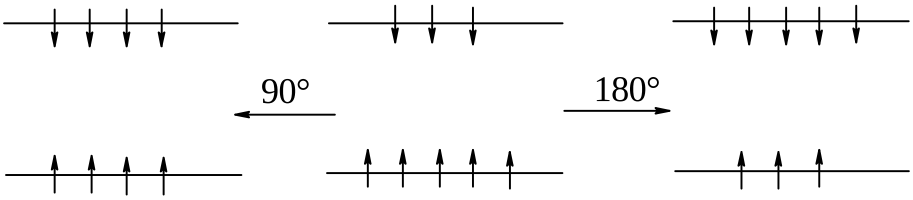
Pulsed Fourier Transform NMR
The rotating frame of reference

The NMR Experiment. The Rotating Frame of Reference.

When we perform a NMR experiment we disturb the equilibrium state of the system and then monitor the response of the system to the disturbance. As a result of the absorption of radiofrequency energy nuclear spins jump from a lower energy level to a higher one.



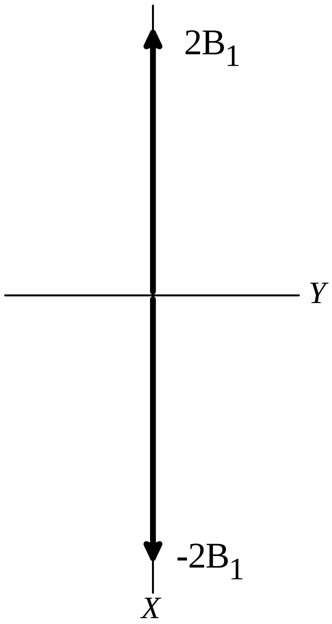
The absorption of energy at this stage is a dominant process due to the population excess in the lower level α at equilibrium. Transitions in the opposite direction correspond to an emission of energy. The probability of the spontaneous emission is very small. Instead, the return of the spin system to its equilibrium state is driven by the presence of “lattice” through a process known as *relaxation*. Each transition is associated with a reversal of the spin orientation (*spin flip*). When more than two energy levels are present ($I \geq 1$) only transitions in which the magnetic quantum number m changes by 1 (*single quantum transitions*) are allowed: $\Delta m = \pm 1$.

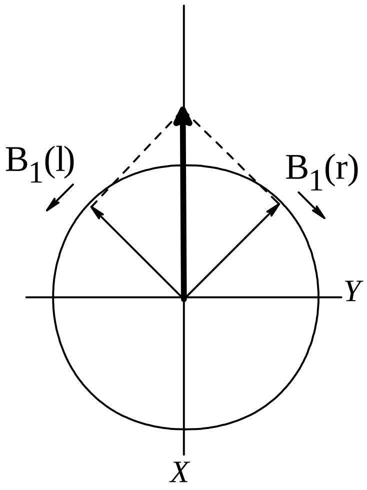
The *resonance condition*:

$$\nu_L = \nu_I = |(\gamma / 2\pi) B_0|$$

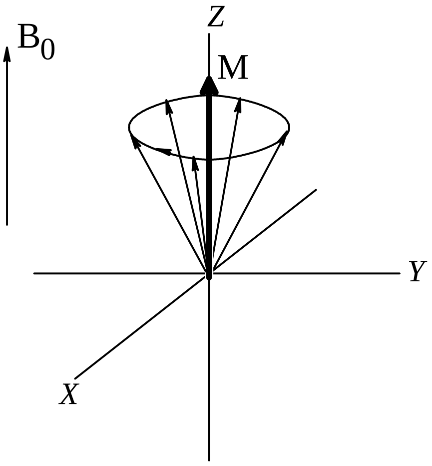
The frequency of the external disturbance (electromagnetic radiation) ν_1 in NMR experiment is chosen so that to match the Larmor frequency ν_L. As a source of the external disturbance an oscillating magnetic field B_1, along the x axis, with frequency $(\gamma/2\pi) B_0$ is used.

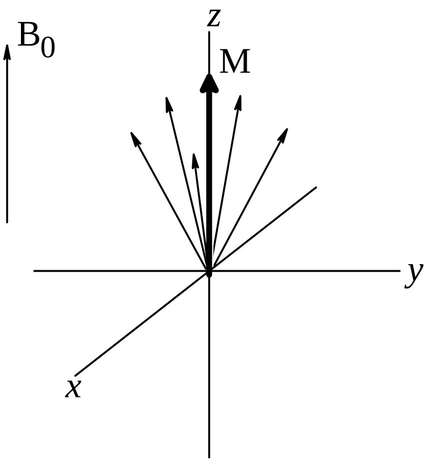
A linear oscillation can be converted into a superposition of two components rotating in opposite directions:





In the rotating frame (*xyz*) representation the *z* axis is parallel to the *Z* axis of the laboratory frame (B_0 is aligned along +*Z* direction) and the *x* and *y* axes are allowed to rotate about the *z* axis at the Larmor frequency. We then assign +*x* direction to B_1 vector.

