Quantum Mechanics of rf Spin Echo in Nuclear magnetic resonance

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The quantum mechanics is used to understand the essential points for the spin echo method of nuclear magnetic resonance (NMR). A static magnetic field is applied along a nuclear spin with angular momentum $\hbar\hat{\boldsymbol{I}}$ and the magnetic moment $\gamma\hbar\hat{\boldsymbol{I}}$, where γ is the gyromagnetic ratio. The static magnetic field is applied along the z axis. The radio frequency (r.f.) field magnetic field is applied along the plane perpendicular to the z axis. Here we consider the case of spin 1/2 system.

1. Gyromagnetic ratio of nuclear spin

(a) Electron

Orbital angular momentum and orbital magnetic moment

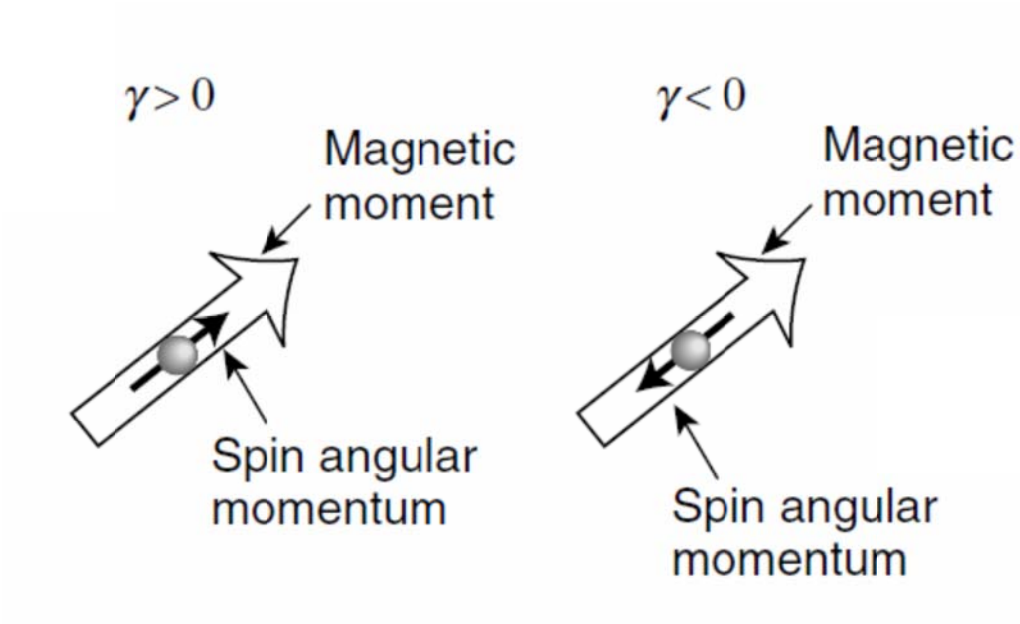
$$\gamma_L = \frac{\boldsymbol{\mu}_L}{\boldsymbol{L}} = \frac{-\mu_B \frac{\boldsymbol{L}}{\hbar}}{\boldsymbol{L}} = -\frac{\mu_B}{\hbar} = -\frac{e}{2mc}$$

Spin angular momentum and spin magnetic moment

$$\gamma_S = \frac{\boldsymbol{\mu}_S}{\boldsymbol{S}} = \frac{-g_e\mu_B \frac{\boldsymbol{S}}{\hbar}}{\boldsymbol{S}} = -\frac{g_e\mu_B}{\hbar} = -g_e\frac{e}{2mc}$$

where $g = 2.0023193043617(15)$.

(b) Proton (neutron); nuclear spin



The gyromagnetic ratio is defined by

$$\gamma_N = \frac{\boldsymbol{\mu}_I}{\hbar \boldsymbol{I}} = \frac{g_n \mu_N \boldsymbol{I}}{\hbar \boldsymbol{I}} = \frac{g_n \mu_N}{\hbar} = g_n \frac{e}{2m_p c}$$

where $\hbar \boldsymbol{I}$ is the angular momentum.

Table-1: Gyromagnetic ratio

Nucleus	(10^6 rad s^{-1} T^{-1})	(MHz T^{-1})
^1H	267.513	42.577 478 92(29)
^2H	41.065	6.536
^3He	−203.789	−32.434
^7Li	103.962	16.546
^{13}C	67.262	10.705
^{14}N	19.331	3.077
^{15}N	−27.116	−4.316
^{17}O	−36.264	−5.772
^{19}F	251.662	40.052
^{23}Na	70.761	11.262
^{27}Al	69.763	11.103
^{29}Si	−53.190	−8.465
^{31}P	108.291	17.235
^{57}Fe	8.681	1.382
^{63}Cu	71.118	11.319
^{67}Zn	16.767	2.669
^{129}Xe	−73.997	−11.777

2. Spin recession

(a) Classical treatment

The magnetic moment of nuclear spin with angular momentum $\hbar I_z$ -s given by

$$\mu_I = \gamma\hbar I_z$$

When a static magnetic field is applied along the z axis, the Hamiltonian has the form of the Zeeman energy, given by

$$H = -\boldsymbol{\mu}_I \cdot B = -\gamma\hbar \boldsymbol{I} \cdot \boldsymbol{B}$$

We consider the equation of motion for the angular momentum

$$\hbar \frac{d\boldsymbol{L}}{dt} = \boldsymbol{\tau} = \boldsymbol{\mu} \times \boldsymbol{B} = \gamma\hbar \boldsymbol{I} \times B$$

$$\frac{d\boldsymbol{I}}{dt} = \gamma(\boldsymbol{I} \times \boldsymbol{B})$$

When the magnetic field is applied along the +z axis,

$$\dot{I}_z = 0 , \qquad \dot{I}_x = \gamma B I_y , \qquad \dot{I}_y = -\gamma B I_x$$

leading to the equation

$$\frac{d}{dt}(I_x + iI_y) = \gamma B I_y - i\gamma B I_x = -i\gamma B(I_x + iI_y)$$

or

$$I_x + iI_y = I_0 \exp(-i\gamma B t) = I_0 e^{i\omega_0 t}$$

where

$$\omega_0 = -\gamma B$$

(clockwise for $\gamma > 0$ and counter clockwise for $\gamma < 0$).

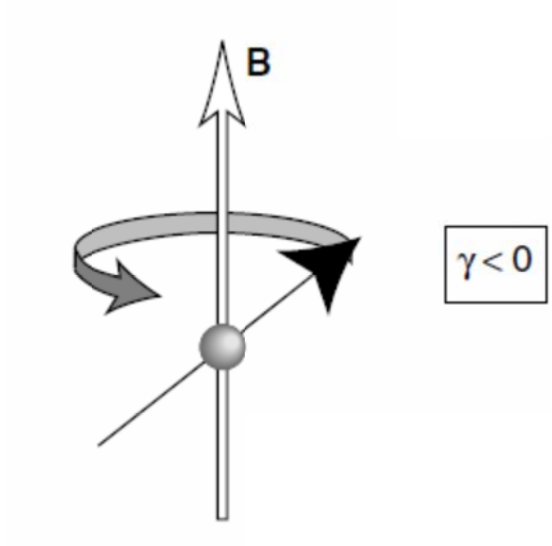


Fig. Precession of nuclear spin. $\omega^0 = -\gamma B > 0$ for $\gamma < 0$. (Counter-clockwise direction). The r.f. field $\boldsymbol{B}_{res}^{RF}(t)$ with $\omega_{ref} > 0$.

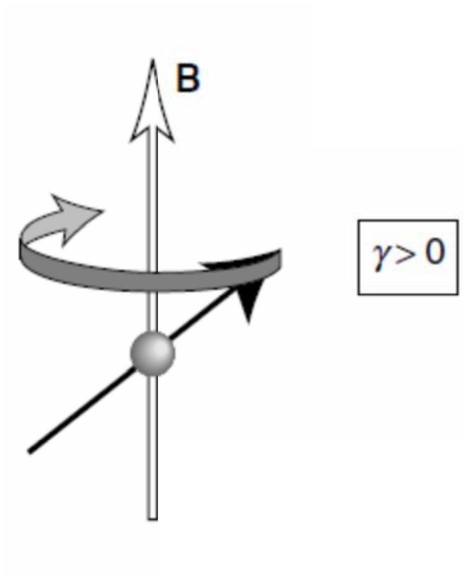


Fig. Precession of nuclear spin. $\omega^0 = -\gamma B < 0$ for $\gamma > 0$. (Clockwise direction). The r.f. foeld $\boldsymbol{B}_{res}^{RF}(t)$ with $\omega_{ref} < 0$

(b) Spin precession using quantum mechanics

The time evolution operator is defined by $\hat{T} = \exp(-\frac{i}{\hbar}\hat{H}t)$. When a static magnetic field is applied along the z axis (in the absence of the r.f. field), the Hamiltonian is given by

$$\hat{H} = -\gamma\hbar\hat{I}_z B = \hbar\omega_0\hat{I}_z$$

where $\omega_0 = -\gamma B$ and $\hat{I}_z = \frac{1}{2}\hat{\sigma}_z$. The state vector at the time t_2 is related to the state vector at the time t_1 through the time evolution operator as

$$\begin{aligned}
|\psi(t_2)\rangle &= \exp(-\frac{i}{\hbar}\hat{H}\tau)|\psi(t_1)\rangle \\
&= \exp(-\frac{i}{\hbar}\hbar\omega_0\hat{I}_z\tau)|\psi(t_1)\rangle \\
&= \exp(-i\omega_0\tau\hat{I}_z)|\psi(t_1)\rangle \\
&= \exp(-i\frac{\omega_0\tau}{2}\hat{\sigma}_z)|\psi(t_1)\rangle
\end{aligned}$$

Here we define the rotation operator as

$$\hat{R}_z(\phi) = \exp(-\frac{i}{2}\phi\hat{\sigma}_z) = \begin{pmatrix} \exp(-\frac{i\phi}{2}) & 0 \\ 0 & \exp(\frac{i\phi}{2}) \end{pmatrix}$$

This means that spin rotates around the *z* axis through the angle $\phi = \omega_0\tau$.

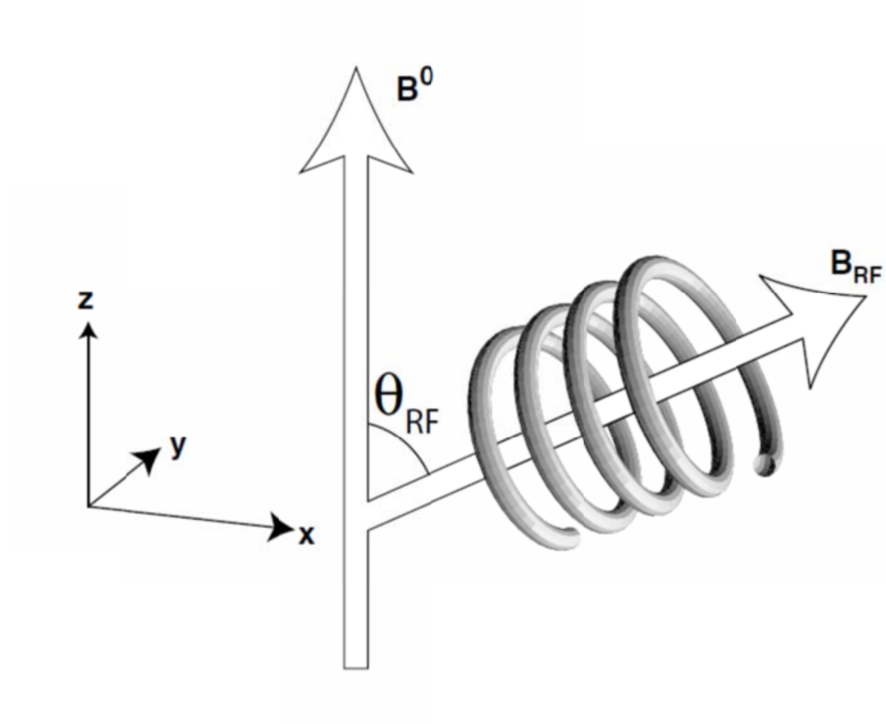
We note that

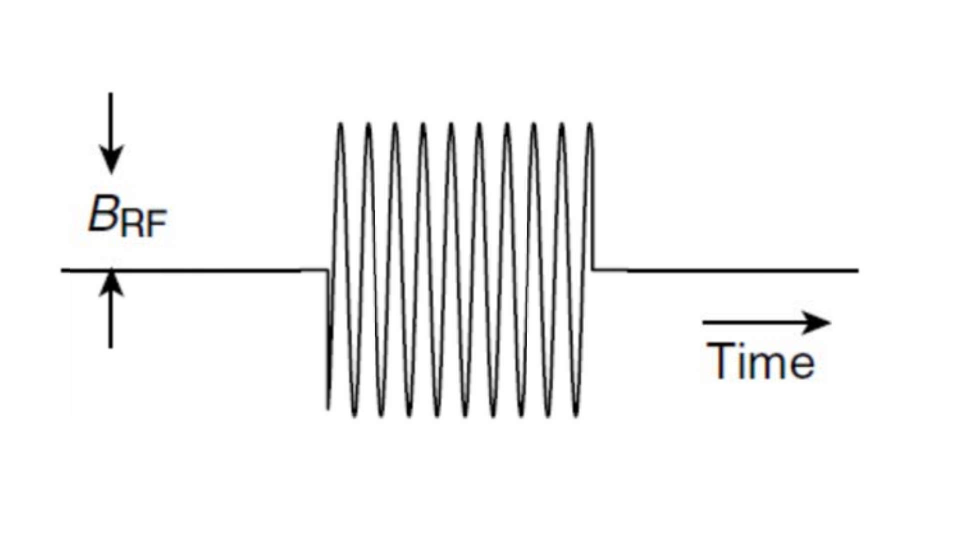
$$\hat{R}_z(\frac{\pi}{2})|+x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i\pi/4} & 0 \\ 0 & e^{i\pi/4} \end{pmatrix}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}e^{-i\pi/4}\begin{pmatrix} 1 \\ i \end{pmatrix} = e^{-i\pi/4}|+y\rangle$$

$$\hat{R}_z(\pi)|+x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i\pi/2} & 0 \\ 0 & e^{i\pi/2} \end{pmatrix}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i\pi/2} \\ e^{i\pi/2} \end{pmatrix} = \frac{1}{\sqrt{2}}e^{-i\pi/2}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = e^{-i\pi/2}|-x\rangle$$

3. r.f. magnetic field

The r.f. coil generates a field $\boldsymbol{B}_{RF}$ along the tilted axis in Fig. During an r.f. pulse on a single spectrometer channel, the magnitude of this field oscillates at the spectrometer reference angular frequency ω_{ref}. Between pulses, the r.f. field is equal to zeo. If the pulse is perfectly rectangular, then the r.f. field has the form:





