Chapter 1

Introduction

1.1 What Is an NMR Probe?

Any kind of physical investigation usually needs a suitable sensor in order to interface the physical phenomenon to the final display of the results. The task is more complicated if the studies are concerning the molecular or atomic level, even at the sub-atomic range nowadays. The principal problem arising when dealing with quantum experiments is how to measure some physical properties at sub-atomic level without perturbing the investigating system by even the measuring process or by the probe we use.

This is precisely the case with Nuclear Magnetic Resonance (NMR) experiment which is based on picking up the signal generated by assemblies of nuclei having a nonzero spin number. The nuclear spins, denoted as s, like hydrogen (s=1/2), phosphorous (s=1/2), carbon 13 (s=1/2), sodium (s=3/2) are involved in the molecular or ionic constitution of a large number of materials (liquids, solids, or living heterogeneous systems). Such a spin assembly defines the sample which is observed by the NMR approach. This is possible since the sample contains a very large number of magnetic moments associated to the spin properties of the considered nuclei. When the spins of the protons and neutrons comprising these nuclei are not paired, the overall spin of the charged nucleus generates a magnetic dipole along the spin axis, the intrinsic magnitude of this dipole is the fundamental nuclear property called the nuclear magnetic moment. Consequently, the nuclear magnetic moment of a nuclei or a nuclear assembly can align with an externally applied magnetic field of strength B, in (2s+1) ways, either reinforcing or opposing B, generating thus a macroscopic magnetization of the whole sample, M. This property is a characteristic of paramagnetic substances for which the magnetization is proportional to the static magnetic field and inversely proportional to the temperature.

More precisely this magnetization is governed by the Boltzmann equilibrium law

$$M = N\frac{\gamma^2 s(s+1)\hbar}{3k_B T}B, \tag{1.1}$$

where N is the number of nuclei present in the sample, γ is the gyromagnetic ration of the nuclei, $\hbar$ is the Planck's constant divided by 2π, k_B is the Boltzmann's constant and T the spin temperature which is equal to the sample temperature at thermal equilibrium between spins and the thermostat made by the sample itself (known also as lattice). Legal and recommended unit to express M is nicked as *ampere· metre*^{2} (notation: Am^2).

The aim of the NMR technique is to quantify the nuclear magnetization of a sample, which is generally a rather small and very specific physical property that cannot be measured by conventional means. For this purpose a resonance approach was developed in 1946 by research groups at Stanford and M.I.T., in the USA [Bloch, F., *et al.*, 1946, Purcell, E.M., *et al.*, 1946]. The radar technology developed during World War II made many of the electronic aspects of the NMR spectrometer possible and thus to observe and determine the predicted nuclear magnetization. The principle of the method is based on the detection of magnetic variable flux provided by the sample similarly to the light signal given by a bicycle alternator. This is possible once the magnetization is tilted from its equilibrium position along and in the sense of the external applied magnetic field, B. After being tilted, the magnetization gets a precession motion around the static magnetic field direction which defines generally the "vertical" direction on pictures (Fig. 1.1). In this particular case, and in this case only, one may consider that the behaviour of the magnetization is comparable to a magnet rotating around an axis (here the axis is given by the static field direction). Then, if a conducting loop is set in a vertical plane, an electromotive force will appear between the two extremities of the wire as shown in Fig. 1.1. The angular frequency of precession is given by

$$\omega = \gamma B\,, \tag{1.2}$$

where γ is the "gyromagnetic" ratio of the considered nuclei, this parameter must be expressed in *radian/second tesla* (notation: $\mathrm{rad\,s^{-1}T^{-1}}$).

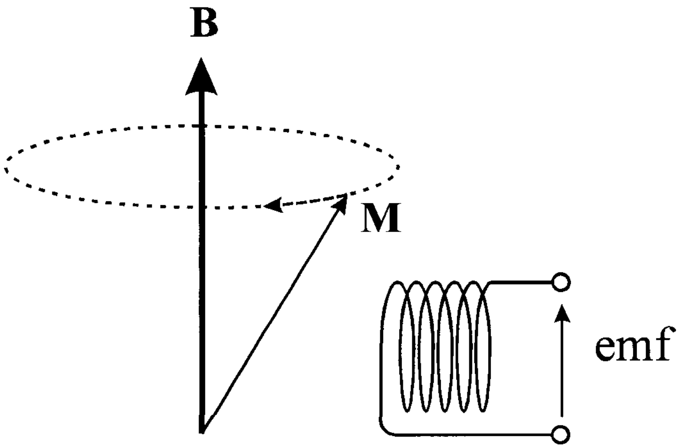

Fig. 1.1. Precession motion of nuclear magnetization around the applied magnetic field and generation of an electromotive force in a "radiofrequency coil" due to the time variation of the magnetic flux.

