# Lecture Note on Senior Laboratory Spin echo method in pulsed nuclear magnetic resonance (NMR) Masatsugu Sei Suzuki and Itsuko S. Suzuki Department of Physics, SUNY at Binghamton 

(February 26, 2011)
Spin echo method is one of the elegant and most useful features in pulsed nuclear magnetic resonance (NMR). In the Phys.427, 429 (Senior laboratory) and Phys. 527 (Graduate laboratory) of Binghamton University (we call simply Advanced laboratory hereafter), both undergraduate and graduate students studies the longitudinal relaxation time $T_{1}$ and the transverse relaxation time $T_{2}$ of mineral oil and water solution of CuSO 4 using the spin echo method. The instrument we use in the Advanced laboratory is a TeachSpin PS1-A, a pulsed NMR apparatus. It focuses on the spin echo method using the CPMG (Carr-Purcell-Meiboom-Gill) sequence with the combinations of $90^{\circ}$ and $180^{\circ}$ pulses for the measurement of $T_{1}$ and $T_{2}$. Through these studies students will understand the fundamental physics underlying in NMR. From a theoretical view point, the dynamics of nuclear spins is uniquely determined by the Bloch equation. This equations are formed of the first order differential equations. The solutions of these equations with appropriate initial conditions can be exactly solved. The motions of the nuclear spin during the application of the $90^{\circ}$ pulse and $180^{\circ}$ pulse for the Carr-Purcell (CP) sequence, and Carr-Purcell-Meiboom-Gill (CPMG) sequence, can be visualized using the Mathematica.

Here we present a lecture note on the principle of the spin echo method in pulsed NMR, which has been given in the class of the Advanced laboratory. This note may be useful to students who start to do the spin echo experiment of pulsed NMR in the Advanced laboratory. One of the authors (MS) has been teaching the Advanced Laboratory course since 2005. He observes very carefully how the students come to understand the principle of the spin echo method and subsequently succeed in doing their experiment. Our students of this course obtained a lot of nice data during the classes. Typical data obtained by them are also shown for $T_{1}$ and $T_{2}$ measurements for the samples of mineral oil and water solution of $\mathrm{CuSO}_{4}$. It is our hope that this note may be useful to their understanding of the underlying physics. Note that the authors are not an expert of the research using the NMR measurements in the condensed matter physics.

Felix Bloch (October 23, 1905 - September 10, 1983) was a Swiss physicist, working mainly in the U.S. Bloch was born in Zürich, Switzerland to Jewish parents Gustav and Agnes Bloch. He was educated there and at the Eidgenössische Technische Hochschule, also in Zürich. Initially studying engineering he soon changed to physics. During this time he attended lectures and seminars given by Peter Debye and Hermann Weyl at ETH Zürich and Erwin Schrödinger at the neighboring University of Zürich. A fellow student in these seminars was John von Neumann. Graduating in 1927 he continued his physics studies at the University of Leipzig with Werner Heisenberg, gaining his doctorate in 1928. His doctoral thesis established the quantum theory of solids, using Bloch waves to describe the electrons.

He remained in European academia, studying with Wolfgang Pauli in Zürich, Niels Bohr in Copenhagen and Enrico Fermi in Rome before he went back to Leipzig assuming a position as privatdozent (lecturer). In 1933, immediately after Hitler came to power, he left Germany, emigrating to work at Stanford University in 1934. In the fall of 1938, Bloch began working with the University of California at Berkeley 37" cyclotron to determine the magnetic moment of the neutron. Bloch went on to become the first professor for theoretical physics at Stanford. In 1939, he became a naturalized citizen of the United States. During WW II he worked on nuclear power at Los Alamos National Laboratory, before resigning to join the radar project at Harvard University.

After the war he concentrated on investigations into nuclear induction and nuclear magnetic resonance, which are the underlying principles of MRI. In 1946 he proposed the Bloch equations which determine the time evolution of nuclear magnetization. He and Edward Mills Purcell were awarded the 1952 Nobel Prize for "their development of new ways and methods for nuclear magnetic precision measurements." In 1954-1955, he served for one year as the first Director-General of CERN. In 1961, he was made Max Stein Professor of Physics at Stanford University.

http://en.wikipedia.org/wiki/Felix_Bloch

Edward Mills Purcell (August 30, 1912 - March 7, 1997) was an American physicist who shared the 1952 Nobel Prize for Physics for his independent discovery (published 1946) of nuclear magnetic resonance in liquids and in solids. Nuclear magnetic resonance (NMR) has become widely used to study the molecular structure of pure materials and the composition of mixtures.

http://en.wikipedia.org/wiki/Edward_Mills_Purcell

Erwin L. Hahn (born 1921) is a U.S. physicist, best known for his work on nuclear magnetic resonance (NMR). In 1950 he discovered the spin echo. He received his B.S. in Physics from Juniata College. He has been Professor Emeritus at the University of California, Berkeley since 1991 and was professor of physics, 1955-91. In 1999 Hahn was awarded the Comstock Prize in Physics from the National Academy of Sciences.
http://en.wikipedia.org/wiki/Erwin_Hahn

## 1. The gyromagnetic ratio and the magnetic moment

We consider a nucleus that possesses a magnetic moment $\boldsymbol{\mu}$ and an angular momentum. $\hbar \mathbf{I}$.

$$
\boldsymbol{\mu}=\gamma \hbar \mathbf{I},
$$

where $\gamma$ is the gyromagnetic ratio and is defined by

$$
\gamma=\frac{\mu}{\hbar I} .
$$

2. Magnetic moment of proton $\left({ }^{1} \mathrm{H}\right)$

The magnetic moment of the proton $\mu_{\mathrm{P}}$ is given by

$$
\begin{aligned}
\mu_{P}= & 2.792 \mu_{\mathrm{N}}=1.410606662 \times 10^{-23} \mathrm{emu} \\
& \text { (NIST, Fundamental Physics constants) }
\end{aligned}
$$

where emu $=\mathrm{erg} / \mathrm{Oe}$ and $\mu_{\mathrm{N}}$ is the nuclear magneton, given by

$$
\mu_{N}=\frac{e \hbar}{2 M_{p} c}=5.05079 \times 10^{-24} \mathrm{emu}
$$

Note that $M_{\mathrm{P}}$ is the mass of the proton, $e$ is the charge of proton, and $c$ is the velocity of light. Note that the value of $\mu_{\mathrm{N}}$ is much smaller than the Bohr magneton for electron,

$$
\mu_{B}=\frac{e \hbar}{2 m c}=9.27400915(23) \times 10^{-21} \mathrm{emu} .
$$

The nuclear spin $I$ of the proton is $I=1 / 2$. The gyromagnetic ratio is positive and is given by

$$
\begin{aligned}
\gamma & =\gamma_{P}=\frac{\mu_{P}}{\hbar I}=\frac{2.792 \mu_{N}}{\hbar(1 / 2)} \\
& =\frac{2.792 \times 5.050951 \times 10^{-24}}{1.0546 \times 10^{-27}(1 / 2)} \\
& =2.675222099 \times 10^{4}\left(s^{-1} O e^{-1}\right)
\end{aligned}
$$

(NIST, Fundamental Physics constants)
Since $\gamma>0$ for proton, the direction of the magnetic moment $\mu_{\mathrm{p}}$ is the same as that of the angular momentum (or nuclear spin $I$ ).

## 3. Zeeman energy

The energy of interaction with the applied magnetic field $\boldsymbol{H}$ is

$$
U=-\boldsymbol{\mu} \cdot \mathbf{B} .
$$

If $\boldsymbol{B}$ is applied along the $z$ axis and is given by $\mathbf{B}=B_{0} \hat{z}$, then we have

$$
U=-\mu_{z} B_{0}=-\gamma \hbar B_{0} I_{z}
$$

The allowed values of $I_{z}$ are

$$
m_{I}=I, I-1, I-2, \ldots,-I,
$$

leading to the splitting of the $(2 I+1)$ energy levels. If $\hbar \omega_{0}$ denotes the energy difference between these levels, then we have

$$
\hbar \omega_{0}=\gamma \hbar B_{0}
$$

or

$$
\hbar \omega_{0}=\hbar(2 \pi \nu)=\gamma \hbar B_{0}
$$

or

$$
v=\frac{\gamma H_{0}}{2 \pi}
$$



Fig. $1 \quad$ Zeeman splitting of the energy level

For proton, we have

$$
v(H z)=\frac{\gamma B_{0}}{2 \pi}=\frac{2.675222099 \times 10^{4} B_{0}}{2 \pi}=4.25775 \times 10^{6} B_{0}(k O e)
$$

or

$$
v(M H z)=4.25775 B_{0}(k O e) .
$$

Note that $1 \mathrm{~T}($ tesla $)=10 \mathrm{kOe}=10^{4} \mathrm{Oe}$. The earth magnetic field at Binghamton, NY is 0.3 Oe.
((Mathematica)) The physics constants from NIST Physics constant (cgs units)

| $k_{\mathrm{B}}$ | Boltzmann constant <br> $\mu_{\mathrm{N}}$ | $(\mathrm{erg} / \mathrm{K})$ <br> $c$ |
| :--- | :--- | :--- |
| nuclear magneton | $(\mathrm{emu})$ |  |
| $\hbar$ | velocity of light | $(\mathrm{cm} / \mathrm{s})$ |
| $M$ | Planck's constant | $(\mathrm{erg} \mathrm{s})$ |
| $\mu$ | mass of proton | $(\mathrm{g})$ |
| $\gamma$ | magnetic moment of proton | $(\mathrm{emu})$ |
|  | gyromagnetic ratio of proton | $\left(\mathrm{s}^{-1} \mathrm{Oe}^{-1}\right)$ |
| $\mathrm{emu}=\mathrm{erg} / \mathrm{Oe}$ |  |  |

## http://physics.nist.gov/cuu/Constants/

((Mathematica))

```
Clear["Global`*"];
Physconst = { }\mu\textrm{N}->5.05079\times1\mp@subsup{0}{}{-24},\textrm{kB}->1.3806504\times1\mp@subsup{0}{}{-16}
```



```
        \gamma->2.675222099 < 104 };
    \mu=\gamma\hbar(1/2) /. Physconst
    1.41061 < 10 -23
    f0 = 渞 B0 /. Physconst
    4257.75 B0
    \DeltaEB = \hbar ( \gamma B0) /. Physconst
    2.82121 * 10 -23 B0
    \DeltaEB = kB T /. Physconst
    1.38065 * 10-16 T
```


## 4. Bloch equation

## A. Equation of motion

The rate of change of the angular momentum is equal to the torque that acts on the system

$$
\hbar \frac{d \mathbf{I}}{d t}=\boldsymbol{\mu} \times \mathbf{B}
$$

where $\boldsymbol{B}$ is the magnetic field. This equation can be rewritten as

$$
\gamma \hbar \frac{d \mathbf{I}}{d t}=\gamma \boldsymbol{\mu} \times \mathbf{B}
$$

or

$$
\frac{d \boldsymbol{\mu}}{d t}=\gamma \boldsymbol{\mu} \times \mathbf{B}
$$

The nuclear magnetization is the sum

$$
\mathbf{m}=\sum_{i} \boldsymbol{\mu}_{i}
$$

where

$$
\boldsymbol{\mu}_{i}=\gamma \hbar \mathbf{I}_{i}
$$

over all the nuclei in a unit volume.

$$
\frac{d \mathbf{m}}{d t}=\gamma \mathbf{m} \times \mathbf{B}
$$

Larmor precession of magnetization


Fig. $2 \quad$ The precession motion of the magnetization $M$ (or spin) around the z axis. The static magnetic field $\boldsymbol{B}_{0}$ is applied along the $z$ axis. When $\gamma>0$, the magnetization $M$ rotates in clockwise.

$$
\begin{aligned}
\frac{d \mathbf{m}}{d t} & =m \sin \theta \frac{d \phi}{d t} \mathbf{e}_{\phi}=m \sin \theta \omega_{0} \mathbf{e}_{\phi} \\
& =-\gamma m B_{0} \sin \theta \mathbf{e}_{\phi}
\end{aligned}
$$

or

$$
\omega_{0}=-\gamma B_{0}
$$

For $\gamma>0$, the rotation is clockwise and for $\gamma<0$, the rotation is counterclockwise. Hereafter we discuss only on the case of $\gamma>0$.