The r.f. field is given by

$$\begin{aligned}\boldsymbol{B}_{RF}(t) &= B_{RF}(\cos\theta_{RF}\boldsymbol{e}_z + \sin\theta_{RF}\boldsymbol{e}_x)\cos(\omega_{ref}t + \phi_p) \\ &= \boldsymbol{B}^{RF}_{res}(t) + \boldsymbol{B}^{RF}_{non-res}(t) + \boldsymbol{B}^{RF}_{long}(t)\end{aligned}$$

during an r.f. pulse. The r.f. field consists of a longitudinal component proportional to $\cos\theta_{RF}$ plus a transverse component proportional to $\sin\theta_{RF}$. It turns out to be useful to imagine that the transverse oscillating field is actually a sum of two rating components. Both components rotae in the *xy*-plane, at the same frequency, but in opposite directions. Note that

$$\boldsymbol{B}_{res}^{RF}(t) = \frac{1}{2} B_{RF} \sin\theta_{RF} [\boldsymbol{e}_x \cos(\omega_{ref} t + \phi_p) + \boldsymbol{e}_y \sin(\omega_{ref} t + \phi_p)]$$

$$\boldsymbol{B}_{non-res}^{RF}(t) = \frac{1}{2} B_{RF} \sin\theta_{RF} [\boldsymbol{e}_x \cos(\omega_{ref} t + \phi_p) - \boldsymbol{e}_y \sin(\omega_{ref} t + \phi_p)]$$

$$\boldsymbol{B}_{long}^{RF}(t) = B_{RF} \cos\theta_{RF} \boldsymbol{e}_z \cos(\omega_{ref} t + \phi_p)$$

where

$$\omega_0 = -\gamma B$$

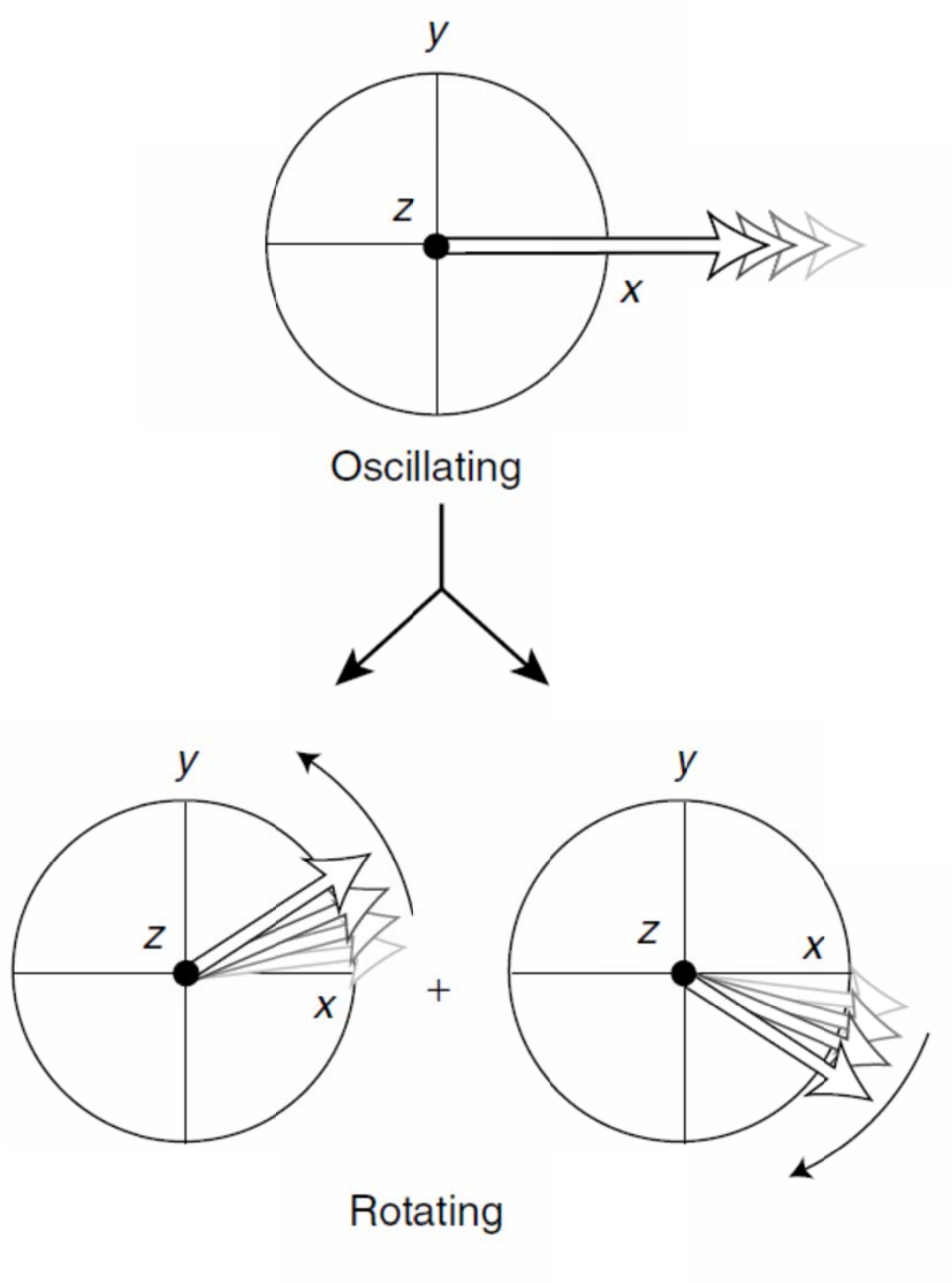
For positive γ, the angular frequency ω_{ref} is negative (clockwise), and for negative γ, the angular frequency ω_{ref} is positive (counter-clock wise). The transverse part of the spin Hamiltonian is approximated as

$$\begin{aligned} \hat{H}_L &= -\gamma\hbar \hat{\boldsymbol{I}} \cdot \boldsymbol{B}_{res}^{RF}(t) \\ &= -\frac{1}{2} \gamma\hbar B_{RF} \sin\theta_{RF} [\hat{I}_x \cos(\omega_{ref} t + \phi_p) + \hat{I}_y \sin(\omega_{ref} t + \phi_p)] \end{aligned}$$

Note that

$$\omega_{nut} = \left| \frac{1}{2} \gamma\hbar B_{RF} \sin\theta_{RF} \right|$$

is the nutation angular frequency.



4. State vector in the rotation frame and Laboratory frame

$$|+x'\rangle = \hat{R}_z(\Phi)|+x\rangle$$

$$\left|+x\right\rangle = \hat{R}_z(-\Phi)\left|+x'\right\rangle$$

Here we use the notations

$\left|+x\right\rangle = \left|+x'\right\rangle_R$ Rotating frame

$\left|+x'\right\rangle = \left|+x\right\rangle_L$ Laboratory frame

Then we have

$$\left|+x'\right\rangle_R = \hat{R}_z(-\Phi)\left|+x\right\rangle_L$$

This relationship may be generalized. Any spin state, viewed from the rotating frame, is related to the spin state, viewed from the fixed frame through

$$\left|\psi\right\rangle_R = \hat{R}_z(-\Phi)\left|\psi\right\rangle, \qquad \left|\psi\right\rangle = \hat{R}_z(\Phi)\left|\psi\right\rangle_R$$

Now we consider the Schrödinger equation in the laboratory frame,

$$i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle = \hat{H}\left|\psi\right\rangle$$

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle_R &= i\hbar\frac{\partial}{\partial t}\hat{R}_z(-\Phi)\left|\psi\right\rangle \\ &= i\hbar[\frac{\partial}{\partial t}\hat{R}_z(-\Phi)]\left|\psi\right\rangle + \hat{R}_z(-\Phi)i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle \end{aligned}$$

Here we note that

$$\hat{R}_z(-\Phi) = \exp(\frac{i}{\hbar}\hat{J}_z\Phi) = \exp(i\Phi\hat{I}_z)$$

where

$$\hat{J}_z = \hbar\hat{I}_z = \frac{\hbar}{2}\hat{\sigma}_z, \qquad \hat{I}_z = \frac{1}{2}\hat{\sigma}_z$$

The derivative of $\hat{R}_z(-\Phi)$ with respect to *t*;

$$\frac{\partial}{\partial t}\hat{R}_z(-\Phi) = \frac{\partial}{\partial t}\exp(i\Phi\hat{I}_z)$$
$$= i\hat{I}_z\frac{d\Phi}{dt}\exp(i\Phi\hat{I}_z)$$
$$= i\omega_{ref}\hat{I}_z\hat{R}_z(-\Phi)$$

where

$$\frac{d\Phi}{dt} = \omega_{ref}, \qquad \Phi = \omega_{ref}t + \phi_{ref}$$

Thus we have

$$i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle_R = -\hbar\omega_{ref}\hat{I}_z\hat{R}_z(-\Phi)\left|\psi\right\rangle + \hat{R}_z(-\Phi)i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle$$
$$= -\hbar\omega_{ref}\hat{I}_z\hat{R}_z(-\Phi)\left|\psi\right\rangle + \hat{R}_z(-\Phi)\hat{H}_L\left|\psi\right\rangle$$
$$= -\hbar\omega_{ref}\hat{I}_z\left|\psi\right\rangle_R + \hat{R}_z(-\Phi)\hat{H}_L\hat{R}_z(\Phi)\left|\psi\right\rangle_R$$
$$= [-\hbar\omega_{ref}\hat{I}_z + \hat{R}_z(-\Phi)\hat{H}_L\hat{R}_z(\Phi)]\left|\psi\right\rangle_R$$
$$= \hat{H}_R\left|\psi\right\rangle_R$$

The Schrödinger equation in the rotating frame is given by

$$i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle_R = \hat{H}_R\left|\psi\right\rangle_R$$

with the Hamiltonian in the rotating frame,

$$\hat{H}_R = -\hbar\omega_{ref}\hat{I}_z + \hat{R}_z(-\Phi)\hat{H}_L\hat{R}_z(\Phi)$$

5. Precession in the rotating frame

The spin Hamiltonian in the static field is

$$\hat{H}_L = \hbar\omega_0\hat{I}_z.$$

So the rotating-frame Hamiltonian is

$$\hat{H}^0{}_R = -\hbar\omega_{ref}\hat{I}_z + \hat{R}_z(-\Phi)\hbar\omega_0\hat{I}_z\hat{R}_z(\Phi)$$
$$= \hbar(\omega_0 - \omega_{ref})\hat{I}_z$$
$$= \hbar\Omega_0\hat{I}_z$$

where

$$\Omega_0 = (\omega_0 - \omega_{ref})$$

Note that

$$\hat{R}_z(-\Phi)\hat{I}_z\hat{R}_z(\Phi) = \hat{I}_z\hat{R}_z(-\Phi)\hat{R}_z(\Phi) = \hat{I}_z$$

6. Rotating-frame Hamiltonian

In the presence of a static field along the *z* axis, the Hamiltonian is given by

$$\hat{H}_0 = \hbar\omega^0\hat{I}_z = \frac{\hbar\omega^0}{2}\hat{\sigma}_z$$

with

$$\hat{I}_z = \frac{1}{2}\hat{\sigma}_z$$

$$\omega_0 = -\gamma B$$

The Hamiltonian due to the r.f. field in the *x*-*y* plane is

$$\hat{H}_{RF} = -\gamma\hbar\hat{\boldsymbol{I}}\cdot\boldsymbol{B}^{RF}_{res}(t)$$
$$= -\frac{1}{2}\gamma\hbar B_{RF}\sin\theta_{RF}[\hat{I}_x\cos(\omega_{rf}t+\phi_p)+\hat{I}_y\sin(\omega_{rf}t+\phi_p)]$$

where

$$\Phi_P = \omega_{rf}t + \phi_P,$$

Then the resulting Hamiltonian is

$$\hat{H}_L = \hat{H}_0 + \hat{H}_{RF}$$
$$= \hbar\omega_0 \hat{I}_z - \frac{1}{2}\gamma\hbar B_{RF} \sin\theta_{RF} [\hat{I}_x \cos(\Phi_p) + \hat{I}_y \sin(\Phi_p)]$$

The Hamiltonian in the rotating frame is

$$\hat{H}_R = -\hbar\omega_{ref} \hat{I}_z + \hat{R}_z(-\Phi)\hat{H}_L \hat{R}_z(\Phi)$$
$$= -\hbar\omega_{ref} \hat{I}_z + \hbar\omega_0 \hat{R}_z(-\Phi)\hat{I}_z \hat{R}_z(\Phi) - \frac{1}{2}\gamma\hbar B_{RF} \sin\theta_{RF} \hat{R}_z(-\Phi)[\hat{I}_x \cos\Phi_P + \hat{I}_y \sin\Phi_P]\hat{R}_z(\Phi)$$
$$= \hbar(\omega_0 - \omega_{ref})\hat{I}_z - \frac{1}{2}\gamma\hbar B_{RF} \sin\theta_{RF} \hat{R}_z(-\Phi + \Phi_P)\hat{R}_z(-\Phi_P)[\hat{I}_x \cos\Phi_P + \hat{I}_y \sin\Phi_P]\hat{R}_z(\Phi_P)\hat{R}_z(\Phi - \Phi_P)$$
$$= \hbar(\omega_0 - \omega_{ref})\hat{I}_z - \frac{1}{2}\gamma\hbar B_{RF} \sin\theta_{RF} \hat{R}_z(-\Phi + \Phi_P)\hat{I}_x \hat{R}_z(\Phi - \Phi_P)$$

where

$$\hat{R}_z(-\Phi_p)[\hat{I}_x \cos\Phi_p + \hat{I}_y \sin\Phi_p]\hat{R}_z(\Phi_p) = \hat{I}_x$$

$$\hat{R}_z(-\Phi + \Phi_P)\hat{R}_z(-\Phi_P) = \hat{R}_z(-\Phi)$$

$$\hat{R}_z(\Phi_P)\hat{R}_z(\Phi - \Phi_P) = \hat{R}_z(\Phi)$$

((**Formula**))

$$\hat{R}_z(\Phi_p)\hat{I}_x \hat{R}_z(-\Phi_p) = \cos(\Phi_p)\hat{I}_x + \sin(\Phi_p)\hat{I}_y$$

$$\hat{R}_z(\Phi_p)\hat{I}_y \hat{R}_z(-\Phi_p) = -\sin(\Phi_p)\hat{I}_x + \cos(\Phi_p)\hat{I}_y$$

or

$$\hat{I}_x = \hat{R}_z(-\Phi_p)[\cos(\Phi_p)\hat{I}_x + \sin(\Phi_p)\hat{I}_y]\hat{R}_z(\Phi_p)$$

$$\hat{I}_y = \hat{R}_z(-\Phi_p)[-\sin(\Phi_p)\hat{I}_x + \cos(\Phi_p)\hat{I}_y]\hat{R}_z(\Phi_p)$$

Thus we have

$$\hat{H}_R = \hbar\Omega_0 \hat{I}_z - \frac{1}{2}\gamma\hbar B_{RF} \sin\theta_{RF} \hat{R}_z(-\phi_{ref} + \phi_p)\hat{I}_x \hat{R}_z(\phi_{ref} - \phi_P)$$

Note that

$$\Omega_0 = \omega_0 - \omega_{ref}$$

$$\Phi = \omega_{ref} t + \phi_{ref}, \qquad \Phi_p = \omega_{rf} t + \phi_p$$

Ω_0 is the resonance offset. Note that the time dependence has vanished from this expression. This is the point of the rotating frame. It transforms a time-dependent quantum-mechanical problem into a time-independent one.

