotating with an arbitrary angular velocity $\vec{\Omega}$.
\[
\frac{\delta \vec{\mu}}{\delta t} + \vec{\Omega} \times \vec{\mu} = \vec{\mu} \times \vec{B}, \text{ or further } \frac{\delta \vec{\mu}}{\delta t} = \vec{\mu} \times (\gamma \vec{B} + \vec{\Omega}) = \vec{\mu} \times \gamma(\vec{B} + \frac{\vec{\Omega}}{\gamma}).
\]

From this equation, we can see that the motion of \(\vec{\mu}\) in the rotating coordinate obeys the same equation as in the laboratory frame if we just replace the actual magnetic field \(\vec{B}\) by the effective magnetic field \(\vec{B}_e = \vec{B} + \frac{\vec{\Omega}}{\gamma}\).

We can now readily solve for the motion of \(\vec{\mu}\) in a static field \(\vec{B} = \hat{k}B_0\) by choose a specific \(\vec{\Omega}\), which makes \(\vec{B}_e = 0\). That is, \(\vec{\Omega} = -\gamma B_0 \hat{k}\). So in this rotating referent frame, we have \(\frac{\delta \vec{\mu}}{\delta t} = 0\), \(\vec{\mu}\) remains fixed with respect to \(\hat{i}, \hat{j}, \hat{k}\), but in the laboratory frame, \(\vec{\mu}\) rotates at angular frequency \(\vec{\Omega} = -\gamma B_0 \hat{k}\). \(\gamma \cdot B_0\) is called “Larmor Frequency”. Now we can reach a surprise conclusion that the classical precession frequency \(\vec{\Omega}\) is identical in magnitude with the angular frequency needed for magnetic resonance absorption, as found by view of quantum mechanics.

Nerveless, instead of having just one single spin, if we have a group of spins with moments \(\vec{\mu}_k\), for the kth spin, their total magnetic moment \(\vec{\mu}\) can be written as: \(\vec{\mu} = \sum_k \vec{\mu}_k\). If the spins do not interact with each other, it is easily to prove that the equation \(\frac{d \vec{\mu}}{dt} = \vec{\mu} \times (\gamma \vec{B})\) still holds. So the experimentally determined bulk magnetization is simply the expectation value of the total magnetic moment. Therefore, the classical equation correctly describes the dynamics of the magnetization, provided the spins may be thought of as not interacting with one another.

3. Alternating Magnetic Fields

Now let’s consider the effect of the altering magnetic field along the x-direction (generally, we create this altering field by using a AC-coil):

\(\vec{B}_x(t) = 2B_1 \cos(\omega \cdot t) \hat{i}\)
And this magnetic field can be divided into two rotating components, each of amplitude $B_1$, one rotating clockwise and the other rotating anti-clockwise.

We denote the two rotating fields by $\vec{B}_R$ and $\vec{B}_L$:

$$\vec{B}_R = B_1 [i \cos(\omega \cdot t) + j \sin(\omega \cdot t)]$$

$$\vec{B}_L = B_1 [i \cos(\omega \cdot t) - j \sin(\omega \cdot t)]$$

Near to the resonance region $\omega \approx \omega_0$, one of the components will contribute heavily to transition absorption, the other can be neglected since its frequency is different by $2\omega$.

Here we assume we only have the field $\vec{B}_L$, and the component of frequency $\omega$ along the z-axis, so $\vec{\omega} = \omega \cdot \hat{k}$. We may therefore write the transverse magnetic field as:

$$B_1(t) = B_1 [i \cos(\omega \cdot t) - j \sin(\omega \cdot t)]$$

Meanwhile we have a static field $\vec{B}_z$ along z-direction, $B_z = k B_0$

So we get the equation: \( \frac{d \mu}{dt} = \mu \times \gamma [k \vec{B}_z + \vec{B}_1(t)] \)

So in a rotating frame with angular velocity referent to the lab frame $\vec{\Omega} = -\omega \hat{k}$, we have:

$$\frac{\delta \mu}{\delta t} = \mu \times \gamma [(\gamma \cdot \vec{B} + \vec{\Omega}) + \vec{B}_1(t)] = \mu \times \gamma \cdot [(B_0 - \frac{\omega}{\gamma}) \vec{k} + \vec{B}_1 \vec{i}]$$

Now \( \frac{\delta \mu}{\delta t} = \mu \times \gamma B_{\text{eff}}, \) where $B_{\text{eff}} = k \cdot (B_0 - \frac{\omega}{\gamma}) + i \cdot B_1 = k \cdot \Delta B + i \cdot B_1$

$$\Delta B \equiv B_0 - \frac{\omega}{\gamma}$$

The equation $B_{\text{eff}} = k \cdot \Delta B + i \cdot B_1$ tells us in the rotating frame, the magnetic moment precesses in a cone of fixed angle about the direction of $B_{\text{eff}}$ at angular frequency $\omega = \gamma B_{\text{eff}}$. We notice that the motion of the moment is periodic. If it is initially oriented along the z-direction, it will return to that direction periodically. As we increase its angle with the z-direction, its magnetic potential energy in the laboratory changes. All the energy it takes to tilt $\mu$ away from $B_0$ is returned in a complete cycle of $\mu$ around the
cone. There is no net absorption of the energy from the altering field but rather alternately receiving and returning of energy.