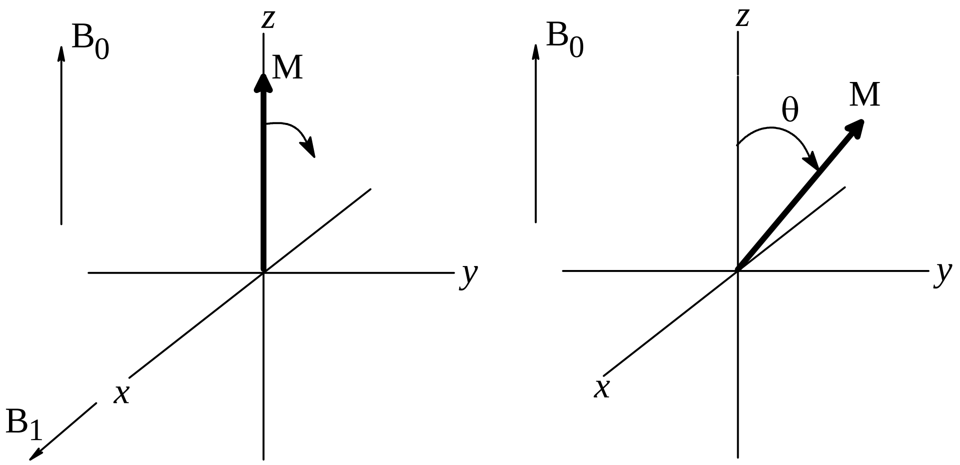




The applied B_1 field is still composed of two counter-rotating vectors: the component vector that rotates in the same direction as the frame appears to be stationary, whereas the other component rotates at frequency $2\omega_0$.

As in the laboratory frame, +*z* direction defines the orientation of the net magnetization vector, M, at equilibrium, although in the rotating frame the B_0-induced precession of the individual magnetizations is “switched off”.

On switching on B_1 field the net magnetization, M, starts precessing along B_1 in the yz plane and is tipped toward the y axis.



The B_1 field is applied as a *pulse* of duration t_p, which usually lasts for a few microseconds. The angle θ (known as the pulse angle) through which the magnetization is tipped from the z axis increases with the amplitude of B_1 and with the length of time, t_p, for which the pulse is applied:

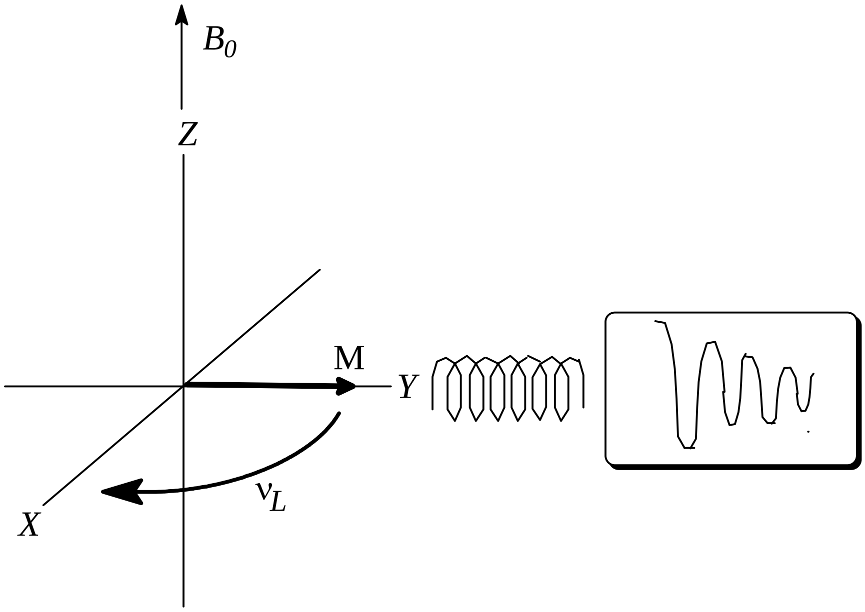
$$\theta\ (\text{rad}) = \gamma\ (\text{rad sec}^{-1}\ \text{G}^{-1})\ B_1\ (\text{G})\ t_{\text{p}}(\text{sec})$$

The transverse magnetization M_y is greatest immediately after a $90°_x$ pulse and is zero for $180°_x$ pulse. M_y is the component of interest, since the receiver coil is aligned along y and as a consequence a signal *(free induction decay)* proportional to M_y is induced in the receiver coil.

