Quantum mechanics on Nuclear Magnetic Resonance with the use of Mathematica

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The fundamental of nuclear magnetic resonance (NMR), mainly rf spin echo method is discussed, based on the quantum mechanics. The expectation values of nuclear spin operators (spin 1/2) over the state vectors are calculated using the Mathematica. The state vector $\left|\psi(t)\right\rangle$ in the laboratory reference frame is related to the state vector $\left|\phi(t)\right\rangle$ in the rotational reference frame through the rotation operator with spin 1/2 angular momentum (in clockwise) as

$$\left|\psi(t)\right\rangle = \exp(\frac{i}{2}\omega t\hat{\sigma}_z)\left|\phi(t)\right\rangle .$$

in our Model (II). The time dependence of $\left\langle\psi(t)\right|\hat{I}_i\left|\psi(t)\right\rangle$ and $\left\langle\phi(t)\right|\hat{I}_i\left|\phi(t)\right\rangle$ will be examined in detail for the rf spin echo method.

Here, we note that there are many standard textbooks on NMR, including the books on *Principles of Magnetic Resonance* (C.P. Slichter) and *Spin Dynamics* (by M.H. Levitt). Nevertheless, we think that the present note may be useful to understanding the principle of MRI (magnetic resonance image) from a view-point of quantum mechanics. In MRI, tissue can be characterized by two different relaxation times – T_1 and T_2. T_1 (longitudinal relaxation time) is the time constant which determines the rate at which excited protons return to equilibrium. It is a measure of the time taken for spinning protons to realign with the external magnetic field. T_2 (transverse relaxation time) is the time constant which determines the rate at which excited protons reach equilibrium or go out of phase with each other. It is a measure of the time taken for spinning protons to lose phase coherence among the nuclei spinning perpendicular to the main field.

Prof. Isidor Isaac Rabi

Isidor Isaac Rabi (July 29, 1898– January 11, 1988) was an American physicist, who won the Nobel Prize in Physics in 1944 for his discovery of nuclear magnetic resonance, which is used in magnetic resonance imaging. He was also one of the first scientists in the United States to work on the cavity magnetron, which is used in microwave radar and microwave ovens.
https://en.wikipedia.org/wiki/Isidor_Isaac_Rabi

1. Nuclear magnetic resonance experiment

In the NMR measurement, the stationary magnetic field $\mathbf{B}_0$ is applied along the *z* axis. The direction of the axis for the solenoidal rf coil is perpendicular to the z axis. In the present case, the rf-field is applied along the *x* axis. The sample (with proton) is positioned in a stationary magnetic field $\mathbf{B}_0$ inside or next to the rf coil. The rf coil is a part of an rf oscillator tuned to the angular frequency ω.

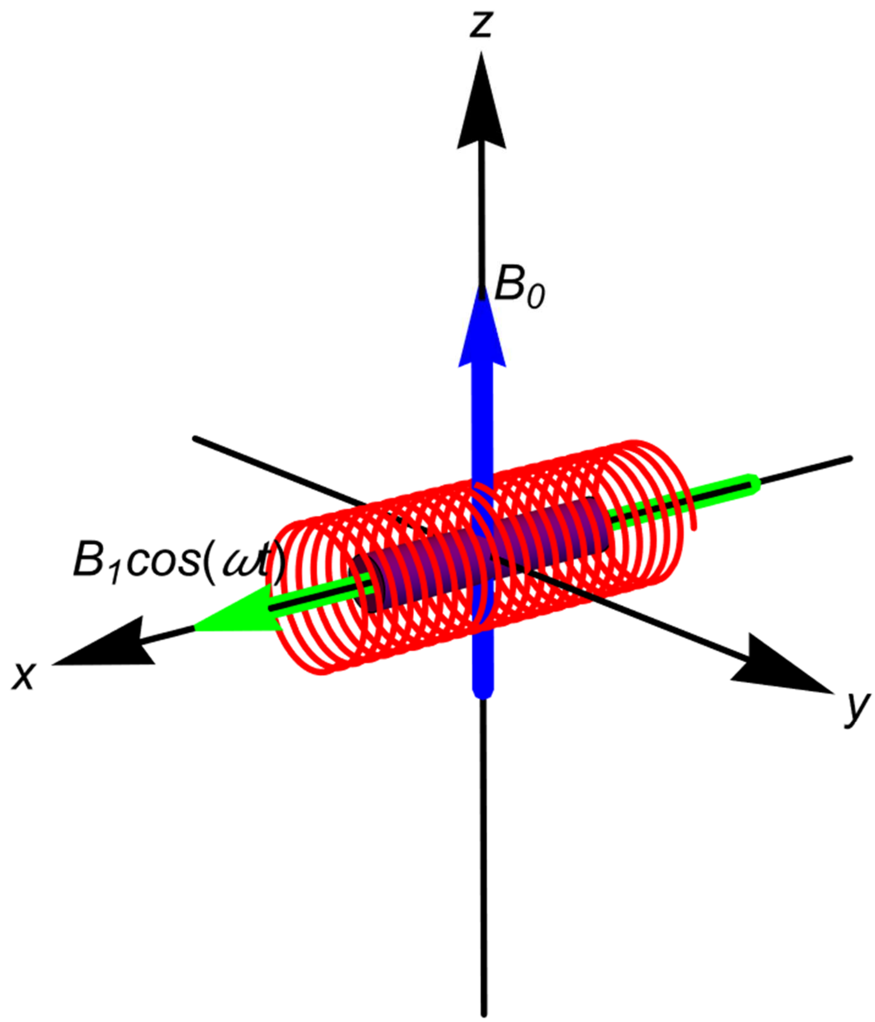


Fig.1 Schematic diagram of typical nuclear magnetic resonance. The direction of axis of the rf coil (rf-magnetic field) is along the *x* axis. The stationary magnetic field is directed along the *z* axis.

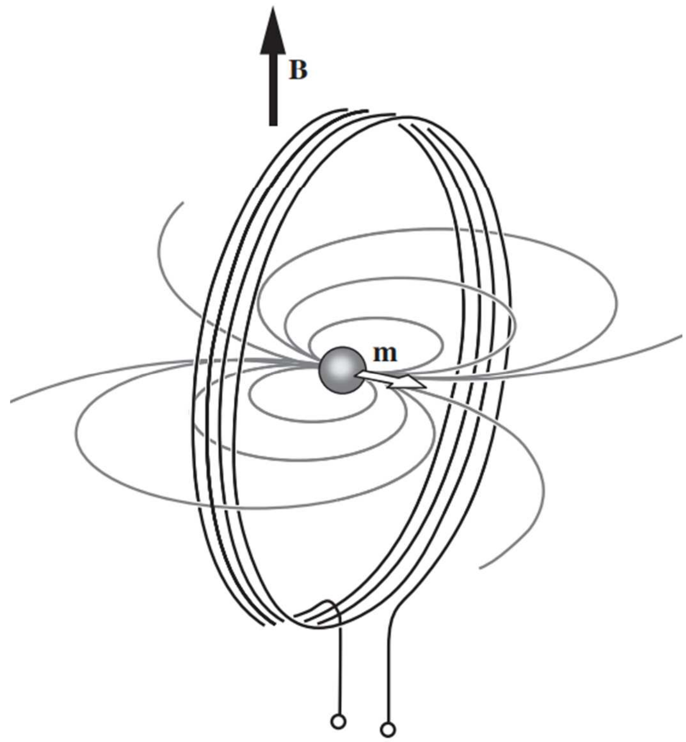


Fig.2 A precessing magnetic moment at the center of a coil causes a periodic change in the flux through the coil, inducing an alternating electromotive force in the coil. Note that the flux from the magnetic moment ***m*** that links the coil is that which loops around outside it (**Purcell and Morin**). $B = B_0$

2. Magnetic moment of proton

Like electron and neutron, proton has a magnetic moment

$$\mu_{proton} = \frac{2}{\hbar}\mu_P I = \gamma_p I \ .$$

where

$$\mu_p = 2.79284734462\mu_N \ ,$$

and I is the nuclear spin angular momentum ($\hbar/2$). The nuclear magneton is

$$\mu_N = \frac{e\hbar}{2m_p c} = 5.050783699 \times 10^{-24} \text{ emu} \qquad \text{(erg/G)}.$$

where m_p is the mass of proton. The gyromagnetic ratio of proton is

$$\gamma_p = \frac{2}{\hbar}\mu_P = 2.675222005 \times 10^4 \text{ rad/(s G)}.$$

Note that proton NMR frequency *f* is related to the magnetic field B_0 as

$$f(MHz) = \frac{\gamma_p B}{2\pi} = 42.5775\, B(\mathrm{T}).$$

where 1 T = 10^4 Oe = 10^4 Gauss.

((**Note**)) **Magnetic moment of neutron** (**comparison**)

We note that the magnetic moment of neutron is given by

$$\mu_{neutron} = \frac{2}{\hbar}\mu_n I = \gamma_n I$$

Note that the values of μ_n and γ_n are negative,

$$\begin{aligned}\mu_n &= -1.91304272(45)\mu_N \\ &= -9.6623647(23) \times 10^{-24} \text{ emu}\end{aligned}$$

and

$$\gamma_n = \frac{2}{\hbar}\mu_n = -1.83247171(43) \times 10^4 \text{ rad/(s G)}$$

3. Model (I) for NMR

First, we consider that the static magnetic field and the rf (radio frequency) field are applied to the magnetic moment of proton as shown in **Fig.3** The corresponding Hamiltonian is given by

$$\hat{H}_I = -\mu_p \hat{\boldsymbol{\sigma}} \cdot [B_0 e_z + B_1 \cos(\omega t)\mathbf{e}_x]$$
$$= -\mu_p [B_0 \hat{\sigma}_z + B_1 \cos(\omega t)\hat{\sigma}_x]$$

We use the Pauli spin operators.

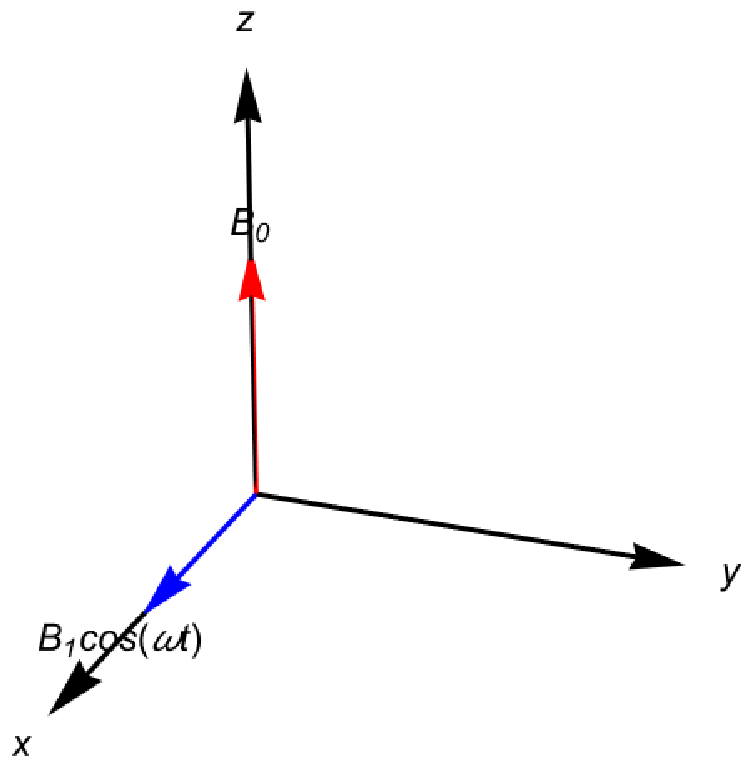


Fig.3 Magnetic field directions. Stationary magnetic field along the z axis and rf magnetic field with angular frequency ω along the x axis. $\mathbf{B} = B_0 \mathbf{e}_z + B_1 \cos(\omega t)\mathbf{e}_x$.

In the absence of any rf field, we have the Hamiltonian

$$\hat{H}_I^{(0)} = -\mu_p B_0 \hat{\sigma}_z .$$

The eigenstate and energy eigenvalue of $\hat{H}_I^{(0)}$ is

$$\hat{H}_I^{(0)} \left|+z\right\rangle = -\mu_p B_0 \hat{\sigma}_z \left|+z\right\rangle = -\mu_p B_0 \left|+z\right\rangle ,$$

$$\hat{H}_I^{(0)}\left|-z\right\rangle = -\mu_p B_0 \hat{\sigma}_z \left|-z\right\rangle = \mu_p B_0 \left|-z\right\rangle .$$

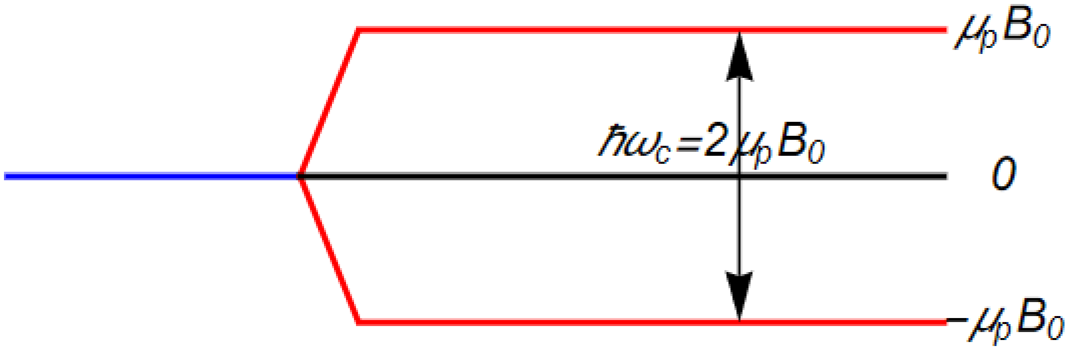


Fig.4 Energy diagram with Zeeman splitting. The lower energy level: $-\mu_p B_0$ (state $\left|+z\right\rangle$. The upper energy level: $\mu_p B_0$ (state $\left|-z\right\rangle$. The energy separation is $2\mu_p B_0 = \hbar\omega_c$

The energy separation is

$$\hbar\omega_c = 2\mu_p B_0 = \hbar\gamma_p B_0 .$$

We now start with the Hamiltonian $\hat{H}_1$,

$$\begin{aligned}
\hat{H}_I &= \hat{H}_I^{(0)} + \hat{H}_I^{(1)} \\
&= -\mu_p B_0[\hat{\sigma}_z + \frac{B_1}{B_0}\cos(\omega t)\hat{\sigma}_x] \\
&= -\frac{1}{2}\hbar\omega_c[\hat{\sigma}_z + \frac{B_1}{B_0}\cos(\omega t)\hat{\sigma}_x] \\
&= -\frac{1}{2}\hbar[\omega_c\hat{\sigma}_z + \omega_1\cos(\omega t)\hat{\sigma}_x]
\end{aligned}$$

where B_0 is the magnitude of the static magnetic field along the z axis, and B_1 is the amplitude of rf magnetic field (along the x axis), and

$$\hat{H}_I = \hat{H}_I^{(0)} + \hat{H}_I^{(1)},$$

$$\hat{H}_I^{(0)} = -\frac{1}{2}\hbar\omega_c\hat{\sigma}_z, \qquad H_I^{(1)} = -\mu_p B_1 \cos(\omega t)\hat{\sigma}_x,$$

For convenience, we newly introduce the notation of ω_1 as

$$\omega_1 = \omega_c \frac{B_1}{B_0}.$$

The time-dependent Schrödinger equation can be written as

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}_I|\psi(t)\rangle,$$

with

$$|\psi(t)\rangle = A_+(t)|+z\rangle + A_-(t)|-z\rangle = \begin{pmatrix} A_+(t) \\ A_-(t) \end{pmatrix},$$

Here, we assume that

$$|\psi(t)\rangle = \exp(-\frac{i}{\hbar}\hat{H}_I^{(0)}t)|\phi(t)\rangle = \exp(\frac{i}{2}\omega_c t\hat{\sigma}_z)|\phi(t)\rangle \qquad \text{(Dirac picture)}$$

with

$$|\phi(t)\rangle = a_+(t)|+z\rangle + a_-(t)|-z\rangle = \begin{pmatrix} a_+(t) \\ a_-(t) \end{pmatrix},$$

and

$$|\psi(t=0)\rangle = |\phi(t=0)\rangle.$$

Note that $\exp(\frac{i}{2}\omega_c t\hat{\sigma}_z)$ is the rotation operator (with angle $\omega_c t$ in clockwise around the z axis). Then, the Schrödinger equation for $|\phi(t)\rangle$ can be obtained as follows.

