Nuts and Bolts

Larmor Precession

Recall from last lecture:

Gyromagnetic ratio: $\gamma = \frac{\vec{\mu}}{\vec{P}}$

If the magnetic dipole (moment) is placed in a (usually static) magnetic field under the influence of a magnetic field, it will experience a torque that will alter the angular momentum

$$\vec{\tau} = \frac{d}{dt}\vec{P} = \frac{d}{dt}(\gamma\vec{\mu}) = \gamma\frac{d}{dt}\vec{\mu}$$

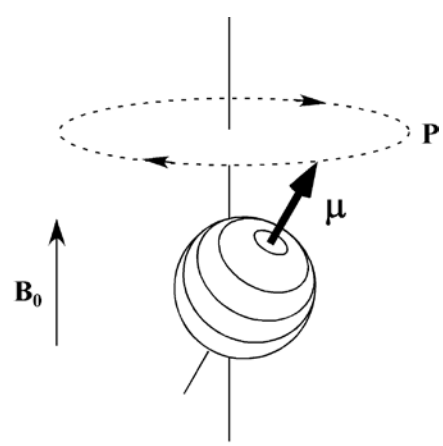
$$\vec{\tau} = \vec{\mu} \times \vec{B} = -\vec{B} \times \vec{\mu}$$

Combining these two expression leads to

$$\frac{d}{dt}\vec{\mu} = -\gamma\vec{B} \times \vec{\mu}$$

This final expression means that the applied torque causes the magnetic moment to precess about the external magnetic field at an angular velocity ω, an effect known as Larmor Precession:

$$\omega = -\gamma B_0$$



Larmor Precession
$\omega = -\gamma \mathbf{B}_0$

Frequency Units?

$$\begin{aligned}\text{Frequency in } \frac{\text{rad}}{\text{sec}} &= 2\pi\left(\text{Frequency in } \frac{1}{\text{sec}}\right)\\ &= 2\pi(\text{Frequency in Hz})\\ &= 2\pi\left(\text{Frequency in } \frac{\text{cycles}}{\text{sec}}\right)\end{aligned}$$

Weak convention:

$$\omega \rightarrow \frac{\text{rad}}{\text{sec}}; \quad \nu \rightarrow \text{Hz}$$

With an applied field of 2.34866 T then

$$\begin{aligned}\omega &= -\left(267.552 \times 10^6 \text{rad s}^{-1} \text{ T}^{-1}\right)(2.3487 \text{ T})\\ &= -628.4 \times 10^6 \text{ rad s}^{-1}\\ &= -100 \times 10^6 \text{ Hz}\end{aligned}$$

Energy Levels

The (Classical) energy of a dipole moment in a magnetic field (**B**$_0$) is given by

$$E = -\mu B_0$$

The quantum mechanical representation of the energy of a spin in a magnetic field is similar, but of course the energy is quantized and there are 2*I*+1 levels with $m_s = \pm 1/2$

$$E = -\hbar \gamma m_s B_0$$

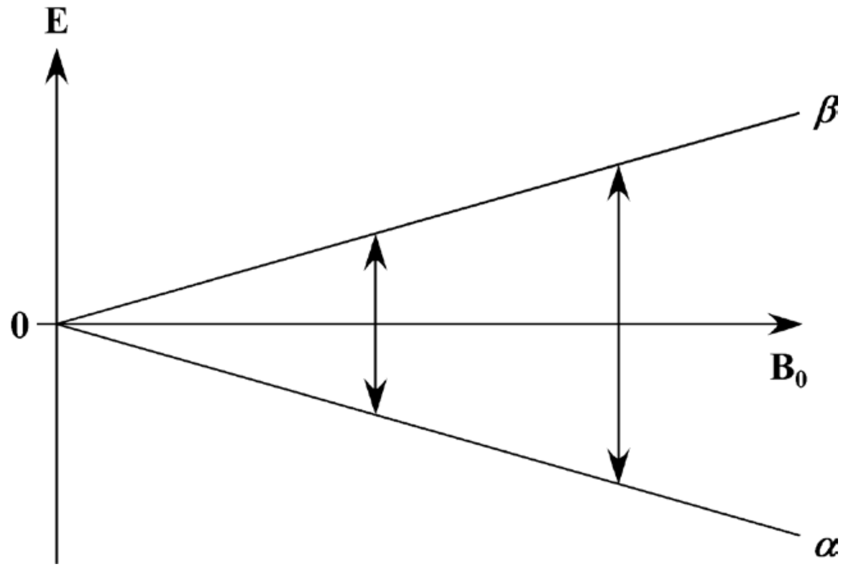
Recall that $\hbar$ is equal to $h/2\pi$. This constant is sometimes called *Planck's reduced constant*.

