Physical basis of NMR spectroscopy

(for a brief introductory textbook on NMR, see P. J. Hore, Nuclear Magnetic Resonance, Oxford University Press, Oxford, 1995)

Where does the magnetization come from?

$^1$H nuclei possess a spin $\frac{1}{2}$ which is associated with an angular momentum and a magnetic dipole moment. Each $^1$H nucleus thus behaves like a little magnet that spins around its dipole axis. A single spin $\frac{1}{2}$ has the quantum mechanical property that, in an external magnetic field $B_0$ (measured in Tesla, abbreviated T), only two orientations (called “parallel” and “antiparallel” or “α” and “β”) with respect to $B_0$ have a defined energy. The energy difference between these two states, $\Delta E$, is given by

$$\Delta E = h\nu = -\frac{\hbar \gamma B_0}{2\pi}$$

$h$ is Planck’s constant, $\gamma$ is the magnetogyric ratio ($2.67 \times 10^8 \text{T}^{-1}\text{s}^{-1}$ for $^1$H). Because of the angular momentum associated with spins, spins don’t align with the magnetic field $B_0$, but precess around an axis parallel to $B_0$ with a frequency $\nu_0$ (the so-called Larmor frequency, $\omega_0 = 2\pi\nu_0 = -\gamma B_0$):

In an NMR experiment, many spins are present. As the energy difference between the states $\alpha$ and $\beta$ is small compared to $kT$ ($k$ Boltzmann constant, $T$ temperature), there is, at room temperature, only a small excess of spins in the energetically lower state, even for the highest available magnetic fields. In thermal equilibrium, the average magnetization from all molecules constitutes a macroscopic magnetization $M$ parallel to the magnetic field:

This macroscopic magnetization (called “longitudinal magnetization”) does not precess, because it is parallel to $B_0$. However, as soon as its direction deviates from that of $B_0$, it precesses around $B_0$ just like the individual spins do.

The NMR experiment in a nutshell:

Put the sample in a magnet, make the macroscopic equilibrium magnetization $M$ of the $^1$H nuclei transverse, e.g. by a 90° pulse, and let it precess in a coil, where the precession of the magnetization will generate an electric current, precisely in the same way as an electricity generator generates alternating current via a magnet rotating in a set of coils. All that’s left is to detect the AC voltage induced by the precessing magnetization.
What is a 90° pulse?

In a magnetic field of several Tesla, equilibrium magnetization can be excited by a radiofrequency pulse (rf pulse). The radiofrequency has to match the Larmor frequency: \( \Delta E = h\nu \). The radiofrequency is delivered by a coil wrapped around the sample, where the axis of the coil is perpendicular to the magnetic field \( B_0 \):

![Diagram of magnetic field and sample with coil]

Like all electromagnetic radiation, the rf field contains an electric and a magnetic component. Only the magnetic component interacts with the spins. When applied to the rf coil, this magnetic component is linearly polarized along the axis of the rf coil (i.e. it oscillates back and forth). This oscillation can also be represented as the sum of two circularly polarized vectors rotating in opposite directions:

![Diagram of circularly polarized vectors]

Only the component precessing around \( B_0 \) with the same speed and direction as the spins effectively interacts with the spins. This component presents the \( B_1 \) field:

![Diagram of B1 field]

In the presence of the \( B_1 \) field (i.e. during the rf pulse), the magnetization \( M \) precesses not only around \( B_0 \) (as far as it deviates in its direction from \( B_0 \)), but simultaneously around \( B_1 \). The resulting overall motion is one where the tip of \( M \) describes a spiral on the surface of a sphere:

![Diagram of spiral motion]

A 90° pulse is an rf pulse of exactly the duration it takes for \( M \) to become transverse (i.e. perpendicular to \( B_0 \)) on its way to the southern hemisphere.
A 180° pulse is twice as long and inverts the magnetization.
A 270° pulse is three times longer than a 90° pulse. It inverts the magnetization and keeps rotating it until it is transverse again.
And so on. (Which way do you think the magnetization points after a 360° pulse?)
The picture becomes much easier by thinking in terms of the “rotating frame”: if we picture ourselves travelling around the spins at their Larmor frequency, they appear stationary (in the “laboratory frame”, of course, they aren’t). In other words, in the rotating frame the precession around $B_0$ goes unnoticed (just like we cannot tell that the earth rotates because we travel at the same speed), so only the rotation around $B_1$ remains:

\[ s(t) = s(0) \exp(-t/T) \]

There are two different relaxation times:

- $T_1$ relaxation: the magnetization returns to equilibrium magnetization.
- $T_2$ relaxation: the magnetization remains transverse, but the spins from different molecules precess with slightly different frequencies, causing dephasing and, hence, decay of the macroscopic magnetization.

(Relaxation is due to interactions with magnetic noise in the environment. Loss of energy by the induced current is unimportant.)

$T_2$ relaxation is always faster than $T_1$ relaxation. The difference between both relaxation times is small for small, rapidly tumbling molecules (e.g. small chemical compounds) but $T_2$ becomes much shorter than $T_1$ for large molecules (MW > 5000).

The NMR spectrum is obtained by Fourier transformation of the FID:

Fourier transformation is a mathematical procedure to represent any signal as a sum of sine and cosine functions with different frequencies. The NMR spectrum is obtained by plotting the amplitude of the sine and cosine functions versus their frequencies. Mathematically:

\[
S(\omega) = \int s(t) \exp(-i\omega t) \, dt = \int s(t) \cos(\omega t) \, dt - i \int s(t) \sin(\omega t) \, dt
\]