Chapter 2
Instrumentation

2.1 System Overview

Questions to be answered in this section include:

1. What are the basic components in an NMR spectrometer?
2. What are their functions?

The basic components of an NMR spectrometer are shown in Fig. 2.1a, and include three major elements: magnet, console, and host computer. The working function of a NMR spectrometer is basically similar to a radio system. Some of the components are called by the terms used in radio systems, such as transmitter, synthesizer, and receiver. The magnet of an NMR spectrometer produces a stable static magnetic field which is used to generate macroscopic magnetization in an NMR sample. The linear oscillating electromagnetic field, B_1 field (see Chap. 1), is induced by a transmitter with a desirable B_1 field strength to interact with nuclei under study. The NMR signal, known as the free induction decay (FID), generated in the probe coil after irradiation by radio frequency (RF) pulses is first amplified by a preamplifier, then detected by a receiver. This detected signal is digitized by an analog-to-digital converter (ADC) for data processing and display, which is done on a host computer.

2.2 Magnet

In this section such questions about the NMR magnet will be addressed as:

1. What is the structure inside a magnet?
2. How is the magnetic field generated and how is the stability of the field maintained?
3. Why does the magnet need to be periodically filled with liquid nitrogen and liquid helium?

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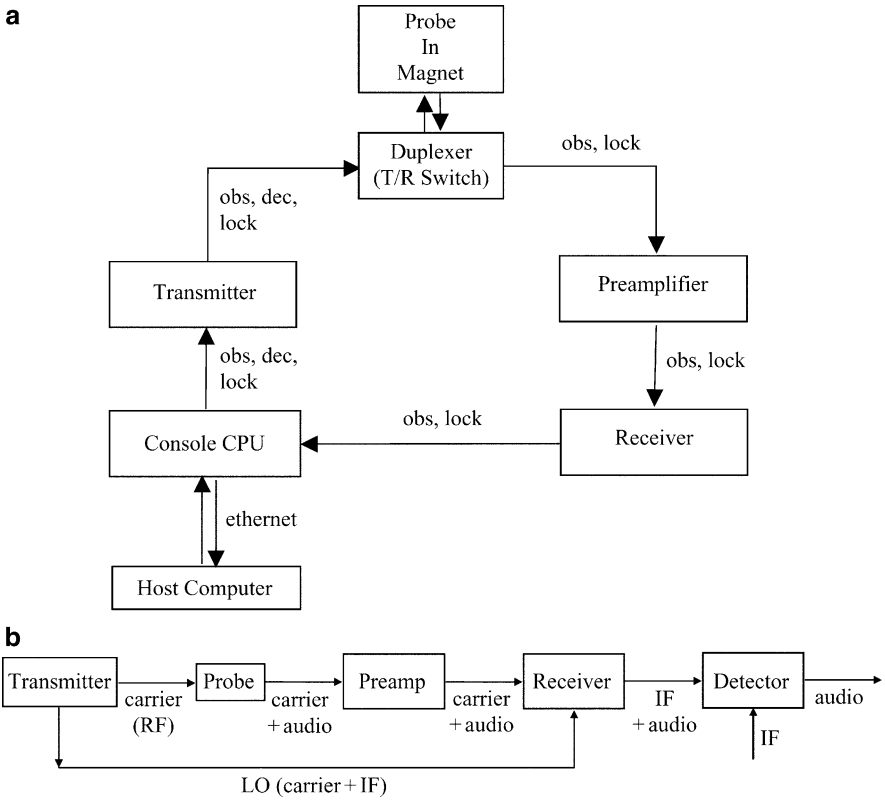

Fig. 2.1 Block diagram of NMR spectrometer.

4. What homogeneity of the field is required for NMR and how can it be obtained?
5. How is the sensitivity increased as the field strength increases?

Almost all high field NMR magnets are made of superconducting (SC) solenoids. In order to achieve superconductivity, an SC solenoid is enclosed in a liquid helium vessel (Fig. 2.2). Liquid nitrogen stored in a vessel outside the liquid helium vessel is used to minimize the loss of liquid helium because the cost of liquid nitrogen is about 40 times less than liquid helium. In addition, insulation of heat transfer between the vessels and the shell of the magnet is achieved by the use of high vacuum chambers. Vacuum is the most effective method of heat insulation, which prevents two of the three heat transfer processes: conduction and convection. The third process of heat transfer, radiation, is prevented through the use of reflective shields which are made of aluminum foil and surrounded by the high vacuum. Because of the efficient heat insulation, an NMR sample can be placed in the probe at room temperature or at other desired temperature and insulated from the liquid helium at 4.2 K just a few inches away. Liquid helium

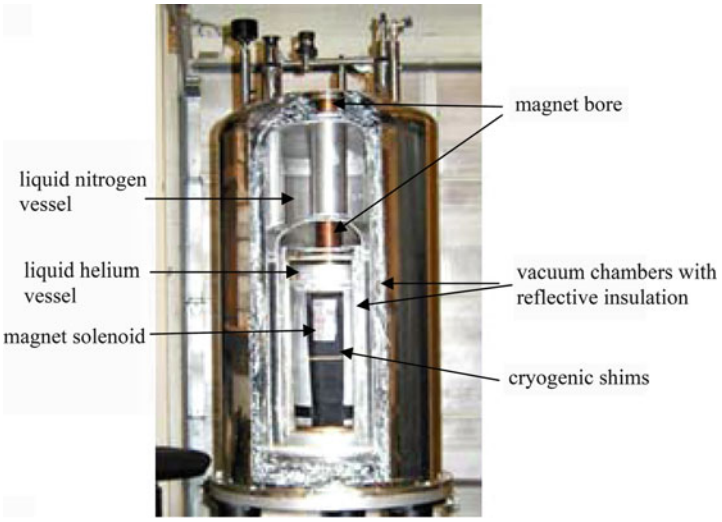

Fig. 2.2 Cutaway of a superconducting (SC) magnet. The magnet solenoid is in a liquid helium vessel, and contains approximately 12 miles of SC wire. The liquid nitrogen vessel is between the inner and outer vacuum chambers. The insulation in the outer vacuum chamber reflects heat radiation from the room temperature surface. The inner 20 K (Kelvin) radiation shield is used to prevent infrared heat radiation transfer from the liquid nitrogen vessel into the liquid helium vessel. The elimination of heat radiation reduces the liquid helium boil-off rate. Both radiation shields are made of aluminum foils (courtesy of JEOL USA, Inc.).

loss can be less than a liter per day for a modern 600 MHz NMR. Low helium loss magnets have a helium holding time longer than 1 year.

Once it is cooled down to operational temperature at or below that of liquid helium, the magnet is energized slowly by conducting DC current into the solenoid over a period of several hours to a few days. (For ultrahigh field such as 800 and 900 MHz, the magnet solenoid is kept below the temperature of liquid helium). When the magnetic field produced by the current reaches operational field strength, the two terminals of the solenoid are closed by a SC switch such as the one shown in Fig. 2.3. The SC switch is open during the entire energization process by turning on the heater nearby the SC wire in the SC switch. The heat causes the SC switch to lose superconductivity. Thus, the current passes through the magnet solenoid from the charging power supply. When the magnet reaches the operational field strength, the SC switch is closed by turning off the heater. As a result, the current passes through the loop formed by the SC switch and the solenoid, and stays inside the solenoid. Normally, an NMR magnetic field drifts less than 10 Hz h^{-1}. Quite frequently, a few months after installation, the field drifts less than 1 Hz h^{-1}.

High homogeneity of the magnetic field is an essential requirement for any NMR magnet. It is achieved with a set of SC shim coils, called cryogenic shims (or cyroshims), located just outside the magnet solenoid. The field homogeneity is

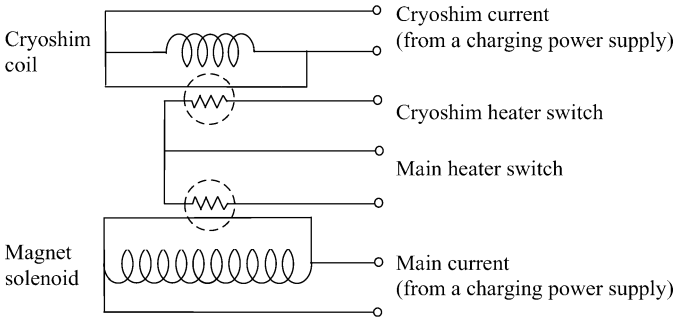

Fig. 2.3 Superconducting (SC) switch. When a heater switch is on, the SC wire inside the heater (the *dotted circle*) becomes a resistor due to the loss of superconductivity as the temperature is raised. The current flows from the power supply to the SC coil. After the heater is turned off, the current remains in the closed coil loops.

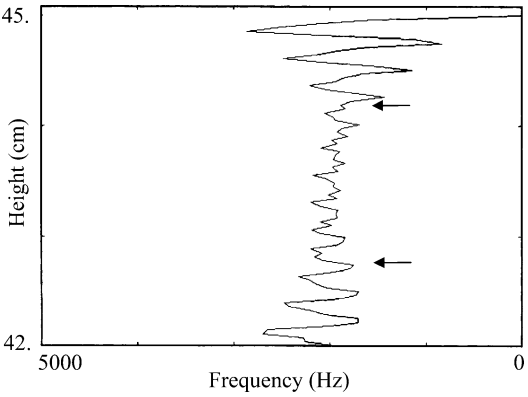

Fig. 2.4 Magnetic field mapping results of cryogenic shims for a 500 MHz magnet. High homogeneity of the magnetic field is obtained across a length over 1.6 cm (indicated by the *arrows*). The deviation of the magnetic field across the 1.6 cm length is about 500 Hz, which is equivalent to 1 ppm (500 Hz/500 MHz). The center of the probe coil is placed at the center of the field.

shimmed by a method called field mapping in which a tiny amount of sample (e.g., a drop of water) is used to obtain signal at different physical locations inside the magnet bore. The sample is moved spirochetically in the bore through the solenoid axis to record the magnetic field gradient. Then, cyroshims are adjusted according to a computer fitting for better field homogeneity. Figure 2.4 shows an example of field mapping results for an Oxford magnet during magnet installation. The results indicate that a field homogeneity of better than 1 ppm is obtained over 1.6 cm by cyroshims. During normal operation of the magnet, cyroshims need not to be changed.

For NMR experiments, a field homogeneity of 1 part per billion (ppb) or better is obtained by using a room temperature (RT) shim set which consists of as many as 40 shim gradients located in the area inside the magnet bore but outside probe.

High resolution NMR experiments require stability of the magnetic field in addition to field homogeneity. The fluctuation of the static magnetic field is corrected by monitoring a locking field frequency using a mini spectrometer, or lock system. The lock system has a lock transmitter (including a lock frequency synthesizer), a lock receiver, and a lock channel in the probe. It continuously observes the deuterium frequency of the NMR sample. The current of the z_0 coil of the RT shim coil assembly residing in the magnet bore is automatically adjusted to maintain the lock frequency at the correct value if the frequency changes. For this purpose, any NMR sample should be made from pure or partially deuterated solvent. ^2H_2O is the most common deuterated solvent used in biological samples. More details are discussed in Chap. 3.

Sensitivity and resolution of NMR signals are the fundamental reasons for the requirement of higher magnetic field strengths. Resolution of NMR spectra at a constant line width in hertz improves linearly with magnetic field strength (B_0). The sensitivity of an NMR signal is proportional to the population difference between two nuclear transition states. Because the energy gap of the two nuclear states is small (in the RF range), the population difference determined by Boltzmann distribution is also small. An increase in field strength will increase the population difference, and thus increases sensitivity (more details in Chap. 1). As a result, the sensitivity of the NMR signal increases in proportion to $B_0^{3/2}$ as the field strength increases and hence the time required to obtain the same signal-to-noise ratio is reduced in proportion to B_0^3.

2.3 Transmitter

Questions to be addressed about the transmitter include:

1. What is the function of the transmitter and what does it consist of?
2. How does a transmitter produce RF pulses with the desired pulse length and desired frequency (the carrier frequency)?
3. How can the amplitude of the pulses be attenuated?
4. What is the relationship between attenuated RF power and pulse length?

