Chapter 2

INSTRUMENTATION

One of the aims of the work reported in this thesis is to set up an experimental facility to undertake nuclear spin lattice relaxation studies over a wide frequency and temperature range. A conventional pulsed NMR spectrometer operating over 5 to 50 MHz of proton frequencies already exists in the laboratory. In order to carry out measurements below 5 MHz, a field cycling NMR (FCNMR) spectrometer has been fabricated as part of the present work. The details of the instrumentation done are presented in three sections in this chapter. The first section covers the general methodologies involved in pulsed NMR experiments and certain common pulse sequences used for the measurement of different relaxation times. The technique and the design considerations of field cycling experiments are discussed in the second section. The instrumentation carried out for setting up the field cycling spectrometer and the control circuit are also described in this section. Further, the details and specifications of the pulsed NMR spectrometer used to do the experiments in the frequency range of 5 - 50 MHz, along with certain accessories are described in the third section. Finally the fourth section describes the experimental procedure used for spin-lattice relaxation measurements in liquid crystals.
2.1 Methodology of pulsed NMR experiments

NMR experiments are generally done either in frequency domain or time domain. In the frequency domain experiments (CW technique), a low power rf radiation is applied to the sample in a high dc magnetic field. Either the frequency of rf or the strength of the dc field is slowly swept through resonance. On the other hand, in a time domain experiment (pulse technique), the response of the spin system excited by intense bursts of high powered resonant rf magnetic fields for short durations is monitored. While, the CW method deals with the study of absorption and dispersion spectra, $F(\omega)$, the pulsed irradiation method deals with the study of time correlation of a specific dynamic quantity $f(t)$ sensitive to the detection system. The two methods are related by Fourier transformation (FT) given by

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) \exp(-i\omega t) dt \quad (2.1)$$

and inversely

$$F(\omega) = \int_{-\infty}^{\infty} f(t) \exp(i\omega t) d\omega \quad (2.2)$$

and hence the same spectral information can in principle be obtained from both methods. However, the time domain method, which is the topic of present work, is more efficient regarding the time consumed and also the sensitivity of the signal obtained, since all the spins are excited simultaneously and not sequentially. Another advantage of time domain experiments is that the response of the system is phase coherent, i.e. there is a definite reference point in time (point of excitation) for measurement of all the components of response (Derek Shaw, 1976).

A nuclear magnetic moment $\mu$ (arising due to a spin $I$ where $\mu = 7/2$), under the influence of an external magnetic field $H$ experiences a torque $\mu \times H$, which is equal
to the rate of change of angular momentum. The resulting equation of motion of the magnetic moment in a fixed coordinate system xyz (Laboratory frame) is given by

$$\frac{d\mu}{dt} = \gamma (\mu \times H)$$

(2.3)

Since \(\sum \mu_i = M\), the total magnetization of the system, the equation of motion for the macroscopically observable total magnetization can be written as

$$\frac{dM}{dt} = \gamma (M \times H)$$

(2.4)

The application of a perturbing rf field, \(H_1(t)\) (with a frequency \(\omega\)), in a plane perpendicular to \(H\) (say along the \(x\) axis), modifies eqn.(2.4) as

$$\frac{dM}{dt} = \gamma M \times [H + H_1(t)]$$

(2.5)

The solution of the above equation is simplified when viewed from a different coordinate system \(x'y'z'\), which is rotating with respect to the Laboratory frame about some axis, say the \(z\)-axis, with an angular frequency, same as that of the rf field (Slichter, 1978). The equation of motion of the magnetization in this rotating coordinate system is similar to that in the Laboratory frame, with the magnetic field replaced by an effective field, \(H_{eff} = [(H + \omega/\gamma) + H_1(t)]\), (Fig. 2.1) i.e.,

$$\frac{\partial M}{\partial t} \bigg|_{rot} = \gamma M \times (H_{eff})$$

(2.6)

Thus the spins precess about an effective field in the rotating frame, with angular frequency \(7 H_{eff}\). Chosing \(H\) to be along the \(z\)-axis of the laboratory frame i.e., \(H = k H_o\) (where \(k\) is an unit vector along \(z\)-axis), the effective field is modified to \(H_{eff} = [(H_o + \omega/k)k + H_1i]\). Also choosing the frequency of the rotating frame to be equal to that of the Larmor frequency, i.e., \(\omega = \omega_o = -\gamma H_o\), it can be seen that
the effective field in the rotating frame is \( i/|i| \) and hence the magnetization that was initially parallel to \( H_0 \) now precesses about \( H_1 \) in the \( y'z' \) plane. If such an rf is applied for a time \( t_w \), the angle by which the magnetization precesses is given by

\[
\theta = \gamma H_1 t_w
\] (2.7)

Thus with an appropriate combination of the intensity and the duration of the rotating field, the magnetization can be rotated by any desired angle. For a given \( H_1 \), a pulse applied such that the magnetization is rotated by 180° is called a \( \pi \) pulse and a pulse applied such that the tilt angle \( \theta = 90° \) is called a \( \pi/2 \) pulse.

In practice, the perturbing field \( H_1 (2) \), which is an alternating magnetic field can be achieved by the application of a sinusoidal voltage across the sample coil. This results in a linearly polarized field along the axis of the coil which can be considered as consisting of two components counter-rotating about an axis perpendicular to the polarization axis. At resonance, the component rotating in the same sense as the magnetic moment alone is effective in exciting the spin system and the other component rotating in the opposite direction is neglected.

Following the turn off of the excitation field, say a \( \pi/2 \) pulse along \( x' \) axis, the magnetization is rotated into the \( y' \) direction in the rotating frame, but precesses with Larmor frequency \( \gamma H_0 \) with respect to the laboratory frame. This precessing magnetization induces an alternating voltage in a pick up coil surrounding the spin system, with its axis perpendicular to the laboratory field. In an actual experiment, the precessing magnetization decays owing to various interactions among the spins which are the objects of NMR study. The interaction between the different nuclei leads to the spins experiencing different fields \( H = H_0 \pm A H \), where \( A H \) is the field due to neighbouring nuclei. This results in the spins precessing with different frequencies and hence leads to a dephasing of the spins in the \( x'y' \) plane. Consequently the magnetization decays exponentially with a time constant \( T_2 \), called the spin-spin relaxation time. This signal induced in the pick up coil is a decaying, free precession signal and hence is called the Free Induction Decay signal (FID).
Fig. 2.1 Effective field \((H_{\text{eff}})\) in the rotating frame and motion of the magnetic moment \(\mu\) around \(H_{\text{eff}}\).
An important factor to note at this point is that any inhomogeneity in the static magnetic field will result in different spins experiencing different static fields, $H_o = H_o \pm \delta H$. This leads to a further spatial distribution of the resonance frequencies of the spins and consequently a faster dephasing of the spins in the $x'y'$ plane. The time constant associated with this process, $T_2^*$, is called the apparent spin-spin relaxation time, which is less than $T_2$.

The decaying magnetization in the $x'y'$ plane, described above, after the removal of $H_1$, simultaneously evolves to the equilibrium value (parallel to the $z'$ and hence $z$ axis), under the influence of the static field $H_o$, with a time constant characterised by the interaction of the spins with external degrees of freedom, $T_1$, called the spin lattice relaxation time. Combining these factors, the equation of motion for the spin system given by eqn. (2.4), can be modified to account for these different relaxation processes as (Bloch, 1946)

\[
\frac{dM_z}{dt} = \gamma (M \times H)_z + \frac{M_o - M_z}{T_1}
\]

\[
\frac{dM_x}{dt} = \gamma (M \times H)_x - \frac{M_x}{T_2}
\]

\[
\frac{dM_y}{dt} = \gamma (M \times H)_y - \frac{M_y}{T_2}
\]

The decay of the magnetization in the transverse plane conserves energy in contrast to the magnetization decay along the longitudinal direction and hence $T_2$ is different from $T_1$. From Fig. 2.2a, it is clear that the time constant of loss of magnetization in the $xy$ plane will never be greater than the time constant of development of magnetization along the $z$-axis i.e., $T_2 < T_2 < T_1$. If the resonance condition is not satisfied, the magnetization vector still relaxes as $e^{-t/T_2}$, but simultaneously processes about the $z'$ axis with the offset frequency, $\omega_i$. The tip of the vector describes a decaying helix as shown in Fig. 2.2b. The component normally detected by the application of magnetic field along $x'$ axis is the $y'$ component of this decaying signal i.e., $M_o e^{-t/T_2} \cos(\omega_i t)$, which on FT yields the Lorentzian signal offset by $\omega_i$ from $\omega_o$. 

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Fig. 2.2a Spin-spin relaxation and spin-lattice relaxation.

(a) Equilibrium magnetization $M_0$ when $H_1 = 0$
(b) Magnetization immediately after $\pi/2$ pulse along $x'$ axis.
(c) Spin-spin relaxation in progress
(d) Free induction decay (i) in the absence and (ii) in the presence of static field inhomogeneity
(e), (f), (g) Spin lattice relaxation in progress.
Fig. 2.2b The off resonance decay and precession of the nuclear magnetization showing the origin of two components
Thus the basic idea of any relaxation time measurement is to disturb the magnetic state from its equilibrium to a given non equilibrium state by an initial pulse (preparation pulse) and then study the evolution of the system back to equilibrium by monitoring the appropriate magnetization component after a variable delay, with another pulse (sampling pulse).

2.1.1 Zeeman Spin-lattice relaxation time \((T_1)\)

During spin lattice relaxation process, the magnetization parallel to the quantizing field \((z\text{-axis})\) in the present case) evolves. Since the pick up coil is sensitive only to the component of magnetization perpendicular to the \(z\text{-axis}\), the magnetization that is developed along \(z\) axis due to \(T_1\) process is detectable only after it is rotated away from the quantizing axis. The different pulse sequences normally used for measuring \(T_1\), their relative merits and demerits are given below.

Saturation recovery sequence \((\pi/2 — T — \pi/2)\)

This sequence consists of a \(\pi/2\) pulse followed by another \(7\pi/2\) pulse applied after a variable delay \(r\). The first \(7\pi/2\) pulse flips the magnetization into the \(xy\) plane (magnetization along the \(z\)-direction is made zero), which is then allowed to evolve for a time \(\tau\) and then sampled by the second \(7\pi/2\) pulse which tilts whatever magnetization that has developed along the \(z\text{-axis}\) into the \(xy\) plane for observation. The amplitude of the FID, \(A(T)\) at a fixed time from the sampling pulse develops from zero at time \(\tau = 0\) to \(A_0\) at time \(\tau = oo\) and satisfies the following equation (Fig. 2.3)

\[
A(\tau) = A_0(1 - \exp(-\tau/T_1))
\] (2.9)

By repeating the experiment for different values of \(\tau\) and then fitting the data to the above equation, \(T_1\) is obtained.

Inversion recovery sequence \((\pi - r - 7\pi/2)\)

This sequence consists of tilting the equilibrium magnetization into the \(-z\) direction using an initial \(\pi\) pulse and then monitoring the evolution along \(z\)-axis by
Fig. 2.3a Saturation recovery sequence for $T_1$ measurements.

Fig. 2.3b Recovery of magnetization in the $z$-direction with time $T$. 
another sampling $7\pi/2$ pulse after a time $\tau$. The preparation ($\pi$) pulse inverts the spin population initially and hence the $z$ component of magnetization recovers from $-M_o$ to $M_o$. The magnetization recovery follows the equation, (Fig. 2.4)

$$A(t) = A_0(1 - 2\exp(-\tau/T_1))$$ (2.10)

$A_o$ being the amplitude of the FID after a time $T = \infty$. A least square fitting of the data to the above equation will give the spin lattice relaxation time, $T_1$.

The advantages of this pulse sequence over saturation recovery sequence are

1. $T_1$ can be roughly estimated by finding the time $\tau_o$ for which the magnetization is zero, as $T_1 = \tau_o/\ln 2$.

2. The data has twice the dynamic range ($-M_o$ to $M_o$) as compared to saturation recovery sequence ($0$ to $M_o$), hence increasing the apparent signal to noise ratio.

