In NMR, the observable which is measured is magnetization and its evolution over time. In order to understand what this means, let us first begin with some simple concepts about magnetism.

1) **Angular momentum and magnetic moment**

An electron moving around a fixed point has an angular momentum associated with it which is given by

\[ \vec{L} = m_e \vec{r} \times \vec{v} = m_e r v \hat{n}. \]  

(1.1)
where \( \vec{n} \) is a normalized unit length vector. This equation is generally valid for any particle rotating about a fixed point.

Given that the area of the circle which the electron describes is given by \( A = \pi r^2 \) and the velocity with which it goes around the circle is given by \( v = 2\pi r / T \), one can rewrite the angular momentum as

\[
\vec{L} = \frac{m_e 2A \vec{n}}{T}.
\]  

(1.2)

Now consider that this electron is moving around in a wire. As a result of this motion, a current will be induced in the wire which in turn gives rise to a magnetic moment. The magnetic moment is given by
\( \vec{\mu} = IA\vec{n} \)  

(1.3)

where \( I \), the current, can be written as 

\[
I = \frac{-e}{T}.
\]

Therefore the magnetic moment is given by 

\[
\vec{\mu} = \frac{-eA\vec{n}}{T}
\]

(1.4)

or using equation 1.1,

\[
\vec{\mu} = \frac{-e\vec{L}}{2m_e} = \gamma_L \vec{L}
\]

(1.5)

where \( \gamma_L \) is the gyromagnetic ratio.

Thus, generally, the gyromagnetic ratio for all types of particles is given by

\[
\vec{\mu} = \gamma \vec{L}.
\]

(1.6)

For nuclei, the gyromagnetic ratio is a characteristic value that is specific to the nucleus in question. For example:
\[
\begin{align*}
\gamma_{1H} &= 42.5759 \times 10^6 \text{Hz.T}^{-1} \\
\gamma_{13C} &= 10.7054 \times 10^6 \text{Hz.T}^{-1} \quad (1.7) \\
\gamma_{15N} &= -4.3142 \times 10^6 \text{Hz.T}^{-1}.
\end{align*}
\]

ref: CRC Handbook.

The magnetic moment, also known as the magnetic dipole moment, when present in a magnetic field \( \vec{B}_0 \) will experience a torque \( \vec{T} \), given by

\[
\vec{T} = \vec{\mu} \times \vec{B}_0. \quad (1.8)
\]

Nuclear spins can be likened to spinning tops because both can precess about an axis, other than the axis of rotation. A spinning top precesses because:

- it has an angular momentum \( \vec{L} \) about its own rotation axis;
- there is a torque \( \vec{T} \) acting on it.
Similarly, a nuclear spin or magnetic dipole will also precess when it is placed in a magnetic field $\vec{B}_0$.

The angular frequency of precession of a magnetic dipole is given by

$$\omega_0 = -\frac{\mu B_0}{L} = -\gamma B_0$$

or in terms of frequency,

$$\nu_0 = \frac{\omega_0}{2\pi}.$$  \hfill (1.10)

The latter frequency (in eq. 1.10) is known as the Larmor frequency and is also characteristic of a given nucleus.
2) *Curie’s Law*

In an NMR experiment the magnetization is measured as the sum of the magnetic dipole moments per unit volume, i.e.

\[
\vec{M} = \frac{1}{V} \sum_{i=1}^{n} \vec{\mu}_i. \tag{1.11}
\]

From quantum mechanics and the results of experiments performed by Stern and Gerlach in 1922, it has been shown that in the presence of a magnetic field, the magnetic moment precesses about \( \vec{B}_0 \) at distinct angles, given by

\[
< \mu_z >= \gamma \hbar m_J \tag{1.12}
\]

where \( m_J \) can adopt the values

\[ m_J = -J, -J + 1, \ldots, J - 1, J. \]

These different precession states have distinct energies associated with them, namely:

\[
E_{m_J} = - < \mu_z > B_0 = -\gamma \hbar m_J B_0 \tag{1.13}
\]

In other words, for a spin 1/2 system (such as \(^1 H\),
\[ E_{m_j} = 0 \]

whereas for a spin 1 (such as \( ^{14}N, ^2H \)), the energy level diagram is:

\[ E_{m_j} = 0 \]

