1) **Spin Intro**

- "Spin" is a highly abstract concept.
- For atomic nuclei that possess “spin,” it can be thought of as if though they have angular momentum but do not experience any bodily rotation.
  
  "Actual", "real"

a) **Combining angular momenta**

- "NMR-active" nuclei can be observed by NMR - they have spin

- The spin of
- The total angular momentum of these nuclei is given by

\[
\langle \mathbf{S} \rangle = \hbar \sqrt{\mathbf{S}(\mathbf{S}+1)}
\]

where \( \mathbf{S} \) is the spin quantum number and \( \hbar \) is Planck’s constant divided by \( 2\pi \).

- If two objects have angular momenta quantum numbers of \( \mathbf{J}_1 \) and \( \mathbf{J}_2 \), the total angular momentum resulting from the addition of \( \mathbf{J}_1 \) and \( \mathbf{J}_2 \) can be:

\[
1 \left| \mathbf{J}_1 - \mathbf{J}_2 \right|
\]

\[
1 \left| \mathbf{J}_1 - \mathbf{J}_2 \right| + 1
\]

\[\vdots\]

\[
1 \left| \mathbf{J}_1 + \mathbf{J}_2 \right|
\]

(works for spin angular momentum as well)

b) **Fundamental particles**

- According to modern physics, everything is made up of quarks, leptons, and force particles.
- Leptons are low mass particles that include electrons. They have a spin of \( \frac{1}{2} \) (quantum number).
- Quarks are heavier. Protons and neutrons are made up of quarks. They have a spin of \( \frac{1}{2} \).
- Force particles mediate the action of one particle on another

i) The neutron
- Two quarks with charge \(-\frac{e}{3}\)
- One quark with charge \(+\frac{2e}{3}\)
- The neutron has an overall spin of \( \frac{1}{2} \)

A neutron:
- Charge = 0
- Spin = \( \frac{1}{2} \)

ii) The proton
- Two quarks with charge \(+\frac{2e}{3}\)
- One quark with charge \(-\frac{e}{3}\)
- The proton has an overall spin of \( \frac{1}{2} \)

A proton:
- Charge = \( +e \)
- Spin = \( \frac{1}{2} \)
c) The atomic nucleus

- Consists of neutrons and protons, collectively known as nucleons.

- Each nucleus has its own quantum spin number.

- The nucleus spin quantum number is usually denoted by "I".

- The $^2$H nucleus has one proton and one neutron. Adding the spin angular momenta, we see it can have a total spin of $I = 0$ or $I = 1$. The energy levels of the nucleus look like

$$^2\text{H} \quad \begin{array}{c}
\uparrow \\
\text{Huge, } \sim 10^{11} \text{ kJ/mol}
\end{array} \quad \begin{array}{c}
\bigcirc \bigcirc \\
I = 0
\end{array} \quad \begin{array}{c}
\downarrow \\
I = 1
\end{array}$$

- Except in very unusual circumstances, $^2$H nuclei have $I = 1$.

- Not easy to predict ground state nuclear spin. However, the following rules of thumb apply.
(1) From equation in (1a), it can be said that isotopes with even mass numbers (even number of nucleons) will have integer spin. Isotopes with an odd number of nucleons will have half-integer spin ($\frac{1}{2}, \frac{3}{2}, \ldots$). Not really just rule of thumb

(2) If the numbers of protons and neutrons are both even, the ground state spin is $I = 0$.

(3) If the numbers of protons and neutrons are both odd, the ground state spin is an integer larger than zero.

- We will only really study $I = \frac{1}{2}$ nuclei for now ($^1\text{H}, ^{13}\text{C}, ^{15}\text{N}, ^{31}\text{P}$, etc.)

2) What is happening in an NMR tube

a) No magnetic field!