((**Note**))

For $\gamma < 0$, $\phi_{ref} = 0$ (definition)

$$\begin{aligned}\hat{H}_R &= \hbar\Omega^0 \hat{I}_z - \frac{1}{2}\gamma\hbar B_{RF} \sin\theta_{RF} \hat{R}_z(\phi_p)\hat{I}_x \hat{R}_z(-\phi_P) \\ &= \hbar\Omega^0 \hat{I}_z - \frac{1}{2}\gamma\hbar B_{RF} \sin\theta_{RF} (\cos\phi_p \hat{I}_x + \sin\phi_p \hat{I}_y)\end{aligned}$$

For $\gamma < 0$, $\phi_{ref} = \pi$ (definition)

$$\begin{aligned}\hat{H}_R &= \hbar\Omega^0 \hat{I}_z - \frac{1}{2}\gamma\hbar B_{RF} \sin\theta_{RF} \hat{R}_z(-\pi + \phi_p)\hat{I}_x \hat{R}_z(\pi - \phi_P) \\ &= \hbar\Omega^0 \hat{I}_z + \frac{1}{2}\gamma\hbar B_{RF} \sin\theta_{RF} (\cos\phi_p \hat{I}_x + \sin\phi_p \hat{I}_y)\end{aligned}$$

where

$$\hat{R}_z(\phi_p)\hat{I}_x \hat{R}_z(-\phi_P) = \cos\phi_p \hat{I}_x + \sin\phi_p \hat{I}_y$$

and

$$\hat{R}_z(-\pi+\phi_p)\hat{I}_x\hat{R}_z(\pi-\phi_P) = \cos(\phi_p-\pi)\hat{I}_x + \sin(\phi_p-\pi)\hat{I}_y$$
$$= -(\cos\phi_p\hat{I}_x + \sin\phi_p\hat{I}_y)$$

Combining these two equations, we get the final result

$$\hat{H}_R = \hbar\Omega^0\hat{I}_z + \hbar\omega_{nut}(\cos\phi_p\hat{I}_x + \sin\phi_p\hat{I}_y)$$

where

$$\omega_{nut} = \left|\frac{1}{2}\gamma\hbar B_{RF}\sin\theta_{RF}\right|$$

For $\gamma > 0$

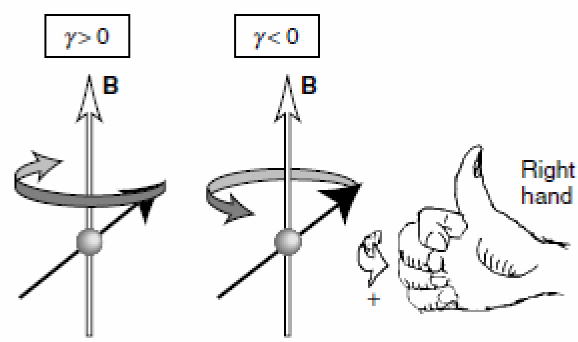


Figure 2.13
Using one's right hand to determine the sense of precession.

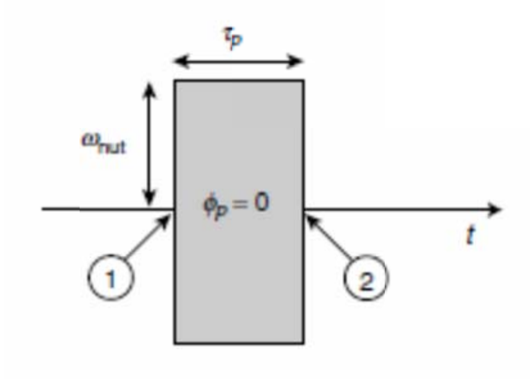
((**Note**))

$\phi_{ref} = \pi$ for $\gamma > 0$

$\phi_{ref} = 0$ for $\gamma < 0$

7. *x*-pulse

We Consider a strong pulse of frequency ω_{ref}, duration τ_p and phase $\phi_p = 0$ (an '*x*-pulse', in the usual NMR jargon). The amplitude of the pulse is specified through the nutation frequency ω_{nut}.



The Hamiltonian in the rotation-frame is

$$\hat{H}_R = \hbar\Omega_0 \hat{I}_z + \hbar\omega_{nut}(\cos\phi_p \hat{I}_x + \sin\phi_p \hat{I}_y)$$

For $\phi_p = 0$ and $\Omega_0 = \omega_0 - \omega_{ref} = 0$ (resonance), the rotating-frame Hamiltonian during the time $\tau_p = t_2 - t_1$,

$$\hat{H}_R = \hbar\omega_{nut}\hat{I}_x$$

$$\left|\psi(t_2)\right\rangle_R = \hat{R}_x(\beta_p)\left|\psi(t_1)\right\rangle_R$$

with

$$\tau_p = t_2 - t_1 .$$

and

$$\hat{R}_x(\beta_p) = \exp(-\frac{i}{\hbar}\hbar\omega_{nut}\tau_p \hat{I}_x) = \exp(-i\omega_{nut}\tau_p \hat{I}_x) = \exp(-i\beta_p \hat{I}_x)$$

or

$$\hat{R}_x(\beta_p) = \begin{pmatrix} \cos\frac{\beta_p}{2} & -i\sin\frac{\beta_p}{2} \\ -i\sin\frac{\beta_p}{2} & \cos\frac{\beta_p}{2} \end{pmatrix}$$

where

$$\beta_p = \omega_{nut}\tau_p$$

Now we start with

$$|\psi(t_1)\rangle_R = \hat{R}_z[\Phi(t_1)]|\psi(t_1)\rangle$$

$$|\psi(t_2)\rangle_R = \hat{R}_z[\Phi(t_2)]|\psi(t_2)\rangle$$

$$\tau_p = t_2 - t_1,$$

where

$$\Phi = \omega_{ref} t ,$$

Thus we get

$$|\psi(t_2)\rangle_R = \hat{R}_x(\beta_p)|\psi(t_1)\rangle_R$$

or

$$\hat{R}_z[-\Phi(t_2)]|\psi(t_2)\rangle = \hat{R}_x(\beta_p)\hat{R}_z[\Phi(t_1)]|\psi(t_1)\rangle$$

or

$$|\psi(t_2)\rangle = \hat{R}_z[\Phi(t_2)]\hat{R}_x(\beta_p)\hat{R}_z[-\Phi(t_1)]|\psi(t_1)\rangle$$

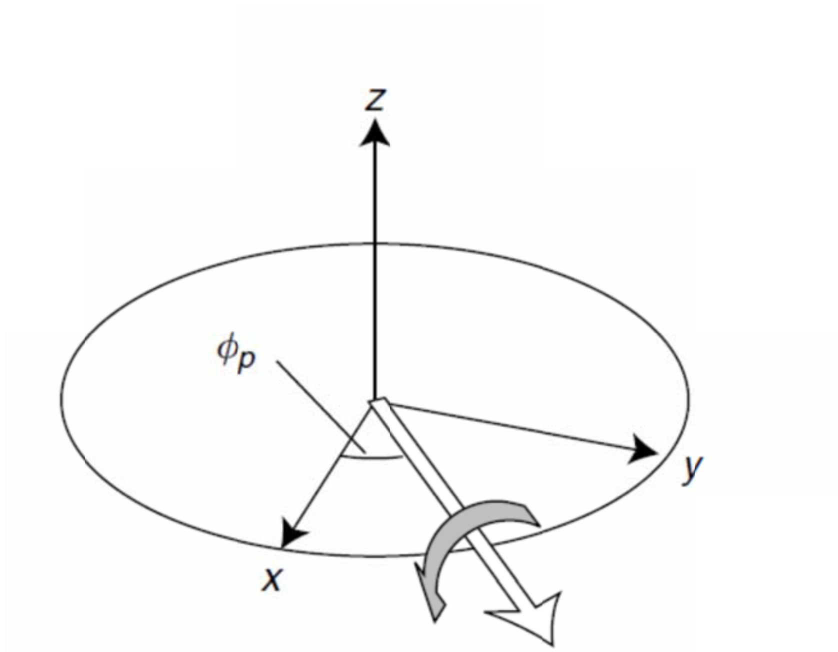
Note that

$$\hat{R}_z(\Phi(t)) = \exp(-i\Phi\hat{I}_z) = \exp(-i\omega_{ref}t\hat{I}_z)$$

Using the **Mathematica**, we get the expression

$$\hat{R}_z[\Phi(t_2)]\hat{R}_x(\beta_p)\hat{R}_z[-\Phi(t_1)] = \begin{pmatrix} e^{-\frac{1}{2}i\tau_p\omega_{ref}}\cos\frac{\beta_p}{2} & -ie^{-\frac{1}{2}i(2t_1+\tau_p)\omega_{ref}}\sin\frac{\beta_p}{2} \\ -ie^{\frac{1}{2}i(2t_1+\tau_p)\omega_{ref}}\sin\frac{\beta_p}{2} & e^{\frac{1}{2}i\tau_p\omega_{ref}}\cos\frac{\beta_p}{2} \end{pmatrix}$$

8. Pulse of general phase



In general, the Hamiltonian in the rotating frame is

$$\hat{H}_R = \hbar\Omega_0\hat{I}_z + \hbar\omega_{nut}(\cos\phi_p\hat{I}_x + \sin\phi_p\hat{I}_y)$$

with $\phi_p \neq 0$ For $\Omega_0 = \omega_0 - \omega_{ref} = 0$ (resonance condition), the rotating-frame Hamiltonian during the time $\tau_p = t_2 - t_1$, is given by

$$\hat{H}_R = \hbar\omega_{nut}(\cos\phi_p\hat{I}_x + \sin\phi_p\hat{I}_y)$$

$$|\psi(t_2)\rangle_R = \hat{R}_{\phi_p}(\beta_p)|\psi(t_1)\rangle_R$$

with

$$\tau_p = t_2 - t_1 .$$

and

$$\hat{R}_{\phi_p}(\beta_p) = \exp[-i\beta_p(\cos\phi_p \hat{I}_x + \sin\phi_p \hat{I}_y)] = \begin{pmatrix} \cos\frac{\beta_p}{2} & -i\sin\frac{\beta_p}{2}e^{-i\phi_p} \\ -i\sin\frac{\beta_p}{2}e^{i\phi_p} & \cos\frac{\beta_p}{2} \end{pmatrix}$$

where

$$\beta_p = \omega_{nut}\tau_p$$

Now we start with

$$\left|\psi(t_1)\right\rangle_R = \hat{R}_z[\Phi(t_1)]\left|\psi(t_1)\right\rangle$$

$$\left|\psi(t_2)\right\rangle_R = \hat{R}_z[\Phi(t_2)]\left|\psi(t_2)\right\rangle$$

$$\Phi(t) = \omega_{ref}t , \qquad \tau_p = t_2 - t_1 ,$$

$$\left|\psi(\tau_2)\right\rangle_R = \hat{R}_{\phi_p}(\beta_p)\left|\psi(t_1)\right\rangle_R$$

$$\hat{R}_z[-\Phi(t_2)]\left|\psi(t_2)\right\rangle = \hat{R}_{\phi_p}(\beta_p)\hat{R}_z[\Phi(t_1)]\left|\psi(t_1)\right\rangle$$

or

$$\left|\psi(t_2)\right\rangle = \hat{R}_z[\Phi(t_2)]\hat{R}_{\phi_p}(\beta_p)\hat{R}_z[-\Phi(t_1)]\left|\psi(t_1)\right\rangle$$

Note that

$$\hat{R}_z(\Phi(t)) = \exp(-i\Phi(t)\hat{I}_z) = \exp(-i\omega_{ref}t\hat{I}_z)$$

Thus we have

$$\hat{R}_z[\Phi(t_2)]\hat{R}_{\phi_p}(\beta_p)\hat{R}_z[-\Phi(t_1)]$$
$$=\begin{pmatrix} e^{-\frac{1}{2}i(\phi_p+\tau_p\omega_{ref})}[\cos(\beta_p)\cos\frac{\phi_p}{2}+i\sin\frac{\phi_p}{2}] & -ie^{-\frac{1}{2}i(\phi_p+\tau_p\omega_{ref})}\cos\frac{\phi_p}{2}\sin(\beta_p) \\ -ie^{\frac{1}{2}i(\phi_p+\tau_p\omega_{ref})}\cos\frac{\phi_p}{2}\sin(\beta_p) & e^{\frac{1}{2}i(\phi_p+\tau_p\omega_{ref})}[\cos(\beta_p)\cos\frac{\phi_p}{2}-i\sin\frac{\phi_p}{2}] \end{pmatrix}$$

9. Off-Resonance effect

For $\Omega_0=\omega_0-\omega_{ref}\neq 0$ (resonance condition), the rotating-frame Hamiltonian during the time $\tau_p=t_2-t_1$, is given by

$$\hat{H}_R=\hbar\Omega_0\hat{I}_z+\hbar\omega_{nut}(\cos\phi_p\hat{I}_x+\sin\phi_p\hat{I}_y)$$

with $\phi_p\neq 0$

$$|\psi(t_2)\rangle_R=\hat{R}_{\phi_p}(\beta_p)|\psi(t_1)\rangle_R$$

with

$$\tau_p=t_2-t_1.$$

and

$$\hat{R}_{off}(\beta_p)=\exp[-i\beta_p(\cos\phi_p\hat{I}_x+\sin\phi_p\hat{I}_y)-i\Omega_0\tau_p\hat{I}_z]$$
$$=\begin{pmatrix} \cos(\frac{\tau_p\omega_{eff}}{2})-i\Omega_0\frac{\sin(\frac{\tau_p\omega_{eff}}{2})}{\omega_{eff}} & \frac{-i\beta_p e^{-i\phi_p}}{\tau_p\omega_{eff}}\sin(\frac{\tau_p\omega_{eff}}{2}) \\ \frac{-i\beta_p e^{i\phi_p}}{\tau_p\omega_{eff}}\sin(\frac{\tau_p\omega_{eff}}{2}) & \cos(\frac{\tau_p\omega_{eff}}{2})+i\Omega_0\frac{\sin(\frac{\tau_p\omega_{eff}}{2})}{\omega_{eff}} \end{pmatrix}$$

where

$$\omega_{eff}=\sqrt{\omega_{nut}^{\ 2}+(\Omega_0)^2}$$

$$\beta_p = \omega_{nut}\tau_p$$

Now we start with

$$|\psi(t_1)\rangle_R = \hat{R}_z[\Phi(t_1)]|\psi(t_1)\rangle$$

$$|\psi(t_2)\rangle_R = \hat{R}_z[\Phi(t_2)]|\psi(t_2)\rangle$$

$$\tau_p = t_2 - t_1$$

$$|\psi(\tau_2)\rangle_R = \hat{R}_{\phi_p}(\beta_p)|\psi(t_1)\rangle_R$$

$$\hat{R}_z[-\Phi(t_2)]|\psi(t_2)\rangle = \hat{R}_{\phi_p}(\beta_p)\hat{R}_z[\Phi(t_1)]|\psi(t_1)\rangle$$

or

$$|\psi(t_2)\rangle = \hat{R}_z[\Phi(t_2)]\hat{R}_{\phi_p}(\beta_p)\hat{R}_z[-\Phi(t_1)]|\psi(t_1)\rangle$$