In explicit terms then, for a spin-1/2 particle in a magnetic field there are 2*I*+1 or 2 energy levels:

$$E_\alpha = -\hbar\gamma B_0/2 \text{ and } E_\beta = \hbar\gamma B_0/2$$

The energy separation of these levels is linearly dependent on the strength of the applied magnetic field

$$\Delta E = \hbar\gamma B_0$$



wherein we explicitly assume that the magnetic field is oriented along the z-axis in our laboratory frame.

In general, the amplitude of the transition energy is given by the Bohr energy expression:

$$\Delta E = h\nu$$

wherein *h* is Planck's constant and *v* is the frequency (Hz).

We set the two expressions describing the energy level change equal:

$$\Delta E = h\nu = \hbar\gamma B_0$$

$$h\nu = \left(\frac{h}{2\pi}\right)\gamma B_0 \text{ or } \nu = \frac{\gamma B_0}{2\pi}$$

A common variation on this development is demonstrated by the following expression:

$$\omega = 2\pi\nu = \gamma B_0$$

wherein *ω* is taken to be frequency in units of *radians per second* $\left(rad \cdot s^{-1}\right)$. The idea here is that there happen to be 2*π* radians in a circle (cycle) and Hz implies cycles per second.

Polarization

In the presence of an applied magnetic field, the individual spin moments add together to form a *bulk* or *macroscopic* magnetic moment

$$\vec{M} = \sum_i \mu_i$$

The distribution of spins into higher energy states may be predicted according to the Boltzmann distribution law:

$$\frac{N_\beta}{N_\alpha} = e^{-\Delta E / k_b T} = e^{-\hbar\gamma B_0 / k_b T}$$

$$\hbar = h/2\pi = 1.0546 \times 10^{-34}\ \mathrm{J\ s^{-1}}\ ; \quad k_\mathrm{b} = 1.3805 \times 10^{-23}\ \mathrm{J}\ K^{-1}$$

at 2.3487 T:

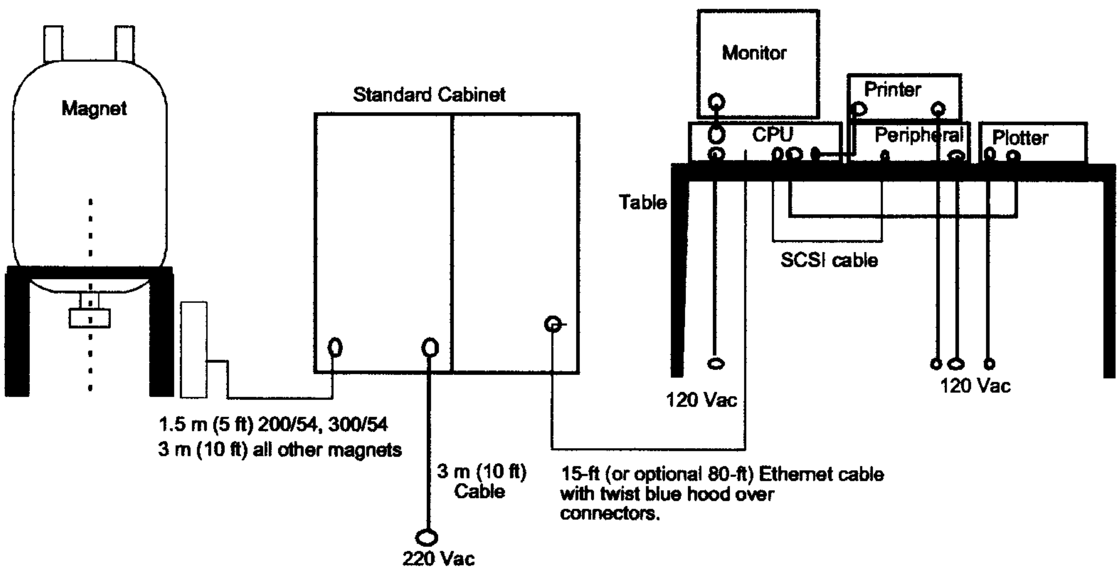
$$\begin{aligned} \frac{N_\beta}{N_\alpha} &= e^{-\hbar\gamma B_0 / k_b T} \\ &= e^{-\left(1.0546\times10^{-34}\right)\left(267.552\times10^{6}\right)\left(2.3487\right) / \left(1.3805\times10^{-23}\right)\left(298\right)} \\ &= 0.999983 \end{aligned}$$

The ratio at 21.49 T:

$$\frac{N_\beta}{N_\alpha} = e^{-\left(1.0546\times10^{-34}\right)\left(267.552\times10^{6}\right)\left(21.49\right)/\left(1.3805\times10^{-23}\right)\left(298\right)}$$

$$= 0.999853$$

The NMR Spectrometer



The NMR spectrometer system consists of the following components:

i) Magnet system (Superconducting magnet and shims)

ii) Probe and Upper-barrel assembly

iii) Radio-frequency (RF) console

iv) Computer

Magnet System

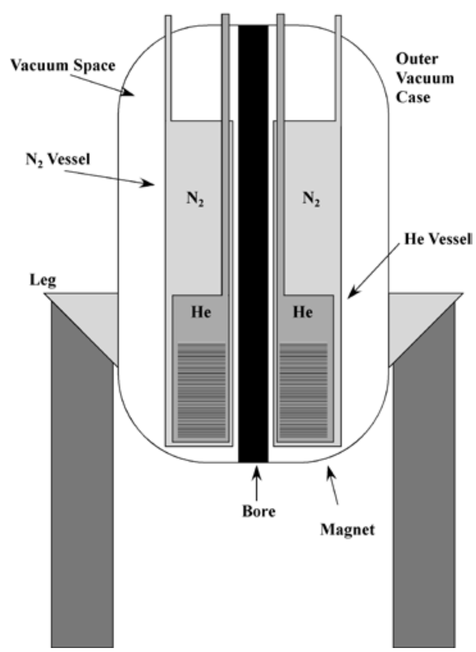
Modern magnet systems employ a superconducting solenoidal (coil) design, with a main winding consisting of Nb_3Sn alloy.

The current flow in the main coil is typically of the order of 10A to 100A and the system remains in a *persistent* state with virtually no loss of energy as long as the source alloy is maintained in the superconductive condition.

The standard operational mode is *passive* and the main field coil is continuously bathed in liquid He at its boiling temperature (4.5K). Failure to maintain the superconducting state leads to uncontrolled release of the stored field energy – a quench!

The homogeneity of the main field is improved by two additional stages of supplementary, or *shim*, coils. The notion of shimming derives from a time when NMR employed electromagnets, wherein the field homogeneity was improved through the use of small thin pieces of iron plate, known as shims. The *cryo-shims* are inside of the OVC and are positioned around the main solenoid, and are themselves superconducting. The RT-shims are outside of the OVC but in the bore tube and provide a level of user-optimized homogeniety.

Cross-Section of Superconducting Magnet



Probe

The NMR probe may be considered to be part of the RF system, but it has specialized functions and physically is located within the bore of the magnet.