If the resonance condition is fulfilled exactly \( \omega = \gamma \cdot B_0 \), the effective field is then simply \( i \cdot B_1 \), so the magnetic moment that is parallel to the static field initially will then precess in the y-z plane. (please refer to Figure. 2). That’s to say, it will precess but remaining always perpendicular to \( B_1 \). Periodically, it will be lined up opposed to \( B_0 \). If we induce the field \( B_1 \) as a pulse with duration time \( t_w \) instead of a continuous wave front, the magnetic moment would precess through an angle \( \theta = \gamma \cdot B_1 \cdot t_w \). If we choose a \( t_w \) which will satisfy \( \theta = \pi \), the pulse will simply invert the moment, such a pulse is referred to in the literature as a “180 degree pulse”. If \( \theta = \frac{\pi}{2} \), the magnetic moment is turned from the z-direction to the y-direction, and the pulse is called “90 degree pulse”. Without other effect, following the turn-off the 90-degree pulse \( B_1 \), the moment would then remain at rest in the rotating frame, and hence precess in the laboratory perpendicular to the static field \( B_0 \). But in fact that is not true, the magnetic moment will go back to the initial z-direction after enough long time due to relaxation, it will bring the spin system back into Boltzmann equilibrium.

4. Equilibrium Magnetization and Bloch Equation

In practice, we can’t measure the magnetic momentum for a single spin; instead, we can only measure the macroscopic magnetization for the whole sample. Now we will try to understand the equilibrium distribution of spin system under the uniformly constant magnetic field along the z-axis \( B_0 \).
As we know, the energy of the magnetic dipole interaction is:

\[ E = -\gamma \cdot J \cdot B_0 = -\gamma \cdot J_z \cdot B_0 \]

If the energy difference between two adjacent states is very small, we can consider the distribution is continuous (Classical Boltzmann Statistics).

\[ E = -\gamma \cdot J \cdot B_0 \cos \theta \]

So the probability that any spin particle in the orientation \((\theta, \varphi)\) in space is given by:

\[ P(\theta, \varphi) = C \cdot \exp \left( -\frac{\gamma J B_0}{k_B T} \cos \theta \right) \]

where \(C\) is the normalized constant.

Generally, in room temperature, we have \(\frac{\gamma J B_0}{k_B T} \ll 1\), then from the equation:

\[ \int d\Omega \cdot P(\theta, \varphi) = C \cdot \int_0^{2\pi} d\varphi \int_0^\pi d\theta \cdot \exp \left( \frac{\gamma J B_0}{k_B T} \cos \theta \right) \sin \theta = 1 \]

we get \(C \approx \frac{1}{4\pi}\).

Thus we get:

\[ < J_z > = \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta \cdot \frac{J \cdot \cos \theta}{4\pi} \left(1 + \frac{\gamma J B_0}{k_B T} \cos \theta \right) = \frac{\gamma J^2 \cdot B_0}{3k_B T} \]

So in thermal equilibrium, only the z-component of the magnetization is non-zero, the x-component and y-component both should be zero due to the azimuthal symmetry.

\[ < \vec{J} > = 0 \cdot \vec{i} + 0 \cdot \vec{j} + \frac{\gamma J^2 \cdot B_0}{3k_B T} \cdot \vec{k} \]

For a system with N non-interaction spins, we have the total angular momentum:

\[ J_0 = N \cdot < J > = N \cdot \frac{\gamma J^2 \cdot B_0}{3k_B T} \]

So the equilibrium magnetization for the spin system should be:

\[ M_0 = \gamma \cdot J_0 = \frac{N \cdot \gamma^2 \cdot J^2 \cdot B_0}{3k_B T} \]
Now if we induce an altering magnetic field (as we discussed before $B_x(t)$), the magnetization will deflect from the equilibrium value.

From the previous equation $\frac{d\mu}{dt} = \mu \times (\gamma \cdot \vec{B})$, we know there should be a similar equation for magnetization $M$, here, we include the thermal relaxation. So the magnetization must wish to be parallel to $B_0$, the x- and y- components must have a tendency to vanish.

Thus

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} + \gamma \cdot (M \times B)_z$$

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} + \gamma \cdot (M \times B)_x$$

$$\frac{dM_y}{dt} = -\frac{M_y}{T_2} + \gamma \cdot (M \times B)_y$$

This set of equations is called Bloch Equations. Here we introduce times, $T_1$ is called longitudinal relaxation time which is different from $T_2$ which is the transverse relaxation time.

Now, we want to figure out what’s the solution of the Bloch Equations when the altering transverse magnetic field is turned on. In order to make the calculation easier, we immediately transform to the coordinate frame rotating at angular velocity $\Omega = -\frac{\omega}{\gamma}$, taking $B_1$ along the rotating x-axis and denoting $B_0 - \frac{\omega}{\gamma}$ by $b_0$.