$$i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle = i\hbar[\frac{i}{2}\omega_c\hat{\sigma}_z\exp(\frac{i}{2}\omega_c t\hat{\sigma}_z)\left|\phi(t)\right\rangle + \exp(\frac{i}{2}\omega_c t\hat{\sigma}_z)\frac{\partial}{\partial t}\left|\phi(t)\right\rangle$$

$$= -\frac{1}{2}\hbar[\omega_c\hat{\sigma}_z + \omega_1\cos(\omega t)\hat{\sigma}_x]\exp(\frac{i}{2}\omega_c t\hat{\sigma}_z)\left|\phi(t)\right\rangle$$

or

$$i\hbar\exp(\frac{i}{2}\omega_c t\hat{\sigma}_z)\frac{\partial}{\partial t}\left|\phi(t)\right\rangle = -\frac{1}{2}\hbar(\omega_1\cos(\omega t)\hat{\sigma}_x\exp(\frac{i}{2}\omega_c t\hat{\sigma}_z)\left|\phi(t)\right\rangle,$$

or

$$i\hbar\frac{\partial}{\partial t}\left|\phi(t)\right\rangle = -\frac{1}{2}\hbar\omega_1\cos(\omega t)[\exp(-\frac{i}{2}\omega_c t\hat{\sigma}_z)\hat{\sigma}_x\exp(\frac{i}{2}\omega_c t\hat{\sigma}_z)]\left|\phi(t)\right\rangle$$

For simplicity, we use $\alpha = \omega_c t$. Then, we have

$$\exp(-\frac{i}{2}\alpha\hat{\sigma}_z)\hat{\sigma}_x\exp(\frac{i}{2}\alpha\hat{\sigma}_z)] = \begin{pmatrix} e^{-i\alpha/2} & 0 \\ 0 & e^{i\alpha/2} \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} e^{i\alpha/2} & 0 \\ 0 & e^{-i\alpha/2} \end{pmatrix}$$

$$= \begin{pmatrix} 0 & e^{-i\alpha} \\ e^{i\alpha} & 0 \end{pmatrix}$$

under the basis of $\{\left|+z\right\rangle, \left|-z\right\rangle\}$. Thus, we have

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix} a_+(t) \\ a_-(t) \end{pmatrix} = -\frac{1}{2}\hbar\omega_1\cos(\omega t)\begin{pmatrix} 0 & e^{-i\omega_c t} \\ e^{t\omega_c t} & 0 \end{pmatrix}\begin{pmatrix} a_+(t) \\ a_-(t) \end{pmatrix}.$$

((**Rotating wave approximation**))

Here we use the rotating wave approximation. We neglect the high frequency term $e^{\pm i(\omega+\omega_c)t}$. is neglected, while the low frequency tern $e^{\pm i(\omega-\omega_c)t}$ is kept. Thus, we have

$$i\hbar\dot{a}_+(t) = -\frac{1}{2}\hbar\omega_1\cos(\omega t)e^{-it\omega_c}a_-(t)$$

$$= -\frac{1}{2}\hbar\omega_1[\frac{e^{i(\omega-\omega_c)t} + e^{-i(\omega+\omega_c)t}}{2}]a_-(t)$$

$$\simeq -\frac{1}{4}\hbar\omega_1 e^{i(\omega-\omega_c)t}a_-(t)$$

$$i\hbar\dot{a}_-(t) = -\frac{1}{2}\hbar\omega_1\cos(\omega t)e^{it\omega_c}a_+(t)$$
$$= -\frac{1}{2}\hbar\omega_1[\frac{e^{-i(\omega-\omega_0)t}+e^{i(\omega+\omega_0)t}}{2}]a_+(t)$$
$$\simeq -\frac{1}{4}\hbar\omega_1 e^{-i(\omega-\omega_0)t}a_+(t)$$

(i) The resonance ($\omega = \omega_c$)

First, we consider the case when $\omega = \omega_c$

$$\dot{a}_+(t) \simeq \frac{1}{4}i\omega_1 a_-(t)$$

$$\dot{a}_-(t) = \frac{1}{4}i\omega_1 a_+(t)$$

From the above two equations, we get

$$\ddot{a}_+(t) + (\frac{1}{4}\omega_1)^2 a_+(t) = 0 \qquad \text{(simple harmonics)}$$

The solution is as follows.

$$a_+(t) = C_1\cos(\frac{\omega_1}{4}t) + C_2\sin(\frac{\omega_1}{4}t)$$

$$a_-(t) = \frac{4}{i\omega_1}\dot{a}_+(t) = i[C_1\sin(\frac{\omega_1}{4}t) - C_2\cos(\frac{\omega_1}{4}t)]$$

The initial conditions [$A_+(0) = a_+(0) = 1$ and $A_-(0) = a_-(0) = 0$] lead to

$$C_1 = 1, \qquad C_2 = 0$$

Thus, we have

$$a_+(t) = \cos(\frac{\omega_1}{4}t), \qquad a_+(t) = i\sin(\frac{\omega_1}{4}t)$$

with the corresponding probability as

$$P_+(t) = |A_+(t)|^2 = \cos^2(\frac{\omega_1}{4}t),$$

$$P_-(t) = |A_-(t)|^2 = \sin^2(\frac{\omega_1}{4}t).$$

Note that

$$A_+(t) = \langle +z|\psi(t)\rangle = \langle +z|e^{i\omega_c t\hat{\sigma}_z}|\phi(t)\rangle = e^{i\omega_c t}\langle +z|\phi(t)\rangle = e^{i\omega_c t}a_+(t).$$

$$A_-(t) = \langle -z|\psi(t)\rangle = \langle -z|e^{i\omega_c t\hat{\sigma}_z}|\phi(t)\rangle = e^{-i\omega_c t}\langle -z|\phi(t)\rangle = e^{-i\omega_c t}a_-(t).$$

(ii) The general case ($\omega \simeq \omega_c$); ω is very close to ω_c

We now solve the general case for the second order differential equation

$$\dot{a}_+(t) = \frac{1}{4}i\omega_1 e^{i(\omega-\omega_c)t}a_-(t),$$

$$\dot{a}_-(t) = \frac{1}{4}i\omega_1 e^{-i(\omega-\omega_c)t}a_+(t),$$

with the initial condition, $A_+(0) = 1$, $A_-(0) = 0$

$$a_+(0) = 1, \qquad a_-(0) = 0$$

$$\dot{a}_+(0) = \frac{1}{4}i\omega_1 a_-(0) = 0, \qquad \dot{a}_-(0) = \frac{1}{4}i\omega_1 a_+(0) = \frac{1}{4}i\omega_1$$

We get the second order differential equation

$$\ddot{a}_+(t) = \frac{1}{4} i\omega_1 i(\omega-\omega_c) e^{i(\omega-\omega_c)t} a_-(t) + \frac{1}{4} i\omega_1 e^{i(\omega-\omega_c)t} \dot{a}_-(t)$$
$$= \frac{1}{4} i\omega_1 i(\omega-\omega_c) e^{i(\omega-\omega_0)t} \frac{4}{i\omega_1} e^{-i(\omega-\omega_c)t} \dot{a}_+(t) + \frac{1}{4} i\omega_1 e^{i(\omega-\omega_c)t} \frac{1}{4} i\omega_1 e^{-i(\omega-\omega_c)t} a_+(t)$$
$$= i(\omega-\omega_c)\dot{a}_+(t) - (\frac{1}{4}\omega_1)^2 a_+(t)$$

or

$$\ddot{a}_+(t) - i(\omega-\omega_c)\dot{a}_+(t) + (\frac{1}{4}\omega_1)^2 a_+(t) = 0.$$

The solution is as follows. Ω is the Rabi angular frequency,

$$\Omega = \sqrt{(\Delta\omega)^2 + \frac{\omega_1^2}{4}}, \qquad \text{with} \qquad \Delta\omega = \omega - \omega_c$$

$$P_+(t) = |a_+(t)|^2$$
$$= \cos^2\left(\frac{\Omega t}{2}\right) + \frac{(\Delta\omega)^2}{\Omega^2}\sin^2\left(\frac{\Omega t}{2}\right)$$
$$= 1 - \frac{\Omega^2 - (\Delta\omega)^2}{\Omega^2}\sin^2\left(\frac{\Omega t}{2}\right) \qquad \text{(the lower energy level)}$$
$$= 1 - \frac{\omega_1^2}{4\Omega^2}\sin^2\left(\frac{\Omega t}{2}\right)$$

$$P_-(t) = |a_-(t)|^2 = \frac{\omega_1^2}{4\Omega^2}\sin^2\left(\frac{\Omega t}{2}\right) \qquad \text{(the upper energy level)}$$

We solve the differential equation with initial conditions by using the Mathematica.

((**Mathematica-1**))

The solution of the model-1 problem using Mathematica

```
Clear["Global`*"];
expr_* := expr /. Complex[a_, b_] :> Complex[a, -b];
rule1 = {Sqrt[-4 (ω - ωc)^2 - ω1^2] → (ⅈ 2 Ω),
   1/Sqrt[-4 (ω - ωc)^2 - ω1^2] → -ⅈ/(2 Ω)};
rule2 = {ω1^2 → 4 Ω^2 - 4 (ω - ωc)^2};
g1 = x''[t] - ⅈ (ω - ωc) x'[t] + (1/4 ω1)^2 x[t] == 0;
g2 = DSolve[{g1, x[0] == 1, x'[0] == 0}, x[t], t] //. rule1 //.
    rule2 // FullSimplify;
x1[t_] := x[t] /. g2
P1 = x1[t]* x1[t] // FullSimplify
```

$$\left\{\mathrm{Cos}\left[\frac{t\,\Omega}{2}\right]^2+\frac{(\omega-\omega c)^2\,\mathrm{Sin}\left[\frac{t\,\Omega}{2}\right]^2}{\Omega^2}\right\}$$

```
P2 = (1 - P1) // Simplify
```

$$\left\{\frac{\left(-\omega^2+\Omega^2+2\,\omega\,\omega c-\omega c^2\right)\,\mathrm{Sin}\left[\frac{t\,\Omega}{2}\right]^2}{\Omega^2}\right\}$$

4. Method (II) with the use of clockwise rotation of rf magnetic field

Here, we show that the physics of the model-II is equivalent to that of the model-I. We note that the Larmor pression of proton is in counterclockwise (CW).

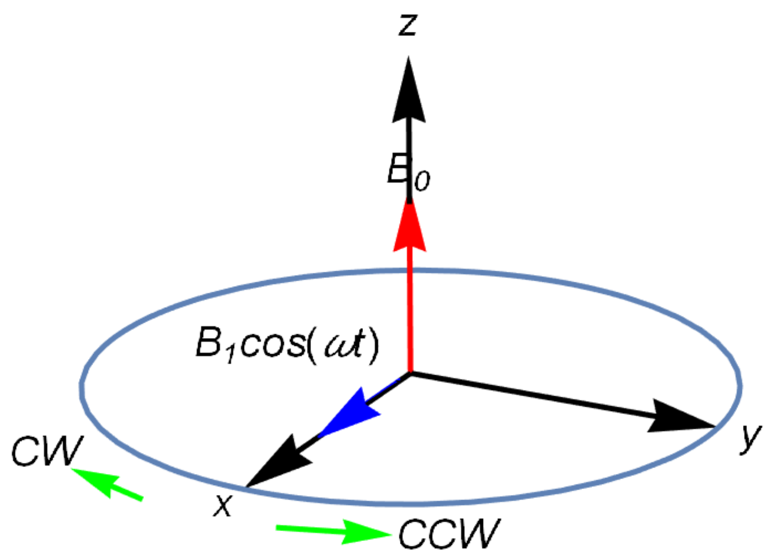


Fig.5 In classical model, The magnetic moment of proton undergoes a clock-wise (CW) Larmor precession with the angular frequency around the z axis in clockwise. The rf magnetic field applied along the x axis consists of CW and CCW rotations of rf magnetic fields. Here we choose the CW rotation of rf magnetic field. The rf field is expressed by $B_1\cos(\omega t)\mathbf{e}_x$

The rf magnetic field applied along the x axis can be written as the combination of CW rotation and CCW rotation,

$$B_1\cos(\omega t)\mathbf{e}_x = \frac{1}{2}[B_1\cos(\omega t)\mathbf{e}_x + B_1\sin(\omega t)\mathbf{e}_y] + \frac{1}{2}[B_1\cos(\omega t)\mathbf{e}_x - B_1\sin(\omega t)\mathbf{e}_y]$$

The first term and second term denote the CCW (rotation) and CW (rotation), respectively.

The CCW rotation of rf magnetic field is neglected, while the CW rotation of rf magnetic field is kept,

$$\frac{1}{2}[B_2\cos(\omega t)\mathbf{e}_x - B_2\sin(\omega t)\mathbf{e}_y],$$

since the magnetic moment of proton undergoes a precession around the z axis in clockwise (CW). We now consider the new Hamiltonian (Zeeman energy) $\hat{H}_2$ (as a model-2), given by

$$\begin{aligned}\hat{H}_{II} &= -\mu_p \hat{\boldsymbol{\sigma}} \cdot [B_0 \mathbf{e}_z + \frac{1}{2} B_1 \cos(\omega t)\mathbf{e}_x - \frac{1}{2} B_1 \sin(\omega t)\mathbf{e}_y] \\ &= -\mu_p B_0 \hat{\sigma}_z - \frac{1}{2}\mu_p B_1 \cos(\omega t)\hat{\sigma}_x + \frac{1}{2}\mu_p B_1 \sin(\omega t)\hat{\sigma}_y\end{aligned}$$

For simplicity, we define the parameters,

$$\mu_p B_0 = \frac{\hbar}{2}\omega_c, \qquad \omega_1 = \omega_c \frac{B_1}{B_0}.$$

Thus, we get the matrix of $\hat{H}_{II}$ (2x2 matrix),

$$\begin{aligned}\hat{H}_{II} &= -\frac{1}{2}\hbar\omega_c \hat{\sigma}_z - \frac{\hbar}{4}\omega_1 \cos(\omega t)\hat{\sigma}_x + \frac{\hbar}{4}\omega_1 \sin(\omega t)\hat{\sigma}_y \\ &= -\frac{1}{2}\hbar[-(\omega - \omega_c)\hat{\sigma}_z + \omega\hat{\sigma}_z] - \frac{\hbar}{4}\omega_1 \cos(\omega t)\hat{\sigma}_x + \frac{\hbar}{4}\omega_1 \sin(\omega t)\hat{\sigma}_y \\ &= -\frac{1}{2}\hbar\omega\hat{\sigma}_z + [\frac{1}{2}\hbar\Delta\omega\hat{\sigma}_z - \frac{\hbar}{4}\omega_1 \cos(\omega t)\hat{\sigma}_x + \frac{\hbar}{4}\omega_1 \sin(\omega t)\hat{\sigma}_y] \\ &= \hat{H}_{II}^{(0)} + \hat{H}_{II}^{(1)}\end{aligned}$$

under the basis of $\{\left|+z\right\rangle$, and $\left|-z\right\rangle\}$. Note that

$$\hat{H}_{II}^{(0)} = -\frac{1}{2}\hbar\omega\hat{\sigma}_z,$$

and

$$\hat{H}_{II}{}^{(1)} = \frac{1}{2}\hbar[\Delta\omega\hat{\sigma}_z - \frac{\omega_1}{2}\cos(\omega t)\hat{\sigma}_x + \frac{\omega_1}{2}\sin(\omega t)\hat{\sigma}_y]$$
$$= \frac{1}{2}\hbar\begin{pmatrix} \Delta\omega & -\frac{\omega_1}{2}e^{i\omega t} \\ -\frac{\omega_1}{2}e^{-i\omega t} & -\Delta\omega \end{pmatrix}$$

We now consider the Schrödinger equation for $\left|\phi(t)\right\rangle$

$$i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle = \hat{H}_{II}\left|\psi(t)\right\rangle, \qquad \text{(Schrödinger picture)}$$

with the time-dependent eigenket $\left|\psi(t)\right\rangle$,

$$\left|\psi(t)\right\rangle = A_+(t)\left|+z\right\rangle + A_-(t)\left|-z\right\rangle = \begin{pmatrix} A_+(t) \\ A_-(t) \end{pmatrix}.$$

We introduce a new ket $\left|\phi(t)\right\rangle$,

$$\left|\psi(t)\right\rangle = \exp(-\frac{i}{\hbar}\hat{H}_{II}{}^{(0)}t)\left|\phi(t)\right\rangle = \exp(\frac{i}{2}\omega t\hat{\sigma}_z)\left|\phi(t)\right\rangle$$

Note that $\exp(-\frac{i}{\hbar}\hat{H}_{II}{}^{(0)}t) = \exp(\frac{i}{2}\omega t\hat{\sigma}_z)$ is the rotation operator around the *z* axis by the angle ωt in clockwise. The new state $\left|\phi(t)\right\rangle$ is given by

$$\left|\phi(t)\right\rangle = a_+(t)\left|+z\right\rangle + a_-(t)\left|-z\right\rangle = \begin{pmatrix} a_+(t) \\ a_-(t) \end{pmatrix},$$

with the initial condition,

$$\left|\psi(t=0)\right\rangle = \left|\phi(t=0)\right\rangle.$$

Note that

$$\begin{pmatrix} A_+(t) \\ A_-(t) \end{pmatrix} = \begin{pmatrix} e^{i\omega t/2} & 0 \\ 0 & e^{-i\omega t/2} \end{pmatrix} \begin{pmatrix} a_+(t) \\ a_-(t) \end{pmatrix} = \begin{pmatrix} e^{i\omega t/2} a_+(t) \\ e^{-i\omega t/2} a_-(t) \end{pmatrix}$$

and

$$A_+(0) = a_+(0), \qquad A_-(0) = a_-(0)$$

Then, the Schrödinger equation for the state $|\phi(t)\rangle$ is obtained as follows.