Typical values for static fields in NMR experiments are presently in the 1 to 23 tesla range, giving frequencies from 42 to 1000 MHz for hydrogen. Such frequencies are typically radio frequency ones and the NMR devices (probes, amplifiers, electronic detectors, *etc*) must operate accordingly.

It is clear from Eq. (1.2) that the larger the static magnetic field, the larger the electromotive force is since the angular frequency is proportional to B for any nuclei observed by NMR. It appears clearly that the sensitivity of the NMR experiment will increase when increasing B, and this explains the expensive efforts towards high static field magnets to perform NMR. Nevertheless, even with the largest magnetic fields presently available (approximately 23 tesla), the NMR signal may still be too poor due to the smallness of the sample volume or to the weakness of the gyromagnetic ratio of the observed nuclei. The signal weakness is also due to the fact that in parallel with manufacturers' efforts to increase the static field, chemists, biochemists and biologists try to observe smaller and smaller samples. Consequently one efficient way to improve the nuclear magnetic signal generated at the sensor output, is to pick it up using a resonant device. Practically, as it will be demonstrated in the following chapter, matching a resonant circuit to the NMR spectrometer means constructing a resonator by tuning its receiving loop with a good quality capacitor to avoid losses. In this case, if Q is the quality coefficient of the resonator, the electromotive force induced in the coil will be multiplied by Q at the resonator output. The voltage thus obtained will be a superposition of useful signal and noise, both multiplied by the same factor. The only advantage brought by this configuration in what concerns the Signal-to-Noise Ratio (SNR) could be the reduction of the pass-band of the system (the SNR is inversely proportional to the pass-band square root). In order to take into account thermal noise, this resonator may be considered a time dependent voltage source in series with a noise source (see Fig. 1.2). The capacitor now acts as a filter at the input of the rest of the circuitry, especially for the noise transmission.

For more than half a century NMR detection was classically based on the generation of an oscillating magnetic flux by an electrically resonating circuit. A recent approach uses the Josephson's effect in semiconductors to observe the nuclear magnetization [McDermott, R., *et al.*, 2002]. This latter technique is sensitive, not to the flux variation, but directly to the flux itself. This innovative way allows NMR experiments without the need for intense polarizing magnetic fields, but rather uses very low fields smaller than the Earth's.

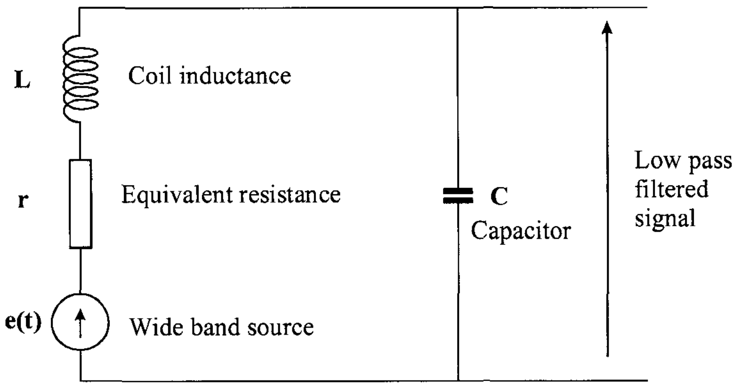

Fig. 1.2. Principle of the NMR resonator using a tuning capacitor.

1.1.1. The basic pulsed NMR experiment

Considering that the precession of the magnetization is able to generate an electromotive force, a current is passing through the receiving loop when this loop is closed by an output circuitry. By reciprocity, when a current is passing through the wire loop during a limited period of time denoted as τ, the sample magnetization is tilted as well. The magnetization excitation is performed provided the angular frequency of the applied current is very close to the precession angular frequency of nuclei. For a given tilt angle θ, the pulsed radio frequency field must be applied along a direction perpendicular to the static magnetic field. Assuming that this alternative field is linearly polarized and that its amplitude is constant and equal to B_{RF}, the angle θ, the pulse length and the radio frequency amplitude are related by the following formula

$$\theta = \gamma \left(\frac{B_{RF}}{2} \right) \tau . \tag{1.3}$$

A rectilinear oscillating field may be decomposed into two opposite circular fields, the preceding result may be derived using the well known rotating frame representation. In this representation the radio frequency field appears as fixed and its amplitude, the half of B_{RF}, is denoted as B_1.

Usually B_1 value is of the order of 10^{-4} tesla, that is considerably smaller than usual static magnetic field values. Consequently, the precession frequency around the direction of B_1, the field which is seen in the rotating frame, is in the kilohertz range for hydrogen (whose gyromagnetic ratio is 2π times 42.57 10^6 rad/s/T). A typical duration for the application of a radio frequency pulse necessary to tilt the magnetization by a 90° angle with respect to its initial orientation, is about 100 microseconds. When reasoning in the rotating frame, one must assume that the motion of the magnetization has to be fast enough compared to the relaxation effects. This condition implies first of all, that the magnetization value remains constant during the pulse. Secondly, once the preceding condition is fulfilled, during any radio frequency pulse, the angle between the radio frequency field direction (which is also the axis of the cone on the surface of which the magnetization is moving) and the magnetization direction should remain constant. Some particular tip angle values are represented in Figure 1.3 to illustrate this remark.