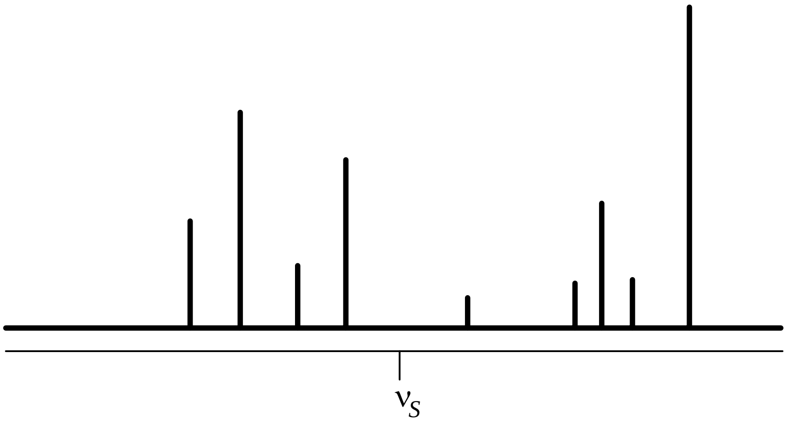
The Free Induction Decay

If the magnetization M is tipped from the z axis to y axis by 90° pulse it would remain indefinitely in the xy plane. In the laboratory frame, M would precess about B_0 at a constant frequency. If we align the receiver coil about the laboratory Y axis, the precessing magnetization will induce in the coil an oscillating voltage which we can detect on an oscilloscope in a form of free induction decay (FID):

free of the influence of the radiofrequency field,
induced in the coil, and
decaying back to equilibrium due to relaxation processes.



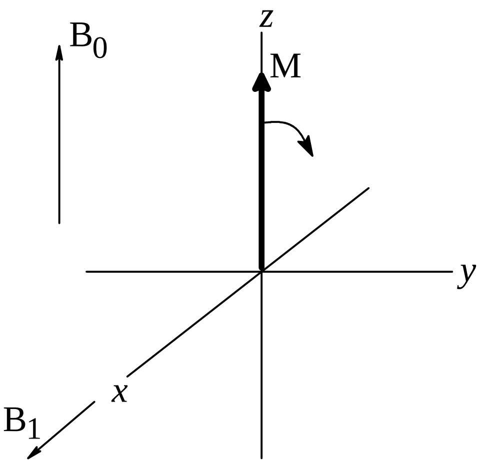
Because the pulse produces a wide range of frequencies (proportional to t_p^{-1}) of almost equal amplitude, the nuclei throughout the entire chemical shift range are all effectively tipped by the same angle. Each chemically shifted nucleus may be considered to belong to a frame rotating at the corresponding Larmor frequency. In order to understand what happens after the pulse, it is necessary to assign the frame to a single frequency, ν_S, the value at the centre of the frequency band (referred to as *carrier frequency*).

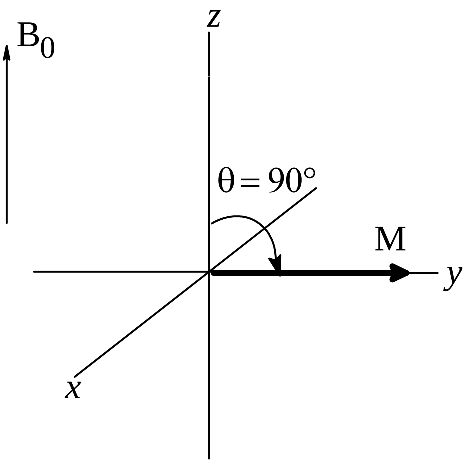


In NMR experiment the difference between the Larmor frequency ν_L and the carrier frequency ν_S is detected: $\delta\nu = \nu_L - \nu_S$. The Larmor frequency for a given type of the nucleus slightly differs from ν_S (*off resonance* conditions) due to chemical shielding effects.

The evolution of the signal seen on the oscilloscope

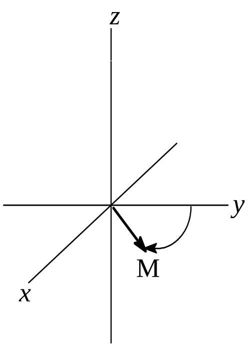
The sample is excited with a 90° pulse along the *x* axis and the magnetization along the *y* axis is observed under off-resonance conditions:

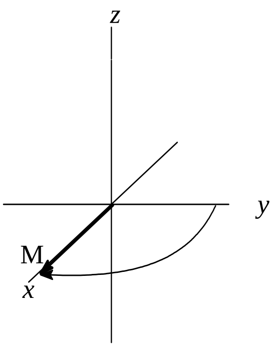


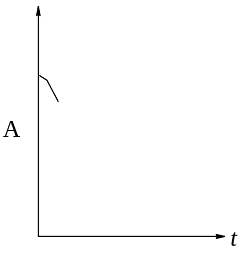


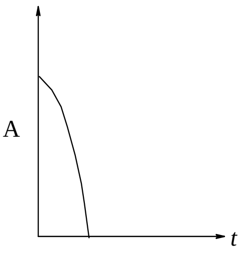
$\gamma\ B_1 t_p = \pi\ /2$

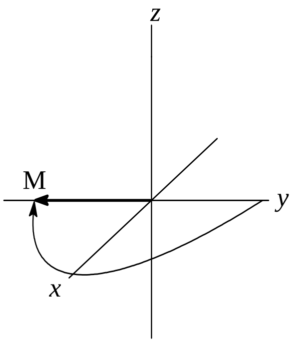
Under the off-resonance condition, the magnetization M is rotating with respect to the frame of observation with offset frequency δν:

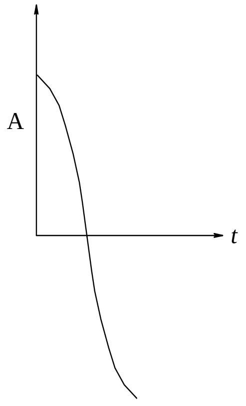




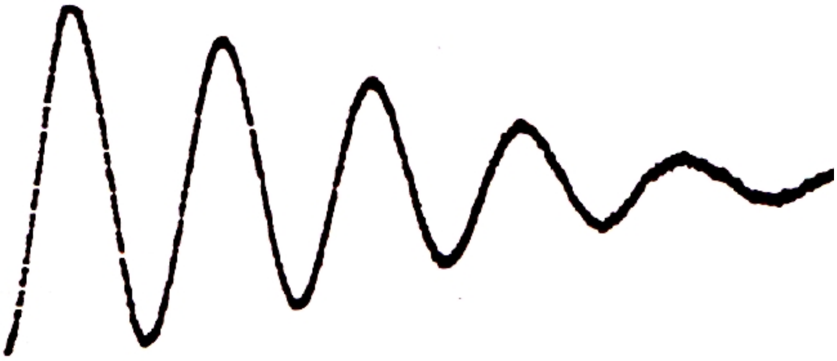




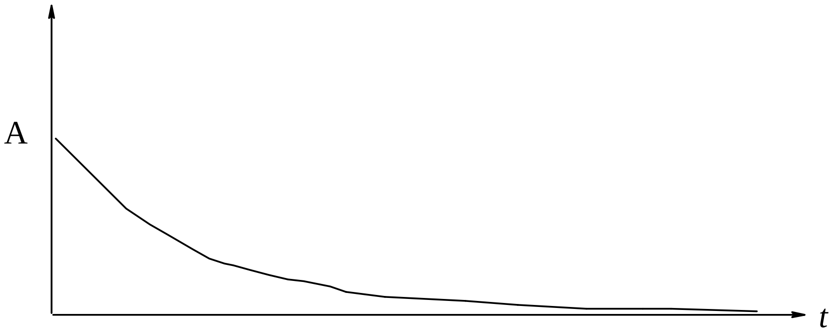




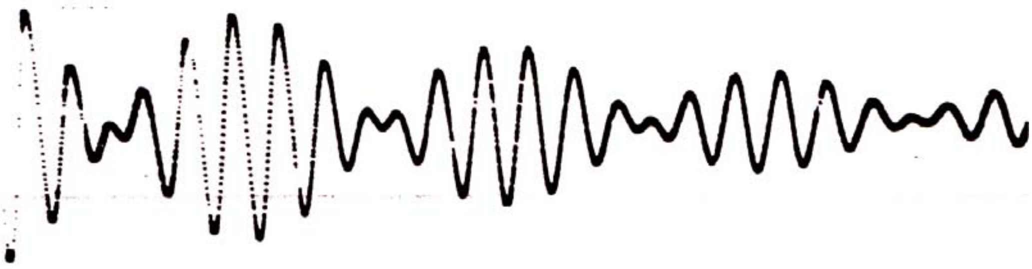
The free-induction decay of protons in water, associated with a 90° pulse along -*x*, and observation along +*y* in the rotating frame:



Under on resonance conditions, we would observe a decaying zero-frequency signal:

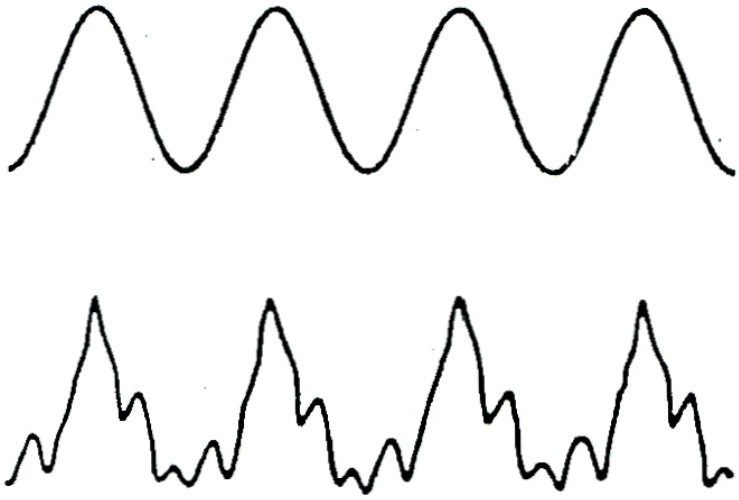


In the case of two or more resonances in the spectrum, the magnetization vectors move in rotating frame at different frequencies $\delta\nu_i$ and produce a signal which is the sum of the components:



Fourier Transformation

The aim of Fourier transformation is to differentiate frequencies present in a complex waveform and to determine intensities corresponding to each frequency (in analogy a with an ordinary prism: a complex wave,“white light”, is dispersed into its components, the spectrum).



Pressure variations produced
by a tuning fork (top) and
a musical instrument (bottom).

Fourier's theorem: *any reasonably well behaved periodic function may be generated by the superposition of a sufficient number of sine and cosine functions*:

$$F(t) = \Sigma\ (A_n \sin n\omega t + B_n \cos n\omega t)$$

where $\omega = 2\pi / T = 2\pi\nu$. The coefficients A_n and B_n indicate the amplitude of the nth harmonic function. The process of determining these coefficients is called Fourier analysis.

A "square wave signal": $F(t) = +1$ between $t=0$ and $t=\pi$

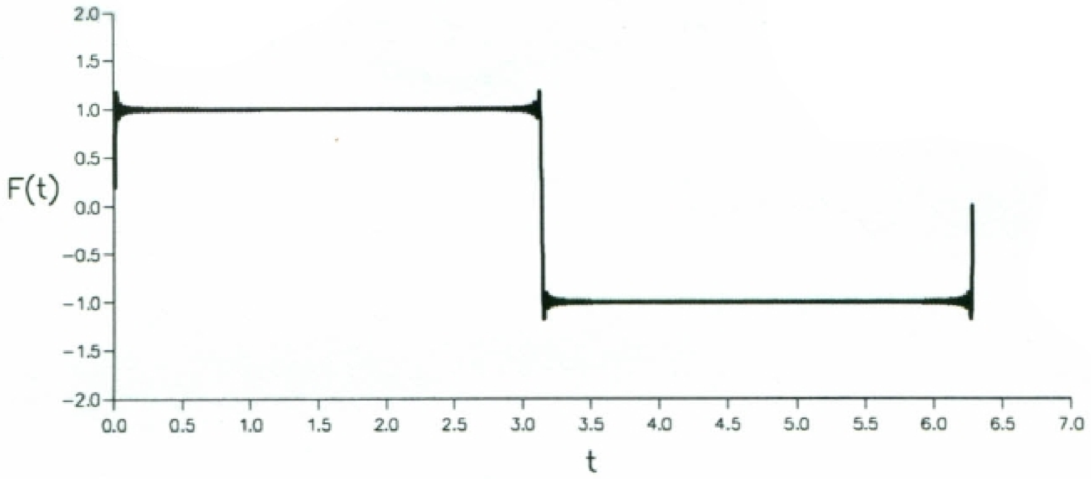
$F(t) = -1$ between $t=\pi$ and $t=2\pi$

$$F(t) = \frac{4}{\pi}\left(\sin\omega t + \frac{1}{3}\sin 3\omega t + \frac{1}{5}\sin 5\omega t + \cdot\ \cdot\ \cdot \right)$$

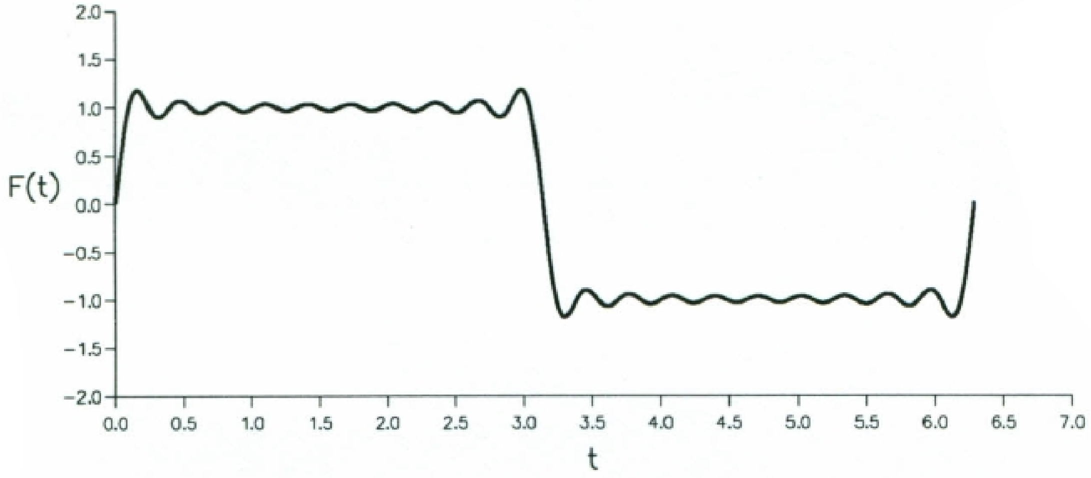
The period T of function F is equal to 2π sec and $\omega = 2\pi / T = 1$ rad/sec.