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle &= i\hbar [\frac{i}{2} \omega \hat{\sigma}_z \exp(\frac{i}{2} \omega t \hat{\sigma}_z) |\phi(t)\rangle + \exp(\frac{i}{2} \omega t \hat{\sigma}_z) \frac{\partial}{\partial t} |\phi(t)\rangle \\ &= [-\frac{1}{2} \hbar \omega_c \hat{\sigma}_z - \frac{\hbar}{4} \omega_1 \cos(\omega t) \hat{\sigma}_x + \frac{\hbar}{4} \omega_1 \sin \omega t \hat{\sigma}_y] \exp(\frac{i}{2} \omega t \hat{\sigma}_z) |\phi(t)\rangle \end{aligned}$$

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\phi(t)\rangle &= \exp(-\frac{i}{2} \omega t \hat{\sigma}_z) \frac{\hbar}{2} [\Delta\omega \hat{\sigma}_z - \frac{\omega_1}{2} \cos(\omega t) \hat{\sigma}_x + \frac{\omega_1}{2} \sin \omega t \hat{\sigma}_y] \exp(\frac{i}{2} \omega t \hat{\sigma}_z) |\phi(t)\rangle \\ &= \exp(-\frac{i}{2} \omega t \hat{\sigma}_z) \frac{\hbar}{2} [\Delta\omega \hat{\sigma}_z - \frac{\omega_1}{2} \cos(\omega t) \hat{\sigma}_x + \frac{\omega_1}{2} \sin \omega t \hat{\sigma}_y] \exp(\frac{i}{2} \omega t \hat{\sigma}_z) |\phi(t)\rangle \end{aligned}$$

or

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\phi(t)\rangle &= \exp(-\frac{i}{2} \omega t \hat{\sigma}_z) \frac{\hbar}{2} [\Delta\omega \hat{\sigma}_z - \frac{\omega_1}{2} \cos(\omega t) \hat{\sigma}_x + \frac{\omega_1}{2} \sin \omega t \hat{\sigma}_y] \exp(\frac{i}{2} \omega t \hat{\sigma}_z) |\phi(t)\rangle \\ &= \exp(-\frac{i}{2} \omega t \hat{\sigma}_z) \hat{H}_{II}{}^{(1)} \exp(\frac{i}{2} \omega t \hat{\sigma}_z) |\phi(t)\rangle \\ &= \hat{H}_{II}{}^{(1)}{}' |\phi(t)\rangle \end{aligned}$$

where

$$\begin{aligned} \hat{H}_{II}{}^{(1)} &= \frac{1}{2} \hbar [\Delta\omega \hat{\sigma}_z - \frac{\omega_1}{2} \cos(\omega t) \hat{\sigma}_x + \frac{\omega_1}{2} \sin(\omega t) \hat{\sigma}_y] \\ &= \frac{1}{2} \hbar \begin{pmatrix} \Delta\omega & -\frac{\omega_1}{2} e^{i\omega t} \\ -\frac{\omega_1}{2} e^{-i\omega t} & -\Delta\omega \end{pmatrix} \end{aligned}$$

Here we note that

$$\begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix} \begin{pmatrix} \Delta\omega & -\frac{\omega_1}{2}e^{i\omega t} \\ -\frac{\omega_1}{2}e^{-i\omega t} & -\Delta\omega \end{pmatrix} \begin{pmatrix} e^{i\omega t/2} & 0 \\ 0 & e^{-i\omega t/2} \end{pmatrix} = \begin{pmatrix} \Delta\omega & -\frac{\omega_1}{2} \\ -\frac{\omega_1}{2} & -\Delta\omega \end{pmatrix} = \Delta\omega\sigma_z - \frac{\omega_1}{2}\hat{\sigma}_x$$

We define the new Hamiltonian defined as

$$\hat{H}_{II} = \hat{H}_{II}{}^{(0)} + \hat{H}_{II}{}^{(1)}{}'$$

$$\hat{H}_{II}{}^{(1)}{}' = \frac{\hbar}{2}(\Delta\omega\hat{\sigma}_z - \frac{\omega_1}{2}\sigma_x).$$

with

$$\hat{H}_{II}{}^{(0)} = -\frac{1}{2}\hbar\omega\hat{\sigma}_z$$

Thus, we have

$$i\hbar\frac{\partial}{\partial t}\left|\phi(t)\right\rangle = \hat{H}_{II}{}^{(1)}{}'\left|\phi(t)\right\rangle,$$

with

$$\left|\psi(t)\right\rangle = \exp(\frac{i}{2}\omega t\hat{\sigma}_z)\left|\phi(t)\right\rangle$$

and

$$\hat{H}_{II}{}^{(1)}{}' = \frac{1}{2}\hbar(\Delta\omega\hat{\sigma}_z - \frac{\omega_1}{2}\hat{\sigma}_x)$$

In the condition of resonance ($\omega = \omega_c$), we have

$$\hat{H}_{II}{}^{(1)}{}' \rightarrow -\frac{\hbar}{4}\omega_1\hat{\sigma}_x.$$

Since the new Hamiltonian is independent of t, we can get the time evolution operator

$$\left|\phi(t)\right\rangle = \exp(-\frac{i\hat{H}_{II}^{(1)}{}' t}{\hbar})\left|\phi(0)\right\rangle = \exp(\frac{i\omega_1 t}{4}\hat{\sigma}_x)\left|\phi(0)\right\rangle .$$

We note that

$$\begin{aligned}\hat{H}_{II}^{(1)}{}' &= -\frac{\hbar}{2}[-\Delta\omega\hat{\sigma}_z + \frac{\omega_1}{2}\hat{\sigma}_x] \\ &= -\frac{\hbar}{2}\Omega(-\frac{\Delta\omega}{\Omega}\hat{\sigma}_z + \frac{\omega_1}{2\Omega}\hat{\sigma}_x) \\ &= -\frac{\hbar}{2}\Omega(\hat{\boldsymbol{\sigma}}\cdot\mathbf{n})\end{aligned}$$

with the unit vector ***n*** as

$$\mathbf{n} = -\frac{\Delta\omega}{\Omega}\mathbf{e}_z + \frac{\omega_1}{2\Omega}\mathbf{e}_x .$$

The initial condition is

$$\left|\phi(0)\right\rangle = \left|+z\right\rangle = \begin{pmatrix}1\\0\end{pmatrix}.$$

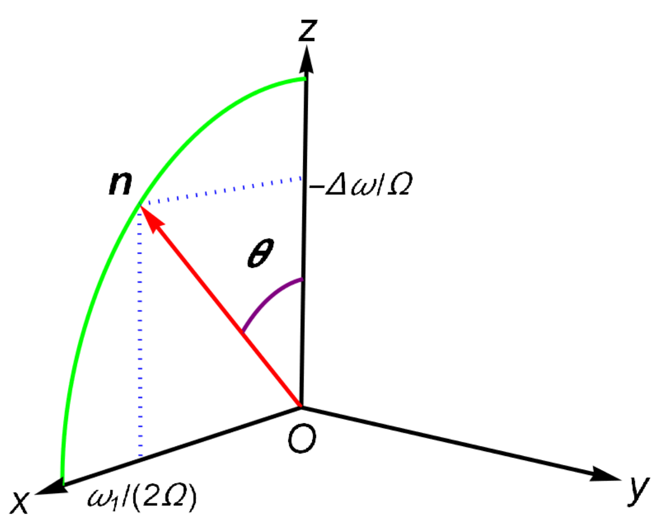


Fig.6 The unit vector $\mathbf{n} = -\frac{\Delta\omega}{\Omega}\mathbf{e}_z + \frac{\omega_1}{2\Omega}\mathbf{e}_x$ which lies in the *x*-*z* plane. $\Omega = \sqrt{(\Delta\omega)^2 + \frac{\omega_1^2}{4}}$; Rabi angular frequency.

Note that the Rabi angular frequency is defined as

$$\Omega = \sqrt{(\Delta\omega)^2 + \frac{\omega_1^2}{4}},$$

with

$$\Delta\omega = \omega - \omega_c .$$

Note that the value of Ω for the model-2 is the same as that for the model-1.
The probability of finding the system in the $|-z\rangle$ state (the excited state in the two-level system)

$$P_-(t) = \frac{\omega_1^2}{4\Omega^2}\sin^2(\frac{1}{2}\Omega t).$$

The probability of finding the system in the $|+z\rangle$ state (the ground state in the two-level-system)

$$P_+(t) = 1 - P_-(t) = 1 - \frac{\omega_1^2}{4\Omega^2}\sin^2(\frac{1}{2}\Omega t),$$

where

$$P_-(t=0) = 0, \qquad P_+(t=0) = 1.$$

For the model-I, we have the parameter ω_1 and the Rabi angular frequency as

$$\omega_1 = \omega_c \frac{B_1}{B_0} \qquad \Omega = \sqrt{(\Delta\omega)^2 + \frac{\omega_1^2}{4}}.$$

Here, we make a plot of the amplitude of $P_{-}(t)$ as a function of $\Delta\omega / \omega_c$ where the parameter ω_1 / ω_c kept as constant.

$$P = \frac{\omega_1^2}{4\Omega^2} = \frac{\frac{1}{4}\omega_1^2}{(\Delta\omega)^2 + \frac{1}{4}\omega_1^2} = \frac{\frac{1}{4}\frac{\omega_1^2}{\omega_c^2}}{\frac{(\Delta\omega)^2}{\omega_c^2} + \frac{1}{4}\frac{\omega_1^2}{\omega_c^2}}.$$

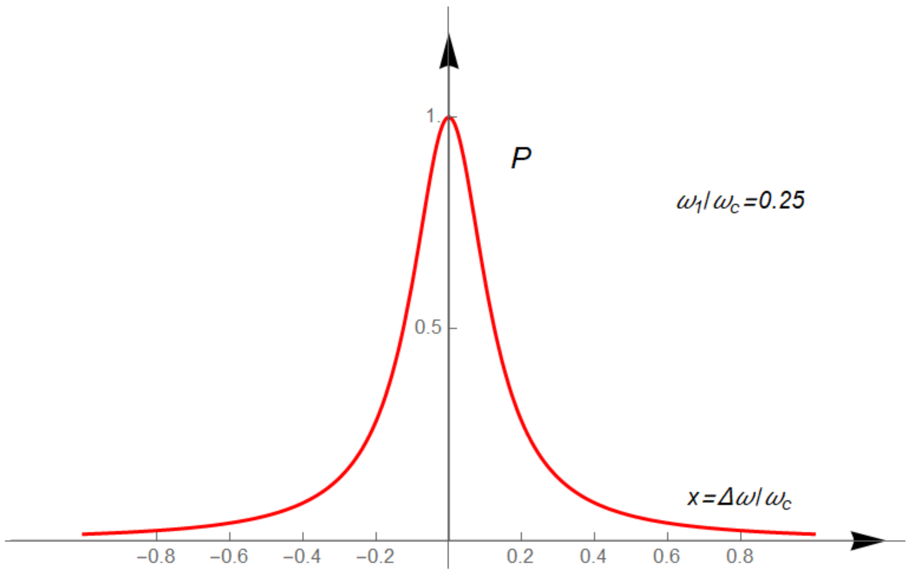


Fig.7 Amplitude of $P_{-}(t)$ as a function of $x = \Delta\omega / \omega_c$ with a parameter $\omega_1 / \omega_c = 0.25$

((Note-1)) **Derivation of the time evolution operator** $\exp(-\frac{i\hat{H}_2^{(1a)}t}{\hbar})$ **without use Mathematica**

We start with the formula,

$$\exp[-\frac{i}{2}\theta(\hat{\boldsymbol{\sigma}}\cdot\mathbf{n})] = \hat{1}\cos\frac{\theta}{2} - i\sin\frac{\theta}{2}(\hat{\boldsymbol{\sigma}}\cdot\mathbf{n}).$$

Then, we have

$$\exp(-\frac{i\hat{H}_2^{(1)}{}'t}{\hbar}) = \exp[\frac{i\Omega t}{2}(\hat{\boldsymbol{\sigma}}\cdot\mathbf{n})$$
$$= \hat{1}\cos(\frac{\Omega t}{2}) + i\sin(\frac{\Omega t}{2})(\hat{\boldsymbol{\sigma}}\cdot\mathbf{n})$$
$$= \hat{1}\cos(\frac{\Omega t}{2}) + i\sin(\frac{\Omega t}{2})(-\frac{\Delta\omega}{\Omega}\hat{\sigma}_z + \frac{\omega_1}{2\Omega}\hat{\sigma}_x)$$
$$= \begin{pmatrix} \cos(\frac{\Omega t}{2}) - i\frac{\Delta\omega}{\Omega}\sin(\frac{\Omega t}{2}) & i\frac{\omega_1}{2\Omega}\sin(\frac{\Omega t}{2}) \\ i\frac{\omega_1}{2\Omega}\sin(\frac{\Omega t}{2}) & \cos(\frac{\Omega t}{2}) + i\frac{\Delta\omega}{\Omega}\sin(\frac{\Omega t}{2}) \end{pmatrix}$$

((**Mathematica-2**)) **Solving the model-2 problem using Mathematica**

```
Clear["Global`*"];
exp_* :=
 exp /. {Complex[re_, im_] :> Complex[re, -im]};
H1 = -ħ/2 ( -Δω    ω1/2
            ω1/2   Δω   );
M1 = MatrixExp[(-ⅈ/ħ) H1 t] // FullSimplify;
rule1 = {Sqrt[4 Δω^2 + ω1^2] → 2 Ω,
   1/Sqrt[4 Δω^2 + ω1^2] → 1/(2 Ω)};
M2 = M1 /. rule1 // FullSimplify;
M2 // MatrixForm
```

$$\begin{pmatrix} \text{Cos}[\frac{t\,\Omega}{2}] - \frac{ⅈ\,\Delta\omega\,\text{Sin}[\frac{t\,\Omega}{2}]}{\Omega} & \frac{ⅈ\,\omega1\,\text{Sin}[\frac{t\,\Omega}{2}]}{2\,\Omega} \\ \frac{ⅈ\,\omega1\,\text{Sin}[\frac{t\,\Omega}{2}]}{2\,\Omega} & \text{Cos}[\frac{t\,\Omega}{2}] + \frac{ⅈ\,\Delta\omega\,\text{Sin}[\frac{t\,\Omega}{2}]}{\Omega} \end{pmatrix}$$