The most traditional representation of an NMR experiment considers a vertical static field and a radio frequency coil with its axis horizontally oriented as depicted in Fig. 1.1. Starting from an equilibrium magnetization, a short alternative current passage in the coil may create a horizontal magnetization which, in turn, is able to modulate the magnetic flux passing through the wires at almost the same frequency.

Since relaxation effects are weak interactions compared to the nuclei coupling with the radio frequency field, they are very efficient because they represent the main interaction between the nuclei and the experimental environment. Spin-lattice relaxation corresponds to the recovery of the longitudinal magnetization, i.e. the component measured along the static field, and is a rather slow process.

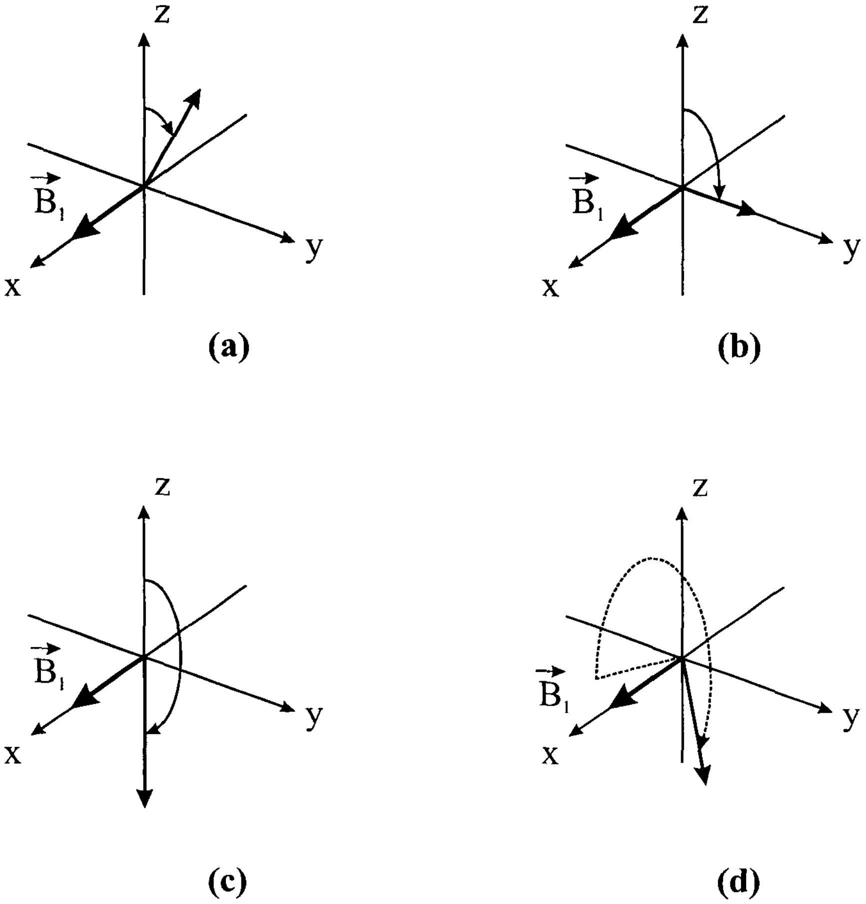

Fig. 1.3. Examples of magnetization tip angles in the rotating frame with magnetization starting from the equilibrium direction: (a) arbitrary pulse; (b) 90° pulse; (c) 180° pulse; (d) 180° pulse with magnetization starting from a direction taken in the Oxy plane.

Spin-spin relaxation acts naturally on the transverse magnetization decay, but this phenomenon is generally shortened by an important out of phase effect generated by the static field non uniformities over the whole observed sample, especially in liquids or heterogeneous samples as the living tissues. Several features must be taken into account in order to understand the magnetization behaviour during the free evolution period which follows the radio frequency excitation:

- the relaxation times (T_1) which govern the recuperation of the longitudinal magnetization is extremely long compared to the period of precession (typically one second for water protons and a few tens of a nanosecond for the precession period),
- the apparent transverse relaxation time (T_2*), shorter than $T_{1,}$ is also very long with respect to the precession period. Notice that this time constant can be defined, only when the static field distribution presents through the sample a very particular repartition said as "Lorentzian", leading, to an exponential decay,
- during a very large number of rotations of the magnetization about the static field direction (more than several thousands) there is no noticeable decay of the amplitude of the transverse magnetization and the same observation works for the induced signal itself.

