

# NMR Spectroscopy

## Introduction

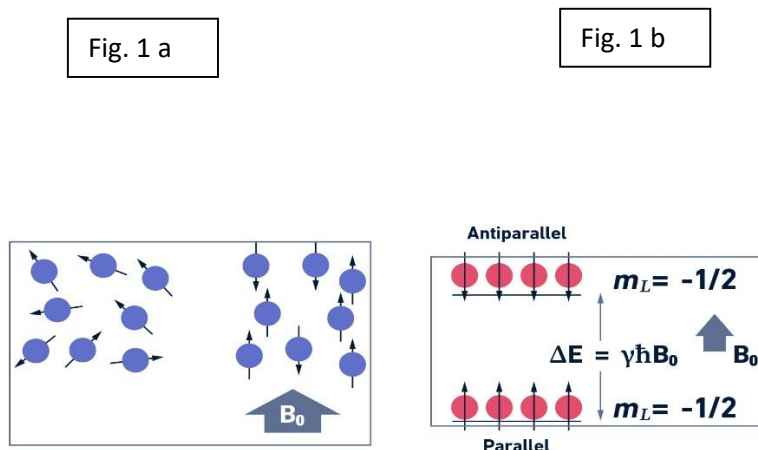
NMR spectroscopy is a physicochemical analysis technique that is based on the interaction of an externally applied radiofrequency radiation with atomic nuclei. During this interaction there is a net exchange of energy which leads to a change in an intrinsic property of the atomic nuclei called **nuclear spin**.

The nuclear spin is defined by a quantum number ( $I$ ), which varies depending on the considered isotope. Only atomic nuclei with  $I \neq 0$  are detectable by NMR spectroscopy (NMR-active nuclei, such as  $^1\text{H}$ ,  $^2\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  etc).

These NMR-active nuclei behave as tiny magnets (magnetic dipoles), capable of aligning with external magnetic fields (a process called **magnetization**). The force of those tiny magnets is defined by a constant known as the magnetogyric ratio ( $\gamma$ ), whose value depends on the isotope.

Nuclear spins of some NMR-active nuclei are able to adopt two different orientations when they align to an external magnetic field ( $B_0$ ).

- One orientation corresponds to the lowest energy level of the nucleus (parallel to the external magnetic field), and
- The other one is associated to the highest energy level of the nucleus (antiparallel to the external magnetic field) (Figure 1 a). The difference between energy levels ( $\Delta E$ ) depends on the magnetic field and the magnetogyric ratio and affects the sensitivity of the technique (Figure 1b).

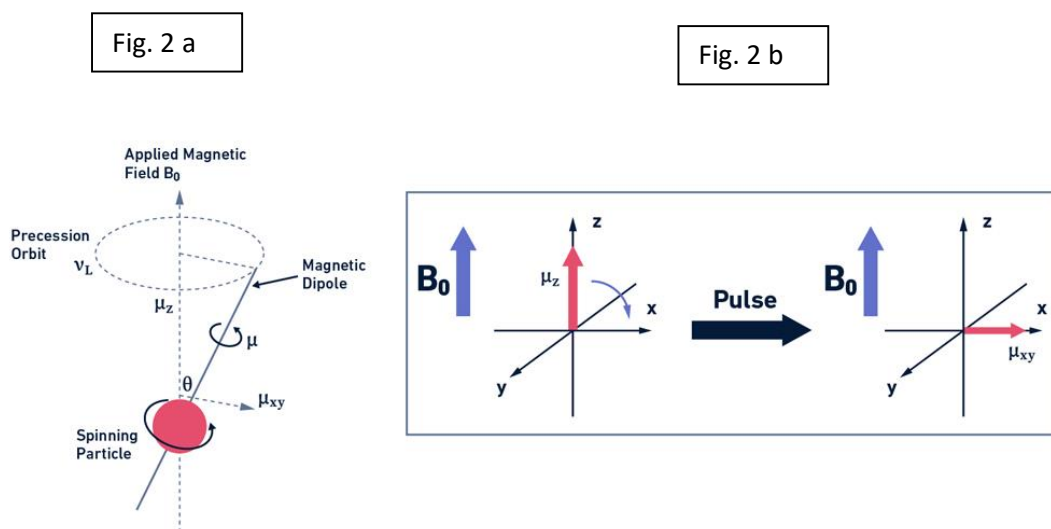


**Figure 1:** Nuclear spin orientations of a sample aligned (parallel and antiparallel) with the direction of an external magnetic field  $B_0$  (Fig 1 a). Distribution of nuclear spin populations in the two possible energy levels in nuclei with  $I = 1/2$  (Fig 1 b).

- **Magnetic resonance** is achieved when nuclei are irradiated with radiofrequency. This causes transitions between energy levels, which involves changes in the orientation of nuclear spins.

When atomic nuclei are under the effect of a magnetic field, nuclear magnetic dipoles are not statically aligned with the magnetic field  $\mathbf{B}_0$ , but rather move like a spinning top (precession movement) around an axis parallel to the direction of the field (Figure 2, a). The frequency of this precession movement, called Larmor frequency ( $\nu_L$ ), is defined by the magnetogyric ratio and the magnetic field.

As a consequence of this precession movement, the magnetic vector ( $\mu$ ) associated with the nuclear magnetic dipoles possesses a component parallel to the magnetic field ( $\mu_z$ ) and another component perpendicular to the magnetic field ( $\mu_{xy}$ ), with this last one having a net value of zero in the absence of external perturbations (In an NMR experiment, it is not possible to measure the signal in the z direction, as the magnetic field is too intense in that direction) Therefore, it is necessary to transfer the magnetization of the z component to the xy plane. For this purpose, a magnetic pulse containing frequencies close to the Larmor frequency is applied perpendicular to  $\mathbf{B}_0$  to reach the resonance of nuclear spins, which generates a non-zero  $\mu_{xy}$  component. After this pulse, a relaxation process takes place and the  $\mu_{xy}$  component gradually recovers its net value of zero (Figure 2, b). As a consequence of this relaxation, energy is emitted as radiofrequency, producing a characteristic signal called **free induction decay (FID)** which is registered by the detector. This FID is subsequently transformed into a plot of intensities versus frequencies known as an **NMR spectrum**.



**Figure 2:** Nuclear spin behavior under the influence of an external magnetic field (left panel). Scheme of a basic NMR experiment in which the magnetization is transferred to the xy plane upon the application of a magnetic pulse (right panel).