- Long after the nuclei in an NMR tube have been perturbed, they reach an equilibrium state where all the "spins" are pointing in random directions (angular momentum axis)

\[ \text{Nucleus}^{\uparrow} \text{ and } \text{"spin" used interchangeably when it has spin angular momentum} \]
- Because the nucleus behaves as if though it is "spinning" (i.e., it has angular momentum) it will, like a "spinning" ball of charge, have a magnetic moment.
- The magnetic moment is related to the spin angular momentum by a proportionality constant, known as the "gyromagnetic ratio," and written as "\( \gamma \)" (also known as "magnetogyric ratio")

\[ \langle \hat{\mu} \rangle = \gamma \langle \hat{S} \rangle \]

- In a magnetic field, a magnetic moment feels a torque \( \vec{T} = \vec{\mu} \times \vec{B} \) that tends to align it with the magnetic field.
- When the spins in a magnetic field reach equilibrium, they tend to be aligned in the direction of the magnetic field. There (at room temps) is still a lot of thermal energy, so it looks like their orientations are random, but there is a very slight tendency to align with the magnetic field.
Even though the magnetic field generated by the alignments of these magnetic dipole moments with the spectrometer field is small, it can be detected.

To get a basic understanding of NMR, it's instructive to analyze how the bulk magnetic moment, resulting from the additive effect of all the nuclear magnetic moments, behaves.
3) The Bloch Equations

a) The precession of a spinning top

\[ \dot{\vec{L}} = \vec{I} \omega \]

- \( \vec{L} \): angular momentum
- \( \vec{I} \): moment of inertia
- \( \omega \): angular speed

The behavior of the bulk magnetic moment is similar to that of a precessing top. This gives a real world, intuitive picture of the NMR phenomenon.

\[ \vec{\omega} = \frac{d\vec{L}}{dt} = \vec{\omega} \times \vec{F}_g \]

- \( \vec{\omega} \): precession
- \( \vec{F}_g \): torque
- \( \vec{\omega} \times \vec{F}_g \)

\[ \vec{F}_g = mg \]

- \( \vec{F}_g \): force
- \( m \): mass
- \( g \): gravitational acceleration

\[ \text{lever arm} = mgr \sin \Theta \]

- \( m \): mass
- \( g \): gravitational acceleration
- \( r \): lever arm
- \( \Theta \): angle
b) Think of the bulk magnetic field as a bar magnet fixed in place at its center.

- Consider that the magnet is if the magnet is not spinning, it will experience a torque acting to align it with the magnetic field. That is, if it is not aligned with the magnetic field already, which is the general case.
- This will cause it to oscillate back and forth.

\[ \tau = \vec{M} \times \vec{B} \]

In a vacuum, the field will be \( \overrightarrow{B} \), physical. Technically, in a medium, it will be \( \overrightarrow{H} \). We'll use \( \overrightarrow{B} \), but this is something to be aware of.

- It is more accurate to imagine the bar magnet as spinning about its long axis.
- If the magnet is spinning about its long axis, the magnetic field will torque the spinning bar magnetic field magnet, causing it to precess.
- A torque causes a change in angular momentum.
\[ \frac{d\vec{L}}{dt} = \vec{M} \times \vec{B} \]

- The magnetic moment should be equal to the angular momentum times \(\gamma\)

\[ \Rightarrow \gamma \frac{d\vec{L}}{dt} = \gamma \vec{M} \times \vec{B} \]

\[ \Rightarrow \frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B} \]

- Solving for the \(x\), \(y\), and \(z\) components:

\[ \frac{dM_x}{dt} = \gamma (M_y B_z - M_z B_y) \]

\[ \frac{dM_y}{dt} = \gamma (M_z B_x - M_x B_z) \]

\[ \frac{dM_z}{dt} = \gamma (M_x B_y - M_y B_x) \]