After frequency subtraction, this signal can be displayed on a narrow spectral range and, if the sample contains isochronal nuclei, this signal has the appearance shown in Fig. 1.4a. A simple Fourier transform of this free induction decay signal gives the complex signal (or phase-amplitude signal) represented in Fig. 1.4b.

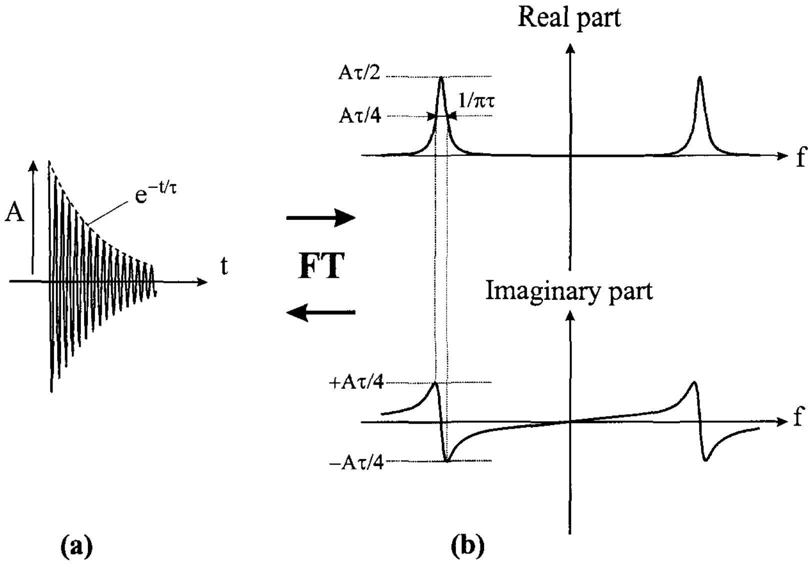

Fig. 1.4. (a) Free induction decay signal in a supposed homogeneous magnetic field leading to an exponential decay. (b) Fourier transform of the signal in phase-amplitude representation.

1.1.2 The head probe on a theoretical point of view

1.1.2.1 The principle of reciprocity and the calculation of the induced emf.

A single conducting coil, (more generally a set of conductors) is the most frequently used way to pick up the electromotive force generated by the transient motion of the nuclear magnetization. From the theoretical point of view, the emf evaluation can be developed either on the basis of the reciprocity principle [Hoult, D.I., and Richards, R.E., 1976; Hoult, D.I., 2000], either from a direct application of the law of electromagnetism [Pimmel, P., 1990]. The second approach will be presented here because it gives detailed information about signal generation and it leads to a comprehensive treatise. One may start the analysis from the schematic drawn in Fig. 1.5 where both the sample and the radio frequency coil are represented.

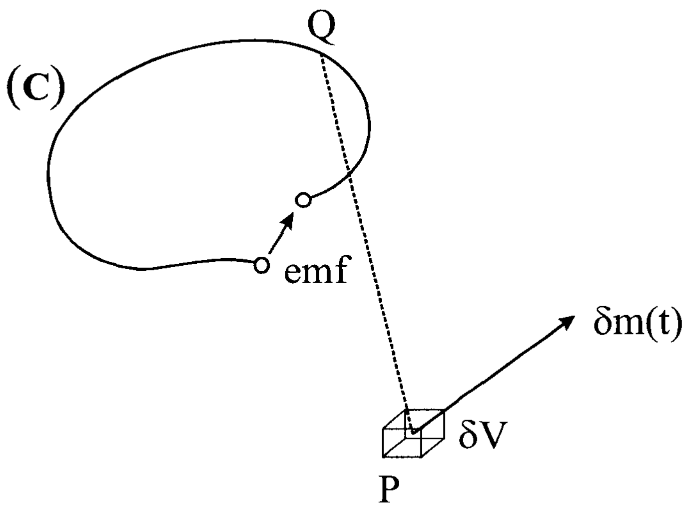

Fig. 1.5. Schematic diagram for the calculation of the electromotive force generated by the magnetization precession.

After the excitation due to a radio-frequency pulse, the time varying magnetization of a volume element placed in P is denoted as $\overrightarrow{\delta m(t)}$. Such a magnetic moment creates in space, especially at the point Q, a magnetic potential vector expressed as:

$$\delta\vec{A}_Q = -\frac{\mu_0}{4\pi}\overrightarrow{\delta m}(t)\wedge\vec{\nabla}_Q\left(\frac{1}{r_{PQ}}\right), \tag{1.4}$$

where μ_0 is the vacuum permeability ($4\pi.10^{-7}$ *Henry/meter*, notation: H/m) and where the reversed delta symbol denotes the "nabla" operator acting at the Q position and r_{PQ} is the distance between P and Q.