The disadvantages of this method over the saturation recovery sequence are that this sequence starts with an initial equilibrium magnetization of the spin system in the $-z$ direction and the magnetization has to evolve into the $z$ direction before repeating the sequence for signal averaging. Hence a considerable amount of time ($> 5T_1$) is to be spent for full recovery of the magnetization before the sequence is repeated and this will be time consuming if $T_1$ is more than a few hundreds of milliseconds.

The spectral width covered by the preparation pulse ($\pi$) in this sequence is less compared to that of the $n/2$ pulse in saturation recovery sequence for a given transmitter power and hence the saturation recovery sequence yields a better lineshape and intensity for broad lines.

One disadvantage of both these pulse sequences is that, if the preparation pulse width is not exactly set ($\pi$ or $7\pi/2$), which is often the case, or if $H_1$ is not homogenous, the initial condition of the magnetizations ($-M_o$ or zero) is not met with, hence leading to reduction in the signal strength.
Fig. 2.4a Inversion recovery sequence, for $T_1$ measurements.

Fig. 2.4b Recovery of magnetization with time $t$ of the sampling pulse.
Saturation burst sequence

A variation of saturation recovery sequence is the saturation burst sequence, where the preparation $\pi/2$ pulse is replaced by a closely spaced burst (usually 5 to 10) of $\pi/2$ pulses which is followed by a sampling $\pi/2$ pulse after a variable time, $r$. The spacing between the pulses in the burst is chosen to be greater than $T_2$, but much less than $T_\lambda$ (Fig. 2.5). The advantage of using this sequence is that the burst ensures the zeroing of magnetization, even if the pulse width is not exactly set to $\pi/2$ or if $H_1$ is slightly inhomogeneous. The evolution of the magnetization after the preparation pulse is given by eqn. (2.9). The other advantage of this sequence over the inversion recovery sequence is that the tedious waiting time ($> 5T_1$) for long $T_\lambda$ measurements is eliminated as there is no need for allowing the magnetization to recover fully before the sequence is repeated. In the actual experiments, the first pulse of the next burst can be used as the sampling pulse.

2.1.2 Slow frequency processes

The relaxation process where the magnetization is allowed to evolve under the influence of $H_1$ in the rotating frame instead of the Zeeman field, is termed as the spin lattice relaxation in the rotating frame, with the corresponding time constant referred to as spin lattice relaxation time in the rotating frame, $T_{1p}$. Similarly, if the magnetization is allowed to decay under the influence of the local dipolar fields, $H_{loc}$ ($H_{loc} \gg H_o$), the corresponding relaxation time is known as the dipolar spin lattice relaxation time, $T_{1D}$. Both $T_{1D}$ and $T_{1p}$ sample low frequencies compared to $T_1$ and hence can give information about slow dynamics of the system under consideration. The different $rf$ pulse sequences necessary for the measurement of the above discussed relaxation times are described below.

Spin lattice relaxation time in the rotating frame ($T_{1p}$):

The methodology for the measurement of $T_{1p}$ involves locking the spin system to a small $rf$ field, $H_1$, in the rotating frame and observing the magnetization as it evolves from the initial equilibrium value corresponding to $H_o$ to the final equilibrium value corresponding to $H_1$ (Fig. 2.6).
Fig. 2.5a Saturation burst sequence for $T_1$ measurements.

Fig. 2.5b Recovery of magnetization with time $r$ of the sampling pulse.
The first \(7\pi/2\) pulse flips the magnetization from \(z\)-axis into the \(x'y'\) plane. The second 90\(^\circ\) phase shifted pulse, applied immediately after the first pulse of variable width, locks the spin system to \(H\) since the \(rf\) field and the magnetization are in the same direction in the rotating frame (Hartmann and Hahn, 1962). Now the magnetization evolving in the presence of the rotating frame magnetic field is given by

\[
A(T) = A_0 \exp(-\tau/T_{1p})
\]  (2.11)

where \(\tau\) is the variable time for which the locking field is applied. Here \(A(\tau)\) corresponds to the amplitude of the FID after an evolution time \(\tau\). By fitting the experimental data (amplitude of the FID as a function of \(\tau\)) to the above equation, \(T_{1p}\) can be calculated.

**Dipolar relaxation time** \((T_{1D})\):

The low frequency motions corresponding to the local dipolar fields can be analyzed by measuring the dipolar spin lattice relaxation time, \(T_{1D}\) which is achieved by transferring the Zeeman order to the dipolar order and measuring the decay of magnetization in the presence of dipolar fields as the system evolves. Two techniques can be used for this purpose (a) adiabatic demagnetization in the rotating frame (ADRF) (Slichter and Holton 1961; Fukushima and Roeder, 1981; Ailion, 1983) and (b) Jeener Broekaert phase shifted pulse sequence (1967). The first technique consists of following a spin locking pulse by an adiabatic demagnetization - remagnetization cycle of the \(rf\) field, while the second technique consists of creating the dipolar order by a pair of phase shifted \(rf\) pulses and then monitoring the decrease of the dipolar order by a third pulse. Though ADRF is an efficient method which enables 100% transfer of Zeeman order to dipolar order the Jeener-Broekaert sequence is used in the present work, due to the convenience in measuring short \(T_{1Ds}\) and also due to the ease with which this sequence can be implemented.

**Jeener Broekaert sequence** \((7\pi/2) o-t -(\pi/4)_{90}-\tau -(\pi/4)\)

In this technique suggested by Jeener and Broekaert (1967), a state of dipolar
Fig. 2.6 Pulse sequence for $T_{1p}$ measurement.

Fig. 2.7 Jeenar-Broekaert (three pulse) sequence for $T_{1D}$ measurement.
order is created by the application of two closely spaced rf pulses which are 90° out of phase (Fig. 2.7). The first $\frac{\pi}{2}$ pulse tilts the magnetization into the $xy$ plane. The magnetization decays under the influence of the local dipolar fields after the second $\frac{\pi}{4}$ pulse. This decay is then observed by applying a third pulse after an evolution time $r$, which transfers the remaining dipolar order to Zeeman order. Since the dipolar order is not aligned about any preferential direction, the condition on the phase of the third pulse is not stringent and it can have any phase. An echo (called dipolar echo) is obtained after the third pulse which is a measure of the remaining dipolar order. The decay of amplitude of the dipolar echo i.e., $A(T)$ as a function of the delay between the second and third pulses is given by

$$A(\tau) = A_x \exp(-\tau/T_{1D})$$

(2.12)

where $\tau$ is the variable time between the second and the third (sampling) pulse. The third pulse is followed by an FID which is 90° out of phase with the dipolar echo, while the second pulse is followed by the solid echo. Hence for detecting the dipolar echo alone, it is ensured that the reference signal to the phase sensitive detector (in the receiver) is 90° out of phase with respect to the FID. In actual experiment, the reference phase to the receiver is adjusted to maximize the FID following the first pulse and the third pulse is set to be 90° out of phase with respect to the first pulse. Also to maximize the echo, it is necessary to place the second pulse at the steepest part of the FID after the first pulse. The efficiency of this sequence in setting up the dipolar order is maximum (56%) when the second and third pulses are $\frac{\pi}{4}$.

Both $T_{1p}$ and $T_{1D}$ measurements can give valuable information about molecular dynamics at very low frequencies (typically up to 100 kHz) where it is not possible to do conventional Zeeman relaxation measurements due to very poor signal to noise ratio. While $T_{1D}$ samples motions corresponding to dipolar fields (around 10 kHz and less), $T_{1p}$ can sample molecular dynamics around 100 kHz (limited by maximum possible locking field strength $H_1$). This restriction is due to the maximum available rf power as well as rf heating of the sample due to the application of high powered rf for longer times. Hence, there exists a considerable gap between the lower limit of
accessible frequency in conventional NMR and high frequency limit of $T_{1p}$ technique, which extends to about two orders of magnitude in frequency. Further information on the molecular dynamics in this frequency range necessitates a more versatile technique. In this regard, Field cycling NMR (FCNMR) technique (Anderson and Redfield 1959; Kimmich and Bachus 1982; Noack, 1986) is more efficient and suited as it facilitates $T_1$ measurements down to 0 Hz. The details of the FCNMR technique along with the design considerations are explained below.

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2.2 Field cycling NMR

Low frequency $T_1$ studies are capable of giving insight into the slow molecular processes. Particularly such studies are extremely useful in liquid crystals where collective fluctuations associated with the director are mostly limited to the frequency region below 1 MHz. But conventional NMR technique can be used only at frequencies above a few MHz (typically 5 MHz). Below this frequency, signal to noise ratio becomes unacceptable, since the NMR induction signal is proportional to $(H_0)^{3/2}$ (the energy levels at equilibrium are more evenly populated as the Zeeman field (and hence frequency) is decreased). On the other hand, an FCNMR spectrometer makes it possible to extend the scope of field dependant measurements to almost zero Larmor frequency, while allowing for the convenience of high frequency signal detection. Further, using the FCNMR technique, any frequency dependant study between a given minimum and maximum obtainable frequencies can be easily done without having to tune the spectrometer independently at each frequency (as the frequency where the signal is detected is not altered in this technique). Another important application of FCNMR is the zero field or low field NMR relaxation (Das and Hahn 1958; Hebel and Slichter 1959; Masuda and Redfield, 1962, 1964; Refield, 1963, 1967; Slusher and Hahn, 1968; Edmonds, 1981) where the Zeeman energy and consequently line broadening caused by the distribution of molecular orientations due to the Zeeman field vanish thus enhancing the spectral resolution.
Apart from just lowering the intensity of the fields (and hence induction $B_0$), field cycling may as well include evolution periods with higher field intensity than the detection field, - or even changing the direction of the field - , and hence this technique offers capabilities which go far beyond the original intentions. Cycling of the orientation at high speed facilitates the angular dependant relaxation and diffusion measurements in liquid crystals with relative ease compared to other cumbersome methods of field rotation. Apart from frequency dispersion studies over a wide frequency range, FCNMR spectrometer can be used in (i) certain level crossing experiments (Hecke and Janssens, 1978; Coppen et al. 1983; Prager et al. 1983) (ii) detection of weak and low frequency resonance signals (Schweikert, 1990) (iii) cross relaxation spectroscopy (Solomon, 1955; Solomon and Bloembergen, 1956; Seliger et al. 1976; Koenig et al. 1978; Vilfan et al. 1980; Winter and Kimmich, 1982a,b; Blinc et al. 1983) and (iv) certain 2d experiments (Dolinsek et al. 1992). Some of the manifold applications of FC were illustrated by Kimmich (1980). The details of the fabricated FCNMR spectrometer taken up as part of the present work are given in this section. The FCNMR spectrometer has been tested and standardized. However, it could not be utilized for actual measurements on the five liquid crystals on which detailed high frequency dispersion study of spin relaxation has been taken up by the author, owing to the limitation on time in completing this project.

2.2.1 Technique

Field cycling technique involves the sample being kept at different Zeeman fields (or magnetic induction) during different times of a relaxation experiment. In other words, the induction is modulated periodically in strength (also direction in case of angular dependent measurements). The nuclear spins are polarized and detected at a sufficiently high field to yield a satisfactory signal to noise ratio ($S/N$). But between the polarization and detection periods, the field (evolution field) is varied from the selected high value to an adjustable lower field. Thus, though the signal is detected at a sufficiently higher field, the properties characteristic of the spins for frequencies between the minimum and maximum can be conveniently studied at a single detection frequency. Comparison of the sensitivity of the induced signal in
the induction coil during an FC experiment with a conventional NMR experiment at low fields (corresponding to evolution fields), clearly shows the signal enhancement in the former case (Noack, 1986). The simplest cycle involving the different periods and times is shown in Fig. 2.8. The polarization field \( B_{OP} \) corresponding to the polarization period \( t_P \) is made as high as possible with moderate requirements on homogeneity. \( B_{OE} \) is the variable evolution field \( (0 < B_{OE} < B_{OP} - B_{OD}) \) and \( B_{OD} \) is the detection field \( (t_D \) is the detection period \) which is again made as high as possible with better homogeneity for signal detection. ‘\( T' \) is the total period of the cycle which is repeated many times during the course of the relaxation time measurements. The transit times \( t_{OFF} \) (\( B_{OP} \rightarrow B_{OE} \)) and \( t_{ON} \) (\( B_{OE} \rightarrow B_{OD} \)) are the times of switching the field OFF and ON respectively. The main conditions to be satisfied by these transit times is that on one hand they should be fast compared to the relaxation times of the spin system under study (to avoid losses of the magnetization) and on the other hand, they should be slow enough such that the Fourier spectrum of the time varying magnetic fields do not contain components in the vicinity of the Larmor frequency. Finally, the cycle has to be synchronized with appropriate intervals of the \( rf \) irradiation \( (H_1(t)) \) common to the conventional NMR to prepare the system into an initial non-equilibrium state or to detect the induced signal.