So $\vec{M}(t) = M_z \hat{z} + M_x \hat{x} + M_y \hat{y}$ and $\vec{B} = b_0 \hat{z} + B_1 \hat{x}$

Then in rotating coordinate

$$\frac{dM_z}{dt} = -\gamma M_y B_1 + \frac{M_0 - M_z}{T_1}$$

$$\frac{dM_x}{dt} = \gamma M_y b_0 - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \gamma (M_z B_1 - M_x b_0) - \frac{M_y}{T_2}$$
In experiment, we choose $B_1$ value low enough to avoid the saturation that will kill the resonance absorption signal. As we know, $M_x$ and $M_y$ must vanish as $B_1 \to 0$, and $M_z$ is in a steady state, it differs from $M_0$ to the order of $B_1^2$. Therefore, we replace $M_z$ by $M_0$ in the last two equations, and neglect the transient term, we get

$$M_x = \chi_0 (\omega_0T_2) \frac{(\omega_0 - \omega)T_2}{1 + (\omega - \omega_0)^2 T_2^2} B_1$$

$$M_y = \chi_0 (\omega_0T_2) \frac{1}{1 + (\omega - \omega_0)^2 T_2^2} B_1$$

Where $\chi_0$ is the magnetic susceptibility, which is equal to $\frac{N\gamma^2 J^2}{3k_B T}$.

So we can see in the rotating referent frame with angular velocity $\omega$, the magnetization is a constant. Therefore, in the lab frame, it must rotate at frequency $\omega$. Typically, we choose the orientation of the coil along the fixed X-direction, we can calculate the time dependent component of magnetization $M_x$ along the coil direction.

By referring to Figure.3, we get $M_x = M_x \cos(\omega \cdot t) + M_y \sin(\omega \cdot t)$

If we regard the magnetic field as a linear filed, we will get

$$B_{x}(t) = B_{x_0} \cos(\omega \cdot t) \quad B_{x_0} = 2 \cdot B_1$$

Then we see both of $M_x$ and $M_y$ are proportional to $B_{x_0}$, and we can write

$$M_x(t) = (\chi' \cos(\omega \cdot t) + \chi'' \sin(\omega \cdot t))B_{x_0} = (\chi' + j\chi'')B_{x_0} \cdot \cos(\omega \cdot t)$$
Where the quantities $\chi'$ and $\chi''$ should be:

$$\chi' = \frac{\chi_0}{2} \left( \frac{(\omega_0 - \omega)T_2}{1 + (\omega - \omega_0)^2} \right)$$
$$\chi'' = \frac{\chi_0}{2} \left( \frac{1}{1 + (\omega - \omega_0)^2} \right)$$

It is convenient to regard both $B_x(t)$ and $M_x(t)$ as being the real parts of the complex functions $B_x^C(t)$ and $M_x^C(t)$. Then if we define $\chi(\omega) = \chi' - I \chi''$ and write $B_x^C(t) = B_x e^{int}$, we find $M_x^C(t) = \chi(\omega) \cdot B_x^C(t)$, and $M_x(t) = \text{Re}\{ \chi(\omega) \cdot B_x e^{int} \}$, where $I = \sqrt{-1}$.

Ordinarily, if a coil of inductance $L_0$ is filled with a material of susceptibility $\chi_0$, the inductance is increased to $L_0(1 + \chi_0)$, since the diamagnetic material will increase the magnetic flux by factor $(1 + \chi_0)$. Similarly, the complex susceptibility produce a flux change from the original value $L_0$, $L = L_0[1 + \chi(\omega)]$

Denoting the coil resistance in the absence of a sample as $R$, the coil impedance when including sample becomes

$$Z = I \cdot L_0 \omega (1 + \chi') + L_0 \omega \chi'' + R.$$  

The real part of the susceptibility $\chi'$ therefore changes the inductance, where as the imaginary part $\chi''$ modifies the resistance. The fractional change in resistance $\frac{\Delta R}{R}$ is:

$$\frac{\Delta R}{R} = \frac{L_0 \omega \chi''}{R}.$$  

If we assume that uniform magnetic field occupy a volume of $V$, the peak stored magnetic energy produced by an altering current, whose peak value is $i_0$, is

$$\frac{1}{2} L_0 \cdot i_0^2 = \frac{1}{2} B_x^2 \cdot V$$

While, we can get the average power dissipated in the nuclei is:

$$\Delta P = \frac{1}{2} i_0^2 \cdot \Delta R = \frac{1}{2} i_0^2 \cdot L_0 \cdot \omega \cdot \chi''$$
So we find $\Delta P = \frac{1}{2} \cdot \omega \cdot B \cdot \chi_0^2 \cdot \chi'' \cdot V$. This equation provides a simple connection between the power absorbed, $\chi''$, and the strength and the frequency of the altering field. So if we can use some detecting system to measure the energy dissipated in the sample during the resonance absorption, we can measure $\chi''$.