The electromotive force induced in the conducting coil, considered here as a thin wire, is given by the Maxwell – Faraday law, or in other words by the circulation along the coil of the magnetic vector potential generated by the magnetic moment

$$\delta e(t) = \int_C \left(-\frac{\partial}{\partial t} \delta \vec{A}_Q \right) d\vec{\ell}, \tag{1.5}$$

where (*C*) is associated to the wire extension.

Using (1.4) in (1.5) one gets

$$\delta e(t) = \frac{\partial}{\partial t} \left\{ \delta \vec{m}(t) \frac{\mu_0}{4\pi} \int_C \vec{\nabla}_Q \left(\frac{1}{r_{PQ}} \right) \wedge d\vec{\ell} \right\}. \tag{1.6}$$

The integral factor of the preceding equation represents exactly the opposite of the magnetic field existing at point *P* when an unit current is passing through the wire. Consequently one may express the electromotive force generated by the motion of $\delta \vec{m}(t)$ as

$$\delta e(t) = -\frac{\partial}{\partial t} \left\{ \delta \vec{m}(t) \vec{B}_1(X, Y, Z) \right\}, \tag{1.7}$$

where $\vec{B}_1(X, Y, Z)$ is the radio-frequency field at *P*, the coordinates of *P* being (*X,Y,Z*), when an unit current is passing through the receiving coil, if the last one is used as a transmitter only.

This result has a practical importance since the bulk sample signal can be evaluated by the superposition of signal rising from a number of elementary volumes. Assuming that the density of nuclei is constant, one may replace the statistical average of (δm) by $M_O \delta V_e$ where M_O is given by Eq. (1.1) and δV_e the volume element at *P*. A linearly polarized radio-frequency field can be denoted as $\vec{B}_{RF} = 2B_1 \cos(\omega t) \vec{I}$, where $\vec{I}$ is the unit vector along the radio-frequency direction which may represent the *OX* axis of the fixed laboratory frame. It can be associated to the current in the coil, $I_B = I_0 \cos(\omega t)$. Assuming that the temporal fluctuations due to transverse relaxation are very slow compared to precession, this can be taken into account in the derivation of Eq. (1.4), then

$$\delta e(t) = a \sin(\omega t) e^{-t/T_2'}, \tag{1.8}$$

where T_2' corresponds to the transverse relaxation time of the magnetization elementary volume δV_e ($T_2 > T_2' > T_2^*$) since T_2^* is observed on the whole sample and the static field inhomogeneity is lower on a volume element than on the entire sample.

From Eq. (1.7) the amplitude a is evaluated as

$$a = \frac{2B_1}{I_0} N_0 \frac{\gamma^3 \hbar^2 s(s+1)}{3k_B T} B^2 (\sin\theta) \delta V_e, \tag{1.9}$$

where N_0 is the number of nuclei per unit sample volume and where the other symbols have their usual significance (the value of "a" is expressed in *Volt*, notation: V).

Since the term $2B_1/I_0$ depends on the position of P where the volume element is taken, one may notice that the amplitude of the signal coming from the sample depends on the uniformity of the radio frequency field. If the uniformity condition is fulfilled one may use Eq. (1.9). Even for a large extension of δV_e, T_2' has to be replaced by T_2^* to express the NMR signal generated in the receiving coil.

In this analysis, Eq.(1.7) plays a particularly important role since it may be pointed out that the time derivation of the scalar product would be equal to zero if one considers a radio-frequency field rotating in the precession sense. Consequently, during the receiving period, the only efficient radio-frequency component is considered to rotate in the opposite sense with respect to the precession motion. This is the reason for changing the phase difference sense when switching from transmitting to receiving for a circularly polarized field for spin excitation.

1.1.2.2 Losses

During the receiving period, the radio-frequency coil can be considered as an electrical voltage source and it can be represented through the equivalent circuit as in Fig. 1.6a, where L corresponds to the self-conductance of all wires and r is the equivalent resistance. To take the thermal noise generated by the resistance into account, the equivalent circuit must be considered as in Fig. 1.6b were a noise source, has been introduced.