- Usually, a large magnetic field is applied along the axis we define as the \(z\)-axis. Then, \(B_x = B_y = 0\). We call the field along \(z\) "\(B_0\)" and it represents the large field of the spectrometer. This gives

\[ \frac{dM_x}{dt} = \gamma M_y B_0 \quad (1) \]

\[ \frac{dM_y}{dt} = -\gamma M_x B_0 \quad (2) \]

\[ \frac{dM_z}{dt} = 0 \quad (3) \]
- Multiplying equation (2) by $\sqrt{-1} = i$ and adding the result to equation (1):

$$\frac{dM_x}{dt} + i \left( \frac{dM_y}{dt} \right) = \gamma M_y B_0 + (i)(-\gamma M_x B_0)$$

$$\Rightarrow \frac{d}{dt} (M_x + i M_y) = \gamma B_0 (-i M_x + M_y)$$

- We define $M_{xy} = M_x + i M_y \Rightarrow -i M_{xy} = -i M_x + M_y$.
  Substituting into the above equation, we get

$$\Rightarrow \frac{dM_{xy}}{dt} = -i \gamma B_0 M_{xy}$$

- We get the following alternate form of the Bloch equations:

$$\frac{dM_{xy}}{dt} = -i \gamma B_0 M_{xy} \quad (4)$$

$$\frac{dM_z}{dt} = 0 \quad (5)$$

- Relaxation can be addressed phenomenologically by adding $-M_{xy}/T_z$ to the right hand side eq. (4). $T_z$ is a time constant that characterizes the rate at which $M_{xy}$ is reduced to $(e^{-1})M_{xy}$. Longitudinal relaxation characterizing the rate at which $z$-magnetization returns to its equilibrium state, where it is aligned with the $B_0$ field, is addressed by adding $-(M_0 - M_z)/T_1$ to the right hand side of eq. (5). $M_0$ is the equilibrium $z$-magnetization in the $B_0$ field. $T_1$ characterizes the time it takes $z$-magnetization to return to $M_0$. $M_{xy}$ relaxation is called "transverse" or "spin-spin" relaxation, $M_z$ relaxation is called "longitudinal" or "spin-lattice."
It is always true that $T_2 \leq T_1$.

The Bloch equations become

\[
\frac{dM_{xy}}{dt} = -i \gamma B_0 M_{xy} - \frac{M_{xy}}{T_2} \tag{6}
\]

\[
\frac{dM_z}{dt} = - \frac{M_0 - M_z}{T_1} \tag{7}
\]

Equation (6) is a homogeneous differential equation. Solving it:

\[
\Rightarrow \frac{dM_{xy}}{M_{xy}} = -i \gamma B_0 \, dt - \left( \frac{1}{T_2} \right) dt
\]

\[
\Rightarrow \ln M_{xy} = -i \gamma B_0 \, t - \frac{t}{T_2} + C
\]

\[
\Rightarrow M_{xy}(t) = M_{xy}(t=0) e^{-i \gamma B_0 \, t} e^{-t/T_2} \tag{8}
\]

\[
= \cos (-\gamma B_0 \, t) + i \sin (-\gamma B_0 \, t), \text{ by Euler's formula.}
\]

The solution to eq. (7), an inhomogeneous differential equation, is:

\[
M_z(t) = M_0 - [M_0 - M_z(t=0)] \exp \left( -\frac{t}{T_1} \right) \tag{9}
\]

It can be seen that magnetization in the transverse plane (i.e., xy-plane) precesses at a frequency $-\gamma B_0$. This is called the "Larmor" frequency and is written $\Omega_0$, if you prefer Hz units or $\omega_0$, if you prefer rad s$^{-1}$.

Let's take a step back and try to imagine what is actually happening in the NMR tube.
The collection of spins look like they are oriented randomly, but they have a slight tendency to point in one particular direction. Each spin precesses at a rate of $\Omega_0$, causing the bulk magnetization, $\hat{M}$, to itself precess at $\Omega_0$.

c) Bloch eqns. in the rotating reference frame

Up until now, all our analyses have been done in the "laboratory frame", where the spectroscopist "lives".

To understand how a radiofrequency (RF) rotating magnetic field impacts the spins and the bulk magnetization of the sample, we have to enter into a rotating reference frame, called simply the "rotating" frame.

Let's return to the vector equation

$$\frac{d\hat{M}}{dt} = \gamma \hat{M} \times \hat{B}$$

Our task is to express this equation in a reference frame rotating at a reference frequency $\Omega$ around $+z$.