### 2.2.2 Magnet

Conventionally the desired cycle can be obtained by two methods. The first is by mechanical movement of the sample between the chosen magnetic fields (Pound, 1951; Schumacher, 1958; Abragam and Proctor, 1958; Pershan, 1960; Johnson and Goldberg 1966; Jones et al. 1968; Blinc et al. 1976; Edmonds, 1977). The other method involves electronic switching wherein the field cycling is achieved by varying the current through an inductive load (magnet) (Packard and Varian, 1954; Bloom and Mansir, 1954). Mechanical cycling can be performed with simple apparatus and also there is no limit on the obtainable polarization and detection field levels. But the switching intervals are limited due to the mechanical movement of the sample. On the other hand, electronic switching results in much faster intervals and is also more suited for automation though the experimental realization for higher fields is
Fig. 2.8 Typical field cycle, with polarization, evolution and detection periods separated by the transit intervals $t_{ON}$ and $t_{OFF}$. 
more involved. In the present case, electronic switching is chosen.

From the simple understanding of the behavior of an inductive load, the maximization of the induction and its rate of variation impose contradicting restrictions. Hence optimization of both these parameters necessitates the critical consideration of the relations between $B_o$ and $dB/dt$.

Optimization of $B_o$ and $dB_o/dt$

Due to the large number of parameters involved, an empirical approach (involving standard formulae on the magnetic field for different geometries) is usually adopted during the construction of an FCNMR magnet. Of the various geometries for the design of the coil available in the literature (Redfield et al. 1968; Kimmich and Noack, 1970; Brown and Koenig, 1977; Wolfel, 1978; Graf, 1980; Voigt and Kimmich, 1980; Rommel et al, 1986), the Helmholtz ring pair and cylindrical geometries are well known (Fig. 2.9). The Helmholtz ring pair arrangement, though has an advantage of well understood mathematics and a convenient radial access to the center, is limited by the marked reduction in the induction at the center of the coil compared to that near the windings. Further good homogeneity is limited to a relatively small area around the center. In this respect, cylindrical coils are found to be superior to Helmholtz ring pairs as regards to many specifications like maximum induction, homogeneity and total field volume since, for a given volume, cylindrical geometry provides a better $B_o/I$ ratio. However the inconvenience of having only axial access to the field (at the center) is a disadvantage to be accepted with the above advantages. Due to the above reasons, in the present case a cylindrical geometry is chosen.

The induction along the axis of a long solenoid of length $l$, radius $r$ and number of turns $n$ in a medium of permeability $\mu$ is given by

$$B_o = \mu H_o = \mu \frac{n}{l} \left[ 1 + \left( \frac{r}{l} \right)^2 \right]^{-1/2} I$$

(2.13)

where $I$ is the current through the coil. The rate of change of current through the coil, $dl/dt$, for an applied voltage ‘$U$’ is given by Faraday’s law of induction as
Fig. 2.9 The two well known geometries for the design of a coil
(a) Helmholtz ring pair \( a \ll R_o \)
(b) Cylindrical geometry (Solenoid) \( d \ll R_o \ll 1 \)

Fig. 2.10 A simple concept of electronic switch for cycling between two current levels \( I_{\text{min}} \) (corresponding to \( BOB \)) and \( I_{\text{max}} \) (corresponding to \( BOP \) and \( BOD \)).
\[
\frac{dI}{dt} = \frac{U - I}{L} R_s 
\]  
(2.14)

where \( R_s \) is the series resistance and \( L \) is the inductance of the coil, given by

\[
L = \frac{\mu n^2 \pi r^2}{l} 
\]  
(2.15)

The above equations clearly indicate that \( B_0 \) and \( dB/dt \) cannot be optimized independently since maximization of one decreases the other. Thus, a compromise has to be found between them for efficient switching. Eqn. (2.13) and eqn. (2.14) can be rewritten in terms of the volume \( V \) of the coil and inductance \( L \) as

\[
B_0 \big|_{\text{max}} = \sqrt{\frac{\mu L}{V}} I \]  
(2.16a)

\[
\frac{dB}{dt} \big|_{\text{max}} = \sqrt{\frac{\mu}{VL}} U \]  
(2.16b)

From the above equations

\[
(B_0)_{\text{max}} \times \left( \frac{dB}{dt} \right)_{\text{max}} \sim \mu/V 
\]  
(2.17)

which clearly shows that simultaneous maximization of \( B_0 \) and \( dB/dt \) depends on the effective volume \( V \) of the coil and the permeability \( \mu \) of the core material used and is independent of other quantities.

Field switch

The simplest realization of the electronic switch is given in Fig. 2.10, which facilitates the switching between two different states. The power supply generates two current levels in the coil of inductance \( L \) and series resistance \( R_s \), through the switch \( S \) and an adjustable parallel resistance \( R_p \). The sum \( R_p + R_s \) determines the lower level of current, \( I_{\text{min}} \), while \( R_s \) determines the upper level of the current, \( I_{\text{max}}. \)
Initially, when the switch $S$ is closed, a voltage $U_o$ applied to the coil increases the current ($I$) exponentially with a time constant $\tau_{on} = L/R$, i.e.,

$$U_o - L \frac{dI}{dt} = IR_s$$

(2.18)

Similarly, when the switch $S$ is open, the voltage across the coil decreases with a time constant $\tau_{off} = L/(R_s + R_p)$ i.e.,

$$U_o - L \frac{dI}{dt} = I(R_s + R_p)$$

(2.19)

From the above two equations, it is clear that the transit times are shorter for larger values of $R_s$ and $R_p$ and smaller values of $L$. The increase in the value of $R_s$ and $R_p$ are limited by the facts that

1. increase in $R_s$ beyond a point results in an enormous increase of supply voltage (for a given maximum current).

2. increase in $R_p$ fails to suppress the excessive voltages induced due to the sudden decrease in the current during turn OFF.

However, from the turn ON and turn OFF characteristics, it is clear that though the equilibrium state is reached faster for higher values of $R_s$ and $R_p$, the fastest rate of increase or decrease of current are independent of $R_s$ and $R_p$, since

$$\frac{dI}{dt} \bigg|_{max} = \frac{|U_o|}{L}$$

(2.20)

In fact, the slope $U_o/L$ for the characteristics is maintained longer for smaller values of $R_s$ and $R_p$ (linear characteristics in Fig. 2.11a and Fig. 2.11b). In other words, the limit $R_s \rightarrow 0$ (cryomagnet limit) results in better transit times than a normal conducting coil. The current through the coil during the transits is given by
Fig. 2.11a Turn OFF characteristics for different values of $R_p$ and $\tau_{\text{off}}$.

$R_p$ is given in terms of arbitrary value $R_{s0}$.

Fig. 2.11b Turn ON characteristics for different values of $R_s$ and $\tau_{\text{on}}$.

The linear increase $\frac{dl}{dt} = \frac{V_o}{L}$ represents the $R_s>0$ limit.

$R_s$ is given in terms of arbitrary value of $R_{s0}$ (Moach, 1986).
Another alternative to reduce the transit times is to reduce the inductance of the coil as evident from eqn. (2.20) i.e., by replacing iron core magnets of larger inductance by air core magnets of small inductance, compatible with other requirements on the cycle like satisfactory induction fields.

Energy storage principle

Another important factor which results in a marked improvement in the transit times is the increase in the voltage across the coil during the transits (eqn. (2.20)). This can be achieved using energy storage principle (Redfield et al. 1968) which is explained below. During major portions of the cycle (i.e. during the low evolution and transit periods) the full power from the supply, \( P_o = I_o U_o \) is not dissipated in the circuit elements. If this redundant energy \( E_{\text{red}} \) can be transferred by a storage device to the turn ON period where it becomes useful and acceptable by the switching circuit, instead of increasing the supply voltage, the switching times can be reduced. The simplest way to achieve this, is by charging a powerful capacitor \( C \) by means of \( E_{\text{red}} \) and then to take advantage of the voltage generated on \( C \) during the transits, to reduce them.

The current characteristics given in eqn. (2.21). are now modified to

\[
I_{\text{ON}}(t^\prime) = I_{\text{min}} + \left( \frac{U_o}{R_s} - I_{\text{min}} \right) \left( 1 - e^{-R_s t^\prime/L} \right) \hspace{1cm} (2.21a)
\]

\[
I_{\text{OFF}}(t^\prime) = I_{\text{min}} + \left( \frac{U_o}{R_s} - I_{\text{min}} \right) \left( e^{-(R_s+R_p) t^\prime/L} \right) \hspace{1cm} (2.21b)
\]

where \( U_+ = U_o + U_c \). Fig. 2.12 shows the improvement in the turn ON transits achieved using the energy storage principle.
Fig. 2.12 Turn ON characteristics after incorporating energy storage principle for different values of $U_e$. (Moak, 1986)
Magnetization during the transits

Unlike in conventional NMR, where the magnetization (under the influence of a constant Zeeman field) at different stages is perturbed by a small field $H_1$, in FCNMR, the Zeeman field itself is modulated and hence the effects of this modulation on the magnetization also is to be considered (since the behavior of spins in the evolution period necessarily depends on the behavior during the other periods of the cycle and especially during transits). Considering the equilibrium value of the magnetization to be $M_o$ and the spin lattice relaxation time, $T_1$ to be field dependent, the Bloch equation for the magnetization parallel to the external field, $M_z$ can be written as

$$\frac{dM_z}{dt} = \gamma [M(t) \times B_o] - \frac{1}{T_1(B_o)} [M_z(t) - M_o(B_o)] \quad (2.23)$$

Let the equilibrium values of $M_z$ in the polarization, evolution and detection periods be $M_{OP}$, $M_{OE}$ and $M_{OD}$ with the corresponding spin lattice relaxation times $T_{1P}$, $T_{1E}$ and $T_{1D}$ respectively. The condition on the transit times is that the switching is fast compared to the relaxation times i.e.,

$$t_{off} + t_{on} \ll T_1(B_o)_{\text{min}} \quad (2.24)$$

but slow enough compared to the Larmor frequency $\omega_o$ so that the magnitude and the angle between $M(t)$ and $B_o(t)$ is preserved.

The above two conditions ensure that there is no change of magnetization during the transits and hence the field after the transits is constant and parallel to the applied field just before the transits i.e.,

$$M_z (B_{OP} \rightarrow B_{OE}) = \text{constant} = M_{OP} \quad (2.25a)$$

$$M_z (B_{OE} \rightarrow B_{OD}) = \text{constant} = M_{OE} \quad (2.25b)$$

The development of the magnetization in the different regimes of the cycle are summarized in Table 2.1 (Fig. 2.13). Thus FC measurements enable the measurement
Table 2.1: Variation of the magnetization $M(t)$ during the different regimes of an ideal Field cycle.

- **Polarization (P)**: $M_z(t) = M_{OD} = M_{OP}$, $(t < t_P)$

- **Transit (P → E)**: $M_z(t) = M_z(t_P) = M_{OP} = \text{constant}$

- **Evolution (E)**: $M_z(t) = M_{OP} - (M_{OP} - M_{OE}) \left[1 - \exp\left(-\frac{t - t_P}{T_{1E}}\right)\right]$, $(t_P < t < t_E)$

- **Transit (E → D)**: $M_z(t) = M_z(t_E) = \text{constant}$

- **Detection (D)**: $M_z(t) = M_z(t_E) + (M_{OD} - M_z(t_E)) \left[1 - \exp\left(-\frac{t - t_E + t_P}{T_{1D}}\right)\right]$, $(t_P + t_E < t < t_P + t_E + t_D)$
Fig. 2.13 Variation of $M_s(t)$ during a typical field cycle
(the switching times $t_{OFF}$ and $t_{ON}$ are neglected).
of $M_z(t)$ as a function of the magnitude of the evolution field $B_{OE}$. Though most FC experiments are concerned with longitudinal relaxation processes, any other NMR quantities which follow general Bloch type relations like diffusion constant, cross relaxation rate etc., are also measurable through standard NMR procedures with suitable $B_o$ cycles.

