

2. Basic Principles

NMR spectrum

Nuclear magnetism

Rotating coordinate frame

NMR spectrometer

Pulse NMR

Fourier transformation

Phase correction

Relaxation

Spin echo

Measurement methods

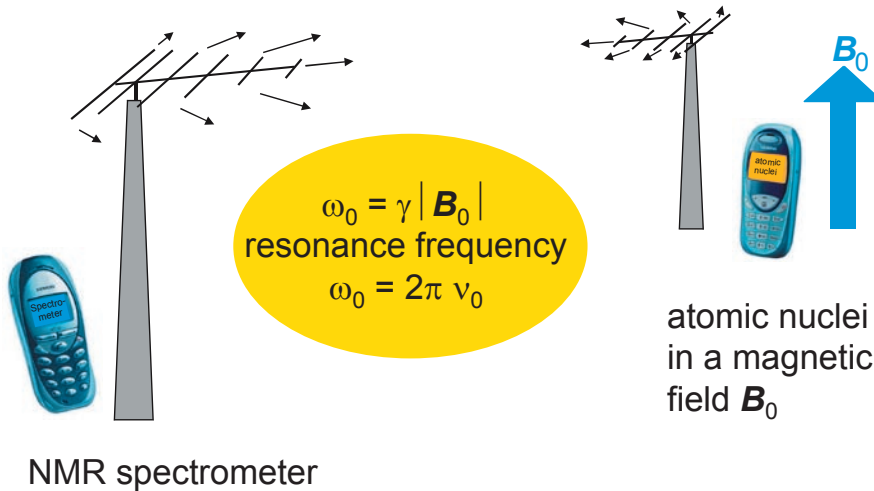
Spatial resolution

Properties of Atomic Nuclei

- When exposed to magnetic fields, magnetic nuclei can receive and emit radio waves. Their *frequency* ν_0 is proportional to the strength B_0 of the magnetic field: $\omega_0 = 2 \pi \nu_0 = \gamma B_0$
- The constant of proportionality is the *gyro-magnetic ratio* γ . It is a characteristic constant of the nuclear isotope
- Examples of isotope abundance and radio frequencies are:

nuclear isotope	nat. abundance	ν_0 at $B_0 = 1.0$ T
^1H	99.98 %	42.57 MHz
^{14}N	99.63 %	3.08 MHz
^{19}F	100.00 %	40.05 MHz
^{13}C	1.108 %	10.71 MHz
^{129}Xe	26.44 %	11.78 MHz

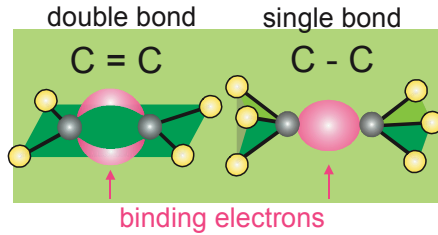
NMR is a Form of Telecommunication in a Magnetic Field



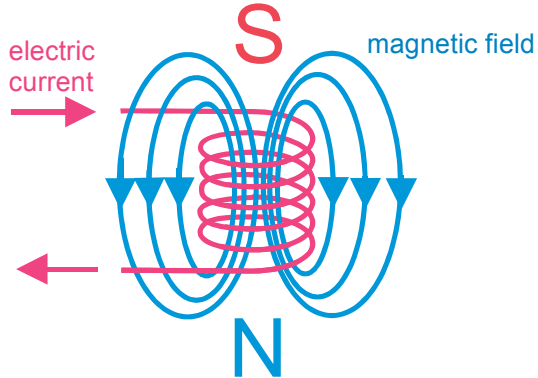
Magnetic Shielding

- The NMR frequency is determined by the magnetic field at the site of the nucleus
- Atomic nuclei are surrounded by electrons
- In molecules, the electrons of the chemical bond are shared by different nuclei
- Electrons of atoms and molecules move in orbitals which are studied in quantum mechanics
- The orbitals of the binding electrons are characteristic of the *chemical structure* of the molecule
- Electrons carry an electric charge
- Electric charges in motion induce a magnetic field
- The internal magnetic field induced by the electrons moving in the external magnetic field \mathbf{B}_0 is usually opposed to \mathbf{B}_0 . It shields the nucleus from \mathbf{B}_0 .

