A. NMR: The Rotating Frame

- The NMR experiment is performed by applying a time dependent field to the nuclear spin system. If the field is linearly polarized and applied along the x axis it has the form $\tilde{B}_1(t) = \tilde{x}B_1 \cos \omega t$.

- As shown in the book in Figure 20.5, a linearly polarized field can be represented by two circularly polarized fields

$$\tilde{x}B_1 \cos \omega t = \frac{B_1}{2} \left( e^{i\omega t} + e^{-i\omega t} \right)$$

$$= \frac{B_1}{2} \left( \tilde{x} \cos \omega t + \tilde{y} \sin \omega t + \tilde{x} \cos \omega t - \tilde{y} \sin \omega t \right)$$

- If we assume the magnetization precesses counter-clockwise around the magnetic field, only the counter-clockwise rotating field $\tilde{B}_1^{cc}(t) = B_1^{cc} (\tilde{x} \cos \omega t + \tilde{y} \sin \omega t)$ can be resonant with the spin system.

- So after neglecting the clockwise rotating component, the torque equation is:

$$\frac{d\tilde{\mu}}{dt} = \gamma \tilde{\mu} \times (\tilde{B}_0 + \tilde{B}_1^{cc}(t))$$

- In a frame rotating with the static field torque at the Larmor frequency, the equation of motion simplifies to

$$\frac{d\tilde{\mu}_R}{dt} = \gamma \tilde{\mu}_R \times \left( \tilde{x}B_1 + \tilde{z} \left( B_0 - \frac{\omega}{\gamma} \right) \right) = \tilde{\mu}_R \times \left( \tilde{x} \gamma B_1 + \tilde{z} \left( \gamma \tilde{B}_0 - \omega \right) \right)$$

$$= \tilde{\mu}_R \times \left( \tilde{x} \gamma B_1 + \tilde{z} \left( \omega_0 - \omega \right) \right) = \tilde{\mu}_R \times \tilde{B}_{eff}$$

- In the rotating frame the magnetic dipole moment vectors experience a torque from a time-independent effective field

$$\tilde{B}_{eff} = \tilde{x} \gamma B_1 + \tilde{z} \left( \omega_0 - \omega \right)$$

- The form of the effective field is shown below. The effective field is composed of three parts: a time independent field in the x direction $\tilde{x} \gamma B_1$ and a field in the z direction composed of the static magnetic field $\tilde{B}_0$ opposed by a “fictitious field $\frac{\omega}{\gamma} \tilde{z}$”. This fictitious field arises from the counter-rotating field.

- At resonance $\omega_0 = \omega$ and the equation now has the very simple form:

$$\frac{d\tilde{\mu}_R}{dt} = \tilde{\mu}_R \times \tilde{x} \gamma B_1$$
where we have dropped the cc superscript on the counter-rotating field. From now on this will be called the radio frequency or r.f. field.

- This means at resonance, the effective field is perpendicular to the z axis and parallel to the x axis. We can understand the effect of this field if we consider the motion of the magnetization vector, whose rotating frame torque equation is:

\[
\frac{d\vec{M}(t)}{dt} = \vec{M}(t) \times \gamma \vec{B}_1
\]

where we understand that the magnetization vector is referenced to the rotating frame. If at \(t=0\) the magnetization is along the z axis: \(\vec{M}(0) = (0,0,M_0)\), the solution to the equation is

\[
\vec{M}(t) = (0,M_0 \sin \gamma B_1 t, M_0 \cos \gamma B_1 t)
\]

- Note the sign correction from equation 20.14 in the book. This equation means that at a time \(\gamma B_1 t_{90} = \omega_1 t_{90} = \frac{\pi}{2}\), the magnetization is

\[
\vec{M}(t_{90}) = (0,M_0,0)
\]

that is the magnetization has been rotated by the r.f. field from along the z axis to along the y axis…a rotation of ninety degree. Such an irradiation is called a ninety degree pulse.