## B. Rotating reference frame



Fig. $3 \quad x_{1}=m_{1} \cdot x_{2}=m_{2} \cdot x_{1}{ }^{\prime}=m_{1}{ }^{\prime} \cdot x_{2}=m_{2}{ }^{\prime}$. Note that $\overrightarrow{O P}$ is fixed. The relation between $\left\{\boldsymbol{e}_{1}, \boldsymbol{e}_{2}\right\}$ and $\left\{\boldsymbol{e}_{1}^{\prime}, \boldsymbol{e}_{2}^{\prime}\right\}$.

We consider the two coordinate systems.

$$
\mathbf{m}=m_{1} \mathbf{e}_{1}+m_{2} \mathbf{e}_{2}=m_{1}{ }^{\prime} \mathbf{e}_{1}{ }^{\prime}+m_{2}{ }^{\prime} \mathbf{e}_{2}{ }^{\prime},
$$

with

$$
\begin{aligned}
m_{1}^{\prime} & =\left(m_{1} \mathbf{e}_{1}+m_{2} \mathbf{e}_{2}\right) \cdot \mathbf{e}_{1}{ }^{\prime}=m_{1} \cos \theta+m_{2} \cos \left(\frac{\pi}{2}-\theta\right) \\
& =m_{1} \cos \theta+m_{2} \sin \theta \\
m_{2}^{\prime} & =\left(m_{1} \mathbf{e}_{1}+m_{2} \mathbf{e}_{2}\right) \cdot \mathbf{e}_{2}^{\prime}=m_{1} \cos \left(\frac{\pi}{2}+\theta\right)+m_{2} \cos \theta \\
& =-m_{1} \sin \theta+m_{2} \cos \theta
\end{aligned}
$$

or

$$
\left(\begin{array}{l}
m_{1}^{\prime} \\
m_{2}^{\prime} \\
m_{3}^{\prime}
\end{array}\right)=\left(\begin{array}{ccc}
\cos \theta & \sin \theta & 0 \\
-\sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{array}\right)\left(\begin{array}{l}
m_{1} \\
m_{2} \\
m_{3}
\end{array}\right),
$$

or

$$
\left(\begin{array}{l}
m_{1} \\
m_{2} \\
m_{3}
\end{array}\right)=\left(\begin{array}{ccc}
\cos \theta & -\sin \theta & 0 \\
\sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{array}\right)\left(\begin{array}{l}
m_{1}{ }^{\prime} \\
m_{2}{ }^{\prime} \\
m_{3}{ }^{\prime}
\end{array}\right) .
$$

We now calculate the time derivative of $\boldsymbol{m}$ such that

$$
\begin{aligned}
\dot{\mathbf{m}} & =\dot{m_{1}} \mathbf{e}_{1}+\dot{m}_{2} \mathbf{e}_{2}=\dot{m}_{1} \mathbf{e}_{1}{ }^{\prime}+\dot{m}_{2} \mathbf{e}_{2}{ }^{\prime}+m_{1} \dot{\mathbf{e}}_{1}{ }^{\prime}+m_{2}{ }^{\prime} \mathbf{e}_{2}^{\prime} \\
& =\left(\dot{m_{1}} \mathbf{e}_{1}{ }^{\prime}+\dot{m}_{2} \mathbf{e}_{2}{ }^{\prime}\right)+\dot{\theta}\left(\mathbf{e}_{3}{ }^{\prime} \times \mathbf{m}\right)
\end{aligned}
$$

## ((Proof))

$$
\begin{aligned}
& \mathbf{e}_{1}{ }^{\prime}=(\cos \theta, \sin \theta, 0), \\
& \mathbf{e}_{2}{ }^{\prime}=(-\sin \theta, \cos \theta, 0), \\
& \mathbf{e}_{1}^{\prime}=(-\dot{\theta} \sin \theta, \dot{\theta} \cos \theta, 0), \\
& \dot{\mathbf{e}}_{2}^{\prime}=(-\dot{\theta} \cos \theta,-\dot{\theta} \sin \theta, 0),
\end{aligned}
$$

Then

$$
\begin{aligned}
& m_{1}{ }^{\prime} \mathbf{e}_{1}{ }^{\prime}+m_{2}{ }^{\prime} \mathbf{e}_{2}^{\prime}=m_{1}{ }^{\prime}(-\dot{\theta} \sin \theta, \dot{\theta} \cos \theta, 0)+m_{2}{ }^{\prime}(-\dot{\theta} \cos \theta,-\dot{\theta} \sin \theta, 0) \\
& =m_{1}{ }^{\prime} \dot{\theta}(-\sin \theta, \cos \theta, 0)-m_{2}{ }^{\prime} \dot{\theta}(\cos \theta, \sin \theta, 0) \\
& =m_{1}{ }^{\prime} \dot{\theta} \mathbf{e}_{2}{ }^{\prime}-m_{2}{ }^{\prime} \dot{\theta} \mathbf{e}_{1}{ }^{\prime}
\end{aligned}
$$

This can be rewritten as

$$
m_{1}^{\prime} \dot{\theta} \mathbf{e}_{2}^{\prime}-m_{2}^{\prime} \dot{\theta} \mathbf{e}_{1}^{\prime}=\dot{\theta}\left(\mathbf{e}_{3}^{\prime} \times \mathbf{m}\right)
$$

where

$$
\mathbf{e}_{3}^{\prime} \times \mathbf{m}=\left|\begin{array}{ccc}
\mathbf{e}_{1}^{\prime} & \mathbf{e}_{2}^{\prime} & \mathbf{e}_{3}^{\prime} \\
0 & 0 & 1 \\
m_{1}^{\prime} & m_{2}^{\prime} & m_{3}{ }^{\prime}
\end{array}\right|
$$

Thus we have the following form,

$$
\frac{d \mathbf{m}}{d t}=\left(\frac{d \mathbf{m}}{d t}\right)_{r e l}+\dot{\theta}\left(\mathbf{e}_{3}^{\prime} \times \mathbf{m}\right)
$$

where

$$
\left(\frac{d \mathbf{m}}{d t}\right)_{r e l}=\dot{m}_{1}^{\prime} \mathbf{e}_{1}^{\prime}+\dot{m}_{2}^{\prime} \mathbf{e}_{2}^{\prime}
$$

and

$$
\frac{d \mathbf{m}}{d t}=\dot{m}_{1} \mathbf{e}_{1}+\dot{m}_{2} \mathbf{e}_{2}
$$



Fig. 4 The rotating coordinates $(X, Y)$ and non-rotating coordinates $(x, y)$. The case for $\omega<0$.

## (c) Equation of the motion

We consider the equation of motion of the magnetic moment in the presence of magnetic fields $\boldsymbol{B}$ given by

$$
\begin{aligned}
& \mathbf{B}=\mathbf{B}_{0}+\mathbf{B}_{r f}, \\
& \mathbf{B}_{0}=\left(0,0, B_{0}\right) .
\end{aligned}
$$

where $\boldsymbol{B}_{0}$ is a static magnetic field along the z axis. We apply the AC magnetic field along the $x$ axis. It is interesting to note that in most experiments the time dependent field is not realized as a rotating field but as a field oscillating in the $x$ direction. It can, however, be expressed as a sum

$$
\begin{aligned}
\mathbf{B}_{r f} & =2 B_{1} \mathbf{e}_{1}=2 B_{1}(\cos \omega t, 0,0) \\
& =\mathbf{B}_{r f 1}+\mathbf{B}_{r f 2} \\
& =\left(B_{1} \cos \omega t, B_{1} \sin \omega t, 0\right)+\left(B_{1} \cos \omega t,-B_{1} \sin \omega t, 0\right)
\end{aligned}
$$



Fig. $5 \quad \mathbf{B}_{r f 1}$ rotates clockwise. The direction of $\mathbf{B}_{r f 1}$ coincides with that of the $X$ axis. The case for $\omega<0$.

The fields $\boldsymbol{B}_{\mathrm{rf} 1}(t)$ and $\boldsymbol{B}_{\mathrm{r} 2}(t)$ rotate in opposite directions. We define a magnetic field $\boldsymbol{B}_{\mathrm{rfl}}$ as

$$
\mathbf{B}_{r f 1}=B_{1} \mathbf{e}_{1}^{\prime}=\left(B_{1} \cos \omega t, B_{1} \sin \omega t, 0\right)
$$

with

$$
\theta=\omega t .
$$

where we assume that $\omega$ is negative, which means that the rotation in clockwise for $\omega<0$ (along the $X$-axis direction). Then we have an equation of motion,

$$
\begin{aligned}
& \frac{d \mathbf{m}(t)}{d t}=\gamma \mathbf{m}(t) \times\left(\mathbf{B}_{0}+\mathbf{B}_{r f 1}\right), \\
& \frac{d \mathbf{m}(t)}{d t}=\gamma \mathbf{m}(t) \times\left(\mathbf{B}_{0}+\mathbf{B}_{r f 1}\right)=\gamma\left|\begin{array}{ccc}
\mathbf{e}_{1} & \mathbf{e}_{2} & \mathbf{e}_{3} \\
m_{1} & m_{2} & m_{3} \\
B_{1} \cos (\omega t) & B_{1} \sin (\omega t) & B_{0}
\end{array}\right| .
\end{aligned}
$$

As a more general case, we use the Bloch equations defined by

$$
\begin{aligned}
& \frac{d m_{1}(t)}{d t}=\gamma\left[\mathbf{m}(t) \times\left(\mathbf{B}_{0}+\mathbf{B}_{r f 1}\right)\right]_{1}-\frac{m_{1}}{T_{2}}, \\
& \frac{d m_{2}(t)}{d t}=\gamma\left[\mathbf{m}(t) \times\left(\mathbf{B}_{0}+\mathbf{B}_{r f 1}\right)\right]_{2}-\frac{m_{2}}{T_{2}} \\
& \frac{d m_{3}(t)}{d t}=\gamma\left[\mathbf{m}(t) \times\left(\mathbf{B}_{0}+\mathbf{B}_{r f 1}\right)\right]_{2}+\frac{M_{0}-m_{3}}{T_{1}},
\end{aligned}
$$

or, in the vector form, we get

$$
\frac{d \mathbf{m}(t)}{d t}=\gamma\left[\mathbf{m}(t) \times\left(\mathbf{B}_{0}+\mathbf{B}_{r f 1}\right)\right]-\frac{1}{T_{2}}\left(m_{1} \mathbf{e}_{1}+m_{2} \mathbf{e}_{2}\right)+\frac{M_{0}-m_{3}}{T_{1}} \mathbf{e}_{3},
$$

where $T_{1}$ is a longitudinal relaxation time (or spin-lattice relaxation time), $T_{2}$ is a transverse relaxation time (or spin-spin relaxation time), and $M_{0}$ is a saturation magnetization. The above equation can be rewritten as

$$
\frac{d \mathbf{m}}{d t}=\left(\frac{d \mathbf{m}}{d t}\right)_{r e l}+\omega\left(\mathbf{e}_{3}{ }^{\prime} \times \mathbf{m}^{\prime}\right)=\gamma \mathbf{m}^{\prime} \times\left(B_{0} \mathbf{e}_{3}{ }^{\prime}+B_{1} \mathbf{e}_{1}{ }^{\prime}\right)-\frac{\left(m_{1} \mathbf{e}_{1}{ }^{\prime}+m_{2}{ }^{\prime} \mathbf{e}_{2}{ }^{\prime}\right)}{T_{2}}+\frac{\left(M_{0}-m_{3}{ }^{\prime}\right) \mathbf{e}_{3}{ }^{\prime}}{T_{1}} .
$$

in the rotating coordinates, where

$$
\begin{aligned}
& m_{1} \mathbf{e}_{1}+m_{2} \mathbf{e}_{2}=m_{1}^{\prime} \mathbf{e}_{1}{ }^{\prime}+m_{2}{ }^{\prime} \mathbf{e}_{2}{ }^{\prime}, \quad \quad m_{3} \mathbf{e}_{3}=m_{3}{ }^{\prime} \mathbf{e}_{3}{ }^{\prime} \\
& \mathbf{B}_{0}=B_{0} \mathbf{e}_{3}=B_{0} \mathbf{e}_{3}^{\prime}, \quad \text { and } \quad \mathbf{B}_{r f 1}=B_{1} \mathbf{e}_{1}{ }^{\prime} .
\end{aligned}
$$

Then we have

$$
\begin{aligned}
\left(\frac{d \mathbf{m}}{d t}\right)_{r e l} & =\dot{m_{1}} \mathbf{e}_{1}{ }^{\prime}+\dot{m}_{2} \mathbf{e}_{2}{ }^{\prime} \\
& =\mathbf{m}^{\prime} \times\left[\gamma\left(B_{0} \mathbf{e}_{3}{ }^{\prime}+B_{1} \mathbf{e}_{1}{ }^{\prime}\right)+\omega \mathbf{e}_{3}{ }^{\prime}\right]-\frac{m_{1}{ }^{\prime} \mathbf{e}_{1}{ }^{\prime}+m_{2}{ }^{\prime} \mathbf{e}_{2}{ }^{\prime}}{T_{2}}+\frac{\left(M_{0}-m_{3}{ }^{\prime}\right) \mathbf{e}_{3}{ }^{\prime}}{T_{1}}
\end{aligned}
$$

We introduce definitions:

$$
\omega_{0}=-\gamma B_{0}, \quad \omega_{1}=-\gamma B_{1},
$$

$$
\begin{aligned}
\gamma\left(B_{0} \mathbf{e}_{3}{ }^{\prime}+B_{1} \mathbf{e}_{1}{ }^{\prime}\right)+\omega \mathbf{e}_{3}{ }^{\prime} & =\left(\omega-\omega_{0}\right) \mathbf{e}_{3}{ }^{\prime}-\omega_{1} \mathbf{e}_{1}{ }^{\prime} \\
& =\Delta \omega \mathbf{e}_{3}{ }^{\prime}-\omega_{1} \mathbf{e}_{1}{ }^{\prime}
\end{aligned}
$$

((Note)) The sign of $\omega_{0}$ and $\omega_{1}$ is negative for $\gamma>0$ (clock-wise). For convenience, we assume $\gamma>0$ hereafter.