Electrons in Motion



distribution of
binding electrons



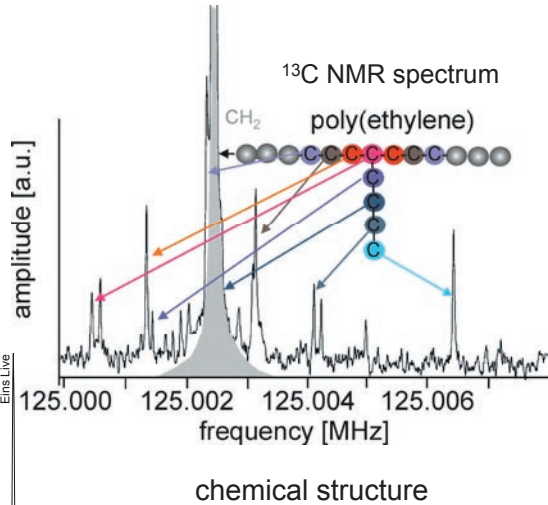
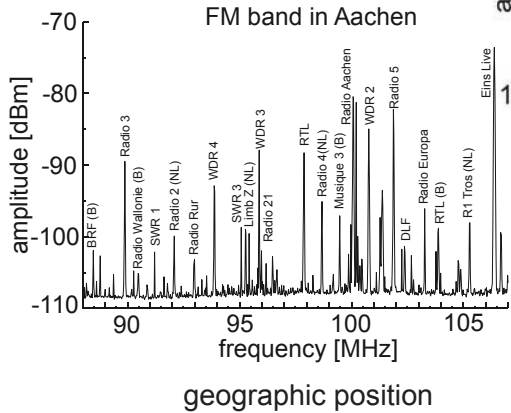
moving charges induce
a magnetic field

example: coil

Chemical Shift

- The induced magnetic field shifts the resonance frequency:
$$\omega_L = 2\pi \nu_L = \gamma (1 - \sigma) B_0$$
- The quantity σ is the *magnetic shielding* for a given chemical group
- The quantity $\delta = (\nu_L - \nu_{\text{ref}}) / \nu_{\text{ref}}$ is the *chemical shift* of a chemical group. It is independent of the magnetic field strength B_0 .
- The chemical shift can be calculated from tabulated chemical shift increments as well as *ab initio* from quantum mechanics
- The quantity ν_{ref} is the reference frequency, for example, the resonance frequency of tetramethyl silane (TMS) for ^1H and ^{13}C NMR
- Magnetically inequivalent chemical groups possess different chemical shifts
- In liquids narrow resonance signals are observed with typical widths of 0.1 Hz
- The distribution of resonance frequencies forms the *NMR spectrum*
- The NMR spectrum is a fingerprint of the molecular structure similar to a distribution of FM signals at a given location which is a fingerprint of the geographical position
- The acquisition of NMR spectra of molecules in solution is a standard method of analysis in following chemical synthesis

Frequency Distributions of Radio Waves



Nuclear Magnetism

- In a sample of material there are roughly 10^{23} atomic nuclei per mole
- Some atomic nuclei have the properties of a *magnetic dipole*
- Examples: ^1H , ^2H , ^{13}C , ^{14}N , ^{19}F , ^{31}P , ^{129}Xe
- Because atomic nuclei consist of a small number of elementary particles, the laws of classical physics do not apply. Instead the laws of *quantum mechanics* do
- According to quantum mechanics an elementary magnetic dipole with a dipole moment μ also possesses an *angular momentum* $\hbar I$ or *spin I*.
- In the laws of physics involving elementary particles Planck's constant h or $\hbar = h / (2\pi)$ appears
- A classical object with angular momentum is the *spinning top*
- A top spinning in a gravitational field formally follows the same laws as a spin in a magnetic field: it precesses around the direction of the field
- In NMR the precession frequency is called the *Larmor frequency*



Arnold Sommerfeld, 1868 – 1951, Heisenberg's teacher, described the spinning top

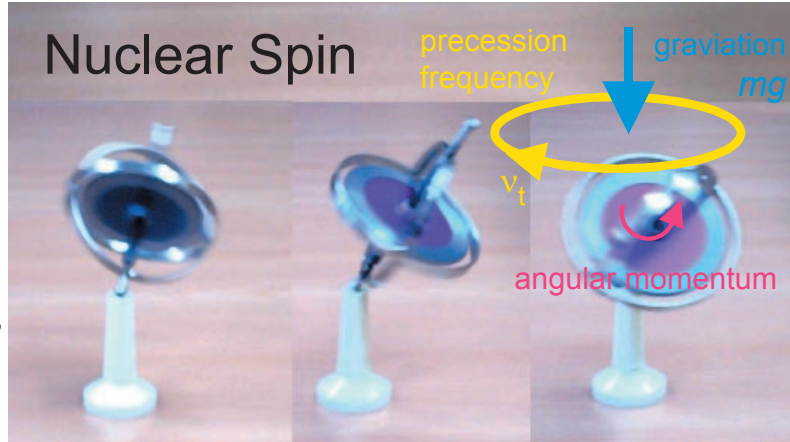


Paul Adrien Maurice Dirac, 1902 – 1984, 1933 Nobel prize in Physics, postulated the existence of the spin