The superposition of (a) three; (b) ten, and (c) one hundred harmonic terms:

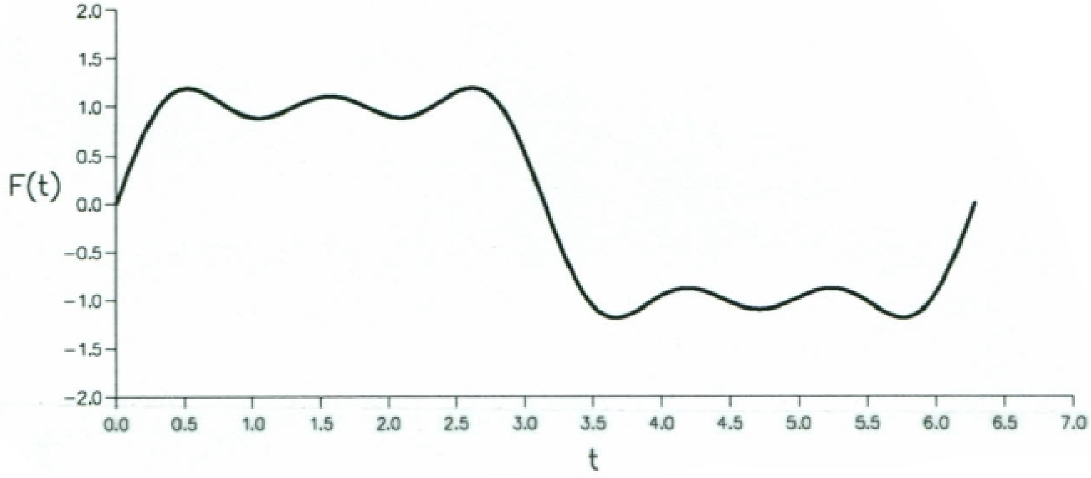
100 components



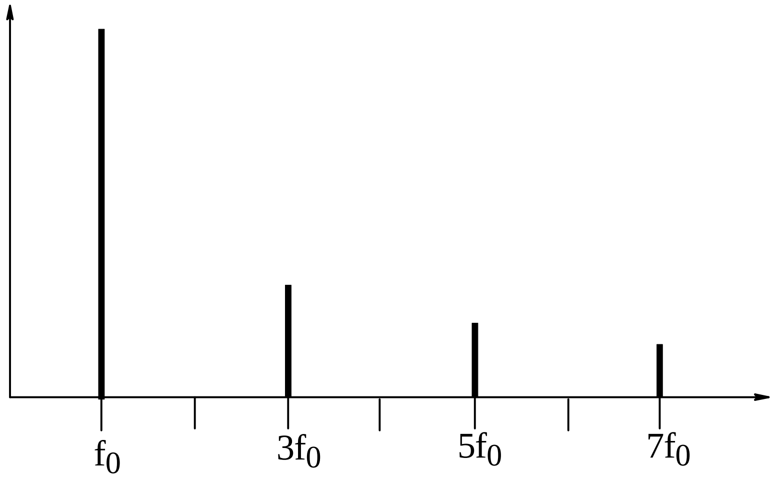
10 components



3 components



The results of Fourier analysis of a function can be presented by its spectrum, in which relative amplitudes of the components in frequency domain are displayed. The square wave has only odd harmonics whose strengths decreases monotonically as the frequency increases:



This representation allows to assess the contribution of low and high frequencies.

The envelope of the rf pulse transmitted to the sample in the probe is close to the shape of the positive half of the square wave function. If the pulse generator is switched on for a short period then the sample is excited with a band of frequencies in the range $\nu_0 \pm 1/t_p$, where t_p is the duration of the pulse. A typical pulse of duration 10 μs gives an effective range of the order of 10^5 Hz, which is adequate for the excitation of all the protons in a sample.