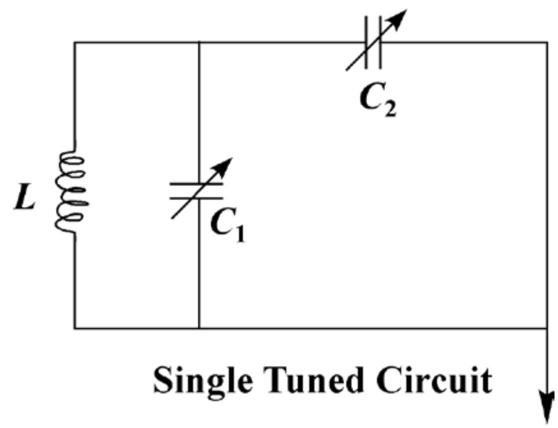
The main functions and attributes of the probe are:

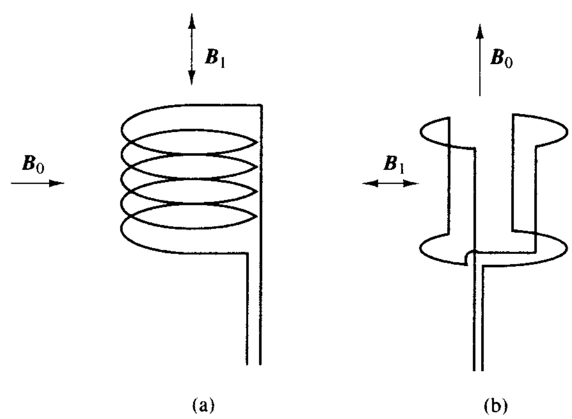
i) Position the sample in the center of the main magnetic field

ii) Passive Electronics for irradiation of the sample and detection of RF signal

iii) Thermocouple and heating coils for temperature control and stabilization

iv) Magnetic field gradient coils





In the figure above (a) corresponds to the solenoidal coil design used in electromagnets and sometimes in solid-state NMR and (b) corresponds to the ‘saddle-coil’ design commonly used with superconducting magnet systems

RF Console

The RF console is essentially a specialized type of radio – a double-conversion superheterodyne transceiver with *phase-sensitive* detection.

In the most common configuration, radio-frequency energy is not *broadcast*, but instead is transmitted to the sample chamber along a coaxial cable known as a transmission line.

The power amplitude of the exciting RF signal ranges from approximately 100 Watts to beyond 1 killowatt.

Due to chemical shielding effects, the resonances of interest will typically be scattering within several kHz of the center frequency of the exciting radiation.

The central frequency of the radiation is called the carrier frequency. In radio communication the carrier frequency encodes the audio (voice or music) information as a modulation of the base frequency, thus conveying the signal through space to the antenna of a receiver.

We sometimes say that the carrier frequency is *modulated* by the voice or music information or NMR information using a transmitter and that it is *demodulated* by the receiver.

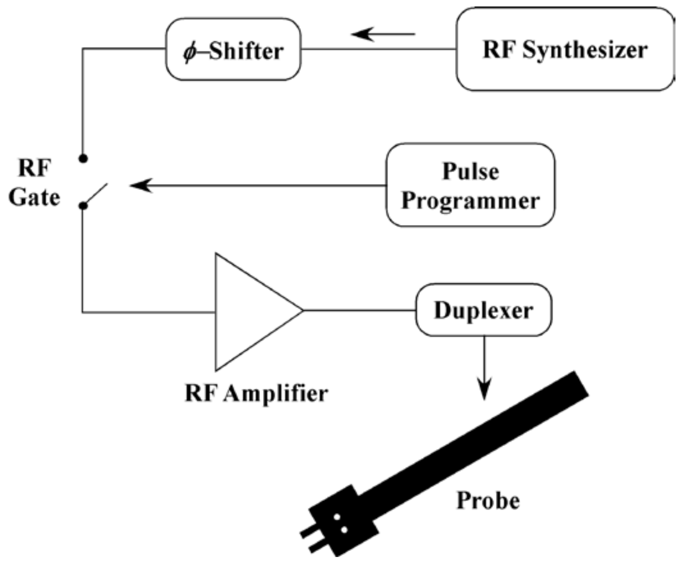
The carrier frequency may be of the order of kHz, as in AM radio, or MHz, as in the case of FM radio.