The function of a transmitter is to provide RF pulses to irradiate the samples with a desired pulse length (or pulse width) and frequency at the correct phase and power level. The transmitter channel consists of a frequency synthesizer, an RF signal generator, a transmitter controller, and an RF amplifier (Fig. 2.5). It provides RF pulses and quadrature phase generation. A frequency synthesizer provides a stable source of signal with the required frequencies using a standard reference frequency. The RF signal is gated by an RF controller to form pulses at a low amplitude level. A transmitter controller is used to create modulated phase, pulse power, and pulse

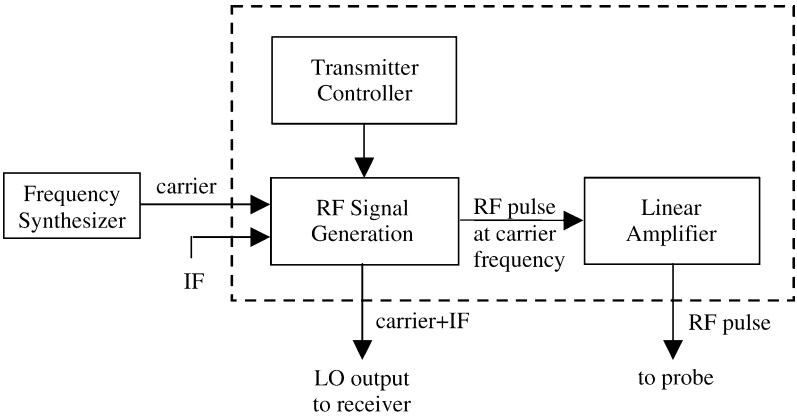

Fig. 2.5 Components of an NMR transmitter—block diagram.

gating (on and off). After it is routed through a computer-controlled attenuator to set the desired amplitude level, the RF signal then goes to the linear power amplifier to obtain the pulse power needed. The pulse from the amplifier is delivered to the probe where the NMR sample is irradiated. The output of the transmitter can be highly monochromic. Because the output power of an amplifier is attenuated linearly, the pulse length for a fixed pulse angle (for instance, a 90° pulse angle) is increased proportional to the power attenuation. The attenuation of the output amplitude is measured in a logarithmic unit, decibel or dB, which is a tenth of 1 Bel. By definition, the decibel of two signals in comparison is

$$\mathrm{dB} = 20 \log \frac{V_2}{V_1} \tag{2.1}$$

in which V_1 and V_2 are two signal amplitudes, or voltage. A signal with twice the amplitude of the other is a 6 dB increase, whereas a signal of one half the amplitude is −6 dB (or a 6 dB attenuation). Twenty decibels represent a tenfold increase in signal amplitude. A signal amplitude V increased by N dB has a value given by

$$N(\mathrm{dB})V = 1.122^N V \tag{2.2}$$

Often the ratio of two signals is measured in terms of power levels:

$$\mathrm{dB} = 10 \log \frac{P_2}{P_1} \tag{2.3}$$

in which P_1 and P_2 are the power levels of the signals and $P = V^2/R$ (R is resistance). In NMR, pulse "power" refers to the amplitude of the transmitter RF field in frequency units, rather than power in watts, because pulse length or pulse

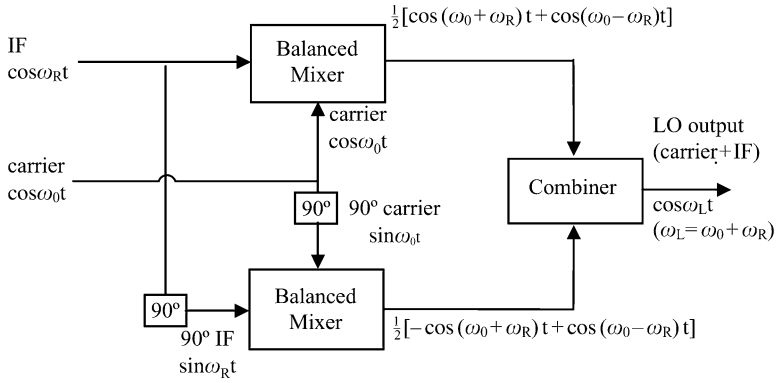

Fig. 2.6 Generation of LO frequency by a transmitter via SSB (single sideband) selection. When mixed at a balanced mixer (BM), two input frequencies are multiplied to produce a pair of sideband frequencies. The phase of the output is also dependent on the phases of the input signals. The output of a balanced mixer contains neither the carrier frequency nor the modulated intermediate frequency (IF) but only the sidebands.

angle is proportional to γB_1, in which γ is the gyromagnetic ratio and B_1 is the amplitude of the transmitter RF field. Therefore, the pulse length will increase to twice as long when attenuation is −6 dB.

One transmitter is required for each channel on an NMR spectrometer. Typically, a triple-resonance experiment requires separated proton, carbon, and nitrogen transmitter channels in addition to a lock channel. A four-channel NMR spectrometer may use the fourth channel for deuterium decoupling or for irradiation on other nuclei. Because of the low gyromagnetic ratios of heteronuclei, a heteronuclear channel has a longer pulse length for the same amplifier output power. A typical amplifier for high resolution NMR has an output power of a few hundred watts on each RF channel (see Sect. 2.8).

The local oscillator (LO) output of a transmitter which is used by a receiver to record the NMR signal (see discussion for receivers) is created by combining an intermediate frequency (IF) signal with the carrier frequency using the technique called single sideband (SSB) selection (Figs. 2.1b and 2.6). The IF is much lower than the carrier frequency, usually a few tens of MHz and is usually obtained from a fixed-frequency source. When the carrier and IF signals are mixed at a balanced mixer (BM is also called phase sensitive detectors, PSD), which is a device with two or more signal inputs that produces one signal output, the carrier multiplies the IF resulting in a pair of frequencies, carrier −IF and carrier +IF, known as a double sideband band suppressed carrier (DSBSC, Fig. 2.7). In order to convert DSBSC to SSB frequency, BMs are used to phase the signals. Quadrature IF and carrier frequencies (Quadrature means that two components of a signal differ in phase by 90°) are met at two BMs whose output contains neither the carrier frequency nor the modulated IF but only the sidebands, resulting in two pairs of mixed IF with the carrier signals: a 90° phase-shifted pair in one path and a non-phase-shifted pair in the other. The output of a BM is a double sideband signal consisting of the

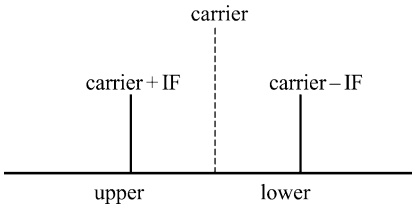

Fig. 2.7 Double sideband suppressed carrier frequency pair. The sidebands above and below the carrier frequency are called upper and lower sideband, respectively.

sum and difference of IF and the carrier frequencies produced by multiplying the two signal inputs:

$$\cos\omega_0 t\cos\omega_R t = \frac{1}{2}[\cos(\omega_0+\omega_R)t + \cos(\omega_0-\omega_R)t]$$
$$\sin\omega_0 t\sin\omega_R t = \frac{1}{2}[-\cos(\omega_0+\omega_R)t + \cos(\omega_0-\omega_R)t]$$

in which ω_0 and ω_R are the carrier frequency and intermediate frequency, respectively. Then, the double-band outputs of the mixers are combined at the combiner, where one sideband is enhanced and the other is canceled. The combination produces a single frequency output, an LO output, which usually is the frequency of the carrier +IF (it can also be designed to produce the frequency of the carrier −IF).

An alternative way to produce an LO is to use a synthesizer to generate an LO frequency. In this case, the carrier frequency of the transmitter is produced from the combination of LO and IF (Fig. 2.8). IF and LO quadrature frequency signals are mixed to produce the carrier frequency for RF pulses. The advantage of this configuration is that LO frequency to be used by the receiver is less noisy than the transmitter configuration represented in Fig. 2.6, and hence it potentially gives better sensitivity.

Since the transmitter provides the energy source for irradiating an NMR sample, it is wise to measure the output of the transmitter when the NMR spectrometer has problems such that no NMR signal can be observed. The convenient way to do this is to connect the transmitter output to an oscilloscope at the point just before the probe. The oscilloscope is set to measure voltage and appropriate attenuation should be used to protect the oscilloscope from damage by the high power of the transmitter amplifier (refer to Sect. 2.9 for operation of an oscilloscope). Attenuation can be done either by setting a transmitter attenuation parameter or by using an attenuator (e.g., 20 dB) between the oscilloscope and the transmitter output.

The dB value describes the relative power levels or amplitudes of two signals. Often, the amplitude of a signal is described relative to a reference power level. For instance, the term dB_m means dB relative to 1 mW into a given load impedance of a device, which is 50 Ω for an NMR instrument (we will assume that impedance is 50 Ω throughout this book unless specified), and dBW to 1 W:

$$1\text{ mW} = 0.2236V_{rms} = 0\text{ dB}_m \tag{2.4}$$

$$dB_m = 10\log P_{mw} \tag{2.5}$$

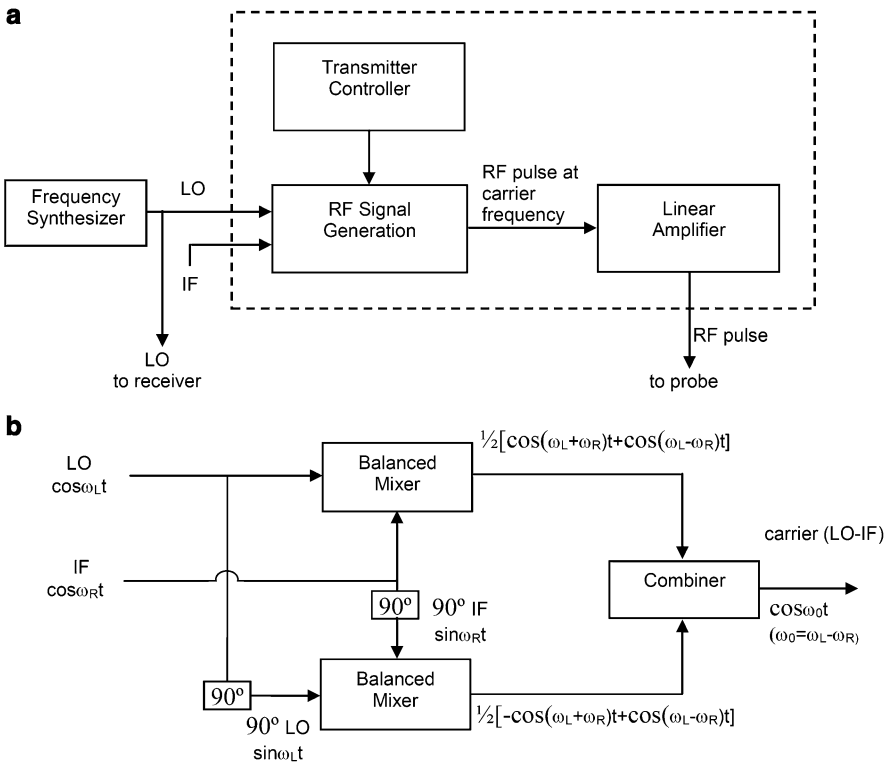

Fig. 2.8 An NMR transmitter using an LO to produce the carrier frequency. The carrier frequency of the transmitter is produced from the combination of LO and IF. IF and LO quadrature frequency signals are mixed to produce the carrier frequency for RF pulses.

$$P_{\mathrm{mw}} = 10^{\mathrm{dB_m}/10} \tag{2.6}$$

in which P_{mw} is the power in mW. A signal into a 50 Ω impedance with 0 $\mathrm{dB_m}$ amplitude has a voltage of 0.2236 V_{rms} $[V = (PR)^{1/2} = (10^{-3} \times 50)^{1/2}]$. The electric signal is also characterized by a peak-to-peak amplitude (V_{pp} which is twice the amplitude) and the root-mean-square amplitude (V_{rms}). For a sinusoidal signal, V_{rms} and V_{pp} have a relationship given by

$$V_{\mathrm{rms}} = \frac{A}{\sqrt{2}} = \frac{V_{\mathrm{pp}}}{2\sqrt{2}} = \frac{V_{\mathrm{pp}}}{2.828} \tag{2.7}$$

$$P_{\mathrm{mw}} = 2.5V_{\mathrm{pp}}^2 \tag{2.8}$$

in which A is the signal amplitude and V_{pp} is the peak-to-peak amplitude that corresponds to the voltage difference between the most positive and most negative

points of a signal waveform (Fig. 2.22). It is two times the amplitude of a sine wave signal. A sine wave signal of 1 V_{pp} has a dB_m value of 3.98, using one of the equations:

$$\begin{aligned} dB_m &= 3.98 + 20 \log V_{pp} \\ &= 13.01 + 20 \log V_{rms} \\ &= 30 + 10 \log P_{rms} \end{aligned} \tag{2.9}$$

in which P_{rms} is the power of the signal in watts. The value of V_{pp} for a given dB_m value can be calculated by

$$V_{pp} = 10^{(dB_m - 3.98)/20} \tag{2.10}$$

When troubleshooting, it is convenient to have a table of V_{pp} vs. dB_m although it can be calculated by (2.10).