P11: Probabilityof finding in the state |+z >

P21: Probability of finding in the state |-z>

with

$$\sqrt{\Delta\omega^2 + \frac{\omega 1^2}{4}} = \Omega$$

```
P1 = {1, 0}.M2.{1, 0} // Simplify;
P11 = P1* P1 // FullSimplify
```

$$\text{Cos}\left[\frac{t\,\Omega}{2}\right]^2 + \frac{\Delta\omega^2\,\text{Sin}\left[\frac{t\,\Omega}{2}\right]^2}{\Omega^2}$$

```
P2 = {0, 1}.M2.{1, 0} // FullSimplify;
P21 = P2* P2 // Simplify
```

$$\frac{\omega 1^2\,\text{Sin}\left[\frac{t\,\Omega}{2}\right]^2}{4\,\Omega^2}$$

5. rf-spin echo method; 90° pulse and 180° pulse

Using the Model-II, we now discuss the rf spin echo method under the resonance condition ($\Delta\omega = \omega - \omega_c = 0$). We note that

$$\exp(-\frac{i\hat{H}_{II}^{(1)}{}'t}{\hbar}) = \begin{pmatrix} \cos\left(\frac{\Omega t}{2}\right) & \frac{i\omega_2}{2\Omega}\sin\left(\frac{\Omega t}{2}\right) \\ \frac{i\omega_2}{2\Omega}\sin\left(\frac{\Omega t}{2}\right) & \cos\left(\frac{\Omega t}{2}\right) \end{pmatrix}$$

$$\cong \begin{pmatrix} \cos\left(\frac{\Omega t}{2}\right) & i\sin\left(\frac{\Omega t}{2}\right) \\ i\sin\left(\frac{\Omega t}{2}\right) & \cos\left(\frac{\Omega t}{2}\right) \end{pmatrix}$$

where $\Omega = \sqrt{(\Delta\omega)^2 + \frac{\omega_1^2}{4}} \to \frac{\omega_1}{2}$. Suppose that $|\phi(0)\rangle = |+z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$. Then we get

$$|\phi(t)\rangle = \exp(-\frac{i\hat{H}_{II}^{(1)}{}'t}{\hbar})|\phi(0)\rangle$$

$$\to \begin{pmatrix} \cos(\frac{\Omega t}{2}) \\ i\sin(\frac{\Omega t}{2}) \end{pmatrix}$$

(i) When $\Omega\ t(90°) = \frac{\omega_2}{2} t(90°) = \frac{\pi}{2}$ (for 90° rf pulse), we have

$$|\phi[t(90°)]\rangle = \begin{pmatrix} \cos(\frac{\pi}{4}) \\ i\sin(\frac{\pi}{4}) \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} = |+y\rangle$$

((**Evaluation of** $t(90°)$))

$$\Omega t(90°) = \frac{\omega_2}{2} t(90°) = \frac{1}{2}\gamma_p B_2\ t(90°) = \frac{\pi}{2}$$

$$B_2\ t(90°) = \frac{\pi}{\gamma_p} = 1.174 \times 10^{-4}\ \text{s G}$$

using the gyromagnetic ratio for proton

$$\gamma_p = \frac{2}{\hbar}\mu_P = 2.675222005 \times 10^4\ \text{rad/(s G)}$$

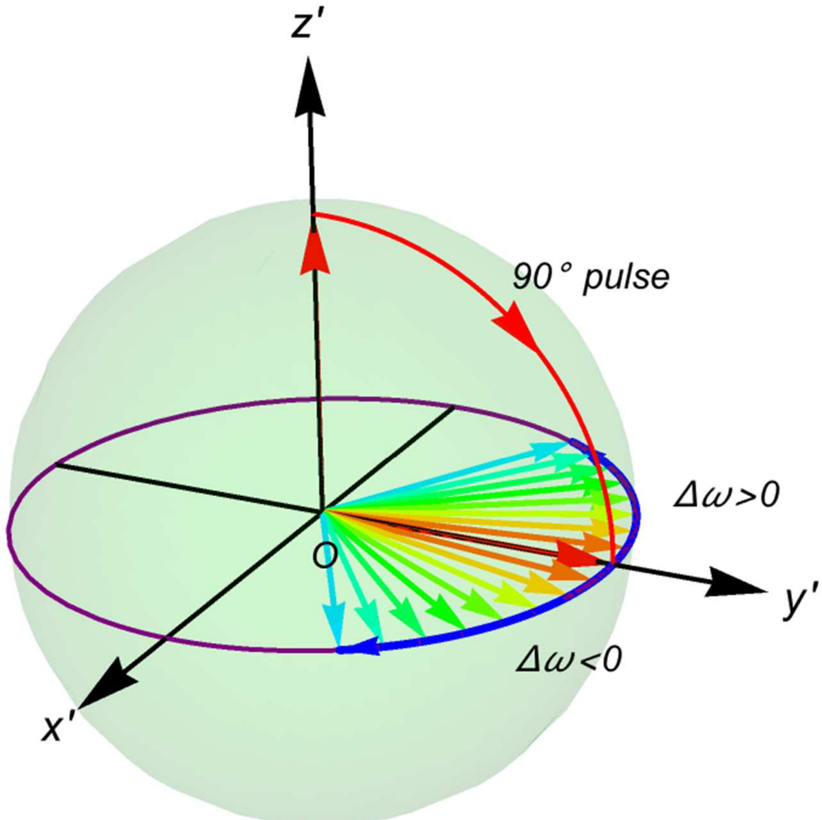


Fig.8 90° rf pulse. Measurement of transverse relaxation time (T_2). x'-y'-z' plane (RCF).

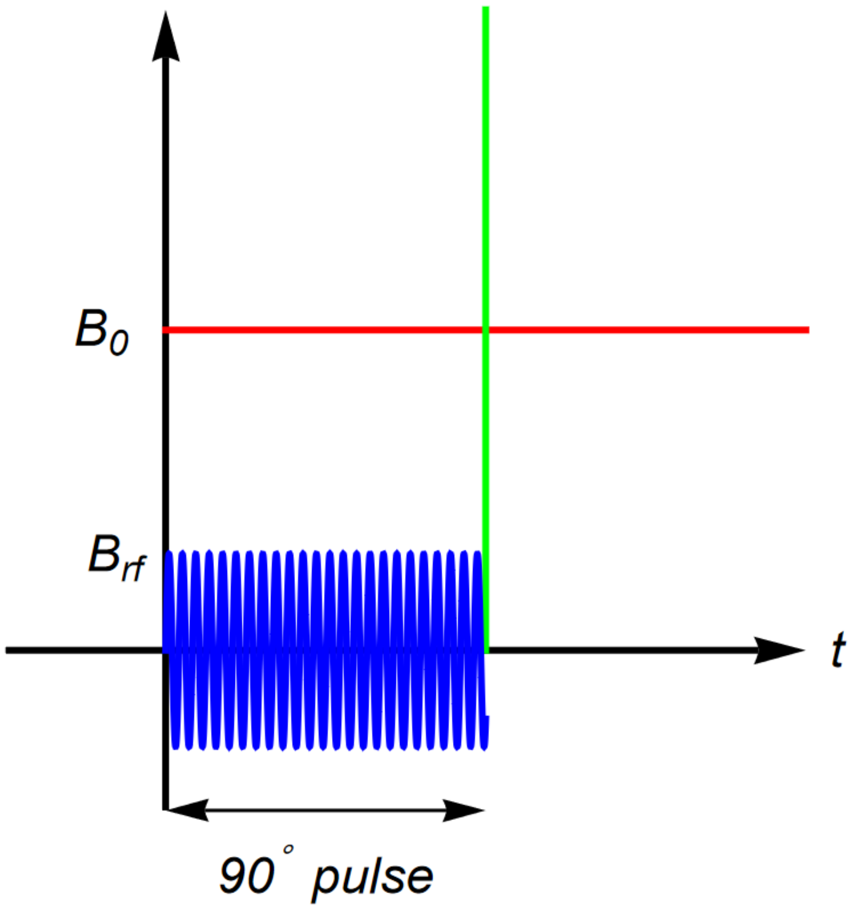


Fig.9 $B_{rf} = B_1$ for the 90° rf-pulse with angular frequency ω. The period $t(90°)$.

(ii) When $\omega_2 t(180°) = \pi$ (for 180° rf pulse), we have

$$\left|\phi[t(180°)]\right\rangle = \begin{pmatrix} \cos(\frac{\pi}{2}) \\ i\sin(\frac{\pi}{2}) \end{pmatrix} = \begin{pmatrix} 0 \\ i \end{pmatrix} = i\left|-z\right\rangle$$

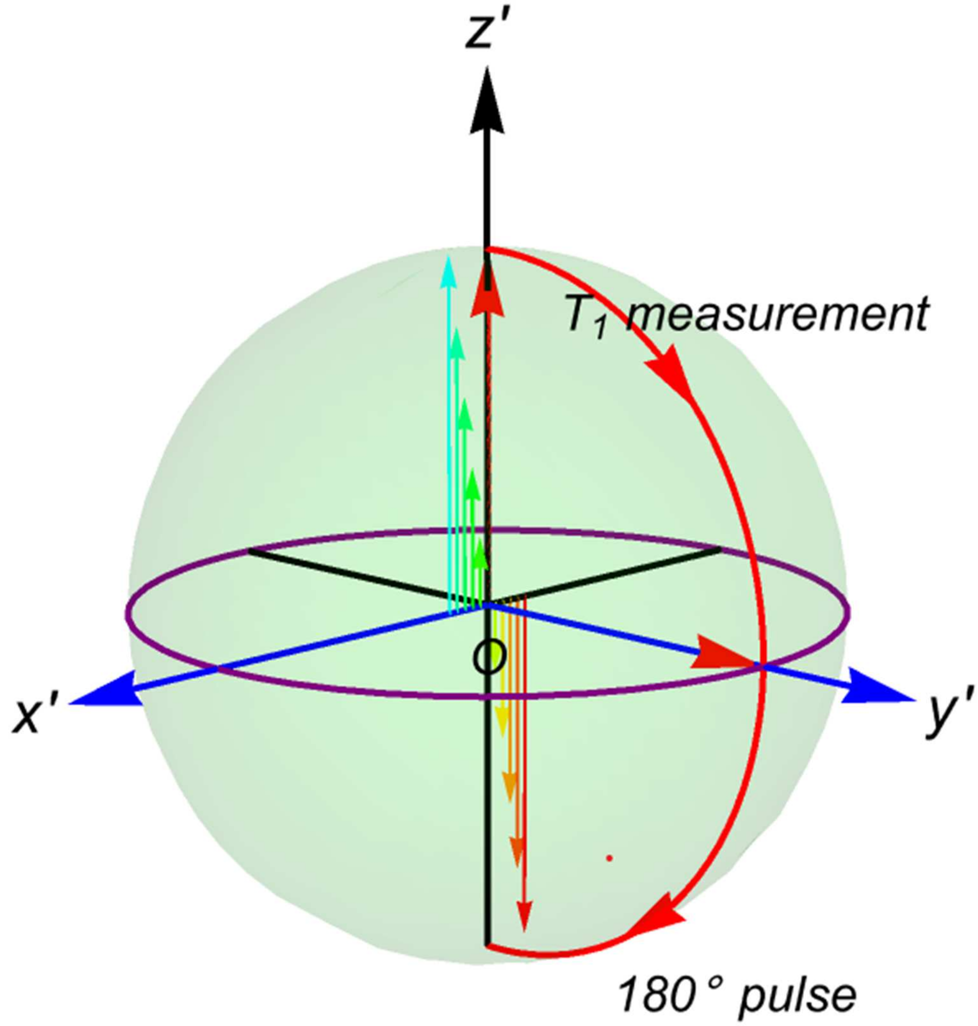


Fig.10 180° rf pulse. Measurement of longitudinal relaxation time or the spin-lattice relaxation time (T_1). Rotating reference frame (RRF). After the 180° rf pulse, the magnetization decays from -*z* direction to +*z* direction with a longitudinal relaxation time T_1. The shift of the red arrows along the x' axis has nothing to do with the spin dynamics.

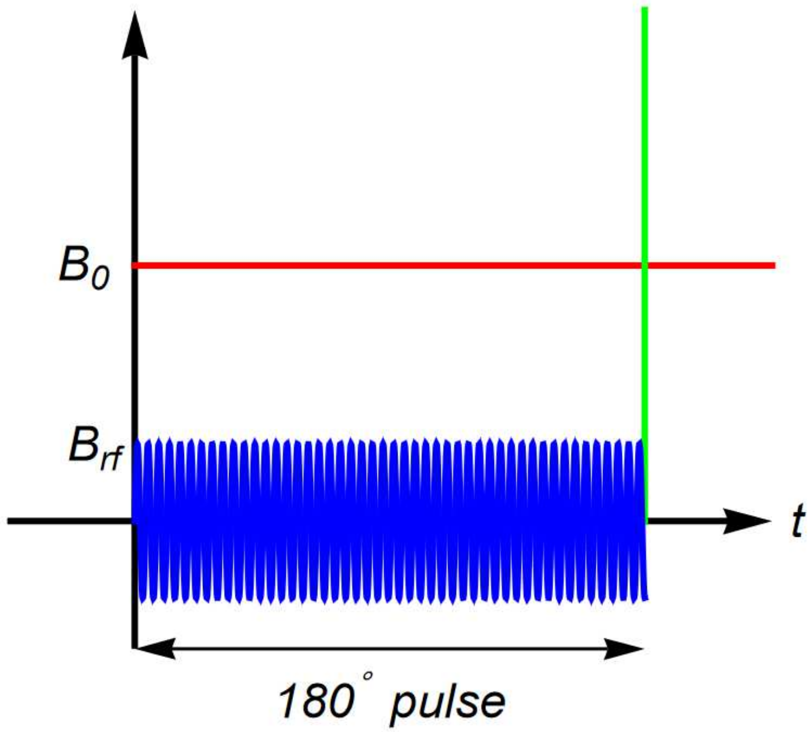


Fig.11 $B_{rf} = B_2$ for the 180° rf-pulse with angular frequency ω. The period $t(180°)$.

((**Evaluation**)) $t(180°)$

$$\omega_2 t(180°) = \frac{1}{2}\gamma_p B_2 t(180°) = \pi$$

$$\gamma_p = \frac{2}{\hbar}\mu_P = 2.675222005 \times 10^4 \text{ rad/(s G)}$$

(iii) When $\frac{\omega_2}{2}T(360°) = 2\pi$ (360° pulse), we have

$$|\phi[T(360°)\rangle = \begin{pmatrix} \cos(\pi) \\ i\sin(\pi) \end{pmatrix} = \begin{pmatrix} -1 \\ 0 \end{pmatrix} = -|+z\rangle$$

which is not equal to $|+z\rangle$. Note that $|\phi[T(720°)\rangle = \begin{pmatrix} \cos(2\pi) \\ i\sin(2\pi) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |+z\rangle$.

