CHEM6154 - Week 19 - Lecture 1: Bloch equations

P.J. Hore, "NMR: The Toolkit", 1st edition - Chapter 1.
J. Keeler, "Understanding NMR Spectroscopy" - Chapter 4.

1. Magnetisation precession

In the classical physics picture of magnetic resonance, a spin is a tiny permanent magnet. This is an approximation, but it works quite well. If we denote the magnetic moment $\vec{M} = \begin{pmatrix} M_X & M_Y & M_Z \end{pmatrix}^T$, its classical equation of motion is:

$$\frac{d\vec{M}(t)}{dt} = \gamma \vec{M}(t) \times \vec{B}(t) \tag{1}$$

where $\times$ denotes vector cross product, γ is the magnetogyric ratio (a fundamental constant for a given nucleus), and $\vec{B}(t)$ is the external magnetic field. In the case of the static magnetic field pointing upwards, we have $\vec{B}(t) = \begin{pmatrix} 0 & 0 & B_0 \end{pmatrix}^T$, and Equation (1) can be written in the component notation as

$$\frac{d}{dt}\begin{pmatrix} M_X(t) \\ M_Y(t) \\ M_Z(t) \end{pmatrix} = \gamma \begin{pmatrix} M_X(t) \\ M_Y(t) \\ M_Z(t) \end{pmatrix} \times \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} = \begin{pmatrix} +\gamma B_0 M_Y(t) \\ -\gamma B_0 M_X(t) \\ 0 \end{pmatrix} \tag{2}$$

Splitting this equation into a system of three differential equations for the components of the magnetization vector and denoting $\omega_0 = -\gamma B_0$, we obtain:

$$\begin{cases} \dfrac{d}{dt} M_X(t) = -\omega_0 M_Y(t) \\ \dfrac{d}{dt} M_Y(t) = +\omega_0 M_X(t) \\ \dfrac{d}{dt} M_Z(t) = 0 \end{cases} \tag{3}$$

These are called *Bloch equations*. We do not have sufficient time in this course to solve this system of equations properly, and will simply write the solutions down:

$$\begin{cases} M_X(t) = a\cos(\omega_0 t + \varphi) \\ M_Y(t) = a\sin(\omega_0 t + \varphi) \\ M_Z(t) = b \end{cases} \tag{4}$$

where a, b and φ are arbitrary constants. Equation (4) makes the tip of the magnetization vector travel along a circle drawn around the direction of the applied magnetic field.

2. Rotating frame transformation

Spin dynamics in the presence of *time-dependent* magnetic fields is more complicated. One way of simplifying the description is to change the perspective: we can rotate the observer together with the spin vector – this essentially amounts to gluing a web camera onto another vector that rotates according to Equations (3) and looking at the system through that web camera so that only the relative motion is observed. In the absence of external perturbations, the camera would not see any motion:

$$\begin{cases} \frac{d}{dt} M_{\mathrm{X}}^{(\mathrm{R})}(t) = 0 \\ \frac{d}{dt} M_{\mathrm{Y}}^{(\mathrm{R})}(t) = 0 \\ \frac{d}{dt} M_{\mathrm{Z}}^{(\mathrm{R})}(t) = 0 \end{cases} \tag{5}$$

In this picture, the primary field $\vec{B}_0$ in the Z direction is effectively absent. If we would like to create some dynamics, we must apply additional magnetic fields.

3. Radiofrequency pulses

A magnetic field that rotates with exactly the same frequency as the rotating frame:

$$\vec{B}_1(t) = B_1 \begin{pmatrix} \cos(\omega_0 t + \varphi) \\ \sin(\omega_0 t + \varphi) \\ 0 \end{pmatrix} \tag{6}$$

would appear static in that picture:

$$\vec{B}_1^{(\mathrm{R})}(t) = B_1 \begin{pmatrix} \cos(\varphi) \\ \sin(\varphi) \\ 0 \end{pmatrix} \tag{7}$$