In a system that is in thermodynamic equilibrium, the population of these energy levels is given by a
Boltzmann distribution:

\[ P_m = \frac{N}{Z} e^{- \frac{E_{mJ}}{kT}} = \frac{N}{Z} e^{\frac{\gamma h m J B_0}{kT}} \quad (1.14) \]

where

\[ Z = \sum_{m,J=\pm J} e^{- \frac{E_{mJ}}{kT}} \quad (1.15) \]

is a normalization constant and \( N \) is the total number of molecules per unit volume. From this now the total magnetization can be determined from (see box 1)

\[ M_z = \frac{N \gamma \hbar}{Z} \sum_{m,J=\pm J} m_J e^{\frac{\gamma h m J B_0}{kT}}. \quad (1.16) \]

This formula can be simplified if one considers two extreme cases: 1) high temperatures, where \( \frac{\gamma h J B_0}{kT} \ll 1 \); and 2) at \( T \to 0 \).
Box 1. Derivation of eq. 16. Given that the total magnetization is given by

$$\vec{M} = \frac{1}{V} \sum_{i=1} \vec{\mu}_i,$$  \hspace{1cm} (1.17)

we can substitute $\vec{\mu}_i$ by a weighted sum of $< \mu_z >$, to give

$$\vec{M} = \sum < \mu_z > P_m = \frac{N \gamma \hbar}{Z} \sum_{m_J = -J}^{J} m_J e^{\frac{\gamma h m_J B_0}{kT}}.$$  \hspace{1cm} (1.18)

This can be rewritten as

$$\vec{M} = N \gamma \hbar \left[ \frac{2J + 1}{2} ctgh((2J + 1) \gamma \hbar B_0 / 2kT) \right. \\
- \left. \frac{1}{2} ctgh(\gamma \hbar B_0 / 2kT) \right].$$  

where

$$ctgh(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}}.$$  \hspace{1cm} (1.19)

At high temperatures, the thermal energy of the system is greater than the magnetic energy $E_{m,J}$. In
this case, 1.16 simplifies to:

\[ M_z = \frac{N(\gamma \hbar)^2 J(J + 1)B_0}{3kT}. \]  (1.20)

This latter equation is known as Curie’s law. At very low temperatures, only the lowest energy level is populated, i.e. \( m_J = J \) and

\[ M_z = N\gamma \hbar J. \]  (1.21)

The magnetization given by 1.20 and 1.21 is the equilibrium magnetization inherent to a system, when placed in a magnetic field \( \vec{B}_0 \). It is often designated as \( M_0 \) (and will be henceforth).
3) *Equations of motion: Bloch Equations*

In NMR we need to perturb the system - to move the magnetization away from equilibrium. We therefore need to describe how magnetization changes as a function of time.

From Newton’s laws, one can write the change in the angular momentum over time as:

\[
\frac{d\vec{L}}{dt} = \vec{T}.
\]  
(1.22)

Given the definitions in equations 1.6 and 1.8, equation 1.22 can thus be rewritten as

\[
\frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \times \vec{B}_0.
\]  
(1.23)

Summing over the unit volume gives the measured magnetization change over time:

\[
\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}_0
\]  
(1.24)

or writing the equations out explicitly:
\[ \frac{dM_x}{dt} = \gamma(M_yB_z - M_zB_y) \]
\[ \frac{dM_y}{dt} = \gamma(M_zB_x - M_xB_z) \]  
\[ \frac{dM_z}{dt} = \gamma(M_xB_y - M_yB_x). \]  

(1.25)

Case 1) Equations of motion in a static magnetic field without relaxation

Consider the case where the static magnetic field is parallel to the z-axis, i.e. \( B_x = B_y = 0 \) and \( B_z = B_0 \). And let us assume that \( M_y(0) = 0 \), i.e. that we apply a 90 degree pulse such that all the magnetization is along the x-axis at time \( t = 0 \). In this case, the equations in 1.25 become:

\[ \frac{dM_x}{dt} = \gamma M_yB_0 \]  
\[ \frac{dM_y}{dt} = -\gamma M_xB_0 \]  
\[ \frac{dM_z}{dt} = 0. \]  

(1.26)  
(1.27)  
(1.28)

Differentiating equation 1.27 and substituting equation 1.28 into this equation, one gets:
\[
\frac{d^2 M_x}{dt^2} = - (\gamma B_0)^2 M_x, \tag{1.29}
\]

which one can then solve to give

\[
M_x(t) = M_x(0) \cos(\omega_0 t)
\]
\[
M_y(t) = M_x(0) \sin(\omega_0 t)
\tag{1.30}
\]
\[
M_z(t) = M_z(0)
\]

where \(\omega_0\) is the Larmor frequency as defined in equation 1.9. Given that \(\gamma\) can either be positive or negative, the direction of precession will therefore either be clockwise or counter-clockwise.