Consider a general function of $\hat{x}$, $\hat{y}$, $\hat{z}$. What happens if we let $\hat{x}$, $\hat{y}$, and $\hat{z}$ rotate at a frequency $\Omega$?

Then

$$\frac{d\hat{u}}{dt} = \hat{\Omega} \times \hat{u}$$

where $\hat{u}$ is any one of $\hat{x}$, $\hat{y}$, $\hat{z}$. 

NOTE THAT WE DID NOT CONSIDER INTERACTIONS B/T SPINS, THAT REQUIRES A QUANTUM MECHANICAL TREATMENT!
\[
\begin{align*}
\frac{\partial}{\partial t} \left( \nabla \times \vec{M} \right) + \frac{1}{\rho} \left( \frac{\partial}{\partial x} \left( x \vec{E} \right) + \frac{\partial}{\partial y} \left( y \vec{E} \right) + \frac{\partial}{\partial z} \left( z \vec{E} \right) \right) &= \left( \nabla \times \vec{E} \right) \\
\frac{\partial}{\partial t} \vec{M} + \frac{1}{\rho} \left( \frac{\partial}{\partial x} \left( x \vec{B} \right) + \frac{\partial}{\partial y} \left( y \vec{B} \right) + \frac{\partial}{\partial z} \left( z \vec{B} \right) \right) &= \vec{H} \\
\end{align*}
\]
- If we replace $\vec{B}$ with $\vec{B}_{\text{eff}} = \vec{B} + \frac{\vec{\Omega} \times}{\gamma}$, we get back our original vector equation:

$$\frac{\dot{\vec{M}}}{\dot{t}} = \vec{M} \times (\gamma \vec{B} + \vec{\Omega} \times) \quad \text{(from previous page)}$$

$$\Rightarrow \frac{\dot{\vec{M}}}{\dot{t}} = \vec{M} \times [\gamma (\vec{B} + \frac{\vec{\Omega} \times}{\gamma})]$$

$$\Rightarrow \frac{\dot{\vec{M}}}{\dot{t}} = \gamma \vec{M} \times (\vec{B} + \frac{\vec{\Omega} \times}{\gamma})$$

$$\Downarrow$$

Substituting using $\vec{B}_{\text{eff}} = \vec{B} + \frac{\vec{\Omega} \times}{\gamma}$

$$\Rightarrow \frac{\dot{\vec{M}}}{\dot{t}} = \gamma \vec{M} \times \vec{B}_{\text{eff}}$$

**Same form as original**

$$\frac{d\vec{M}_{xy}}{dt} = \gamma \vec{M} \times \vec{B}$$

- Ignoring relaxation, we see that the equation for $M_{xy}$ in the rotating frame becomes (note that we are using "\"d\" instead of "\"s\" for the derivative from now on, relying on context to know whether the rotating or lab frame is being used)

$$\frac{dM_{xy}}{dt} = -i \gamma \vec{B}_{\text{eff}} M_{xy} = -i \gamma (B_0 + \frac{\Omega \times}{\gamma}) M_{xy}$$

- We see that if we set $\Omega_x = -\gamma B_0$, $\frac{dM_{xy}}{dt} = 0$.

- In a frame rotating at the speed of $M_{xy}$'s precession, $M_{xy}$ appears "frozen".
For the purposes of an NMR experiment, we will want to apply an RF field, which, in the rotating frame, will remain constant in the transverse plane. In order to analyze the behavior of magnetization in the rotating frame when a constant field is present in its transverse plane, we will have to revisit the assumption we made earlier about the \( B \) field being along +z.

d) Applying an RF field, as viewed in the rotating frame

- Let's set \( \Omega r = -yB_0 \), so that \( B_{\text{eff}} = B_0 - \frac{yB_0}{\gamma} = 0 \).

- We apply a field \( B_1 \), which remains constant in the rotating reference frame (a frame rotating at \( \Omega r \)). Note that, from the perspective of the lab frame, the \( B_1 \) field will rotate at radiofrequency.

- For simplicity, we ignore \( T_1 \) and \( T_2 \) relaxation.