2.4 Receiver

Questions about the receiver are addressed in this section, including:

1. What kind of signal is detected by the receiver and how is it detected?
2. How is the signal separated from the carrier frequency by the receiver?
3. How is quadrature detection achieved?

A receiver is used to detect the NMR signal generated at the probe and amplify the signal to a level suitable for digitization. Detection is the process of demodulating the NMR signal (in audio frequency, kHz range) from the carrier frequency (in RF, MHz range), and measures not only the amplitude or voltage of the signal, but also the phase modulation. Because the RF signal is very weak coming from the probe, it is amplified first by a preamplifier that is located near or inside the probe to reduce the loss of signal, before it is transferred to the receiver inside the console. The process of signal detection includes preamplification, several stages of RF signal amplification, quadrature detection (separation of the NMR signal from the carrier frequency), and amplification of the NMR (audio) signals.

In the simplest method, several stages of tuned RF amplification are used, followed by a detector. The frequencies of all amplification stages are tuned to a narrow range near the carrier frequency in order to amplify RF signals for detection. When signals pass through the amplifier, noise is also amplified along with the input signals which have very low amplitude. To reduce the effect of noise it is necessary to filter noise outside the signal frequency bandwidth and to only allow signals and noise with the same bandwidth as the signals to come through. For this reason, a bandpass filter is used with the center frequency tunable over a desired frequency range.

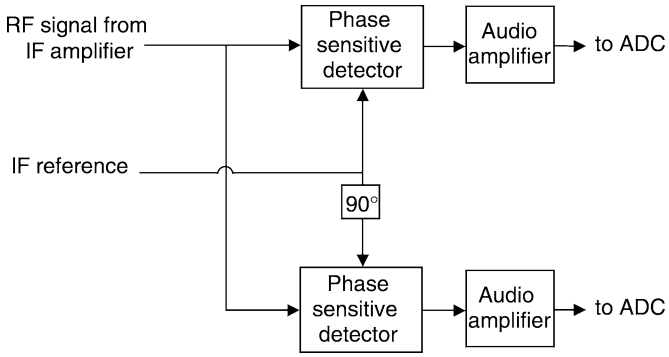

Fig. 2.9 Quadrature detection using two phase sensitive detectors (PSDs). The PSDs compare the frequencies of two input signals, and then generates an output. The output is the measure of phase and frequency differences of the input signals. When two signals with the same frequency are mixed at a PSD, the output is the measure of the phase difference of the two inputs.

Furthermore, all stages of amplification must have amplitude linearity over the full band frequency range. This configuration of NMR receiver is undesirable because it is difficult to construct amplifiers with linear response and accurate selectivity at all stages over the range of several hundred MHz. The tunable filters usually lack passband flatness over a wide frequency range. As a result, the resolution of the tuned receiver is dependent on frequency. This causes problems such as lack of sensitivity and resolution, and signal distortion.

The solution to the problem is the superheterodyne receiver (narrowband receiver). It differs from the tuned receiver in that the RF signals are adjusted to pass through fixed passband amplifiers and filters instead of tuning the amplifiers and filters for the RF signals. Unlike the transmitter which must use Larmor frequency RF pulses to irradiate sample in order to generate NMR signals, the receiver may be set to a fixed frequency to detect the signals. The incoming signals are amplified by a preamplifier (single stage tuned amplification), then mixed with an LO frequency to produce signals at a fixed IF. After the preamplifier, the signal at IF passes through a set of IF amplifiers and filters in the receiver. Finally, IF RF signals are terminated at a quadrature detector that subtracts the IF from the NMR signals using the reference IF, and NMR signals with audio frequency (kHz) are amplified by an audio amplifier for digitization. Tuning the IF receiver for different carrier frequencies is achieved by alternating the LO frequency so that an input carrier frequency gets mixed down to the IF frequency. Receivers that have one mixing stage are called single conversion receivers, whereas they are called multiple-conversion receivers if mixed in more than one stage. The single-conversion superheterodyne receiver has become very popular for modern NMR spectrometers. It offers higher sensitivity and better performance in the presence of interfering signals.

Detection of NMR signals is done by a quadrature detector, involving a phase detector shown in Fig. 2.9. The phase detector is a circuit that compares the

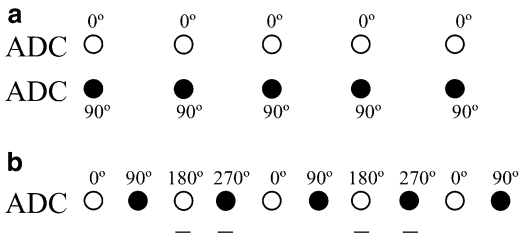

Fig. 2.10 Quadrature detection by (**a**) the simultaneous acquisition method and (**b**) the sequential method. The *open circles* represent the data points detected by the zero-phased detector (PSD) and the *filled circles* represent those detected by the 90°-phased detector in Fig. 2.9. The data points multiplied by −1 are indicated by the *minus sign* below the *circles* in (**b**). The receiver phases are shown above or below the data points.

frequencies of two input signals, and then generates an output. The output is the measure of phase and frequency differences of the input signals. The internal circuitry of a phase detector is actually a BM. When two signals with the same frequency are mixed at a phase detector, the output is the measure of the phase difference of the two inputs. The RF signal coming out of the IF amplifier is divided at a splitter. The two split signals are fed into separate phase detectors where they are mixed with quadrature IF reference signals generated by a phase shifter. Finally the output of each phase detector is amplified by an audio amplifier and digitized at the ADC (see the Sect. 2.7) as real and imaginary components of an FID.

Practically, quadrature detection in the observed dimension can be done either by two ADCs or by a single ADC (Fig. 2.10). The first method (known as simultaneous acquisition) uses one ADC for each PSD to simultaneously sample the data from two channels with one ADC acquiring the real part of the FID and the other recording the imaginary part of the data. Fourier transformation of the complex data produces a spectrum with the carrier in the center of the spectral window (SW). The second method (known as sequential acquisition or the Redfield method) uses a single ADC to sample the data from the two PSDs one after the other with the same time intervals set by the dwell time. The ADC digitizes the signal at a sample rate twice as fast as normal. The ADC switches between the two PSDs after sampling each point. Therefore, the odd number data points come from the first PSD and the even number from the second PSD, which is 90° out of phase to the first one. Additionally, every second pair of data points is multiplied by −1. The net result is that the phases of all the points are increased sequentially by 90° (=¼ cycle), which is known as time-proportional phase increment (TPPI). If a real Fourier transform is applied to the data, the sign of the frequency (the direction of the magnetization rotation) cannot be distinguished (−SW to SW), because the data does not contain an imaginary part. Since the sampling rate is twice as fast as in the simultaneous method, the spectral window now is −½SW to +½SW (real Fourier transformation produces a spectral window with 2SW from −SW to +SW and the ½ factor is caused by the doubled sampling rate). In addition, the effect of TPPI on the time domain is to increase the frequency by +½SW. This can be understood by

considering that the spectral width is doubled because the real Fourier transformation cannot distinguish the sign of the spectrum, the 90° phase increment introduces a factor of ¼ because 90°/360° = ¼, and hence 2SW × ¼ = ½SW. Considering all the factors, the spectral window of the sequentially acquired data ranges from 0 to SW after the real Fourier transformation with the carrier in the center of the spectrum and the correct sign for all frequencies. The results obtained from the two methods are essentially identical. Some spectrometers (such as Bruker systems) allow users to use either of the acquisition methods, whereas others acquire the data simultaneously using two ADCs (such as Agilent or JEOL).

2.5 Probe

Probe circuits are usually characterized by three quantities: resonance frequency, total impedance at resonance, and the *Q* factor of the circuits. In the current section, simple circuits are discussed to illustrate the function of an NMR probe. Questions to be addressed include the following:

1. What are the electronic components inside a probe?
2. What are the inductor–capacitor (*LC*) parallel and series circuits and what are their resonance frequencies and impedance?
3. How is the quality factor or *Q* factor of the probe defined and what are the *Q* factors of the circuits?
4. What do probe tuning and matching mean and why must a probe be tuned before setting up experiments?
5. How are probe tuning and matching achieved?
6. What is a cryogenic probe and how is high sensitivity of a cryogenic probe obtained?
7. Why can a moderate salt concentration degrade the performance of cryogenic probes?
8. What is the radiation damping effect and what causes it?

NMR probes are basically resonant circuits (frequency dependent) in which capacitors and inductors are combined (Fig. 2.11). The sample coil in the probe

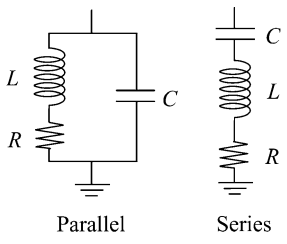

Fig. 2.11 Parallel and series *LC* circuits. *C* is the capacitance of the circuit and *L* is the inductance with resistance *R*.

circuit is used to generate a B_1 electromagnetic field to interact with the nuclei of the sample. Used with RF pulses, the probe circuit must have its impedance matched to the specific impedance of the cables, which means that the impedance of the cable terminated at the probe equals the characteristic impedance of the cable (50 Ω). This allows the RF pulses to be transferred to the probe without reflection so that all the power of the pulses is used by the probe without loss. In order to understand the function and working principle of probes, it is necessary to review the relationship between voltage and current, which are the two quantities characterized in electronic circuits. An important characteristic of capacitors and inductors is their frequency dependence. A device made from these components will produce an output waveform that is also frequency dependent, but maintains linearity in the amplitude of waveforms. The generalized Ohm's law is well used in analyzing the inductor–capacitor (*LC*) devices:

$$I = \frac{V}{Z} \tag{2.11}$$

$$V = IZ \tag{2.12}$$

in which Z is impedance in complex form, considered as a generalized resistor of a circuit, I is current and V is voltage. The capacitor with capacitance C and the probe coil with inductance L have impedances in the following terms:

$$\text{Capacitor: } Z_{\mathrm{C}} = -\frac{j}{\omega C} = \frac{1}{i\omega C} \tag{2.13}$$

$$\text{Inductor: } Z_{\mathrm{L}} = j\omega L \tag{2.14}$$

$$\text{Resistor: } Z_{\mathrm{R}} = R \tag{2.15}$$

in which ω is the angular frequency of the waveform ($\omega = 2\pi v$) and j is the imaginary unit, $\sqrt{-1}$. Like resistors, impedance in parallel and series circuits has the formulas:

$$Z_{\mathrm{p}} = \frac{1}{(1/Z_1) + (1/Z_2) + (1/Z_3) + \cdots} \tag{2.16}$$

$$Z_{\mathrm{s}} = Z_1 + Z_2 + Z_3 + \cdots \tag{2.17}$$

The simplest *LC* circuits are parallel and series *LC* circuits, in which an inductor is combined with a capacitor in parallel and series, respectively (Fig. 2.11). Since the *LC* circuits are connected to the input in series where the current is the same for the input and the output at the junction and ground, the output voltage is

proportional to the total impedance of the LC circuit. For a parallel LC, the impedance is given by

$$Z = \frac{1}{(1/Z_L) + (1/Z_C)} = \frac{1}{(1/(j\omega L + R)) + j\omega C} = \frac{j\omega L + R}{1 - \omega^2 LC + j\omega RC} \tag{2.18}$$

By multiplying both the numerator and denominator of (2.18) by $(R - j\omega L)$, the total impedance is

$$Z = \frac{\omega^2 L^2 + R^2}{R - j\omega L(1 - \omega^2 CL - R^2 C/L)} \tag{2.19}$$

At resonance frequency ω_0, the circuit has real impedance. Therefore, the imaginary part of (2.19) must be zero:

$$1 - \omega_0^2 CL - R^2 C/L = 0 \tag{2.20}$$

Because R is always much smaller than L in the circuit, $R^2 C/L \approx 0$. Then

$$\omega_0 \approx 1/\sqrt{LC} \tag{2.21}$$

The impedance Z at resonance approximately equals [R^2 in (2.19) is negligible compared to L]:

$$Z = \frac{\omega^2 L^2}{R} \tag{2.22}$$

producing a sharp peak of output voltage as shown in Fig. 2.12.