Then we have

$$
\begin{aligned}
\left(\frac{d \mathbf{m}}{d t}\right)_{r e l} & =\dot{m}_{1} \mathbf{e}_{1}{ }^{\prime}+\dot{m}_{2}{ }^{\prime} \mathbf{e}_{2}{ }^{\prime} \\
& =\mathbf{m}^{\prime} \times\left(\Delta \omega \mathbf{e}_{3}{ }^{\prime}-\omega_{1} \mathbf{e}_{1}{ }^{\prime}\right)-\frac{m_{1} \mathbf{e}_{1}{ }^{\prime}+m_{2}{ }^{\prime} \mathbf{e}_{2}{ }^{\prime}}{T_{2}}+\frac{\left(M_{0}-m_{3}{ }^{\prime}\right) \mathbf{e}_{3}{ }^{\prime}}{T_{1}} \\
& =\gamma \mathbf{m}^{\prime} \times \mathbf{B}_{e f f}-\frac{m_{1} \mathbf{e}_{1}{ }^{\prime}+m_{2}{ }^{\prime} \mathbf{e}_{2}{ }^{\prime}}{T_{2}}+\frac{\left(M_{0}-m_{3}{ }^{\prime}\right) \mathbf{e}_{3}{ }^{\prime}}{T_{1}}
\end{aligned}
$$

where

$$
\Delta \omega=\omega-\omega_{0}
$$

and

$$
\gamma \mathbf{B}_{e f f}=\Delta \omega \mathbf{e}_{3}{ }^{\prime}-\omega_{1} \mathbf{e}_{1}{ }^{\prime} . \quad \text { or } \quad \mathbf{B}_{e f f}=\frac{\Delta \omega \mathbf{e}_{3}{ }^{\prime}-\omega_{1} \mathbf{e}_{1}{ }^{\prime}}{\gamma}=\frac{\Delta \omega}{\gamma} \mathbf{e}_{3}{ }^{\prime}+\frac{-\omega_{1}}{\gamma} \mathbf{e}_{1}{ }^{\prime}
$$

We introduce

$$
\Omega=\sqrt{(\Delta \omega)^{2}+\omega_{1}^{2}} .
$$

Then $B_{\text {eff }}$ is related to $\Omega$,

$$
B_{e f f}=\frac{\Omega}{\gamma}
$$



Fig. 6

$$
\mathbf{B}_{e f f}=\frac{\Delta \omega \mathbf{e}_{3}{ }^{\prime}-\omega_{1} \mathbf{e}_{1}{ }^{\prime}}{\gamma}=\frac{\Delta \omega}{\gamma} \mathbf{e}_{3}{ }^{\prime}+\frac{-\omega_{1}}{\gamma} \mathbf{e}_{1}{ }^{\prime}=\left(B_{0}+\frac{\omega}{\gamma}\right) \mathbf{e}_{3}{ }^{\prime}+B_{1} \mathbf{e}_{1}{ }^{\prime} \cdot \omega_{0}=-\gamma B_{0} .
$$

$\omega_{1}=-\gamma B_{1} . \Delta \omega=\omega-\omega_{0}$. In this rotating reference frame, $B_{1}$ along the $X$ direction is a DC magnetic field. The case for $\omega<0$.

When $\Delta \omega=0$ (the resonance condition is satisfied), we have only the magnetic field $B_{1}$ along the $X$ direction.


Fig. 7
The configuration where $\Delta \omega=0$ is satisfied. Only the magnetic field $B_{1}$ is applied along the $X$ direction.
5. Bloch equation in the rotating reference frame

For simplicity we introduce $\boldsymbol{M}$ defined by

$$
\begin{aligned}
& \mathbf{m}^{\prime}=\mathbf{M}=M_{X} \mathbf{e}_{1}{ }^{\prime}+M_{Y} \mathbf{e}_{2}{ }^{\prime}+M_{Z} \mathbf{e}_{3}{ }^{\prime} \\
& \gamma \mathbf{M} \times \mathbf{B}_{e f f}=\left|\begin{array}{ccc}
\mathbf{e}_{1}^{\prime} & \mathbf{e}_{2}{ }^{\prime} & \mathbf{e}_{3}{ }^{\prime} \\
M_{X} & M_{Y} & M_{Z} \\
-\omega_{1} & 0 & \Delta \omega
\end{array}\right|=\left(M_{Y} \Delta \omega,-M_{X} \Delta \omega-M_{Z} \omega_{1}, M_{Y} \omega_{1}\right)
\end{aligned}
$$

Thus we have the following Bloch equation

$$
\begin{aligned}
\dot{M}_{X} \mathbf{e}_{1}{ }^{\prime}+\dot{M}_{Y} \mathbf{e}_{2}{ }^{\prime}+\dot{M}_{Z} \mathbf{e}_{3}{ }^{\prime} & =M_{Y} \Delta \omega \mathbf{e}_{1}{ }^{\prime}-\left(M_{X} \Delta \omega+M_{Z} \omega_{1}\right) \mathbf{e}_{2}{ }^{\prime}+M_{Y} \omega_{1} \mathbf{e}_{3}{ }^{\prime} \\
& -\frac{\left(M_{X} \mathbf{e}_{1}{ }^{\prime}+M_{Y} \mathbf{e}_{2}{ }^{\prime}\right)}{T_{2}}+\frac{\left(M_{0}-M_{Z}\right) \mathbf{e}_{3}{ }^{\prime}}{T_{1}}
\end{aligned}
$$

or

$$
\dot{M}_{X}=M_{Y} \Delta \omega-\frac{M_{X}}{T_{2}}
$$

$$
\begin{aligned}
& \dot{M}_{Y}=-\left(M_{X} \Delta \omega+M_{Z} \omega_{1}\right)-\frac{M_{Y}}{T_{2}} \\
& \dot{M}_{Z}=M_{Y} \omega_{1}+\frac{M_{0}-M_{Z}}{T_{1}}
\end{aligned}
$$

(a)

$$
\begin{aligned}
\dot{M}_{X}+i \dot{M}_{Y} & =\left(M_{Y} \Delta \omega-\frac{M_{X}}{T_{2}}\right)-i\left(M_{X} \Delta \omega+M_{Z} \omega_{1}\right)-i \frac{M_{Y}}{T_{2}} \\
& =-\frac{M_{X}+i M_{Y}}{T_{2}}-i\left(M_{X}+i M_{Y}\right) \Delta \omega-i M_{Z} \omega_{1} \\
& =-\left(i \Delta \omega+\frac{1}{T_{2}}\right)\left(M_{X}+i M_{Y}\right)-i M_{Z} \omega_{1}
\end{aligned}
$$

(b)

$$
\begin{aligned}
\dot{M}_{Z}+i \dot{M}_{Y} & =M_{Y} \omega_{1}+\frac{M_{0}-M_{Z}}{T_{1}}+i\left[-\left(M_{X} \Delta \omega+M_{Z} \omega_{1}\right)-\frac{M_{Y}}{T_{2}}\right] \\
& =-i \omega_{1}\left(M_{Z}+i M_{Y}\right)+\frac{M_{0}-M_{Z}}{T_{1}}-i \Delta \omega M_{X}-i \frac{M_{Y}}{T_{2}}
\end{aligned}
$$

Note that

$$
\begin{aligned}
& \dot{M}_{X} M_{X}+\dot{M}_{Y} M_{Y}+\dot{M}_{Z} M_{Z} \\
= & M_{X} M_{Y} \Delta \omega-\frac{M_{X}^{2}}{T_{2}}-\left(M_{X} M_{Y} \Delta \omega+M_{Y} M_{Z} \omega_{1}\right)-\frac{M_{Y}{ }^{2}}{T_{2}} \\
+ & M_{Y} M_{Z} \omega_{1}+\frac{M_{0} M_{Z}-M_{Z}^{2}}{T_{1}} \\
= & -\frac{M_{X}^{2}+M_{Y}{ }^{2}}{T_{2}}+\frac{M_{0} M_{Z}-M_{Z}^{2}}{T_{1}} \\
= & \frac{M_{Z}^{2}-M_{0}{ }^{2}}{T_{2}}-\frac{M_{Z}{ }^{2}-M_{0} M_{Z}}{T_{1}} \\
= & \left(M_{Z}-M_{0}\right)\left(\frac{M_{Z}+M_{0}}{T_{2}}-\frac{M_{Z}}{T_{1}}\right) \\
= & M_{0}{ }^{2} \frac{1}{T_{2}}\left(\frac{M_{Z}}{M_{0}}-1\right)\left(\frac{M_{Z}}{M_{0}}+1-\frac{T_{2}}{T_{1}} \frac{M_{Z}}{M_{0}}\right)
\end{aligned}
$$

Furthermore we use the following non-dimensional notation,

$$
\begin{aligned}
& \xi=\frac{M_{X}}{M_{0}} \\
& \eta=\frac{M_{Y}}{M_{0}} \\
& \varsigma=\frac{M_{Z}}{M_{0}}
\end{aligned}
$$

Then we get the equations

$$
\begin{aligned}
& \frac{d \xi}{d t}=(\Delta \omega) \eta-\frac{1}{T_{2}} \xi \\
& \frac{d \eta}{d \tau}=-(\Delta \omega) \xi-\omega_{1} \varsigma-\frac{1}{T_{2}} \eta \\
& \frac{d \varsigma}{d t}=\omega_{1} \eta+\frac{1}{T_{1}}(1-\varsigma)
\end{aligned}
$$

These equations can be solved under appropriate conditions.
6. The case of $\Delta \omega=0$ and $B_{1}=0$ (thermal equilibrium)

We consider the case for $\Delta \omega=0$ (resonance condition). We aslso suppose that $\omega_{1}=0$ ( $B_{1}=0$ ).

$$
\begin{aligned}
& \frac{d \xi}{d t}=-\frac{1}{T_{2}} \xi \\
& \frac{d \eta}{d t}=-\frac{1}{T_{2}} \eta \\
& \frac{d \varsigma}{d t}=\frac{1}{T_{1}}(1-\varsigma)
\end{aligned}
$$

or

$$
\begin{aligned}
& \frac{d \varsigma}{d t}=\frac{1}{T_{1}}(1-\varsigma) \\
& \frac{d}{d t}(\xi+i \eta)=-\frac{1}{T_{2}}(\xi+i \eta)
\end{aligned}
$$

The stationary state of these equations is given by

$$
\xi=0, \eta=0, \varsigma=1 \|
$$

in thermal equilibrium. The saturated magnetization is directed along the $z$ axis.