- Recall that the Bloch eqns. have the same form in the rotating and laboratory frames; the only difference is that, in the rotating frame, \( B_0 \) is replaced with \( B_0 + \Omega r / \gamma \). Therefore, we go back to the Bloch eqns. in the lab frame, which should still be valid here, in the rotating frame (see part b):

\[
\frac{dM_x}{dt} = \gamma (M_y B_z - M_z B_y) \\
\frac{dM_y}{dt} = \gamma (M_z B_x - M_x B_z) \\
\frac{dM_z}{dt} = \gamma (M_x B_y - M_y B_x)
\]
- Note that, in the rot. frame, $B_x = B_1$, and $B_y = B_z = 0$. Substituting into the Bloch eqns. we get
\[
\frac{dM_x}{dt} = 0 \implies M_x = \text{const.} = M_x(t=0)
\]
\[
\frac{dM_y}{dt} = \gamma M_z B_1 \quad (1)
\]
\[
\frac{dM_z}{dt} = -\gamma M_y B_1 \quad (2)
\]
- Let's not shy away from solving this set of two coupled differential equations by using a complex-valued variable $M_{yz}$! *if you are confused by the ensuing maths, see the appendix which follows, "Solving second-order linear differential equations".

- We solve equation (2) for $M_y$:
\[
\implies M_y = -\left(\frac{1}{\gamma B_1}\right) \frac{dM_z}{dt} \quad (3)
\]
- We substitute for $M_y$ in equation (1) using equation (3):
\[
\implies -\frac{d}{dt} \left[ \left(\frac{1}{\gamma B_1}\right) \frac{dM_z}{dt} \right] = \gamma M_z B_1
\]
\[
\implies \frac{d^2 M_z}{dt^2} = -\gamma^2 B_1^2 M_z
\]
\[
\implies \frac{d^2 M_z}{dt^2} + \gamma^2 B_1^2 M_z = 0 \quad (4)
\]
- We write the characteristic equation (auxiliary equation) for the above second-order linear differential equation, a.k.a. equation (4):
\[
\lambda^2 + \gamma^2 B_1^2 = 0
\]
The roots of the characteristic equation are:
\[ \lambda = \pm i \gamma B, \quad \text{(complex roots!)} \]

In general, when the roots of the characteristic equation are complex numbers \( \lambda_1 \) and \( \lambda_2 \), which we can write as

\[ \lambda_1 = \alpha + i \beta \]
\[ \lambda_2 = \alpha - i \beta \]

we can write the solution to the differential equation as

\[ M_2 = \exp(\alpha t) \left[ C_1 \cos(\beta t) + C_2 \sin(\beta t) \right] \]

Here, \( \alpha = 0 \) and \( \beta = \gamma B \), so the solution to the differential equation is:

\[ M_2(t) = C_1 \cos(\gamma B_1 t) + C_2 \sin(\gamma B_1 t) \]

At \( t = 0 \), \( M_2 = M_2(t=0) \), which implies:

\[ M_2(0) = M_2(0) \cos(\gamma B_1 t) + C_2 \sin(\gamma B_1 t) \] (5)

Solving for \( M_y(t) \) in the same way we solved for \( M_2(t) \), we get:

\[ M_y(t) = M_y(0) \cos(\gamma B_1 t) + C_4 \sin(\gamma B_1 t) \] (6)

Recall that in the lab frame, magnetization rotated about the \( z \)-axis, where the \( B_0 \) field pointed. Our term for this rotation was "precession". Here, our physical intuition would suggest that magnetization should rotate about the \( x \)-axis of the rotating frame, where \( B_1 \) is pointed. This is called "nutation".
Assuming that magnetization nutates about the x-axis in the same manner as it precessed about the z-axis in our earlier analysis (part b), the position of \( \hat{M} \)'s projection into the yz-plane at a time \( t = 0 \) will be related to its position at a time \( t = \frac{\pi}{2 \gamma B_1} \) as:

\[
\begin{align*}
\phi + \frac{\pi}{2} & \quad \text{(initial)} \\
\phi + \frac{\pi}{2} + \frac{\gamma B_1 t}{\gamma B_1} & \quad \text{(final)}
\end{align*}
\]

