Chapter 1

Nuclear Magnetization, Larmor Resonance, Excitation and Bloch Equations

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I. Nuclear spin and magnetic moment

Let's start with a little bit of quantum mechanics. Physical observables $\Rightarrow$ operators in quantum mechanics

$$\hat{P}_x = -i\hbar \frac{\partial}{\partial x}, \qquad \hat{x} = x$$

$$\left.\begin{array}{l} \hat{l}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{l}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{l}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \end{array}\right\}$$

$$\hat{l} = \hat{r} \times \hat{p} = -i\hbar\hat{r} \times \mathbf{V}$$

$$l^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$$

$$\begin{cases} \hat{l}^2\phi = \hbar^2 l(l+1)\phi \\ \hat{l}_z\phi = m_l\hbar\phi \end{cases}$$

ϕ : eigen function

ℓ : eigenvalues or quantum number of $\hat{\ell}$

m_l: -l, -l+1,…l

true for spin angular momentum: $\hat{s}$

And total angular momentum: $\hat{j} = \hat{s} + \hat{l}$ spin-orbit coupling

Also true for a nucleus (aggregate of nucleons) as an entity: $\vec{J} = \sum \vec{j}$

$$\begin{cases} \hat{J}^2\phi = \hbar^2 (I)(I+1)\phi \\ \hat{J}_z\phi = m_I\hbar\phi \end{cases}$$

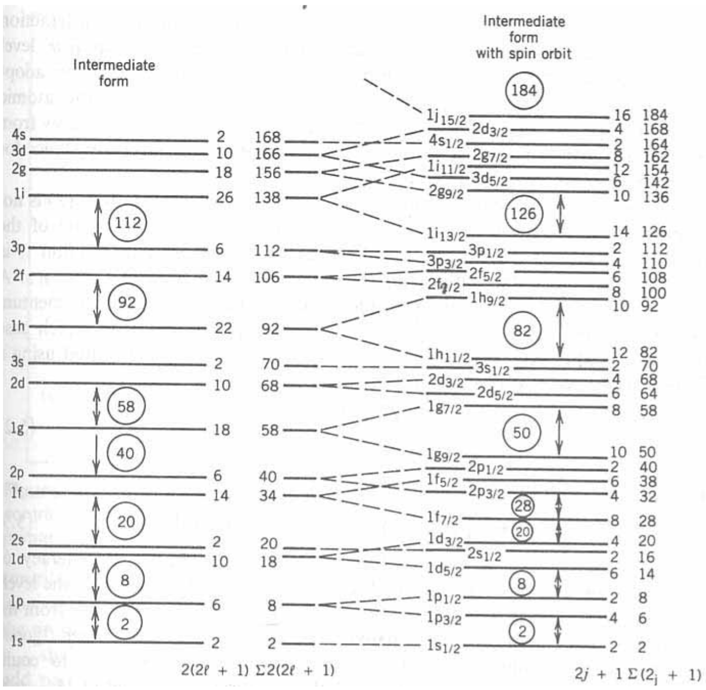
So, the measurement of $\vec{J}$ will give

or $\left|\hat{J}\right| = \hbar\sqrt{I(I+1)}$ I: nuclear spin quantum number

and, the measurement of $\vec{J}_z$ will give the following possibilities

$$\left|\hat{J}_z\right| = m_I\hbar \qquad m_I : -I, -I+1, \ldots\ldots I-1, I$$

"I" can be predicted by the shell model of the nucleus with spin-orbital coupling (Mayer, Haxel Suess, Jensen, 1949).



The shell model explains the magic numbers found in the stable nuclei.