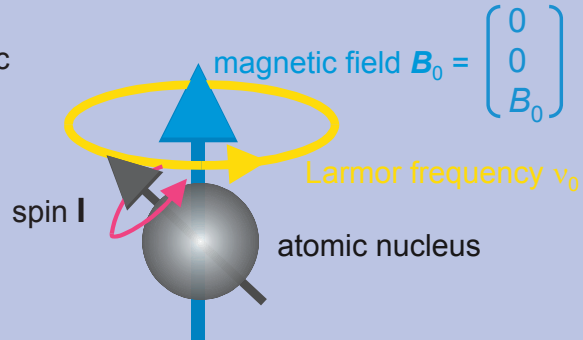


Otto Stern 1888 – 1963, 1943 Nobel prize in Physics, experimental discovery of the spin

Nuclear Spin



magnetic moment
 $\mu = \gamma \hbar I$



Properties of Nuclear Spins

- Following Heisenberg's uncertainty principle, only the component of the spin in the direction of the magnetic field can be measured
- From quantum mechanics it is known that a spin with the *spin quantum number* I can assume $2I + 1$ stable orientations in a magnetic field
- The projection of the spin angular momentum along the direction of the magnetic field is proportional to the *magnetic quantum number* m , where $m = I, I-1, \dots, -I$
- $I = \frac{1}{2}$ is valid for the nuclei ^1H , ^{13}C , ^{19}F , ^{31}P , ^{129}Xe and $I = 1$ for ^2H , ^{14}N
- For nuclei with spin $I = \frac{1}{2}$ there are two possible orientations of its projection along the axis of the magnetic field: \uparrow und \downarrow
- Both orientations differ in the interaction energy $E_m = -\hbar \gamma m B_0$ of the nuclear magnetic dipoles with the magnetic field
- According to Bohr's formula $\Delta E = h \nu_0$ the energy difference $\Delta E = E_{-1/2} - E_{+1/2} = \hbar \gamma B_0$ associated with both orientations corresponds to the frequency $\omega_0 = 2\pi \nu_0 = \gamma B_0$
- Here ν_0 is the precession frequency of the nuclear spins in the magnetic field

Quantum Mechanics



Niels Henrik David Bohr
1885 - 1962,
1922 Nobel prize in Physics: $\Delta E = h \nu$

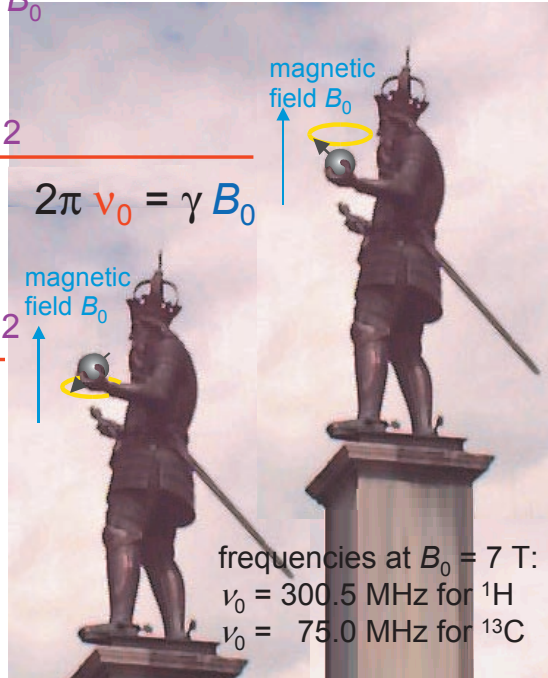
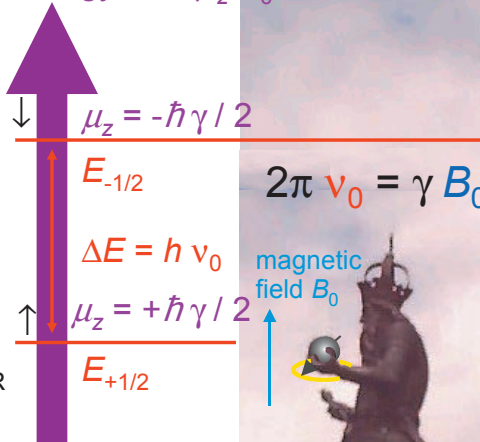