Note: Left-handed sense of nutation, same as sense of precession in part b! For \( Y > 0 \), the sense of nutation/precession is left-handed (see section 2.6.2 of Schmidt-Rehr \& Spiess, "Multidimensional Solid-State NMR and Polymers," Academic Press, San Diego, 1994)

- This allows us to solve for the \( C_2 \) and \( C_4 \) unknowns:

\[
\begin{align*}
M_z(t) &= M_z(0) \cos(\gamma B_1 t) - M_y(0) \sin(\gamma B_1 t) \\
M_y(t) &= M_y(0) \cos(\gamma B_1 t) + M_z(0) \sin(\gamma B_1 t)
\end{align*}
\]

- The frequency of nutation, \( \gamma B_1 \), is called the "Rabi frequency" and is sometimes written \( \Omega_r \) (in Hz) or \( \omega_r \) (in rad/s).

- When \( \Omega_r = -\gamma B_0 \), as it does in the above analysis, the RF field is said to be "on resonance." This is the "resonance" part of "nuclear magnetic resonance." If we apply an RF field for a time of \( t_p = (\frac{\pi}{2})(\frac{1}{2 \pi \Omega_r}) \), we can tip bulk magnetization by an angle of \( \frac{\pi}{2} \) radians in the yz-plane. This pulsed RF field (or, simply, "RF pulse") is used to tilt equilibrium...
magnetization (at equilibrium in a $B_0$ field, magnetization can be defined to be $\mathbf{M} = N_0 \mathbf{\hat{z}}$) into the transverse plane (xy-plane).

- Often, a coil that looks like a solenoid (other coil geometries are possible — will be covered later) is used to create this $B_1$ field.

- It is hard to create a rotating field with a solenoid. Instead, a linearly oscillating field is often created. This linearly oscillating field can be decomposed into two counter-rotating fields. A linearly oscillating RF pulse ($\mathbf{B}_r$) is decomposed as shown below:

\[
\begin{align*}
\mathbf{B}_r & \quad t=0 \\
\mathbf{B}_r^+ + \frac{1}{3} \mathbf{B}_r^- & \quad t=\Delta t \\
\mathbf{B}_r^- & \quad t=2\Delta t \\
\mathbf{B}_r^+ + \frac{1}{3} \mathbf{B}_r^- & \quad t=3\Delta t \\
\mathbf{B}_r^- & \quad t=4\Delta t \\
\mathbf{B}_r^+ & \quad t=5\Delta t
\end{align*}
\]
- Mathematically, this can be expressed as
  \[ \overrightarrow{B}_r = 2B \cos(2\pi \Omega_r t) \hat{x} + B \cos(2\pi \Omega_r t) \hat{x} + B \sin(2\pi \Omega_r t) \hat{y} = \overrightarrow{B}_1^+ + \overrightarrow{B}_1^- \]

where \( \Omega_r \) is the reference frequency (the frequency at which the RF pulse is applied).

- One of the fields, \( \overrightarrow{B}_1^+ \) or \( \overrightarrow{B}_1^- \), will be on resonance with the precession of the spins, the other will be far off resonance.

- In most cases, we can ignore the \( B_1 \) field that is off resonance, however it can have an effect, especially when the magnitude of the RF field is very large. This effect is called the "Bloch-Siegert effect."

- One important thing to note is that although, technically, the senses of precession and nutation are left-handed for \( Y > 0 \) and right-handed for \( Y < 0 \), it is often more convenient if the rotations produced are right-handed. Therefore, from now on, we are assuming the senses of precession and nutation are right-handed for \( Y > 0 \).

  It turns out this gives equivalent results. Except in unusual circumstances, you will not have to worry about the sense of precession/nutation.