Magnetic moment:

$$\vec{\mu} = \frac{e\hbar}{2m} g \qquad \vec{J} \swarrow \begin{cases} \vec{\mu} \,//\, \vec{J} \\ |\vec{\mu}| = g\dfrac{e\hbar}{2m}|\vec{J}| = \gamma|\vec{J}| \end{cases} \qquad \gamma : \text{gyromagnetic ratio}$$

Classical Picture:

$$l = m v r$$

$$\mu = iA = \frac{e}{T}\pi r^2 = \frac{e}{(2\pi r / v)}\pi r^2 = \frac{evr}{2} = \frac{e}{2m} l$$

$$\therefore \gamma = \frac{e}{2m}$$

In Quantum Mechanics, $\mu = \frac{e\hbar}{2m} l$

$\frac{e\hbar}{2m} \equiv b$ b: "Bohr magneton" $\mu_B \sim 10^{-5}\, eV/T$ for electrons

"nuclear magneton" $\mu_N \sim 10^{-8}\, eV/T$ for nucleons

$|\vec{\mu}| = gb|\vec{J}|$ g: "g factor"

$= \gamma|\vec{J}|$ $g\begin{cases} proton \approx 5.6 \\ neutron \approx -3.8 \\ electron \approx 2.0 \end{cases}$

II. Magnetization

Let $\vec{\mu}_i$ in a magnetic field $\vec{B}_0 = B_0 \vec{k}$

<1> $\vec{\mu}$ is quantized in $\vec{k}$:

$$|\vec{\mu}_z| = \gamma m_I \hbar \qquad m_I = -I, -I+1, \ldots I$$

$$\Rightarrow \text{Cos}\,\theta = \frac{\mu_z}{\mu} = \frac{\gamma m_I \hbar}{\gamma\hbar\sqrt{I(I+1)}} = \frac{m_I}{\sqrt{I(I+1)}}$$

$\vec{\mu}_{xy} = \mu_x \vec{i} + \mu_y \vec{j}$ $\vec{\mu}_{xy}$ is @ any phase angle (random)

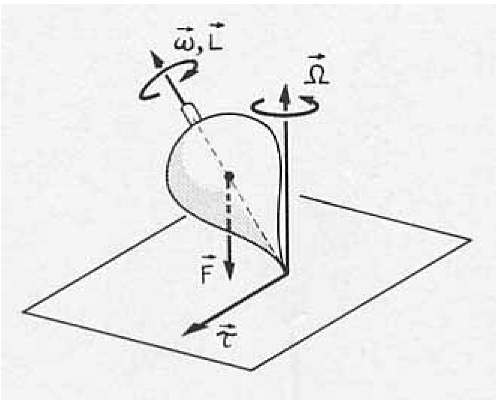
$$|\vec{\mu}_{xy}| = \sqrt{\mu^2 - \mu_z^2} = \gamma\hbar\sqrt{I(I+1) - m_I^2}$$

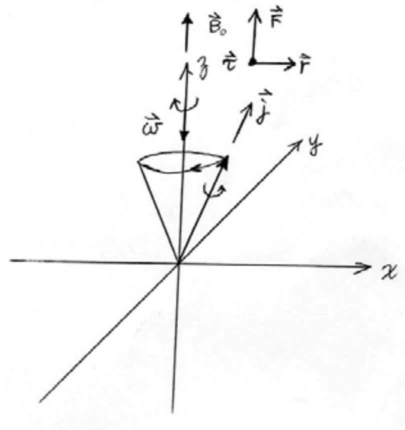
for $I = \frac{1}{2}$,

$$\theta = \pm 54°.44$$

$$|\vec{\mu}_{xy}| = \frac{\gamma\hbar}{\sqrt{2}}$$

<2> $\vec{\mu}$ precession around $\vec{k}$: classical picture





Therefore, $\vec{\tau} = \frac{d}{dt}\vec{J} = \vec{\mu} \times \vec{B}_0$ (classical picture)

Or $\frac{d\vec{\mu}}{dt} = \gamma\vec{\mu} \times \vec{B}_0$ (microscopic Bloch Eq.)