The resonance condition is phase-resonance, meaning that the capacitance and inductance of the circuit are equal. The frequency function of the voltage ratio (V_{out}/V_{in}) in Fig. 2.12 shows that the output voltage of the parallel LC circuit is the same as the input voltage at the resonance frequency. Practically, the ratio is less than 1 due to imperfections in the electronic components.

The circuit is characterized by the quality factor of the circuit, Q, which is dependent on the resonance frequency:

$$Q = \omega_0 L/R \tag{2.23}$$

The practical significance of Q represents that the smaller the value of R, the greater the value of Q, resulting in a sharper resonance peak. In addition, the higher Q is, the more sensitive the probe. Changing C and L will alter the impedance of the circuit while tuning to the desired resonance frequency.

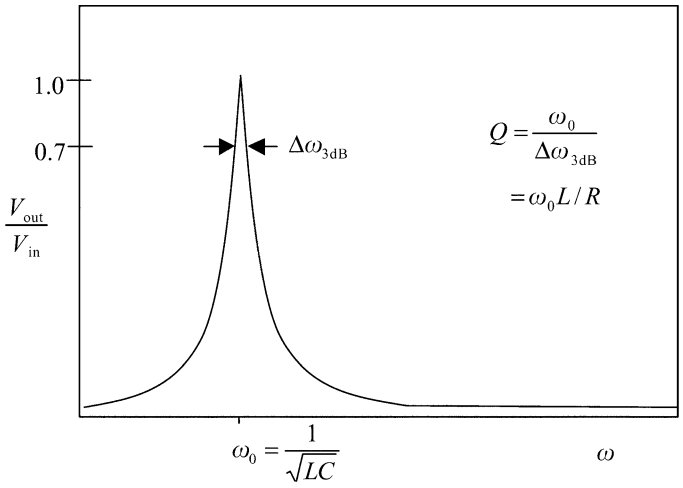

Fig. 2.12 Output voltage curve in a parallel *LC* circuit as a function of frequency. The maximum is at the resonance frequency ω_0 and is dependent on the capacitance and inductance of the circuit.

Another type of *LC* resonance circuit is the series *LC* circuit as shown in Fig. 2.11, which has impedance in the terms of

$$Z = Z_L + Z_C = R + j\omega L + \frac{1}{j\omega C} = \frac{\omega CR + j(\omega^2 LC - 1)}{\omega C} \tag{2.24}$$

By applying the resonance condition that the imaginary term of the impedance is zero, the resonance frequency has the same formula as that of parallel circuit, $\omega_0 = 1/\sqrt{LC}$. The series resonance circuit is different than the parallel in that it is a trap circuit which holds all input voltage at the resonance frequency (Fig. 2.13). There is no voltage through the circuit at the resonance condition, as if it is a short circuit. However, the individual components have voltage across them. In fact, the capacitor and inductor have the same amplitude and opposite voltages. In addition, they are larger than the input voltage and 90° out of phase with the input. The circuit has a Q factor of $\omega_0 L/R$ and the resonance impedance of the circuit equals the resistance R of the conductor (probe coil).

For the above circuits, to achieve the highest Q factor, L is chosen to be as large as possible and R as small as possible. The desired resonance frequency can be obtained by changing C for the given L. However, the impedance cannot be set to a desired value once L, C and R are selected for a resonance frequency and Q factor. As a result, matching the impedance is impractical for these kinds of circuits. The solution to the problem is to integrate an additional adjustable capacitor as shown in Fig. 2.14. For the series–parallel circuit the total impedance can be approximated to

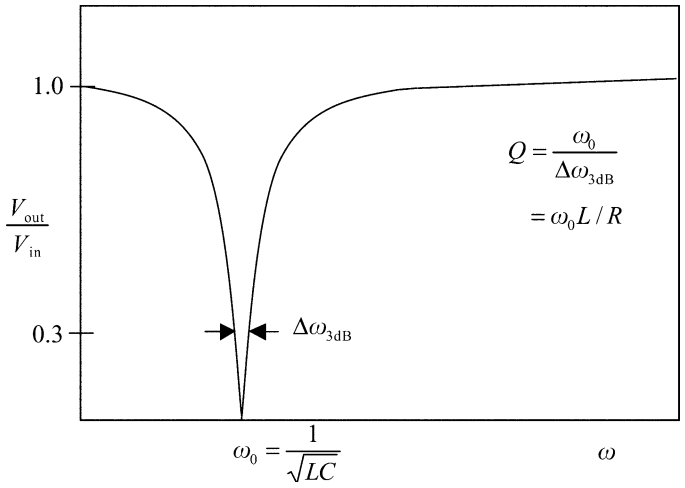

Fig. 2.13 Output voltage curve in a series *LC* circuit as a function of frequency. It becomes a short circuit at the resonance frequency ω_0.

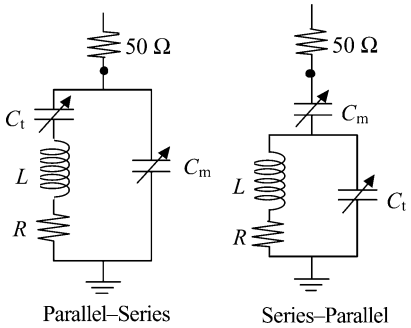

Fig. 2.14 Examples of probe circuits: parallel–series and series–parallel *LC* circuits. C_t and C_m are the adjustable capacitors for tuning and matching, R is the resistance of the probe coil, and 50 Ω is the impedance of the cable connected to the probe at the dot point.

$$Z_{LC} = \frac{1}{(1/Z_L) + (1/Z_{C_t})} + Z_{C_m} = \frac{1}{(1/j\omega L) + j\omega C_t} + \frac{1}{j\omega C_m}$$
$$= \frac{j(\omega^2 L C_t + \omega^2 L C_m - 1)}{(1 - \omega^2 L C_t)\omega C_m} \tag{2.25}$$

$$\omega_0^2 L(C_t + C_m) - 1 = 0 \tag{2.26}$$

$$\omega_0^2 = \frac{1}{\sqrt{LC}} \tag{2.27}$$

in which $C = C_t + C_m$. To obtain the Q factor and total impedance at resonance, the resistance R should be considered as treated earlier (refer to (2.18)). Q is the same at resonance as previously obtained for the resonance circuit, $Q = \omega L/R$.

The impedance at resonance is close to $Q\omega L/a$, which is the same as the parallel circuit except it is scaled by a factor of $a = (1 + C_m/C_t)^2$. Therefore, for a probe circuit with high Q obtained by large L, the impedance is brought down to 50 Ω by increasing C_m and simultaneously decreasing C_t to maintain the resonance frequency.

For a parallel–series circuit, the modification is obtained by adding a parallel capacitor to the series circuit. Using a similar treatment, the resonance frequency is proved to be approximately equal to $(LC_t)^{-1/2}$ for the situation of $C_m \gg C_t$ and the impedance at resonance is given by $Q\omega LC_t^2/(C_t + C_m)^2$. When such a circuit is used for an NMR probe, the resonance frequency is achieved by high L and small C_t to obtain high Q and to meet the condition of $C_m \gg C_t$. For such a probe, the matching capacitor has little effect on the tuning of the resonance frequency and the 50 Ω matching is achieved by adjusting the matching capacitor after the probe is tuned to ω_0.

Tuning the probe means adjusting the circuit capacitance and inductance to be on resonance at a desired frequency. For probe tuning, it is difficult and expensive to change the inductance of the probe circuit. Therefore, the frequency and impedance adjustment of the probe is achieved by changing the capacitance as described above. During the probe tuning, the impedance of the probe circuit is also adjusted to match impedance of the cable connected to the probe at 50 Ω. The probe acts as an RF load of the cable. In the case of mismatch, when the impedance of the probe circuit is not 50 Ω, the cable produces a reflected wave when an RF pulse is applied to the probe, and thus reflects a portion of the RF power delivered to the probe. The ratio of reflected power to the applied power (power loss due to the mismatch) is dependent on the impedance of the probe, Z_L and the characteristic impedance of the cable, Z_0:

$$\rho = \frac{Z_L - Z_0}{Z_L + Z_0} \tag{2.28}$$

A probe with an impedance smaller than 50 Ω produces a reflected wave with opposite polarity, whereas the reflected wave is not inverted if Z_L is larger than 50 Ω. At the matching condition ($Z_L = Z_0$), there is no power loss and hence all applied power remains in the probe, which in turn produces the shortest 90° pulse length.

As mentioned in Chap. 1, NMR spectroscopy is an insensitive technique owing to the small energy gap between the transition energy states. This insensitivity limits the application of NMR to samples with high concentration. Much effort has been carried out to develop more sensitive probes in parallel with the development of higher field magnets. The sensitivity of the probe is proportional to its Q factor, which means that the higher Q is, the higher the sensitivity:

$$\frac{S}{N} \propto \sqrt{\frac{\eta Q}{T}} \tag{2.29}$$

in which S/N is the signal-to-noise ratio, η is the filling factor of the probe coil and T is temperature in K. As discussed previously, the Q factor is inversely proportional to the resistance of the probe coil. Reduction in the resistance will significantly increase the Q value of the probe. Using high temperature superconducting material

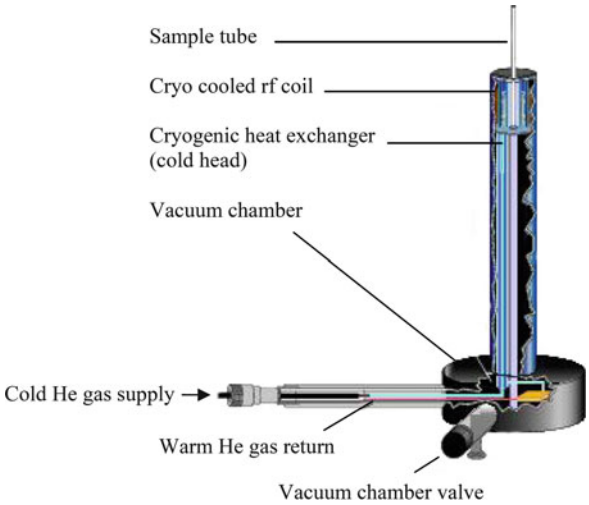

Fig. 2.15 Diagram example of a cryogenic NMR probe. The probe operates at cryogenic temperature (e.g., 25 K) and the temperature of the sample is regulated by a variable temperature (VT) control unit. The probe coil and preamplifier are cooled by the cold helium gas. After heat exchange at the cold head near the probe coil, the warm helium gas returns to helium compressor of a close-cycled cooling (CCC) system. The probe body is insulated by the vacuum chamber pumped continuously (courtesy of Agilent Technologies).

for the probe coil is an effective way to reduce the resistance. It has also been recognized that thermal noise generated at the probe coil limits the sensitivity of the probe. Cooling the probe coil made from the normal conductor and preamplifer to 25 K can significantly reduce the noise contribution and improve the sensitivity. For a cryogenic probe, the Q factor can be as high as 20,000 compared to 250 of conventional probes. In addition, a considerable amount of thermal noise in the probe is eliminated at the low temperature, which in turn increases the sensitivity of the probe. For this same reason, preamplifier circuits are integrated inside the cryogenic probe and cooled to the cryogenic temperature. An example diagram of a cryogenic probe for high resolution NMR is shown in Fig. 2.15. With the use of cryogenic probes, the sensitivity can be improved dramatically by a factor of 3–4-fold compared to a conventional probe as evidenced by the comparison of HNCA TROSY slices shown in Fig. 2.16. This leads to a reduction in experiment time of 9–16 fold or the ability to obtain data for more dilute samples.