The following figure (Figure. 4) shows the theoretical relationship between $\chi'$, $\chi''$ with the oscillation frequency of the altering magnetic field. “$\chi'$ vs. $(\omega_0 - \omega)$” is called the dispersion curve, and the other one ------ “$\chi''$ vs. $(\omega_0 - \omega)$” is called the absorption curve. We can see when the frequency is near to the resonance frequency, the absorption curve will get close to its peak value.

![Fig. 4](image)

By using sensitive electronic circuit, we can change both of these two magnetic susceptibilities to electronic signals and measure them by using digital oscilloscope. If we tune it well, we can get clear experimental signals, where the absorption and dispersion are corresponding to the “In-Phase Signal” and “Out-Phase Signal” respectively.

5. Pulsed NMR Experiment and Free Induction Decays

Since the static magnetic field has a small inhomogeneity across the sample in the coil, so from the definition of the Larmor Frequency $\omega_0 = \gamma \cdot B_0$, we know there will be a distribution of the values of Larmor Frequencies as well. If the distribution function is denoted by $g(\omega_0)$, the number of particles $dn$ with Larmor Frequencies between $\omega_0$ and $\omega_0 + d\omega_0$ is:

$$dn = N \cdot g(\omega_0) \cdot d\omega_0$$
In order to solve the problem of the time dependence of the net magnetization \( \vec{M}(t) \), we first estimate the average angular momentum of the spin system:

Instead of using \( \vec{J} = \sum_k \vec{j}_k \), we have

\[
\vec{J}(t) = \int J_{\omega_0}(t) \cdot dn = N \int J_{\omega_0}(t) \cdot g(\omega_0) \cdot d\omega_0
\]

Now we examine the response of our sample to a rotating magnetic field of magnitude \( B_1 \), angular speed \( \omega_0 \) and its lasting time \( t_w \). Let us view the behavior of the spin system from the reference frame rotating with \( B_1 \), and this time due to convenience, we choose \( B_1 \) along the \( -\vec{j} \) direction. (please refer to Figure 5.)

![Fig. 5](image)

So now the effective field in the rotating frame becomes:

\[
\vec{B}_{\text{eff}} = \Delta B_0 \vec{k} - B_1 \vec{j}, \quad \text{where} \quad \Delta B_0 = B_0 - \frac{\omega}{\gamma}.
\]

At the resonance case, \( \sqrt{\frac{1}{2}} \ll B_1 \) is a good approximation, we can set \( \vec{B}_{\text{eff}} = -B_1 \vec{j} \).

Just before the application of the rotating pulsed field, we have \( \vec{j}_{\omega_0}(0) = j(0) \vec{k} \), where \( \vec{j}_{\omega_0}(t) \) is the so-called isochromat. After we induced the transverse field, each of
the isochromats will precess about the \( \vec{j} \) axis in time \( t_w \) by an amount \( \theta = \gamma \cdot B \cdot t_w \), so that \( \vec{j}_{\omega_0}(t_w) = j(0) \cdot (\cos \theta \cdot \vec{k} + \sin \theta \cdot \vec{i}) \).

So the total angular momentum over the sample is:

\[
\vec{J}_{\omega_0}(t_w) = N \int d\omega_0 \cdot g(\omega_0) \cdot j(0)(\cos \theta \cdot \vec{k} + \sin \theta \cdot \vec{i})
= Nj(0) \cdot (\cos \theta \cdot \vec{k} + \sin \theta \cdot \vec{i}) = J(0) \cdot (\cos \theta \cdot \vec{k} + \sin \theta \cdot \vec{i})
\]

where \( J(0) = Nj(0) \).

So we find

\[
\vec{J}(t_w) = J(0) \vec{i} \quad \text{for} \quad \theta = 90^\circ \quad (90^\circ \text{ pulse})
\]

\[
\vec{J}(t_w) = -J(0) \vec{k} \quad \text{for} \quad \theta = 180^\circ \quad (180^\circ \text{ pulse})
\]

After the pulse turned off \((t > t_w)\), we get \( \vec{B}_{\text{eff}} = \Delta B \vec{k} \) and each isochromat precesses about the \( \vec{k} \) axis at an angular speed of \( \Delta \omega_0 = \gamma \cdot \Delta B \). Thus

\[
\vec{j}_{\omega_0}(t) = j(0) \cos \theta \vec{k} + j(0) \sin \theta[\cos(\Delta \omega_0(t - t_w)) \vec{i} - \sin(\Delta \omega_0(t - t_w)) \vec{j}]
\]

If we redefine \( t_1 = t - t_w \), and do the integral over \( dn(\omega_0) \), we find

\[
\vec{J}_{\omega_0}(t_w + t_1) = J(0) \cos \theta \vec{k} + J(0) \sin \theta \cdot [i \int g(\Delta \omega_0) \cos(\Delta \omega_0 t_1) \cdot d\Delta \omega_0 - j \int g(\Delta \omega_0) \sin(\Delta \omega_0 t_1) \cdot d\Delta \omega_0]
\]

Generally, \( g(\Delta \omega_0) \) is a symmetric function of \( \Delta \omega_0 \), so the second integral vanishes, while it predicts that the \( \vec{k} \) component of the angular momentum is time invariant and the \( \vec{i} \) or \( \vec{j} \) (if we choose the rotation field along another orientation) components decays to zero slowly.

