Chapter III

EXPERIMENTAL TECHNIQUES - WIDELINE N.M.R. SPECTROMETER

Abstract

A general description of the requirements and functioning of the different systems of a typical wideline NMR spectrometer set up is given in this chapter. The necessity for adequate magnetic field homogeneity and stability is discussed along with the means of meeting these stringent conditions. The purpose of the field modulation as well as the field sweep arrangements is also discussed. Following this, conventional NMR detector circuits are outlined. The role of phase-sensitive detection in the processing of NMR signal is then given, followed by a discussion of the essential conditions for the observation of NMR absorption. At the end of the chapter a typical wideline NMR experimental set up and its operation are briefly described.

As the interaction energy between the nuclear magnetic moment and the static magnetic field is very small (~ $10^{-5}$ to $10^{-7}$ eV) the detection of nuclear magnetism is inherently a problem of very low signal-to-noise (S/N). On a microscopic level, these energies, at least at room temperature, are significantly smaller than the thermal noise [1]. However, by virtue of the resonance phenomenon and coherence effects we are able to observe the nuclear magnetism indirectly through NMR. In this context it is worthwhile to consider the different experimental techniques and the various spectrometer systems that enable one to extract the weak NMR signal deeply embedded in noise.

3.1 : The spectrometer - basic requirements

All resonance detection techniques (in principle) and NMR (in practise) can be implemented by two basic approaches, which are called CW (continuous wave) and pulsed (transient response) methods in the case of NMR. In the first approach, either the static magnetic field or the radiofrequency is swept slowly and the absorbed (or emitted) energy monitored as a function of either of these quantities. A resonance will thus be characterised as a peak in the corresponding parameter (the spectrum). In the second case, energy of a wide frequency range is given as input to the system for a short period of time and the subsequent output is observed. The system itself provides information by its transient "ringing" after the excitation [1].

For wideline NMR studies the CW method is usually adopted. The basic requirements of a typical CW spectrometer are as follows:
(i) A powerful magnet into which the sample is placed. A net magnetization will then be induced in the sample in the direction of the applied magnetic induction.
(ii) A radiofrequency transmitter, which supplies the (Larmor) frequency appropriate for the particular field strength and nucleus under examination. The linearly oscillating r.f.field is applied perpendicular to the direction of $B_0$ and the magnetic vector of this field has a component rotating at the Larmor frequency.
(iii) A radiofrequency receiver, which detects the resonance absorption.
(iv) A recorder, to provide a permanent record of the signals observed by the receiver.
The detection and display of the resonance signal usually involves some more additional subsystems, such as slow linear field sweep, field modulation, detection systems involving signal recovery techniques etc.

3.2 : Magnet - field homogeneity and field stability

The two main requirements to be met by the magnetic field employed in NMR experiments are high degree of homogeneity in space and excellent stability in time [2].

3.2.1 : Field homogeneity

The magnetic field employed for NMR experiments should be homogeneous within the volume of space occupied by the sample. The basic requirement for such homogeneity lies in very precise pole-piece design; these must be metallurgically uniform, precisely parallel to each other and free from machining marks [3]. Besides polepieces should have a diameter about ten times larger than the air gap in order to achieve better field uniformity [4]. The requirement of better field homogeneity will indirectly restrict the sample volume that can be adopted for the experiment.

For wideline NMR studies in the solid-state the magnetic field should be uniform to about 0.1 gauss over the sample volume. Otherwise, inhomogeneities in the magnetic field will completely mask the resonance signal [5].

3.2.2 : Field stability

For achieving the maximum field stability three steps are to be adopted: a high-precision current stabilizer, a flux stabilizer (or ‘super stabilizer’) and a field-frequency lock. With the first device, the magnet current is stabilized to about 1 part in 10^6. The flux stabilizer is designed to compensate for rapid fluctuations in the magnetic field. For this purpose, pick up coils are mounted on the polepieces; the voltage induced in these coils by field fluctuations are amplified, integrated and fed as a correction signal to the current stabilizer, giving a field stability of around 1 part in 10^10 per second. As a last step, long-term variations are compensated by a correction signal derived from the ‘lock circuit’ and this signal is fed to the input of the flux stabilizer [4].