6. Expectation value $\langle\psi(t)|\hat{S}_i|\psi(t)\rangle$ in the Model-II (laboratory reference frame)

We just take a look at the form of the new Hamiltonian for the model-2

$$\hat{H}_{II}^{(1)}{}' = \frac{\hbar}{2}(\Delta\omega\hat{\sigma}_z - \frac{\omega_1}{2}\hat{\sigma}_x), \qquad \hat{H}_{II}^{(0)} = -\frac{1}{2}\hbar\omega\hat{\sigma}_z.$$

The time evolution operator is obtained as

$$\hat{T}(t) = \exp(-\frac{i}{\hbar}\hat{H}_{II}^{(1)}{}'t).$$

which is the rotation operator for the rotation around the x-axis by angle $\omega_1 t/2$ in clockwise.

$$|\phi(t)\rangle = \hat{T}(t)|\phi(t=0)\rangle = \exp(-\frac{i}{\hbar}\hat{H}_{II}^{(1)}{}'t)|\phi(t=0)\rangle$$

It is reasonable to assume that in thermal equilibrium, $|\phi(t=0)\rangle = |+z\rangle$. Finally, we have

$$\begin{aligned}|\psi(t)\rangle &= \exp(\frac{i}{2}\omega t\hat{\sigma}_z)|\phi(t)\rangle \\ &= \exp(\frac{i}{2}\omega t\hat{\sigma}_z)\exp(-\frac{i}{\hbar}\hat{H}_{II}^{(1)}{}'t)|\phi(0)\rangle \\ &= \exp(\frac{i}{2}\omega t\hat{\sigma}_z)\exp(-\frac{i}{\hbar}\hat{H}_{II}^{(1)}{}'t)|+z\rangle\end{aligned}$$

Now we discuss the expectation value $\langle I_i\rangle_t = \langle\psi(t)|\hat{I}_i|\psi(t)\rangle$ ($i = x, y, z$) in the laboratory reference frame (LFF)

$$\begin{aligned}\langle I_i\rangle_t &= \langle\psi(t)|\hat{I}_i|\psi(t)\rangle \\ &= \frac{\hbar}{2}\langle\phi(t)|\exp(-\frac{i}{2}\omega t\hat{\sigma}_z)\hat{\sigma}_i\exp(\frac{i}{2}\omega t\hat{\sigma}_z\omega t)|\phi(t)\rangle \\ &= \frac{\hbar}{2}\langle +z|\exp(\frac{i}{\hbar}\hat{H}_{II}^{(1)}{}'t)\exp(-\frac{i}{2}\omega t\hat{\sigma}_z)\hat{\sigma}_i\exp(\frac{i}{2}\omega t\hat{\sigma}_z)\exp(-\frac{i}{\hbar}\hat{H}_{II}^{(1)}{}'t)|+z\rangle\end{aligned}$$

with $i = x, y, z$. Using the **Mathematica**, we get the expectation value in LFF

$$X = \frac{\hbar\omega_1}{4\Omega^2}[-2\Delta\omega\cos(\omega t)\sin^2\left(\frac{\Omega t}{2}\right) + \Omega\sin(\omega t)\sin(\Omega t)],$$

$$Y = \frac{\hbar\omega_1}{4\Omega^2}[2\Delta\omega\sin(\omega t)\sin^2\left(\frac{\Omega t}{2}\right) + \Omega\cos(\omega t)\sin(\Omega t)],$$

$$Z = \frac{\hbar}{16\Omega^2}\{4[(\Delta\omega)^2 + \Omega^2] - \omega_1^{\ 2} + [-4(\Delta\omega)^2 + 4\Omega^2 + \omega_1^{\ 2}]\cos(\Omega t)\}.$$

In the resonance condition ($\Delta\omega = 0$ and $\Omega = \frac{\omega_1}{2}$), we have the expectation values in LFF

$$X = \frac{\hbar}{2}\sin(\omega t)\sin(\frac{\omega_1 t}{2}), \qquad Y = \frac{\hbar}{2}\cos(\omega t)\sin(\frac{\omega_1 t}{2}), \qquad Z = \frac{\hbar}{2}\cos\left(\frac{\omega_1 t}{2}\right).$$

((**Mathematica-3**))

```
Clear["Global`*"];
expr_* := expr /. Complex[a_, b_] :> Complex[a, -b];
σx = PauliMatrix[1]; σy = PauliMatrix[2];
σz = PauliMatrix[3]; A1 = 1/2 ω σz;
H1 = 1/2 (Δω σz - ω1/2 σx) // FullSimplify;
H1P = MatrixExp[ⅈ H1 t];
H1M = MatrixExp[-ⅈ H1 t];
A1P = MatrixExp[ⅈ A1 t];
A1M = MatrixExp[-ⅈ A1 t];
rule1 = {Sqrt[4 (Δω)^2 + (ω1)^2] → 2 Ω,
   1/Sqrt[4 (Δω)^2 + (ω1)^2] → 1/(2 Ω)};
Sx = ℏ/2 H1P.A1M. σx.A1P.H1M /. rule1 // FullSimplify;
Sy = ℏ/2 H1P.A1M. σy.A1P.H1M /. rule1 // FullSimplify;
Sz = ℏ/2 H1P.A1M. σz.A1P.H1M /. rule1 // FullSimplify;
X1 = Sx[[1, 1]]
```

$$\frac{\omega 1\, \hbar \left(-2\, \Delta\omega \operatorname{Cos}[t\, \omega] \operatorname{Sin}\left[\frac{t\,\Omega}{2}\right]^2 + \Omega \operatorname{Sin}[t\,\omega] \operatorname{Sin}[t\,\Omega]\right)}{4\,\Omega^2}$$

```
Y1 = Sy[[1, 1]]
```

$$\frac{\omega 1\, \hbar \left(2\, \Delta\omega \operatorname{Sin}[t\, \omega] \operatorname{Sin}\left[\frac{t\,\Omega}{2}\right]^2 + \Omega \operatorname{Cos}[t\,\omega] \operatorname{Sin}[t\,\Omega]\right)}{4\,\Omega^2}$$

```
Z1 = Sz[[1, 1]]
```

$$\frac{\hbar \left(4 \left(\Delta\omega^2 + \Omega^2\right) - \omega 1^2 + \left(-4\,\Delta\omega^2 + 4\,\Omega^2 + \omega 1^2\right) \operatorname{Cos}[t\,\Omega]\right)}{16\,\Omega^2}$$

7. The expectation values of spin operator in the rotating reference frame

Mathematically, the expectation of spin operator in the rotation coordinate frame (RFF) is related to that in the LFF

$$X'\mathbf{e}_x' + Y'\mathbf{e}_y' + Z'\mathbf{e}_z' = X\mathbf{e}_x + Y\mathbf{e}_y + Z\mathbf{e}_z,$$

for the rotation around the *z* axis by angle $\phi = \omega t$ with

$X'\mathbf{e}_x' + Y'\mathbf{e}_y' + Z'\mathbf{e}_z'$; expectation in the RFF,

$X\mathbf{e}_x + Y\mathbf{e}_y + Z\mathbf{e}_z$; expectation in the LFF.

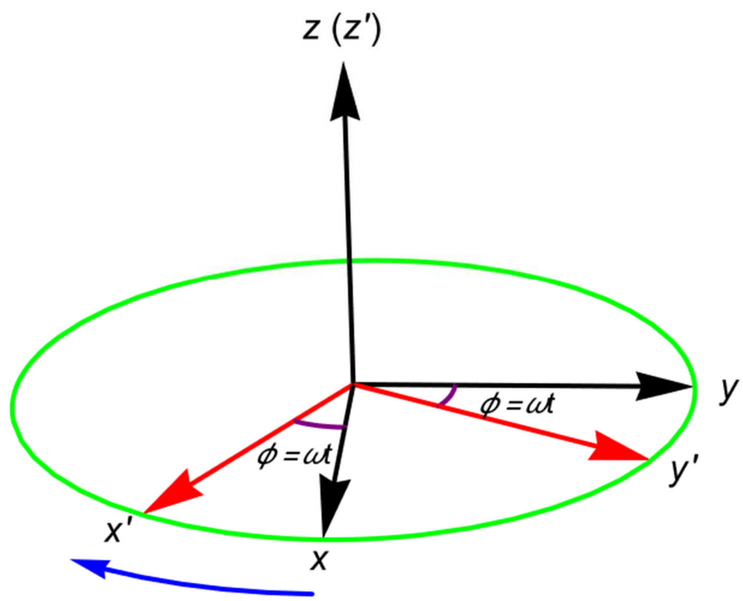


Fig.12 *x*, *y*, *z* (LFF; laboratory reference frame). *x'*, *y'*, *z'* (RFF; rotational reference frame). *z'*=*z*. Rotation around the *z* axis by the angle $\phi = \omega t$.

Thus, we have

$$\begin{aligned} X' &= X\mathbf{e}_x \cdot \mathbf{e}_x' + Y\mathbf{e}_y \cdot \mathbf{e}_x' + Z\mathbf{e}_z \cdot \mathbf{e}_x' \\ &= X\cos\phi - Y\sin\phi \\ &= \frac{\hbar\omega_1\Delta\omega}{4\Omega^2}[-1 + \cos(\Omega t)] \end{aligned}$$

$$\begin{aligned}
Y' &= X\mathbf{e}_x \cdot \mathbf{e}_y' + Y\mathbf{e}_y \cdot \mathbf{e}_y' + Z\mathbf{e}_z \cdot \mathbf{e}_y' \\
&= X\sin\phi + Y\cos\phi \\
&= \frac{\hbar\omega_1}{4\Omega}\sin(\Omega t)
\end{aligned}$$

$$\begin{aligned}
Z' &= X\mathbf{e}_x \cdot \mathbf{e}_z' + Y\mathbf{e}_y \cdot \mathbf{e}_z' + Z\mathbf{e}_z \cdot \mathbf{e}_z' \\
&= Z \\
&= \frac{\hbar}{16\Omega^2}\{4[(\Delta\omega)^2 + \Omega^2] - \omega_1^{\ 2} + [-4(\Delta\omega)^2 + 4\Omega^2 + \omega_1^{\ 2}]\cos(\Omega t)\}
\end{aligned}$$

where $\phi = \omega t$

$$\begin{pmatrix} X' \\ Y' \\ Z' \end{pmatrix} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}.$$

In the resonance condition ($\Delta\omega = 0$), we have $\Omega = \frac{\omega_1}{2}$

$$X' = 0, \qquad Y' = \frac{\hbar\omega_1}{2}\sin(\frac{\omega_1 t}{2}), \qquad Z' = \frac{\hbar}{2}\cos\left(\frac{\omega_1 t}{2}\right)\}$$

((**Mathematica 3S**))

```
X2 = X1 Cos[ω t] - Y1 Sin[ω t] // FullSimplify;
Y2 = X1 Sin[ω t] + Y1 Cos[ω t] // FullSimplify;
Z2 = Z1;
```

```
X2
```

$$\frac{\Delta\omega\ \omega 1\ \hbar\ (-1 + \mathrm{Cos}[t\,\Omega])}{4\,\Omega^2}$$

```
Y2
```

$$\frac{\omega 1\ \hbar\ \mathrm{Sin}[t\,\Omega]}{4\,\Omega}$$

```
Z2
```

$$\frac{\hbar\ \left(4\ \left(\Delta\omega^2 + \Omega^2\right) - \omega 1^2 + \left(-4\,\Delta\omega^2 + 4\,\Omega^2 + \omega 1^2\right)\ \mathrm{Cos}[t\,\Omega]\right)}{16\,\Omega^2}$$

```
X2 /. {Δω → 0, Ω → ω1/2}
```

0

```
Y2 /. {Δω → 0, Ω → ω1/2, ℏ → 1}
```

$\frac{1}{2}\text{Sin}\left[\frac{t\,\omega 1}{2}\right]$

```
Z2 /. {Δω → 0, Ω → ω1/2, ℏ → 1}
```

$\frac{1}{2}\text{Cos}\left[\frac{t\,\omega 1}{2}\right]$

```
Z2 /. t → π/(2 Ω) // Simplify
```

$$\frac{\left(4\left(\Delta\omega^2+\Omega^2\right)-\omega 1^2\right)\hbar}{16\,\Omega^2}$$

8. The expectation values: Method-II using the quantum mechanics

Now we discuss the expectation value of $\langle I_i\rangle_t = \langle\phi(t)|\hat{I}_i|\phi(t)\rangle$ ($i = x, y, z$).

$$\langle\phi(t)|\hat{I}_i|\phi(t)\rangle = \frac{\hbar}{2}\langle +z|\exp(\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}{}'t)\hat{\sigma}_i\exp(-\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}{}'t)|+z\rangle,$$

where

$$\hat{H}_{II}{}^{(1)}{}' = \frac{\hbar}{2}(\Delta\omega\hat{\sigma}_z - \frac{\omega_1}{2}\hat{\sigma}_x),$$

$$X' = \langle\phi(t)|\hat{I}_x|\phi(t)\rangle$$
$$= \frac{\hbar\omega_1\Delta\omega}{4\Omega^2}[-1+\cos(\Omega t)]$$

$$Y' = \langle \phi(t) | \hat{I}_y | \phi(t) \rangle$$
$$= \frac{\hbar \omega_1}{4\Omega} \sin(\Omega t)$$

$$Z' = \langle \phi(t) | \hat{I}_z | \phi(t) \rangle$$
$$= \frac{\hbar}{16\Omega^2} \{4[(\Delta\omega)^2 + \Omega^2] - \omega_1{}^2 + [-4(\Delta\omega)^2 + 4\Omega^2 + \omega_1{}^2] \cos(\Omega t)\}$$

So that, the results of *X*', *Y*', and *Z*' agree with those obtained from the mathematical calculation above described,

((**Mathematica-4**))

```
Clear["Global`*"];
expr_* := expr /. Complex[a_, b_] :> Complex[a, -b];
σx = PauliMatrix[1]; σy = PauliMatrix[2];
σz = PauliMatrix[3];
```

$$H1 = \frac{1}{2}\left(\Delta\omega\, \sigma z - \frac{\omega 1}{2}\sigma x\right) \text{ // FullSimplify;}$$

```
H1P = MatrixExp[ⅈ H1 t];
H1M = MatrixExp[-ⅈ H1 t];
```

$$\text{rule1} = \left\{\sqrt{4(\Delta\omega)^2 + (\omega 1)^2} \to 2\,\Omega,\ \frac{1}{\sqrt{4(\Delta\omega)^2 + (\omega 1)^2}} \to \frac{1}{2\,\Omega}\right\};$$

$$Sx1 = \frac{\hbar}{2} \text{ H1P.σx.H1M /. rule1 // FullSimplify;}$$

$$Sy1 = \frac{\hbar}{2} \text{ H1P.σy.H1M /. rule1 // FullSimplify;}$$

$$Sz1 = \frac{\hbar}{2} \text{ H1P.σz.H1M /. rule1 // FullSimplify;}$$

```
X2 = Sx1[[1, 1]]
```

$$\frac{\Delta\omega\, \omega 1\, \hbar\, (-1 + \mathrm{Cos}[t\,\Omega])}{4\,\Omega^2}$$

```
Y2 = Sy1[[1, 1]]
```

$$\frac{\omega 1\, \hbar\, \mathrm{Sin}[t\,\Omega]}{4\,\Omega}$$

```
Z2 = Sz1[[1, 1]]
```

$$\frac{1}{16\,\Omega^2}\hbar\left(4\left(\Delta\omega^2 + \Omega^2\right) - \omega 1^2 + \left(-4\,\Delta\omega^2 + 4\,\Omega^2 + \omega 1^2\right)\mathrm{Cos}[t\,\Omega]\right)$$

((**Note**)) The calculation of the matrix elements with the use of Mathematica (version 13).

```
HXH // MatrixForm
```

$$\begin{pmatrix} \frac{\Delta\omega\,\omega1\,(-1+\mathrm{Cos}[t\,\Omega])}{2\,\Omega^2} & \frac{-4\,\Delta\omega^2+4\,\Omega^2+\omega1^2+\left(4\,\left(\Delta\omega^2+\Omega^2\right)-\omega1^2\right)\,\mathrm{Cos}[t\,\Omega]+8\,i\,\Delta\omega\,\Omega\,\mathrm{Sin}[t\,\Omega]}{8\,\Omega^2} \\ \frac{-4\,\Delta\omega^2+4\,\Omega^2+\omega1^2+\left(4\,\left(\Delta\omega^2+\Omega^2\right)-\omega1^2\right)\,\mathrm{Cos}[t\,\Omega]-8\,i\,\Delta\omega\,\Omega\,\mathrm{Sin}[t\,\Omega]}{8\,\Omega^2} & \frac{\Delta\omega\,\omega1\,\mathrm{Sin}\left[\frac{t\,\Omega}{2}\right]^2}{\Omega^2} \end{pmatrix}$$