Note that

$$\hat{R}_z(\Phi) = \exp(-i\Phi\hat{I}_z)$$

where

$$\Phi = \omega_{ref}t$$

$$\hat{R}_z[\Phi(t_2)]\hat{R}_{\phi_p}(\beta_p)\hat{R}_z[-\Phi(t_1)$$

$$= \begin{pmatrix} \dfrac{e^{-\frac{i}{2}\tau_p\omega_{ref}}[-i\Omega_0\sin(\frac{\omega_{eff}\tau_p}{2}) + \omega_{eff}\cos(\frac{\omega_{eff}\tau_p}{2})]}{\omega_{eff}} & \dfrac{-i\beta_p\sin(\frac{\omega_{eff}\tau_p}{2})e^{-\frac{i}{2}[2\phi_p+(2t_1+\tau_p)\omega_{ref}+\tau_p\omega_{eff}]}}{\tau_p\omega_{eff}} \\ \dfrac{-i\beta_p\sin(\frac{\omega_{eff}\tau_p}{2})e^{\frac{i}{2}[2\phi_p+(2t_1+\tau_p)\omega_{ref}]}}{\tau_p\omega_{eff}} & \dfrac{e^{\frac{i}{2}\tau_p\omega_{ref}}[i\Omega_0\sin(\frac{\omega_{eff}\tau_p}{2}) + \omega_{eff}\cos(\frac{\omega_{eff}\tau_p}{2})]}{\omega_{eff}} \end{pmatrix}$$

10. Rabi formula

Suppose that

$t_1 = 0$, and $t_2 = t$, $\tau_p = t$

$|\psi(0)\rangle = |+z\rangle$

$$|\psi(t)\rangle = \hat{R}_z[\Phi(t)]\hat{R}_{\phi_p}(\beta_p)\hat{R}_z[-\Phi(0)]|\psi(0)\rangle$$

$$= \begin{pmatrix} \dfrac{e^{-\frac{i}{2}\omega_{ref}t}[-i\Omega^0 \sin(\frac{\omega_{eff}t}{2}) + \omega_{eff}\cos(\frac{\omega_{eff}t}{2})]}{\omega_{eff}} & \dfrac{-i\beta_p \sin(\frac{\omega_{eff}t}{2})e^{-\frac{i}{2}[2\phi_p + (\omega_{ref}+\omega_{eff})t]}}{t\omega_{eff}} \\ \dfrac{-i\beta_p \sin(\frac{\omega_{eff}t}{2})e^{\frac{i}{2}[2\phi_p + \omega_{ref}t]}}{t\omega_{eff}} & \dfrac{e^{\frac{i}{2}\omega_{ref}t}[i\Omega^0 \sin(\frac{\omega_{eff}t}{2}) + \omega_{eff}\cos(\frac{\omega_{eff}t}{2})]}{\omega_{eff}} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$= \begin{pmatrix} \dfrac{e^{-\frac{i}{2}\omega_{ref}t}[-i\Omega^0 \sin(\frac{\omega_{eff}t}{2}) + \omega_{eff}\cos(\frac{\omega_{eff}t}{2})]}{\omega_{eff}} \\ \dfrac{-i\beta_p \sin(\frac{\omega_{eff}t}{2})e^{\frac{i}{2}[2\phi_p + \omega_{ref}t]}}{t\omega_{eff}} \end{pmatrix}$$

with

$\beta_p = \omega_{nut}t$

The probability of finding the system in the state $|-z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$,

$$\langle -z|\psi(\tau_p)\rangle_L = \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} \dfrac{e^{-\frac{i}{2}\omega_{ref}\tau_p}[-i\Omega^0 \sin(\frac{\omega_{eff}\tau_p}{2}) + \omega_{eff}\cos(\frac{\omega_{eff}\tau_p}{2})]}{\omega_{eff}} \\ \dfrac{-i\beta_p \sin(\frac{\omega_{eff}\tau_p}{2})e^{\frac{i}{2}[2\phi_p + \omega_{ref}\tau_p]}}{\tau_p\omega_{eff}} \end{pmatrix}$$

$$= \frac{-i\beta_p \sin(\frac{\omega_{eff}\tau_p}{2})e^{\frac{i}{2}[2\phi_p + \omega_{ref}\tau_p]}}{\tau_p\omega_{eff}}$$

$$\left|\langle -z|\psi(\tau_p)\rangle_L\right|^2 = \left|\frac{-i\beta_p \sin(\frac{\omega_{eff}\tau_p}{2})e^{\frac{i}{2}[2\phi_p+\omega_{ref}\tau_p]}}{t\omega_{eff}}\right|^2$$

$$= \frac{\omega_{nut}^{\;2}}{\omega_{nut}^{\;2}+(\Omega^0)^2}\sin^2\left(\frac{\omega_{eff}\tau_p}{2}\right)$$

where

$$\omega_{eff} = \sqrt{\omega_{nut}^{\;2}+\left(\Omega^0\right)^2}$$

11. Density operator:

$$R_x(\beta) = \begin{pmatrix} \cos\frac{\beta}{2} & -i\sin\frac{\beta}{2} \\ -i\sin\frac{\beta}{2} & \cos\frac{\beta}{2} \end{pmatrix}$$

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

The density operator is defined by

$$\hat{\rho} = \overline{|\psi\rangle\langle\psi|} = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} = \begin{pmatrix} \overline{C_1^{\,*}C_1} & \overline{C_1^{\,*}C_2} \\ \overline{C_2^{\,*}C_1} & \overline{C_2^{\,*}C_2} \end{pmatrix}$$

$$\hat{\rho}^+ = \hat{\rho} \qquad\qquad \rho_{21}^{\;*} = \rho_{12}$$

$$Tr[\hat{\rho}] = 1, \qquad\qquad \rho_{11} + \rho_{22} = 1$$

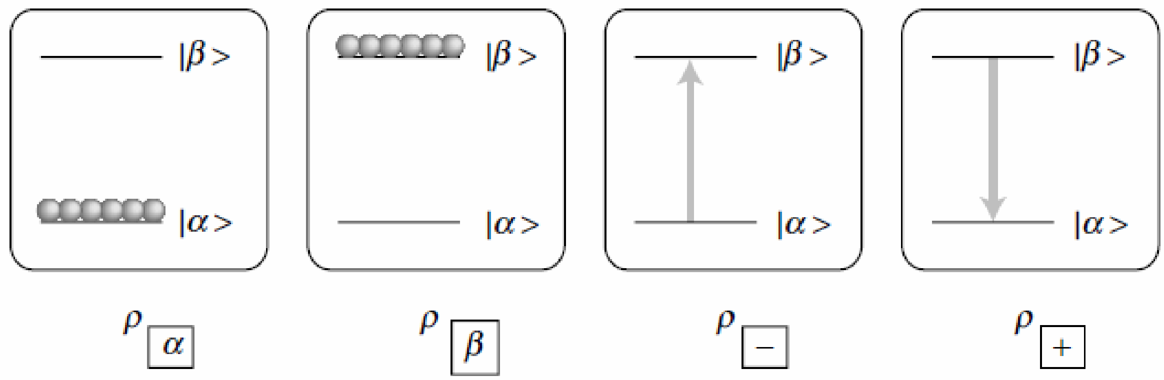
ρ_{11}, ρ_{22}; Populations of states $|1\rangle$ and $|2\rangle$.

ρ_{11}, ρ_{22}; Coherences of states $|1\rangle$ and $|2\rangle$.

Note that

$$\rho_{11} = \langle 1|\hat{\rho}|1\rangle, \qquad \rho_{12} = \langle 1|\hat{\rho}|2\rangle$$

$$\rho_{21} = \langle 2|\hat{\rho}|1\rangle, \qquad \rho_{22} = \langle 2|\hat{\rho}|2\rangle$$



$$\begin{aligned}\langle I_z\rangle &= Tr[\hat{I}_z\hat{\rho}] \\ &= \frac{1}{2}Tr[\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}\rho_{11} & \rho_{12}\\ \rho_{21} & \rho_{22}\end{pmatrix}] \\ &= \frac{1}{2}Tr\begin{pmatrix}\rho_{11} & \rho_{12}\\ -\rho_{21} & -\rho_{22}\end{pmatrix} \\ &= \frac{1}{2}(\rho_{11}-\rho_{22})\end{aligned}$$

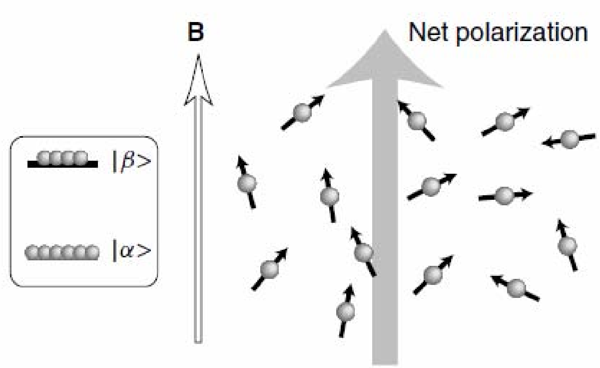


Figure 11.3
Net spin polarization along the field.

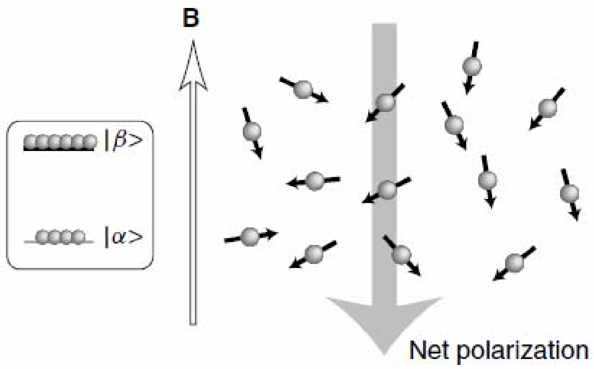


Figure 11.4
Net spin polarization against the field.

$$
\begin{aligned}
\langle I_x \rangle &= Tr[\hat{I}_x \hat{\rho}] \\
&= \frac{1}{2} Tr[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}] \\
&= \frac{1}{2} Tr \begin{pmatrix} \rho_{21} & \rho_{22} \\ \rho_{11} & \rho_{12} \end{pmatrix} \\
&= \frac{1}{2} (\rho_{21} + \rho_{12}) \\
&= |\rho_{21}| \cos\phi
\end{aligned}
$$

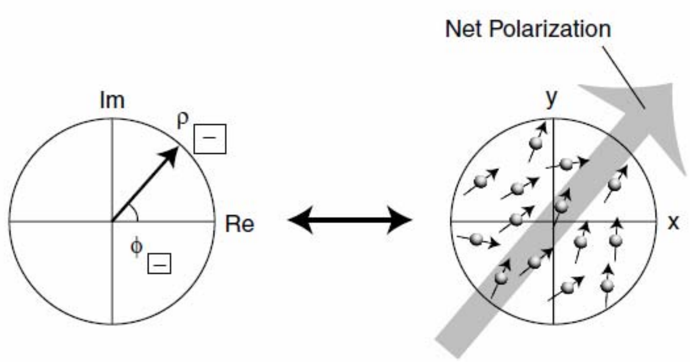


Figure 11.7
Phase of the (−1)-quantum coherence and the direction of the transverse polarization.

$$
\begin{aligned}
\langle I_y \rangle &= Tr[\hat{I}_y \hat{\rho}] \\
&= \frac{1}{2} Tr[\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}] \\
&= \frac{1}{2} Tr\begin{pmatrix} -i\rho_{21} & -i\rho_{22} \\ i\rho_{11} & i\rho_{12} \end{pmatrix} \\
&= \frac{1}{2}(-i\rho_{21} + i\rho_{12}) \\
&= |\rho_{21}| \sin\phi
\end{aligned}
$$

where

$$\rho_{21} = |\rho_{21}| e^{i\phi}$$

12. The density operator in thermal equilibrium

$$
\begin{aligned}
\hat{\rho}_{eq} &= \frac{1}{Z} \exp(-\beta \hat{H}) \\
&= \begin{pmatrix} \rho_{11} & 0 \\ 0 & \rho_{22} \end{pmatrix} \\
&= \frac{1}{\exp(\frac{\beta\hbar\omega_0}{2}) + \exp(-\frac{\beta\hbar\omega_0}{2})} \begin{pmatrix} \exp(-\frac{\beta\hbar\omega_0}{2}) & 0 \\ 0 & \exp(\frac{\beta\hbar\omega_0}{2}) \end{pmatrix}
\end{aligned}
$$

where

$$\omega_0 = -\gamma B_0$$

$$\hat{H} = -\gamma\hbar \hat{I}_z B_0 = \hbar\omega_0 \hat{I}_z = \frac{\hbar\omega_0}{2} \hat{\sigma}_z$$

with

$$\hat{I}_z = \frac{1}{2} \hat{\sigma}_z$$

$\gamma\hbar\hat{I}_z$ is the magnetic moment of nuclear spin.

$$\hat{H} = \hbar\omega_0 \hat{I}_z = \frac{\hbar\omega_0}{2}\hat{\sigma}_z$$

with

$$\hat{I}_z = \frac{1}{2}\hat{\sigma}_z$$

From the condition that $Tr[\hat{\rho}] = 1$

$$\rho_{11} + \rho_{22} = 1$$

((**Approximation**))

$$\begin{aligned}\hat{\rho}_{eq} &= \frac{1}{Z}\exp(-\beta\hat{H}) \\ &\approx \frac{1}{2}\begin{pmatrix} 1 - \frac{\beta\hbar\omega_0}{2} & 0 \\ 0 & 1 + \frac{\beta\hbar\omega_0}{2} \end{pmatrix} \\ &= \frac{1}{2}\hat{1} - \frac{\beta\hbar\omega_0}{4}\hat{\sigma}_z\end{aligned}$$

Here we note that

$$-\beta\hbar\omega_0 = -\beta\hbar(-\gamma B) = \beta\hbar\gamma B$$

Thus we have

$$\hat{\rho}_{eq} = \frac{1}{2}\hat{1} + \frac{\beta\hbar\gamma B}{4}\hat{\sigma}_z = \frac{1}{2}\hat{1} + \frac{\beta\hbar\gamma B}{2}\hat{I}_z = \frac{1}{2}\hat{1} + \frac{1}{2}\tilde{B}\hat{I}_z$$

where

$$\tilde{B} = \beta\hbar\gamma B.$$

13. The density operator in the rotating frame

The rotating frame density operator is defined by

$$\hat{\rho}_R = \overline{|\psi_R\rangle\langle\psi_R|}$$

Using the relations

$$|\psi\rangle_R = \hat{R}_z(-\Phi)|\psi\rangle_L, \qquad {}_R\langle\psi| = {}_L\langle\psi|\hat{R}_z(\Phi)$$