$$\therefore \quad \frac{d}{dt}\vec{\mu} = \gamma\vec{\mu} \times \vec{B}_0 \quad \rightarrow \quad \begin{cases} \frac{d}{dt}\mu_x = \gamma\mu_y B_0 = w_0\mu_y \\ \frac{d}{dt}\mu_y = -\gamma\mu_x B_0 = -w_0\mu_x \\ \frac{d}{dt}\mu_z = 0 \end{cases}$$

$$\rightarrow \begin{cases} \dfrac{d^2\mu_x}{dt^2} = -w_0^2 \mu_x \\ \dfrac{d^2\mu_y}{dt^2} = -w_0^2 \mu_y \end{cases} \qquad \rightarrow \begin{cases} \mu_x(t) = \mu_x(0)\cos(w_0 t) + \mu_y(0)\sin(w_0 t) \\ \mu_y(t) = -\mu_x(0)\sin(w_0 t) + \mu_y(0)\cos(w_0 t) \\ \mu_z(t) = \mu_z(0) \end{cases}$$

$\Rightarrow$ ① $\vec{w}_0 = -\gamma \vec{B}_0$ "Larmor Frequency" γ : gyromagnetic ratio

② prcession: clockwise, "Left-hand rule"

$$\rightarrow \underbrace{\begin{bmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}}\begin{bmatrix} \mu_x(0) \\ \mu_y(0) \\ \mu_z(0) \end{bmatrix} = \begin{bmatrix} \mu_x(t) \\ \mu_y(t) \\ \mu_z(t) \end{bmatrix} \qquad \alpha = w_0 t$$

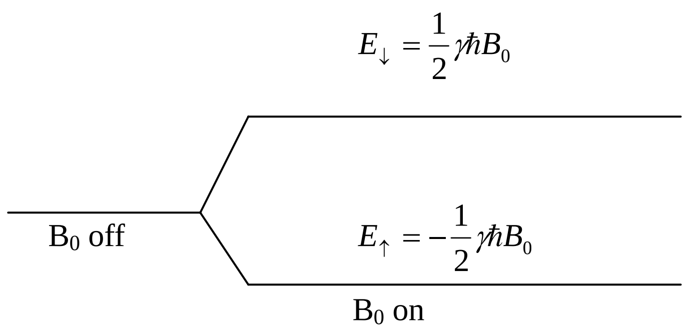
$$\hat{R}_z(w_0 t)\vec{\mu}(0) = \vec{\mu}(t)$$

<3> Net Magnetization: $\vec{M}_0 = \sum_{n=1}^{N} \vec{\mu}_n$

spin- $\frac{1}{2}$ system

$$E = -\vec{\mu}\cdot\vec{B}_0 = -\mu_z B_0 = -\gamma\hbar m_I B_0 = \begin{cases} E_\uparrow = -\gamma\hbar \frac{1}{2} B_0 & (m_I = \frac{1}{2}) \\ E_\downarrow = \gamma\hbar \frac{1}{2} B_0 & (m_I = -\frac{1}{2}) \end{cases}$$

$$\Delta E = E_\downarrow - E_\uparrow = \gamma\hbar B_0$$



$N_\uparrow = Ae^{-E_\uparrow/KT}$ $\qquad N_\downarrow = Ae^{-E_\downarrow/KT}$ Boltzmann distribution

$$\frac{N_\uparrow}{N_\downarrow} = e^{(E_\downarrow - E_\uparrow)/KT} = e^{\Delta E / KT} = e^{\gamma\hbar B_0 / KT}$$

$$\approx 1 + \frac{\gamma\hbar B_0}{KT}$$

$$\therefore N_\uparrow - N_\downarrow = \frac{\gamma\hbar B_0}{KT} N_\downarrow \approx \frac{\gamma\hbar B_0}{2KT} N$$