Because of its high sensitivity, the performance of the cryogenic probe is more vulnerable to the salt concentration of the NMR sample. The sensitivity of a probe has a dependence on the conductivity of a sample according to the following relationship:

$$\frac{S}{N} \propto r_s \sqrt{\eta \sigma \omega_0} \tag{2.30}$$

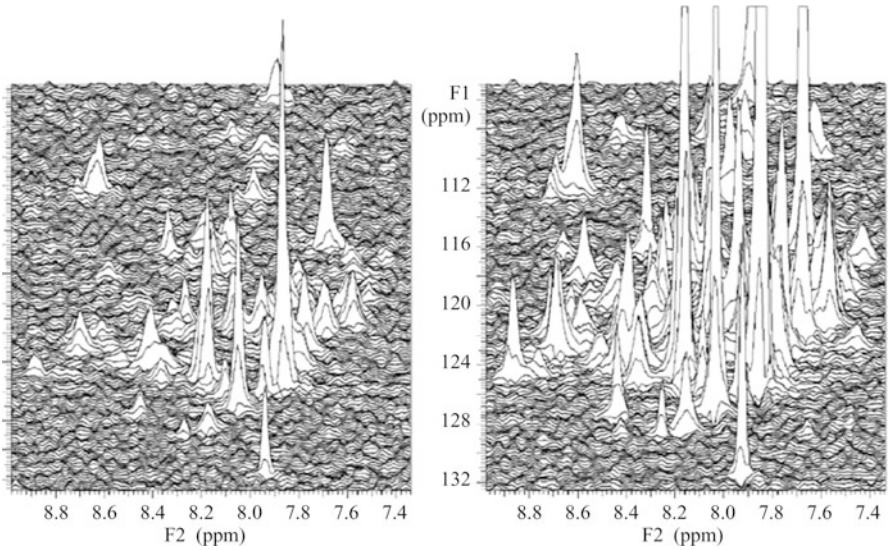

Fig. 2.16 HNCA TROSY slices of 2.3 mM ^{13}C, ^{15}N, ^{2}H DAGK (Oxenoid et al. 2004) obtained at 600 MHz field strength using a conventional triple-resonance probe (*left*) and a cryogenic probe (*right*) (courtesy of Agilent Technologies).

in which r_S is the radius of a cylindrical sample with conductivity of σ, η is the filling factor of the probe coil, and ω_0 is the resonance frequency. The high Q value of cryogenic probes is dramatically diminished by the increased resistance due to the presence of salts in the solution, whereas the function of a conventional probe is stable over a relatively wide range of salt concentrations. Even a moderate dielectric loss by a salt concentration of about 100 mM may substantially weaken the advantage of cryogenic probes. Therefore, careful attention must be paid when the sample is prepared with a buffer solution containing salts.

At high magnetic fields (>500 MHz), the radiation damping effect from water signal of an aqueous sample causes problems and artifacts such as artifacts and spurious harmonics in multidimensional spectra and distorted line shapes in T_1 and T_2 relaxation measurements. It has long been recognized that radiation damping is not signal dissipation but a process in which transverse magnetization is transformed to the longitudinal magnetization due to the coupling of water magnetization to the probe coil. The effect can be explained by considering the oscillating magnetic field produced by the water transverse magnetization. After an RF pulse, the water magnetization near the carrier frequency precesses in the xy plane of the laboratory frame (Augustine 2002). This rotating magnetization produces an oscillating magnetic field that induces an electromotive force (EMF) or a current flowing in the probe coil according to Faraday's law. The current will in turn produce an RF magnetic field inside the probe coil with the same frequency that rotates the water magnetization back to the z axis. The rate at which the water transverse magnetization generated by a 90° pulse returns to the z axis by the

oscillating RF magnetic field can be described in terms of the radiation damping time constant T_{RD} (Bloembergen and Pound 1954), which is given by

$$R_{RD} = \frac{1}{T_{RD}} = 2\pi M_0 \gamma Q \eta \tag{2.31}$$

in which γ is the gyromagnetic ratio, Q and η are defined as in (2.29). For a high-Q NMR probe (specially a cryogenic probe), the water transverse magnetization can be transformed to longitudinal magnetization by the radiation damping effect on the order of milliseconds compared to the water ^{1}H T_1 relaxation times on the order of seconds (Lippens et al. 1995). Larger T_{RD} gives a slower rate (or a smaller R_{RD}).

Radiation damping can cause problems such as line width broadening, rapid sample repolarization, and solute signal distortion. Many methods have been developed to remove the radiation damping effects by either pulse sequences or probe hardware design. The active feedback-suppression method (Szoke and Meiboom 1959; Broekaert and Jeener 1995) uses hardware to feed the signal generated by the radiation damping back to the probe coil after the signal is phase shifted by 180°. As a result, the oscillating current in the probe coil is canceled in real time. Other methods include the overcoupling method, which uses overcoupled probe circuits (Picard et al. 1996) and hence increases T_{RD} and decreases the radiation damping rate, and Q-switching method which uses low Q during RF pulsing and switches to high Q during acquisition. As a result, T_{RD} is increased by decreasing the Q value.

The radiation damping effect has also been utilized to obtain information on the water/solute interactions and to achieve solvent suppression. For instance, the radiation damping was used to study the hydration of the protein BPTI without the feedback (Bockmann and Guittet 1995), to generate selective inversion pulse using the feedback to investigate the water/solute interaction (Abergel et al. 1996), and to suppress solvent signals in the measurement of the self-diffusion coefficients of biomolecules (Krishnan et al. 1999).

2.6 Quarter-Wavelength Cable

Questions to be addressed in the present section include the following:

1. What is a quarter-wavelength cable?
2. What are the functions of a quarter-wavelength cable?
3. What can it be used for?

If the load impedance of a cable matches the characteristic impedance of the cable, all applied power goes into the load and no power is reflected. This is true regardless of cable length or wavelength of the RF signal. However, when the impedance of the cable is mismatched, for a given cable length, the portion of the signal reflected back at the input terminal has a phase shift with respect to the input signal and the phase

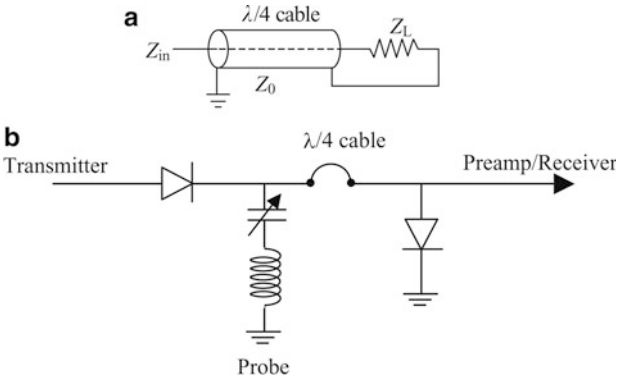

Fig. 2.17 (**a**) Quarter-wave coaxial cable whose input impedance is determined by (2.33) and (**b**) its application in a T/R (transmitter/receiver) switch.

depends on the frequency of the input signal (Parker et al. 1984). Consequently, the impedance at the input terminal will contain the reflected component and depends on the load impedance of the cable, the characteristic impedance, cable length ℓ and the wavelength λ corresponding to the applied frequency. The wavelength is 0.66 times the wavelength of light at a given frequency for a typical coaxial cable using solid dielectric spacing material (polyethylene). For a cable with length ℓ, characteristic impedance Z_0, and load impedance Z_L (Fig. 2.17), the input impedance is given by

$$Z_{in} = Z_0 \frac{Z_L \cos(2\pi\ell/\lambda) + jZ_0 \sin(2\pi\ell/\lambda)}{Z_0 \cos(2\pi\ell/\lambda) + jZ_L \sin(2\pi\ell/\lambda)} \tag{2.32}$$

The equation describes the dependence of the impedance transformation on the cable length. If the cable length equals an odd number of quarter-wavelength:

$$\ell = n\frac{\lambda}{4} \quad (n = 1, 3, 5, 7, \ldots)$$

then the input impedance experienced by the cable is

$$Z_{in} = \frac{Z_0^2}{Z_L} \tag{2.33}$$

For a short-circuited ¼ wavelength cable which has zero load impedance ($Z_L = 0$) such as by grounding, the input impedance becomes infinitely large according to (2.33), which means that the cable becomes open for its corresponding frequency. Thus, no signal with the frequency of the quarter-wavelength cable can pass through, and a signal with a different frequency will be attenuated by passing through the cable. This can be understood by considering that a shorted

¼ wavelength line must always have zero voltage and maximum current at the shorted end because $Z_L = 0$. At the input end which is a quarter-wavelength away from the shorted end, the voltage is maximum and the current is zero. Therefore, it looks like an open circuit for the signal with the corresponding frequency. This property of the quarter-wavelength cable (sometimes called quarter wave cable) is applied in a T/R (transmitter/receiver) switch to isolate the probe from the preamplifier during the transmitter pulse so that the RF power does not go into the preamplifier. A quarter-wavelength cable with actively shut diodes is connected to the receiver part of the T/R switch. When an RF pulse is applied by the transmitter, the diodes become one-way conductors (because of the high voltage of the pulse, Fig. 2.17b). The quarter-wavelength cable is shorted by the closed diode connected to it, becomes an open line for the specific frequency RF pulse, and hence separates the receiver from the transmitter during pulsing. Conversely, for an open-circuited ¼-wavelength cable (without transmitter pulsing), the input impedance becomes zero because of the infinite load impedance (according to (2.33)), and hence the line looks like a shorted circuit, resulting in attenuation of the signal with a frequency corresponding to that of the quarter-wavelength cable.

2.7 Analog/Digital Converters

Questions to be answered related to the topics of this section include the following:

1. What are analog-to-digital converters (ADC) and digital-to-analog converters (DAC)?
2. What are the basic principles used to make the devices?
3. What are their functions and applications to NMR instrumentation?