The density operator in the rotating frame is related to that in the laboratory frame as

$$\begin{aligned}\hat{\rho}_R &= \overline{\hat{R}_z(-\Phi)|\psi\rangle\langle\psi|\hat{R}_z(\Phi)} \\ &= \hat{R}_z(-\Phi)\overline{|\psi\rangle\langle\psi|}\hat{R}_z(\Phi) \\ &= \hat{R}_z(-\Phi)\hat{\rho}\hat{R}_z(\Phi)\end{aligned}$$

or

$$\hat{\rho} = \hat{R}_z(\Phi)\hat{\rho}_R\hat{R}_z(-\Phi)$$

We have

$$Tr[\hat{\rho}_R] = Tr[\hat{R}_z(-\Phi)\hat{\rho}\hat{R}_z(\Phi)] = Tr[\hat{\rho}] = 1$$

from the property of Tr. Note that

$$\hat{\rho} = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}$$

$$\hat{R}_z(\Phi) = \exp(-\frac{i}{\hbar}\Phi\hat{I}_z) = \exp(-\frac{i}{2}\Phi\hat{\sigma}_z) = \begin{pmatrix} e^{-\frac{i}{2}\Phi} & 0 \\ 0 & e^{\frac{i}{2}\Phi} \end{pmatrix}$$

$$\hat{R}_z(-\Phi) = \exp(\frac{i}{\hbar}\Phi\hat{I}_z) = \exp(\frac{i}{2}\Phi\hat{\sigma}_z) = \begin{pmatrix} e^{\frac{i}{2}\Phi} & 0 \\ 0 & e^{-\frac{i}{2}\Phi} \end{pmatrix}$$

Thus we get

$$\hat{\rho}_R = \begin{pmatrix} e^{\frac{i}{2}\Phi} & 0 \\ 0 & e^{-\frac{i}{2}\Phi} \end{pmatrix} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \begin{pmatrix} e^{-\frac{i}{2}\Phi} & 0 \\ 0 & e^{\frac{i}{2}\Phi} \end{pmatrix}$$

$$= \begin{pmatrix} e^{\frac{i}{2}\Phi} & 0 \\ 0 & e^{-\frac{i}{2}\Phi} \end{pmatrix} \begin{pmatrix} \rho_{11} e^{-\frac{i}{2}\Phi} & \rho_{12} e^{\frac{i}{2}\Phi} \\ \rho_{21} e^{-\frac{i}{2}\Phi} & \rho_{22} e^{\frac{i}{2}\Phi} \end{pmatrix}$$

$$= \begin{pmatrix} \rho_{11} & \rho_{12} e^{i\Phi} \\ \rho_{21} e^{-i\Phi} & \rho_{22} \end{pmatrix}$$

The thermal equilibrium density operator contains only populations, and is the same in both frames

$$(\hat{\rho}_{eq})_R = \hat{\rho}_{eq},$$

since

$$\hat{\rho}_{eq} = \frac{1}{2}\hat{1} + \frac{1}{2}\tilde{B}\hat{I}_z$$

is diagonal.

14. Free particle without relaxation

Suppose that there is no r.f. field between t_1 and t_2. We note that

$$|\psi(t)\rangle_R = |\psi(t)\rangle$$

We still assume that ω_{rf} remains unchanged. For $t_2 - t_1 = \tau_p$

$$\hat{H} = \hbar\Omega_0 \hat{I}_z$$

Then we have

$$
\begin{aligned}
\left|\psi(t_2 = t_1 + \tau)\right\rangle &= \exp(-\frac{i}{\hbar}\hat{H}\tau)\left|\psi(t_1)\right\rangle \\
&= \exp(-\frac{i}{\hbar}\hbar\Omega_0\hat{I}_z\tau)\left|\psi(t_1)\right\rangle \\
&= \exp(-i\Omega_0\hat{I}_z\tau)\left|\psi(t_1)\right\rangle \\
&= \hat{R}_z(\Omega_0\tau)\left|\psi(t_1)\right\rangle
\end{aligned}
$$

Density operator

$$
\begin{aligned}
\hat{\rho}(t_2) &= \overline{\left|\psi(t_2)\right\rangle\left\langle\psi(t_2)\right|} \\
&= \hat{R}_z(\Omega_0\tau)\overline{\left|\psi(t_1)\right\rangle\left\langle\psi(t_1)\right|}\hat{R}_z(-\Omega_0\tau) \\
&= \hat{R}_z(\Omega_0\tau)\hat{\rho}(t_1)\hat{R}_z(-\Omega_0\tau)
\end{aligned}
$$

where

$$
\hat{R}_z(\Omega_0\tau) = \exp(-\frac{i}{2}\Omega_0\tau\hat{\sigma}_z) = \begin{pmatrix} e^{-\frac{i}{2}\Omega_0\tau} & 0 \\ 0 & e^{\frac{i}{2}\Omega_0\tau} \end{pmatrix}
$$

$$
\hat{R}_z(-\Omega_0\tau) = \exp(\frac{i}{2}\Omega_0\tau\hat{\sigma}_z) = \begin{pmatrix} e^{\frac{i}{2}\Omega_0\tau} & 0 \\ 0 & e^{-\frac{i}{2}\Omega_0\tau} \end{pmatrix}
$$

Suppose that

$$
\hat{\rho}(t_1) = \hat{\rho}_R(t_1) = \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}\hat{I}_z
$$

Thus we have

$$
\begin{aligned}
\hat{\rho}(t_2) &= \hat{R}_z(\Omega_0\tau)\hat{\rho}(t_1)\hat{R}_z(-\Omega_0\tau) \\
&= \hat{R}_z(\Omega_0\tau)(\frac{1}{2}\hat{1}+\frac{1}{2}\widetilde{B}\hat{I}_z)\hat{R}_z(-\Omega_0\tau) \\
&= \frac{1}{2}\hat{1}+\frac{1}{2}\widetilde{B}\hat{R}_z(\Omega_0\tau)\hat{I}_z\hat{R}_z(-\Omega_0\tau) \\
&= \frac{1}{2}\hat{1}+\frac{1}{2}\widetilde{B}\hat{I}_z\hat{R}_z(\Omega_0\tau)\hat{R}_z(-\Omega_0\tau) \\
&= \frac{1}{2}\hat{1}+\frac{1}{2}\widetilde{B}\hat{I}_z \\
&= \hat{\rho}(t_1)
\end{aligned}
$$

$$
\begin{aligned}
\hat{\rho}_R(t_2) &= \hat{R}_z(-\Omega_0\tau)\hat{\rho}_R(t_1)\hat{R}_z(\Omega_0\tau) \\
&= \hat{R}_z(-\Omega_0\tau)(\frac{1}{2}\hat{1}+\frac{1}{2}\widetilde{B}\hat{I}_z)\hat{R}_z(\Omega_0\tau) \\
&= \frac{1}{2}\hat{1}+\frac{1}{2}\widetilde{B}\hat{R}_z(-\Omega_0\tau)\hat{I}_z\hat{R}_z(\Omega_0\tau) \\
&= \frac{1}{2}\hat{1}+\frac{1}{2}\widetilde{B}\hat{I}_z\hat{R}_z(-\Omega_0\tau)\hat{R}_z(\Omega_0\tau) \\
&= \frac{1}{2}\hat{1}+\frac{1}{2}\widetilde{B}\hat{I}_z \\
&= \hat{\rho}_R(t_1)
\end{aligned}
$$

15. The magnetization vector using the density operator

$$M_x = \gamma\hbar Tr[\hat{I}_x\hat{\rho}] = \frac{\gamma\hbar}{2}(\rho_{12}+\rho_{21}) = \gamma\hbar\,\mathrm{Re}[\rho_{12}]$$

$$M_y = \gamma\hbar Tr[\hat{I}_y\hat{\rho}] = \frac{\gamma\hbar}{2}i(\rho_{12}-\rho_{21}) = -\gamma\hbar\,\mathrm{Im}[\rho_{12}]$$

$$M_z = \gamma\hbar Tr[\hat{I}_z\hat{\rho}] = \frac{\gamma\hbar}{2}(\rho_{11}-\rho_{22})$$

where

$$Tr[\hat{\rho}] = 1, \qquad (\rho_{11}+\rho_{22}=1)$$

$$\hat{\rho}^{+} = \hat{\rho} \qquad (\rho_{21}=\rho_{12}{}^{*})$$

Thus we have

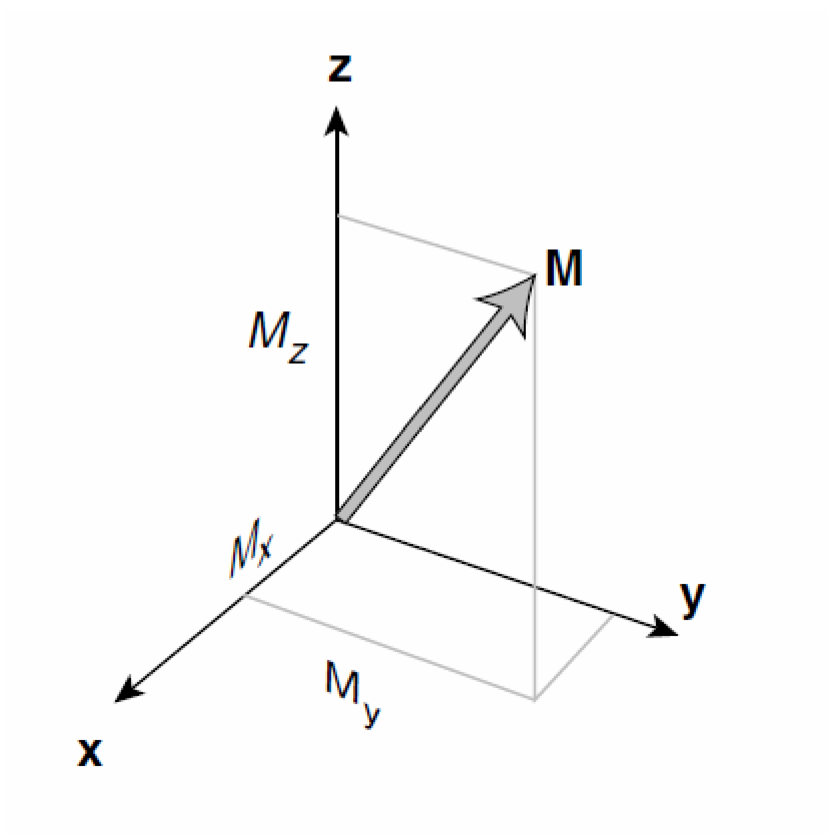
$$\rho_{11} = \frac{1}{2}(1 + \frac{2}{\gamma\hbar} M_z), \qquad \rho_{22} = \frac{1}{2}(1 - \frac{2}{\gamma\hbar} M_z)$$

$$\rho_{12} = \frac{1}{\gamma\hbar}(M_x - iM_y), \qquad \rho_{21} = \frac{1}{\gamma\hbar}(M_x + iM_y)$$

leading to the density matrix as

$$\hat{\rho} = \frac{1}{2}\hat{1} + \frac{1}{\gamma\hbar}(M_x\hat{\sigma}_x + M_z\hat{\sigma}_z + M_z\hat{\sigma}_z) = \frac{1}{2}\hat{1} + \frac{1}{\gamma\hbar}\boldsymbol{M} \cdot \hat{\boldsymbol{\sigma}}.$$

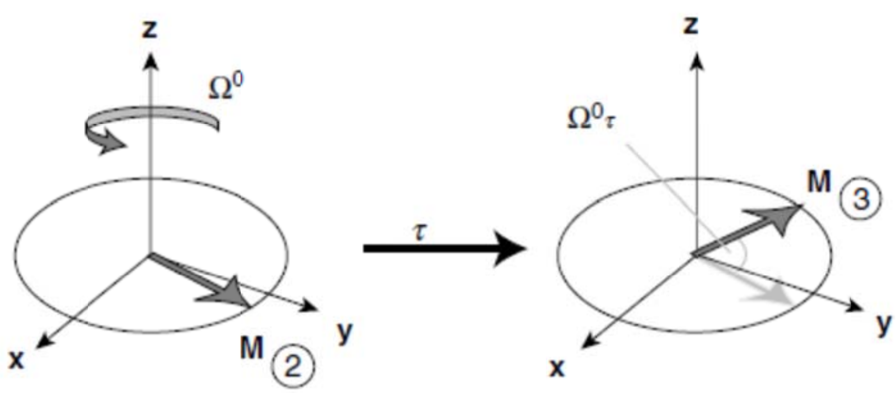
16. Magnetization vector (II) in general case



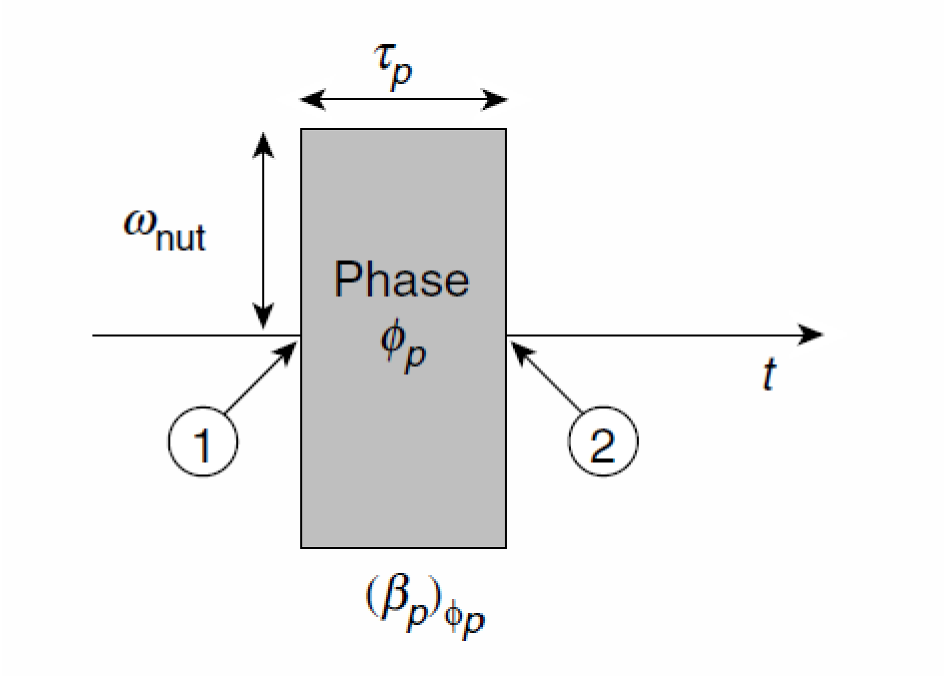
$$
\begin{aligned}
M_x(t_3) &= \gamma\hbar\,\mathrm{Re}[\rho_{12}(t_3)] \\
&= \gamma\hbar\,\mathrm{Re}[\rho_{12}(t_2)e^{-i\omega_0\tau}] \\
&= \gamma\hbar\,\mathrm{Re}\{[(\mathrm{Re}\,\rho_{12}(t_2) + i\,\mathrm{Im}\,\rho_{12}(t_2)][\cos(\omega_0\tau) - i\sin(\omega_0\tau)] \\
&= \gamma\hbar[\mathrm{Re}\,\rho_{12}(t_2)\cos(\omega_0\tau) + \mathrm{Im}\,\rho_{12}(t_2)\sin(\omega_0\tau)] \\
&= M_x(t_2)\cos(\omega_0\tau) - M_y(t_2)\sin(\omega_0\tau)
\end{aligned}
$$

$$
\begin{aligned}
M_y(t_3) &= -\gamma\hbar\,\mathrm{Im}[\rho_{12}(t_3)] \\
&= -\gamma\hbar\,\mathrm{Im}[\rho_{12}(t_2)e^{-i\omega_0\tau}] \\
&= -\gamma\hbar\,\mathrm{Im}\{[(\mathrm{Re}\,\rho_{12}(t_2) + i\,\mathrm{Im}\,\rho_{12}(t_2)][\cos(\omega_0\tau) - i\sin(\omega_0\tau)] \\
&= -\gamma\hbar[\mathrm{Im}\,\rho_{12}(t_2)\cos(\omega_0\tau) - \mathrm{Re}\,\rho_{12}(t_2)\sin(\omega_0\tau)] \\
&= M_x(t_2)\sin(\omega_0\tau) + M_y(t_2)\cos(\omega_0\tau)
\end{aligned}
$$

$$
\begin{aligned}
M_z(t_3) &= \frac{\gamma\hbar}{2}[\rho_{11}(t_3) - \rho_{22}(t_3)] \\
&= \frac{\gamma\hbar}{2}[\rho_{11}(t_3) - \rho_{22}(t_3)] \\
&= M_z(t_2)
\end{aligned}
$$