- At the conclusion of an RF pulse (generated as described above), magnetization present in the transverse plane will precess around the \( B_0 \)-field of the spectrometer. This magnetization, freely precessing, will induce a current in the solenoid coil. Over time, relaxation processes (treated
phenomenologically here) will cause the magnetization to decay. The trace of the current induced in the coil is recorded by a spectroscopist, and it is called a **Free Induction Decay** (FID).

c) When an RF pulse is applied slightly off-resonance - In practice, spins are located in slightly different environments. Electrons traveling around in molecular orbitals near the spin will "shield" the spin from the spectrometer $B_0$-field to various degrees. Say you have a tripeptide LAF dissolved in some solvent and you are getting an NMR spectrum of the $^{15}$N spins. The situation might look like:

![Diagram of a tripeptide molecule with labeled N atoms and spin environments](image)
Generally, you will have only one RF coil to tilt the spins in environments A and B (hereafter referred to as spins A and B) into the transverse plane.

This means you cannot make a $B_1$-field that is exactly on-resonance for both spins A and B!

The magnetic field at spin A is "shifted" relative to that of a bare $^{15}$N nucleus without electrons to "shield" it from the external $B_0$-field of the spectrometer. This shifting of the field the $^{15}$N nucleus experiences is quantified by defining a "chemical shift" parameter. We will get more into that later. However, for now, let's refer to the field experienced by spin A as $B_{0A}$ and the field experienced by spin B as $B_{0B}$. If we plot the field strength at various sites, it might look like (ONLY ILLUSTRATIVE, NOT NECESSARILY ACCURATE)

![Diagram showing the fields $B_{0A}$ and $B_{0B}$]

We can now plot the frequency of the various $^{15}$N spins. The frequency of the rotating frame (the $B_1$ field is constant in this frame) is also shown.
- Note: We have redefined $B_{\text{eff}}$ to be $\Delta B$! We will use $B_{\text{eff}}$ for something else here!

- We have $\Delta B^B = B^B_0 + \Omega r/\gamma$ and $\Delta B^A = B^A_0 + \Omega r/\gamma$

- In the $xz$-plane, there is an "effective field" (we use $B_{\text{eff}}$ for this here) which is the sum of the $B_i$ field and $\Delta B$ (either $\Delta B^A$ or $\Delta B^B$, depending on which spin's behavior you're analyzing), in the frame rotating at $\Omega r$

- You can solve for the Bloch eqns. in this case. Magnetization rotates in a cone about $B_{\text{eff}} = \sqrt{B_i^2 + (\Delta B)^2}$

- It might look like
This could be compared with the on-resonance case:

- If one applies an RF pulse for a time $t_p = \left(\frac{\pi}{2}\right) \left(\frac{1}{2\pi\Omega_0}\right)$, equilibrium on-resonance, magnetization will end up along $-y$ (using right-handed convention). On the other hand, if the RF pulse is applied slightly off-resonance, it will make an angle $\phi$ with the $-y$ axis. $\phi$ will vary ALMOST linearly with $\Delta B$, as shown below.
APPENDIX: Solving second-order linear differential equations

- A second-order linear differential equation has the form:

\[ P(x) \frac{d^2 y}{dx^2} + Q(x) \frac{dy}{dx} + R(x)y = G(x) \]

- Linear refers to the manner in which the solution set of the differential equation can be expressed. It tells us that if \( y_1 \) and \( y_2 \) are both solutions to the diff. eqn., then a linear combination \( y = c_1 y_1 + c_2 y_2 \) is also a solution to the diff. eqn.

- Second-order means that there is a second order derivative (which is the highest order derivative). In this case, \( \frac{d^2 y}{dx^2} \) is the highest order derivative in the above expression. (there's also a first order derivative \( \frac{dy}{dx} \) and a zeroth order derivative \( y \)).

- It is easier to solve homogeneous differential equations. The above equation becomes homogeneous when \( G(x) = 0 \). Then it has the form

\[ P(x) \frac{d^2 y}{dx^2} + Q(x) \frac{dy}{dx} + R(x)y = 0 \quad (1) \]

- We can show that, given a diff. eqn., has to form shown above, if \( y_1 \) and \( y_2 \) are solutions of the diff. eqn., any linear combination \( c_1 y_1 + c_2 y_2 \) will also be a solution of the diff. eqn.
- The proof is pretty easy, so I'll leave it to you if you want to practice a bit of math.
- Another fact we require to make sure we have ALL the solutions to the differential eqn. (the complete set of solutions) is:

  The general solution (i.e. complete set of solutions) is a linear combination of two \textit{linearly independent} solutions \(y_1\) and \(y_2\).