Here φ is called the *phase*. It is an angle set by the spectrometer electronics that controls the direction of the $\vec{B}_1^{(\mathrm{R})}(t)$ field in the rotating frame. The in the rotating frame, the magnetisation would now rotate around that direction. For example, when $\varphi = 0$:

$$\vec{B}_1(t) = \begin{pmatrix} B_1 \\ 0 \\ 0 \end{pmatrix}; \qquad \frac{d}{dt}\begin{pmatrix} M_{\mathrm{X}}^{(\mathrm{R})}(t) \\ M_{\mathrm{Y}}^{(\mathrm{R})}(t) \\ M_{\mathrm{Z}}^{(\mathrm{R})}(t) \end{pmatrix} = \gamma \begin{pmatrix} M_{\mathrm{X}}^{(\mathrm{R})}(t) \\ M_{\mathrm{Y}}^{(\mathrm{R})}(t) \\ M_{\mathrm{Z}}^{(\mathrm{R})}(t) \end{pmatrix} \times \begin{pmatrix} B_1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ +\gamma B_1 M_{\mathrm{Z}}(t) \\ -\gamma B_1 M_{\mathrm{Y}}(t) \end{pmatrix} \tag{8}$$

the magnetisation will be rotating clockwise around the X axis in the YZ plane:

$$\begin{cases} M_{\mathrm{X}}^{(\mathrm{R})}(t) = 0 \\ M_{\mathrm{Y}}^{(\mathrm{R})}(t) = M_{\mathrm{Y}}^{(\mathrm{R})}(0)\sin(\omega_1 t), \\ M_{\mathrm{Z}}^{(\mathrm{R})}(t) = M_{\mathrm{Z}}^{(\mathrm{R})}(0)\cos(\omega_1 t) \end{cases} \qquad \omega_1 = -\gamma B_1 \tag{9}$$

Because the phase of the pulse is set by the user, it is in practice possible to move spins in an arbitrary way. Magnetisation always rotates clockwise around the direction of the radiofrequency field in the rotating frame – the famous corkscrew rule is a convenient mnemonic.

RF phase	**Name**	**Direction of magnetisation rotation**
$\varphi = 0$	+X pulse	clockwise when looking along the direction of X
$\varphi = \pi/2$	+Y pulse	clockwise when looking along the direction of Y
$\varphi = \pi$	–X pulse	counter-clockwise when looking along the direction of X
$\varphi = 3\pi/2$	–Y pulse	counter-clockwise when looking along the direction of Y

A period during which the $\vec{B}_1$ field is active is called a *pulse*. This is because these periods are short (microseconds) and require strong radiofrequency outputs (kilowatts) from the spectrometer electronics.

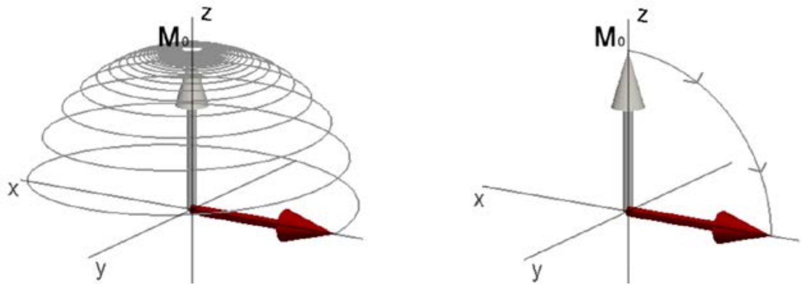

Figure 1. *Schematic illustration of the effect of a resonant (meaning that the frequency is the same as spin precession frequency) radiofrequency pulse on the direction of the magnetisation that was initially pointing along the Z axis.* ***Left:*** *laboratory frame picture.* ***Right:*** *rotating frame picture. The direction of the B_1 field is along the Y axis of the rotating frame, pointing away from the viewer.*

Manipulating magnetization using radiofrequency pulses is the essence of magnetic resonance spectroscopy. In the rotating frame, the nuclear magnetization precesses around the direction of the $\vec{B}_1$ field – an *X pulse* would rotate the magnetization around the X axis, and a *Y pulse* would rotate it around the Y axis. Due to the engineering limitations of NMR instruments, electronics performing direct Z pulses is not usually available, but Z rotations may be achieved indirectly by performing multiple X and Y rotations.

4. Pulse rotation angles

Magnetisation tilt angle α achieved by the pulse is determined by the amplitude of the $\vec{B}_1$ field and the duration of the pulse Δt in exactly the same way as any other precession:

$$\alpha = -\gamma B_1 \Delta t \qquad (10)$$

Typical amplitudes of $\vec{B}_1$ fields are in the milliTesla range. As an example, let us calculate the $\vec{B}_1$ field required to tilt proton magnetisation by exactly 90 degrees (π/2 radians) in 5.0 microseconds:

$$B_1 = \left|\frac{\pi/2}{\gamma_{\mathrm{H}}\Delta t}\right| = \left|\frac{\pi/2}{2.675\cdot 10^8 \cdot 5.0\cdot 10^{-6}}\right| = 1.2\cdot 10^{-3}\ \mathrm{T}$$