To summarize, the requirements and demands for optimization of FC spectrometer are

1. The transit times must be fast compared to relaxation times but slow compared to $\omega_o$.
2. The polarization field should be sufficiently high for initial magnetization.
3. The detection field should be sufficiently high and homogenous to ensure good $S/N$ ratio.
4. The maximum induction and the rate of change of the induction must be optimised simultaneously.

Lastly, the limit on homogeneity and transit times depends on the type of systems under investigation i.e., liquids have smaller line widths and hence require more homogeneous fields even with poor transit times. On the other hand, solids require enhanced $B_o$ and $dB/dt$, with a moderate homogeneity since they have larger line widths. Keeping these factors in view, the field cycling magnet and the necessary electronics to control and switch the field are designed, the details of which are given below.

Design considerations

The crucial part of the instrumentation involved in setting up an FCNMR spectrometer is the design and construction of the switchable magnet. Apart from the usual specifications of an NMR magnet like maximum induction, homogeneity and stability etc., an FC magnet is characterized by an additional feature i.e., the geometry of the coil which enables fast switching. The highest obtainable field $(B_o)_{\text{max}}$
and the fastest rate of change of induction \((dB/dt)_{\text{max}}\) characterizing the magnet are interdependent through the coil parameters like inductance, permeability, volume etc., (eqn. (2.16a) and eqn. (2.16b)). Hence the performance of the magnet can not be ascertained by optimizing any single parameter. The obvious choice thus is to maximize both the quantities simultaneously i.e., 
\[(B_o)_{\text{max}} \times (dB/dt)_{\text{max}} \approx \mu/V,\]
where \(V\) is the effective volume enclosed by the coil. Thus, a good FC coil should be very small and filled with magnetic material of large permeability (in the regions not occupied by the sample). However, both aspects are bound by mathematical and technical problems which are complicated. For example, the choice of the magnetic material is limited since ferromagnetic materials are completely inadequate due to poor frequency response and hysteresis effects, while ferrimagnetic materials are not very promising due to their low \(\mu(B_o)\) saturation. Thus, air core magnets seem to be best choice. Similarly, reduction of volume is limited by the technical requirements on the cooling facility and also a minimum size of the sample and cryostat required for temperature variation measurements.

Homogeneity

Suitable refinements to the cylindrical geometry due to finite length of cylindrical coils result in improved homogeneity. For example, uniform induction can be obtained by (i) linearly varying the number of windings per length (Hak, 1936) (ii) adding outer notches (Grossl et al, 1985) (iii) graduating the spacing between the conductor loops (Cesnak and Kabat, 1972) etc. (Fig. 2.14). Considering all the above factors, a cylindrical geometry with outer notches is chosen in the present case for the design of the magnet.

The optimization method of Grossl (1985), with external notches is followed since it has the advantage of providing accurate field values in a considerable volume around the neighborhood of the center of the coil. The geometrical parameters of a general solenoid (Fig. 2.15 ) are denoted as \(\alpha = R_o/R_i, \beta = 1/2R_i, \theta = fc/i^*, \eta = l_k/l. R = \frac{1}{2}\alpha R_i\) is the mean radius and \(C\) is the layer thickness given by \((a - 1)R_i\). The relative axial and radial variables are \(x = l_o/l\) and \(y = R_o/R_i\). The procedure consists of optimizing the quantity \(B \times dB/dt\) for a given peak input power. The solutions
Fig. 2.14 Variations in the cylindrical geometry to improve the homogeneity of the field
(a) Linear variation of the number windings per length
(b) Addition of outer notches
(b) Graduating the spacing between the conductor loops
Fig. 2.15 The different geometrical parameters of a solenoid to be optimized for homogeneity (ftub'ssL et al. 1985).
of the elliptic integrals obtained (Grossl et al., 1985) result in the switching time, \( r \) being proportional to the square of the flux density. This optimization procedure leads to the different parameters of the coil as given in Table 2.2. The final design of the magnet is given in Fig. 2.16a. The maximum magnetic field obtained in the present case is 1.2 kG with a stability of 1 in \( 10^5 \) in an hour. The requirement of a low ohmic and low inductive magnet is satisfied by winding the coil with copper wire of appropriate dimensions.

The large currents through the coil result in a large power dissipation which necessitates critical cooling requirements. Compressed air, liquid nitrogen, water and oil are convenient cooling agents to remove the heat from the coil, each with its own advantages and disadvantages. Air is not very effective though it is easy to handle. Liquid nitrogen is very effective but is expensive and difficult to regulate. Though water is effective, necessary measures to avoid corrosion by electrolysis are required. Oil is more effective than water but requires a more closed cooling arrangement than water. Considering all the above factors, in the present case, the magnet is enclosed in a closed oil bath which is cooled with chilled running water (Fig. 2.16b).

**Construction details**

The basic circuit used to control and switch the current through the magnet based on the energy storage principle (Noack, 1986) is shown in Fig. 2.17. Here semiconductor devices such as metal oxide semiconductor field-effect transistors (MOSFET’s) are used to control electric currents, since they combine the advantages of bipolar transistors as well as switching components like Gate turn off (GTO) thyristors. The GTO is used to switch the capacitor in and out of the magnet circuit during transits. Here the specifications of the current source determine the maximum induction obtained while the specification of the switching devices (GTO and MOSFET’s) limit the maximum switching times of the cycle. The use of the energy storage principle and the most recent switching devices to overcome the high voltage surges makes the circuit more versatile.

\( N_1 \) is the main power supply (180V/25, APLAB make, No. 7146S), which provides the maximum current needed during the polarization period. The decoupling diodes
Table 2.2: Specifications of the magnet coil.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Geometry</td>
<td>Cylinder with outer notches</td>
</tr>
<tr>
<td>2</td>
<td>material</td>
<td>Copper wire</td>
</tr>
<tr>
<td>3</td>
<td>Total No. of windings</td>
<td>2552</td>
</tr>
<tr>
<td>4</td>
<td>Number of windings in notches</td>
<td>352</td>
</tr>
<tr>
<td>5</td>
<td>Coil length</td>
<td>22 cm</td>
</tr>
<tr>
<td>6</td>
<td>Diameter of the bore</td>
<td>5 cm</td>
</tr>
<tr>
<td>7</td>
<td>Inductance</td>
<td>66 mH</td>
</tr>
<tr>
<td>8</td>
<td>Max. induction</td>
<td>0.15T</td>
</tr>
<tr>
<td>9</td>
<td>Homogeneity</td>
<td>1 in $10^5$</td>
</tr>
<tr>
<td>11</td>
<td>Maximum current</td>
<td>10 A</td>
</tr>
<tr>
<td>12</td>
<td>Cooling agent</td>
<td>Oil</td>
</tr>
<tr>
<td>12</td>
<td>Transit times</td>
<td>5 msec.</td>
</tr>
</tbody>
</table>
Fig. 2.16a Optimized dimensions of the magnet.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total No. of windings</td>
<td>2552</td>
</tr>
<tr>
<td>No. of windings in the notch</td>
<td>352</td>
</tr>
<tr>
<td>Inductance of the coil</td>
<td>66mH</td>
</tr>
<tr>
<td>Resistance of the coil</td>
<td>7 ohms</td>
</tr>
</tbody>
</table>

![Diagram of optimized magnet dimensions](image)
Fig. 2.16b  Cooling arrangement for the coils.
Fig. 2.17  Electronic field switch with power MOSFET's, GTO and energy storage principle.

Fig. 2.18  RCD snubber network to protect the GTO from high voltages.
D₁ (BY 127, 20 of them in parallel) decouples the coil from the mains during the transit times. The action of the storage capacitor, C (three capacitors in parallel, each 3000μF/300V) is enhanced by precharging with the help of an additional power supply N₂ with negligible current demand (1200V/1Amp, APLAB make, 7323), so as to provide extra driving power for the transits. The charging diode D₂ allows the charging of the capacitor C and also decouples the coil from the source N₂ during the transits. The free wheel diode D₃ (Nihon inter elect. corp. model no. 45MLA), provides a path for current during the turn off interval, where the energy of the coil is transferred to the capacitor. The transistor arm T consists of 20 MOSFETs (IBRFPG 40) which enables the control of the fields. The GTO thyristor G (Model No. 358RGA100 of Nihon Interelec. Corpn.) used during turn ON period is protected against excessive voltages or current transients using a snubber network (Fig. 2.18 ) consisting of a combination of a resistor R, a capacitor C and a diode D. The working of the circuit during different time intervals is broadly explained below (Fig. 2.19).

1. During high or low field periods the coil current is regulated at any chosen value, by the MOSFET control circuit (Fig. 2.19a).

2. During the transit from high to low fields (turn off of the field), the signal corresponding to the required low field is given to the MOSFET control circuit, resulting in the reduction of the current and also generation of large voltage at the coil. The energy storage condenser C is precharged by N₂ and is further charged with the coil voltage to a higher voltage Uₑ, during this period. If the precharged voltage is close to Uₑ, the capacitor charges quickly to the maximum value resulting in a faster decay of the current through the coil (Fig. 2.19b)

3. As soon as the applied lower current level (the required evolution period) is reached, the MOSFET transistors control the field and hence a steady evolution field is obtained (Fig. 2.19c). Thus the operation in both the high and low fields is indistinguishable, as regards the operation of the control circuit.

4. During the transit from the low evolution field to the detection period, the high voltage Uₑ from the condenser is fed back to the coil, through the ignition of
Fig. 2.19 Current paths during different field levels and transits.
(a) High field (Polarization and detection field)
(b) Transit high to low
(c) Low field (Evolution field)
(d) Transit low to high.
the GTO thyristor $G$ (by applying suitable pulses to its gate). The current through the coil, thus increases from the low value to that corresponding to the detection field (Fig. 2.19d).

5. Finally, when the detection field is reached, the GTO is switched OFF (by applying a suitable pulse at its gate) and the MOSFET transistors are switched ON to regulate the field, resulting in the initial condition. In the present case, the operation is simplified by making the polarization and detection field levels equal. This cycle is repeated at regular intervals depending on the relaxation times of the system under investigation. The details of the control circuit using MOSFETs, the switching circuit using GTO and the current regulating circuit are given below.

Control circuit

If the maximum and minimum realizable Larmor frequencies i.e., polarization (or detection) and evolution fields are to be achieved with the same control circuit, a regulation of more than 1 in $10^5$ is required. In other words, if a stable magnetic field (either high or low) is to be achieved as soon as the cycling is done, the voltage levels to be applied to the gates of the MOSFET's during the different phases of the cycle are to be very stable. A drift free and modulation free regulation circuit serves the purpose (Schweikert, 1990). The block diagram of the control circuit is given in Fig. 2.20. In the present case, a fast, noiseless operational amplifier (OP27) which results in a minimum offset voltage of $1\mu V$ and a drift of $0.01 \mu V/\text{degree}$ is used to achieve high current stability and fast response times.

The input current levels to the control circuit are obtained through a stable 1.5 V dry cell. To facilitate a variation in the input level, the output from the dry cell is given through a variable resistor. Any fluctuations or variations in the coil current are to be fed back to the controller in the right sense (opposite sign, in the present case) with respect to the reference, so that the variations are annulled, resulting in a stable signal at the output of the control circuit. The feedback input to the controller is given from a measuring resistor $R_{\text{meas}}$, which is in the path of the coil current, and is sensitive to the changes in the coil current. The most important part of the
Fig. 2.20 Block diagram of the control circuit

Fig. 2.21 Pole zero pair amplifier
controller circuit is a pole zero pair amplifier circuit (Fig. 2.21). The typical response characteristics of the pole zero circuit are shown in Fig. 2.22. The low frequency part $I_1$ is responsible for the stability with the drift compensated input. The second part $I_2$ coupled with the high frequency region adjusts the control parameter to a high frequency limit. The third part p allows the controller to work in the proportional region (regulation). The pole and the zero of the circuit are given by

$$f_p = -\frac{1}{R_2 C_2}$$  \hspace{1cm} (2.26a)

$$f_z = \frac{R_3 R_2 C_2}{R_3 + R_2}$$  \hspace{1cm} (2.26b)

The dc gain of this amplifier is given by

$$A_o = \frac{R_2 + R_3}{R}$$  \hspace{1cm} (2.26c)

In the present case, the gain is chosen to be 1000. The pole and zero of the circuit are adjusted by trial and error method to obtain high stability during the polarization and detection periods ($f_p = 5$ Hz and $f_z \gg 1$ kHz).

