3.4 Principles of NMR and MRI

NMR spectroscopy is mainly used to determine the structure of complex chemical or biological molecules and for studying condensed matter in solid or liquid form. A detailed description of how NMR works would take us too far afield, and so we shall only touch upon the subject. The sample under study is placed in a uniform field $\vec{B}_0$ of several teslas, the maximum field accessible at present being about 20 T (Fig. 3.5). An NMR is characterized by the resonance frequency.[10] $\nu_0 = \omega_0/2\pi = \gamma_p B_0/(2\pi\hbar)$ for a proton: a field of 1 T corresponds to a frequency $\simeq 42.6$ MHz, and so we can speak of an NMR of 600 MHz if the field B_0 is 14 T. Owing to the Boltzmann law, the level $|0\rangle$ is more populated than the level $|1\rangle$, at least for $\gamma > 0$, which is the usual case. The ratio of the populations p_0 and p_1 at thermal equilibrium at absolute temperature T is, from the Boltzmann law,

$$\frac{\mathsf{p}_0(t=0)}{\mathsf{p}_1(t=0)} = \exp\left(\frac{\hbar\omega_0}{k_B T}\right), \tag{3.33}$$

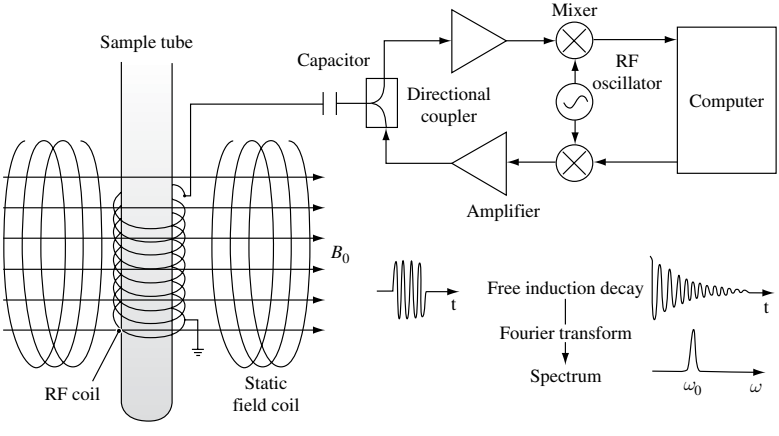

Figure 3.5 Schematics of the NMR principle. The static field $\vec{B}_0$ is horizontal and the radiofrequency field is generated by the vertical solenoid. This solenoid also serves as the signal detector (FID Free Induction Decay). The RF pulse and the signal are sketched at the lower right of the figure. The decreasing exponential form of the signal and the peak of its Fourier transform at $\omega = \omega_0$ should be noted. Adapted from Nielsen and Chuang (2000).

[10] More rigorously, ω is an *angular frequency*, measured in rad/s, whereas the *frequency* $\nu = \omega/2\pi$ is measured in Hz. Since we shall use ω almost exclusively, we shall refer to it somewhat casually as the frequency.

where k_B is the Boltzmann constant, $k_B = 1.38 \times 10^{-23}\,\mathrm{J/K}$. At the ambient temperature for an NMR of 600 MHz the population difference

$$\mathsf{p}_0 - \mathsf{p}_1 \simeq \frac{\hbar\omega_0}{2k_B T}$$

between the levels $|0\rangle$ and $|1\rangle$ is $\sim 5 \times 10^{-5}$.

The application at time $t = 0$ of a radiofrequency field $\vec{B}_1(t)$ during a time t such that $\omega_1 t = \pi$ with frequency ω_1 lying near the resonance frequency ω_0, that is, a π pulse, makes the spins of the state $|0\rangle$ go to the state $|1\rangle$ and vice versa, resulting in a *population inversion* with respect to the equilibrium populations, so that the sample is out of equilibrium. The return to equilibrium is characterized by a relaxation time [11] T_1, the *longitudinal relaxation time*. In practice, a $\pi/2$ pulse is used: $\omega_1 t = \pi/2$. This corresponds geometrically to rotating the spin by an angle $\pi/2$ about an axis of the xOy plane (Exercise 3.5.1). If the spin is initially parallel to $\vec{B}_0$, it ends up in a plane perpendicular to $\vec{B}_0$, a transverse plane (whereas a π pulse takes the spin to the longitudinal direction $-\vec{B}_0$). The return to equilibrium is then governed by a relaxation time T_2, the *transverse relaxation time*. The time T_1 is of the order of a second and $T_2 \lesssim T_1$; generally, $T_2 \ll T_1$. In any case, the return to equilibrium occurs with the emission of electromagnetic radiation of frequency $\simeq \omega_0$, and Fourier analysis of the signal gives a frequency spectrum which permits the structure of the molecule in question to be reconstructed. This is done on the basis of the following properties.