Transmitter Section

Superheterodyning, is the process by which means that the RF signal is produced by adding two frequencies together and that all of part of the transmitter and receiver sections are shared, i.e., use the exact same components. This sharing is primary to insure mod/demod stability rather than for economic reasons.

Conversion is the process by which two frequencies are mixed – when two signals, say one at 10 MHz (LO) and one at 490 MHz (IF), the result is the sum, 500 MHz (RF high-band) and difference, 480 MHz (RF low-band) of the two input frequencies. The exciting RF frequencies are usually generated in one mixing step, thus single-conversion. During reception, the IF is first mixed off and then the audio signal is obtained by a second mixing step with the LO, thus double-conversion.

The transmitter produces radiofrequency signals at high power, typically in the range of 100 W to 1 kW, that excite the resonances.

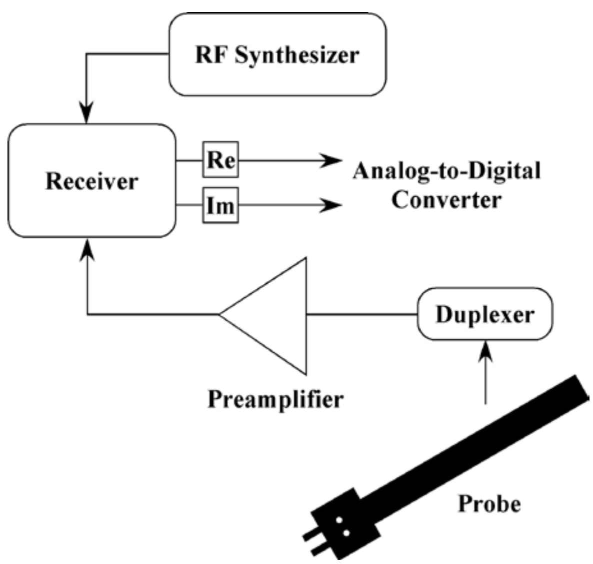


The power of the transmitter may be varied over a very large range, typically up to 70dB of more at the software control level (**tpwr**, **dpwr**):

$$\text{dB}=10\ \log\frac{P_2}{P_1}=20\ \log\frac{V_2}{V_1}$$

Receiver Section

The receiver section records the NMR signal induced in the Probe and converts the RF analog signal into a digital audio signal.



The receiver section provides several levels of amplification including up to 60 dB at the software control level (**gain**).