The signals generated at the probe coil and detected by the receiver are in continuous or analog form, meaning that their amplitudes change smoothly, such as in a sine wave. However, the signals to be processed by computers and other electronic devices in the NMR spectrometer are a digital or discrete type, which means that their amplitudes can only exist in certain levels or ranges, such as binary digits. On the other hand, the output controlled by the computer needs to be converted to analog form, for example, numbers for gradient pulse levels and RT shims must be converted to analog currents into gradient coil or RT shim coils. Therefore, for NMR spectrometers it is necessary to accurately convert an analog signal to a digital number proportional to its amplitude (ADC), and vice versa (DAC). These conversions are essential in a wide variety of processes in which the analog information is converted (ADC) for data processing and display such as the Fourier transformation of the time domain data, and the digital information is converted to analog (DAC) for a computer controlling the experimental setup such as shimming, gradient pulse amplitude, or waveform generation. The conversions are also necessary for measurement instruments such as signal generators as well as digital oscilloscopes. An ADC is a device that converts the information obtained in

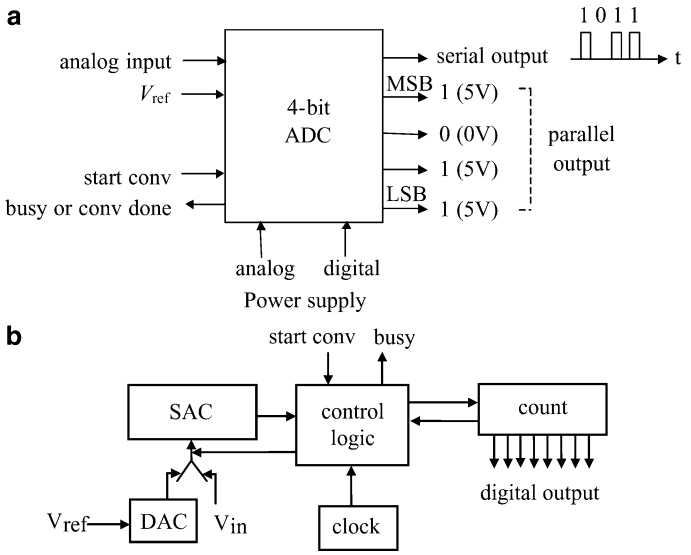

Fig. 2.18 Analog-to-digital conversion. (**a**) Block diagram of a 4-bit ADC converting an input signal with a amplitude of 11 to a parallel and serial output of 1011. The reference voltage is often produced within the converter. The ADC usually has two control lines to receive "start conversion" input and send status "busy" (conversion in progress) or "conversion done" output. The serial output is in the form of a pulse train with MSB first, whereas the parallel output is done simultaneously via four separate output lines. MSB and LSB mean most significant bit and least significant bit, respectively. (**b**) Successive approximation conversion (SAC). All bits of output are first set to zero. Then, each bit is compared to the DAC output, starting with the MSB. If the input signal voltage is larger than or equal to the DAC output, the register is set to 1, otherwise, it is set to 0. The process continues until the LSB is compared.

analog form such as the amplitude of the input signal to the information described in numerical values with respect to a reference signal, whereas the DAC is a device for the reverse conversion. They are integrated circuits and can have resolution higher than 16 bit and conversion rates faster than 50 MHz.

The ADC process includes quantizing and encoding. The analog input signal is first partitioned by a comparator unit during the quantization and then the partitioned signal is assigned to a unique digital code corresponding to the input signal during the encoding process. Usually, the binary number system is used in the conversion. For an n-bit converter, there are 2^n digital codes (numbers), resulting in a dynamic range of $2^{n-1}-1$ (which represents numbers between -2^{n-1} and $2^{n-1}-1$). The code is a set of n physical two-value levels (i.e., bits, 0 or 1). For example, a signal with a scale of 11 will be coded as 1011 by a 4-bit ADC as shown in Fig. 2.18a. Frequently, the signal is digitized by converting the electric voltage of the input signal into a set of coded binary electrical levels such as +5 or 0 V and the digitized signal is output in parallel (simultaneous) form or in series (pulse-train) form with the most significant bit first (MSB), and sometimes both.

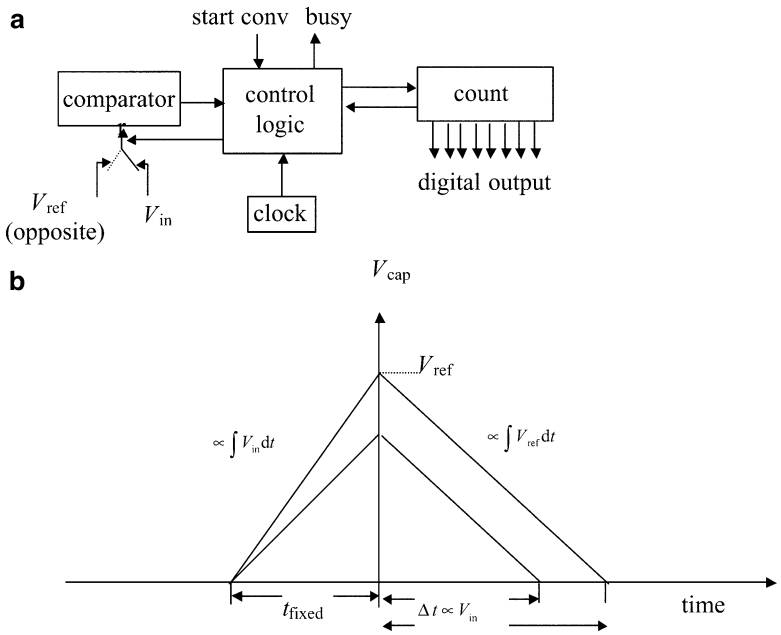

Fig. 2.19 Dual-slope integration conversion. (**a**) Block diagram of the ADC, (**b**) conversion cycle. The voltage of the reference is proportional to the input voltage, V_{in}, and hence the time to discharge the capacitor, Δt, is proportional to V_{in}. Because the current for discharging the capacitor is constant, the slope of the reference integration is unchanged for all V_{in}, while Δt is different for different V_{in}.

There are many techniques for analog-to-digital conversion, among which the successive-approximation (Fig. 2.18b) and dual-slope (Fig. 2.19) ADC remain popular because of their conversion speed and accuracy (Dooley, 1980; Sheingold, 1977). The dual-slope integration converters provide excellent accuracy with high sensitivity and resolution (Fig. 2.19). During the conversion, the input signal is integrated for a fixed time interval by charging a capacitor with a current accurately proportional to the input signal amplitude. The final value of the signal integral becomes the initial condition for integration of the reference in the reverse process, which is achieved by discharging the capacitor with a constant current. When the net integral is zero, as indicated by the voltage of the capacitor reaching zero again, integration of the reference stops. The time of reference integration (to discharge the capacitor) is counted by a counter driven from a clock, which is proportional to the input signal amplitude. Therefore, the result of the time count is a digital output proportional to the input signal amplitude. The drawback of the dual-slope integration conversion is the slow conversion rate.

The successive approximation conversion (SAC) is a popular high speed technique used primarily in data acquisition. The conversion is achieved by comparing the input signal with a reference set produced by a DAC, resulting in various output

codes (Fig. 2.18b). Initially, all bits of output are set to zero. Then each bit is compared to the DAC output, starting with the MSB. If the input signal voltage is larger than or equal to the DAC output, the register is set to 1; otherwise, it is set to 0. It is a binary search starting from the middle of the full scale. The MSB is tried by the DAC output of ½ full scales. The MSB code is set to 1 or 0, respectively, if the input signal is at least equal to or does not exceed the DAC output. Then, the second bit is tried with ¼ full scale and assigned to 1 or 0 accordingly. The process continues until the least significant bit (LSB) is compared. An n-bit ADC has an n-step process. The maximum output is always 2^n-1, in which all bits are set to 1. The final digital output is usually provided in both the parallel form of all bits at once on n-separated output terminals and the series form of n-sequential output bits with the MSB first on one single output terminal. For NMR applications, the current typical conversion time is 500 kHz with a dynamic range of 16 bits.

The DAC is a device to convert an input signal representing binary numbers (or binary-coded decimals, BCDs) to information in the form of current or voltage proportional to the input signal. There are a variety of conversion methods, in which the reference voltage source, resistor network, and digital switches are the essential elements (Sheingold, 1977; Dooley, 1980). The reference voltage source and the resistor network are used to generate binary scaled currents, whereas digital switches are turned to the output terminal or to the ground under the control of the digital input code. The output signal voltage V (or current) is given by

$$V = V_{\text{ref}} \sum_{i=1}^{n} \frac{2^{n-i}}{2^n} \delta_{\text{i}} \tag{2.34}$$

in which V_{ref} is the voltage of the reference source, δ_{i} is the input digital code which is equal to 0 or 1, and n is the bit of the converter. The MSB (i = 1) is converted first and the LSB (i = n) last. The maximum output voltage is limited to $V_{\text{ref}}(2^n - 1)/2^n$ because the maximum digital input is 2^n-1. For instance, if a digital input of 1011 is converted by the 4-bit DAC, the output has a voltage given by

$$V_{\text{out}} = V_{\text{ref}} \left(\frac{8}{16} + \frac{0}{16} + \frac{2}{16} + \frac{1}{16} \right) = \frac{11}{16} V_{\text{ref}} \tag{2.35}$$

2.8 Instrument Specifications

In the current section, typical specifications of an NMR instrument are discussed which are useful to describe a desired NMR spectrometer. When purchasing an NMR spectrometer, there are certain specifications that must be considered and specified. The typical specifications to be discussed below are categorized based on the basic components of NMR spectrometer.

Specifications for the NMR magnet include bore size, number of shims, actively vs. passively shielded, days between refills for liquid nitrogen and liquid helium, field drift rate and warranty period. NMR magnets are made with either a standard bore size (e.g., 51 mm diameter) or a wide bore (e.g., 69 mm). The wide bore magnets are usually used for micro imaging or solid state NMR because there is more space inside the bore, but they cost much more than the standard bore magnets due to the usage of more SC material. In recent probe development, solid state NMR probes have been built to fit in a standard bore magnet for solid state NMR research. The standard bore magnet may have as many as 40 RT shims for a field strength higher than 500 MHz whereas the wide bore type does not need more than 30 shims because of the large volume inside the magnet. An actively shielded magnet has a much shorter 5 Gauss line diameter than an unshielded magnet, which saves lab space. (A 5 Gauss line is the circle from the magnet center, where the fringe magnetic field strength outside the circle is less than 5 Gauss.) The time between refills should be $>$14 days for liquid nitrogen and $>$120 days for liquid helium. Although the drift rate is usually specified to $<$10 Hz h^{-1}, in most cases, the drift rate is in the range of 0.5–3 Hz h^{-1} for the magnets of 600 MHz or lower. For magnets of 500 MHz or higher, a set of antivibration posts should be included in the specifications. Homogeneity of the magnetic field is usually $<$1 ppm after cryogenic shimming.

Specifications for the console are more complicated than those for magnets, and are categorized based on the components of the console: RF channels (transmitter, amplifier, synthesizer, receiver, and digitizer), lock channel, and probes. The number of RF channels defines the spectrometer's capability of simultaneously delivering RF pulses to different nuclei. For consoles of 400 MHz or lower, the standard configuration has two RF channels with one full band and one low band frequency synthesizer, whereas three or four channel configuration with two full band and one low band synthesizer is the typical choice for 500 MHz or higher. An RF channel with a ^{1}H only frequency synthesizer is not a wise choice although it probably costs less than a full band RF channel. Full band is defined as the frequency range from ^{15}N resonance (or lower) up to ^{1}H resonance frequency and low band covers the frequency range from ^{15}N resonance up to ^{31}P resonance. Amplifier output power is $>$50 W for the frequency range of $\pm$50 MHz about the ^{1}H resonance (~100 W for solid state NMR) and ~300 W for the heteronuclear frequency range. The additional specifications for transmitter include $<$500 ns event timing, $>$4,000 steps amplitude control over at least 60 dB range, $<$50 ns time constant for phase and amplitude change, and 0.1 Hz frequency resolution. The console should have at least two waveform generators with $<$50 ns pulse time resolution, and $<$200 ns minimum event time, and $>$1,000 linear steps. The lock channel should have the capability of automatic switching for ^{2}H gradient shimming and for ^{2}H decoupling. The frequency range of the lock is ~$\pm$5 MHz about the ^{2}H resonance frequency, which is necessary to adjust spectrometer frequency when needed (such as in the case of z_0 out of range due to field drift). An active T/R switch with $<$1.5 μs timing, a 16 bit ADC with 500 kHz speed and digital signal processing capability are the standard features of NMR spectrometers.