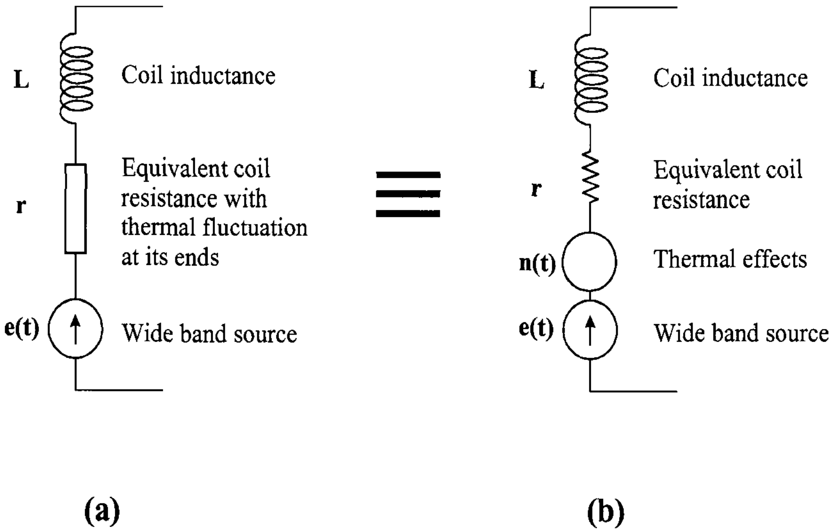

Fig.1.6. (a) Equivalent voltage source for the signal generation. (b) Equivalent circuit for the radio-frequency coil used as receiving coil (taking into account the noise equivalent source).

The resistance value includes the "ohmic" values of all wires in presence of high frequency oscillating currents. This contribution is larger than the static resistance due to skin effect that reduces the current penetration in conductors. A second contribution is caused by the leakage due to the induced currents in the conducting samples at the operating radio-frequency; this effect depends on the electrical conductivity of the sample medium. For example, in biological samples, the conductivity is approximately equal to the electrical conductivity of a saline solution of 9 kg/m^3 of sodium chloride. Such leakages are designed as *magnetic losses*. The third contribution in the overall resistance is caused by the electrical losses. They are due to the potential differences between ground and some circuit parts reaching high potential values during the radio-frequency excitation. Such potential differences create high frequency electric field passing through the sample medium and consequently dipolar losses due to the presence of dipolar "carriers" such as water.

Finally, the equivalent resistance of the radio-frequency probe may be written as

$$r = r_\Omega + r_M + r_E, \tag{1.10}$$

where r_Ω corresponds to conventional Joule effects in the wires, r_M is the resistance due to magnetic losses, and r_E is generated by electrical losses, mainly through the sample.

A quantitative estimation of each term can be derived on the basis of electromagnetic law, provided the sample shape and its electrical characteristics are known. For a spherical sample of radius b, calculation leads to the following results

$$r_M = R_M \sigma n^2 \omega^2 b^5, \tag{1.11}$$

where R_M depends on the coil geometry and n is the number of conducting turns, σ being the electrical conductivity of the sphere medium, and

$$r_E = R_E \omega^3 L^2 C_d, \tag{1.12}$$

where R_E is the loss factor of the coil having an auto inductance L and a capacitive value C_d.

The effect of these latter resistances can be reduced via some symmetrical arrangements, when designing the NMR probe, described in detail in the following chapters.

1.1.2.3 The ultimate sensitivity

The knowledge of the equivalent resistance r permits one to evaluate the probe sensitivity, assuming an extremely high quality factor for the tuning capacitor. The quality factor of the radio-frequency coil itself which is simply the ratio of its admittance ($L\omega$) by the equivalent resistance r

$$Q = \frac{L\omega}{r}. \tag{1.13}$$

In these conditions, if ω is the Larmor pulsation for nuclei, this quality factor is also the NMR probe quality factor. Notice that, from Eq. (1.13), r is inversely proportional to Q.

Consider the thermal fluctuations due to the presence of the resistance of an equivalent noise voltage source introduced in Figure 1.6b. This may be derived from thermodynamics consideration provided noise is considered as thermal white noise with a null mean value and a mean square value given by

$$\sigma_n = \sqrt{4 r k_B T \delta f}\,, \tag{1.14}$$

where k_B is the Boltzmann's constant, T the temperature of the probe and δf the bandwidth of the NMR receiving system. Using legal units system, the second member of Eq. (1.14) leads to a voltage value (expressed in *Volts*) with the root mean square σ_n.

The ultimate sensitivity can be defined considering the amplitude of signal to noise ratio in the time domain, and according to Eqs. (1.9) and (1.14), this gives

$$S = \frac{2B_1}{I_0} N_0 \frac{\gamma^3 \hbar^2 s(s+1)}{3k_B T} B^2 (\sin\theta) \delta V_e \frac{1}{\sqrt{4 r k_B T \delta f}}\,. \tag{1.15}$$

This rather complicated formula can be used as a guide for improving the NMR experiment. For a given nuclear species (γ and s fixed), for a given number of nuclei (N_0) and observed using a given device (B, θ, δV_e, δf fixed), the sensitivity is proportional to $B_1/I_0\sqrt{r}$. This result means that losses must be strongly limited (small value of r) and that the radio frequency coil must exhibit the highest possible efficiency since it must generate the largest radio frequency field amplitude at a given current passing through the wires. Assuming that the radio frequency field generated by the coil is uniformly distributed through the inner space of the coil, the proportionality to $B_1/I_0\sqrt{r}$ can be replaced by a proportionality to $\sqrt{\eta Q}$ where η is the filling factor of the resonator coil, i.e. the ratio of the sample volume to the inner volume of the coil.