The input current levels corresponding to the different evolution periods are obtained from a pulse programmer, which provides the control signal for the cycles, the driving signal for the rf pulses, triggering pulse for the recording of the relaxation time measurements and finally a trigger pulse to two switches during the transits.

However, due to the finite time constant of the pole zero circuit, the change of the current from one value to the other (switching) results in overmodulation of the current level. In other words, a completely false output signal results before the current stabilizes at the required new value (Fig. 2.23). Due to this overmodulation, the voltage at the gates of the MOSFET's has the correct value only after a time $t = t_o + t_z$. In an FC experiment, where the field is periodically varied, correction of such periodic overmodulations is compulsory to obtain stable currents through the magnet.
Fig. 2.22 Frequency characteristics of Pole zero pair amplifier
Fig. 2.23a Over modulation of the MOSFET gate voltage due to finite time constant of the Pole. *zero pour amplifier.*

Fig. 2.23b MOSFET gate voltage & Magnet current after overmodulation correction
A simple but logical option to correct the overmodulated voltage at the MOSFET gate is to disable the pole zero amplifier during the transits. This is achieved by enabling a strong negative feedback arm $A_f$ (by switching ON the electronic switch $S_1$ in Fig. 2.20). This reduces the gain of the pole zero amplifier drastically during the transits (resulting in a simple inverter). However, this leads to a change of input voltage and hence the output voltage. Thus this voltage has to be compensated to obtain the required evolution field. This is done by enabling the compensating arm $A_c$ by switching ON the electronic switch $S_2$ in Fig. 2.20. The compensating signal is obtained through an oppositely directed feedback signal from $R_{mes}$ and amplified appropriately. The compensating amplifier $C_A$ has a variable gain in order to vary the evolution field. Two n-channel MOSFET's (IBRFPG40) are used for the switching purposes in Fig. 2.24. The required pulses to the gates of the switches are obtained from the pulse programmer described in section 2.2.3 (Fig. 2.24). Thus the circuit works as a simple proportional amplifier with a strong negative feedback during the transits and the evolution period. However, it acts like a full fledged pole zero circuit resulting in a stable output signal immediately after the field is changed to the detection level.

After the turn ON i.e., in the detection period, the switches $S_1$ and $S_2$ are open and the circuit now works as a controller with good stability. The pulses with variable levels from the pole zero amplifier are buffered before being fed to the gates of the controlling MOSFET's. The Darlington pair (Fig. 2.20) provides enough current to drive the large number of MOSFETs.

With the correction for overmodulation and reduction in the turn ON time due to the induction of the magnet, the other possible sources for the drift of the magnetic field are the oscillations of the magnetic coils due to the vibrations of the cooling arrangement around the coil and fluctuations in the temperature of the coil due to the main current. These deviations can be corrected by correcting the coil current, the required signal being obtained from the temperature measurement system of the magnet. In the present arrangement, the drift due to these two sources is found to be negligible and hence no such precautions are needed. It is found that the magnetic field has high stability of $1 \times 10^5$ in an hour.
Fig. 2.24 Configurations of the switches $S_1$ and $S_2$ (MOSFET's) to compensate the overmodulation.

Fig. 2.25 MOSFET gate driver
The power MOSFETs used in the circuit are solid state devices, the current through them being controlled by applying appropriate signals at the gates. The constant current characteristics of the MOSFET is used in regulating the current. However the MOSFET has to withstand the large amounts of current during the cycle, and hence a large number of them (in the present case 20 are found to be adequate) are connected in parallel. Unless the cutoff frequencies and input capacities of all the MOSFETS match, they tend towards oscillations during the transits. This complication due to the parallel connection can be eliminated by decoupling the individual gates and is achieved by driving each MOSFET independently using a separate driver circuit (Fig. 2.25). This arrangement of gate driver circuit partially linearizes the voltage-current characteristics. The LEDs in each of the gate driver help in visualising the function of each gate driver and hence any problem in the MOSFET circuit can be localized and detected easily.

Since the feedback signal to the controller is given from the measuring resistor, it is necessary that the resistor measures the current through the magnet without any error. Several positions can be chosen in the circuit for placing $R_{mes}$ (Fig. 2.26) depending on the relative merits and demerits. Positions $a$ and $6$ do not hold the ON, OFF current correctly and are at a high variable potential to the ground. Hence a direct and precise transmission of the signal to the control circuit is not possible. Positions $c$ and $d$ are directly in the magnet power supply lines and hence measure the current without any error but they are at a higher potential with respect to the ground. The positions $e.$ and $f.$ are at easily operating positions but at $e,$ the driving current for the MOSFET driver falsifies the data apart from improper OFF current measurement. Hence the position $e$ has the most favorable characteristics and is chosen for positioning the measuring resistor. This circuit is modified slightly to hold the input current properly (Fig. 2.17).

The choice of the value of $R_{mes}$ is also very critical. On one hand, it must be large enough so that the voltage drop from the control signal is large enough (i.e., even minute changes in the control signal should result in perceptible voltage drop across $R_{mes}$ for better resolution). On the other hand, $R_{mes}$ should be small enough so that the power loss and hence the heat dissipated should be small to ensure a stable
Fig. 2.26 Several possible positions for the measuring resistor ($R_{mes}$).

Fig. 2.27 Pulses to the GTO driver.
operation. In the present case, 150 mΩ resistor satisfies the above requirements since it results in a maximum voltage drop of \( \sim 1 \text{V} \) (corresponding to the polarization and the detection period) and a maximum power dissipation of only 7 Watts across \( R_{mes} \).

**Switching circuit**

Apart from the overmodulation correction, the turn ON time of the magnet, as explained earlier can be reduced by increasing the voltage at the coil (by the use of energy storage capacitor) through the switching of a GTO thyristor. The details of this switching circuit are given below.

The GTO thyristor used to impress high voltages across the magnet during turn ON period is Model No. 358RGA100 of Nihon interelect. corpn. Unlike in ordinary thyristors, which can be triggered ON with the help of a signal at the gate but can be switched OFF only by breaking the anode circuit, a GTO can be controlled through a trigger pulse given at the gate. The trigger and quenching pulses needed for the control of the thyristor are obtained through a commercial gate driving circuit GK2AN. The input pulses to this gate driver are obtained from the pulse programmer (Fig. 2.27). The GTO is protected from the dangerous high voltages developed during switch OFF and switch ON through the use of an external protection circuit shown in Fig. 2.18 (Snubber network). The values of the components in this circuit are \( R = 5\Omega ; C = 0.3 \mu\text{F} \). The diode used in the snubber network is 20MLA with 0.1 \( \mu\text{F} \) capacitor connected across it.

Due to the large voltages developed and high currents flowing in the circuit, a large power is dissipated in different parts of the circuit and hence necessitates cooling arrangements. The MOSFETs, GTO thyristor, free wheel diode, decoupling diodes and the measuring resistor, \( R_{mes} \) are mounted on a thick aluminium sheet cooled by circulating chilled water.

**2.2.3 3.5 MHz Pulsed NMR Spectrometer**

The details of the fixed frequency (3.5 MHz) spectrometer fabricated as part of the FCNMR spectrometer is described in this section. The block diagram of the spectrometer is given in Fig. 2.28. It consists of (1) a transmitter (2) a matching network
Fig. 2.28 Block diagram of the pulsed NMR spectrometer
Fig. 2.29 rf amplifier using 2N2369

Fig. 2.30 Pulse generator using IC74121
(probe) and (3) a receiver. The ideal requirements of these three parts with their subunits is described below. The transmitter should be capable of providing strong rf pulses (typically in the range of a few hundreds of watts with sharp rising and falling edges) of short duration (1-100 μsec). The ON/OFF ratio of the rf pulses should be very large so as to ensure that there is no leakage of rf voltage into the receiver during the transmitter OFF time. The rf field \(H_1\) provided by the transmitter should be as homogeneous as possible over the sample volume. The power from the transmitter should be efficiently transferred to the system (sample coil) by an impedance matching network. This matching network along with the sample coil is termed as the probe.

The signal induced in the sample coil after the transmitter pulse is very small (typically in μV), and hence it should be amplified by the receiver to a few hundreds of times, and then demodulated to recover the decaying pattern. Apart from this, the receiver should be capable of withstanding overload voltages and also recover fast from these overload voltages (due to leakages during pulse ON periods). The recovery time (dead time) of the receiver (from overloading) should be as small as possible to ensure that the signal is not lost during the dead time of the receiver. Also the reciever should be capable of detecting only the carrier wave in order to increase the signal strength. The various units mentioned above are described in detail below.

**Transmitter**

The transmitter essentially consists of an rf source, a pulse programmer capable of generating the required pulse sequences, a pulsed rf mixer, a medium power amplifier and a gated high power amplifier.

**rf source**

The rf source used is a commercial unit (Kikusui, Model No. 4100) capable of generating rf of high spectral purity from 0.1 kHz to 110 MHz with a stability of about 1 in \(10^9\) s. This is further amplified using 2N2369 transistors to a required level of about 3V peak to peak (Fig. 2.29). The rf thus obtained is power divided into two parts, the first part is used for pulse modulation and the other is used as reference (through a phase shifter) for the phase sensitive detector.
Pulse programmer

The required pulses and the pulse sequence for the field switching with necessary delays are obtained through a commercial four channel digital delay generator DG (EG&G make, Model No. 9650) and a home made pulse generator. IC74121 (Fig. 2.30) is used to obtain the rf pulse, which is triggered by DG. Pulse outputs are also available for triggering the oscilloscope and the gated high power amplifier. Complexed rf pulse sequences (for example two pulse or three pulse sequences) can also be generated using a combination of home made pulse generators and delay generators as explained latter (Fig. 2.42 and Fig. 2.43).

rf gate

The pulse modulation of rf is achieved using a quad two input NAND gate (74LS00) connected as shown in Fig. 2.31, with a good rf suppression ratio (> 100dB) during the OFF time of the pulse. The rise and fall times obtained are very sharp (10 nsec typically). The rf suppression during the pulse OFF periods can be further improved by increasing the number of gates.

Medium rf power amplifier

The fluctuation spectrum of the different mechanisms mediated through the dipolar interaction in solids results in considerable increase of line width and hence results in very short FIDs. As explained earlier, the inhomogeneity in the Zeeman magnetic field leads to a further shortening of $T_2$ to $T_2^*$. In order to excite all the spins equally in such a broadened spectrum, the pulse width should be as small as possible. Normally pulsed rf in the range of a few KW is needed to get a $\pi/2$ pulse width of about 2-3 $\mu$sec for proton. This is achieved in two stages. The gated rf obtained from the NAND gates is amplified to 20 Vpp using a gated medium power amplifier which subsequently is used to drive a gated high power amplifier to get the required pulsed rf power.

The medium power amplifier is built using a power transistor 2N3553 (Shenoy, 1978) (Fig. 2.31). The - 5 Vdc and the TTL pulses at the base of the transistor provide the necessary biasing and ensure that the transistor is OFF during the pulse OFF period. On the other hand, during the pulse ON period, the transistor is forward
Fig. 2.31 Mixer or rf gate and medium power amplifier.
biased, thereby forcing the input pulsed rf to be amplified by $\beta = 10$ times the input current. The additional gating provided by the pulses synchronous with the pulsed rf, further suppresses the rf leakage during the OFF period. The inductors $L_1$ and $L_2$ are adjusted to match the input and output impedances to the previous and following stages respectively. The rf chokes are adjusted to obtain the necessary gain during the ON period. A peak voltage of 20V is obtained at the output of this medium power amplifier (typical input of about 200 mV of pulsed rf).

*Gated rf high power amplifier*

This amplifier is constructed using 3E29 dual tetrode tubes operating in push pull configuration (Lowe and Tarr, 1968) and is gated with a 0 to -150 V pulse amplifier. The 0 to -150 V synchronous, gating pulses and the input pulsed rf are given to the tubes through a wide band input transformer (model NH0900B of North Hills make). This is capable of amplifying pulsed rf with negligible rise and fall times, the 3 dB bandwidth being 5 to 30 MHz. The rise and fall times of the final pulsed rf from the power amplifier are determined by the rise and fall times of the grid pulses (typically < 50 nsec). The circuits of the gated pulse amplifier and the tube amplifier (Fig. 2.32) are discussed individually below.