$$\therefore \vec{M}_0 = \sum_{n=1}^{N} (\vec{\mu}_x + \vec{\mu}_y + \vec{\mu}_z) = \sum_{n=1}^{N} \vec{\mu}_z = \left(\sum_{n=1}^{N_\uparrow} \frac{1}{2}\gamma\hbar - \sum_{n=1}^{N_\downarrow} \frac{1}{2}\gamma\hbar \right) \vec{k}$$

$$= \frac{1}{2}\gamma\hbar (N_\uparrow - N_\downarrow) \vec{k} = \frac{\gamma^2 \hbar^2 B_0 N}{4KT} \vec{k}$$

for spin-I system

$$M_0 = \frac{\gamma^2 \hbar^2 B_0 N (I+1) I}{3KT} \qquad \text{(see the Appendix)}$$

For a spin-$\frac{1}{2}$ system at room temperature:

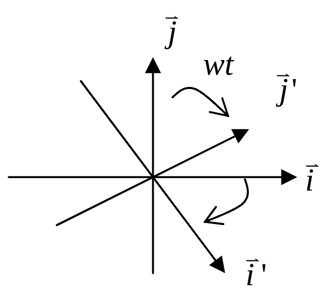
calculate $\frac{N_\uparrow - N_\downarrow}{N} = \frac{\gamma\hbar B_0}{2KT}$

$\approx 3 \times 10^{-6}$

γ = 42.58×10^{6} Hz/T
h = 6.6×10^{-34} J-S
T_s = 300 K
K = 1.38×10^{-23} J/K
B_0 = 1T

<4> Rotating Frame vs. Lab Frame

$$\begin{cases} \vec{i}\,' = \cos(wt)\vec{i} - \sin(wt)\vec{j} \\ \vec{j}\,' = \sin(wt)\vec{i} + \cos(wt)\vec{j} \\ \vec{k}\,' = \vec{k} \end{cases}$$



or

$$\begin{cases} \vec{i} = \cos(wt)\vec{i}\,' + \sin(wt)\vec{j}\,' \\ \vec{j} = -\sin(wt)\vec{i}\,' + \cos(wt)\vec{j}\,' \end{cases}$$

$$\vec{k} = \vec{k}'$$

Also,

$$\begin{cases} \dfrac{d\vec{i}\,'}{dt} = \vec{w} \times \vec{i}\,' \\ \dfrac{d\vec{j}\,'}{dt} = \vec{w} \times \vec{j}\,' \\ \dfrac{d\vec{k}\,'}{dt} = \vec{w} \times \vec{k}\,' \end{cases} \qquad \left(\vec{w} = -w\vec{k}\right)$$

$$\begin{aligned} \vec{M} &\equiv M_x \vec{i} + M_y \vec{j} + M_z \vec{k} \\ \vec{M}_{rot} &\equiv M_{x'} \vec{i}\,' + M_{y'} \vec{j}\,' + M_{z'} \vec{k}\,' \end{aligned} \qquad \left(\vec{M} = \vec{M}_{rot}\right)$$

$$\therefore \quad \begin{bmatrix} M_{x'} \\ M_{y'} \\ M_{z'} \end{bmatrix} = \begin{bmatrix} Coswt & -Sinwt & 0 \\ Sinwt & Coswt & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} M_x \\ M_y \\ M_z \end{bmatrix}$$

Now, $$\frac{d\vec{M}}{dt} \equiv \frac{dM_x}{dt}\vec{i} + \frac{dM_y}{dt}\vec{j} + \frac{dM_z}{dt}\vec{k} \qquad \left(= \frac{d\vec{M}_{rot}}{dt} \right)$$

$$\frac{\partial \vec{M}_{rot}}{\partial t} \equiv \frac{dM_{x'}}{dt}\vec{i}\,' + \frac{dM_{y'}}{dt}\vec{j}\,' + \frac{dM_{z'}}{dt}\vec{k}\,'$$

Then

$$\frac{d\vec{M}}{dt} = \frac{\partial \vec{M}_{rot}}{\partial t} + \vec{w} \times \vec{M}_{rot}$$