Other remarks concern the presence of temperature factor in the sensitivity formula. Here it is assumed that the coil wires and the NMR sample are both at the same temperature which is represented by the common T symbol. In fact, these two temperatures may be significantly different, and it is possible to lower the temperature of the receiving wires in order to reduce thermal noise generation and to increase sensitivity.

Some interesting points can also be discussed about the concept of ultimate sensitivity. In the preceding section, it is pointed out that two kinds of sensitivity formulation are possible: proportional to $B_1/I_0\sqrt{r}$ or to$\sqrt{\eta Q}$.[1] The first formulation is certainly more rigorous than the second one since it can be considered as a direct expression of the principle of reciprocity. But it does not explicitly involve the electrical resonance phenomenon which is created in the probe circuit, the resonator. The fact that the resonating frequency of the electrical circuit made by the loop and the capacitor, is equal to the precession frequency of the observed magnetization is a very important feature of NMR detection and can justify the use of the word "resonance" on the experimental scope. The electromotive force taken at the terminals of the circuit is almost Q times the electromotive force generated by the magnetization flux variation in the receiving coil. As already said, in the schematic representation of Fig. 1.6b, the noise voltage associated to the equivalent resistance and occurring at the same spectral position is also multiplied by Q at the resonating circuits output. Consequently, the signal to noise ratio in the time domain does not depend on the electrical resonating configuration. The only advantage of this resonating arrangement is that higher voltages are available now, for both signal and noise since they are multiplied by Q factor. Nevertheless, one should not forget the presence of $\sqrt{r}$ in the first expression for sensitivity. When choosing a very good quality capacitor and when reducing the coupling between the sample and its environment, the equivalent resistor is made as small as possible; this corresponds to the biggest value of Q for the given probe system. Moreover it may be interesting to have some idea about the signal to noise ratio in the frequency domain, even when the corresponding quantity is already defined and known in the time domain. This question

[1] At this point it should be mentioned that Q represents the "true" quality factor of the probe coil and not the Q factor of the whole electrical circuit including the tuning/matching network.

may be easily solved when using the Discrete Fourier Transform, a mathematical method to pass from time to frequency domain in digital spectroscopy. Simply speaking, if N is the number of transformed samples (which is also the number of signal samples in the frequency domain) the signal to noise ratio is roughly $\sqrt{N}$ times larger in the frequency domain than in the time one. This result, even approximately expressed here, is sufficient to explain that the easiest way to observe the NMR signal from noise is to perform the Fourier Transform on the Free Induction Decay signal. Nevertheless the signal processing can not replace an efficient instrumental design and a well done experiment, so a careful design and construction of the probe will represent the ultimate condition to observe the NMR signal with the optimum signal to noise ratio.

1.2 What Probes For a Specific NMR Experiment

In the preceding sections we have considered the principle of the NMR probe only, i.e. the technical process which is presently used to observe the magnetization precession motion in order to get magnetization measurement. This is based on the generation of an induced electromotive force, and it works like in an electric alternator. This is the principle working since the beginning of the NMR experimental adventure which started almost sixty years ago. Other techniques based on Superconducting Quantum Interferences Devices (SQUID) permit one to determine directly the magnetic flux with a very high sensitivity[McDermott, R., *et al.*, 2002; Wong-Foy, A., *et al.*, 2002].

Consequently these systems which are employed for magneto-graphic applications which may concern extremely low magnetic fields (few femtotesla) generated by living organs (heart, brain,..) are now considered for the future design of NMR probes. The present use of super conducting materials for NMR probes is based on high critical temperature super conducting materials, and the system is still based on magnetic flux detection. Indeed, the advantage of super conducting loops is that the equivalent resistance can be fixed at a very low value provided the magnetic and electrical losses through the sample are negligible. At high field values – more than 3 tesla – this assumption is valid with small size probes only and considering the difficulty to perform high critical temperature super conducting surface deposits, the application domain is presently very restricted. Consequently it is still pertinent to design NMR probes from the principles described above and one must, at least, consider three main domains of application.