High power amplification and good ON/OFF ratio is accomplished by biasing the grids of the dual tetrodes with 0 V during pulse ON period and -150V during the pulse OFF period. The working of the pulse amplifier can be understood as follows. During the pulse OFF period, the transistor $T_1$ is OFF, resulting in -150V at the bases of $T_2$, $T_3$ and $T_4$. Since both the pnp transistors $T_2$ and $T_3$ are conducting and the npn transistor, $T_4$ is not conducting, -150V appears at the grids of the tubes. Thus, during the pulse OFF period, no amplification is done resulting in an improved ON/OFF ratio. During the pulse ON period, $T_1$ conducts making the voltage at the base of $T_2$, $T_3$ and $T_4$ 0 V from -150 V. Thus $T_2$ and $T_3$ are OFF and $T_4$ is ON resulting in 0V at the grids of the tubes. The output of the amplifier is taken through another wide band transformer (North Hills NH1703BA). Since the plates of the tetrodes are at about 800V, very high amplification ($\sim 10$) of the input pulsed rf is achieved during the pulse ON period.
Fig. 2.32 High power gated amplifier.
Matching network

The most important part of a pulsed NMR spectrometer is the coupling system (probe) which couples the power from the transmitter to the sample coil during pulse ON period and converts the precession magnetization into a detectable signal at the input of the receiver immediately following the pulse. The matching network should be capable of coupling the sample coil to the transmitter during pulse ON period and should also couple the sample coil to the receiver during the pulse OFF period. It should also decouple the receiver from the transmitter during the pulse ON period. The important considerations during the construction of the probe are given below. The size of $H_1$ and hence the $\pi/2$ pulse width is determined by the transmitter coil and the final $S/N$ ratio is determined by the sensitivity of the receiver coil. One crucial factor in the design of the size of the sample is that since $H_1 \propto (V)^{-1/2}$, where $V$ is the effective volume of the sample, a probe built for a larger sample will have smaller $H_1$ for the same power. Also since signal to noise ratio ($S/N) \propto (f)^{1/2}$, where $f$ is the filling factor of the coil, it is necessary that the probe should have a filling factor close to unity. Finally, the receiver coil in the probe should not give rise to spurious signals (for example, from the mechanical oscillations of the inadequately secured $rf$ coil or generation of acoustic waves and signals which interfere with the actual signal).

The above factors can be satisfied by using tunable circuits consisting of LCR networks. Either crossed coil method (Bloch et al., 1946), where separate transmitter and receiver coils are used or single coil method (Clark and McNeil, 1973; Ailion, 1983), where a single coil is used for both the transmitter and the receiver can be used for this purpose. The single coil arrangement is simpler and has advantages over the crossed coil probe, like, the coil can be tightly wound around the sample and hence has maximum power efficiency. Since the coil is common to both the transmitter and the receiver, care should be taken to protect the receiver from leakage of $rf$ pulses from the transmitter, i.e., the probe should isolate the receiver from the transmitter. This can be achieved by using crossed diodes and $\lambda/4$ transmission lines which appear as short circuit to high voltages and open circuit to the small signals.
Two matching circuits available in the literature are used in the present studies and their relative merits are discussed below. Both the circuits are single coil circuits which are easier to handle and also efficient compared to the crossed coil probe as explained earlier.

Series resonant circuit

This matching network (Clark and McNeil, 1973) consists of three resonant circuits; \( L_1C_1 \), \( L_2C_2 \) and \( L_3C_3 \), each tuned independently at the Larmor frequency (Fig. 2.33). The crossed diodes \( (D_1) \) at the input act as a short circuit to the high power \textit{rf} pulses (during pulse ON period) and as an open circuit to the small signal voltages (during pulse OFF period). The series combination, \( L_2C_2 \) represents a low impedance path in parallel with that of \( L_3C_3 \) so that the entire transmitter voltage is dropped across \( L_2 \) and very little voltage is fed into the receiver during the pulse ON period. Also, since the diode pair \( (D_2) \) represents short circuit to ground, voltage at \( E \) is dropped across \( L_3 \) before reaching the receiver. After the transmitter pulse, the diode pair \( D_1 \) effectively disconnects it from \( E \) and \( D_2 \) acts as an open circuit to the low voltage induced resonant signals, thereby forcing the signal into the receiver through \( L_3C_3 \). Hence, \( L_2C_2 \) and \( L_3C_3 \) represent a composite series circuit tuned at the Larmor frequency. The FID is received at \( F \) (a high impedance point to ground). The tuned input receiver circuit \( (L_3C_3) \) provides good coupling of \( L_2 \) to the receiver and hence increases the \( S/N \). Thus the circuit ensures an efficient transfer of power from the transmitter to the sample coil and also good protection of the receiver from destructive overloads.

Tuning

The three resonant circuits are to be tuned independently such that maximum transmitter power is transferred to the sample coil. The tuning should also ensure a good coupling between the sample coil and receiver. This is achieved using the following procedure.

1. Initially, the switch \( S_1 \) is closed and \( L_1C_1 \) is tuned to maximize the amplitude of the pulsed \( rf \) at \( A \) by tuning \( C \).
Fig. 2.33 Series resonant matching network.
2. The pair \( L_3C_3 \) is tuned by closing \( S_2 \) and giving a low level rf at the tune input and then maximizing the voltage at \( F \) by tuning \( C_3 \).

3. Finally, the tank circuit \( L_2C_2 \) is tuned by opening the switches \( S_1 \) and \( S_2 \). The pulsed rf from the transmitter is given at the input and the voltage across \( L_2 \) is maximized by tuning \( C_2 \). However, some final adjustments are to be made by observing the signal to optimize the pulse width and signal strength.

The values of the different components and capacitors are chosen following the procedure of Clark and McNeil (1973). Typical values of the various components at 3.5 MHz for \( R_o = 50 \text{ft} \) (the output impedance of the circuit) are \( L_1 = L_3 = 0.45 \mu \text{H} \); \( L_2 = 0.9 \mu \text{H} \). A sample coil of radius 1 cm with 17 turns is found to be the proper choice for optimum signal strength. The major precaution to be taken in the process of designing the probe is to avoid using cables of A/4 length or its multiples from the transmitter to the sample coil since they act as open circuit to the high powered transmitter pulses at the designed frequency. The bandwidth of this circuit is about 2 MHz.

**Parallel resonant circuit:**

The second circuit (Ailion, 1983), given in Fig. 2.34, consists of a single resonant tank circuit \( L\cap C \), in series with a capacitor \( C_2 \). The crossed diodes at the input of the circuit allow the high power rf voltages to pass through the sample coil, while acting as open circuit to the small signals induced in the coil. The diodes at the output of the circuit allow any rf power leaked into the ground, thus protecting the receiver from the rf pulses, while acting as open circuit to the small NMR signals thereby forcing them to go entirely into the receiver. These crossed diodes also remove low level noise and other transients originating in the transmitter and hence improve the S/N ratio of the system. In addition, presence of quarter wave network before the diode pair offers a high impedance for transmitter pulses thus protecting the receiver from overload further. The input and output impedances of the tuned coil is chosen to be equal to 50 ft. \( C_2 \) is chosen to be as small as possible in order to minimize the degradation of \( L/C \) ratio and in turn the quality factor \( Q \) of the circuit. The conditions for tuning the circuit are given by
Fig. 2.34 Parallel resonant matching network.
Here \( Q \) is the quality factor of the coil which is made as large as possible to optimize S/N ratio and power transfer efficiency. On the other hand very large \( Q \) would result in a long ringing time and hence a long system recovery time of the receiver, following the turn OFF of the rf. Hence for broad signals, it is advantageous to reduce \( Q \) at the cost of a lower S/N ratio. \( L \) is determined from eqn. (2.27b) and \( C_1 \) from eqn. (2.27a). Typical values of the components at 3.5 MHz are \( Q = 100, \ C_2 = 150 \text{pF}, \ C_1 = 900 \text{pF} \), the coil \( L_1 \) has 21 turns with an inductance of \( 2.3 \mu \text{H}, \ C_3 = 900 \text{pF} \) and finally the coil \( L_3 \) has 21 turns with an inductance of \( \mu \text{H} \).

Tuning

The tuning of the circuit is done by tuning the tank circuit for maximum power at the coil. Fine tuning can be done further by observing the ringing pattern after the pulse. The \( Q \) of the circuit is optimized to reduce the ringing time sufficiently. The A/4 circuit acts as an impedance transformer network. When shorted at one end, the A/4 line transmits the low voltage signals at the designed frequency and hence attenuate all other frequencies (equivalent to a selective filter). In the present case this line consists of an inductor, \( L_3 \) and two capacitors, \( C_3 \) (connected as a \( \pi \) section) wherein the active elements are chosen to offer an impedance of 50 Ohms (as in eqn. (2.27c)) at the designed frequency i.e., \( L_3 \omega = 1/C_3 \omega = 50 \Omega \). The signal strength is maximized at each frequency by tuning the capacitors \( C_3 \). The tuning of this probe is relatively easier compared to the Clark's circuit since there is only a single capacitor to be tuned. Also for a given geometry of the sample coil, the parallel resonant probe offers a much higher \( Q \) and hence better sensitivity. However the high \( Q \) of the parallel resonance circuit results in an increase in the recovery time of the reciever and hence it is advantageous to use Clark's probe for broad signals (and hence short FID's).
Receiver

The receiver consists of a fast recovery preamplifier, a tuned amplifier, a phase sensitive detector, a filter and finally a signal averager for signal acquisition and averaging purposes. The details of these subunits are given below.

Fast recovery pre-amplifier:

The NMR signal from the probe is very weak (typically a few $\mu V$) and hence has to be amplified by a few orders of magnitude before detection. Hence the receiver should have a gain of about $10^5$. But, despite the many precautions taken, the receiver is always overloaded by the large rf pulses from the transmitter resulting in two problems, the dead time of the receiver and the baseline shift after the detection due to asymmetry of saturation together with ac coupling. A fast recovery pre-amplifier (Ramadan et al., 1974) is used to overcome these problems.

The amplifier (Fig. 2.35) possesses high sensitivity and short recovery time besides a large band width. The diodes $D_1$ and $D_2$ protect the input of the receiver from large rf pulses. Diodes $D_3$ and $D_4$ in the feedback circuit limit the high voltage rf pulses to the receiver to approximately $\pm 0.5V$. The dc level of the feedback circuit is adjusted by a variable resistor $R_1$ such that the positive and negative limit of the rf pulses are symmetric about the baseline. The amplifier has a gain of 10 and a bandwidth from 1 kHz to 15 MHz. The recovery of the system is about $5\mu S$ with this amplifier.

MOSFET tuned amplifier:

The signal from the pre-amplifier is further amplified using a low distortion and a stable gain MOSFET amplifier which is stagger tuned (Landee et al. 1957) around the Larmor frequency, $\omega_0$. The amplifier consists of three identical stages followed by a source follower (Fig. 2.36). The first three stages are made of n-channel insulated gate FET with a gain of 20 dB each. A source follower using a JFET after the third stage provides the impedance matching and the final output is taken through a broadband transformer (North Hlls 0900BB). The high input impedance of the MOSFETs ensures a low noise figure and negligibly small distortions of the amplified signal. In the stagger tuned mode the last stage is tuned to the frequency $f_0$ whereas
Fig. 2.35 Fast recovery pre-amplifier.
Fig. 2.36 MOSFET tuned amplifier.
the first two stages are detuned symmetrically on either side of $f_o$. The staggered tuning is done to achieve a band width of 2 MHz so as to allow the FID signals of short duration. The $Q$ value of the last stage is chosen to be equal to half of that of the symmetrically detuned stages. The interstage coupling is done using series tuned $LC$ circuits between each stage which effectively block out any low frequency transient and allow the $rf$ signal without any attenuation.