Fig. $8 \quad \Delta \omega=0$ and $B_{1}=0$. The magnetization $\boldsymbol{M}_{0}$ is directed along the $z$ axis in thermal equilibrium.
7. The case of $\Delta \omega=0$ and $B_{1} \neq 0\left(90^{\circ}\right.$ pulse and $180^{\circ}$ pulse)

Let $\boldsymbol{M}$ is parallel to the $z$ axis at $t=0$. We have the initial condition such that $\zeta(0)=1$, $\xi(0)=0, \eta(0)=0$.

$$
\begin{aligned}
& \frac{d \xi}{d t}=(\Delta \omega) \eta \\
& \frac{d \eta}{d t}=-(\Delta \omega) \xi-\omega_{1} \varsigma \\
& \frac{d \varsigma}{d t}=\omega_{1} \eta
\end{aligned}
$$

Note that

$$
\xi \frac{d \xi}{d t}+\eta \frac{d \eta}{d t}+\varsigma \frac{d \varsigma}{d t}=0 .
$$

or

$$
\xi^{2}+\eta^{2}+\varsigma^{2}=\xi(0)^{2}+\eta(0)^{2}+\varsigma(0)^{2}=1 \quad \text { (conserved) }
$$

In other words, $(\xi, \eta, \zeta)$ is located on the unit sphere. Furthermore we assume that $\omega / \omega_{0}=1$ (the resonance condition). Then we have

$$
\begin{aligned}
& \frac{d \xi}{d t}=0 \\
& \frac{d \eta}{d t}=-\omega_{1} \varsigma \\
& \frac{d \varsigma}{d \tau}=\omega_{1} \eta
\end{aligned}
$$

or

$$
\frac{d \eta}{d t}+i \frac{d \varsigma}{d t}=i \omega_{1}(\eta+i \varsigma)
$$

or

$$
\begin{aligned}
& \eta+i \varsigma=\text { conste }^{i \omega_{1} t} \\
& \xi=0
\end{aligned}
$$

This means that the magnetization $M$ (or spin) rotates in the $Y Z$ plane with an angular frequency $\omega_{1}\left(=-\gamma B_{1}\right)<0$. The application of the magnetic field $B_{1}$ along the $X$ axis leads to the rotation of the magnetization $M_{0}$ in clock-wise.
(i) $\quad \mathbf{9 0}{ }^{\circ}$ pulse. At $t=\pi /\left(2\left|\omega_{1}\right|\right)$, the magnetization $\boldsymbol{M}$ is parallel to the $Y$ axis. The system is in the excited state. This implies the transition of the system from the ground state at $t=0$ to the excited state at $t=\pi /\left(2\left|\omega_{1}\right|\right) . \quad\left(90^{\circ}\right.$ pulse $)$.


Fig. 9 The spin is directed along the $Z$ axis in the thermal equilibrium. When the $90^{\circ}$ pulse is applied, the spin rotates in clockwise from the $Z$ axis to the $Y$ axis. The case for $\omega_{1}<0$.
(ii) $\quad \mathbf{1 8 0}^{\circ}$ pulse. At $t=\pi /\left|\omega_{1}\right|$, the magnetization $\boldsymbol{M}$ is antiparallel to the $Z$ axis. All spins are antiparallel to $\boldsymbol{B}_{0}(/ / Z)$. The system is in the excited state. This implies the transition of the system from the ground state at $t=0$ to the excited state at $t=$ $\pi / \omega_{1}$. ( $180^{\circ}$ pulse).

$180^{\circ}$ pulse

Fig. $10 \quad$ The spin is directed along the $Z$ axis in the thermal equilibrium. When $180^{\circ}$ pulse is applied, the spin rotates in clockwise from the $Z$ axis to the $Y$ axis. The case for $\omega_{1}<0$.

## 8. $B_{1}=0$ and $\Delta \omega \neq 0$

Suppose that $\Delta \omega$ is very close to zero (near the resonance condition). When the field $B_{1}$ is switched on,, the magnetization is directed along the $z$ (or $Z$ ) axis. Then we apply a $90^{\circ}$ pulse. The magnetization rotates from the $z$ axis to the $Y$ axis. After the field $B_{1}$ is switched off, the free induction decay (FID) takes place and the individual vectors in the $X Y$ plane fan out.


Fig. 11 The $90^{\circ}$ pulse leads to the rotation of the spin from the Z axis to the $Y$ axis around the $Z$ axis. Then spin fans out in the $X-Y$ plane, in counterclockwise for $\Delta \omega<0$ or in clock-wise for $\Delta \omega>0$.
(a) The $90^{\circ}$ pulse.
(b) The spin rotates in the counter-clockwise for $\Delta \omega<0$ and in the clockwise for $\Delta \omega>0$.

We consider the motion such that

$$
\begin{aligned}
& \frac{d \xi}{d t}=\Delta \omega \eta-\frac{1}{T_{2}} \xi \\
& \frac{d \eta}{d t}=-\Delta \omega \xi-\frac{1}{T_{2}} \eta
\end{aligned}
$$

with the initial condition,

$$
\xi(0)=0, \text { and } \eta(0)=1 .
$$

where

$$
\Delta \omega=\omega-\omega_{0} \quad \text { and } \quad \omega_{1}=0\left(\text { since } B_{1}=0\right) .
$$

The solution of the differential equation is obtained as

$$
\xi(t)=\exp \left(-\frac{t}{T_{2}}\right) \sin (\Delta \omega t), \quad \text { and } \quad \eta(t)=\exp \left(-\frac{t}{T_{2}}\right) \cos (\Delta \omega t)
$$

or

$$
\begin{aligned}
\xi(t)+i \eta(t) & =\exp \left(-\frac{t}{T_{2}}\right)[\sin (\Delta \omega t)+i \cos (\Delta \omega t)] \\
& =\exp \left(-\frac{t}{T_{2}}\right) i[\cos (\Delta \omega t)-i \sin (\Delta \omega t) \\
& =\exp \left(-\frac{t}{T_{2}}\right) \exp \left[-i(\Delta \omega t)+i \frac{\pi}{2}\right]
\end{aligned}
$$

This means that
(1) The spin is at $\xi=0$ and $\eta=1(t=0)$.
(2) The spin fans out in counter-clockwise for the case of $\Delta \omega<0$.
(3) The spin fans out in clockwise for the case of $\Delta \omega>0$

## ((Mathematica))

```
Clear["Global`*"];
\(\mathrm{f} 1=\mathrm{D}[\xi[\mathrm{t}], \mathrm{t}]=\Delta \omega \eta[\mathrm{t}]-\frac{1}{\mathrm{~T} 2} \xi[\mathrm{t}] ;\)
\(\mathrm{f} 2=\mathrm{D}[\eta[\mathrm{t}], \mathrm{t}]=-\Delta \omega \xi[\mathrm{t}]-\frac{1}{\mathrm{~T} 2} \eta[\mathrm{t}] ; \mathrm{f} 3=\{\xi[0]=0, \eta[0]==1\}\);
eq1 = DSolve[Join[\{f1, f2\}, f3], \{ \([\mathrm{t}], \eta[\mathrm{t}]\}, \mathrm{t}] / /\) Simplify
\(\left\{\left\{\eta[\mathrm{t}] \rightarrow \mathbb{e}^{-\frac{\mathrm{t}}{\mathrm{T} 2}} \operatorname{Cos}[\mathrm{t} \Delta \omega], \xi[\mathrm{t}] \rightarrow e^{-\frac{\mathrm{t}}{\mathrm{T} 2}} \operatorname{Sin}[\mathrm{t} \Delta \omega]\right\}\right\}\)
\(\eta\left[t_{-}\right]=\eta[t] / . \operatorname{eq1}[[1]]\)
\(e^{-\frac{t}{T 2}} \operatorname{Cos}[t \Delta \omega]\)
\(\xi\left[t_{-}\right]=\xi[t] / . \operatorname{eq1}[[1]]\)
\(e^{-\frac{t}{T 2}} \operatorname{Sin}[t \Delta \omega]\)
```

We make a ParametricPlot of $\{\xi(t), \eta(t)\}$ as a function of t in the $(X, Y)$ plane.


Fig. 12 The time dependence of $\{\eta(t), \xi(t)\}$ in the units of $T_{2}$, where $\{\eta(0), \xi(0)\}$ $=\{1,0\}$. We choose the value of $\alpha$ as $\alpha=|\Delta \omega| T_{2}=6.0$. The red arrows (clockwise) for $\Delta \omega>0$. The blue arrows (counterclockwise) for $\Delta \omega<0$. The spin rotates around the $Z$ axis. The spins starts to rotate at $t=0$ from the Y axis and fans out in the $X Y$ plane.

In the limit of $\Delta \omega \rightarrow 0$ (the resonance condition is satisfied),

$$
\xi(t)=\exp \left(-\frac{t}{T_{2}}\right) \sin (\Delta \omega t) \rightarrow \xi_{0}(t)=0
$$

and

$$
\eta(t)=\exp \left(-\frac{t}{T_{2}}\right) \cos (\Delta \omega t) \rightarrow \eta_{0}(t)=\exp \left(-\frac{t}{T_{2}}\right)
$$

## 9. Spin rotation during the $180^{\circ}$ pulse for the CP (Carr-Purcell) sequence

We consider the motion of spins during the $180^{\circ}$ pulse for the CP (Carr-Purcell) sequence, which is governed by the following differential equations,

$$
\begin{aligned}
& \frac{d \xi}{d t}=(\Delta \omega) \eta-\frac{1}{T_{2}} \xi \\
& \frac{d \eta}{d t}=-(\Delta \omega) \xi-\omega_{1} \varsigma-\frac{1}{T_{2}} \eta \\
& \frac{d \varsigma}{d t}=\omega_{1} \eta+\frac{1}{T_{1}}(1-\varsigma)
\end{aligned}
$$

with initial condition,

$$
\xi(0)=-\sin \theta_{0}, \quad \eta(0)=\cos \theta_{0}, \text { and } \quad \varsigma(0)=0 .
$$

where $\theta_{0}$ is the angle from the $Y$ axis to the $-X$ axis side. Further we assume that

$$
T_{1}=\infty . \quad T_{2}=\infty .
$$

for simplicity. Then we have

$$
\begin{aligned}
& \frac{d \xi}{d t}=(\Delta \omega) \eta \\
& \frac{d \eta}{d t}=-(\Delta \omega) \xi-\omega_{1} \varsigma \\
& \frac{d \varsigma}{d t}=\omega_{1} \eta
\end{aligned}
$$

We note that

$$
\xi \frac{d \xi}{d t}+\eta \frac{d \eta}{d t}+\varsigma \frac{d \varsigma}{d t}=0
$$

or

$$
[\xi(t)]^{2}+[\eta(t)]^{2}+[\varsigma(t)]^{2}=1 . \quad \text { (conservative) }
$$

When $\omega_{c}$ is newly defined as

$$
\omega_{c}=\sqrt{(\Delta \omega)^{2}+\omega_{1}^{2}}(>0),
$$

Using the Mathematica, we get

$$
\begin{aligned}
& \xi(\phi)=-\cos ^{2} \delta \sin \theta_{0}+\sin \delta\left(-\sin \theta_{0} \sin \delta \cos \phi+\cos \theta_{0} \sin \phi\right) \\
& \eta(\phi)=\cos \theta_{0} \cos \phi+\sin \theta_{0} \sin \delta \sin \phi \\
& \varsigma(\phi)=-\cos \delta\left(2 \sin \theta_{0} \sin \delta \sin ^{2} \frac{\phi}{2}+\cos \theta_{0} \sin \phi\right)
\end{aligned}
$$

where

$$
\phi=\omega_{c} t
$$

and

$$
\alpha=-\frac{\omega_{1}}{\omega_{c}}=\cos \delta, \quad \beta=\frac{\Delta \omega}{\omega_{c}}=\sin \delta
$$



Fig. $13 \quad(\alpha, \beta)$ diagram. We are interested in the regions where $\Delta \omega>0$ and $B_{1}>0$ (red region) and $\Delta \omega<0$ and $B_{1}>0$ (green region).

When $\theta_{0}=0$, we have

$$
\xi(\phi)=\sin \delta \sin \phi, \quad \eta(\phi)=\cos (\phi)
$$

$$
\varsigma(\phi)=-\cos \delta \sin (\phi)
$$

(i) $\quad B_{1}>0, \Delta \omega<0$


Fig.14(a) The spin fans out from the $Y$ axis in clockwise around the $Z$ axis. At the angle $\theta_{0}(>0)$, the $180^{\circ}$ pulse is applied. The spin undergoes a rotation from the position (denoted by the red arrow) to the position (denoted by blue arrow) around the $X$ axis in clock-wise. $B_{1}>0 . \Delta \omega<0$.