17. Strong radio-frequency pulse



$$\left|\psi(t_2)\right\rangle_R = \hat{R}_{\phi_p}(\beta_p)\left|\psi(t_2)\right\rangle_R$$

$$\hat{\rho}_R(t_2) = \hat{R}_{\phi_p}(\beta_p)\hat{\rho}_R(t_1)\hat{R}_{\phi_p}(-\beta_p)$$

where

$$\begin{aligned}\hat{\rho}_R(t) &= \hat{R}_z[-\Phi(t)]\hat{\rho}(t)\hat{R}_z[\Phi(t)] \\ &= \begin{pmatrix} e^{\frac{i}{2}\Phi(t)} & 0 \\ 0 & e^{-\frac{i}{2}\Phi(t)} \end{pmatrix}\begin{pmatrix} \rho_{11}(t) & \rho_{12}(t) \\ \rho_{21}(t) & \rho_{22}(t) \end{pmatrix}\begin{pmatrix} e^{-\frac{i}{2}\Phi(t)} & 0 \\ 0 & e^{\frac{i}{2}\Phi(t)} \end{pmatrix} \\ &= \begin{pmatrix} \rho_{11}(t) & e^{i\Phi(t)}\rho_{12}(t) \\ e^{-i\Phi(t)}\rho_{21}(t) & \rho_{22}(t) \end{pmatrix}\end{aligned}$$

or

$$\hat{\rho}_R(t) = \begin{pmatrix} \rho_{11}(t) & e^{i\Phi(t)}\rho_{12}(t) \\ e^{-i\Phi(t)}\rho_{21}(t) & \rho_{22}(t) \end{pmatrix}$$

where

$$\hat{R}_z[\Phi(t)] = \exp[-\frac{i}{\hbar}\Phi(t)\hbar\hat{I}_z] = \exp[-\frac{i}{2}\Phi(t)\hat{\sigma}_z] = \begin{pmatrix} e^{-\frac{i}{2}\Phi(t)} & 0 \\ 0 & e^{\frac{i}{2}\Phi(t)} \end{pmatrix}$$

and

$$\hat{\rho}(t) = \hat{R}_z[\Phi(t)]\hat{\rho}_R(t)\hat{R}_z[-\Phi(t)]$$
$$= \begin{pmatrix} \rho_{R11}(t) & e^{-i\Phi(t)}\rho_{R12}(t) \\ e^{i\Phi(t)}\rho_{R21}(t) & \rho_{R22}(t) \end{pmatrix}$$

((**Diagram**))

$$\hat{\rho}_1 = \hat{\rho}_{eq} = \frac{1}{2}\hat{1} + \frac{1}{2}\tilde{B}\hat{I}_z$$

$$\downarrow \qquad (\beta_p)_{\phi_p}$$

$$\hat{\rho}_2 = \frac{1}{2}\hat{1} + \frac{1}{2}\tilde{B}\hat{R}_{\phi_p}(\beta_p)\hat{I}_z\hat{R}_{\phi_p}(-\beta_p)$$

where

$$\hat{R}_{\phi_p}(\beta_p)\hat{I}_z\hat{R}_{\phi_p}(-\beta_p) = \frac{1}{2}\begin{pmatrix} e^{-i\phi_p}(\cos\phi_p + i\cos\beta_p\sin\phi_p) & \sin\beta_p\sin\phi_p \\ \sin\beta_p\sin\phi_p & e^{i\phi_p}(-\cos\phi_p + i\cos\beta_p\sin\phi_p) \end{pmatrix}$$
$$= (\cos^2\phi_p + \cos\beta_p\sin^2\phi_p)\hat{I}_z + i\sin\phi_p\cos\phi_p(-1+\cos\beta_p)\hat{1} + \sin\beta_p\sin\beta_p\hat{I}_x$$

18. Example: $\left(\frac{\pi}{2}\right)_x$ pulse with $\phi_p = 0$

For the $(\pi/2)_x$ with $\phi_p = 0$. we have

$$\hat{R}_{\phi_p=0}(\beta_p) = \hat{R}_x(\beta_p) = \exp(-i\beta_p\hat{I}_x)$$

with

$$\beta_p = \omega_{nut}\tau = \frac{\pi}{2}$$

At $t = t_1$,

$$\hat{\rho}(t_1) = \hat{\rho}_R(t_1) = \hat{\rho}_{eq} = \frac{1}{2}\hat{1} + \frac{1}{2}\tilde{B}\hat{I}_z \qquad \text{(in thermal equilibrium)}$$

$$\hat{R}_x(\beta_p = \frac{\pi}{2}) = \exp(-i\frac{\pi}{2}\hat{I}_x)$$

The density operator in the rotating frame is

$$\begin{aligned}
\hat{\rho}_R(t_2) &= \hat{R}_x(\frac{\pi}{2})\hat{\rho}_R(t_1)\hat{R}_x(-\frac{\pi}{2}) \\
&= \hat{R}_x(\frac{\pi}{2})(\frac{1}{2}\hat{1} + \frac{1}{2}\tilde{B}\hat{I}_z)\hat{R}_x(-\frac{\pi}{2}) \\
&= \frac{1}{2}\hat{1} + \frac{1}{2}\tilde{B}\hat{R}_x(\frac{\pi}{2})\hat{I}_z\hat{R}_x(-\frac{\pi}{2}) \\
&= \frac{1}{2}\hat{1} - \frac{1}{2}\tilde{B}\hat{I}_y
\end{aligned}$$

or

$$\hat{\rho}_R(t_2) = \frac{1}{2}\hat{1} - \frac{1}{2}\tilde{B}\hat{I}_y .$$

where

$$\hat{R}_x(\frac{\pi}{2})\hat{I}_z\hat{R}_x(-\frac{\pi}{2}) = -\hat{I}_y \qquad \text{(using Mathematica)}$$

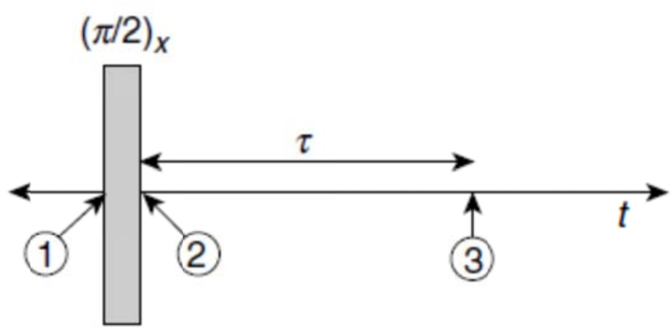
We note that

$$\hat{\rho}(t_2) = \hat{R}_z[\Phi(t_2)]\hat{\rho}_R(t_2)\hat{R}_z[-\Phi(t_2)]$$
$$= \hat{R}_z[\Phi(t_2)](\frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}\hat{I}_y)\hat{R}_z[-\Phi(t_2)]$$
$$= \frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}\hat{R}_z[\Phi(t_2)]\hat{I}_y\hat{R}_z[-\Phi(t_2)]$$
$$= \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}[\sin(\omega_{ref}t_2)\hat{I}_x - \cos(\omega_{ref}t_2)\hat{I}_y]$$

where

$$\hat{R}_z[\Phi(t)]\hat{\sigma}_y\hat{R}_z[-\Phi(t)] = \begin{pmatrix} 0 & -ie^{-i\omega_{ref}t} \\ ie^{i\omega_{ref}t} & 0 \end{pmatrix} = -\sin(\omega_{ref}t)\hat{\sigma}_x + \cos(\omega_{ref}t)\hat{\sigma}_y$$

19. Example: $\left(\frac{\pi}{2}\right)_x$ pulse, followed by a free precession interval



From the above discussion,

$$\hat{\rho}_R(t_2) = \frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}\hat{I}_y$$

We note that

$$\hat{\rho}_R(t_2) = \hat{\rho}(t_2) = \frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}\hat{I}_y$$

since there is no r.f. field in the period between t_2 and t_3,

$\Phi = \omega_{ref} t = 0$.

$$|\psi(t)\rangle_R = \hat{R}_z[\Phi(t)]|\psi(t)\rangle = |\psi(t)\rangle$$

Then we have

$$\begin{aligned}
\hat{\rho}(t_3) &= \hat{R}_z(\Omega_0\tau_{23})\hat{\rho}(t_2)\hat{R}_z(-\Omega_0\tau_{23}) \\
&= \frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}\hat{R}_z(\Omega_0\tau_{23})\hat{I}_y\hat{R}_z(-\Omega_0\tau_{23}) \\
&= \frac{1}{2}\hat{1} - \frac{1}{4}\widetilde{B}\begin{pmatrix} 0 & -ie^{-i\Omega_0\tau_{23}} \\ ie^{i\Omega_0\tau_{23}} & 0 \end{pmatrix} \\
&= \frac{1}{2}\hat{1} + \frac{1}{4}\widetilde{B}[\sin(\Omega_0\tau_{23})\hat{\sigma}_x - \cos(\Omega_0\tau_{23})\hat{\sigma}_y] \\
&= \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}[\sin(\Omega_0\tau_{23})\hat{I}_x - \cos(\Omega_0\tau_{23})\hat{I}_y]
\end{aligned}$$

or

$$\hat{\rho}(t_3) = \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}[\sin(\omega_0\tau_{23})\hat{I}_x - \cos(\omega_0\tau_{23})\hat{I}_y]$$

((**Diagram**))

$$\hat{\rho}_1 = \hat{\rho}_{eq} = \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}\hat{I}_z$$

$$\downarrow \qquad \left(\frac{\pi}{2}\right)_x$$

$$\hat{\rho}_2 = \frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}\hat{I}_y$$

$$\downarrow \qquad \tau$$

$$\hat{\rho}_3 = \frac{1}{2}\widetilde{B}[-\hat{I}_y\cos(\Omega_0\tau) + \hat{I}_x\sin(\Omega_0\tau)].$$

where

$$\hat{R}_x(\frac{\pi}{2})\hat{I}_z\hat{R}_x(-\frac{\pi}{2}) = -\hat{I}_y$$

$$\hat{R}_z(\theta)\hat{I}_x\hat{R}_z(-\theta) = \hat{I}_x\cos\theta + \hat{I}_y\sin\theta$$

$$\hat{R}_z(\theta)\hat{I}_y\hat{R}_z(-\theta) = -\hat{I}_x\sin\theta + \hat{I}_y\cos\theta$$

In the case of the presence of transverse relaxation and longitudinal relaxation,

$$\hat{\rho}(t) = \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}(1-e^{-t/T_1})\hat{I}_z + \frac{1}{2}\widetilde{B}[\sin(\omega_0\tau_{23})\hat{I}_x - \cos(\omega_0\tau_{23})\hat{I}_y]e^{-t/T_2}$$

((**Diagram**))

$$\hat{\rho}_1 = \hat{\rho}_{eq} = \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}\hat{I}_z$$

$$\downarrow \qquad (\frac{\pi}{2})_x$$

$$\hat{\rho}_2 = \frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}\hat{I}_y$$

$$\downarrow \qquad \tau$$

$$\hat{\rho}_3 = \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}(1-e^{-\tau/T_1})\hat{I}_z - \frac{1}{2}\widetilde{B}[\cos(\Omega_0\tau)\hat{I}_y - \sin(\Omega_0\tau)\hat{I}_x]e^{-\frac{\tau}{T_2}}$$

where

$$\hat{R}_z(\Omega_0\tau)\hat{I}_y\hat{R}_z(-\Omega_0\tau) = -\sin(\Omega_0\tau)\hat{I}_x + \cos(\Omega_0\tau)\hat{I}_y$$

---

20. Example: $\phi_p = 0$. $(\pi)_x$ pulse

For the $(\pi)_x$ with $\phi_p = 0$. we have

$$\hat{R}_{\phi_p=0}(\beta_p) = \hat{R}_x(\pi) = \exp(-i\pi\hat{I}_x)$$

The density operator in the rotation frame is

$$\begin{aligned}\hat{\rho}_R(t_2) &= \hat{R}_x(\pi)(\frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}\hat{I}_z)\hat{R}_x(-\pi) \\ &= \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}\hat{R}_x(\pi)\hat{I}_z\hat{R}_x(-\pi) \\ &= \frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}\hat{I}_z\end{aligned}$$

where

$$\hat{R}_x(\pi)\hat{I}_z\hat{R}_x(-\pi) = -\hat{I}_z \qquad \text{(using Mathematica).}$$

---

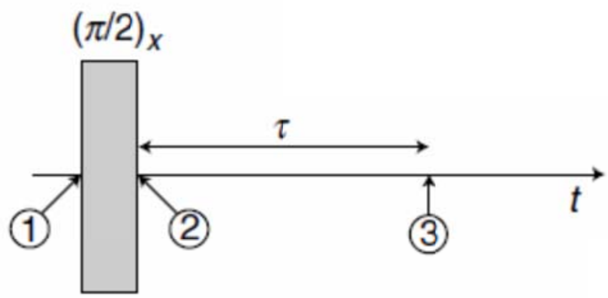
21. Transverse relaxation time T_2

The phenomological equation for the polulation is given by

$$\rho_{21}(t_2) = \rho_{21}(t_1)\exp[(i\Omega_0 - \frac{1}{T_2})\tau]$$

$$\rho_{12}(t_2) = \rho_{12}(t_1)\exp[(-i\Omega_0 - \frac{1}{T_2})\tau]$$

We consider the following case. At $t = t_1$, $\hat{\rho} = \hat{\rho}_{eq}$. the $\left(\frac{\pi}{2}\right)_x$ pulse is applied between t_1 and t_2. After that the r.f. pulse is turned off.