Proof:

$$\frac{d\vec{M}}{dt} = \frac{d\vec{M}_{rot}}{dt} = \left(\frac{dM_{x'}}{dt}\vec{i}\,' + \frac{dM_{y'}}{dt}\vec{j}\,' + \frac{dM_{z'}}{dt}\vec{k}\,'\right) +$$

$$\left(M_x' \frac{d\vec{i}\,'}{dt} + M_y' \frac{d\vec{j}\,'}{dt} + M_z' \frac{d\vec{k}\,'}{dt}\right)$$

$$= \frac{\partial \vec{M}_{rot}}{\partial t} + \left[M_{x'}\left(\vec{w}\times\vec{i}\,'\right) + M_{y'}\left(\vec{w}\times\vec{j}\,'\right) + M_{z'}\left(\vec{w}\times\vec{k}\,'\right)\right]$$

$$= \frac{\partial \vec{M}_{rot}}{\partial t} + \vec{w}\times\vec{M}_{rot}$$

* self exercise: Prove that $\frac{d\vec{i}\,'}{dt} = \vec{w}\times\vec{i}\,'$

<5> Bloch Eq. $\frac{d\vec{M}}{dt} = \gamma\vec{M}\times\vec{B}_0 - \frac{M_x\vec{i} + M_y\vec{j}}{T_2} - \frac{\left(M_z - M_z^0\right)}{T_1}\vec{k}$ (Macroscopic Bloch Eq.)

neglect these for the moment

$$\frac{\partial \vec{M}_{rot}}{\partial t} = \gamma\vec{M}_{rot}\times\vec{B}_0 - \vec{w}\times\vec{M}_{rot}$$

$$= \gamma\vec{M}_{rot}\times\left(\vec{B}_0 + \frac{\vec{w}}{\gamma}\right)$$

$$= \gamma\vec{M}_{rot}\times\vec{B}_{eff}$$

if $\vec{w} = -B_0\gamma\vec{k}$, $\vec{B}_{eff} = 0$

$\therefore$ In rotating frame, $w = w_0$, $\vec{M}_{rot}$ is constant

III. On-Resonance excitation

RF pulse: $\vec{B}_1(t) = 2B_1^e(t)Cos(w_{rf}t + \varphi)\vec{i}$

$$= B_1^e(t)\left[Cos(w_{rf}t + \varphi)\vec{i} - Sin(w_{rf}t + \varphi)\vec{j}\right]$$

$$+ B_1^e(t)\left[Cos(w_{rf}t + \varphi)\vec{i} + Sin(w_{rf}t + \varphi)\vec{j}\right]$$

or in complex form $B_1(t) = B_1^e(t)e^{-i(w_{rf}t + \varphi)}$

w_{rf} : carrier frequency, $B_1^e(t)$: pulse envelop function

φ : initial phase

Now, on resonance Excitation $w_{rf} = w_0$

$\vec{B}_{1,rot} = B_1^e(t)\vec{i}'$ in rotating frame where $w = w_{rf}$

$$\vec{B}_{eff} = \left(B_0 - \frac{w_{rf}}{\gamma}\right)\vec{k}' + B_1^e(t)\vec{i}'$$

Since $w_{rf} = w_0$, $B_0 - \frac{w_{rf}}{\gamma} = 0$

$\vec{B}_{eff} = B_1^e(t)\vec{i}'$

$$\therefore \quad \frac{\partial \vec{M}_{rot}}{\partial t} = \gamma \vec{M}_{rot} \times \vec{B}_{eff} = \gamma \vec{M}_{rot} \times B_1^e(t)\vec{i}'$$