- Linearly independent means one solution (i.e. \(y_1\)) is not just another solution \(\times\) (i.e. \(y_2\)) times some constant factor. That is \(f(x) = x^2\) and \(f(x) = 3x^2\) are not linearly independent solutions because \(3x^2 = 3(x^2)\).

- We can now make an educated guess as to what the solution of eqn. (1) might be. If we find two linearly independent solutions, we have found the general solution!

- It is not always easy to find the general solution to equation (1). However, if \(P(x)\), \(Q(x)\), and \(R(x)\) are not functions of \(x\) and, instead are just constants, then it is relatively easy to solve. Now the differential eqn. becomes

  \[ ay'' + by' + cy = 0 \quad (2) \]

  where \(a\), \(b\), and \(c\) are constants and \(a \neq 0\).
We propose the solutions to eqn. (2) have the form

\[ y = e^{\lambda x} \quad (3) \]

Substituting into eqn. (2) using equation (3), we get

\[ a\lambda^2 e^{\lambda x} + b\lambda e^{\lambda x} + c e^{\lambda x} = 0 \]

\[ \Rightarrow (a\lambda^2 + b\lambda + c) e^{\lambda x} = 0 \]

Either the part boxed in red is zero or \( e^{\lambda x} \) is zero. But \( e^{\lambda x} \) is never zero. Thus, \( y = e^{\lambda x} \) is a solution to eqn. (2) if

\[ a\lambda^2 + b\lambda + c = 0 \quad (4) \]

This equation is called the characteristic or auxiliary equation.

We solve for the roots of the characteristic equation using the quadratic formula

\[ \lambda = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

... there are three different cases:
CASE 1: $b^2 - 4ac > 0$

In this case, the roots of the characteristic eqn. $\lambda_1$ and $\lambda_2$ are real and distinct, leading to two linearly independent solutions $y_1 = e^{\lambda_1 x}$ and $y_2 = e^{\lambda_2 x}$. The general solution is

$$y = c_1 e^{\lambda_1 x} + c_2 e^{\lambda_2 x} \quad (5)$$

CASE 2: $b^2 - 4ac = 0$

In this case, the roots of the characteristic eqn. are real and equal (degenerate). $\lambda = -\frac{b}{2a}$ will give one solution. The other solution is given as $y_2 = xe^{\lambda x}$. You can verify this for yourself by substituting into eqn. (4). The general solution is

$$y = c_1 e^{\lambda x} + c_2 x e^{\lambda x} \quad (6)$$

CASE 3: $b^2 - 4ac < 0$

In this case, the roots to the characteristic eqn. are complex numbers which we can write as:

$$\lambda_1 = \alpha + i\beta \quad \text{and} \quad \lambda_2 = \alpha - i\beta$$

Recall Euler's equation:

$$e^{i\theta} = \cos \theta + i \sin \theta$$

We can write the general solution as
$y = C_1 e^{\lambda_1 x} + C_2 e^{\lambda_2 x}$

$= C_1 e^{(\alpha + i\beta)x} + C_2 e^{(\alpha - i\beta)x}$

$= C_1 e^{\alpha x} e^{i\beta x} + C_2 e^{\alpha x} e^{-i\beta x}$

$= C_1 e^{\alpha x} (\cos \beta x + i \sin \beta x) + C_2 e^{\alpha x} (\cos \beta x - i \sin \beta x)$

$= e^{\alpha x} \left[ (C_1 + C_2) \cos \beta x + i (C_1 - C_2) \sin \beta x \right]$  

\[\text{define as } C_1' \quad \text{define as } C_2'\]

$= e^{\alpha x} \left( C_1' \cos \beta x + C_2' \sin \beta x \right)$