For wideline NMR experiments, since a field stability of the order of 1 part in 10^6 is adequate, only a precision current stabilizer need be employed for achieving the required field stability. For this purpose highly regulated alternating currents are rectified, and the direct current that is supplied to the magnet is stabilized using a feedback system. The magnet current is passed through a standard resistor and the resultant voltage is compared with that from a reference source of high stability (e.g. a Weston cell); the difference voltage is amplified and fed as an error signal to the current control through which the magnet current has passed and this causes self-compensation. By this method a field stability of the order of 1 part in 10^6 can be obtained [3].

In the case of wideline NMR, because of the width of the line, the requirements for field homogeneity and field stability are not as critical as in high resolution NMR. Besides larger sample volumes can also be used in this case.
3.3 : Field modulation system

In order to display the nuclear magnetic resonance absorption or dispersion line on an oscillograph it is necessary to modulate the 'steady' magnetic field at a low audio frequency, often about 30Hz. Usually, a sinusoidally varying field having an amplitude of several times the width of the absorption line is applied by means of auxiliary coils. Now, if the mean value of the steady field is close to the resonant value, the field is swept twice through the resonance condition in each cycle, providing an audio-amplitude modulation of the r.f. carrier. After rectification, the audio signal is further amplified and it is then displayed on a CRO, the time-base of which is synchronised with the modulation.

On the other hand, when a phase-sensitive amplifier is employed during the recording of the signal, the modulation current is so adjusted that the maximum variation in the field at the sample is much less than the width of its resonance line. The output signal of the lock-in amplifier is then sinusoidal with an amplitude proportional to the first derivative of the line shape; strictly this is only true for a very small amplitude of modulation such that the portion of the line shape which is traversed during the field sweep can be treated as linear. On the contrary, if the modulating field is set too high considerable distortion, known as 'modulation broadening' of the output, occurs; its elimination becomes essential for the observation of true lineshapes. Provided the modulation amplitude is not more than about one-sixth of the linewidth, the curve obtained is a reasonably faithful reproduction of the derivative [6].

The process of field modulation will lead to the generation of some additional noise in the spectrometer. It has been shown that the sensitivity of NMR spectrometers with signal modulation and subsequent detection is limited to a considerable extent by the noise at the modulation frequency [7]. Since the modulation noise in the gap of the electromagnet are determined mostly by the modulating field and is proportional to it, the problem of attenuation of modulation noise reduces to stabilization of the amplitude and phase of the modulating magnetic field. Using feedback which is sensitive to variations of the amplitude and phase of the modulating field, the modulation current is stabilized, and this lowers the noise level.

3.4 : Field Sweep arrangement

Field sweep at a very slow rate is necessary for the convenient recording of NMR signal (there being a limit to the fast response capability of the recording system). The field sweep is effected either by scanning the reference voltage of the magnet current stabilizer between appropriate limit and at the desired rate [5,8,9] or by using a separate field sweep unit, having independent field sweep coils, that generate linearly varying fields of desired strength and duration [3,10,11]. For the faithful recording of the resonance spectra this field sweep should be highly linear.

The correct choice of sweep rate is important as well as complicated because there are a number of requirements which contradict one another [4]. The best procedure for recording single scan spectrum consists of using the lowest possible sweep rate mainly determined by the maximum allowed recording time - and the corresponding optimum saturation parameter. For systems with a high $T_1/T_2$ ratio, however, it may be preferable that the sweep rate be raised as this has the advantage of saving time without loss of sensitivity or resolution.
3.5 : The NMR probe

The NMR probe is the system which performs the dual function of transmitting the r.f. field as well as detecting the resonance signal. The conventional methods for detecting the existence of the NMR effect can be broadly split into two categories: 

(i) Single coil method in which the change in susceptibility of the sample when resonance occurs changes the effective inductance of a coil which is part of a tuned circuit and which surrounds the sample.

(ii) Double coil method in which one coil is fed from an r.f. signal generator and the second coil, mutually orthogonal to the transmitting coil axis and to the steady magnetic induction \( B_0 \), has a voltage induced in it due to the forced precession of the nuclear spins at their Larmor frequency.

Method (i) is often referred to as 'nuclear magnetic resonance absorption', since one picture of the process is of a heating of the spin system due to the absorption of energy at resonance, resulting in a decrease in the effective \( Q \) of the resonant circuit. Method (ii) is aptly described as 'nuclear induction'.