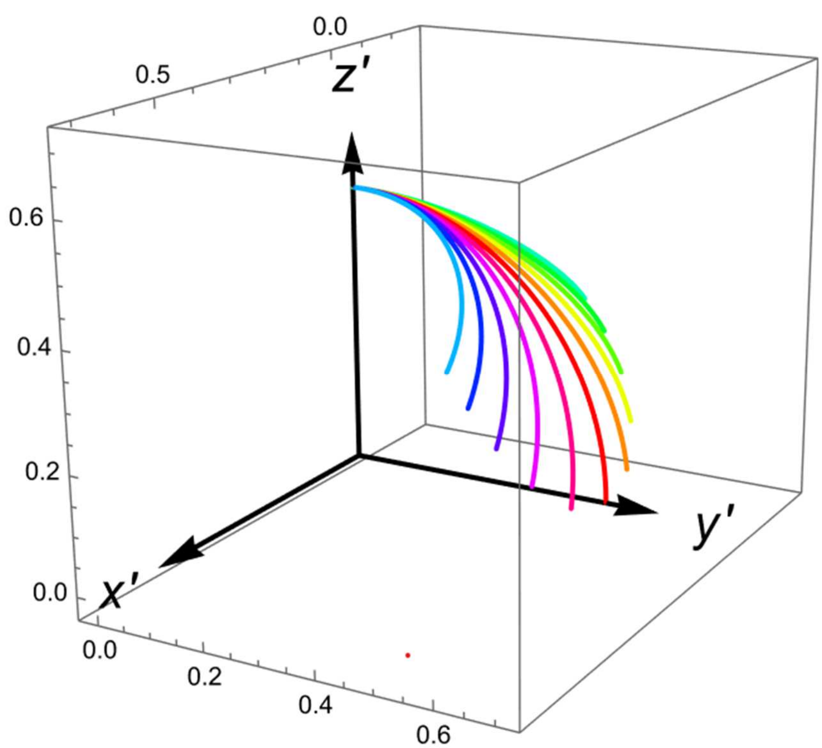
```
HYH = H1P.σy.H1M /. rule1 // FullSimplify; HYH // MatrixForm
```

$$\begin{pmatrix} \frac{\omega1\,\mathrm{Sin}[t\,\Omega]}{2\,\Omega} & -\frac{i\,\left(-4\,\Delta\omega^2+4\,\Omega^2-\omega1^2+\left(4\,\left(\Delta\omega^2+\Omega^2\right)+\omega1^2\right)\,\mathrm{Cos}[t\,\Omega]+8\,i\,\Delta\omega\,\Omega\,\mathrm{Sin}[t\,\Omega]\right)}{8\,\Omega^2} \\ \frac{i\,\left(-4\,\Delta\omega^2+4\,\Omega^2-\omega1^2+\left(4\,\left(\Delta\omega^2+\Omega^2\right)+\omega1^2\right)\,\mathrm{Cos}[t\,\Omega]-8\,i\,\Delta\omega\,\Omega\,\mathrm{Sin}[t\,\Omega]\right)}{8\,\Omega^2} & -\frac{\omega1\,\mathrm{Sin}[t\,\Omega]}{2\,\Omega} \end{pmatrix}$$

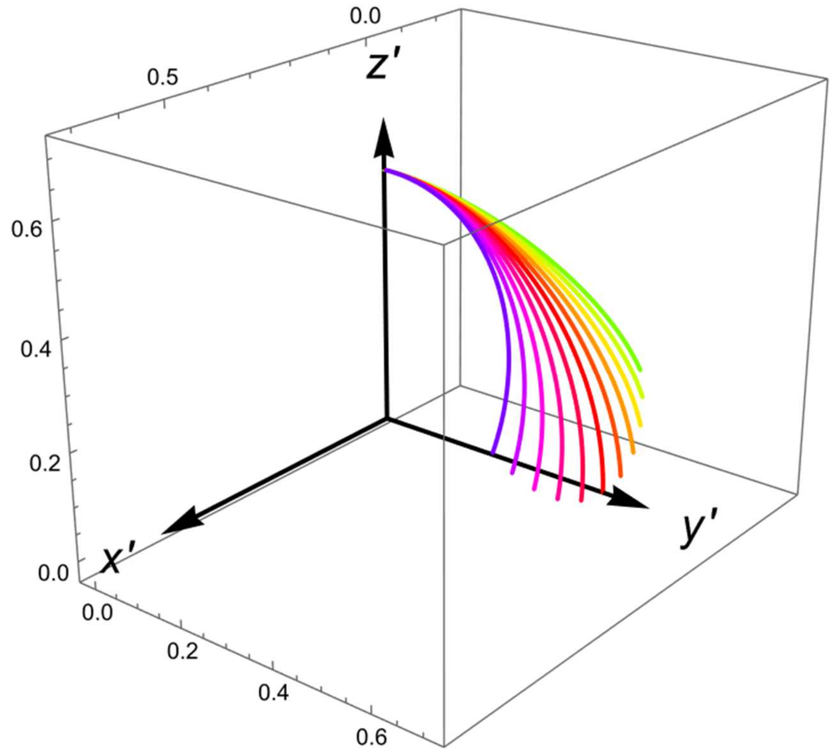
```
HZH = H1P.σz.H1M /. rule1 // FullSimplify; HZH // MatrixForm
```

$$\begin{pmatrix} \frac{4\,\left(\Delta\omega^2+\Omega^2\right)-\omega1^2+\left(-4\,\Delta\omega^2+4\,\Omega^2+\omega1^2\right)\,\mathrm{Cos}[t\,\Omega]}{8\,\Omega^2} & \frac{\omega1\,(\Delta\omega\,(-1+\mathrm{Cos}[t\,\Omega])+i\,\Omega\,\mathrm{Sin}[t\,\Omega])}{2\,\Omega^2} \\ \frac{\omega1\,(\Delta\omega\,(-1+\mathrm{Cos}[t\,\Omega])-i\,\Omega\,\mathrm{Sin}[t\,\Omega])}{2\,\Omega^2} & \frac{-4\,\left(\Delta\omega^2+\Omega^2\right)+\omega1^2+\left(4\,\Delta\omega^2-4\,\Omega^2-\omega1^2\right)\,\mathrm{Cos}[t\,\Omega]}{8\,\Omega^2} \end{pmatrix}$$

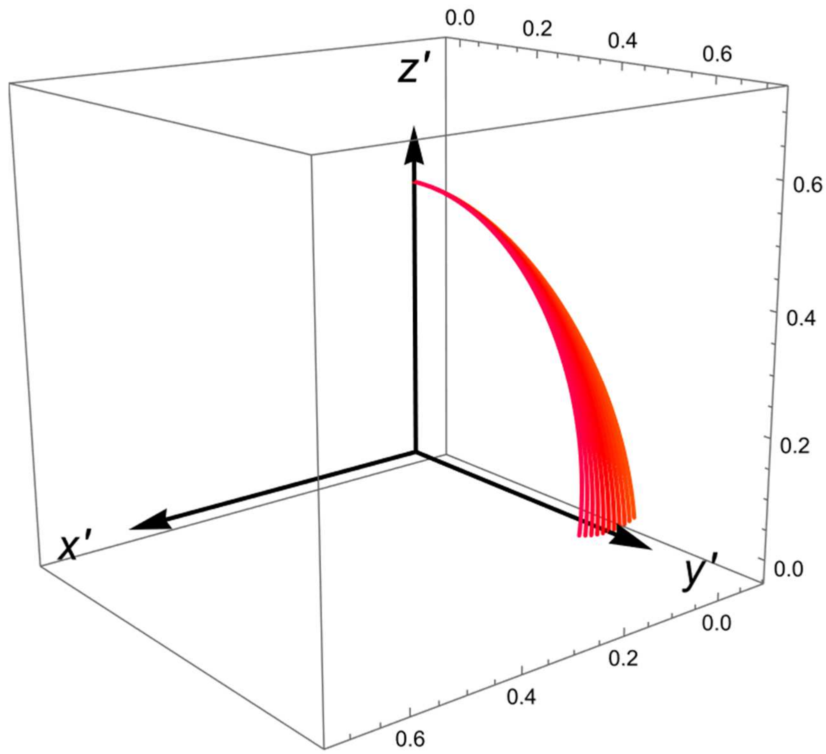
9. ParametricPlot3D of (*X*', *Y*', *Z*') [rotational reference frame (RRF)]



(a) The off-resonance condition. $\omega_1 = 0.08$, $\Delta\omega = 0.009$ k (*k*=-5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5). *x*'-*y*'-*z*' plane.



(b) The off resonance condition. $\omega_1 = 0.08$, $\Delta\omega = 0.005$ k (k=-5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5).



(c) Near the resonance condition. $\omega_1 = 0.08$, $\Delta\omega = 0.001$ k (*k*=-5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5)

Fig.13 (a), (b), and (c)
The ParametricPlot3D of $(X', Y' Z')$ [RRF] as a function of time during the rf 90° pulse period.

10. ParametricPlot3D of (*X*, *Y*, *Z*) [LRF] and (*X'*, *Y'*, *Z'*) [RRF]

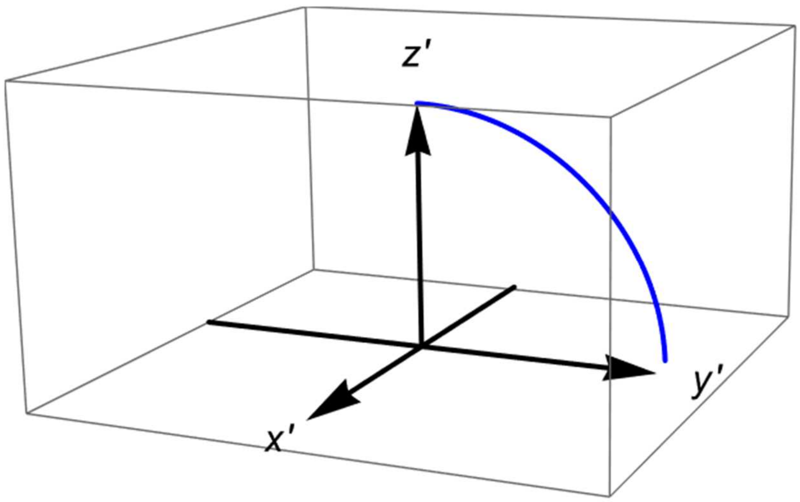
We make a ParametricPlot3D of (X, Y, Z) [LRF] as

$$(X, Y, Z)=\{\langle\psi(t)|\hat{I}_x|\psi(t)\rangle, \langle\psi(t)|\hat{I}_y|\psi(t)\rangle, \langle\psi(t)|\hat{I}_z|\psi(t)\rangle\} \qquad \text{(LRF)}$$

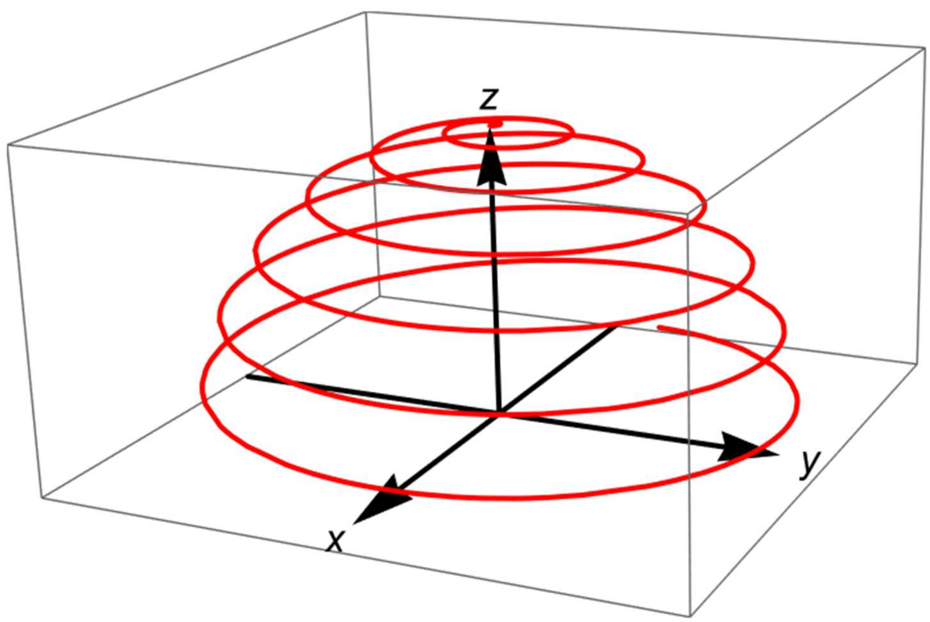
and

$$(X', Y', Z')=\{\langle\phi(t)|\hat{I}_x|\phi(t)\rangle, \langle\phi(t)|\hat{I}_y|\phi(t)\rangle, \langle\phi(t)|\hat{I}_z|\phi(t)\rangle\} \qquad \text{(RRF)}$$

as function of *t*, with parameters of $\Delta\omega$, ω_1 in the rf pulse period. Note that after the rf pulse period, we need to put $\omega_1 \to 0$.



(a) Rotational reference frame (RRF).



(b) Laboratory reference frame (LRF).

Fig.14(a) and (b)

ParametricPlot3D. $\omega_1 = 0.08$, $\Delta\omega = 0.005$. $\omega = 1$.

(a) blue (rotation, RRF). (b) Red (laboratory; LRF).

(b) $(X, Y, Z)=\{\langle\psi(t)|\hat{I}_x|\psi(t)\rangle, \langle\psi(t)|\hat{I}_y|\psi(t)\rangle, \langle\psi(t)|\hat{I}_z|\psi(t)\rangle\}$ (LCF)

11. Resonance condition

In resonance, we have

$$\Delta\omega = 0, \qquad \Omega = \omega_1$$

$$\langle I_x \rangle_t = X = \frac{\hbar}{2}\sin(\omega t)\sin(\omega_1 t)],$$

$$\langle I_y \rangle_t = Y = \frac{\hbar}{2}\cos(\omega t)\sin(\omega_1 t)],$$

$$\langle I_z \rangle_t = Z = \frac{\hbar}{2}[\cos^2\left(\frac{\omega_1 t}{2}\right) - \sin^2\left(\frac{\omega_1 t}{2}\right)] = \frac{\hbar}{2}\cos(\omega_1 t).$$

Note

$$\omega_1 = \omega_c \frac{B_1}{B_0}.$$

When $\omega_1 t = \frac{\pi}{2}$,

$$X = \frac{\hbar}{2}\sin(\omega t), \qquad Y = \frac{\hbar}{2}\cos(\omega t), \qquad Z = 0.$$

12. Spin dynamics after the rf 90° pulse

After the rf 90° pulse, the system is in the $|+y\rangle$ state. The rf field is turned off ($\omega_1 = 0$) at $t = 0$.

$$\begin{aligned}\hat{H}_{II} &= \hat{H}_{II}^{(0)} + \hat{H}_{II}^{(1)} \\ &= -\frac{1}{2}\hbar\omega\hat{\sigma}_z + \frac{1}{2}\hbar(\omega - \omega_c)\hat{\sigma}_z \\ &= -\frac{1}{2}\hbar\omega\hat{\sigma}_z + \frac{1}{2}\hbar\Delta\omega\hat{\sigma}_z\end{aligned}$$

with

$$\hat{H}_2^{(0)} = -\frac{1}{2}\hbar\omega\hat{\sigma}_z, \qquad \hat{H}_2^{(1)} = \frac{1}{2}\hbar\Delta\omega\hat{\sigma}_z,$$

$$\left|\phi(0)\right\rangle = \left|+y\right\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ i\end{pmatrix}, \qquad \text{(initial state)}$$

$$\left\langle\phi(t)\right|\hat{I}_i\left|\phi(t)\right\rangle = \frac{\hbar}{2}\left\langle\phi(0)\right|\exp(\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t)\hat{\sigma}_i\exp(-\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t)\left|\psi(0)\right\rangle$$
$$= \frac{\hbar}{2}\left\langle+y\right|\exp(\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t)\hat{\sigma}_i\exp(-\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t)i\left|+y\right\rangle$$

where

$$\exp(\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t)\hat{\sigma}_x\exp(-\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t) = \begin{pmatrix}0 & e^{it\Delta\omega}\\ e^{-it\Delta\omega} & 0\end{pmatrix},$$

$$\exp(\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t)\hat{\sigma}_y\exp(-\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t) = \begin{pmatrix}0 & -ie^{it\Delta\omega}\\ ie^{-it\Delta\omega} & 0\end{pmatrix},$$

$$\exp(\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t)\hat{\sigma}_z\exp(-\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t) = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.$$

Using these relations, we have

$$X' = -\frac{\hbar}{2}\sin(\Delta\omega t), \qquad Y' = \frac{\hbar}{2}\cos(\Delta\omega t), \qquad Z' = 0.$$

The spin vector rotates in either clockwise or counterclockwise with angular frequency (ω_c) in the *x*-*y* plane. At t = 0 (just after the 90° rf pulse is turned off), $X' = 0$, $Y' = \frac{\hbar}{2}$, Z'=0. For *t*>0, the spin rotates around the *z*' axis in the *x*'-*y*' plane.