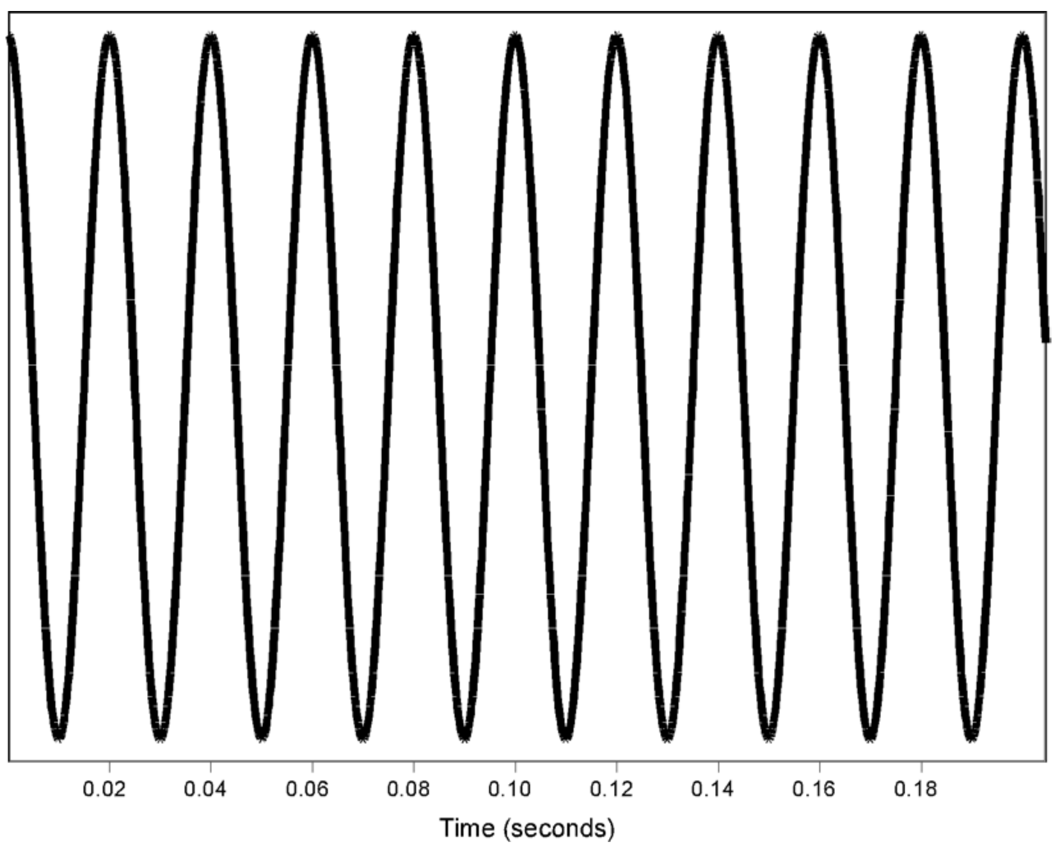
The receiver section also contains a digital-to-analog converter that transforms the audio signal into a digitized waveform.

There are several dedicated CPUs that control attributes of the RF pulse generation, including gating controls and waveform generation (shaped pulses).

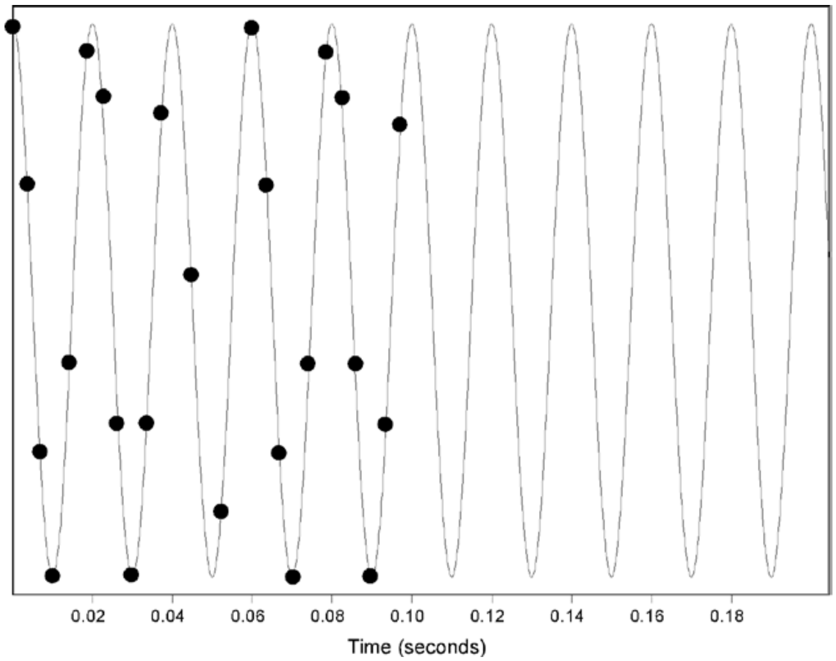
An important dedicated computer is the acquisition CPU. This computer may be thought of as being part of the receiver section, since it often contains the analog-to-digital converter. In addition, the acquisition CPU stores signals and supports some basic memory manipulations (summation).