One important piece of information which the nuclear induction method yields, but which the resonance absorption method does not yield, is the sign of the nuclear magnetic moment. However, apart from this advantage, which is not of importance in all types of work, there is little to choose between the single- and double- coil methods of observing nuclear magnetic resonance. In practise the choice is frequently determined by local experience and tradition. For work at low temperatures one frequently desires simplicity within the cryostat even at the expense of complication outside it. The single-coil methods are preferable in such cases, since only one coil and two leads are required inside the cryostat, while the nuclear induction methods require two coils, flux leakage controls and at least three electrical leads within the cryostat [12]. Based on these considerations the single coil method of NMR detection has been adopted for the investigations presented in this work.

3.6 : Phase sensitive detection

In conventional broadline NMR the principle objective is to obtain the lineshape of the broad signal as accurately as possible, often over a wide range of temperature. The main difficulty encountered here is the very weak signal strength of the broad lines. This difficulty arises from the spread of the absorption over a range of field values due to the large nuclear spin-spin interactions which are dominant in many solids. The signal strength at any one point in the spectrum is comparable with the inherent noise of the system and invariably signal recovery techniques have to be used [13].

For extracting the weak NMR signal embedded in large interference noise, a lock-in amplifier is the most ideal signal processing instrument that can be used [14]. This is a sophisticated low-level signal measurement system using phase sensitive detection principle. The system has two inputs: a signal that is to be measured (which in a NMR spectrometer corresponds to the output of the NMR probe that varies at the modulation frequency), and a reference that has the same frequency as the input (here, the modulation frequency) and having an arbitrary but constant phase shift with respect to the input. The signal is prefiltered after amplification and is fed to a phase-sensitive detector (PSD). The reference signal is also filtered and, after passing through a 0 to 360° continuously-
controllable phase shifter, is fed to the PSD through a driver.

The operation of a phase-sensitive detector is similar to that of a half-wave detector. The reference voltage at the modulation frequency (often transformed into a square wave) switches on and off a gate into which the signal and noise are fed. The gate will be opened for one half of each cycle. Over several hundred periods any random signals present tend to cancel out provided the integrating time is long enough. This time determines the effective bandwidth of the system and, provided the speed of traverse through the line is slow enough, the important factor is the time constant of the smoothing circuit. A relatively large value for the time constant helps to narrow down the effective bandwidth considerably. This will then be equivalent to passing the input through a tuned circuit having a very high Q-factor, so that the noise components outside the bandwidth will get eliminated. Only the Fourier components of the input at the reference frequency (and odd harmonics) will contribute to the net d.c.component [13]. When the magnetic field is swept, the output of the PSD will vary in amplitude and in phase as the field modulation effected at different region of the normal signal line shape. As a result the original signal will get converted into its derivative at the detector's output. This output of the PSD is low-pass filtered and after further amplification, becomes the final output of the lock-in amplifier. The setting of the 0 to 360° phase shifter is in general adjusted to optimize the output signal.

The main advantage of phase sensitive detection is that only those components of the noise in the input which occur at the reference frequency are detected, whereas in normal detectors all frequencies contribute to the electrical noise of the output: thus a considerable gain in S/N ratio ensues. As its name implies, the output from the phase-sensitive detector depends on the phase of the input signal and since it also depends on the slope of the normal line the final output will constitute the derivative of the original signal [15].

3.7 : Condition for the observation of NMR absorption

If a nuclear magnetic resonance signal is to be detected at all, it must be discriminated from the background of random electrical fluctuations or 'noise'; in fact the signal power available at the detection apparatus must be at least of the same order as the noise power. If, further, accurate measurements are to be made of the shape of the resonance absorption line, the ratio of signal power to noise power must be much greater than unity [12].

Bloembergen, Purcell and Pound have derived an expression for the signal-to noise voltage ratio [16], which for a given nuclear species can be shown as

\[
\frac{V_s}{V_n} \propto \zeta N \left( \frac{\nu_0^3 V_c Q T_2}{(T^3 B_x F T_1)} \right)^{1/2}, \quad \text{where}
\]

\(\zeta\) \(\rightarrow\) is the filling factor denoting the proportion of the effective coil area which is occupied by the spin system

\(N\) \(\rightarrow\) is the total number of nuclei per cc

\(\nu_0\) \(\rightarrow\) is the applied radio frequency

\(V_c\) \(\rightarrow\) is the effective volume in which the r.f.magnetic field energy is stored and is very nearly equal to the volume of the coil

\(Q\) \(\rightarrow\) is the quality factor of the coil
\( T_2 \rightarrow \) is the spin-spin interaction time
\( T \rightarrow \) is the temperature of the experimental sample
\( B_2 \rightarrow \) is the effective bandwidth of the phase sensitive amplifier
\( F \rightarrow \) is the noise factor of the detection apparatus and
\( T_1 \rightarrow \) is the spin-lattice relaxation time.