If one were to observe the magnetization along the x-axis, for example, one would observe an infinite oscillation between \(+M_x(0)\) and \(-M_x(0)\) over time, i.e.
As with a spinning top, however, this infinite oscillation of the magnetization is not possible. A spinning top eventually stops precessing because of frictional forces. Similarly, spins will eventually stop precessing, i.e. the magnetization will decay. The phenomenon leading to this decay is known as relaxation.
Case 2) Equations of motion in a static magnetic field with relaxation

Let us consider again the case where the static magnetic field is parallel to the z-axis, i.e. $B_x = B_y = 0$ and $B_z = B_0$. And let us assume that $M_y(0) = 0$.

Let us define the longitudinal magnetization component to be $M_z$ and the transverse components to be $M_x$ and $M_y$.

There are two types of relaxation mechanisms which can affect a spin: a) longitudinal relaxation (i.e. affecting the $M_z$ component) and b) transverse relaxation (i.e. affecting the $M_x$ and $M_y$ components) (see box 2 for a more detailed description of relaxation mechanisms).

Keep in mind: THIS IS A PHENOMENOLOGICAL DESCRIPTION

a) Longitudinal Relaxation

Longitudinal relaxation arises from the interaction between a spin and its surrounding ”lattice” (e.g. a gas molecule and the walls of a container). As a
result of this interaction, the energy generated by having the spin in a magnetic field will dissipate to the surroundings such that an equilibrium is reached. This means that the $M_z$ component decays as:

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1} \quad (1.31)$$

where $M_0$ is the equilibrium magnetization and $T_1$ is the longitudinal relaxation time. Solving this differential equation yields

$$M_z(t) = M_0 + (M_z(0) - M_0)e^{-\frac{t}{T_1}}. \quad (1.32)$$

b) Transverse Relaxation

Transverse relaxation arises from the interactions of spins between each other. As a result of this interaction, the energy which causes a spin to precess in the xy-plane will decay such that for long times the magnetization in the xy-plane will become zero. In other words,
\[ M_x(t) = M_x(0)\cos(\omega_0 t)e^{-\frac{t}{T_2}} \]
\[ M_y(t) = M_x(0)\sin(\omega_0 t)e^{-\frac{t}{T_2}} \]

(1.33)

where \( T_2 \) is the transverse relaxation time. Or pictorially,

\[ \text{cos}(x)\exp(-x/1000) \]

for the \( x \)-component, or overall:
Taking both mechanisms for the decay of magnetization into account, the corresponding equations to equations 1.25 are:
\[
\begin{align*}
\frac{dM_x}{dt} &= \gamma (M_y B_0) - \frac{M_x}{T_2} \\
\frac{dM_y}{dt} &= -\gamma (M_x B_0) - \frac{M_y}{T_2} \\
\frac{dM_z}{dt} &= -\frac{M_z - M_0}{T_1}.
\end{align*}
\] (1.34)

or in a general form

\[
\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}_0 - R[\vec{M} - \vec{M}_0]
\] (1.35)

where

\[
R = \begin{pmatrix}
\frac{1}{T_2} & 0 & 0 \\
0 & \frac{1}{T_2} & 0 \\
0 & 0 & \frac{1}{T_1}
\end{pmatrix}
\] (1.36)

These equations are known as the Bloch equations (ref. F. Bloch, Phys. Rev., 70, 460 (1946)). As we will see in later chapters, the relaxation matrix above only applies for two level systems.

Solving equations 1.34 for the case where \( B_x = B_y = 0, B_z = B_0 \) and \( M_y(0) = 0 \) yields the equations given in 1.33 and 1.32.
Box 2. Relaxation mechanisms. Relaxation mechanisms depend on whether the spin system being considered is spin 1/2 or > 1/2.

For spin 1/2 systems, magnetization will relax because of: 1- changes in the dipole-dipole interaction due to molecular tumbling or translation; 2- changes in the local field due to the chemical shift anisotropy (CSA); 3- spin rotation. These interactions affect relaxation in decreasing order, i.e. 1 > 2 > 3.

For spin > 1/2 systems, the mechanisms listed above also apply. In addition to these, however, there is also the quadrupolar interaction, which is the dominant mechanism. I.e. in this case, the relaxation mechanisms in order of decreasing importance are: quadrupolar >> 1 > 2 > 3.