For simplicity, we assume that the function of \( g(\omega_0) \) is a constant \( \frac{1}{2a} \) in the range of \( (\omega_0 - a < \omega_0 < \omega_0 + a) \); other wise, it has value of zero:

So we will get
\[ \int_{-\infty}^{+\infty} g(\Delta \omega_0) \sin(\Delta \omega_0 t_1) \cdot d\Delta \omega_0 = \int_{-a}^{+a} \frac{1}{2a} \sin(\Delta \omega_0 t_1) \cdot d\Delta \omega_0 = 0 \]

\[ \int_{-\infty}^{+\infty} g(\Delta \omega_0) \cos(\Delta \omega_0 t_1) \cdot d\Delta \omega_0 = \int_{-a}^{+a} \frac{1}{2a} \cos(\Delta \omega_0 t_1) \cdot d\Delta \omega_0 = \frac{\sin at_1}{at_1} \]

So we get

\[ \vec{J}_{\theta_0} (t_\omega + t_1) = J(0) \cos \theta \cdot \vec{k} + J(0) \sin \theta \frac{\sin at_1}{at_1} \cdot \vec{i} . \]

Since \( M_0 = \gamma \cdot J_0 \), so the magnetization has the same time dependent function.

Since the orientation of the coil is along the y-direction, the magnetization along that direction in the lab frame should be \( M_X(t) = M_j \cos(\omega \cdot t) + M_i \sin(\omega \cdot t) \), so the average magnetization along that fixed direction is \( |M_X| = \frac{M_0}{2} \sin \theta \frac{\sin at_1}{at_1} \). So it will decay after the pulse as time increases. Meanwhile, we also know that the amplitude of Fid signal will be proportional to the magnetization of the direction of the coil, so we know the fid signal will also decay to zero after the pulsed transverse magnetic field is turned off.

Now let us consider the effect of a second pulse of the transverse field. We assume that the second pulse comes at time \( \tau \) after the first pulse. This time in order to differentiate the two pulses, the rotation produced by the first pulse is labeled by \( \theta_1 \), and that by the second is labeled by \( \theta_2 \). This time, we still choose the second \( B_1 \) along the \(- \vec{j}\) direction. To simplify future discussion, we think the \( \vec{i} \) and \( \vec{j} \) components of \( \vec{J}(t) \) have died to zero due to the transverse relaxation. So just before the 2nd pulse comes, we have \( \vec{J}(t) = J(0) \cos \theta_1 \vec{j} \). Use the same analysis as we used for discussing the response of the system to the first pulse, the response to the second pulse should be:

\[ \vec{J}(\tau + t_w + t_2) = J(0) \cos \theta_1 \cos \theta_2 \vec{k} + J(0) \cos \theta_1 \sin \theta_2 (i \int g(\Delta \omega_0) \cos(\Delta \omega_0 t_2) d\Delta \omega_0 - j \int g(\Delta \omega_0) \sin(\Delta \omega_0 t_2) d\Delta \omega_0) \]

\[ = J(0) \cos \theta_1 \cos \theta_2 \vec{k} + J(0) \cos \theta_1 \sin \theta_2 \frac{\sin at_2}{at_2} \cdot \vec{i} \]

It shows how the angular momentum, or magnetization of the sample functions as time \( t_2 \) after the 2nd pulse. From this equation, we can draw the conclusion that the 2nd
fid has the same shape as the fid curve, and its amplitude is proportional to \( \cos \theta_1 \sin \theta_2 \), instead of proportional to \( \sin \theta_1 \) as the first fid. So if \( \theta_1 = 90^\circ \) or \( \theta_2 = 180^\circ \) or both, the second fid is zero. However, this is true just for the case there is no longitudinal relaxation; that is to say, after the first pulse, the angle between the magnetization and the static field is unchanged, stays \( \theta_1 \). But for the real experiment, the ideal case is not true. After the first pulse, the magnetization wishes to go back to the z-direction (the direction of magnetic field), so the angular \( \theta_1 \) will decreases with time, when the 2\(^{nd} \) pulse comes, it will become \( \theta_1(\tau)' \).

So we get the first fid and the second fid are the following respectively:

\[
\vec{F}_1(t_{w1} + t_1) = J(0) \sin \theta_1 \frac{\sin at_1}{at_1} \cdot \vec{i} \\
\vec{F}_2(\tau + t_{w2} + t_2) = J(0) \cos \theta_1' \sin \theta_2 \frac{\sin at_2}{at_2} \cdot \vec{i}
\]

As we know, when it is in resonance, the average resonance frequency range \( \Delta \omega \) should be the smallest value, the fid signal will decay to the zero slower, so the wiggle of the fid curve will become smaller (Figure 6 ---- Indication of Resonance).