Felix Bloch,
scholar of Heisenberg:
1905 - 1983,
1952 Nobel prize in Physics: NMR



Edward Mills Purcell
1912 - 1997,
1952 Nobel prize in

energy $E = -\mu_z B_0$



Nuclear Magnetization in Thermodynamic Equilibrium

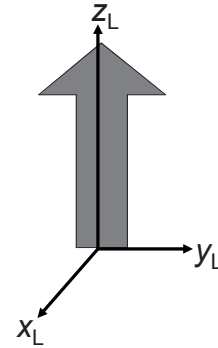
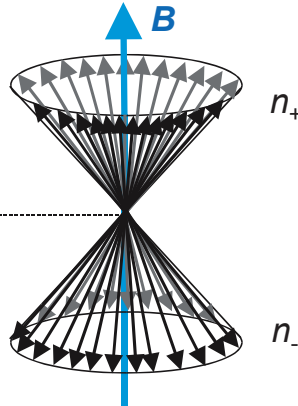
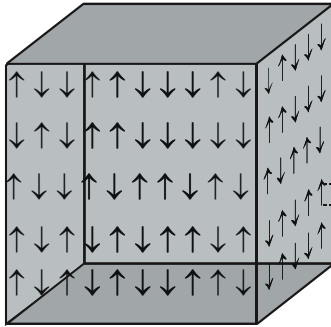
- All magnetic dipole moments are added as vectors; their components in each space direction are additive
- The sum of transverse components (if observable) vanishes
- The sum of longitudinal components constitutes the *longitudinal magnetization*
- This component is referred to as the *magnetic polarization* of the nuclei or the *nuclear magnetization*
- At room temperature only about 10^{18} spins of all 10^{23} spins contribute to the macroscopic nuclear magnetization of the sample
- In the thermodynamic equilibrium state, the nuclear magnetization is oriented parallel to the direction of the magnetic field
- The direction of the magnetic field is referred to as the z direction of the *laboratory coordinate frame* LCF (index L)

Macroscopic Magnetization

macroscopic sample:
 10^{23} nuclear spins

$$n_-/n_+ = \exp\{-\Delta E/k_B T\}$$

vector sum:
macroscopic
magnetization M



Bloch's Equation

- When the magnetization \mathbf{M} is not aligned with the z_L direction, it precesses around z_L with the frequency ν_0 in complete analogy with the precession of a top spinning in a gravitational field \mathbf{g}
- The precession is described by the equation for the magnetic *spinning top*:

$$\frac{d}{dt} \mathbf{M} = \gamma \mathbf{M} \times \mathbf{B}$$

- This equation states that any change $d\mathbf{M}$ of the magnetization \mathbf{M} is perpendicular to \mathbf{M} and \mathbf{B} ; therefore \mathbf{M} precesses
- In general any macroscopic precessional motion is attenuated. This is why Felix Bloch introduced phenomenological attenuation terms:

$$\mathbf{R} = \begin{pmatrix} 1/T_2 & 0 & 0 \\ 0 & 1/T_2 & 0 \\ 0 & 0 & 1/T_1 \end{pmatrix}$$

- The resultant equation is the *Bloch equation*,

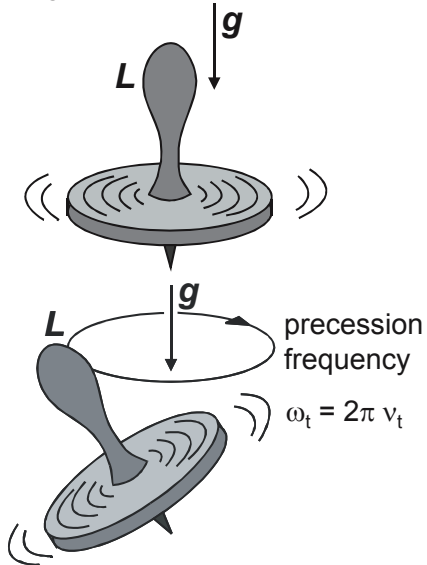
$$\frac{d}{dt} \mathbf{M} = \gamma \mathbf{M} \times \mathbf{B} - \mathbf{R} (\mathbf{M} - \mathbf{M}_0)$$

where \mathbf{M}_0 : initial magnetization, T_1 : longitudinal relaxation time,
 T_2 : transverse relaxation time