**Phase sensitive detector and phase shifter:**

The signal from the probe often consists of all frequency components, apart from the frequency of interest, and hence has to be demodulated before signal averaging. This can be done either using diode detection or phase sensitive detection. A phase sensitive detector (PSD) has many advantages over a diode detector. A PSD has a smaller bandwidth than a diode detector and hence a better $S/N$ ratio (Farrar and Becker, 1971). Since PSD is sensitive to the phase of the signal, the phase information is retained. Finally, it discriminates heavily against signals which do not have the same phase as the reference signal and hence can be used in signal averaging experiments when the $S/N$ ratio is larger than one (Stejskal, 1963).

The phase sensitive detector used in the present case is a double balanced mixer (Hewlett Packard make, model 10534A). The signal (of frequency $f$) is applied at the LO port while the reference (of frequency $f_o$) is fed into the $rf$ port (Fig. 2.37). The detected output which is proportional to $(f_o - f)$ and the difference of the frequencies of two inputs $(f_o - f)$ is taken out from the IF port. Thus when the frequency of the reference is same as the signal, an output corresponding to zero (i.e., $dc$) is obtained. The signal strength is further maximized by adjusting the phase difference between the two inputs.

If the reference signal given at the $rf$ port is $A_1 \sin \omega t$ and the signal at LO port, $A_2 \sin(\omega t + \phi)$, $\phi$ being the difference in phase between the two inputs, then the output signal at the IF port is $A_1 A_2 \cos \phi$. When the phase difference is zero, maximum output will be obtained. The reference signal is given from the $rf$ source through an adjustable phase shifter for maximising the signal strength. An electronically tunable phase shifter (Merrimac make) is used for this purpose, where the phase of the output
Fig. 2.37 Arrangement of phase sensitive detector with the phase shifter.
with respect to the input can be varied from 0 - $2\pi$ by using a variable dc voltage from 0 to 30 V. The arrangement of the PSD along with the phase shifter is given in Fig. 2.37.

**Filter and signal averager:**

The detected output signal has along with the dc, a component at $2f_0$ and other noise components which can be filtered using a low pass (< 2 MHz) filter made using RC network. The filtered output is then given to a digital storage oscilloscope (Tektronix 2230) for signal averaging purposes.

**Temperature controller:**

A home built, temperature controller is used for temperature variation measurements covering all the mesophases. The details of this temperature controller (Chiu et al., 1979) which works in the range of 85 to 400 K with a stability of 0.1 K (Fig. 2.46) are given in section 2.3.

Various subunits of the spectrometer described above require different regulated power supplies, which are home built through the use of bridge rectifier, filter and three pin regulator (78XX series for positive and 79XX series for negative supplies). The pulsed rf spectrometer built thus is standardized at 3.5 MHz by observing the Nitrogen NQR signal from NaNO$_2$ with a typical unaveraged $S/N$ of about 3 to 4 and a $7\pi/2$ pulse width of about $10\mu$sec. This rf spectrometer is to be coupled with the magnet so that the field switching and the rf pulses are synchronised.

### 2.2.4 Synchronization of FC magnet and rf spectrometer

The switching cycle for the solenoid magnet and rf pulses in the 3.5 MHz spectrometer are to be synchronised in order to perform the NMR relaxation time measurements (the methodology involved is discussed in section 2.2.6). The typical timing diagram of input pulses to the different components in the controller circuit of the magnet during a cycle are given in Fig. 2.38. As explained earlier, a four channel digital delay generator is used to generate the necessary input pulses (Fig. 2.39). The delay of channel A is set to zero. The delay of B is adjusted to provide the evolution period...
Fig. 2.38 Timing diagram of the various pulses to the different subunits during a typical $T_1$ measurement using field cycling.
Fig. 2.3d Pulse programmer with different pulse generators and digital delay generators to get the required field cycle and rf pulse sequences.
(\(t_E\)). The gated output A.B provides the necessary input pulse to the switches \(S_1\) and \(S_2\) (Fig. 2.39). The pole-zero pair amplifier is disabled during the entire period of \(t_E\) by closing the switch \(S_1\) and the necessary signal to obtain the appropriate evolution period is obtained by closing the switch \(S_2\) with the help of A.B signal (Fig. 2.39). Further, the delay of channel C is made equal to the delay of B and the delay D is adjusted to be the sum of the delay B and \(t_{ON}\) so that the gate output CD provides the necessary pulse to switch ON the GTO during the \(t_{ON}\) period. The trigger pulse at the channel D is synchronous with the edge of \(t_{ON}\) and hence it can be used to trigger the pulse programmer in the \(rf\) spectrometer. In case where a single \(\pi/2\) pulse is sufficient following the field cycle, the trigger output of D can be directly used to generate the \(\pi/2\) pulse. The FCNMR spectrometer is automated by interfacing the delay generator and the signal averager (digital storage oscilloscope) to a PC/AT through IEEE 488 parallel port. The details of the automation are given in section 2.3.2.
**Specifications of the spectrometer**

The specifications of the spectrometer described so far are summarized below. The estimated errors in the measurement of $T_1$ using this spectrometer are generally within 5% and within 10% for $T_{1D}$ measurements.

1. Operating frequency range 0 kHz to 3.5 MHz
2. Polarization and detection frequency 3.5 MHz to 5 MHz
3. Maximum OFF time 1 msec
4. Maximum turn ON time 25 msec
5. Field stability 1 in $10^5$
6. Field homogeneity 1 in $10^{-5}$
7. Bandwidth 2 MHz at a given frequency
8. Pulsed rf power upto 1 kV (peak to peak) into 50 Ohms
9. Typical $\pi/2$ pulse width 2 - 3 $\mu$ sec for proton
10. ON/OFF ratio of rf pulse 100 dB
11. Transmitter isolation 60 dB minimum
12. Recovery time 15 $\mu$ sec (typical)
13. Interface bus with PC GPIB
14. Temperature range 77 K to 400 K (with 0.05 K stability over one hour).
2.2.5 Methodology of FCNMR

The methodology of the experiments using FC can be approximated to that of the conventional NMR, by taking into account the Zeeman field modulation and the transit times.

*Longitudinal relaxation time* (\(T_1\))

The methodology adopted to measure the longitudinal relaxation using FC is similar to that with constant Zeeman field apart from application of adequate \(B_o\) cycle. The usual method of disturbing the spin system to a known non-equilibrium value is through the \(B_o\) cycle itself \((Bop \rightarrow B_{OE})\) and is combined with a \(B_1(t)\) sequence to sample the evolving magnetization or the spin temperature belonging to the evolution period i.e.,

\[
M_z(t_E) = M_z(t_E = 0) - (M_z(t_E = 0) - M_{OE})[1 - \exp(-t_E/T_{1E})] \tag{2.28}
\]

During the polarization period \((t_p\) is sufficiently long), \(M_z\) increases to an equilibrium value \(M_{OP}\). Following the downward switch to a selected level of \(B_{OE}\), the magnetization \(M_z(t)\) relaxes in the evolution period with a time constant \(T_{1E}\) towards the new lower equilibrium value \(M_{OE}\). The system is allowed to evolve in the evolution period for a time \(r\) before the sampling \(n/2\) is applied immediately after the upward switch. The sampling pulse flips the \(M_z(t_D = 0)\), into the plane perpendicular to \(B_{OD}\). This transverse magnetization \(M_\perp(t_D= 0)\) i.e., \(M_z\) \((t = t_E)\), now relaxes under the influence of \(B_{OD}\) with Larmor frequency \(\omega_o\) giving rise to the familiar FID in the sample coil wound around the sample. The initial height of the FID, \(U_{\text{sig}}(t_D = 0)\) decays proportional to the magnitude of \(M_z\) at \(t - t_E\) i.e., the height of the FID obtained decays exponentially with a time constant \(T_{1E}\) as a function of the evolution period time, \(t_E\).

Thus the relaxation time \(T_{1E}\) (corresponding to the evolution period) at the selected field strength is measured directly from the envelope of \(U_{\text{sig}}(t)\) obtained by cycling with different durations of \(t_E\). The \(T_{1E}\) corresponding to the other values of
the evolution periods $B_{OE}$ is obtained by readjusting the $BOE$ switch amplitude and repeating the above procedure without additional changes. The correlations between the various quantities involved in the cycle $(B_{o}(t), M_{z}(t), B_{1}(t)$ and $U_{\text{sig}}(t))$ are shown in Fig. 2.40. The total time $T$ needed to get a single FID signal is determined by the duration of $BOP$ i.e., $top — 10T_{1P}$. The sampling pulse and the induction signal are in the reference frame rotating with the Larmor frequency and hence are designated by $B'(t)$ and $U'_{\text{sig}}(t)$. The $T_{1}$ experiment using FC is very much simplified compared to the conventional $T_{1}$ experiment at constant Zeeman field, since $Bop \rightarrow B_{OE}$ transit already generates the non equilibrium magnetization, without the use of a separate preparation pulse ($\pi$ or $\pi/2$). Even the anisotropy studies of $T_{1E}$ can be obtained very easily by splitting the evolution field into components parallel to the $z$ and $x$ axes without any significant modification of the scheme, except for high levels of $B_{OE}$, where the transit fails to deviate the magnetization from equilibrium at $t_{E} — 0$ and hence necessitating a $\pi$ or a $\pi/2$ preparation pulse.

One crucial point to remember during FC experiments is to make $BOD$ homogeneous, otherwise $T_{2}^{*}$ will be very short making it difficult to detect the full FID due to instrument dead times. This can be overcome to some extent by using a spin echo sequence $(n/2 — \tau — \pi)$ where $r$ is small compared to spin spin relaxation time. The echo amplitude and area of echo vary as $M(t_{E})$ and hence allow one to determine $T_{1E}$ without the resolution problem involved in an FID.

Transverse relaxation time ($T_{2}$)

Similar to the spin lattice relaxation, the methodology used to determine the transverse relaxation using $FC$ is same as that with constant Zeeman field. Nevertheless their applications are limited to only liquid like systems with long $T_{2}^{*}$ ($T_{2} \simeq T_{1}$) due to the time scales involved.

The transverse nuclear magnetization $M_{\perp}$ following a $\pi/2$ pulse is given by the familiar Bloch equation

$$\frac{dM_{\perp}}{dt} = \gamma [M(t) \times B_{o}] - \frac{M_{\perp}(t)}{T_{2}}$$

(2.29)
Fig. 2.40 Simple FC scheme to measure the field dependence of the longitudinal relaxation time $T_{1E}$. The sign (') refers to the quantities in the rotating frame
(a) Zeeman field cycle $B_o(t)$
(b) Longitudinal magnetization $M_z(t)$
(c) rf pulse and recovery of magnetization in the z direction.
The relaxation time $T_{2E}$ in the evolution period may in principle be measured from the FID, created by a $n/2$ pulse in polarization period, and sampled as a function of the time, $t_E$. However, the inhomogeneities in the dc field necessitates measurements through spin echo techniques. A typical spin echo sequence ($\pi/2 - T - \pi$) compatible with $B_o$ cycles is (Carr-Purcell) given in Fig. 2.41. Shortly before the end of polarization period, $M_{OP}$ is flipped into the $xy$ plane by the $7\pi/2$ pulse. The subsequent field switch changes the relaxation time from $T_{2P}$ to $T_{2E}$. The $\pi$ pulse which refocuses the dephasing spins is applied in the middle of the evolution period with a spacing of $At = t_E/2$. Since the available techniques do not allow change of $B_1(t)$ sufficiently fast to the evolution period, it must be cycled to the $Bop$ level during the $\pi$ pulse. The inhomogeneously distributed magnetization in the transverse direction is rephased resulting in a spin echo at $t_E = 2At$. The pulses and transits must be positioned in such a way that the echo maximum occurs immediately after switching to $BOD$ in order to avoid any mixing with $T_{2D}$. The height of the signal obtained from the echo at $t_D = 0$ will be proportional to $M\pm$ at $t = t_E$ and the signal envelope as a function of $t_E$ yields $T_{2E}$. The full relaxation dispersion can be obtained by repeating for other BOE levels. As mentioned for $T_1$ processes, the value of $t_{OFF}$ and $t_{ON}$ set a lower bound to the accessible $T_2$ range.