1.2.1 High resolution NMR in solution

Organic chemical and biochemical applications of NMR are generally devoted to elucidate molecular structure and it requires a very high resolution power, 10^8 to 10^9 or better; the resolution power being the inverse ratio of the spectral resolution to the resonance frequency. Fortunately the samples under analysis are often in the liquid state or, more simply, dissolved in a solution of very mobile liquid molecules. In this case, the weakness of interactions leads to extremely short correlation times for molecular translation and reorientation, typically in the range of pico seconds. Consequently, in liquids, the relaxation times T_1 (spin-lattice) and T_2 (spin-spin) are rather long, of the order of one second or more. Long T_2 values make the resonance line widths very fine. Such line widths are mainly limited by the spatial distribution of the static magnetic field through the sample. This sample fills the bottom part of a calibrated NMR tube and usually the mechanical design of the probe keeps this tube in a vertical position. In order to improve the homogeneity of the static field it is possible to rotate the tube about its vertical axis during the measurements. For variable temperature measurements, the insert can be cooled until rather low temperature values (almost –160°C) or warmed to temperatures of the order of 200°C. Such performances require a specific Dewar assembly with particular glass properties in order to prevent undesired effects caused by dilatation. For the vertical orientation of both static magnetic field direction and tube axis, the radio frequency coils must generate a horizontal high frequency field. This is generally achieved using a saddle coil wound around a vertically oriented cylindrical glass form. Nevertheless, there are cases where the orientation of the NMR probe may have other degrees of freedom in the gap of the magnet due to their specifically small dimensions. This is the particular case of the microcoil probes or nanoprobes where the geometry of the coil is not imposed by the direction of the external magnetic field.

For a transmit and receive configuration, a single coil system can be easily built. For a quadrature transmit and receive coil system or a transmit coil associated to a separate receiving one, the design requires two orthogonal saddle coils and the building may be rather complicated. Particular caution, must be taken in order to avoid direct coupling between the two coils. For double or multiple resonance experiments this configuration is still valid. One may notice that, in order to obtain the best radio frequency field uniformity, the shape of the saddle coil must respect canonical proportions: the length value must be two times the diameter and the longitudinal opening angle of the saddle must be equal to 120°.

When using for both transmitting and receiving radio frequency, this simple and naïve coil structure can be advantageously replaced by a more efficient ones such as the Alderman and Grant (or slotted tube) design which will be discussed in this book.

1.2.2 Solid state NMR

The most important set-back of solid state high resolution NMR is caused by dipolar interaction between spins which cannot move freely, as in the liquid state, to give zeroed interactions and small line widths. The secular term of Hamiltonian interaction can be nulled out by magic angle spinning (54°) of the tube sample with respect to the static magnetic field. The spinning rate should be quite fast. Simply speaking, this particular design and radio frequency high powered pulse trains render the interactions of the spin system of the solid sample rather similar to interactions occurring in the liquid state. The aim is to reduce spectral dipolar widths considerably and to obtain, subsequently to the Fourier transform, reasonable line widths. Considering fast rotation inertial effects, the sample tube must be rather small. Moreover the important value of the magic angle, permits one to efficiently use a solenoid coil around the sample. In this scope, variable path solenoids can be designed in order to improve the radio frequency field uniformity.

The present practice of solid state NMR necessitates particularly well designed probes, not only due to rotation capabilities but also to perform measurements under controlled atmosphere in several applications like catalysis material characterization. Consequently it is not highly recommended, except for experts, to develop home-made probe for solid-state NMR experiments.

1.2.3 Biomedical and biophysical applications

This field of application is rather wide since it includes NMR studies for biochemistry, biology, pharmacology and medicine and it will be widely developed in the following chapters. The choice of the resonator design for a given application depends on several parameters, on the sample or on the kind of experiment used. It also depends on the bore magnet accessibility. In this case the two main different features for the coils are required according to the horizontal or vertical configuration. Roughly speaking, the vertical configuration, even with small animal studies, and developed with rather high magnetic fields constrains the users to develop radio frequency probe units very similar to high resolution system used for liquid spectroscopy, except that the coil itself must be updated to the particular location within the sample. Generally a surface coil, of one turn of copper or silver wire can be employed since it is well suited for brain, heart, liver configuration. In this case, the rest of the probe is quite identical to a high resolution one. Notice that the vertical position is not the best physiological position for animals. Nevertheless this configuration works well for perused organs such as excised heart or excised kidney and, in this case, the common saddle shaped coil can be very efficient. A large variety of NMR resonator designs can be considered when using an horizontal magnet because the accessibility is easier than in the vertical case. For some small samples, one may use a simple solenoid coil which is orthogonal to the field axis direction, in order to take advantage of the sensitivity of this design. More generally, the radio-frequency coil access is oriented along the direction of the magnet bore axis and several resonator structures have been extensively developed on this symmetry basis: the Alderman and Grant resonator, the Hayes coil or the birdcage configuration are among the most popular designs. They are interesting because they are wound on a cylindrical form that fits the cylindrical symmetry of the magnet and gradients coils geometry well. Such radio-frequency coil configurations will be described and studied in the following chapters. Generally, there are two conditions to be met for probe construction. The first fact to take into account is the geometrical structure which is generally imposed by sample shape or volume requirements. The second is related more to the electrical coupling modes between coils themselves, between coils and the output of radio-frequency power amplifier and also between coils with the input of the electronic chain for signal detection and processing. All these particular features will be developed in the following chapters.