$$\hat{\rho}^{eq} = \frac{1}{2}\hat{1} + \frac{1}{2}\tilde{B}\hat{I}_z = \begin{pmatrix} \frac{1}{2}+\frac{1}{4}\tilde{B} & 0 \\ 0 & \frac{1}{2}-\frac{1}{4}\tilde{B} \end{pmatrix}$$

Just after the $\left(\frac{\pi}{2}\right)_x$ pulse is turned off,

$$\hat{\rho}(t_2) = \frac{1}{2}\hat{1} - \frac{1}{2}\tilde{B}\hat{I}_y = \begin{pmatrix} \frac{1}{2} & \frac{i}{4}\tilde{B} \\ -\frac{i}{4}\tilde{B} & \frac{1}{2} \end{pmatrix}$$

So we get

$$\rho_{12}(t_3 = t_2 + \tau) = \frac{i}{4}\tilde{B}\exp[(-i\Omega_0 - \frac{1}{T_2})\tau] = \frac{i}{4}\tilde{B}e^{-\frac{\tau}{T_2}}[\cos(\Omega_0\tau) - i\sin(\Omega_0\tau)]$$

$$\rho_{21}(t_3 = t_2 + \tau) = -\frac{i}{4}\tilde{B}\exp[(i\Omega_0 - \frac{1}{T_2})\tau] = -\frac{i}{4}\tilde{B}e^{-\frac{\tau}{T_2}}[\cos(\Omega_0\tau) + i\sin(\Omega_0\tau)]$$

$$\rho_{11}(t_3 = t_2 + \tau) = \frac{1}{2}, \qquad \rho_{22}(t_3 = t_2 + \tau) = \frac{1}{2}$$

or

$$\hat{\rho}(t_3 = t_2 + \tau) = \begin{pmatrix} \frac{1}{2} & \frac{1}{4}\tilde{B}e^{-\frac{\tau}{T_2}}[i\cos(\Omega_0\tau) + \sin(\Omega_0\tau)] \\ \frac{1}{4}\tilde{B}e^{-\frac{\tau}{T_2}}[-i\cos(\Omega_0\tau) + \sin(\Omega_0\tau)] & \frac{1}{2} \end{pmatrix}$$

or

$$\hat{\rho}(t_3 = t_2 + \tau) = \frac{1}{2}\hat{1} + \frac{1}{2}\tilde{B}e^{-\frac{\tau}{T_2}}[-\cos(\Omega_0\tau)\hat{I}_y + \sin(\Omega_0\tau)\hat{I}_x]$$

---

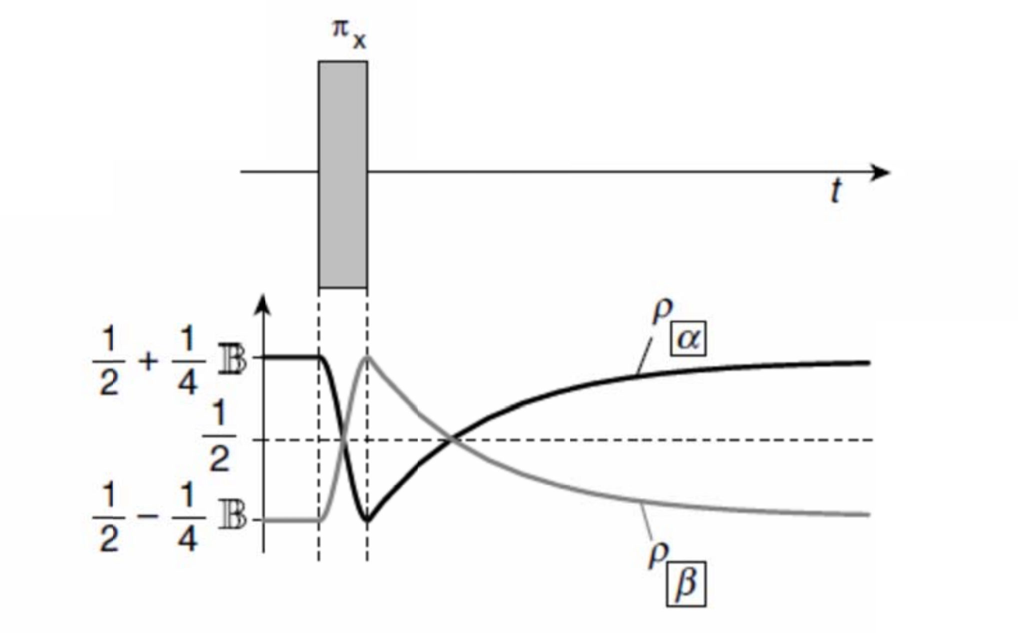
22. Longitudinal relaxation time T_1

The phenomological equation for the population is given by

$$\rho_{11}(t_2) = [\rho_{11}(t_1) - \rho_{11}{}^{eq}]\exp(-\frac{\tau}{T_1}) + \rho_{11}{}^{eq}$$

$$\rho_{22}(t_2) = [\rho_{22}(t_1) - \rho_{22}{}^{eq}]\exp(-\frac{\tau}{T_1}) + \rho_{22}{}^{eq}$$

We consider the following case. At $t = t_1$, $\hat{\rho} = \hat{\rho}_{eq}$. the $(\pi)_x$ pulse is applied between t_1 and t_2. After that the r.f. pulse is turned off.



$$\hat{\rho}^{eq} = \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}\hat{I}_z = \begin{pmatrix} \frac{1}{2} + \frac{1}{4}\widetilde{B} & 0 \\ 0 & \frac{1}{2} - \frac{1}{4}\widetilde{B} \end{pmatrix}$$

Just after the $(\pi)_x$ pulse is turned off,

$$\hat{\rho}(t_2) = \frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}\hat{I}_z = \begin{pmatrix} \frac{1}{2} - \frac{1}{4}\widetilde{B} & 0 \\ 0 & \frac{1}{2} + \frac{1}{4}\widetilde{B} \end{pmatrix}$$

Using the above equations

$$\rho_{11}(t_3 = t_2 + \tau) = \{\left(\frac{1}{2} - \frac{1}{4}\widetilde{B}\right) - \left(\frac{1}{2} + \frac{1}{4}\widetilde{B}\right)\}e^{-\frac{\tau}{T_1}} + \left(\frac{1}{2} + \frac{1}{4}\widetilde{B}\right)$$
$$= \frac{1}{2} + \frac{1}{4}\widetilde{B}(1 - 2e^{-\frac{\tau}{T_1}})$$

Similarly, we have $\rho_{11}(t_3)$ as

$$\rho_{22}(t_3) = \{\left(\frac{1}{2} + \frac{1}{4}\widetilde{B}\right) - \left(\frac{1}{2} - \frac{1}{4}\widetilde{B}\right)\}e^{-\frac{\tau}{T_1}} + \left(\frac{1}{2} - \frac{1}{4}\widetilde{B}\right)$$
$$= \frac{1}{2} - \frac{1}{4}\widetilde{B}(1 - 2e^{-\frac{\tau}{T_1}})$$

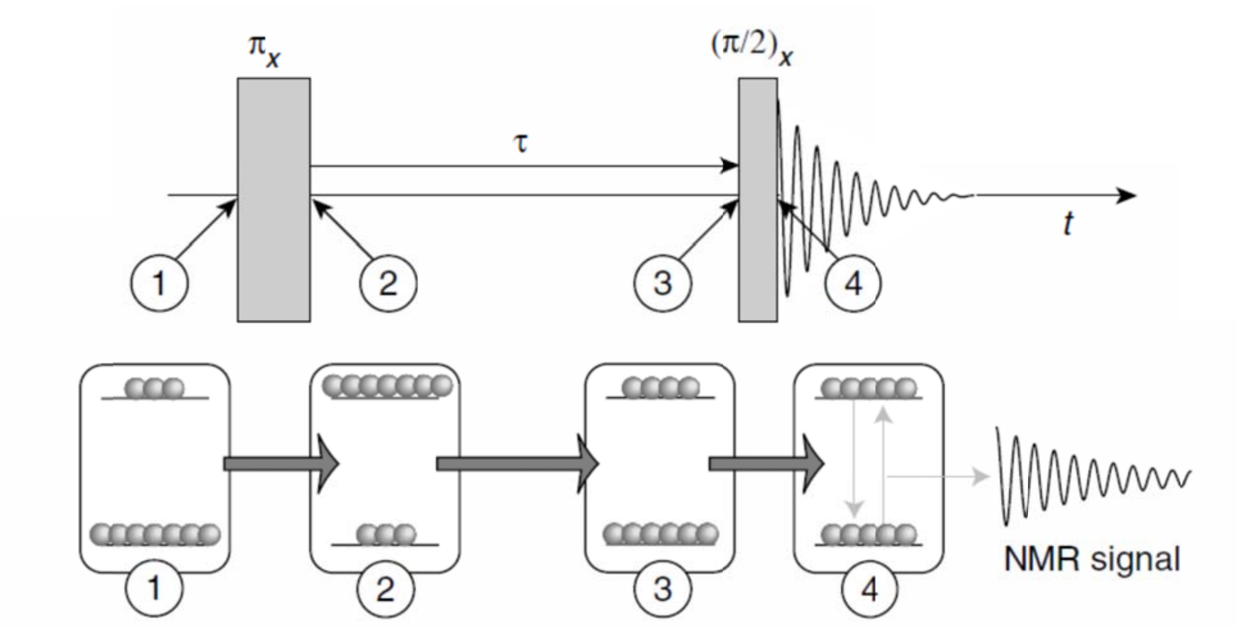
where

$$\tau = t_3 - t_2$$

In summary we get the expression

$$\hat{\rho}(t_3) = \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}(1 - 2e^{-\frac{\tau}{T_1}})\hat{I}_z$$

23. rf spin echo method for determination of T1



$$\hat{\rho}_1 = \hat{\rho}_{eq} = \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}\hat{I}_z$$

$$\downarrow \qquad \pi_x$$

$$\hat{\rho}_2 = \hat{R}_x(\pi)\hat{\rho}_1\hat{R}_x(-\pi) = \frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}\hat{I}_z$$

$$\downarrow \qquad \tau$$

$$\hat{\rho}_3 = \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}(1 - 2e^{-\frac{\tau}{T_1}})\hat{I}_z$$

$$\downarrow \qquad (\frac{\pi}{2})_x$$

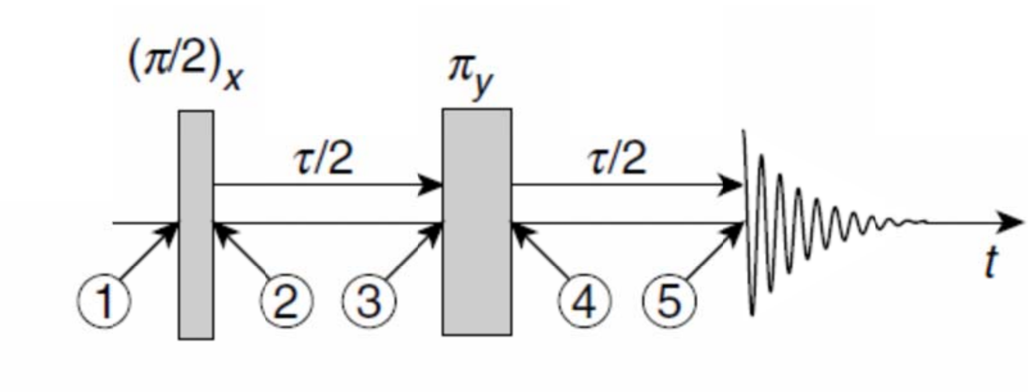
$$\hat{\rho}_4 = \hat{R}_x(\frac{\pi}{2})\hat{\rho}_3\hat{R}_x(-\frac{\pi}{2}) = \frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}(1 - 2e^{-\frac{\tau}{T_1}})\hat{I}_y$$

where

$$\hat{R}_x(\pi)\hat{I}_z\hat{R}_x(-\pi) = -\hat{I}_z$$

$$\hat{R}_x(\frac{\pi}{2})\hat{I}_z\hat{R}_x(-\frac{\pi}{2}) = -\hat{I}_y$$

24. r.f. spin echo for determination of T_2



$$\hat{\rho}_1 = \hat{\rho}_{eq} = \frac{1}{2}\hat{1} + \frac{1}{2}\widetilde{B}\hat{I}_z$$

$$\downarrow \quad \left(\frac{\pi}{2}\right)_x$$

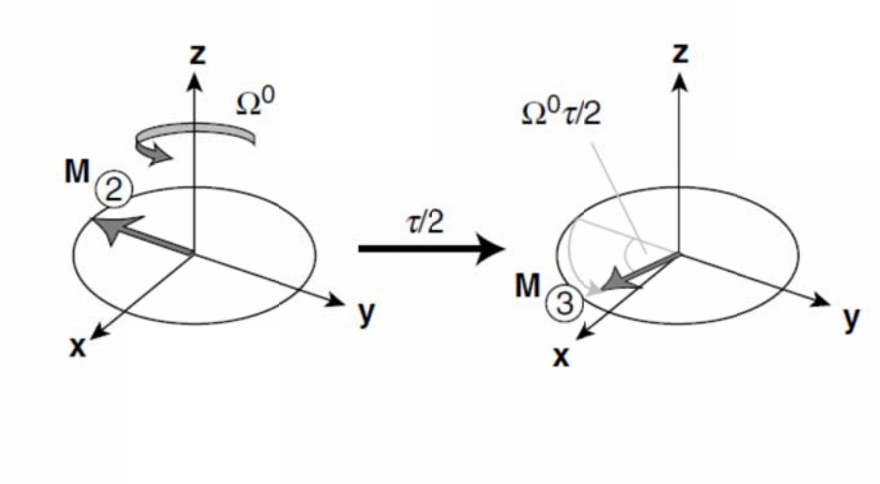
$$\hat{\rho}_2 = \frac{1}{2}\hat{1} - \frac{1}{2}\widetilde{B}\hat{I}_y$$

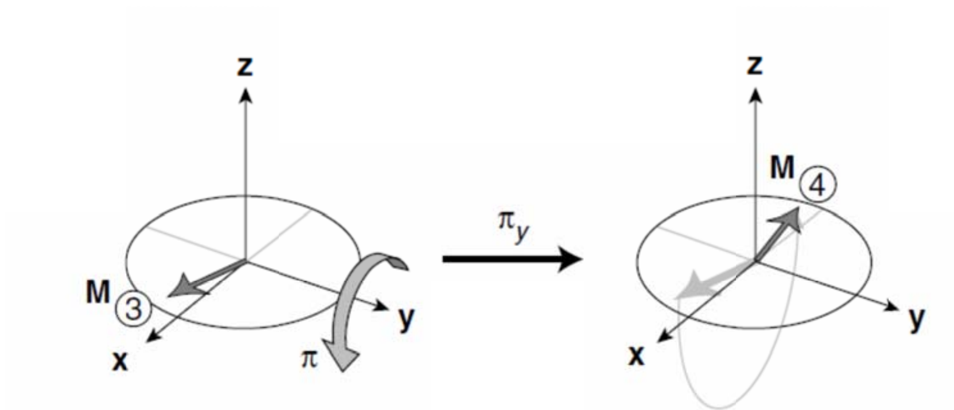
$$\downarrow \quad \frac{1}{2}\tau$$

$$\hat{\rho}_3 = \frac{1}{2}\widetilde{B}[-\hat{I}_y\cos(\frac{1}{2}\Omega_0\tau) + \hat{I}_x\sin(\frac{1}{2}\Omega_0\tau)]e^{-\frac{\tau}{2T_2}}$$

$$\downarrow \quad (\pi)_y$$

$$\hat{\rho}_4 = \frac{1}{2}\widetilde{B}[-\hat{I}_y\cos(\frac{1}{2}\Omega_0\tau) - \hat{I}_x\sin(\frac{1}{2}\Omega_0\tau)]e^{-\frac{\tau}{2T_2}}$$





where

$$\hat{R}_x(\frac{\pi}{2})\hat{I}_z\hat{R}_x(-\frac{\pi}{2}) = -\hat{I}_y$$

$$\hat{R}_y(\pi)\hat{I}_x\hat{R}_y(-\pi) = -\hat{I}_x$$

$$\hat{R}_y(\pi)\hat{I}_y\hat{R}_y(-\pi) = \hat{I}_y$$

REFERENCES

M.H. Levitt, Spin Dynamics, Basics of Nuclear Magnetic Resonance, second edition (John Wiley & Sons).