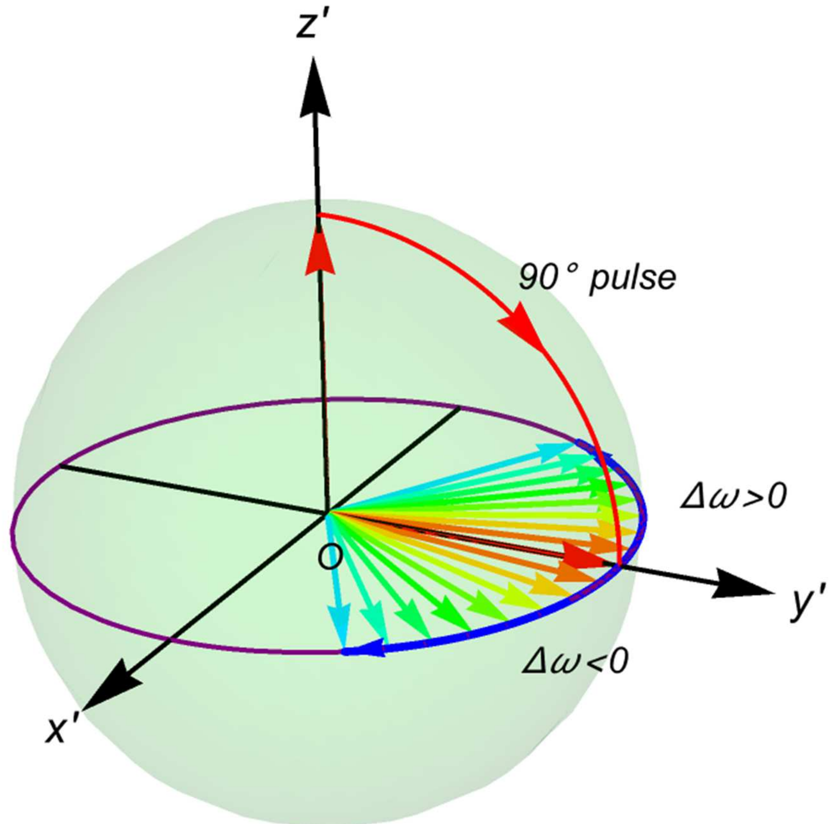


Fig.15 Rotation of spin after the rf 90° pulse is turned off. Counterclockwise ($\Delta\omega > 0$). Clockwise ($\Delta\omega < 0$)

((**Mathematica-5**))

After the turning off of 90 degrees rf pulse

```
Clear["Global`*"];
expr_* := expr /. Complex[a_, b_] :> Complex[a,
σx = PauliMatrix[1]; σy = PauliMatrix[2];
σz = PauliMatrix[3];
H1 = 1/2 (Δω σz) // FullSimplify;
H1M = MatrixExp[-ⅈ H1 t ];
H1P = MatrixExp[ⅈ H1 t ]; ψy1 = 1/√2 (1
                                      ⅈ);

ψy2 = 1/√2 (1 -ⅈ );

X1 = ℏ/2 ψy2.H1P. σx.H1M.ψy1 // FullSimplify;

Y1 = ℏ/2 ψy2.H1P. σy.H1M.ψy1 // FullSimplify;

Z1 = ℏ/2 ψy2.H1P. σz.H1M.ψy1 // FullSimplify;

{X1[[1, 1]], Y1[[1, 1]], Z1[[1, 1]]}
```

$$\left\{-\frac{1}{2}\hbar\,\mathrm{Sin}[t\,\Delta\omega],\ \frac{1}{2}\hbar\,\mathrm{Cos}[t\,\Delta\omega],\ 0\right\}$$

13. Spin dynamics after the rf 180° pulse

After the rf 180° pulse, the system is in the $i\left|-z\right\rangle$ state. The rf field is turned off ($\omega_1 = 0$) at $t = 0$.

$$\begin{aligned}\hat{H}_{II} &= \hat{H}_{II}{}^{(0)} + \hat{H}_{II}{}^{(1)} \\ &= -\frac{1}{2}\hbar\omega\hat{\sigma}_z + \frac{1}{2}\hbar(\omega-\omega_c)\hat{\sigma}_z \\ &= -\frac{1}{2}\hbar\omega\hat{\sigma}_z + \frac{1}{2}\hbar\Delta\omega\hat{\sigma}_z\end{aligned}$$

$$\left|\psi(0)\right\rangle = i\left|-z\right\rangle = i\begin{pmatrix}0\\1\end{pmatrix} \qquad \text{(initial state)}$$

$$\begin{aligned}\left\langle I_i\right\rangle_t &= \left\langle\phi(t)\right|\hat{I}_i\left|\phi(t)\right\rangle \\ &= \frac{\hbar}{2}\left\langle\phi(0)\right|\exp(\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t)\hat{\sigma}_i\exp(-\frac{i}{\hbar}\hat{H}_{II}{}^{(1)}t)\left|\phi(0)\right\rangle\end{aligned}$$

$$\left\langle S_x\right\rangle_t = X' = 0, \qquad \left\langle S_y\right\rangle_t = Y' = 0, \qquad \left\langle S_z\right\rangle_t = Z' = -\frac{\hbar}{2}$$

14, Measurement of T_2 using the rf-pulse method

What is the role of rf 180° pulse? It is the analogy of egalitarian foot race for the kindergarten class.

((egalitarian foot race for the kindergarten class))

The 180° 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° pulse is like that whistle. The spins in the larger field get out of phase by $+\Delta\theta$ in a time τ. After the 180° pulse, they continue to precess faster than M but at 2τ they return to the in-phase condition. The slower precessing spins do just the opposite, but again rephase after a time 2τ. (**Teachspin instruction manual**).

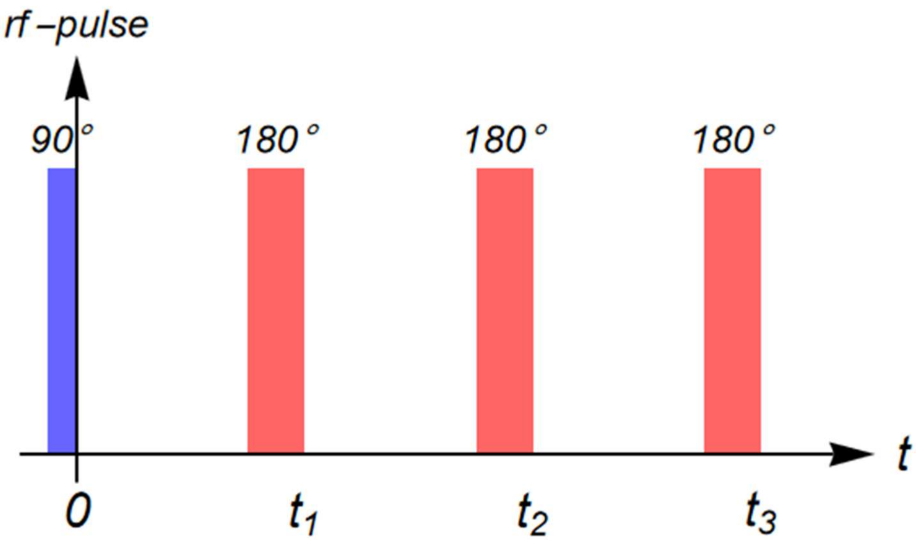
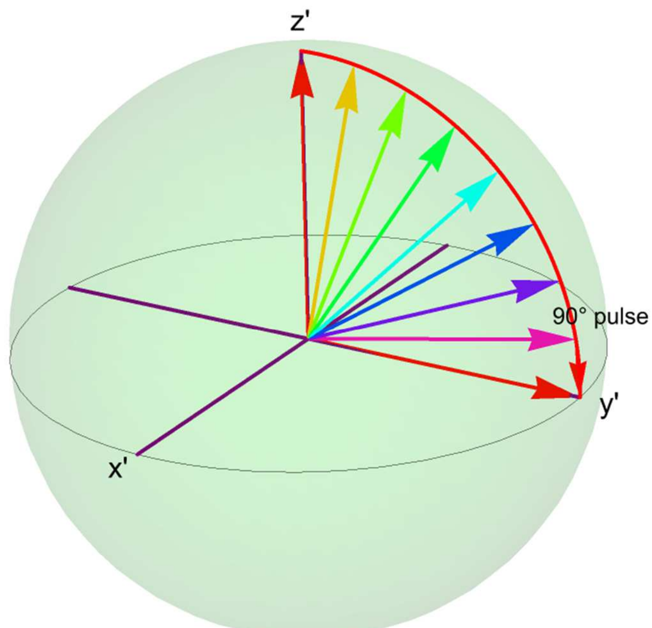
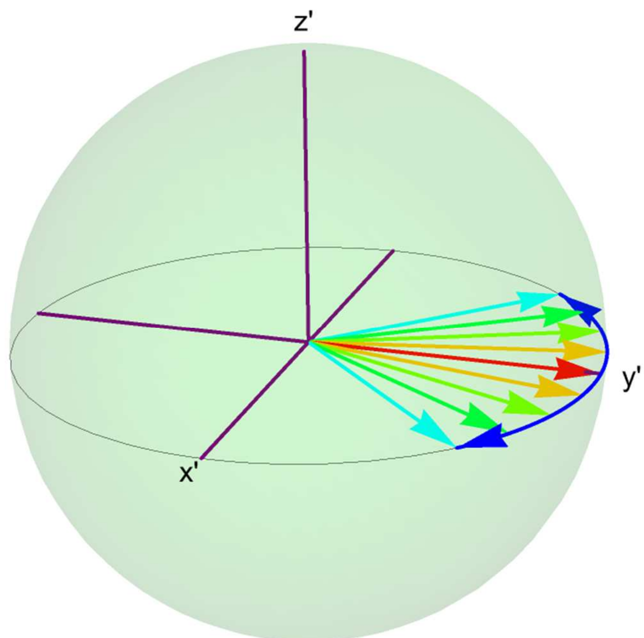


Fig.16 Pulse sequence for the rf spin echo experiment with 90° pulse and 180° pulses.

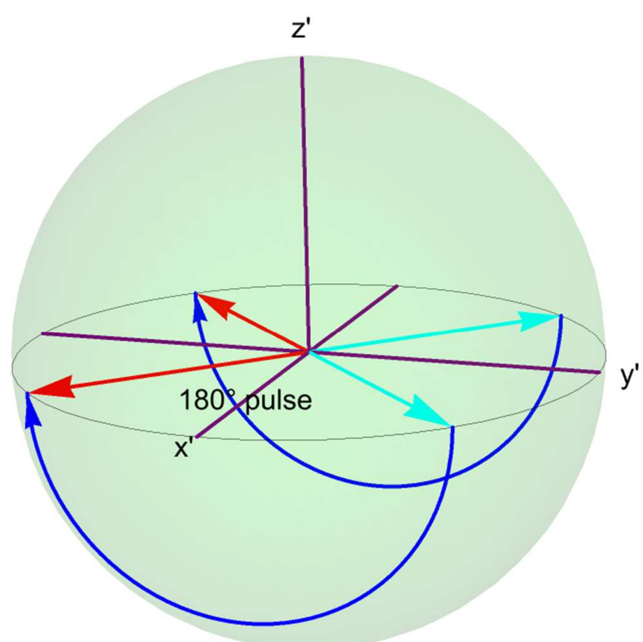
Sequence of rf pulse. rf 90° (*x'* axis) and rf 180° (*x'* axis) [counterclockwise]



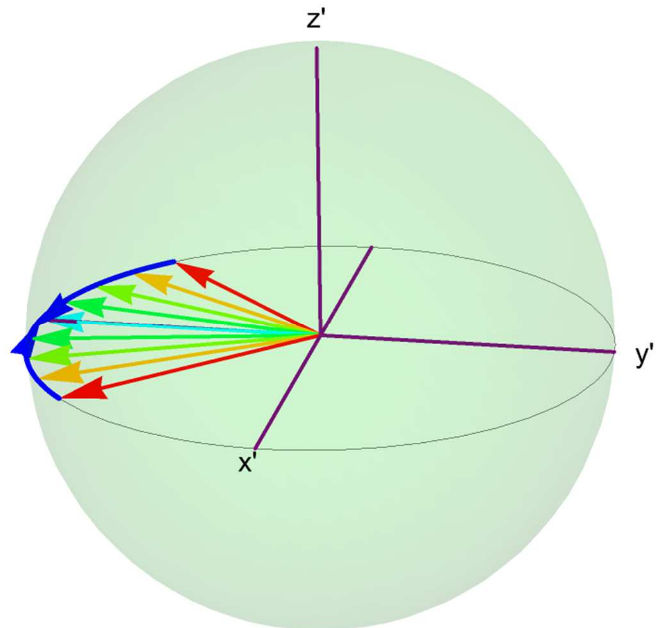
$t \simeq t_0$ (rf-90° pulse)

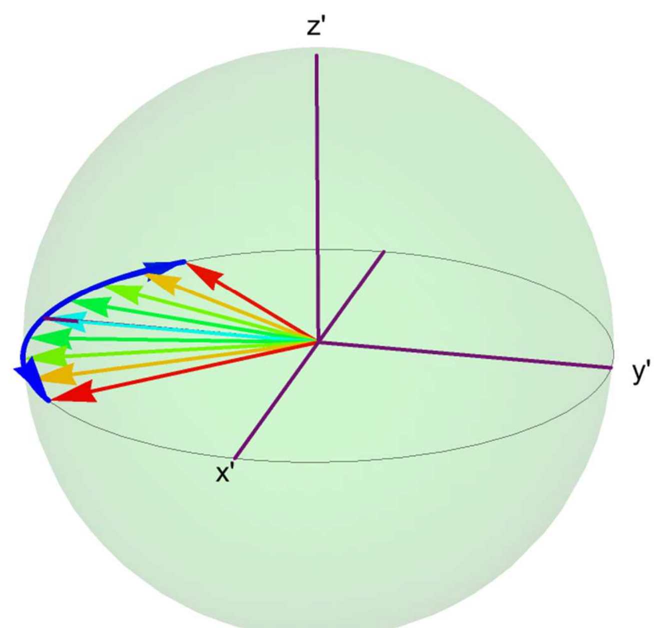


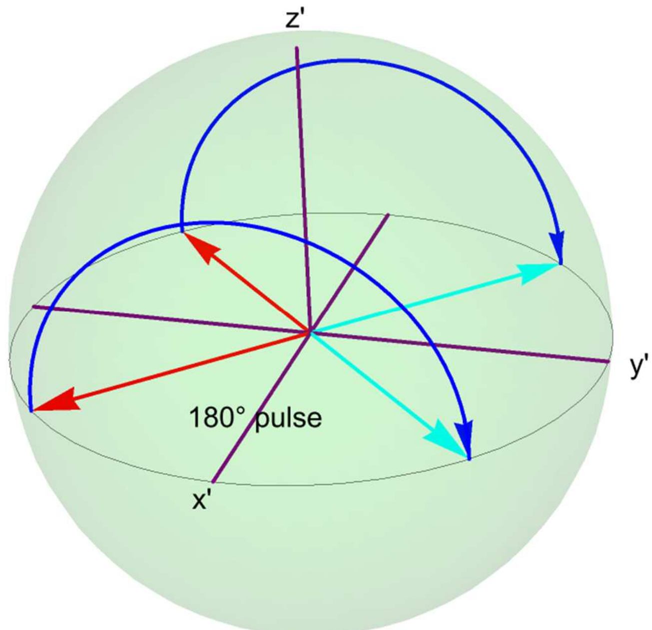
$t = t_0 - t_1$



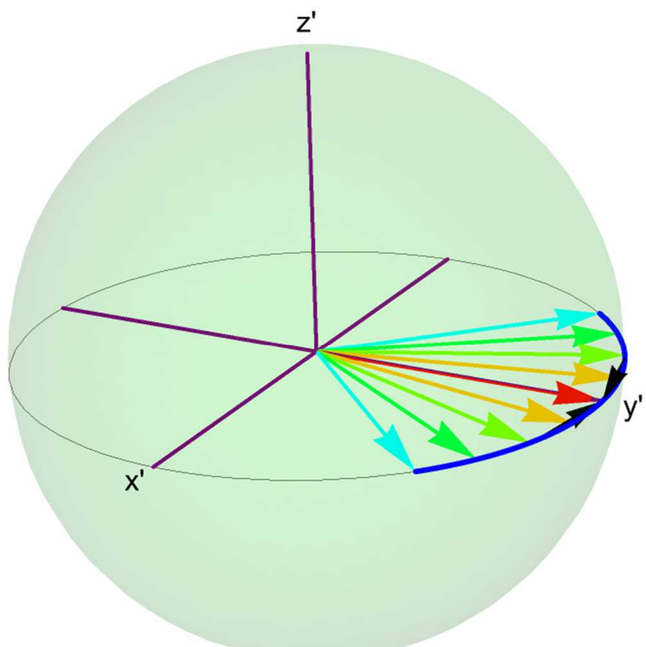
$t \simeq t_2$ (rf-180° pulse)