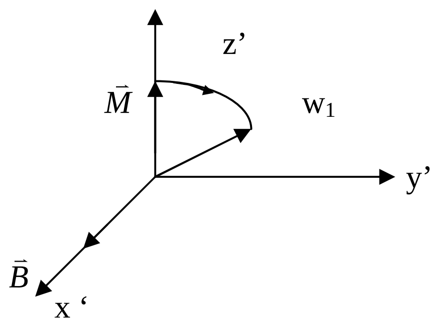
$$\rightarrow \begin{cases} \dfrac{\partial M_{x'}}{\partial t} = 0 \\ \dfrac{\partial M_{y'}}{\partial t} = \gamma B_1^e(t) M_{z'} \\ \dfrac{\partial M_{z'}}{\partial t} = -\gamma B_1^e(t) M_{y'} \end{cases}$$

if $\vec{M}_{0^-} = M_z^o \vec{k}'$

$$\rightarrow \begin{cases} M_{x'}'(t) = 0 \\ M_{y'}'(t) = M_z^0 \sin\left(\int_0^t \gamma B_1^e(\tau) d\tau \right) \\ M_{z'}'(t) = M_z^0 \cos\left(\int_0^t \gamma B_1^e(\tau) d\tau \right) \end{cases}$$

if $B_1^e(t) = B_1 II\left(\dfrac{t - \tau p/2}{\tau p} \right) = \begin{cases} B_1 & 0 \le t \le \tau_p \\ 0 & Otherwise \end{cases}$

$$\rightarrow \begin{cases} M_{x'}(0) = 0 \\ M_{y'}'(0) = M_z^0 \sin(w_1 t) \\ M_{z'}'(0) = M_z^0 \cos(w_1 t) \end{cases}$$



Flip angle $\alpha = \int_0^{\tau_p} w_1(t) dt$

$$= \int_0^{\tau_p} \gamma B_1^p(t) dt = \gamma B_1 \tau_p$$

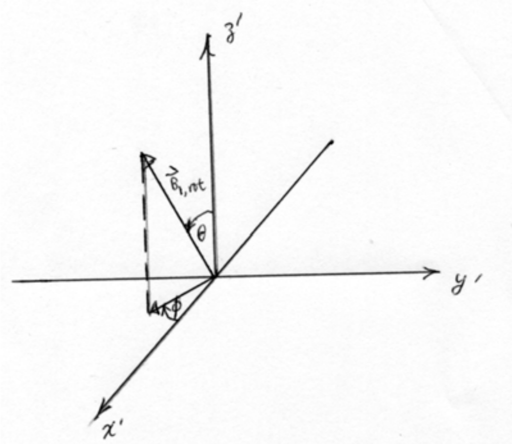
Left-hand rule: $\vec{B}_1$ is the axis of rotation

$$\hat{R}_{x'}(\alpha) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & Cos\alpha & Sin\alpha \\ 0 & -Sin\alpha & Cos\alpha \end{bmatrix}$$

$$\hat{R}_{y'}(\alpha) = \begin{bmatrix} Cos\alpha & 0 & -Sin\alpha \\ 0 & 1 & 0 \\ Sin\alpha & 0 & Cos\alpha \end{bmatrix}$$

$$\hat{R}_{z'}(\alpha) = \begin{bmatrix} Cos\alpha & Sin\alpha & 0 \\ -Sin\alpha & Cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\begin{cases} \hat{R}_{-x'}(\alpha) = R_{x'}(-\alpha) \\ \hat{R}_{-y'}(\alpha) = R_{y'}(-\alpha) \end{cases}$$



In general,

$$\vec{M}_{rot}(0_+) = \hat{R}_{z'}(\varphi)\hat{R}_{y'}(\hat{\theta})\hat{R}_{x'}(\alpha)\hat{R}_{y'}(-\hat{\theta})\hat{R}_{z'}(-\varphi)\vec{M}_{rot}(0_-)$$

where $\hat{\theta} = 90 - \theta$

First rotate, $\vec{B}_1$ & $\vec{M}_{rot}(0\_)$ through

$$\hat{R}_{z'}(-\phi) \text{ then } \hat{R}_{y'}(-\hat{\theta})$$

Second, let $\vec{B}_1^{'}$ in new position in $\vec{i}\,'$ act on $\vec{M}_{rot}(0\_) \rightarrow \vec{M}^{'}_{rot}(0.)$