APPENDIX

Mathematica

```
Clear["Global`*"];
σx = PauliMatrix[1];
σy = PauliMatrix[2];
σz = PauliMatrix[3];
```

$$Rx[\theta\_] := MatrixExp\left[\frac{-i\,\theta}{2}\,\sigma x\right];$$

$$Ry[\theta\_] := MatrixExp\left[\frac{-i\,\theta}{2}\,\sigma y\right];$$

$$Rz[\theta\_] := MatrixExp\left[\frac{-i\,\theta}{2}\,\sigma z\right];$$

Rz[θ]

$$\left\{\left\{e^{-\frac{i\,\theta}{2}},\,0\right\},\,\left\{0,\,e^{\frac{i\,\theta}{2}}\right\}\right\}$$

Rx[θ]

$$\left\{\left\{\mathrm{Cos}\left[\frac{\theta}{2}\right],\,-i\,\mathrm{Sin}\left[\frac{\theta}{2}\right]\right\},\,\left\{-i\,\mathrm{Sin}\left[\frac{\theta}{2}\right],\,\mathrm{Cos}\left[\frac{\theta}{2}\right]\right\}\right\}$$

Ry[θ]

$$\left\{\left\{\mathrm{Cos}\left[\frac{\theta}{2}\right],\,-\mathrm{Sin}\left[\frac{\theta}{2}\right]\right\},\,\left\{\mathrm{Sin}\left[\frac{\theta}{2}\right],\,\mathrm{Cos}\left[\frac{\theta}{2}\right]\right\}\right\}$$

$$Rxy[\theta\_] := MatrixExp\left[-i\,\beta p\left(\frac{\mathrm{Cos}[\theta]}{2}\,\sigma x+\frac{\mathrm{Sin}[\theta]}{2}\,\sigma y\right)\right];$$

```
k1 = Rxy[ϕp] // ExpToTrig // FullSimplify;
k1 // MatrixForm
```

$$\begin{pmatrix} \text{Cos}\left[\frac{\beta p}{2}\right] & \text{Sin}\left[\frac{\beta p}{2}\right] (-\mathbb{i}\,\text{Cos}[\phi p] - \text{Sin}[\phi p]) \\ \text{Sin}\left[\frac{\beta p}{2}\right] (-\mathbb{i}\,\text{Cos}[\phi p] + \text{Sin}[\phi p]) & \text{Cos}\left[\frac{\beta p}{2}\right] \end{pmatrix}$$

```
k11 = Rxy[π / 2] // ExpToTrig // FullSimplify;
k11 // MatrixForm
```

$$\begin{pmatrix} \text{Cos}\left[\frac{\beta p}{2}\right] & -\text{Sin}\left[\frac{\beta p}{2}\right] \\ \text{Sin}\left[\frac{\beta p}{2}\right] & \text{Cos}\left[\frac{\beta p}{2}\right] \end{pmatrix}$$

```
k12 = Rxy[0] // ExpToTrig // FullSimplify;
k12 // MatrixForm
```

$$\begin{pmatrix} \text{Cos}\left[\frac{\beta p}{2}\right] & -\mathbb{i}\,\text{Sin}\left[\frac{\beta p}{2}\right] \\ -\mathbb{i}\,\text{Sin}\left[\frac{\beta p}{2}\right] & \text{Cos}\left[\frac{\beta p}{2}\right] \end{pmatrix}$$

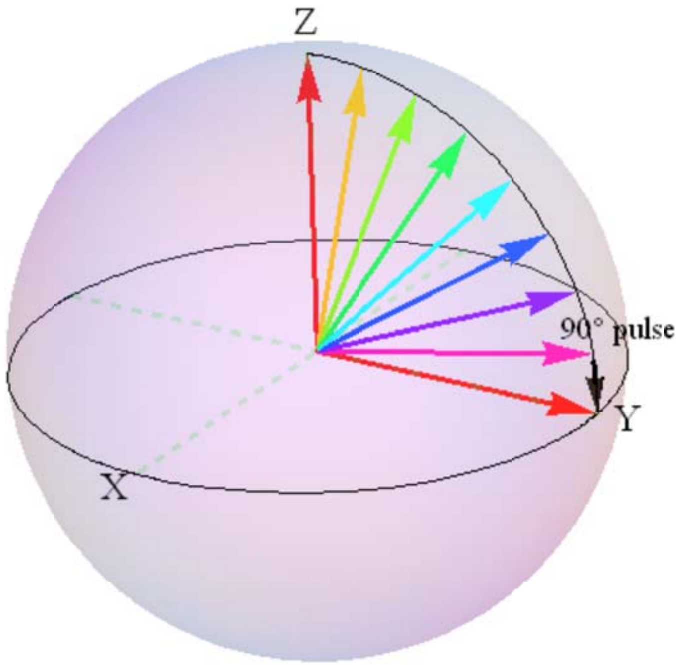
```
k13 = Rxy[π] // ExpToTrig // FullSimplify;
k13 // MatrixForm
```

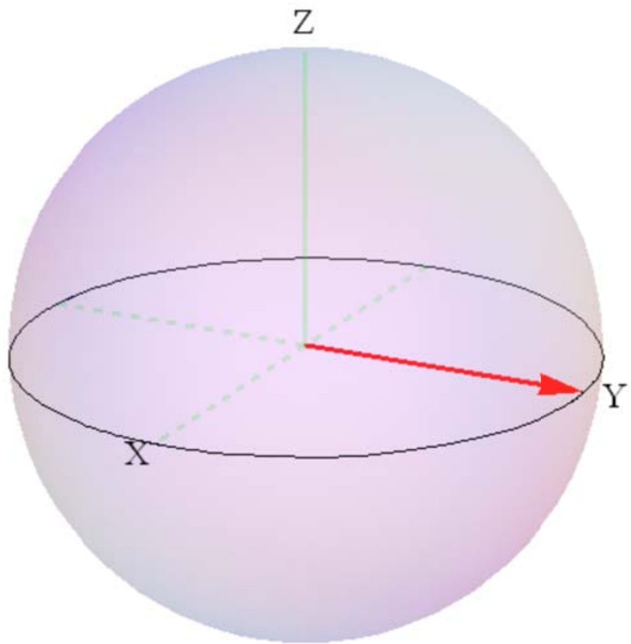
$$\begin{pmatrix} \text{Cos}\left[\frac{\beta p}{2}\right] & \mathbb{i}\,\text{Sin}\left[\frac{\beta p}{2}\right] \\ \mathbb{i}\,\text{Sin}\left[\frac{\beta p}{2}\right] & \text{Cos}\left[\frac{\beta p}{2}\right] \end{pmatrix}$$

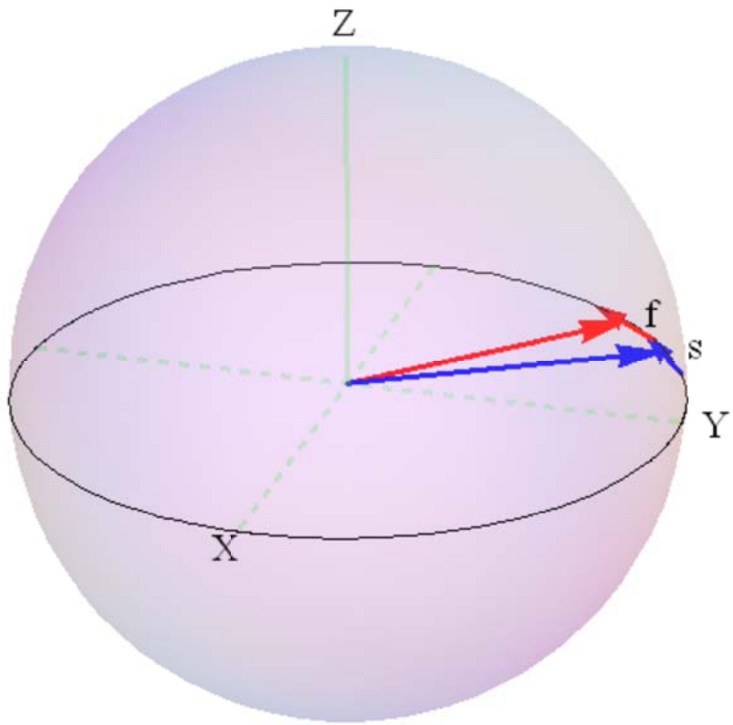
```
Roff[θ_] :=
  MatrixExp[-ⅈ βp (Cos[θ]/2 σx + Sin[θ]/2 σy) -
    ⅈ (Ω0 τp)/2 σz];

Roff[θ_] :=
  MatrixExp[-ⅈ βp (Cos[θ]/2 σx + Sin[θ]/2 σy) -
    ⅈ (Ω0 τp)/2 σz];

s1 =
 Roff[ϕp] /. {Sqrt[βp^2 + τp^2 Ω0^2] → τp ωeff,
    1/Sqrt[βp^2 + τp^2 Ω0^2] → 1/(τp ωeff)} // FullSimplify;

s1 // MatrixForm
```

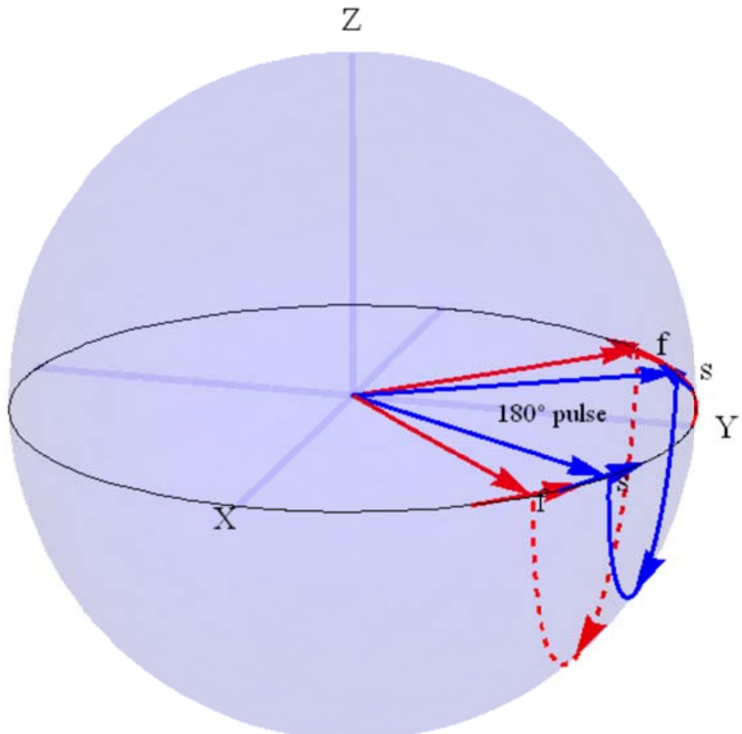
$$\begin{pmatrix} \mathrm{Cos}\left[\frac{\tau p\, \omega eff}{2}\right] - \frac{i\, \Omega 0\, \mathrm{Sin}\left[\frac{\tau p\, \omega eff}{2}\right]}{\omega eff} & \frac{\beta p\, (-i\, \mathrm{Cos}[\phi p] - \mathrm{Sin}[\phi p])\, \mathrm{Sin}\left[\frac{\tau p\, \omega eff}{2}\right]}{\tau p\, \omega eff} \\ \frac{\beta p\, (-i\, \mathrm{Cos}[\phi p] + \mathrm{Sin}[\phi p])\, \mathrm{Sin}\left[\frac{\tau p\, \omega eff}{2}\right]}{\tau p\, \omega eff} & \mathrm{Cos}\left[\frac{\tau p\, \omega eff}{2}\right] + \frac{i\, \Omega 0\, \mathrm{Sin}\left[\frac{\tau p\, \omega eff}{2}\right]}{\omega eff} \end{pmatrix}$$

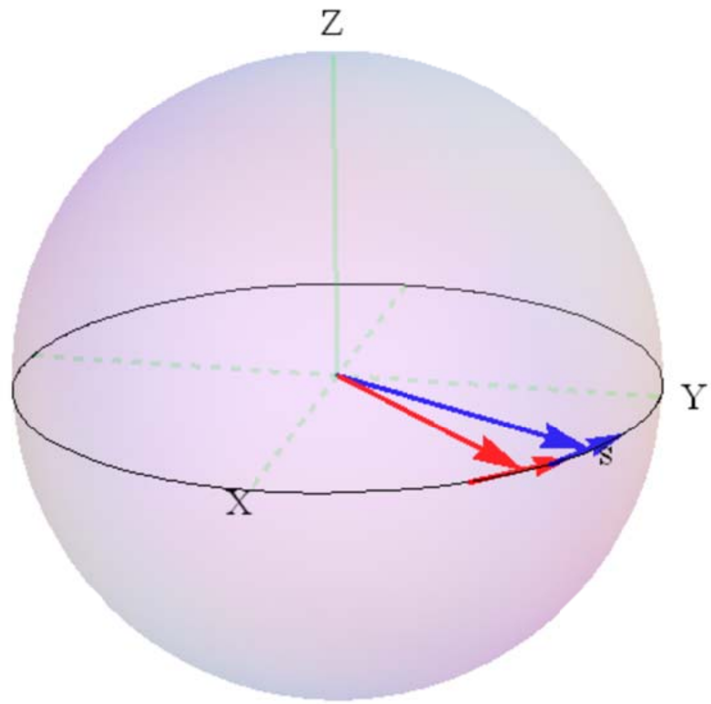
((From Lecture Note on rf spin echo method))


Z
90° pulse
Y
X


Z
Y
X


Z
f
s
Y
X


Z
f
s
180° pulse
Y
X
f
s


Z
Y
X
s