Analog-to-digital conversion is an essential part of signal acquisition, since it allows us to store signals and to implement *data processing* strategies that enhance the raw signal.

For example, an analog sine wave appears at shown below



A *digitized* sine wave is shown below



In the ADC, the amplitude of the analog (continuous) signal is sampled at regular intervals.

The length of the sampling interval is called the *dwell-time* and is symbolized as Δt.

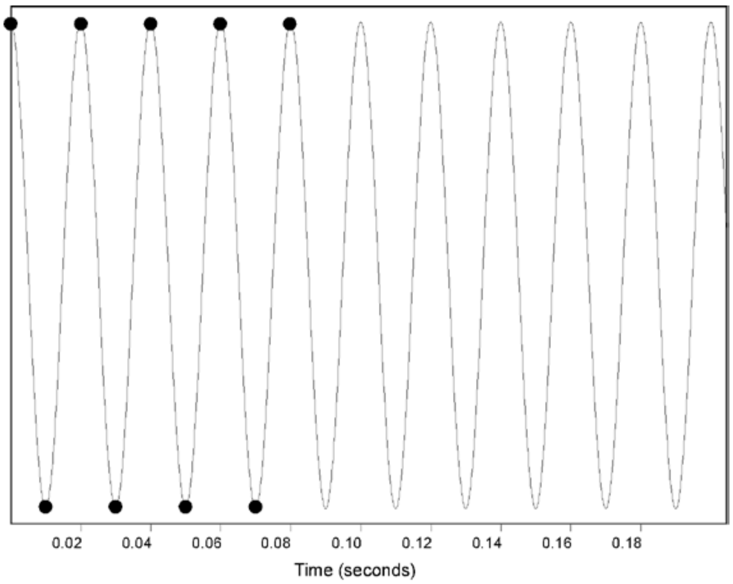
A major consideration of the digitization process involves the frequency at which the analog waveform is sampled.

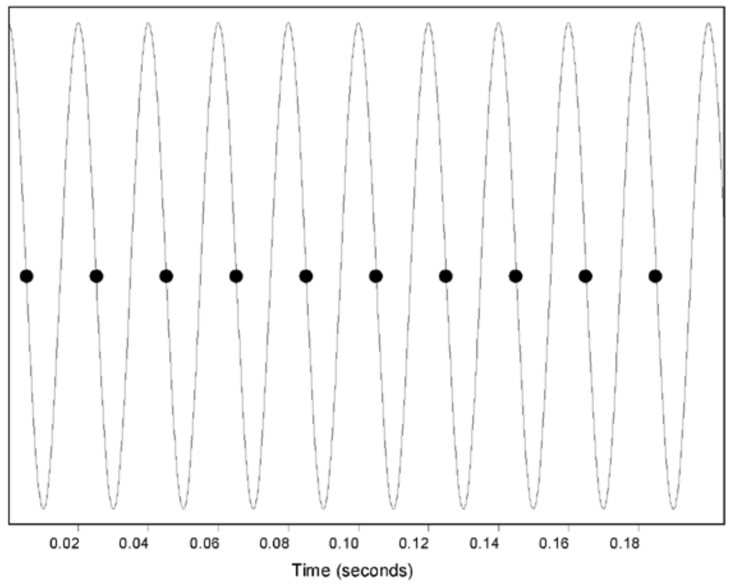
For sinusoidal waveforms we must sample the waveform at least twice in every cycle (period) – this frequency is named the Nyquist frequency

$$f_N = \frac{1}{2\Delta t}$$

and follows from a specification named the sampling theorem stated below (quoted from S.L. Marple, *Digital Signal Processing*, Prentice Hall, Englewood Cliffs, NJ 1987)

> If a continuous signal, $s(t)$ is bandwidth-limited to frequencies smaller in magnitude than some value f_c, then the continous function is completely determined by the discretely sampled sequence, $s(k\Delta t)$, provided that the sampling interval Δt is such that $f_N \geq f_c$.