Now, rotate the $\vec{B}_1^{'}$ & $\vec{M}^{'}_{rot}(0.)$ back to $\vec{B}_1$ and $\vec{M}_{rot}(0_+)$ through

$\hat{R}_{y'}(\hat{\theta})$ then $\hat{R}_{z'}(\phi)$

We have

$$\vec{M}_{rot}(0_+) = \hat{R}_{z'}(\varphi)\hat{R}_{y'}(\hat{\theta})\hat{R}_{x'}(\alpha)\hat{R}_{y'}(-\hat{\theta})\hat{R}_{z'}(-\varphi)\vec{M}_{rot}(0_-)$$

<6> off-resonance excitations

Magnetic field inhomogeneities } ⟹ heterogeneous
Chemical-shift effects } isochromats

The effective field an isochromat sees

$$\vec{B}_{eff} = \left(B_0 - \frac{w_{rf}}{\gamma}\right)\vec{k}' + B_1^e(t)\vec{i}'$$

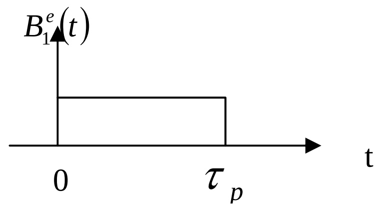
$$= \frac{\Delta w_0}{\gamma}\vec{k}' + B_1^e(t)\vec{i}', \qquad \Delta w_0 = w_0 - w_{rf} \text{ is the off-resonance}$$

So the corresponding Bloch Eq.:

$$\frac{\partial \vec{M}}{\partial t} = \gamma \vec{M} \times B_{eff} = \gamma \vec{M} \times \left(\frac{\Delta\omega}{\gamma}\vec{k}' + B_1^e(t)\vec{i}'\right)$$

$$\begin{cases} \dfrac{\partial M_{x'}}{\partial t} = \Delta w_0 M_{y'} \\ \dfrac{\partial M_{y'}}{\partial t} = -\Delta w_0 M_{x'} + \gamma B_1^e(t) M_{z'} \\ \dfrac{\partial M_{z'}}{\partial t} = -\gamma B_1^e(t) M_{y'} \end{cases}$$

For Top-hat RF $B_1^e(t) = B_1 \Pi\left(\dfrac{t - \tau_p/2}{\tau_p}\right)$:



A close form solution exists:

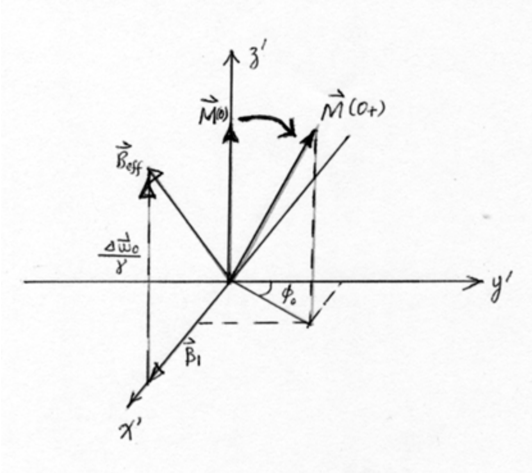
$$\begin{cases} M_{x'}(t) = M_z^0 \sin\theta\cos\theta\left[1 - \cos(w_{eff}t)\right] \\ M_{y'} = M_z^0 \sin\theta \sin(w_{eff}t) \qquad\qquad 0 \le t \le \tau_p \\ M_{z'} = M_z^0\left[\cos^2\theta + \sin^2\theta\cos(w_{eff}t)\right] \end{cases}$$