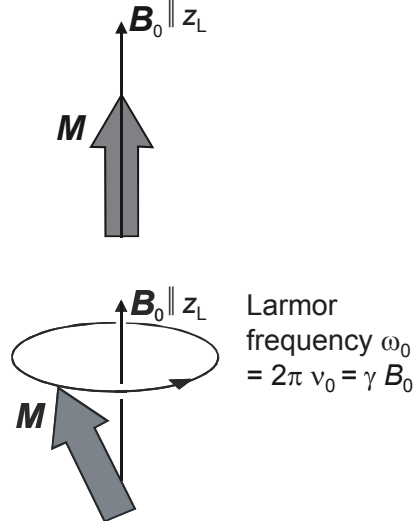
- Note: The Bloch equation formulates a left-handed rotation of the transverse magnetization. But for convenience sake a right handed one is followed throughout this text and many others in the literature

Precession of Nuclear Magnetization

spinning top in a
gravitational field



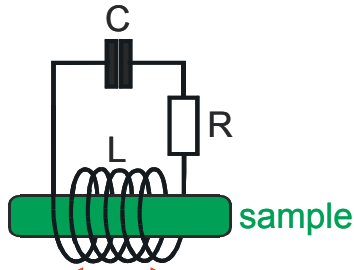
macroscopic nuclear
magnetization



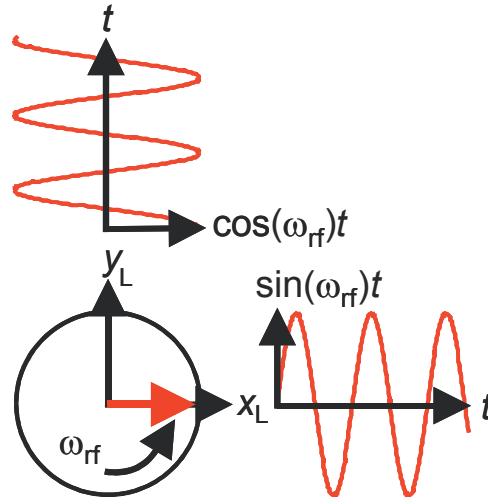
Contacting Nuclear Magnetization

- Nuclear magnetization can be rotated away from the direction z_L of the magnetic polarization field \mathbf{B}_0 by radio-frequency (rf) irradiation
- To this end one generates a magnetic field which rotates around \mathbf{B}_0 with frequency ω_{rf}
- For maximum interaction of the rotating field with the nuclear magnetization the *resonance condition* $\omega_{\text{rf}} = \omega_0$ is chosen
- Because $\nu_0 = \omega_0/2\pi$ is a frequency in the radio-frequency regime, the rotating magnetic field is an electromagnetic *radio-frequency wave*
- High frequency electromagnetic waves are emitted from transmission antennas or oscillating electronic rf circuits
- An *electronic oscillator* consists of a *coil* with inductance L , a capacitor with capacitance C , and a resistor with resistance R
- The coil generates a linearly polarized, oscillating magnetic field $2B_1 \sin\omega_{\text{rf}}t$
- Two orthogonal, linearly polarized waves $\cos\omega_{\text{rf}}t$ and $\sin\omega_{\text{rf}}t$ generate a rotating wave
- A linearly polarized wave $\sin\omega_{\text{rf}}t$ can be decomposed into a right rotating wave $\frac{1}{2} \exp\{i\omega_{\text{rf}}t\}$ and a left rotating wave $\frac{1}{2} \exp\{-i\omega_{\text{rf}}t\}$
- For optimum use of the oscillating magnetic field, the sample to be investigated is placed inside the coil

Magnetic Fields in an Oscillator Circuit



$2 B_1 \sin(\omega_{rf} t)$
 magnetic field B_1
 oscillating with
 frequency ω_{rf}