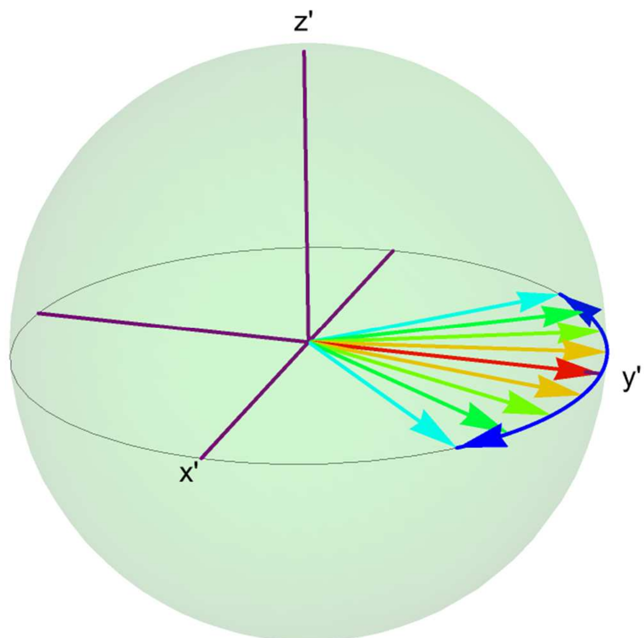

z'
y'
x'


z'
y'
x'

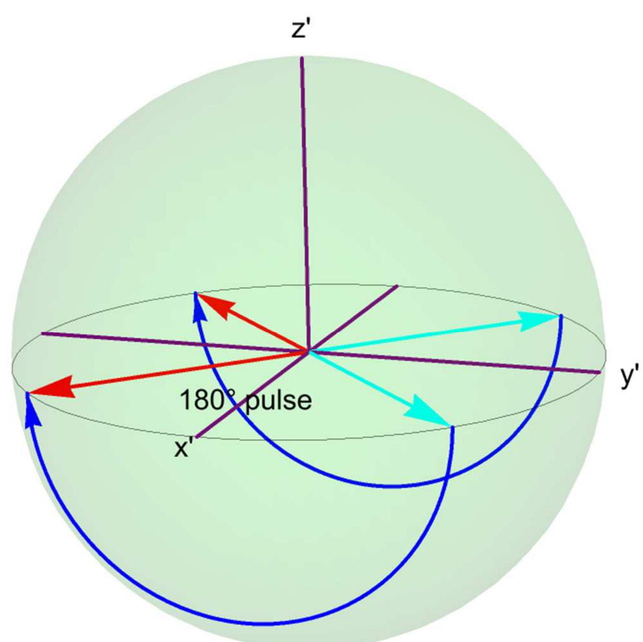


$t \simeq t_3$ (rf-180° pulse)





$t = t_0 - t_1$



$t \simeq t_3$ (rf-180° pulse)

Fig.17 rf spin echo method with a sequence of 90° and 180° rf pulses to determine the transverse relaxation time T_2.

((**Wikipedia**)) Spin echo method

We find a very interesting article on the rf-spin echo method for determination of the transverse relaxation time.in
https://en.wikipedia.org/wiki/Spin_echo

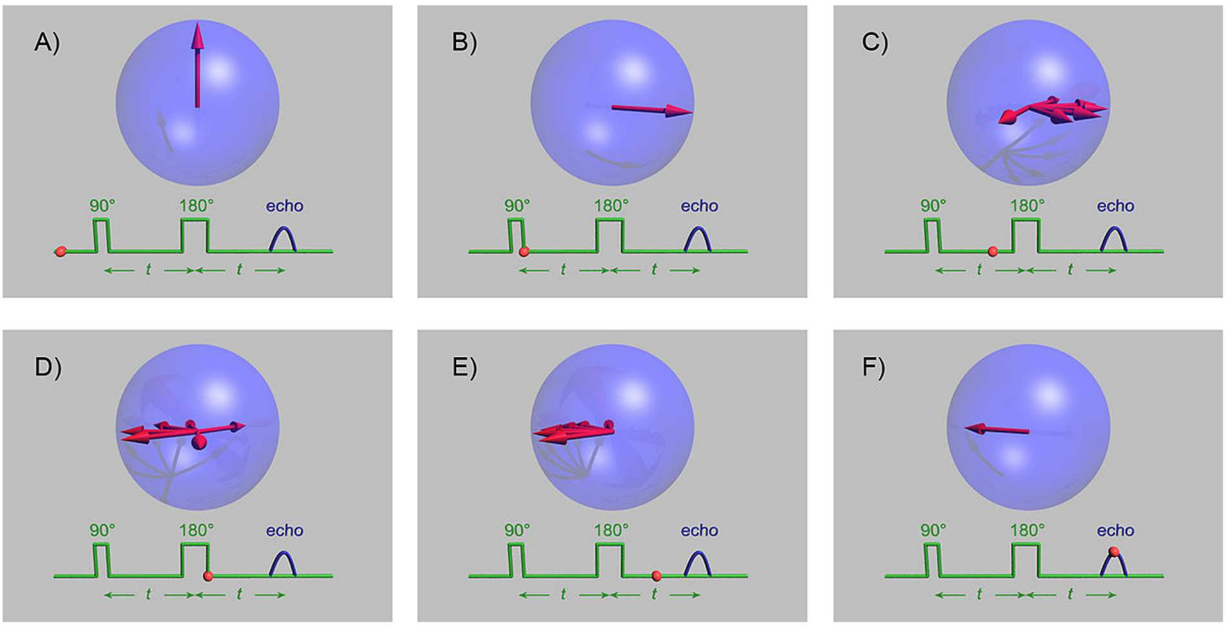


Fig.18

(a) The vertical red arrow is the average magnetic moment of a group of spins, such as protons. All are vertical in the vertical magnetic field and spinning on their long axis, but this illustration is in a rotating reference frame where the spins are stationary on average.

(b) A 90° pulse has been applied that flips the arrow into the horizontal (x'-y') plane.

(c) Due to local magnetic field inhomogeneities (variations in the magnetic field at different parts of the sample that are constant in time), as the net moment precesses, some spins slow down due to lower local field strength (and so begin to progressively trail behind) while some speed up due to higher field strength and start getting ahead of the others. This makes the signal decay.

(d) Progressively, the fast moments catch up with the main moment and the slow moments drift back toward the main moment. At some moment between E and F the sampling of the echo starts.

(e) Complete refocusing has occurred and at this time, an accurate T_2 echo can be measured with all T_2^* effects removed. Quite separately, return of the red arrow towards the vertical (not shown) would reflect the T_1 relaxation. 180 degrees is π radians so 180° pulses are often called π pulses.

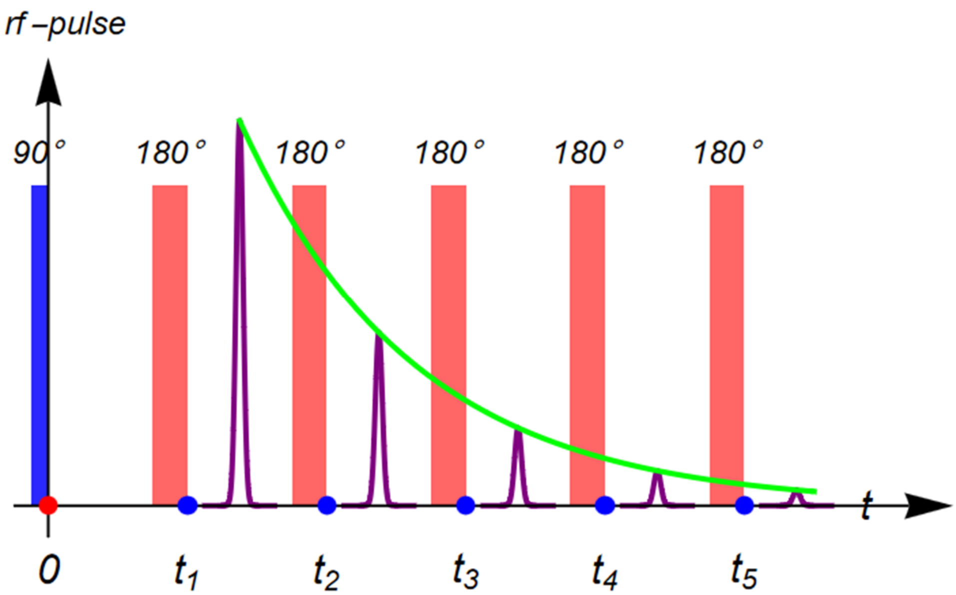


Fig.19 Free induction decay. Measurement of the relaxation time T_2 for the exponential decay such as $\exp(-t/T_2)$.

15. Summary

We discussed the principle of nuclear magnetic resonance (rf echo method) based on the quantum mechanics [Model-(II))]. The expectation value of spin can be easily calculated with the use of Mathematica. Experimentally the rf field is applied along the *x* axis. Since this rf field consists of the rf fields with CW (clockwise) and CCW (counterclockwise) in the rotating reference frame. Experimentally, we use only the CW rf field since the nuclear spins undergo a precession (CW rotation) around the *z* axis (magnetic field direction). In the rf echo method, the application of rf field along the *x*'-direction of rotating reference frame is equivalent to that of the rf field along the x-direction of the laboratory reference frame. The use of rotational reference frame is essential to understanding the principle of the measurement of relaxation time in the rf spin echo method. In quantum mechanics, the state vector $|\psi(t)\rangle$ in the laboratory reference frame is related to the state vector $|\phi(t)\rangle$ in the rotational reference frame through the rotation operator (rotation around the *z* axis by angle ωt in clockwise,

$$|\psi(t)\rangle = \exp(\frac{i}{2}\omega t\hat{\sigma}_z)|\phi(t)\rangle .$$

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APPENDIX I Formula in quantum mechanics

(a) Baker-Campbell-Hausdorff theorem (I)

$$\exp(x\hat{A})\hat{B}\exp(-x\hat{A}) = \hat{B} + \frac{x}{1!}[\hat{A},\hat{B}] + \frac{x^2}{2!}[\hat{A},[\hat{A},\hat{B}]] + \frac{x^3}{3!}[\hat{A},[\hat{A},[\hat{A},\hat{B}]]] + ...$$

(b) Baker-Campbell-Hausdorff theorem (II)

If the commutator of two operators $\hat{A}$ and $\hat{B}$ commutes with each of them ($\hat{A}$ and $\hat{B}$)

$$[\hat{A},[\hat{A},\hat{B}]] = \hat{0}, \qquad [\hat{B},[\hat{A},\hat{B}]] = \hat{0}.$$

One has an identity

$$\exp(\hat{A}+\hat{B}) = \exp(\hat{A})\exp(\hat{B})\exp(-\frac{1}{2}[\hat{A},\hat{B}]).$$

(c) Rotation operator

$$\exp(-\frac{i}{2}\hat{\sigma}_x\theta) = \hat{1}\cos\frac{\theta}{2} - i\sin\frac{\theta}{2}\hat{\sigma}_x,$$

$$\exp(-\frac{i}{2}\hat{\sigma}_y\theta) = \hat{1}\cos\frac{\theta}{2} - i\sin\frac{\theta}{2}\hat{\sigma}_y,$$

$$\exp(-\frac{i}{2}\hat{\sigma}_z\theta) = \hat{1}\cos\frac{\theta}{2} - i\sin\frac{\theta}{2}\hat{\sigma}_z,$$

$$\exp[-\frac{i}{2}(\hat{\boldsymbol{\sigma}}\cdot\mathbf{n})\theta] = \hat{1}\cos\frac{\theta}{2} - i\sin\frac{\theta}{2}(\hat{\boldsymbol{\sigma}}\cdot\mathbf{n}).$$ (***n***: unit vector in the 3D space)

(d)

$$(\hat{\boldsymbol{\sigma}}\cdot\mathbf{A})(\hat{\boldsymbol{\sigma}}\cdot\mathbf{B}) = \hat{1}(\mathbf{A}\cdot\mathbf{B}) + i\hat{\boldsymbol{\sigma}}\cdot(\mathbf{A}\times\mathbf{B})$$

(e) Pauli operator

$$[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z, \qquad [\hat{\sigma}_y, \hat{\sigma}_z] = 2i\hat{\sigma}_x, \qquad [\hat{\sigma}_z, \hat{\sigma}_x] = 2i\hat{\sigma}_y.$$

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

$$\hat{\sigma}_x^{\ 2} = \hat{\sigma}_y^{\ 2} = \hat{\sigma}_z^{\ 2} = \hat{1}.$$

(f) Eigenstates of spin 1/2

$$|+z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |-z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

$$|+x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}, \qquad |-x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix},$$

$$|+y\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}, \qquad |-y\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}.$$

((Nomenclature))

Rotation operator
Pauli matrices
Eigenstate and eigenvalue
Free induction decay (FID)
Rotating wave approximation
Rotational reference frame (RRF)
Laboratory reference frame (FRF)
The 90° pulse
The rephasing 180° pulse (refocusing pulse)
Rabi angular frequency
Time evolution operator
Schrődinger equation
Time evolution operator
Dirac picture and Schrődinger picture in quantum mechanics
Transverse relaxation time
Longitudinal relaxation time
Baker-Campbell-Haudorff theorem

APPENDIX II

The discovery of the spin echo method by Erwin.L. Hahn (1921-2016)
https://arxiv.org/ftp/arxiv/papers/1906/1906.03428.pdf

Erwin Louis Hahn was one of the most innovative and influential physical scientists in recent history, impacting generations of scientists through his work in nuclear magnetic resonance (NMR), optics, and the intersection of these two fields. Starting with his discovery of the spin echo, a phenomenon of monumental significance and practical importance, **Hahn** launched a major revolution in how we think about spin physics, with numerous implications to follow in many other areas of science. Students of NMR and coherent optics quickly discover that many of the key concepts and techniques in these fields derive directly from his work.

Hahn was happy to tell the story of his "accidental" discovery of the spin echo, the most famous of his achievements. He was a post-doctoral fellow when he discovered spin echoes, though he emphasized that at that time he was given freedom to work more like an independent research scientist. While studying nuclear spin coherence relaxation, he applied not one but two driving pulses separated by a time interval. What he saw (and what he at first thought to be a "glitch") was that, in addition to decaying FID (free induction decay) signals following each of the two separate pulses, there was a third "ghost" signal appearing at a time following the second pulse equal to the time separation between the two pulses. This was puzzling because it was not clear where the signal came from; the echo occurred long after the FID following each of the pulses died out due to dephasing, then thought of as an irreversible process in the thermodynamic sense. Eventually, **Hahn** recognized that the "echo" signal was due to "refocusing" of the precession of different nuclei in the sample occurring at slightly different frequencies due to magnetic-field inhomogeneities and that the system's order was "hidden" but not gone. The second pulse, in effect, creates a kind of time reversal, where the relative phases accumulated by the spins during the evolution between the pulses are undone during the evolution after the second pulse. Today, the spin echo and its countless generalizations, for instance to sequences of not two but up to thousands of pulses, constitute the basis of essentially all magnetic resonance applications, including the familiar medical-diagnostic magnetic resonance imaging (MRI).