Fig.14(b) $\quad B_{1}>0 . \Delta \omega<0$. The spin rotates from an angle (denoted by red point, near the $Y$ axis) to an angle (denoted by blue point, near the $-Y$ axis) in the $Y-Z$ plane in clock-wise around the $X$ axis. $\delta=-\pi / 120 . \phi=-0.02 \pi-$ $0.98 \pi(\Delta \phi=\pi)$.
(ii) $\quad B_{1}>0, \Delta \omega>0$


Fig.15(a) The spin fans out from the $Y$ axis around the $Z$ axis in counterclockwise. At the angle $\theta_{0}(<0)$, the $180^{\circ}$ pulse is applied. The spin undergoes a rotation from the position (denoted by the red arrow) to the positions (denoted by blue arrow) around the $X$ axis in clock-wise. $B_{1}>0 . \Delta \omega>0$.


Fig.15(b) $\quad B_{1}>0 . \Delta \omega>0$. The spin rotates from a angle (denoted by red, near the $Y$ axis) to an angle (denoted by blue point, near the $-Y$ axis) in clock-wise around the $X$ axis. $\delta=\pi / 120 . \phi=-0.02 \pi-0.98 \pi .(\Delta \phi=\pi)$
((Mathematica))

```
Clear["Global`*"];
\(\mathbf{f 1}=\mathbf{D}[\xi[\mathrm{t}], \mathrm{t}]=\mathrm{s} \omega \eta[\mathrm{t}]\);
\(\mathrm{f} 2=\mathrm{D}[\eta[\mathrm{t}], \mathrm{t}]=-\Delta \omega \xi[\mathrm{t}]-\omega 1 \zeta[\mathrm{t}]\);
f3 = D [ [ [t], t] = \(\omega 1 \eta[t]\);
\(\mathrm{f} 4=\{\xi[0]=-\operatorname{Sin}[\theta 0], \eta[0]==\operatorname{Cos}[\theta 0], \zeta[0]==0\}\);
eq1 = DSolve[Join[\{f1, f2, f3\}, f4],
    \(\{\xi[t], \eta[t], \zeta[t]\}, t] / /\) Simplify;
rule1 \(=\left\{\sqrt{-\Delta \omega^{2}-\omega 1^{2}} \rightarrow \dot{\mathrm{I}} \omega \mathrm{c}, \frac{1}{\sqrt{-\Delta \omega^{2}-\omega 1^{2}}} \rightarrow-\dot{\mathrm{i}} \frac{1}{\omega \mathrm{c}}, \Delta \omega^{2}+\omega 1^{2} \rightarrow \omega \mathrm{c}^{2}\right\} ;\)
eq11 = eq1 / . rule1 // FullSimplify;
rule1 \(=\left\{\omega 1 \rightarrow-\operatorname{Cos}[\delta] \omega c, \Delta \omega \rightarrow \operatorname{Sin}[\delta] \omega c, t \rightarrow \frac{\phi}{\omega c}\right\} ;\)
\(\xi 1\left[\tau_{-}\right]=\xi[t] / . \operatorname{eq11}[[1]] /\). rule1 // Simplify
\(-\operatorname{Cos}[\delta]^{2} \operatorname{Sin}[\theta 0]+\operatorname{Sin}[\delta](-\operatorname{Cos}[\phi] \operatorname{Sin}[\delta] \operatorname{Sin}[\theta 0]+\operatorname{Cos}[\theta 0] \operatorname{Sin}[\phi])\)
\(\eta \mathbf{1}\left[\tau_{-}\right]=\eta[\mathrm{t}] / . \operatorname{eq11[[1]]/.}\) rule1 // Simplify
\(\operatorname{Cos}[\theta 0] \operatorname{Cos}[\phi]+\operatorname{Sin}[\delta] \operatorname{Sin}[\theta 0] \operatorname{Sin}[\phi]\)
ऽ1[ \(\left.\tau_{-}\right]=\zeta[t] /\). eq11[[1]] /. rule1 // Simplify
\(-\operatorname{Cos}[\delta]\left(2 \operatorname{Sin}[\delta] \operatorname{Sin}[\theta 0] \operatorname{Sin}\left[\frac{\phi}{2}\right]^{2}+\operatorname{Cos}[\theta 0] \operatorname{Sin}[\phi]\right)\)
\(\boldsymbol{\xi 1}[\tau] / . \theta 0 \rightarrow 0\)
Sin[ \(\delta] \operatorname{Sin}[\phi]\)
\(\eta \mathbf{1}[\tau] / . \theta 0 \rightarrow 0\)
\(\operatorname{Cos}[\phi]\)
\(\varsigma 1[\tau] / . \theta 0 \rightarrow 0\)
- \(\operatorname{Cos}[\delta] \operatorname{Sin}[\phi]\)
```

10. Spin rotation during the $180^{\circ}$ pulse: the MG (Meiboom-Gill) sequence

We now consider the phase change in $B_{\mathrm{rf}}$ by $\pi / 2$, which is required for the MG sequence. Mathematically, under such a phase change, $\mathbf{B}_{r f}$ can be rewritten as

$$
\begin{aligned}
\mathbf{B}_{r f} & =2 B_{1}\left[\cos \left(\omega t+\frac{\pi}{2}\right), 0,0\right] \\
& =B_{1}(-\sin (\omega t), \cos (\omega t), 0)+B_{1}(-\sin (\omega t),-\cos (\omega t), 0) \\
& =B_{1}(\sin (-\omega t), \cos (-\omega t), 0)+B_{1}(\sin (-\omega t),-\cos (-\omega t), 0)
\end{aligned}
$$

We pick up only the magnetic field $\boldsymbol{B}_{1}$ along the $Y$ axis,

$$
\mathbf{B}_{r f 1}=B_{1}(-\sin (\omega t), \cos (\omega t), 0)=B_{1} \mathbf{e}_{2}^{\prime}
$$

Using

$$
\gamma \mathbf{M} \times \mathbf{B}_{e f f}=\left|\begin{array}{ccc}
\mathbf{e}_{1}{ }^{\prime} & \mathbf{e}_{2}{ }^{\prime} & \mathbf{e}_{3}{ }^{\prime} \\
M_{X} & M_{Y} & M_{Z} \\
0 & -\omega_{1} & \Delta \omega
\end{array}\right|=\left(M_{Y} \Delta \omega+M_{Z} \omega_{1}\right) \mathbf{e}_{1}{ }^{\prime}-M_{X} \Delta \omega \mathbf{e}_{2}{ }^{\prime}-M_{X} \omega_{1} \mathbf{e}_{3}{ }^{\prime}
$$

we get the equation of motion

$$
\begin{aligned}
\dot{M}_{X} \mathbf{e}_{1}{ }^{\prime}+\dot{M}_{Y} \mathbf{e}_{2}{ }^{\prime}+\dot{M}_{Z} \mathbf{e}_{3}{ }^{\prime} & =\left(M_{Y} \Delta \omega+M_{Z} \omega_{1}\right) \mathbf{e}_{1}{ }^{\prime}-M_{X} \Delta \omega \mathbf{e}_{2}{ }^{\prime}-M_{X} \omega_{1} \mathbf{e}_{3}{ }^{\prime} \\
& -\frac{\left(M_{X} \mathbf{e}_{1}{ }^{\prime}+M_{Y} \mathbf{e}_{2}\right)}{T_{2}}+\frac{\left(M_{0}-M_{Z}\right) \mathbf{e}_{3}{ }^{\prime}}{T_{1}}
\end{aligned}
$$

or

$$
\begin{aligned}
& \dot{\xi}=(\Delta \omega) \eta+\omega_{1} \varsigma-\frac{\xi}{T_{2}} \\
& \dot{\eta}=-(\Delta \omega) \xi-\frac{\eta}{T_{2}} \\
& \dot{\varsigma}=-\omega_{1} \xi+\frac{(1-\varsigma)}{T_{1}}
\end{aligned}
$$

When $T_{1}=T_{2}=\infty$ (for simplicity)

$$
\begin{aligned}
& \frac{d \xi}{d t}=(\Delta \omega) \eta+\omega_{1} \varsigma \\
& \frac{d \eta}{d t}=-(\Delta \omega) \xi \\
& \frac{d \varsigma}{d t}=-\omega_{1} \xi
\end{aligned}
$$

with initial condition;

$$
\xi(0)=-\sin \theta_{0}, \quad \eta(0)=\cos \theta_{0}, \text { and } \quad \varsigma(0)=0 .
$$

We note that

$$
\xi \frac{d \xi}{d t}+\eta \frac{d \eta}{d t}+\varsigma \frac{d \varsigma}{d t}=0
$$

or

$$
[\xi(t)]^{2}+[\eta(t)]^{2}+[\varsigma(t)]^{2}=1 \quad \text { (conserved). }
$$

The solution of the above differential equations is given by

$$
\begin{aligned}
& \xi(\phi)=-\sin \theta_{0} \cos (\phi)+\sin \delta \cos \theta_{0} \sin \phi, \\
& \left.\eta(\phi)=\cos \theta_{0} \cos ^{2} \delta+\sin ^{2} \delta \cos \theta_{0} \cos \phi\right]+\sin \delta \sin \theta_{0} \sin \phi, \\
& \varsigma(\phi)=-\cos \delta\left[\sin \delta \cos \theta_{0}(-1+\cos \phi)+\sin \theta_{0} \sin \phi\right]
\end{aligned}
$$

where

$$
\begin{aligned}
& \omega_{c}=\sqrt{(\Delta \omega)^{2}+\omega_{1}^{2}}>0, \\
& \alpha=-\frac{\omega_{1}}{\omega_{c}}=\cos \delta, \quad \beta=\frac{\Delta \omega}{\omega_{c}}=\sin \delta
\end{aligned}
$$

(i) $\quad B_{1}>0, \Delta \omega<0$


Fig.16(a) The spin fans out from the $Y$ axis in counterclockwise around the $Z$ axis. At the angle $\theta_{0}$, the $180^{\circ}$ pulse is applied. The spin undergoes a rotation from the position (denoted by the red arrow) to the positions (denoted by blue arrow) around the $Y$ axis in clock-wise. $B_{1}>0 . \Delta \omega<0$


Fig.16(b) $\quad B_{1}>0 . \Delta \omega<0$. The spin rotates from the red point (near $Y$ axis) to the blue point (near the $Y$ axis) in clock-wise around the $Y$ axis. $\theta_{0}=\pi / 6$ (red point) and $\pi / 4$ (red point). $\delta=-\pi / 120>0 . \phi=0-\pi$.
(ii) $B_{1}>0, \Delta \omega>0$


Fig.17(a) The spin fans out from the $Y$ axis in clockwise around the $Z$ axis. At the angle $\theta_{0}(<0)$, the $180^{\circ}$ pulse is applied. The spin undergoes a rotation from the position (denoted by the red arrow) to the positions (denoted by blue arrow) around the $Y$ axis in clock-wise.

$$
B_{1}>0, \Delta \omega>0, \mathrm{CW}
$$



Fig.17(b) $\quad B_{1}>0 . \Delta \omega>0$. The spin rotates from the red point (near the $Y$ axis to the blue point (near the $X$ axis) in clock-wise around the $Y$ axis. $\theta_{0}=-\pi / 6$ (red point) and $-\pi / 4$ (blue point). $\delta=\pi / 120 . \phi=0-\pi$.