After finding the Resonance condition, we focus our attention on two specific cases.
(1) The "90° − τ−90°" pulse sequence(Figure 7):

\[ \theta_1 = \theta_2 = \gamma B_1 t_w \approx 90° \]

Fig. 7

More ever, we can see if we add "90° − 90°" pulses (\( \theta_1 = \theta_2 = 90° \)) to the spin system, the amplitude of the first fid is the maximal of all the values it could be. The amplitude of the 2\(^{nd}\) fid depends on the delay time from the 2\(^{nd}\) pulse to the 1\(^{st}\) pulse \(\tau\). When the delay time \(\tau\) is a constant, we can tune our detecting circuit until we get the maximum of the second fid, when it shows the second pulse is also a 90° pulse.

Using Bloch Equations, let \( B_i = 0 \) (since the pulse is turned off), and change magnetization \( M \) to \( J \), so we have:

\[
\frac{dJ_z}{dt} = \frac{J_0 - J_z}{T_1} \\
\frac{dJ_x}{dt} = \gamma J_x \Delta B_0 - \frac{J_x}{T_2} \\
\frac{dJ_y}{dt} = -\gamma J_y \Delta B_0 - \frac{J_y}{T_2}
\]

Solving this equation, we get:

\[
J_z(t) = J_0 + (J_z(0) - J_0) e^{-\frac{t}{T_1}}
\]

\[
J_x(t) = J_x(0) e^{-\frac{t}{T_1}} \cos(\Delta \omega_0 t) \quad \text{(where } \Delta \omega_0 = \gamma \cdot \Delta B_0 \text{)}
\]

So we can see that the longitudinal angular momentum \( J_z(t) \) will go back to the equilibrium value \( J_0 \) as function of \( (1 - e^{-\frac{t}{T_1}}) \) after the pulsed transverse field is turned off;
the transverse angular momentum \( J_x(t) \) will decay as \( e^{-\frac{t}{T_1}} \) from its initial value \( J_x(0) \) after pulse \( (J_x(t) \) has a similar performance as \( J_x(t) \).)

The fid curve is: 
\[
\vec{F}_{\text{fid}}(t, \tau) = J_0(1 - e^{-\frac{t}{T_1}}) \cdot f(t) \hat{i}
\]

Where function \( f(t) \) should be \( \frac{\sin a(t-\tau-t_2)}{a(t-\tau-t_2)} \hat{i} \).

So we can also measure the amplitudes of a series of second fid curves with different \( \tau \), there should satisfy a relation of \( (1 - e^{-\frac{\tau}{T_1}}) \). By using this method, we can measure the longitudinal relaxation time \( T_1 \).

(2) The "90°−τ−180°" pulse sequence (Figure 8):

Now let's discuss about another special case "90°−180°" pulses and the phenomenon of "echo". Firstly, we follow a typical isochromat \( \vec{j}_{\omega_0}(t) \). At the time \( \tau \), before the application of the second pulse, this isochromat will have accumulated an azimuthal phase \( \phi = -\Delta \omega_0 \tau \) relative to the \( \hat{i} \) axis. The inducing of the \( 2^{\text{nd}} \) pulse will make it nutate by 180° about the \( -\hat{j} \) axis, so that its phase immediately following the second pulse is now \( \phi' = \pi - \Delta \omega_0 \tau \) (please refer to Figure 9, I didn’t show it here). As the accumulation of the transverse phase should be proportional to the time, so at the time \( t = \tau + t_2 \), the phase should be \( \phi'' = \pi - \Delta \omega_0 \tau + \Delta \omega_0 t_2 \).

Thus we have the transverse component differential:
\[ \vec{J}_{\omega_0}(\tau + t_2) = J(0) \cos[\theta'(\tau + t_2)] \sin[\theta'(t_2)] \left[ \cos(\pi + \Delta \omega_0 (t_2 - \tau)) - \sin(\pi + \Delta \omega_0 (t_2 - \tau)) \right] \]

\[ \vec{J}(\tau + t_2) = \int \vec{J}_{\omega_0}(t) \cdot d\omega = N \int \vec{J}_{\omega_0}(t) \cdot g(\omega) \cdot d\omega = J(0) \cos(\theta') \sin(\theta') \times \left[ -i \int g(\Delta \omega_0) \cos(\Delta \omega_0 (t_2 - \tau)) \cdot d\omega_0 + j \int g(\Delta \omega_0) \sin(\Delta \omega_0 (t_2 - \tau)) \cdot d\omega_0 \right] \]

As we know before, the integral

\[ [-i \int g(\Delta \omega_0) \cos(\Delta \omega_0 (t_2 - \tau)) \cdot d\omega_0 + j \int g(\Delta \omega_0) \sin(\Delta \omega_0 (t_2 - \tau)) \cdot d\omega_0] \approx \frac{\sin a(t_2 - \tau)}{a(t_2 - \tau)} \]

So

\[ \vec{J}(\tau + t_2) = J(0) \cos(\theta') \sin(\theta') \times \frac{\sin a(t_2 - \tau)}{a(t_2 - \tau)} \]

If \( t_2 \) is different with \( \tau \), since \( a \) is a significant number, this term will go to zero quickly. So generally, we can see nothing after turning off the 2\textsuperscript{nd} fid signal. But when \( t_2 = \tau \), the factor \( \frac{\sin a(t_2 - \tau)}{a(t_2 - \tau)} \) will become quite large ---- 1, which is very significant compared to the other cases: \( t_2 \neq \tau \), it will increase the probability for us to detecting the fid signal. This phenomenon (when \( t_2 = \tau \)) is called spin refocusing, the signal shows up at time \( t = t_2 + \tau = 2\tau \) is called echo.