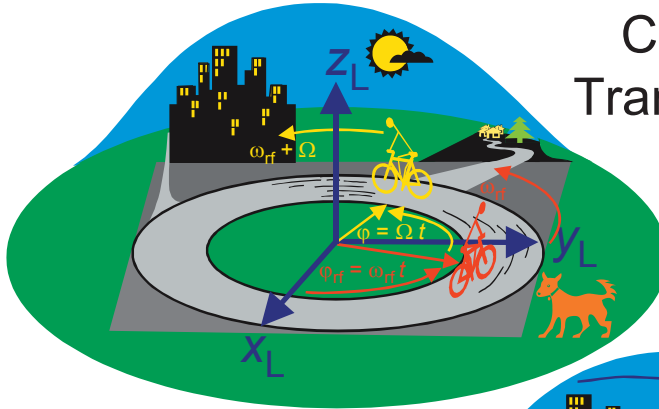
$$\exp\{i\omega_{rf} t\} = \cos(\omega_{rf} t) + i \sin(\omega_{rf} t)$$

$$2 B_1 \sin(\omega_{rf} t) = -i B_1 [\exp\{i\omega_{rf} t\} - \exp\{-i\omega_{rf} t\}]$$

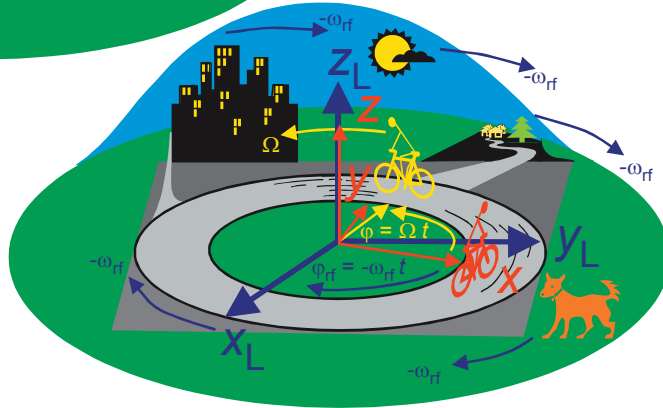
Rotating Coordinate Frame

- Transformations from one coordinate frame into another change the point of view, i. e. they change the mathematics but not the physics
- As the precession of nuclear magnetization is a rotational motion and the rf excitation is a rotating wave, the magnetization is conveniently studied in a *rotating coordinate frame* (RCF)
- The dog at the traffic circuit is positioned in the *laboratory coordinate frame* (LCF): For him the bicycles are driving in the traffic circuit with angular velocities ω_{rf} and $\omega_{\text{rf}} + \Omega$
- The cyclists on the bicycles are viewing the world from the RCF. They are at rest in their respective RCF
- For the red cyclist the world is rotating against the direction of his bicycle with angular velocity $-\omega_{\text{rf}}$
- For the red cyclist the yellow bicycle rides with angular velocity Ω in his RCF
- The connecting vectors from the center of the traffic circle to the bicycles correspond to the magnetization vectors in the transverse xy plane
- The angular velocity of the RCF as seen in the LCF corresponds to the frequency ω_{rf} of the rf wave

Coordinate Transformation



rotating coordinate frame
 x, y, z : the red bicycle rider looks at the dog

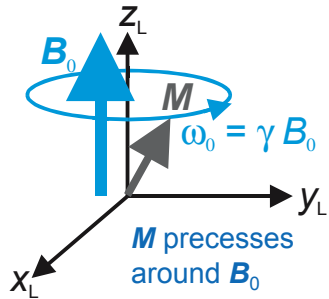


Radio-Frequency Pulses

- In a coordinate system, which rotates with frequency ω_0 around the z axis the magnetization \mathbf{M} appears at rest even if it is not parallel to the magnetic field \mathbf{B}_0
- When the magnetization is not rotating, there is no magnetic field active in that frame which produces a torque on the magnetization
- On resonance $\omega_{\text{rf}} = \omega_0$, and the rf field \mathbf{B}_1 is time independent and appears static in the RCF when turned on
- In the RCF, which rotates in the LCF with $\omega_{\text{rf}} = \omega_0$ around \mathbf{B}_0 , the magnetization rotates around the \mathbf{B}_1 field with frequency $\omega_1 = \gamma |\mathbf{B}_1|$ in analogy to the rotation with frequency $\omega_0 = \gamma |\mathbf{B}_0|$ around the \mathbf{B}_0 field in the LCF
- If \mathbf{B}_1 is turned on in a pulsed fashion for a time t_p , a 90° pulse is defined for $\omega_1 t_p = 90^\circ$ and a 180° pulse for $\omega_1 t_p = 180^\circ$
- The phase φ_0 of the *rotating rf field* $B_1 \exp\{i\omega_{\text{rf}}t + i\varphi_0\}$ defines the direction of the \mathbf{B}_1 field in the xy plane of the RCF
- Using this phase the magnetization can be rotated in the RCF around different axes, e. g. 90°_y denotes a positive 90° rotation around the y axis of the RCF and 180°_x a positive 180° rotation around the x axis