## ((Mathematica))

```
Clear["Global`*"];
f1 = D[\xi[t], t] == \Delta\omega \eta[t] + \omega1 \zeta[t];
f2 = D[\eta[t], t] == - \Delta\omega \xi[t] ;
f3 = D[\zeta[t], t] == - \omega1 \xi[t];
f4 = {\xi[0] == - Sin[00], \eta[0] == Cos[00], \zeta[0] == 0};
eq1 = DSolve[Join[{f1, f2, f3}, f4],
    {\varepsilon[t], \eta[t], \zeta[t]}, t] // Simplify;
```

rule1 $=\left\{\sqrt{-\Delta \omega^{2}-\omega 1^{2}} \rightarrow \dot{\mathrm{i}} \omega \mathrm{c}, \frac{1}{\sqrt{-\Delta \omega^{2}-\omega 1^{2}}} \rightarrow-\dot{\mathrm{i}} \frac{1}{\omega \mathrm{c}}, \Delta \omega^{2}+\omega 1^{2} \rightarrow \omega \mathrm{c}^{2}\right\} ;$
eq11 = eq1 / . rule1 // FullSimplify;
eq11

$$
\begin{aligned}
\{\{\zeta[t] & \rightarrow \frac{\omega 1(\Delta \omega \operatorname{Cos}[\theta 0](-1+\operatorname{Cos}[t \omega c])+\omega c \operatorname{Sin}[\theta 0] \operatorname{Sin}[t \omega c])}{\omega c^{2}}, \\
\eta[t] & \rightarrow \frac{\operatorname{Cos}[\theta 0]\left(\omega 1^{2}+\Delta \omega^{2} \operatorname{Cos}[t \omega c]\right)+\Delta \omega \omega c \operatorname{Sin}[\theta 0] \operatorname{Sin}[t \omega c]}{\omega c^{2}}, \\
\xi[t] & \left.\left.\rightarrow-\operatorname{Cos}[t \omega c] \operatorname{Sin}[\theta 0]+\frac{\Delta \omega \operatorname{Cos}[\theta 0] \operatorname{Sin}[t \omega c]}{\omega c}\right\}\right\}
\end{aligned}
$$

$$
\text { rule2 }=\left\{\omega 1 \rightarrow-\operatorname{Cos}[\delta] \omega c, \Delta \omega \rightarrow \operatorname{Sin}[\delta] \omega c, t \rightarrow \frac{\phi}{\omega c}\right\} ;
$$

$\xi\left[\phi_{-}\right]=\xi[t] / . \operatorname{eq11[[1]]/.rule2//Simplify}$
$-\operatorname{Cos}[\phi] \operatorname{Sin}[\theta 0]+\operatorname{Cos}[\theta 0] \operatorname{Sin}[\delta] \operatorname{Sin}[\phi]$
$\eta\left[\phi_{-}\right]=\eta[t] / . e q 11[[1]] /$. rule2 // Simplify
$\operatorname{Cos}[\delta]^{2} \operatorname{Cos}[\theta 0]+\operatorname{Sin}[\delta](\operatorname{Cos}[\theta 0] \operatorname{Cos}[\phi] \operatorname{Sin}[\delta]+\operatorname{Sin}[\theta 0] \operatorname{Sin}[\phi])$
$\zeta\left[\phi_{-}\right]=\zeta[t] / . e q 11[[1]] /$. rule2 // Simplify
$-\operatorname{Cos}[\delta](\operatorname{Cos}[\theta 0](-1+\operatorname{Cos}[\phi]) \operatorname{Sin}[\delta]+\operatorname{Sin}[\theta 0] \operatorname{Sin}[\phi])$
$\xi[\phi] / . \theta 0 \rightarrow-\pi / 2$
$\operatorname{Cos}[\phi]$
$\eta[\phi] / . \theta 0 \rightarrow-\pi / 2$
-Sin[ $\delta$ ] Sin [ $\phi$ ]
$\zeta[\tau] / . \theta 0 \rightarrow-\pi / 2$
$\operatorname{Cos}[\delta] \operatorname{Sin}[\tau]$

## 11. The expression of signal obtained from picking coil along the $x$ axis

 We know that$$
\left(\begin{array}{l}
m_{x} \\
m_{y} \\
m_{z}
\end{array}\right)=\left(\begin{array}{ccc}
\cos (\omega t) & -\sin (\omega t) & 0 \\
\sin (\omega t) & \cos (\omega t) & 0 \\
0 & 0 & 1
\end{array}\right)\left(\begin{array}{l}
M_{X} \\
M_{Y} \\
M_{Z}
\end{array}\right) .
$$

Experimentally, we detect the $m_{\mathrm{x}}$ component since the axis of the detecting coil is the $x$ axis.

$$
\begin{aligned}
m_{x} & =\cos (\omega t) M_{X}-\sin (\omega t) M_{y} \\
& =M_{0}[\xi(t) \cos (\omega t)-\eta(t) \sin (\omega t)] \\
& =M_{0} \exp \left(-\frac{t}{T_{2}}\right)[\sin (\Delta \omega t) \cos (\omega t)-\cos (\Delta \omega t) \sin (\omega t)] \\
& =M_{0} \exp \left(-\frac{t}{T_{2}}\right) \sin (\Delta \omega-\omega) t \\
& =M_{0} \exp \left(-\frac{t}{T_{2}}\right) \sin \left(-\omega_{0} t\right)=-M_{0} \exp \left(-\frac{t}{T_{2}}\right) \sin \left(\omega_{0} t\right)
\end{aligned}
$$

since $\Delta \omega=\omega-\omega_{0} \approx 0$ and $\omega<0$ in the present case.

Suppose that $f_{0}=15 \mathrm{MHz}$. The value of $T_{2}$ is assume to be $\approx 15 \mathrm{~ms}$ for the mineral oil. Then we have

$$
\left|\omega_{0}\right| T_{2}=2 \pi f_{0} T_{2}=2 \pi \times 15 \times 10^{6} \times 15 \times 10^{-3}=1.41 \times 10^{6} .
$$

So we note that

$$
\left|\omega_{0}\right| T_{2} \gg 1 .
$$

The voltage generated in the solenoid coil is given by

$$
\begin{aligned}
V_{\text {coil }} & =-k_{1} \frac{d m_{x}}{d t}=k M_{0} \frac{d}{d t}\left[\exp \left(-\frac{t}{T_{2}}\right) \sin \left(\omega_{0} t\right)\right] \\
& =\frac{k_{1} M_{0}}{T_{2}} \exp \left(-\frac{t}{T_{2}}\right)\left[T_{2} \omega_{0} \cos \left(\omega_{0} t\right)-\sin \left(\omega_{0} t\right)\right] \\
& \approx \frac{k_{1} M_{0}}{T_{2}} \exp \left(-\frac{t}{T_{2}}\right) T_{2} \omega_{0} \cos \left(\omega_{0} t\right)=k_{1} M_{0} \omega_{0} \exp \left(-\frac{t}{T_{2}}\right) \cos \left(\omega_{0} t\right)
\end{aligned}
$$

since $\left|\omega_{0}\right| T_{2} \gg 1$, where $k_{1}$ is a constant parameter.

## 12. The expression for the mixer signal

A mixer is a nonlinear device that effectively multiplies the CW (continuous wave) rf signal from the oscillator with rf signals from the precessing nuclear magnetization. The frequency output of the mixer is proportional to the difference frequencies between the two rf signals.

$$
\begin{aligned}
V_{\text {mixer }} & =k_{2} V_{\text {coil }} \sin (\omega t)=k_{1} k_{2} M_{0} \omega_{0} \exp \left(-\frac{t}{T_{2}}\right) \cos \left(\omega_{0} t\right) \sin (\omega t) \\
& =\frac{1}{2} k_{1} k_{2} M_{0} \omega_{0} \exp \left(-\frac{t}{T_{2}}\right)\left[\sin \left(\omega-\omega_{0}\right) t+\sin \left(\omega+\omega_{0}\right) t\right]
\end{aligned}
$$

We neglect the second term which has a frequency of $\left(\omega+\omega_{0}\right)$. Then we get the expression for the mixer signal as

$$
V_{\text {mixer }} \approx \frac{1}{2} k_{1} k_{2} M_{0} \omega_{0} \exp \left(-\frac{t}{T_{2}}\right)\left[\sin \left(\omega-\omega_{0}\right) t\right]
$$

If the oscillator properly tuned to the resonance, the signal output of the mixer should no beats, but if the two rf signals have different frequencies a beat structure will be superimposed on the signal.









Fig. 18 Signals of the mixer as a function of $t / T_{2} . \alpha=(\Delta \omega) T_{2}$ is changed as a parameter. $\alpha=-2,-4,-6,-8,-10,-12,-14,-16$ and $-18 . \alpha=0$ corresponds to the resonance condition. The case for $\Delta \omega<0$.

## 13. How to find the resonance condition in TeachSpin pulsed NMR

In the pulsed NMR experiment, we use the mineral oil. It is placed in the carriage and the mixer out and detector out outputs are plugged into the oscilloscope channels. The frequency generator is set around 15 MHz . Using the formula $f=\gamma \mathrm{B}_{0} / 2 \pi$, it is found that a magnetic field of 3.55888 kOe will correspond to a resonant frequency of 15.1516 MHz .

After the $90^{\circ} \mathrm{rf}$ pulse is applied at $t=0$, the resonance can be seen on the oscilloscope when the mixer out (denoted by orange lines) and detector out (denoted by the blue lines) show approximately the same thing. If the circuit is out of resonance, beats will be seen on the mixer's signal. Below are three pictures, each getting closer to resonant frequency. The first one is fairly far out of resonance and the beats are very close together. The second is getting closer and only a few beats can be seen in the signal. The third one shows the resonance.

The Free Induction Decay (the blue line) is the due to the pulse pushing the magnetization down to the $X-Y$ plane, then they are slowly fanning out in the the $X-Y$ plane.


Fig. 19 (Far from resonance, too many beats): The $90^{\circ} \mathrm{rf}$ pulse is applied at $t=0$. The output of the detector (blue). The output of mixer (orange). The data are obtained from the Report of G. Parks (Binghamton University).


Fig. 20 (Closer, only a few beats seen). The $90^{\circ}$ rf pulse is applied at $t=0$. The data are obtained from the Report of G. Parks (Binghamton University).


Fig. 21 (Resonance Found). The $90^{\circ}$ rf pulse is applied at $t=0$. The data are obtained from the Report of G. Parks (Binghamton University).
14. CP process for spin echo method: measurement of $\boldsymbol{T}_{\mathbf{2}}$
(a) Initially $(t=0)$ the system is in thermal equilibrium and all the spin vectors are lined up in the $Z$ direction parallel to the static magnetic field.
(b) During the application of the $90^{\circ}$ pulse (the $B_{1}$ field is turned on for $t_{\mathrm{w}} / 2$ ), the vectors are tipped away from the $Z$ direction toward the $Y$ direction in the rotating frame by the rf field in the $X$ direction. $\gamma B_{1} t_{w} / 2=\pi / 2$.
(c) At the end of the $90^{\circ}$ pulse the magnetic moments are all in the equatorial plane in the $Y$ direction. If the pulse duration $t_{\mathrm{w}}$ is sufficiently short, there will have been no relaxation of fanning out due to field inhomegenities.
(d) After the field $B_{1}$ is switched off, free induction decay (FID) takes place and the individual spins in the $X Y$ plane fan out.
(e) After a time $\tau$, a second $180^{\circ}$ pulse is applied, lasting for a period $2 t_{\mathrm{w}} \cdot \gamma B_{1} t_{w}=\pi$. This turns the whole fanned system of spins through $180^{\circ}$ about the $X$ axis. After the second pulse, each individual spin continues to move in the rotating frame in the same direction as before. Now, however, this fanning motion will lead to a closing up of the spins.
(f) At time $2 \tau$, the set of vectors in the $X Y$ plane will be completely re-clustered, leading to a strong resultant moment in the negative $Y$ direction. This will lead to a signal in the detector coil and is the echo.
(g) After the echo, the vectors again fan out and a normal decay is observed.
(h). These processes are repeated to get the spin echo pattern.

$t=0\left(90^{\circ} \mathrm{pulse}\right)$

$$
t=0-\tau .
$$


$t=\tau\left(180^{\circ}\right.$ pulse $)$

$$
t=\tau-2 \tau .
$$


$t=2 \tau-3 \tau$

$$
t=3 \tau\left(180^{\circ} \text { pulse }\right)
$$


$t=3 \tau-4 \tau$

$$
t=4 \tau-5 \tau
$$


$t=5 \tau\left(180^{\circ}\right.$ pulse $)$

$t=6 \tau-7 \tau$

$$
t=7 \tau\left(180^{\circ} \text { pulse }\right)
$$

Fig. $22 \quad$ CP (Carr-Purcell) sequence for the measurement of $T_{2} . t=0\left(90^{\circ}\right.$ pulse). $t$ $=\tau, 3 \tau, 5 \tau, 7 \tau, 9 \tau \ldots\left(180^{\circ}\right.$ pulse $)$.


Fig. 23
Spin echo in the CP sequence. Application of a $90^{\circ}$ pulse at $t=0$, followed by successive $180^{\circ}$ pulse ( $X$-axis) at $t=\tau, 3 \tau, 5 \tau, 7 \tau, 9 \tau$... The width of $180^{\circ}$ pulse is twice longer than that of $90^{\circ}$ pulse. The resultant exponential decay (dotted green line) of the echoes (free induction decay). The unit of the time axis (horizontal) is $t / \tau$. The peaks appear at $t / \tau=0,2,4,6, \ldots$.

## 15. Intrinsic transverse relaxation time

Two factors contribute to the decay of transverse magnetization.
(1) Spin-spin interactions (said to lead to an intrinsic $T_{2}$ ).
(2) variations in $B_{\mathrm{o}}$ (said to lead to an inhomogeneous $T_{2}$ effect.