In the case of the spectral analysis, it is convenient to deal with the corresponding integrals:

$$f(\nu) = \int_{-\infty}^{\infty} F(t)\exp(-i2\pi\nu t)dt$$

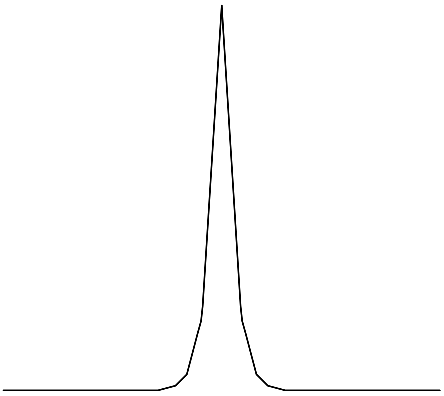
$$F(t) = \int_{-\infty}^{\infty} f(\nu)\exp(+i2\pi\nu t)d\nu$$

$$\{\exp(i\,2\pi\nu t) = \cos(2\pi\nu t) + i\sin(2\pi\nu t)\}$$

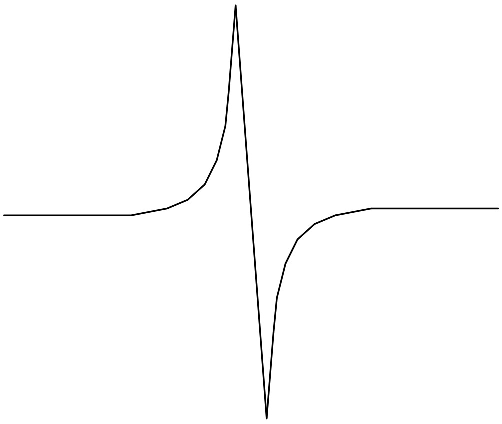
This mathematical procedure is known as *Fourier transformation*, which relates time and frequency domains.