Action of rf Pulses

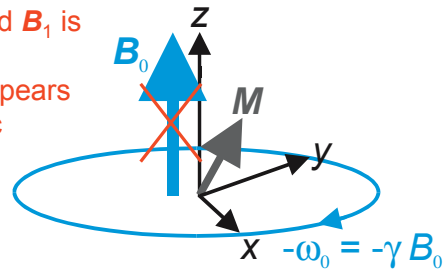
laboratory coordinate frame



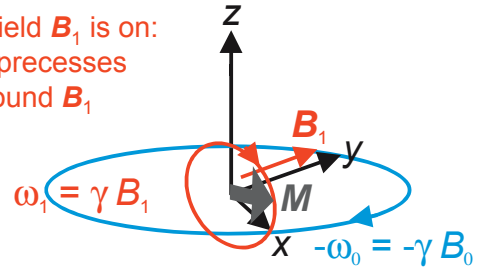
90° pulse: $\omega_1 t_p = \pi/2$
 180° pulse: $\omega_1 t_p = \pi$

rotating coordinate frame

rf field B_1 is off:
 M appears static



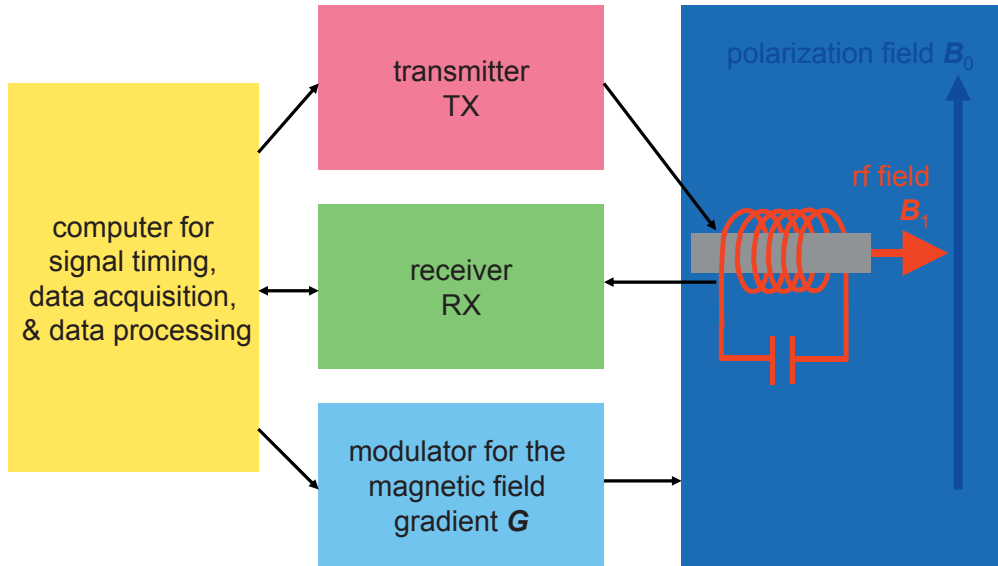
rf field B_1 is on:
 M precesses around B_1



NMR Spectrometer

- The sample is positioned in a magnetic field \mathbf{B}_0 inside a rf coil which is part of a *rf oscillator* tuned to the frequency ω_{rf}
- The oscillator is connected under computer control either to the rf *transmitter* (TX) or to the *receiver* (RX)
- A 90° rf pulse from the transmitter rotates the magnetization from the z_L direction of the \mathbf{B}_0 field into the transverse plane
- Following the pulse, the transverse magnetization components precess around the z_L axis of the LCF with frequency ω_0
- According to the dynamo principle, the precessing magnetization induces a voltage in the coil which oscillates at frequency ω_0
- In the receiver, this signal is mixed with a reference wave at frequency ω_{rf} , and the audio signal at the difference frequency is filtered for acquisition
- This step is the transition into the *rotating coordinate frame*
- Depending on the phase $\phi_0 = 0^\circ$ and 90° of the reference wave $\sin(\omega_{\text{rf}}t + \phi_0)$ the *quadrature components* $\sin(\omega_0 - \omega_{\text{rf}})t$ and $\cos(\omega_0 - \omega_{\text{rf}})t$ of the transverse magnetization are measured in the RCF, respectively
- Usually both quadrature components are measured simultaneously
- For imaging and flow measurements the spectrometer is equipped with switchable *gradient fields* in x_L , y_L , and z_L directions of the LCF