The combination of these two factors is what actually results in the decay of transverse magnetization. The combined time constant is called $T_{2}$ star and is given the symbol $T_{2}{ }^{*}$. The relationship between the $T_{2}$ from molecular processes and that from inhomogeneities in the magnetic field is as follows.

$$
\frac{1}{T_{2} *}=\frac{1}{T_{2}}+\frac{1}{T_{2 i \mathrm{hhom}}}
$$

We note that

$$
\frac{1}{T_{2} *}=\frac{1}{T_{2}}+\frac{1}{T_{2 i n \mathrm{hom}}}>\frac{1}{T_{2}}
$$

or

$$
T_{2}>T_{2} *
$$

This implies that the measured value $T_{2}{ }^{*}$ is smaller than the intrinsic value $T_{2}$.

## 16. Physical meaning on the $180^{\circ}$ pulse

The $180^{\circ}$ pulse allows the $X-Y$ spin to re-phase to the value it would have had with perfect magnet. This is analogous to an egalitarian foot race for the kindergarten class, the race that makes everyone in the class a winner. Suppose that you made the following rules. Each kid would run in a straight line as fast as he or she could and when the teacher blows the whistle, every child would turn around and run back to the finish line at the same time. The $180^{\circ}$ pulse is like that whistle. The spins in the larger field get out of phase by $+\Delta \theta$ in a time $\tau$. After the $180^{\circ}$ pulse, they continue to precess faster than $M$ but at $2 \tau$ they return to the in-phase condition. The slower precessing spins do just the opposite, but again rephase after a time $2 \tau$. (Teachspin instruction manual).


Fig. 24 Consider the spins 1 (denoted by red arrow) and 2 (denoted by blue arrow) [spatially separated, that have slightly different frequencies $\left[(\Delta \omega)_{i}=\omega-\left(\omega_{0}\right)_{i}\right.$ for spins 1 and 2 , respectively $\left.(i=1,2)\right]$. After a $90^{\circ}$ pulse, the two spins are parallel, pointing along the $Y$ axis. After some time $\tau_{0}$, the two spins are no longer in phase. Now a $180^{\circ}$ pulse is applied at $\tau_{0}$. This leads to a rotation of $180^{\circ}$ of both spins about the $X$ axis. So that the phase difference is reversed. The spin 1 (denoted by red arrow), which is ahead of the spin 2 (denoted by blue arrow), is now behind. Another interval $\tau_{0}$, the two spins becomes back in phase.


Fig. $25 \quad$ CP sequence for the $180^{\circ}$ pulse. We assume that at $t=0$ the spin is directed along the $Y$ axis (at the point A). For $\Delta \omega<0$, the spin fans out in counter-clockwise from the point A to B. At $t=\tau$, we apply the $180^{\circ}$ pulse ( $X$ axis). The spin rotates through the points $\mathrm{B}, \mathrm{C}$, and D in clockwise. The point D is in the $X-Y$ plane. The spin starts to fan out from the point D to the point E , leading to the peak in the observed spin echo intensity $(t=$ $2 \tau)$. After that it further fans out from the point E to the point F . Then we again apply the $175^{\circ}$ pulse ( $X$ axis). The spin rotates through the points F , G , and H in clockwise. Note that the point $H$ is in the $X-Y$ plane. The spin fans out from the point H to the point E , leading to the peak of the spin echo intensity at $t=4 \tau$. This process is repeated.


Fig. 26 CP sequence for the $175^{\circ}$ pulse. What happens to the above behavior when the $175^{\circ}$ pulse is applied, instead of the $180^{\circ}$ pulse along the $X$ axis. We assume that at $t=0$ the spin is directed along the $Y$ axis (at the point A). The spin rotates in counter-clockwise from the point A to B . At $t=\tau$, we apply the $175^{\circ}$ pulse $X$ axis). The spin rotates through the points B, C, and D . The point D is not in the $X-Y$ plane and is slightly above the point $\mathrm{D}_{1}$ in the $X-Y$ plane. The spin starts to rotate from the point D to the point E just above the point $E_{1}$ in the $X-Y$ plane, leading to the peak in the observed spin echo intensity $(t=2 \tau)$, Aftr that it further rotates from the point E to the point F (just above the point $\mathrm{F}_{1}$ in the $X-Y$ plane). Then we again apply the $175^{\circ}$ pulse ( $X$ axis). The spin rotates through the points F , G , and H . Note that the point $H$ is below the $X-Y$ plane. The spin rotates from the point $A_{1}$ which is well below the point $A$, leading to the peak of the spin echo intensity at $t=4 \tau$. This process is repeated.

## 17. Example for the measurement of $\boldsymbol{T}_{\mathbf{2}}$ using TeachSpin (CPMG sequence)

The spin echo is created when the phases of the magnetic moments rephrase. When the moments are pushed down to the $X-Y$ plane, they begin to precess around the origin.

There moments have a slow and fast precession, so when the $180^{\circ}$ pulse flips the moments back around they will rephrase. They then create the echo that can be seen and measured. To do this experimentally, the pulse programmer is set to make a $90^{\circ}$ pulse, then an $180^{\circ}$ pulse. The distance between the echo and the second pulse is the same as the distance between the first and second pulses. The picture below shows the pulse sequence then the pulse.


Fig. 27
The spin echo method. $90^{\circ}$ pulse and $180^{\circ}$ pulse. The data are obtained from the Report of G. Parks (Binghamton University).

The measurement of $T_{2}$ can be made by changing the delay time measuring the height of the echo. The easier way of measuring $T_{2}$ is by creating a pulse train. This is known as a Carr-Purcell train. It is a $90^{\circ}$ pulse followed by at least twenty $180^{\circ}$ pulses. This creates an echo train, and the peaks of the echoes can be quickly measured and plotted. The picture below is a screen shot of the Carr-Purcell train. This gives a quick measurement of $T_{2}$, but it can be fairly in accurate. If the $180^{\circ}$ pulse is off by just a few degrees, after 20 pulses the train can be off by $60^{\circ}$ or more. Also when the B pulse width is changed slightly the whole decay changes a lot. To correct this problem Meiboom and Gill created a method of cancelling out the error that can accumulate using the Carr-Purcell train. The Meiboom-Gill train uses an $180^{\circ}$ pulse followed by a $-180^{\circ}$ pulse, this way the error will not be carried through out the entire train. This method creates less error in the answer and gives a more accurate measurement of $T_{2}$. The measurement is made the same way as the previous part. The picture below shows the train with the Meiboom-Gill correction. It is easy to see the echo train is smoother and thus more accurate.


Fig. 28
The spin echo method for the measurement of $T_{2}$ under the Carr-Purcell-Meiboon-Gill (CPMG) sequence. The data are obtained from the Report of J. Berger (Binghamton University).
18. Carr-Purcell-Meiboom-Gill (CPMG) sequence

(a) $90^{\circ}$ pulse ( $X$ axis)
(b)


Fig. 29

The Carr-Purcell-Meiboom-Gill (CPMG) sequence as shown above is derived from the Hahn spin-echo sequence. This sequence is equipped with a "built-in" procedure to self-correct pulse accuracy error. For a description of the first half of the sequence, look above in the Hahn echo section. In the picture above, only the first shift is shown but with field inhomogeneity. The letters $f$ and $s$ means that those spins affected by the inhomogeneity of the magnet precess faster and slower than the chemical shift respectively. If the first inversion pulse applied is shorter (e.g. $175^{\circ}$ ) than a $180^{\circ}$ pulse, a systematic error is introduced in the measurement. The echo will form above the XY plane (e.g. $5^{\circ}$ ) and therefore the signal will be smaller than expected. To correct that
error, instead of sampling immediately the echo, a third tau delay is introduced, during which, the magnetization evolve as before but slightly above the XY plane (see figure above). If the second inversion pulse, also shorter than a 180 degree pulse (e.g. 175 degree), is applied, as the spin is already above the plane, this shorter inversion pulse will put the spin exactly in the $X-Y$ plane. At the end of the last tau delay, the echo will form exactly in the $X Y$ plane self correcting the pulse error!


Fig. $30 \quad$ MG sequence for the ideal $180^{\circ}$ pulse. Just after the $90^{\circ}$ pulse $(t=0)$, the spins are directed along the $Y$ axis. Mainly due to the magnetic field inhomogenity, we assume that the spin (f) will rotates fast in counterclockwise and that the spin (s) rotates slowly. After a time $\tau(t=\tau)$, the $180^{\circ}$ pulse is applied along the ( $-Y$ axis), the spins rotates around the $Y$ axis. After that, both the spin (f) and spin (s) starts to rotates in counterclockwise and reach at the Y axis at the same time $(t=2 \tau)$. The observed spin echo intensity drastically increases. This process is repeated, leading to the peak of the intensity at $t=2 n \tau(n-1,2,3, \ldots)$.


Fig. 31 MG sequence for the $175^{\circ}$ pulse. What happens to the above behavior when the $175^{\circ}$ pulse is applied, instead of the $180^{\circ}$ pulse along the $Y$ axis. We assume that at $t=0$ the spin is directed along the $Y$ axis (at the point A). The spin rotates in counter-clockwise from the point A to B (path-1). At $t=\tau$, we apply the $175^{\circ}$ pulse ( $Y$ axis). The spin rotates through the points $\mathrm{B}, \mathrm{C}$, and D (paths 2 and 3 ). The point D is not in the $X-Y$ plane and is slightly above the point H . The spin starts to rotate from the point D to the point E (just above the point A ) leading to the peak in the observed spin echo intensity $(t=2 \tau)$ and further rotates from the point E to the point F (just above the point B). We again apply the $175^{\circ}$ pulse ( $Y$ axis). Then the spin rotates through the points $\mathrm{F}, \mathrm{G}$, and H . Note that the point $H$ is in the $X$ - $Y$ plane. The spin rotates from the point $H$ to the point A, leading to the peak of the spin echo intensity at $t=4 \tau$. This process (ML) is repeated.


Fig. 32
CPMG. Application of a $90^{\circ}$ pulse at $t=0$, followed by successive $180^{\circ}$ pulse ( $Y$-axis). The width of $180^{\circ}$ pulse is twice longer than that of $90^{\circ}$ pulse. The resultant exponential decay (dotted green line) of the echoes (free induction decay). The unit of the time axis (horizontal) is $t / \tau$. The peaks appear at $t / \tau=0,2,4,6, \ldots$.

## 19. Spin echo method: the measurement of $T_{1}$

We assume the initial condition such that $\zeta(0)=-1, \xi(0)=0, \eta(0)=0$. The resonance condition is also satisfied. Here $\omega_{1}=0\left(B_{1}=0\right.$ after the operation of $180^{\circ}$ pulse $)$.
or

$$
\frac{d \varsigma}{d t}=\frac{1}{T_{1}}(1-\varsigma), \quad \text { with } \zeta(0)=-1
$$

The solution is given by

$$
\varsigma(t)=1-2 \exp \left(-\frac{t}{T_{1}}\right)
$$



Fig. 33
The tangential line at $\mathrm{t}=0$ (blue line) for $\zeta(t)$ vs t becomes 1 at $t / T_{1}=1$.


Fig. 34
Time dependence of $M_{\mathrm{z}}$ to measure the longitudinal relaxation time $T_{1}$. We need to apply the $90^{\circ}$ pulse to measure the value of $M_{z}$.

After the nuclear magnetization has reached its equilibrium value $M_{0}$, a $180^{\circ}$ pulse gives to it the value $M_{z}=-M_{0}$. From then on the time-dependent value of $M_{z}$, resulting from the equation

$$
\frac{d M_{z}}{d t}=\frac{M_{0}-M_{z}}{T_{1}},
$$

is given by

$$
M_{z}=M_{0}\left(1-2 e^{-t / T_{1}}\right)
$$

and can be measured by the size of the signal following a $90^{\circ}$ pulse applied a time $t$ after the first $180^{\circ}$ pulse.
(i) To obtain the curve $M_{z}(t)$, one must wait a time several times $T_{1}$ after each $90^{\circ}$ pulse, before again applying a $180^{\circ}$ pulse and a $90^{\circ}$ pulse a time $t$ later (one-by one measurement)
(ii) First, application of the $180^{\circ}$ pulse inverts the macroscopic magnetization. During the inversion time, the macroscopic magnetization shrinks along the negative $z$ axis, eventually passes through $z=0$ and re-grows along the positive along the positive thermal equilibrium. Before the macroscopic magnetization is fully relaxed, the $90^{\circ}$ pulse flips the partially relaxed longitudinal magnetization into the transverse plane in order to measure the signal induced in an RF coil (sequential measurement).