Section - 3

2.3 High field pulsed NMR

A variable frequency, home made pulsed NMR spectrometer (Venu,1986) is available in the laboratory. The details of this spectrometer, which has been used for the relaxation measurement at high frequencies (> 3 MHz) are briefly described in this section. The various subunits of this spectrometer are similar to that of the FC spectrometer described in section 2 except for a few modifications. The magnet used is manufactured by Bruker Spectrospin (Model BE25) and is energized using a power supply (Bruker, Model No. B-MN 155/45 A6). The pole caps are 10° in diameter and the pole gap is adjustable upto 4°. The magnet has a stability of 1 in 10⁶ with
Fig. 2.41 Simple FC scheme to measure the **field** dependence of the transverse relaxation time $T_{2E}$. The sign ($) refers to the quantities in the rotating frame

(a) **Zoeman** field cycle $B_0(t)$

(b) rf pulse and recovery of the magnetization in the transverse direction.
a very good homogeneity over about \(1 \text{cm}^3\). A maximum magnetic field of about 1.2 T with a long term stability can be obtained with good cooling arrangements.

### 2.3.1 Spectrometer

The pulses of required widths with necessary delays between them are obtained from two commercial pulse generators (BNC, model 8010) in conjunction with a commercial delay generator (BNC, model 7010) (Fig. 2.42). The three pulse sequence for dipolar echo is obtained with the above three units and a home made pulse generator using IC74121 (Fig. 2.43). A commercial synthesizer capable of giving \(rf\) from 0.1 kHz to 110 MHz with a stability of 1 in \(10^8\) is used (Wavetek, Model No. 2500A) to get the required \(rf\). Pulse modulation is done using double balanced mixers with a current driving circuit as described below.

**Pulse modulation**

**Mixer**

Pulse modulation of the \(rf\) with very high ON/OFF ratio is achieved using double balanced mixers (Mini Circuits, Model No. SRA-3H). It consists of three ports IF, LO and RF perfectly isolated from each other. The circuit diagram of a typical double balanced mixer (DBM) is shown in Fig. 2.44 and the working of the circuit is explained below. If the diodes \(D_1\) and \(D_2\) are matched and the transformers \(T_1\) and \(T_2\) are symmetrical, the voltage at A is equal to the voltage at the center tap of \(T_1\) i.e., ground. Similarly if \(D_3\) and \(D_4\) are matched, the voltage at B is equal to ground. Thus the secondary ends of the Transformer \(T_2\) are at ground potential and hence LO port is isolated from both \(rf\) and IF ports. Now looking from \(rf\) port, since all the diodes are matched, the voltage at C is equal to the voltage at D i.e., ground. Hence no \(rf\) voltage appears at the LO port. Due to symmetry, the voltage at IF port is same as that at C and D i.e., zero. Thus there is no \(rf\) output at IF port and hence all the three ports are isolated.

With the pulses applied at the IF port and an \(rf\) signal at the \(rf\) port, the current at the IF port rises suddenly during the pulse ON period. This turns on the diodes and hence the \(rf\) appears at the LO port. When the transmitter pulse is OFF, as
Fig. 2.42 Pulse programmer for generating different pulse sequences
(a) Arrangement for two pulse sequence
(b) Arrangement for saturation burst sequence.
Fig. 2.43 Arrangement for Jeener Broekaert three pulse sequence for $T_{1D}$ measurements.
Fig. 2.44  Double Balance Mixer (DBM).
explained above, the IF and rf port are isolated resulting in a pulse modulated rf with negligible rise and fall times (less than $0.1 \mu s$).

Practically as the frequency of operation is increased, isolation tends to fall off at the rate of 5 dB/octave. As the current through the IF port is varied, the balance between LO and RF will be altered. Since the IF port response extends from dc to some high frequency, very fast switching is practical. Assumptions for balance are based on transformer symmetry and diodes being equal. Diode junction capacity differences and transformer winding mismatch leads to imbalance in the bridge and subsequent drop in isolation.

Addition of one more DBM in series, results in a better ON/OFF ratio and hence a better $S/N$ at the cost of higher insertion loss (Fig. 2.45a). Better isolation can be achieved using a current driving circuit (McLachlan, 1982) to drive the DBMs (Fig. 2.45b). This circuit enables the adjustment of the amplitude of the pulsed rf over a ten fold range by varying the gating pulse current from about 1 to 30 mA. The working of the circuit is briefly described below. The transistors ($Q_1$ and $Q_2$) are independent current drivers and have their collector currents adjusted by the $1K\Omega$ trimpot. When the transmitter pulses are OFF, the collector currents switch ON the transistors $Q_4$ and $Q_5$ respectively and hence no pulses appear at the IF inputs of the DBMs. During the pulse ON period $Q_3$ and $Q_4$ are ON and the collector currents of $Q_1$ and $Q_2$ are steered to the IF ports of the corresponding DBMs. Since the transistors used (BC 558) are PNP transistors, inverted TTL pulses are given at the inputs. This circuit has two driving channels and hence different phase shifted pulses can be pulse modulated simultaneously.

The pulsed rf from the mixers is initially amplified to a nominal level of $30 \text{ V}_{pp}$, using a commercial medium power amplifier (ENI make, model 350L), which is used to drive a subsequent high power gated tube amplifier. The matching network used is either a parallel or series resonant circuit described in section - 2. The receiver used is a broad band receiver (Matec, model No. 625) with a narrow band double tuned preamplifier (Matec make, model No. 252) along with a phase sensitive detector, filter and a signal averager, the functioning of which are explained earlier. The temperature
Fig. 2.45b Current driving circuit to drive the DBM's.
controller used is similar to that of the FC spectrometer.

**Temperature controller**

To enable the temperature variation measurements covering all the mesophases of the liquid crystals, a temperature variation facility is used. Since the orientation ordering of the molecules in LC is sensitive to the temperature, maintaining the sample at a particular temperature during the course of the measurement is an essential factor. Various temperature controller circuits are available in the literature. For the present purpose, a slight modification of the circuit (Chiu et al., 1979) is used which works in the range of 85 K to 400 K with a stability of 0.1 A'. Dry air is used for temperatures above room temperature while Liquid Nitrogen vapor is used for low temperatures.

The circuit mainly consists of an error amplifier (A) which gets a reference signal through a 10 turn calibrated helipot and the sensed voltage from the sample (Fig. 2.46). The difference is amplified and buffered before being fed to the heater through power transistors (2N 3055 in parallel). The temperature required is set by adjusting the helipot which is calibrated to give 1 mV for each turn. The polarity of the reference voltage is so chosen that the output of the error amplifier is positive whenever the sensor temperature is less than the set temperature. The precise measurement of the sample temperature and the reference temperature is obtained using two different thermocouples (Copper-Constantan).

The working of the circuit is explained briefly below. When the reference voltage is more than the sensor voltage, a positive voltage appears at the output of the error amplifier, thereby turning ON the power transistors. Thus current flows through the heater and the temperature of the sensor (sample) rises. The increase in the sensor voltage decreases the error at the input of the error amplifier, thus making the output of the error amplifier less positive and less current through the heater. This happens until the sensor emf is more than the reference voltage. Now the heater is turned OFF. This turning ON and OFF of the heater happens quite a number of times until an equilibrium temperature is reached, thus maintaining the sample temperature constant.
Fig. 2.46 Temperature controller.
The sample is placed in a copper can and is kept inside a double walled evacuated \(10^{-5} \text{T}\) glass cryostat (Fig. 2.47) which is used to minimize the heat losses. The heater coil is placed in the path of the air or liquid nitrogen vapors for homogeneous temperature variation of the sample. Since the stability of the sample temperature is crucial, a few precautions are to be followed. A low thermal mass inside the cryostat enables the sample to reach the required temperature quickly but reducing the stability since any fluctuations at the heater are immediately felt by the sample. An increase in thermal mass, although improves the stability, will take very long time to reach the required temperature. Hence the thermal mass of the sample has to be optimized. Apart from this, the rate of gas flow, position of the sensor, position of the heater coil also play an important role in the process of attaining stabilized temperature. All these factors are optimized by trial and error methods to obtain temperature stability of \(0.1K\) within an acceptable time of 30 to 45 mts, typical time taken for a given \(T_1\) experiment.

### 2.3.2 Automation of the spectrometer

The high frequency pulsed NMR spectrometer and the FC spectrometer described earlier are connected to PC/AT's through IEEE 488 interface bus for automatic controlling of the spectometer for data transfer. The parameters to be changed during the course of the experiment are the delays from the digital delay degenerators. The signals to be processed for measuring the relevant relaxation time are acquired and averaged by the digital storage oscilloscope (through automation).

The necessary programs for this purpose are written in BASIC language and are executed through an assembly level program after suitable conversion. These programs differ depending on the pulse sequence required, but in general have a 'declaration block' which defines the different devices on the IEEE bus. Each device has a primary address. A given string of data can be transferred to different devices (talkers and listeners) by executing specific subroutine calls. In a typical program, for the measurement of \(T_1\) using 'saturation burst' sequence, the clock provides the repetition rate \(r\) (Fig. 2.42), while the pulse generator PG1 produces the gating pulse.
Fig.2.47 Sample assembly with temperature variation facility.
(which essentially determines the number of pulses in the burst). The delay between any two pulses in a single burst is determined by the second pulse generator PG2.

The signal averager is programed to perform the required number of averages for a given delay with specified weightages and to display the data and waveforms before repeating for other delays. The PC is programed to control the pulse programmer, clock and the signal averager by proper handshaking procedures. The algorithm used for the above procedure is given in Fig. 2.48.
Fig. 2.48 The algorithm for a typical automated $T_1$ measurement using saturation bunt sequence.
Specifications of the high frequency NMR spectrometer

1. Operating frequency range : 3 to 50 MHz

2. Bandwidth : 2 MHz at a given frequency

3. Pulsed rf power : up to $1kV(\text{peak})$ to peak
   into 50 Ohms

4. Typical $7\tau/2$ pulse width : 2 - 3 $\mu$ sec for proton

5. Pulse sequences used : Two pulse sequence

6. Recovery time : $20\mu S$ maximum

7. rf gain after detection : $100dB$

8. ON/OFF ratio of rf pulse : $100dB$

9. Transmitter isolation : 60 dB minimum

10. Temperature range : 77 K to 400 K (with 0.1 K
    stability over one hour).

11. Interface bus with PC : GPIB
2.4 Experimental details

The work reported in this thesis involves proton spin lattice relaxation measurements done as a function of frequency (\(\omega\)) in the range of 5 to 50 MHz and temperature covering all the mesophases in a few liquid crystals. These measurements are carried out using the high rf frequency spectrometer described in the earlier section. The spectrometer is tuned to obtain the best possible signal using a standard sample (viz., water with a paramagnetic impurity) at each frequency with an unaveraged S/N of 50 at the maximum frequency and an S/N of about 15 at the minimum frequency. This variation in S/N as a function of frequency accounts for the variable scatter obtained as a function of frequency. Inversion recovery and saturation burst sequence are used for the \(T_1\) measurements, while Jeenar-Broekaert three pulse sequence is used for \(T_{1D}\) measurements. The signal in the isotropic phase (I) is usually very narrow (a long FID) due to the averaging of the dipolar interaction and hence only inversion recovery sequence is used for \(T_1\) measurement. On the other hand, FID is short in the nematic phase (\(\sim 100\mu\) sec) and hence saturation burst is used, whenever \(T_1\) is above 100 msec. The maximum error in the measurement of \(T_1\) is estimated to be about 5% and about 10% for \(T_{1D}\) measurements.

The liquid crystalline samples are obtained from Frinton Laboratories (USA) and used without further purification. The transition temperatures of the systems studied are obtained from differential scanning calorimetry (DSC) and are found to be agreeing with the literature to within 1°C. The isotropic to nematic phase and nematic to smectic phase transitions are also confirmed by observing the change in the length of the FID at these transitions. The FID begins to shorten near the \(T_{NI}\) (isotropic to nematic transition) as the temperature is decreased from isotropic phase and finally collapses to a very short FID (broad line) at the transition.

The samples are sealed in 6 mm diameter glass tubes at about \(10^{-5}\) Torr after removing the dissolved oxygen by freeze-pump-thaw method. The measurements are
made by first heating the system well into the isotropic phase and then cooling to the required temperature in the presence of high fields (about 10 kG) to ensure the proper alignment of the molecules in the mesophase. The temperature variation is done with a home built temperature controller (with a stability of about 0.1 A over a period of an hour) and the data points are collected in intervals of 2° C in all the mesophases.