- The resonance frequency depends on the nuclei through γ.
- For a given nucleus the resonance frequency is slightly modified by the chemical environment of the atom to which the nucleus belongs, and this can be taken into account by defining an effective magnetic field B_0' acting on the nucleus:

$$B_0' = (1 - \sigma)B_0, \qquad \sigma \sim 10^{-6},$$

  where σ is called the *chemical shift*. There are strong correlations between σ and the nature of the chemical grouping to which the nucleus in question belongs.
- The interactions between neighboring nuclear spins provoke a splitting of the resonance frequencies into several subfrequencies which are also characteristic of the chemical groupings.

This is summarized in Fig. 3.6, where a typical NMR spectrum is given. It is important to observe that an NMR measurement has nothing to do with a projective measurement, as defined in Section 2.4. In fact, the NMR signal is a *collective* signal built up by spins located on $\sim 10^{18}$ molecules. When returning

[11] When a field $\vec{B}_0$ is applied, thermodynamical equilibrium (3.33) is not established instantaneously, but only after a time $\sim T_1$.

to equilibrium, these spins build up a a macroscopic polarization which precesses about the constant field $\vec{B}_0$. This precession induces an emf in a solenoid (the same solenoid which served to bring the spins to nonequilibrium), and this emf can be measured by standard methods. This gives rise to the free induction signal (FID) schematized in Fig. 3.5. This FID is Fourier analyzed, which allows one to determine the resonance frequencies, as in Fig. 3.6. The reason why the NMR measurement is a purely classical one is that spontaneous emission from a spin in an excited state, which must be described in a quantum framework, is completely negligible, so that the NMR measurement is best described in classical terms.

In the case of magnetic resonance imaging (MRI), it is only the protons contained in water and fats which are of interest. The sample is placed in a nonuniform field $\vec{B}_0$, which makes the resonance frequency depend on the spatial point. Since the signal amplitude is directly proportional to the spin density and therefore to the proton density, by complex computer calculations it is possible to deduce a three-dimensional image of the density of water in biological tissues. At present the spatial resolution is of the order of a millimeter, and an image can be made in 0.1 s. This has allowed the development of functional MRI (fMRI), which can be used, for example, to watch the brain in action by measuring local variations of the blood flow. The longitudinal and transverse relaxation times T_1 and T_2 play a major role in obtaining and interpreting MRI signals.

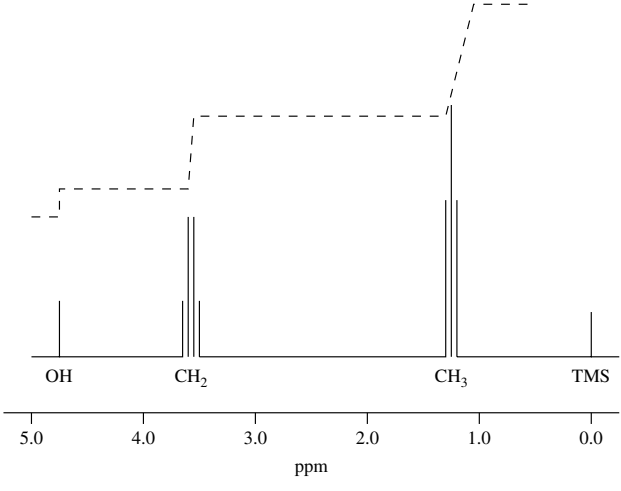

Figure 3.6 NMR spectrum of protons of ethanol CH_3CH_2OH obtained using an NMR of 200 MHz. The three peaks associated with the three groupings OH, CH_3, and CH_2 are clearly seen. The dashed line represents the integrated area of the signals. TMS (tetramethylsilane) is a reference signal.