Specifications for the probe include signal-to-noise ratio, line width, gradient profile, gradient recovery time, 90° pulse lengths, and RF homogeneity. For a triple-resonance probe with a *z*-axis gradient, a typical 90° pulse length at 3 dB lower than the maximum pulse power is <7 μs for ^{1}H, <15 μs for ^{13}C, <40 μs for ^{15}N and <40 μs for ^{31}P. The gradient coil should be shielded with a strength >50 G/cm^{-1} (>20 G/cm^{-1} for 400 MHz or lower instruments) and a recovery time <0.1 ms. The sensitivity of a conventional (or room temperature, RT) triple-resonance probe is >1,000:1 for 500, >1,300:1 for 600 MHz and >1,800:1 for 800 MHz using the standard ^{1}H sensitivity sample (0.1 % ethylbenzene in $CDCl_3$), whereas cryogenic probes have a sensitivity of 3–4 fold higher. For instance, the cryogenic probe of a 600 MHz instrument should have a sensitivity of >4,500:1. RF homogeneity is >80 % for ^{1}H 450°/90° (which means that the intensity of the peak obtained by the 450° pulse is greater than 80 % the intensity obtained by the 90° pulse), >70 % for ^{1}H 810°/90°, 70 % for ^{13}C decoupler 360°/0°, and 55 % for ^{13}C decoupler 720°/0°. A typical ^{1}H non spinning line width should be better than 1/10/15 Hz at 50 %/0.55 %/0.11 % of peak amplitude using a 5 mm standard line shape sample for a RT probe and 1/10/20 Hz for a cryogenic probe. Spinning sidebands should be less than 1 % at a spin rate of 25 Hz. The variable temperature (VT) range is typically over −60 to 100 °C for a conventional probe and 0–40 °C for a cryogenic probe.

Additional specifications include quadrature image with one scan <0.4 %, with four scans <0.04 %, phase cycling cancelation (four scans) <0.25 %, and pulse turn-on time <0.05 μs.

2.9 Test or Measurement Equipment

The test equipment to be discussed in the present section are those routinely used in instrument setup or trouble-shooting, including the reflection bridge, oscilloscope, and spectral analyzer. Questions to be addressed about the test equipment are:

1. What is the test equipment needed for?
2. How are they operated?
3. What is the noise figure of a system?
4. How can it be measured?

2.9.1 Reflection Bridge

Although a reflection bridge (also known as duplexer or magic *T*, Parker et al. 1984) is not exactly a test instrument, it is a broadband device with four ports that is useful in tuning an NMR probe (Fig. 2.20). There is complete isolation (infinite impedance) between A and C or between B and D, but no isolation between the two terminals of any other combination. An RF signal fed into any port is equally split

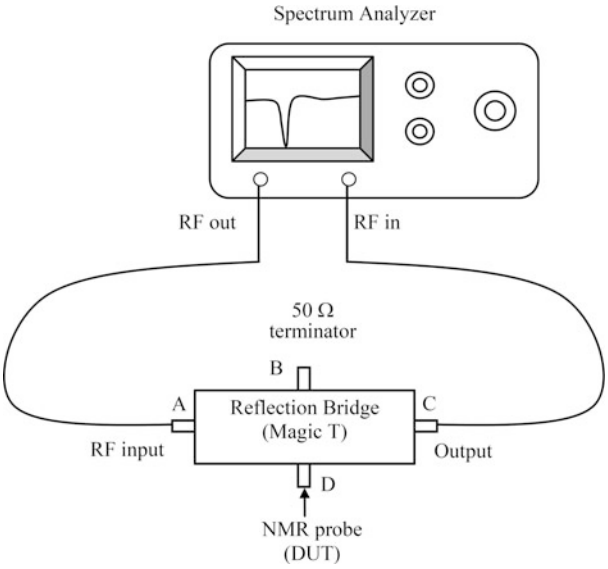

Fig. 2.20 Reflection bridge used for NMR probe tuning. There is complete isolation (infinite impedance) between A and C or between B and D, but no isolation (near zero impedance) between the two terminals of any other combination. An RF signal fed into port A is equally split into two output signals at ports B and D. If the impedances of the two output ports (B and D) are mismatched (unequally loaded), the reflected power is directed into the isolated port, resulting in an output at port C from port A. By monitoring the output RF signal (at C), a probe can be tuned for a desired resonance frequency at the desired impedance (50 Ω in this case). *DUT* device under test.

into two output signals at the closest ports with a specific phase shift (usually 0 or 180°). If the impedances of the two output ports (B and D) are mismatched (unequally loaded), the reflected power is directed into the isolated port, resulting in an output at port C from port A. By monitoring the output RF signal, a probe can be tuned for a desired resonance frequency at the desired impedance (50 Ω).

2.9.2 Oscilloscope

The two time-dependent physics quantities from electronic circuits we want to measure are current and voltage. An oscilloscope (Oliver and Cage 1971; Parker et al. 1984), or scope, is an essential and very useful test instrument because it measures the voltages or current (sometimes) in a circuit as a function of time and displays waveforms of the measured signals (Fig. 2.21). It is an electronic instrument which produces a graphical plot on its screen showing the relationship of two or more independent variables such as voltage vs. time. It can be adjusted for amplitude measurement or time measurement. For amplitude measurement, the scope

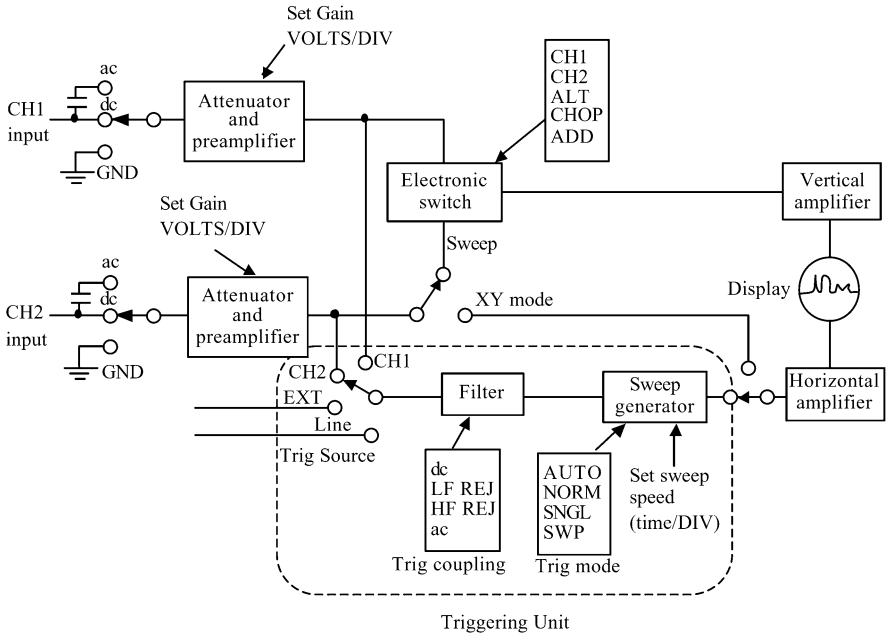

Fig. 2.21 Block diagram of an oscilloscope.

measures vertical deflection such as peak-to-peak voltage (V_{pp}) displayed on the oscilloscope screen (Fig. 2.22). If the effective voltage (V_{rms}) is needed to measure a sinusoidal signal, V_{pp} can be converted to V_{rms} according to (2.7). For time measurement, the time base setting is adjusted to observe time-dependent properties of the circuit, such as the frequency of the signal, the pulse rise time of the voltage step, or the phase difference of two signals.

Oscilloscopes usually have two or more input channels. Each channel has an input attenuation control knob labeled as VOLTS/DIVISION for vertical amplitude measurement (Fig. 2.21). Turning the knob increases or decreases the intensity of the measured signal in a calibrated condition. The knob is automatically rendered inactive if the channel related to it is set to ground input mode, GND, which lets the user observe the position of zero voltage on the scope screen. In ground mode, the signal is cut off from the scope input. The input of the scope is grounded, but the signal is not shorted to ground. There is also a VARIABLE control knob for each channel allowing the user to set the desired number of divisions. Turning the VAR knob adjusts the magnitude of a given signal, and the vertical deflection becomes uncalibrated as indicated on screen. The attenuation must be in the calibrated condition (VAR knob is not activated) when making an accurate measurement of signal voltage such as for the output of an amplifier.

There are other controls for vertical display, including input modes (DUAL, ADD and XY mode), Y POSITION control and an INVERT switch. Y POSITION (vertical position) allows one to change the vertical trace position. When there is no

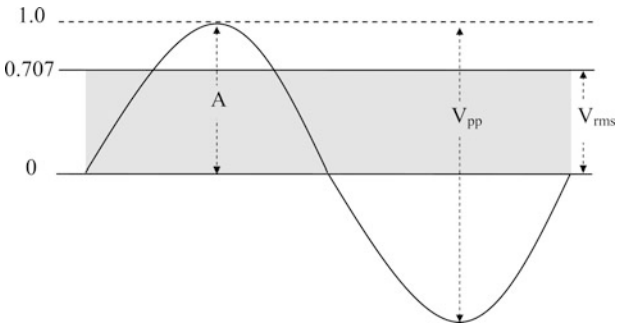

Fig. 2.22 Relationship between rms voltage, V_{rms}, signal amplitude, A, and peak-to-peak voltage, V_{pp}.

signal applied at the input, the vertical trace represents 0 V. The invert function is used to invert the signal display by 180°. This function is useful when looking at the difference of two signals in ADD mode. If the input mode is switched to DUAL mode, vertical signals from both channels are displayed on the screen either in ALTERNATE mode whereby the scope internally switches over from one channel to the other after each time base sweep or CHOPPED mode in which channel switching occurs constantly during each sweep. In XY mode, one channel is used for vertical (Y) deflection whereas the other causes horizontal (X) deflection (the amplitude change is displayed horizontally), which is useful for such measurements as frequency and phase comparisons of two signals. What is displayed on the screen is one signal vs. another (X–Y) rather than against time. The time unit controls the z axis and can be triggered internally from the vertical portion of the X–Y display.

Time related amplitude changes on an input signal are displayed in vertical mode as discussed above, deflecting the beam up and down whereas the time base generator moves the beam from left to right on the screen (time deflection). This gives a display of voltage vs. time. Similar to vertical attenuation control, calibrated TIME/DIV and VAR controls are used to change time deflection. Because test signals to be displayed are repetitive waveforms, the time base must accordingly repeat the time deflection periodically. To produce a stable display, the time base is triggered only if LEVEL and SLOPE (+ or −) on a waveform match with the previous time base. The slope is relative to rising or falling edge of the test signal. Triggering can be performed by measuring the signal itself (internal triggering) or by an externally supplied but synchronous voltage. In AUTO trigger mode, the sweep is free running without a trigger signal. A baseline will not disappear from the screen even if no signal is present. This is the best mode to use for all uncomplicated measuring tasks. The NORMAL trigger mode produces a waveform display by manually adjusting the trigger LEVEL control. When the trigger LELVEL is mismatched or signal is weak, no waveform is displayed.

Sometimes it is hard to get a signal to show on the screen. The following are tips for a quick start. Start by connecting the input to channel 1, setting the triggering on

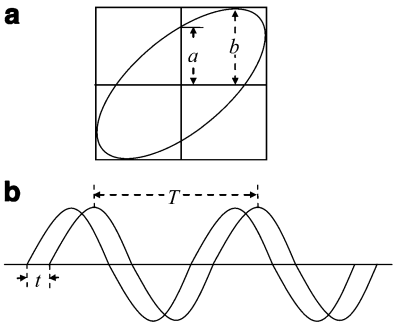

Fig. 2.23 Measurement of phase shift using (**a**) the Lissajous figure and (**b**) alternate mode methods.

AUTO, DC, CH1 and setting time (horizontal) deflection at calibrated 1 ms per div with the *X*-magnifier off (1×). Next, ground the input signal by setting the input mode to ground input mode, GND, and adjust the display intensity and vertical position controls until the reference horizontal line appears. Now apply signal to the scope by ungrounding the input and adjust the time base switch TIME/DIV accordingly.

