These notes are intended to be aids in covering the material in chapter 20. Typos are indicated.

A. Nuclear Magnetic Resonance (NMR): Equilibrium Aspects

- NMR refers to the resonant absorption of radio frequency power by nuclei with magnetic dipole moments that arise from spin angular momentum.
- Spin angular momentum should NOT be confused with the angular momentum associated with the orbital motion of electrons, which is also quantized. See Lecture 8.
- Nuclear spin angular momentum is associated with internal motions of the nucleus. We make the classical analog, the an atomic nucleus with “spin” is a sphere of positive charge rotating around its polar axis like a planet rotating around its polar axis. This is not an accurate nor rigorous rendition of spin, but this classical view nevertheless gives us useful results. See below and see sections 20.1 and 20.2.
- An angular momentum can be classically viewed as arising from a rotational motion wherein a mass m, displaced from the orbital axis by a vector \( \vec{r} \) rotates in a circular orbit with a velocity \( \vec{v} \). This rotational motion generates an angular momentum \( \vec{I} \) according to:
  \[
  \vec{I} = \vec{r} \times \vec{p} = \vec{r} \times m\vec{v}
  \]
  where \( \vec{p} \) is the linear momentum.
- Suppose the direction of the angular momentum \( \vec{I} \) changes in time. Then the time rate of change is
  \[
  \frac{d\vec{I}}{dt} = \frac{d}{dt}(\vec{r} \times \vec{p}) = \frac{d\vec{r}}{dt} \times \vec{p} + \vec{r} \times \frac{d\vec{p}}{dt} = \vec{r} \times \frac{d\vec{p}}{dt} = \vec{r} \times \vec{F}
  \]
  The quantity \( \vec{r} \times \vec{F} = \vec{\Gamma} \) is called a torque, and it means that if an force is exerted on a rotating body the angular momentum experiences a torque that changes the direction of the angular momentum: \( \frac{d\vec{I}}{dt} = \vec{\Gamma} \).
- The spin angular momentum of the nucleus is associated with a particle property called the magnetic dipolar moment: \( \vec{\mu} = \gamma \vec{I} \). Note the difference with the text which inserts an h-bar into the definition of the magnetic moment. This is convention. It changes the units of the magnetic moment and you have to remember to add h-bar when you calculate the energy.
One imagines that the rotational motion of the charged nucleus induces this magnetic moment. Like the electric dipole moment, which is a vector pointing from the positive to the negative charge centers of a molecule, the magnetic dipole moment is a vector that points from the south pole to the north pole of the tiny bar magnet that nuclear spin rotation induces.

If such a nuclear magnetic dipole moment is exposed to a magnetic field \( \vec{B}_0 \) which is set to point along the z axis, the energy of interaction is

\[
E = -\hbar \vec{\mu} \cdot \vec{B}_0 = -\hbar \gamma \vec{I} \cdot \vec{B}_0
\]

Note energy is an inner product, a scalar Therefore the result of the calculation is that the inner product yields the product of the component of the spin angular momentum parallel to the magnetic field:

\[
E = -\hbar \gamma \vec{I} \cdot \vec{B}_0 = -\hbar \gamma I_z B_0
\]

The z component of the spin angular momentum is quantized. This means that the energy has certain discrete values according to \( E = \hbar \gamma I_z B_0 = \hbar \gamma m_z B_0 \). For a nucleus with spin S, \( m_z \) varies integrally from \(-S\) to \(+S\). For nuclei like \(^1\text{H}\), \(^3\text{H}\), \(^13\text{C}\), \(^15\text{N}\), and \(^31\text{P}\), the spin angular momentum \( S=1/2 \). For “spin ½ nuclei” and so \( m_z=-1/2 \) or \(-1/2\) and there are two energy levels corresponding to two orientation of the magnetic dipole moment relative to the external magnetic field.

Not the energy level splitting is

\[
\Delta E = E_{-1/2} - E_{+1/2} = \hbar \gamma B_0 = \hbar \omega_0 \quad \text{where } \omega_0 \text{ is}
\]

called the Larmor frequency.

There is a second effect from the magnetic field, which exerts a torque on each magnetic dipole moment according to

\[
\vec{\Gamma} = \gamma \vec{\mu} \times \vec{B}_0
\]

\[
\frac{\gamma d\vec{I}}{dt} = \frac{d\vec{\mu}}{dt} = \gamma (\vec{\mu} \times \vec{B}_0) = \vec{\mu} \times \vec{\omega}_0
\]

This equation means the magnetic moments precesses around the magnetic field at the Larmor frequency.
This very dynamic view of individual nuclear spin precession can be simplified if we view the vector sum of the individual moments...called the magnetization $\hat{M}$. The magnetization is a vector and is related to the nuclear moment vectors by

$$\hat{M} = \sum_i \vec{\mu}_i$$

Because only the z component of the individual magnetic dipole moments (i.e. the spin angular momentum) are quantized, the x and y components of the magnetic moments are not quantized and in fact are randomly distributed. Therefore, only the z components add and the summation simplifies to

$$\hat{M}_z = \sum_i \hat{\mu}_z = \gamma \sum_i \hat{I}_z,$$

In the equation above, the z component of the angular momentum is quantized and hence the vector points in the z direction and has a magnitude of $\frac{1}{2}$, or points down with a magnitude of $\frac{1}{2}$. So the summation can be written as

$$\hat{M}_0 = \gamma \sum_i \hat{I}_z = \frac{\gamma}{2} (N_{1/2} - N_{-1/2}) \hat{z}$$

$\hat{M}_0$ is called the equilibrium or longitudinal magnetization, because it points in the z direction. It is also called the Curie magnetization. The quantity $N_{1/2} - N_{-1/2}$ is the difference between the number of nuclear spins that are “spin-up” and the number that are “spin-down”. Note the ratio is given by

$$\frac{N_{-1/2}}{N_{1/2}} = e^{-\Delta E/k_B T} = e^{-\hbar \gamma B_0/k_B T}$$

For magnetic fields currently available and at ambient temperatures $k_B T \gg \hbar \gamma B_0$ and so while $N_{1/2} > N_{-1/2}$, the difference $N_{1/2} - N_{-1/2}$ is not large.