where $w_{eff} = \sqrt{\Delta w_0^2 + w_1^2}$

$$\theta = \arctan\left(\frac{w_1}{\Delta w_0}\right)$$

$$@\ t = \tau_p,\quad \alpha = w_{eff}\tau_p$$

$$\begin{cases} M_{x'} = M_z^0 \sin\theta\cos\theta[1-\cos\alpha] \\ M_{y'}(\tau_p) = M_z^0 \sin\theta\sin\alpha \\ M_{z'}(\tau_p) = M_z^0(\cos^2\theta + \sin^2\theta\cos\alpha) \end{cases}$$



phase shift φ_0

$$\tan\ \varphi_0 = \frac{M_x(\tau_p)}{M_y(\tau_p)}$$

$$= \frac{\sin\theta\cos\theta[1-\cos\alpha]}{\sin\theta\sin\alpha} = \frac{(1-\cos\alpha)}{\sin\alpha}\frac{\Delta w_0}{w_{eff}} = \tan\frac{\alpha}{2}\frac{\Delta w_0}{w_{eff}} \Rightarrow \phi_0 \propto \Delta w_0$$

$$M_{xy'}(0_+) = \sqrt{M_{x'}^2(0_+) + M_{y'}^2(0_+)}$$

$$= M_z^0 \sin\theta\sqrt{\sin^2\alpha + (1-\cos\alpha)^2\cos^2\theta} \Rightarrow 0$$

when $\theta\downarrow$ (when $\vec{B}_{eff} \sim \frac{\Delta\vec{w}_0}{\gamma}$).

APPENDIX

Bulk Magnetization of a spin-I system

Given a spin-I system, the energy levels are quantized into 2I+1 levels, denoting m_I = -I, -I+1, ……I-1, I.

Each energy level in the state m_I is:

$$E_{m_I} = -\gamma m_I \hbar B_0 \,,$$

and the number of nuclear spins per unit volume in state m_I, $N(m_I)$, is related to other state $N(m_I')$ by the Boltzmann principle:

$$\frac{N(m_I)}{N(m_I^{'})} = \frac{e^{-E_{m_I}/k_B T}}{e^{-E_{m_I^{'}}/k_B T}} = e^{-\left(E_{m_I} - E_{m_I^{'}}\right)/k_B T}$$

Since $N = \sum_{m_I} N(m_I)$ = the total number of spins per unit volume

We have $N(m_I) = N \dfrac{e^{-E_{m_I}/k_B T}}{Z}$

Where $Z = \sum_{m_I} e^{-E_{m_I}/k_B T}$ “ partition function”

So, the magnetization, which is the total magnetic moment per unit volume, is:

$$M_0 = \langle M_z \rangle = \sum_{m_I} N(m_I)\mu_z = \sum_{m_I} N(m_I)\gamma\hbar m_I$$

$$= \frac{N\sum_{m_I} e^{-E_{m_I}/k_B t}\gamma\hbar m_I}{Z} = \frac{N\sum_{m} e^{+\beta m}\gamma\hbar m}{\sum_{m} e^{+\beta m}} \qquad \left(\beta \equiv \gamma\hbar B_0 / k_B T\right)$$

Since $\beta = \gamma\hbar B_0 / k_B T \cong 6.83\times 10^{-6}$ if B_0 = 1 Tesla, T = 300k

$$\therefore\ M_0 = \frac{N\gamma\hbar \sum_m (1+\beta m) m}{\sum_m (1+\beta m)}$$

knowing that $\sum_m 1 = 2I+1$, $\sum_m m^2 = I(I+1)(2I+1)/3$, $\sum_m m = 0$,

we have

$$M_0 = \frac{\beta N\gamma\hbar I(I+1)(2I+1)}{3(2I+1)} = \frac{N\gamma^2\hbar^2 I(I+1)}{3k_B T} B_0 = X_0 B_0$$