## 20. Measurement of $\boldsymbol{T}_{1}$ (TeachSpin)

The relaxation time T1 is measured using the FID. Since no direct measurements can be made of the magnetization along the $z$ axis, so a series of pulses is used to indirectly measure the magnetization. First a $180^{\circ}$ pulse knocks the magnetization into the $-z$ axis, then a time later a $90^{\circ}$ pulse pushes the magnetization that are left in the $-z$ axis into the $x-y$ plane to be measured. The figure below shows the pulse sequence that allows the measurement of $T_{1}$. The $180^{\circ}$ pulse can be seen by a little blip on the scope, then $90^{\circ}$ pulse that is follows creating the FID. Note that the $180^{\circ}$ pulse should create no FID as is seen in the picture. In order to get a measurement of $T_{1}$ the delay time must be changed and the peak voltage of the decay is measured.


Fig. 35 The measurement of $T_{1} .180^{\circ}$ pulse (not clearly seen) and $90^{\circ}$ pulse. The data are obtained from the Report of G. Parks (Binghamton University).

## 21. CW (continuous wave method)

In the stationary state, $\dot{M}_{X}=\dot{M}_{Y}=\dot{M}_{Z}=0$

$$
\begin{aligned}
& \left(\begin{array}{ccc}
-\frac{1}{T_{2}} & \Delta \omega & 0 \\
-\Delta \omega & -\frac{1}{T_{2}} & -\omega_{1} \\
0 & \omega_{1} & -\frac{1}{T_{1}}
\end{array}\right)\left(\begin{array}{l}
M_{X} \\
M_{Y} \\
M_{Z}
\end{array}\right)=\left(\begin{array}{c}
0 \\
0 \\
-\frac{M_{0}}{T_{1}}
\end{array}\right) \\
& M_{X}=-\frac{M_{0} T_{2}^{2} \Delta \omega \omega_{1}}{1+T_{2}^{2}(\Delta \omega)^{2}+T_{1} T_{2} \omega_{1}^{2}} \\
& M_{X}=-\frac{M_{0} T_{2} \omega_{1}}{1+T_{2}^{2}(\Delta \omega)^{2}+T_{1} T_{2} \omega_{1}^{2}} \\
& M_{Z}=\frac{M_{0}+M_{0} T_{2}^{2}(\Delta \omega)^{2}}{1+T_{2}^{2}(\Delta \omega)^{2}+T_{1} T_{2} \omega_{1}^{2}} \\
& \left(\begin{array}{l}
m_{x} \\
m_{y} \\
m_{z}
\end{array}\right)=\left(\begin{array}{ccc}
\cos (\omega t) & -\sin (\omega t) & 0 \\
\sin (\omega t) & \cos (\omega t) & 0 \\
0 & 0 & 1
\end{array}\right)\left(\begin{array}{l}
M_{X} \\
M_{Y} \\
M_{Z}
\end{array}\right)
\end{aligned}
$$

Then we have

$$
\begin{aligned}
& m_{x}=-\frac{M_{0} T_{2} \omega_{1}\left[T_{2} \Delta \omega \cos (\omega t)-\sin (\omega t)\right]}{1+T_{2}^{2}(\Delta \omega)^{2}+T_{1} T_{2} \omega_{1}^{2}} \\
& m_{y}=-\frac{M_{0} T_{2} \omega_{1}\left[T_{2} \Delta \omega \sin (\omega t)+\cos (\omega t)\right]}{1+T_{2}^{2}(\Delta \omega)^{2}+T_{1} T_{2} \omega_{1}^{2}} \\
& m_{z}=\frac{M_{0}+M_{0} T_{2}^{2}(\Delta \omega)^{2}}{1+T_{2}^{2}(\Delta \omega)^{2}+T_{1} T_{2} \omega_{1}^{2}}
\end{aligned}
$$

We define the dispersion and absorption by

$$
m_{x}=\operatorname{Re}\left[\tilde{m}_{x} e^{i o t}\right],
$$

with

$$
\begin{aligned}
& \widetilde{m}_{x}=-i \frac{M_{0} T_{2} \omega_{1}\left(-i T_{2} \Delta \omega+1\right)}{1+T_{2}^{2}(\Delta \omega)^{2}+T_{1} T_{2} \omega_{1}{ }^{2}} \\
& B_{1 x}=\operatorname{Re}\left[B_{1}{ }^{\prime} e^{i \omega t}\right]
\end{aligned}
$$

with

$$
\begin{aligned}
& B_{1}^{\prime}=2 B_{1} \\
& \omega_{1}=-\gamma B_{1}
\end{aligned}
$$

The complex susceptibility is defined by

$$
\widetilde{m}_{x}=\left(\chi^{\prime}-i \chi^{\prime \prime}\right) B_{1}^{\prime},
$$

with the dispersion

$$
\chi^{\prime}=\frac{M_{0} T_{2} \gamma T_{2} \Delta \omega}{1+T_{2}^{2}(\Delta \omega)^{2}+T_{1} T_{2} \omega_{1}^{2}},
$$

and the absorption

$$
\chi^{\prime \prime}=\frac{M_{0} T_{2} \gamma}{1+T_{2}^{2}(\Delta \omega)^{2}+T_{1} T_{2} \omega_{1}^{2}}=\frac{M_{0} T_{2} \gamma}{1+T_{2}^{2}\left(\omega-\omega_{0}\right)^{2}+T_{1} T_{2} \omega_{1}^{2}}
$$

The absorption energy is

$$
\bar{P}=\frac{\omega B_{1}^{\prime 2}}{2} \chi^{\prime \prime}=2 \omega B_{1}^{2} \chi^{\prime \prime}
$$

((Note))
The energy generated by the system is

$$
\begin{aligned}
P(t) & =\operatorname{Re}\left(B_{1}{ }^{\prime} e^{i \omega t}\right) \frac{d}{d t} \operatorname{Re}\left[\widetilde{m}_{x} e^{i \omega t}\right] \\
& =\operatorname{Re}\left(B_{1}{ }^{\prime} e^{i \omega t}\right) \operatorname{Re}\left[(i \omega) \chi B_{1}{ }^{\prime} e^{i \omega t}\right] \\
& =\frac{1}{4} B_{1}{ }^{\prime 2}\left(e^{i \omega t}+e^{-i \omega t}\right)\left[i \omega \chi e^{i \omega t}-i \omega \chi^{*} e^{-i \omega t}\right] \\
& =\frac{1}{4} B_{1}{ }^{\prime 2}\left[i \omega \chi e^{2 i \omega t}-i \omega \chi^{*} e^{-2 i \omega t}+i \omega \chi-i \omega \chi^{*}\right]
\end{aligned}
$$

The time average over the period $2 \pi / \omega$ is

$$
\begin{aligned}
\bar{P} & =\frac{B_{1}^{\prime 2}}{4} i \omega\left(\chi-\chi^{*}\right) \\
& =\frac{B_{1}^{\prime 2}}{4} i \omega\left[\left(-2 i \chi^{\prime \prime}\right)\right] \\
& =\frac{\omega B_{1}^{\prime 2}}{2} \chi^{\prime \prime}
\end{aligned}
$$

The frequency dependence of the dispersion and absorption is schematically shown in the following figure.


Fig. $36 \quad \chi^{\prime}$ vs $\omega$ and $\chi^{\prime \prime}$ vs $\omega . \omega_{0}=-10$. The values of $M_{0}, T_{1}, T_{2}, \omega_{1}, \gamma$, and so on are appropriately chosen.

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## APPENDIX

## A1. APPARATUS (TeachSpin)

The apparatus that is used in this experiment is supplied by TeachSpin. There are three panels used, the receiver, the pulse programmer, and the oscillator amplifier mixer.


Fig. 37 TeachSpin apparatus for the pulsed NMR.
These three things work together with the probe to create NMR conditions. Above is a picture of the control panel used in the experiment. By following the TeachSpin manual it is easy to learn what each of these input, outputs, and switches do. The figure below is a block diagram of how the circuit is set up. What is happening is pretty self explanatory.


Fig. 38 TeachSpin. A block diagram of the pulsed NMR apparatus used in the Advanced laboratory.

The only other set up that is needed to start running the experiment is to prepare the sample. The sample used is mineral oil, it has a fast relaxation time and much is known about it. The sample is placed in a small vile that can fit into the carriage, which holds the probe circuitry. Placing only about 5 mm of sample into the vile is crucial for producing
accurate data. This is because if there is too much in the vile the magnetic field will not be homogeneous throughout, and fringing effects will cause error. The probe can also only make measurements when the spins are in the $X-Y$ plane. This is important to note because the only way to take data is if the atoms are in the $X-Y$ plane, so at least one $90^{\circ}$ pulse has to be used.
For the mineral oil, we use $\quad B_{0}=3.55888 \mathrm{kOe}$ and $f_{0}=15.1516 \mathrm{MHz}$.

## A2. RESULTS

For the experiment of the mineral oil (TeachSpin) we use the following pulse width for the $90^{\circ}$ and $180^{\circ}$ pulse.

$$
\begin{aligned}
& \gamma B_{0}=\omega=2 \pi(15 \mathrm{MHz}) \\
& \gamma B_{1} \tau=\phi \\
& t_{w}=\frac{B_{0}}{B 1} \frac{1}{\omega} \phi=\frac{3000 O e}{12 O e} \frac{\phi}{2 \pi(15 \mathrm{MHz})}=2.653 \phi(\mu s)
\end{aligned}
$$

(1) $90^{\circ}$ pulse

$$
t_{w}=2.653 \cdot \frac{\pi}{2}=4(\mu s) \quad \text { (typically) }
$$

(2) $180^{\circ}$ pulse

$$
t_{w}=2.653 \cdot \pi=8(\mu s) \quad \text { (typically) }
$$

## (1) Mineral oil

The values of $T_{1}$ and $T_{2}$ for mineral oil obtained in the Advanced laboratory (Binghamton University)

$$
\begin{array}{lll}
T_{1}=25.9 \pm 0.1 \mathrm{~ms} & T_{2}=12.1 \pm 0.1 \mathrm{~ms} & \text { (Michael Schauber, Spring 2006) } \\
T_{1}=29.4 \pm 0.3 \mathrm{~ms} & T_{2}=21.3 \pm 0.7 \mathrm{~ms} & \text { (Jeffrey Burger, Spring 2007) } \\
T_{1}=24.0 \pm 2.4 \mathrm{~ms} & T_{2}=19.4 \pm 0.9 \mathrm{~ms} & \text { (Gregory Parks, Spring 2008) } \\
T_{1}=26.9 \pm 0.4 \mathrm{~ms} & T_{2}=15.4 \pm 0.3 \mathrm{~ms} & \text { (Yong Han, Spring 2010) }
\end{array}
$$

- Free Induction Decay Amplitude (V)


Fig. 39 Least squares fit of the data (voltage vs time (ms) for the $T_{1}$ measurement. The data are obtained from the Report of Yong Han (Binghamton University).

$$
-0 \text { Spin Echo (M) }
$$



Fig. 40 Least squares fit of the data [voltage vs time (ms) for the $T_{2}$ masurement]. The data are obtained from the Report of Yong Han (Binghamton University). $T_{2}=15.4 \pm 0.3 \mathrm{~ms}$.

## (2) Water solution of $\mathrm{CuSO}_{4}$

$\mathrm{H}_{2} \mathrm{O}$ with $\mathrm{CuSO}_{4}$ is a good choice because $T_{1}$ is shortened to a few ms by the paramagnetic $\mathrm{Cu}^{+}$ions. In the Advanced laboratory, copper sulphate solutions with various concentrations are used. The solution's concentration could be calculated by the following equation:

$$
\text { concentration }=\frac{m_{\mathrm{CuSO}_{4}}}{m_{\mathrm{CuSO}_{4}}+m_{\mathrm{H}_{2} \mathrm{O}}} \text {. }
$$

For each solution the same procedures were followed to determine spin-lattice relaxation time and spin-spin relaxation time. The results were then plotted against the concentration.

- Spin-lattice relaxation time (ms)


Fig. 41 The concentration dependence of $T_{1}$ (the spin-lattice relaxation time). The data are obtained from the Report of Yong Han (Binghamton University).


Fig. 42 The concentration dependence of $T_{2}$. The data are obtained from the Report of Yong Han (Binghamton University).

We use water solution of $\mathrm{CuSO}_{4}$, where paramagnetic ions $\mathrm{Cu}^{2+}$ ions with large electronic magnetic moment profoundly effect the relaxation times of the protons in water. Such an effect can be measured over a wide range of concentration. It can be seen that the trend is an exponential decay curve, with both $T_{1}$ and $T_{2}$ decreasing as the concentration of $\mathrm{CuSO}_{4}$ increases.