- The torque equation also means that at a time \(\gamma B_1 t_{180} = \omega_1 t_{80} = \pi\) the magnetization is

\[
\vec{M}(t_{180}) = (0,0,-M_0)
\]

- This type of pulse is called a 180 degree pulse because its effect is to point the magnetization anti-parallel to the field. Note in the configuration the spin populations are inverted and \(N_{-1/2} > N_{1/2}\). Recall an inversion of populations in a two level system cannot be achieved thermally, because it would require a negative temperature.
B. Relaxation

- Suppose the magnetization is rotated by the r.f. field so that it is parallel to the y axis, as shown in frame a, above. Once the magnetization is entirely in the x-y or transverse plane, the r.f. field is turned off and the magnetization precesses about the magnetic field, i.e. the z axis. As we learned in organic chemistry, not all spins have exactly the same Larmor frequencies. Due to the chemical shift effect, spins precess at different rates in the transverse plane. In the x-y plane, as viewed from the laboratory frame (not the rotating frame) the rotating magnetization of a particular type of spin is

$$\tilde{M}_i(t) = \tilde{M}_x(t) + i\tilde{M}_y(t) = \tilde{M}_x \cos(\gamma B_0 (1 - \sigma_i)) + i\tilde{M}_y \sin(\gamma B_0 (1 - \sigma_i))$$

where $\sigma_i$ is the chemical shift of spin i.

- Transverse magnetization does not simply rotate in the x-y plane. Its behavior is more complicated. Suppose we view the magnetization in a frame that rotates at the Larmor frequency. We would expect that the x and y components of the magnetization would appear stationary. But this is not the case. In fact the magnitude of the x and y components of the magnetization decay according to the equations
The solutions to these decay equations are:

\[ M_x(t) = M_x e^{-t/T_2} \quad M_y(t) = M_y e^{-t/T_2} \]

The decay of transverse magnetization is called transverse relaxation. Transverse relaxation is a radiationless process where the magnetization vectors of individual spins get out of phase due to tiny fluctuating magnetic fields generated by molecular motions. As the precessing spins get out of phase, they cannot get back into phase as the processes that generate the fluctuations are not reversible. Therefore the magnetization decays to \(1/e\) of its original value at a time \(T_2\) and will eventually relax to zero. All transverse magnetization will be gone after a time \(t \gg T_2\), but the system may not be back to equilibrium.

The spin system will not return to equilibrium until the longitudinal magnetization \(M_z\) returns to its equilibrium value of \(M_0\). This may occur at a time \(T_2\), but never sooner. Transverse magnetization must disappear entirely before equilibrium can be reached. As the transverse magnetization decays as described above, the longitudinal magnetization also decays according to

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

which has the solution \(M_z(t) = M_0 \left(1 - e^{-t/T_1}\right)\)

This equation means that at \(t=0\) the longitudinal magnetization is zero because all magnetization is in the transverse plane. But as time elapses, the transverse magnetization decays and the longitudinal magnetizations grows, as shown in the figure above. Once transverse magnetization disappears entirely, the longitudinal magnetization may not be back to its original value...meaning the energy level populations \(N_{1/2}\) and \(N_{-1/2}\) may not yet be restored to their equilibrium values. This can only occur by “flipping spins from -1/2 to +1/2. If motions of the environment, i.e. the molecular structure or the “lattice” occur near the Larmor frequency, tiny magnetic fields will be generated that accomplish these spin flips. The spin-lattice relaxation time \(T_1\) characterizes the time that it takes to accomplish this.

Taking the results for the transverse relaxation and returning to eh lab frame, the transverse magnetization has the form:

\[ \tilde{M}_i(t) = \left(\tilde{M}_x \cos(\gamma B_0 (1 - \sigma_i)) + i\tilde{M}_y \sin(\gamma B_0 (1 - \sigma_i))\right)e^{-t/T_2} \]

The sum over all spins is called the free induction decay \(f(t)\):

\[ f(t) = \sum_i \tilde{M}_i(t) = \sum_i \left(\tilde{M}_x \cos(\gamma B_0 (1 - \sigma_i)) + i\tilde{M}_y \sin(\gamma B_0 (1 - \sigma_i))\right)e^{-t/T_2} \]