Here, the transverse angular momentum \( J_z(t) \) will decay as \( e^{-\frac{t}{T_2}} \) from its initial value \( J_z(0) \) after pulse.

Now, based on the previous discussion, we can estimate the fid curves and echo including the spin-relaxation.

The echo should be like the following term:

\[ \vec{F}_{\text{echo}}(t) = -J_0 \cdot \exp(-\frac{t}{T_2}) \cdot g(t) \cdot i \]

Where \( g(t) \) should be

\[ \frac{\sin a(t_2 - \tau)}{a(t_2 - \tau)} = \frac{\sin a(t - 2\tau)}{a(t - 2\tau)} \]
So using echo signal, we can measure the echo peak values of different delay time $\tau$, then fit the experimental data, we can obtain the transverse relaxation time $T_2$.

The height of echo should decay as function of $\exp\left(\frac{2\tau}{T_2}\right)$.

After this point, we see the main experiment we can do for pulsed NMR:

1. For the "90 $- \tau - 90$ " pulse sequence:

   \[ (1 - e^{-\frac{\tau}{T_1}}) \text{ vs. } \tau \], fid curve fitting to get $T_1$.

2. For the "90 $- \tau - 180$ " pulse sequence:

   \[ \exp\left(\frac{2\tau}{T_2}\right) \text{ vs. } \tau \], echo curve fitting to get $T_2$.

Experiment SET-UP

This experiment is evolved a lot of equipments including a complicated structure of circuit, now we will introduce the essential parts briefly.

The following block diagram (Figure 10.) shows the main contents.
A: Pulse Programmer                B: Modulator
C: Power Amplifier                   D: Protection and Coupling Circuit
E: Receiver                                F: Oscillator
G: Phase Detector                     H: Oscilloscope
I: Sample in coil                       N (S): North Pole or South Pole of Permanent Magnetic Filed

The Oscillator (F) outputs a continuous radio frequency signal. The frequency can be adjusted by different scales. When we are doing pulsed NMR experiment, we can change the frequency until we are close to the Larmor Frequency $\omega_0$ of the resonance.

The Pulse Programmer (A) generates D.C pulses that are used to determine when the RF (radio frequency) pulse are applied to the sample to excite sample from equilibrium state. The programmer can determine the repetition rate of series of identical pulse sequences, the length of each of the D.C pulse ($t_{w1}$ and $t_{w2}$), and the delay time between the two individual pulses.

The Modulator (B) modulates the signal from the Oscillator with the pulses from the programmer. It can be looked as a switch that opens and closes according to the pulse signals from the programmer.

The main function of Power Amplifier (C) is to take the RF pulses from the modulator and amplifies them from about 0.1 volts to 100 volts, but keeping the same shape.

The 100 volts out of power amplifier will damage the receiver and cause it to “block”, so that the signal following the RF pulse is unobservable. The Protection Circuit (D) connects the resonant circuit of the probe to the power amplifier during the excitation pulse, while disconnecting the receiver. Following the excitation pulse, it connects the resonant circuit of the probe to the receiver and disconnects it from the transmitter. So spurious noise from the transmitter doesn’t reach the receiver, and almost all of the signal from the resonant circuit goes the receiver.

The Receiver (E) is a high gain, low noise, radio frequency amplifier. It takes the signal coming from the sample coil and amplifies it from $1 \mu Volt \sim 100 \mu Volt$ to about 0.1 volt, then send it to the phase detector.

The Phase Detector (G) takes the signal from the receiver and changes it to D.C. It can be viewed as a switch that opens and closes in synchronism with the reference signal from the oscillator. In fact, the output of the phase detector seems as the vector sum of the signal from the receiver and the reference signal.

There is one thing I have to mention left ----- the resonance circuit around the sample. When the RF frequency is tuned to the Larmor Frequency $\omega_0$, it uses the power
from the power amplifier to create an oscillating magnetic field to excite the sample. It can also pick up a signal from the precessing magnetization to relay to the receiver.

Experimental Data and Discussion

In our experiment, we used three different concentrations of CuBr$_2$ solution. The following are data table and plots.