The inverse of the dwell-time is called the sampling bandwidth or the *spectral width*, and its value determines the range of frequencies that may be accurately represented.

$$\text{spectral width} = \text{SW}=2\,f_N = \frac{1}{\Delta t}$$

In additional to the various dedicated CPU elements, the entire system is controlled by a *host computer* system.

The computer is usually a unix-based workstation that has dedicated software for design and execution of pulsed experiments and data processing.

The most common task executed in modern NMR data processing is the Fourier transformation, or FT.

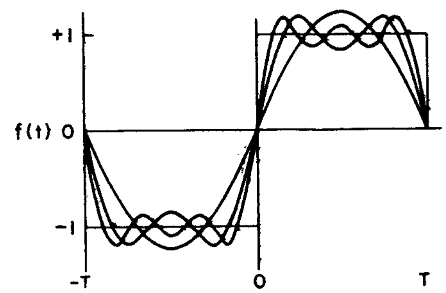
Fourier Transform NMR

Ernst, R.R. and Anderson, W.A. (1966) Application of Fourier Transform Spectroscopy to Magnetic Resonance. *Rev. Sci. Instr.* **37**, 93-102.

The Fourier Hypothesis: An arbitrary function, *f*(*t*), may be approximated to arbitrary precision as a sum of cosine and sine functions

$$f(t) = \sum_{n=0}^{\infty} A_n \cos(n\pi/T)t + \sum_{n=0}^{\infty} B_n \sin(n\pi/T)t$$

Figure 1.6. Approximation of a square wave by Fourier sine series of 1, 3, and 5 terms.



From *Pulse and Fourier Transform NMR*, T.C. Farrar and E.D. Becker, Academic Press 1971

Fourier Pairs:

$$F(\omega) = \int_{-\infty}^{\infty} f(t) \exp[-i\omega t] dt$$

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) \exp[i\omega t] d\omega$$

We will normally employ the FT to extract frequency-domain information from a time-domain signal.

One simple example is the use of the FT to predict the bandwidth of an RF-pulse:

Assume a normalized pulse of length t_p and amplitude $1/t_p$ – the time-domain function may be written as follows

$$f(t)=\begin{cases}0; & t<-t_p/2\\ 1/t_p; & -t_p/2<t<t_p/2\\ 0; & t>t_p/2\end{cases}$$

Then we may write that

$$F(\omega)=\int_{-\infty}^{-1/t_p} f(t)e^{-i\omega t}dt+\int_{-1/t_p}^{+1/t_p} f(t)e^{-i\omega t}dt+\int_{1/t_p}^{\infty} f(t)e^{-i\omega t}dt$$

$$F(\omega)=\int_{-1/t_p}^{+1/t_p} f(t)e^{-i\omega t}dt$$

$$F(\omega)=\frac{1}{t_p}\int_{-1/t_p}^{+1/t_p} e^{-i\omega t}dt$$

$$F(\omega)=\frac{1}{t_p}\int_{-1/t_p}^{+1/t_p} e^{-i\omega t}dt=\frac{1}{t_p}\left(\int_{-1/t_p}^{+1/t_p}\cos(\omega t)dt-i\int_{-1/t_p}^{+1/t_p}\sin(\omega t)dt\right)$$

It is sufficient to consider only the real part of $F(\omega)$, thus

$$F(\omega)=\frac{1}{t_p}\int_{-1/t_p}^{+1/t_p}\cos(\omega t)dt=\frac{2}{t_p}\int_{0}^{+1/t_p}\cos(\omega t)dt$$

$$F(v)=\frac{2}{t_p}\int_{0}^{+1/t_p}\cos(2\pi\omega t)dt=\frac{\sin(\pi v t_p)}{\pi v t_p}$$

wherein v is the carrier frequency in Hz.

The normal NMR signal is generally more complex than the simple cases we have looked at thus far