$$\mathrm{Re}[f(\nu)] = \int_{-\infty}^{\infty} F(t)\cos(2\pi\nu t)\,dt$$

$$\mathrm{Im}[f(\nu)] = \int_{-\infty}^{\infty} F(t)\sin(2\pi\nu t)\,dt$$

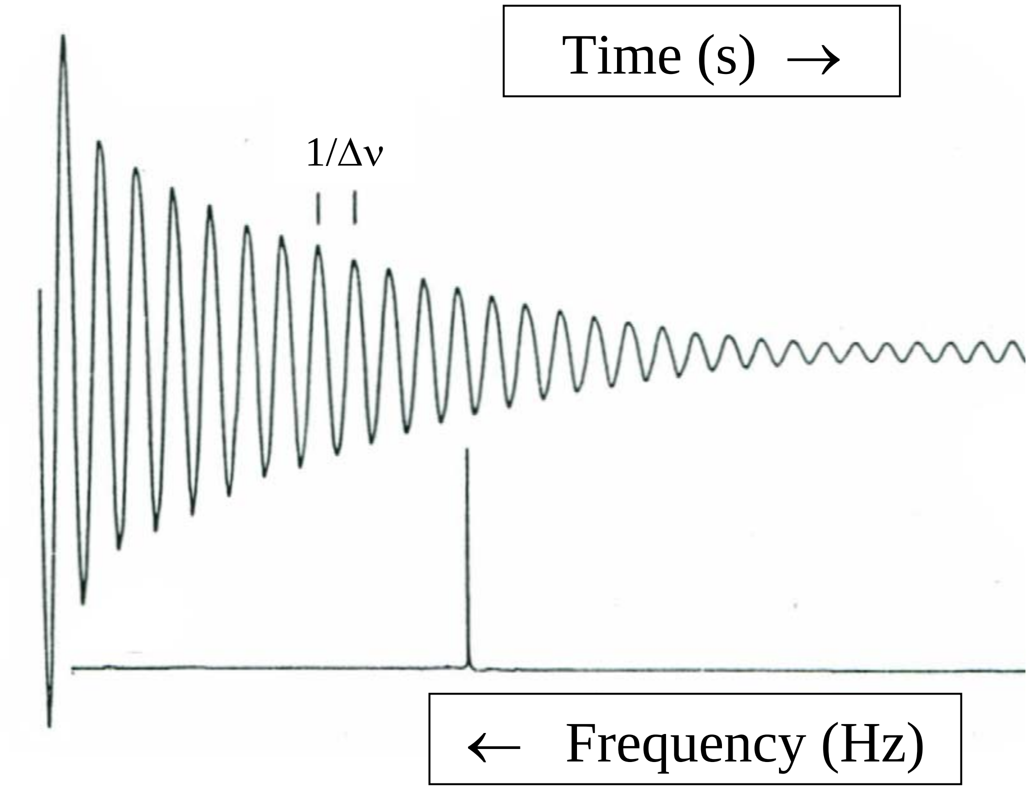


Absorption mode

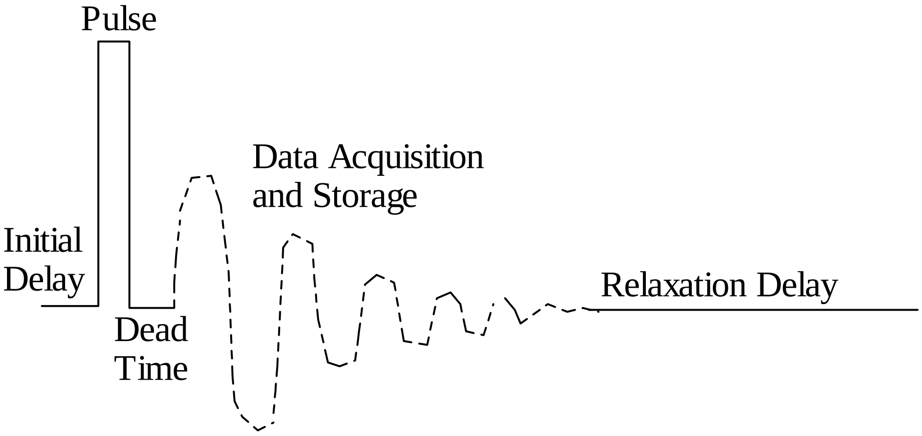


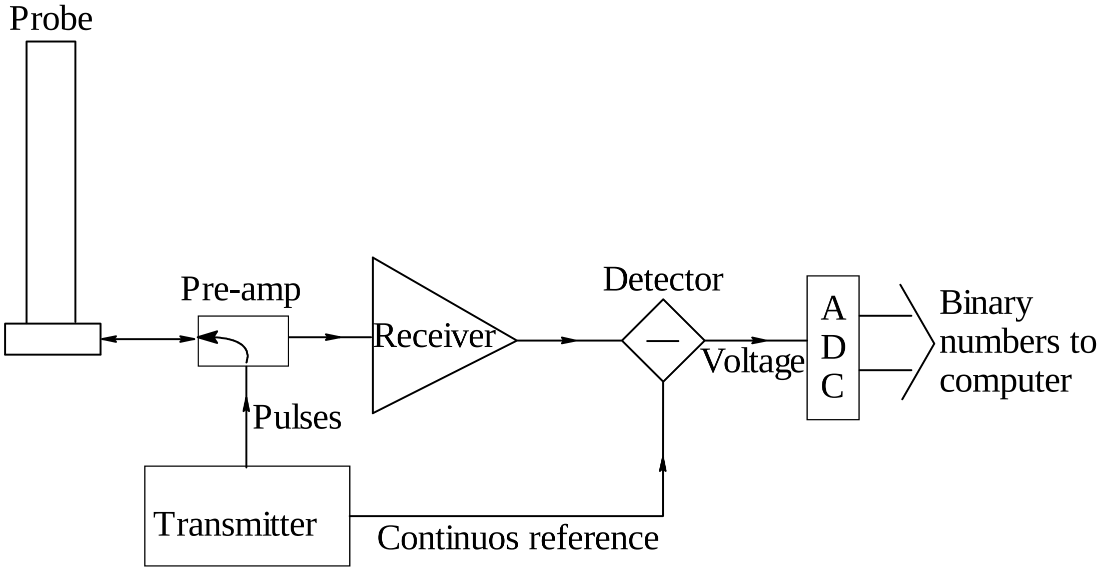
Dispersion mode

In a single line NMR spectrum the time interval between successive maxima in the FID is $1/\Delta\nu$, where $\Delta\nu$ is the difference in frequency between the carrier frequency ν_S and the resonance frequency ν_i of the nuclei.



Single Pulse Experiment





ADC – analog-to-digital converter.

ADC resolution – the number of bits used in the binary representation (usually 12-bit resolution – if the receiver has been adjusted so that the maximum signal just fills the ADC, then no signal less than 2^{11}-1 of the largest signal (i.e. 1/2047) should be detectable [*dynamic range* 2047:1])

Signal Averaging

The single pulse experiment is repeated for *NS* times until the desired signal-to-noise ratio is achieved. For best sensitivity there is an optimum combination of the tip angle, the T_1 relaxation time, and the time between pulses, given by Ernst's equation:

$$\cos\theta = \exp(-\,t_{\mathrm{rep}} / T_1)$$

NMR fits the definition of a “detector-noise-limited”: the process of time-averaging a large number of FID’s results in a theoretical improvement in signal-to-noise ratio by a factor equal to $\sqrt{NS}$.

Field frequency locking is used in order to ensure that the relation of the spectrometer frequency and the Larmor frequencies of the nuclei does not change during signal acquisition. Usually the frequency of a deuterium resonance of the solvent is compared to a fixed frequency derived from the master clock used to generate the spectrometer frequency.