<table>
<thead>
<tr>
<th>Concentration 0.0375 M (CuBr$_2$)</th>
<th>90 Deg ~ 90 Deg Sequence</th>
<th>90 Deg ~ 180 Deg Sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delay Time 1 (ms)</td>
<td>Amplitude of 2$^{nd}$ Pulse (mV)</td>
<td>Delay Time 2 (ms)</td>
</tr>
<tr>
<td>5</td>
<td>15.6</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>17.2</td>
<td>15</td>
</tr>
<tr>
<td>50</td>
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</tr>
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</table>

<table>
<thead>
<tr>
<th>Concentration 0.15 M (CuBr$_2$)</th>
<th>90 Deg ~ 90 Deg Sequence</th>
<th>90 Deg ~ 180 Deg Sequence</th>
</tr>
</thead>
<tbody>
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<td>Delay Time 1 (ms)</td>
<td>Amplitude of 2$^{nd}$ Pulse (mV)</td>
<td>Delay Time 2 (ms)</td>
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<td>5</td>
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<tr>
<td>10</td>
<td>4.64</td>
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<td>50</td>
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<tr>
<td>100</td>
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<td>200</td>
<td>8.64</td>
<td>50</td>
</tr>
<tr>
<td>500</td>
<td>9.8</td>
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</tr>
</tbody>
</table>
Concentration 0.75 M (CuBr$_2$)

<table>
<thead>
<tr>
<th>90 Deg ~ 90 Deg Sequence</th>
<th>90 Deg ~ 180 Deg Sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delay Time 1 (ms)</td>
<td>Amplitude of 2nd Pulse (mV)</td>
</tr>
<tr>
<td>5</td>
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<tr>
<td>10</td>
<td>20.8</td>
</tr>
<tr>
<td>50</td>
<td>44.4</td>
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<tr>
<td>100</td>
<td>48</td>
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<tr>
<td>200</td>
<td>49.6</td>
</tr>
<tr>
<td>300</td>
<td>50.4</td>
</tr>
</tbody>
</table>

Longitudinal Relaxation Time T1
Measurement for 0.0375 M CuBr2 (90~90 Pulse Sequence)

Where we get the fit curve is $V_{Fid_2}(\tau) = 13 + 31 \cdot (1 - e^{-\frac{\tau}{390}})$. 

![Graph showing Longitudinal Relaxation Time T1 Measurement for 0.0375 M CuBr2 (90~90 Pulse Sequence)](image-url)
Longitudinal Relaxation Time T1 Measurement for 0.15 M CuBr2 (90~90 Pulse Sequence)

Where we get the fit curve is $V_{\text{Fid}2} (\tau) = 4 + 9 \cdot (1 - e^{-\frac{\tau}{275}})$

Longitudinal Relaxation Time T1 Measurement for 0.75 M CuBr2 (90~90 Pulse Sequence)

Where we get the fit curve is $V_{\text{Fid}2} (\tau) = 50 \cdot (1 - e^{-\frac{\tau}{30}})$
Transverse Relaxation Time T2 Measurement
for 0.0375 M CuBr2 (90~180 Pulse Sequence)

\[ y = 308.69e^{-0.049x} \]
\[ R^2 = 0.8996 \]

Where we get the fit curve is:

\[ V_{\text{echo}}(\tau) = 308.9 \cdot e^{\frac{-2\tau}{40.8}}. \]

Transeverse Relaxation Time T2
Measurement for 0.15 M CuBr2 (90~180 Pulse Sequence)

\[ y = 33.995e^{-0.043x} \]
\[ R^2 = 0.9816 \]

Where we get the fit curve is:

\[ V_{\text{echo}}(\tau) = 34.0 \cdot e^{\frac{-2\tau}{46.5}}. \]
Transeverse Relaxation Time T2 Measurement for 0.75 M CuBr2 (90~180 Pulse Sequence)

\[ y = 161.93 e^{-0.1489x}, \quad R^2 = 0.9995 \]

Where we get the fit curve is:

\[ V_{echo}(\tau) = 161.93 e^{-\frac{\tau}{13.43}}. \]

After fitting our experimental curves, we obtained the longitudinal relaxation time and transverse relaxation time for the three different samples:

<table>
<thead>
<tr>
<th>Concentration of CuBr(_2)</th>
<th>Longitudinal Relaxation Time T1 (ms)</th>
<th>Transverse Relaxation Time T2 (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0375 M</td>
<td>390</td>
<td>40.8</td>
</tr>
<tr>
<td>0.150 M</td>
<td>275</td>
<td>46.5</td>
</tr>
<tr>
<td>0.750 M</td>
<td>30</td>
<td>13.43</td>
</tr>
</tbody>
</table>

Adjustment and tuning of the apparatuses of this experiment is really a challenge job, we try our best to improve the signal, but it turns out that we couldn’t finally make it as good as we desired. Tuning both of the fid curves and echoes need a lot of diligence and patience, Professor Donna Naples (Faculty Member in Dept. of Physics & Astronomy, Univ. of Pittsburgh) also afforded me lots of help which I really feel appreciated, however, unfortunately the whole system seems not working consistently and appropriately. So the best suggestion here is to update the whole experiment set up, and make it work well. Looking at our experiment data, we can see that as the concentration of the salt solvent increases, both of the longitudinal and transverse relaxation times decrease. Since our data are not good, so it is quite difficult for us use it to make a plot of “Relaxation Time vs. Solution Concentration”. The most valuable thing of doing this experiment is to get a chance to review all the physics details in pulsed NMR experiment and give a reasonable analysis and estimation.