The above expression leads to the following conclusions:

(a) Frequency \( \nu_0 \): The radio frequency occurs explicitly as \( \nu_0^{3/2} \), but also enters implicitly into \( Q \) (which usually increases more slowly with frequency), \( F \) and \( V_c \) (which may slowly decrease with an increase of frequency). Hence it can be concluded that it generally pays to work at as high a frequency as possible. This frequency is often limited by the magnetic fields available, which should therefore be as high as possible.

(b) Number of nuclei present: The proportionality of S/N ratio to \( \xi N V_c^{1/2} \) indicates that the specimen should contain as many resonating nuclei as possible.

(c) Temperature: The factor \( T^{3/2} \) in the expression indicates that a very low sample temperature will considerably enhance the S/N, though at the expense of experimental simplicity.

(d) Relaxation times: The term \( (T_2/T_1)^{1/2} \) implies that the linewidth should be small, as for example in a liquid, and that the spin lattice relaxation time should be short. \( T_1 \) may often be shortened by the addition of a paramagnetic impurity to the specimen.

(e) Detection system: The factor \( (Q/B_2 F)^{1/2} \) leads to the obvious statement that the S/N ratio is improved by use of a high-Q coil, an amplifier of low noise-factor, and a narrow bandwidth. \( B_2 \) is of the order of \( 1/t_e \), where \( t_e \) is the time constant of the output circuit of the phase-sensitive amplifier; therefore \( B_2 \) is only reduced at the expense of a slower speed of recording information.

Thus the main choices that permits optimisation of the signal strength will be (i) a high, steady magnetic field, (ii) a large sample volume and (iii) as low a specimen temperature as possible.

The basic requirements for observing nuclear magnetic resonance absorption can now be considered. A sample of material, containing large number of nuclei in which one is interested, is subjected to a strong and steady magnetic field \( H_0 \). It is then necessary to wait for a period several times longer than the spin-lattice relaxation time for the spin system to come into thermal equilibrium with the lattice. Facilities must now be provided for subjecting the sample to a radiofrequency magnetic field of appropriate strength in a direction at right angles to \( H_0 \). This is achieved by winding a coil around the sample, its axis in the direction of the desired oscillatory field, and by passing an r.f. current through the coil. Provision must now be made for adjustment either of the magnitude of the steady field \( H_0 \), or of the radio frequency \( \nu \), until the resonance condition is reached. Under this condition the maximum power is absorbed from the radiofrequency field. This resonance condition is detected by observing the additional power flow, equivalent to extra losses in the coil supplying the radiofrequency [12].

3.8: A Typical wideline NMR spectrometer

A typical arrangement for wideline continuous wave NMR spectrometer is as shown in Fig.3.1. The magnetic field is \( -1 \) Tesla (10,000 gauss) with reasonable (but not necessarily outstanding) stability and homogeneity, capable of being swept linearly over
Fig. 3.1: Block diagram of typical CW wideline NMR spectrometer
field ranges up to \(-5\text{mT}\) at rates varying down to \(-0.1\text{mT}\) per minute. Additional audio frequency field modulation is used by superimposing a small sinusoidal field variation by modulation coils fixed round the polecaps. The absorption signal detected by the NMR probe can be displayed on an oscilloscope, in which case the modulation strength should be around five to ten times the width of the resonance line under investigation.

For recording of the NMR signal, the output of the NMR probe is fed into the lock-in amplifier, the reference for which is derived from the modulation oscillator. Besides, to avoid any distortion of the lineshape, the amplitude of field modulation is reduced to less than one fourth the linewidth [13]. The derivative output of the lock-in amplifier is then recorded either on a strip chart recorder or on an X-Y recorder, whose X-sweep is linked with the slow linear field sweep.
REFERENCES

[12] E.R Andrew; Nuclear Magnetic Resonance (Great Britain; Oxford University Press1969)