The peak-to-peak voltage of a signal can be directly measured by counting the amplitude scales on the scope. If V_{rms} is needed, V_{pp} can be converted according to the relationship shown in Fig. 2.22 or (2.7). The frequency of a sinusoidal signal may be measured by reading the time necessary for one full cycle and inverting the reading result. The relative phase of two waveforms is usually measured by means of a Lissajous figure as shown in Fig. 2.23a. Each of two signals is applied to each individual channel of the scope in XY mode. The phase angle can be determined from the dimensions of the ellipse according to the relationship:

$$\sin\theta = \pm\frac{a}{b} \tag{2.36}$$

in which the minus sign is for a ellipse 90° rotated from the one in Fig. 2.23a. A more convenient method is to display both of the signals in alternate mode. Alter the full cycles of the waveforms are obtained by setting the appropriate time scale, the phase shift is determined by the quantities t and T:

$$\theta = 360\frac{t}{T} \tag{2.37}$$

2.9.3 Spectrum Analyzer

A spectrum analyzer is another widely used test instrument, particularly in tuning an NMR probe. A scope observes signal voltage as a function of time, whereas a spectrum analyzer allows one to look at the signal voltage in the frequency domain, the graphical representation of signal amplitude as a function of frequency

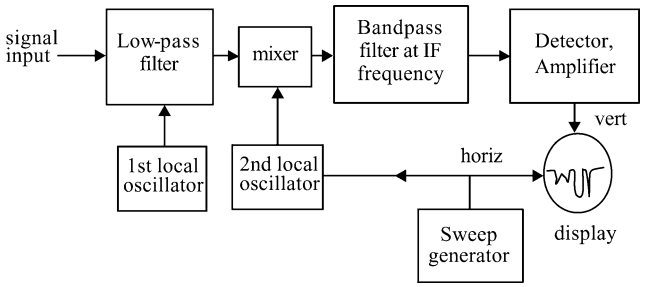

Fig. 2.24 Block diagram of a swept-tune (ST) spectrum analyzer. ST analyzers are tuned by a sweeping local oscillator (LO) of a superheterodyne receiver over its range of frequencies. The LO is mixed with the input signal to produce an intermediate frequency (IF). The signal frequency whose difference with LO frequency is equal to IF can pass through the IF amplifier and filter, and consequently is detected and displayed. As LO is swept through its frequency range, different input frequencies are successfully mixed to be observed.

(Coombs 1972; Parker et al. 1984). The time domain is used to view the relative timing and phase information of a characterized circuit. However, not all circuits can be appropriately characterized by time domain information. Circuit elements such as NMR probes, amplifiers, filters, receivers and mixers are best characterized by their frequency dependent information. In the time domain, all frequency components of a signal are overlapped together, whereas in the frequency domain, they are separated in frequency axis and voltage level at each frequency displayed. Therefore, a spectrum analyzer is useful in measuring resonance frequency, low level distortion and noise, etc.

There are two basic types of spectrum analyzers: swept-tuned (ST) and real-time (RT). ST analyzers are the most common type and they tuned by a sweeping LO of a superheterodyne receiver over its range of frequencies (Fig. 2.24). The LO is mixed with the input signal to produce an IF which can be detected and displayed on the analyzer screen. The signal frequency whose difference with LO frequency is equal to an IF can pass through the IF amplifier and filter, and consequently is detected and displayed. As the LO is swept through its frequency range, different input frequencies are successfully mixed to be observed. High sensitivity is obtained for this type of spectrum analyzers due to the use of IF amplifiers and filters, and it can be tuned up to a few gigahertz bandwidth. Since the input frequencies are sampled sequentially in time, only a small portion of the input signal is used at a given time. It is impossible to display transient responses on an ST analyzer. RT analyzers have lots of flexibilities in terms of sweep range, center frequency, filter bandwidth, display scale, etc. The instruments are able to simultaneously display the amplitudes of all signals in a wide frequency range. This preserves the time dependent relationship among signals, which allows one to analyze the phase change of signal vs. frequency. An RT analyzer can display transient events as well as random and periodic signals. A Digital analyzer is an RT analyzer which makes use of digital Fourier transformation. After the detection and

filtering processes, it converts an analog input signal to digital using an ADC, and then generates a digital spectrum using Fourier transformation. It is particularly useful for low frequency signals because the sweep rate of swept analyzer is slow for practical use at low frequency.

Usually a tracking generator is used either in conjunction with a spectrum analyzer or as an integrated part of the spectrum analyzer. This is a special signal source whose RF output frequency tracks (checks) the analyzer signal with itself. It produces a signal with frequency precisely tracking the spectrum analyzer tuning. Precision tracking means that at any instant of time the tracking generator frequency is in the center of the spectrum analyzer passband. Certain spectrum analyzers have a tracking generator installed, whereas others require an external tracking source for accurate measurement.

Similar to an oscilloscope but with fewer controls, a spectrum analyzer has vertical (amplitude) and horizontal (frequency) controls. Attenuation control (dB/DIV) sets vertical scale unit per division, whereas SPAN/DIV adjusts the displayed spectral width of the signal. The center frequency is tuned by a dial "FREQUENCY." The tuning rate is dependent on the selected SPAN/DIV setting. The sweep rate is selected by TIME/DIV. For general operation, after turning the analyzer on, set attenuation to 0 dB, TIME/DIV to AUTO, SPAN/DIV to max, and adjust the center FREQUENCY control. Once the input signal is displayed, adjust SPAN/DIV to the desired spectral window. Figure 2.20 shows the connection of the probe to a spectrum analyzer using a reflection bridge for probe tuning.

2.9.4 System Noise Measurement

By definition, noise is the electrical interference which causes reduction of the signal being measured. Instrument sensitivity is affected by both the noise coming with the signal and the noise generated internally by the instrument. Generally, system noise is described by the amount of noise in dB, or the noise figure, which numerically equals the logarithm of the ratio of signal-to-noise ratios at the input and output of a system (Mazda 1987):

$$F = 10 \log \frac{\mathrm{SN}_{\mathrm{in}}}{\mathrm{SN}_{\mathrm{out}}} \tag{2.38}$$

in which F is in dB, SN is the input or output signal-to-noise ratio of the system. If the noise source of the system has excess power E, the noise figure is determined by the noise power N_{c} with noise source off (cold) and N_{w} with noise source on (warm):

$$F = 10 \log E - 10 \log \left(\frac{N_{\mathrm{w}}}{N_{\mathrm{c}}} - 1 \right) \tag{2.39}$$

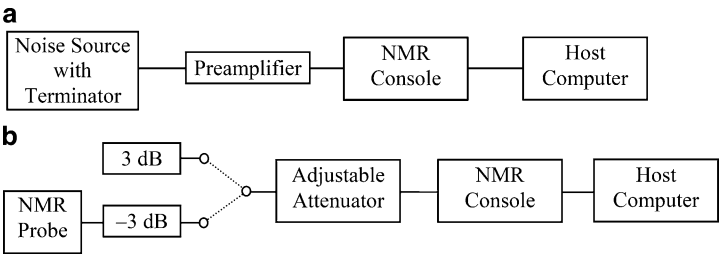

Fig. 2.25 Methods of noise figure measurement. (**a**) Cold/warm method separately measures the rms noise by placing the noise source at liquid nitrogen temperature and 20 °C. (**b**) Twice power method measures the rms noise with or without a probe. The source-off rms noise is measured with 3 dB attenuator and without the probe, whereas the probe and −3 dB attenuation are used for the measurement of the source-on rms noise.

E is also known as excess noise ratio and N_w/N_c is commonly called as Y factor. The noise figure can also be expressed in terms of noise temperature:

$$F = 10\log\left[\left(\frac{T_w}{290} - 1\right)\frac{N_c}{N_w} + \left(1 - \frac{T_c}{290}\right)\right] - 10\log\left(1 - \frac{N_c}{N_w}\right) \tag{2.40}$$

in which N_c and N_w are the noise measured at the cold T_c and warm T_w temperature, respectively. If the warm noise is measured at 290 K and cold noise measured in liquid nitrogen, the noise figure can be obtained by:

$$F = -1.279 - 10\log\left(1 - \frac{N_c}{N_w}\right) \tag{2.41}$$

In practice, the noise is measured as a V_{rms} value and hence $N = V_{rms}^2$. For an NMR system, the system noise figure should be less than 2 dB.

There are two methods to measure the noise figure based on (2.39) and (2.41), respectively. The cold/warm method measures the rms noise using a noise source in liquid nitrogen and at about 20 °C (Fig. 2.25a). Because the impedance of the NMR system is 50 Ω, the noise source for the cold measurement is constructed using the coaxial cable terminated with a 50 Ω resistor. After disconnecting the probe from the preamplifier, the noise source is connected to the preamplifier. The noise is measured with pulse length of 0, a ^{1}H SW of 50 ppm, maximum receiver gain and single scan. N_c is equal to the square of rms noise calculated after the Fourier transformation without any line broadening. N_w is measured in the same way except the noise source is warmed to 20 °C. Finally, the noise figure is calculated using (2.41).

The second method called twice-power measurement (Fig. 2.25b) is to make the noise ratio equal to 2 so that the noise figure is solely dependent on the first term of (2.39). The noise is first measured without the probe and the 3 dB attenuation using a pulse length of 0, an SW of 50 ppm, maximum receiver gain in the linear range and a single scan, which is N_c because switching off the noise source is equivalent to the cold

condition. The probe is then connected to the preamplifier to allow the measurement of N_w with the −3 dB attenuation. The −3 dB attenuation can be achieved by decreasing the receiver gain according to the linear response of the instrument receiver gain. The next step is to adjust the inline attenuator to obtain the rms noise (N_w) at about the same level as the first measurement. In this condition, N_w has a value twice to N_c because of the −6 dB attenuation $[(-3\,\mathrm{dB})_{N_w} - (+3\,\mathrm{dB})_{N_c} = -6\,\mathrm{dB}]$, resulting in the cancelation of the second term in (2.39). Therefore, the noise figure of the system is determined solely by the value of the first term in (2.39), which is equal to the value of the inline attenuator. This method does not require making noise sources but needs an adjustable attenuator. In addition, it may introduce error when using instrument receiver gain to attenuate the noise for the N_w measurement. The error of the twice-power measurement is in the range of 0.1–0.5 dB greater than that of the cold/warm method.

Questions

1. Which part of an NMR instrument generates NMR signals and which part detects? Where are they located?
2. How much are sensitivity and resolution of NMR signals on a 900 MHz instrument increased compared to a 500 MHz instrument? Assuming that the 900 MHz instrument has a cryogenic probe which has a gain in sensitivity by 3.5 fold, how much is the sensitivity increased compared to a 500 MHz with conventional probe? What field strength with a conventional probe is the sensitivity of the cryogenic probe on 500 MHz NMR equivalent to?
3. What is the function of ¼ wavelength cables? Where are they used in a NMR spectrometer? What could happen if the wrong ¼ wavelength cable is used during an experiment?
4. What is a T/R switch? Why does a NMR spectrometer have it?
5. What is the function of IF? And what is the value on an instrument you have used?
6. What part of an NMR spectrometer generates frequency? And what are the frequency ranges of the RF channels on an NMR spectrometer you have used?
7. If a 90° ^{1}H pulse length is much longer than the normal one (e.g., twice longer), what are the three things you should check before you conclude that something is wrong with the instrument?
8. Why does a magnet still have a magnetic field when the power is out?
9. If a 90° ^{1}H pulse length is 6.2 μs, what are the 90° ^{1}H pulse lengths after the RF field strength generated by a linear amplifier is reduced by 3 and 6 dB?
10. Why must the probe be tuned before the setup of an experiment? If a probe is tuned with the filters or without, which method gives the correct pulse length? Explain why.
11. What is the dynamic range (ratio of the largest to smallest signals) of a 16-bit ADC?
12. Where is a preamplifier located and what is its primary function?

13. Why is the ^{13}C sensitivity of a triple-resonance probe on a 600 MHz NMR spectrometer much lower than that of a broadband probe on a 400 MHz instrument?
14. Why can a cryogenic triple-resonance probe be used to directly observe ^{13}C?
15. Why is it necessary to fill two different cryogens in an SC magnet?
16. How is the heat insulation achieved in an SC magnet?
17. What is the function of LO in a NMR console?
18. How can a spectrum analyzer be used for probe tuning?

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