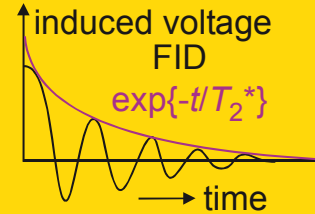
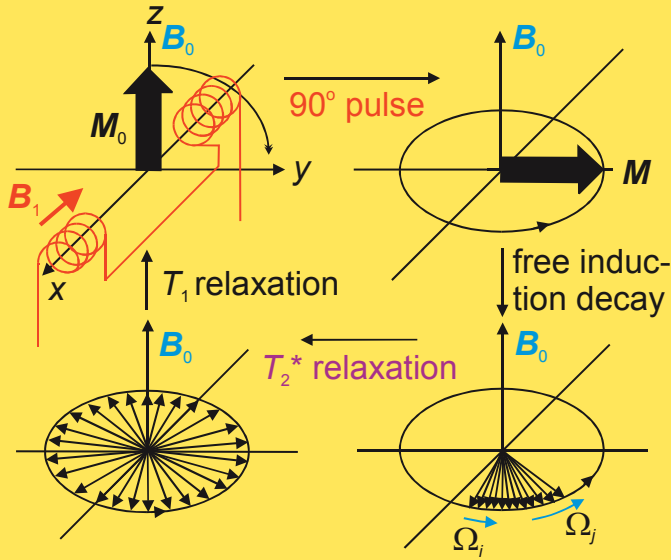
Spectrometer Hardware



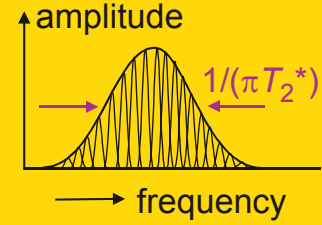
Pulse Excitation

- Outside a magnetic field the nuclear magnetic dipole moments are oriented in random directions in space
- When introducing the sample into the magnetic field \mathbf{B}_0 , the *longitudinal magnetization* M_0 is formed parallel to \mathbf{B}_0 with the time constant T_1 by aligning the nuclear magnetic moments according to the Boltzmann distribution: $M_z(t) = M_0 (1 - \exp\{-t/T_1\})$
- A 90° rf pulse from the transmitter rotates the magnetization from the z direction of the magnetic field \mathbf{B}_0 into the transverse plane of the RCF
- After the rf pulse the transverse components M_i of the magnetization precess around the z axis of the RCF with the difference frequencies $\Omega_i = \omega_{L_i} - \omega_{\text{rf}}$
- Each component M_i corresponds to a different chemical shift or another position in the sample with a different magnetic polarization field
- The vector sum of the *transverse magnetization* components decays with the time constant T_2^* due to interference of the components with different precession frequencies Ω_i
- T_2^* is the *transverse relaxation time* due to time-invariant and time-dependent local magnetic fields
- The signal decay is often exponential: $M_{xy}(t) = M_z(0) \exp\{-t/T_2^*\}$
- The signal induced in the coil after pulse excitation is the *free induction decay (FID)*
- The frequency analysis of the FID by *Fourier transformation* produces the *NMR spectrum* with a *linewidth* $\Delta\Omega = 1/(\pi T_2^*)$

Fourier NMR



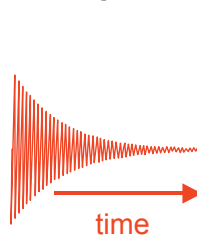
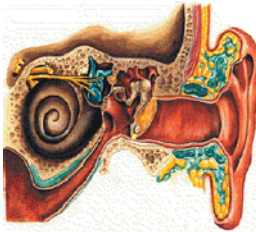
Fourier transformation



Fourier Transformation

- Fourier introduced the transformation named after him when studying thermal conductivity
- The *Fourier transformation* (FT) is a decomposition of a function $s(t)$ into harmonic waves $\exp\{i\omega t\} = \cos\omega t + i \sin\omega t$ with variable frequency ω
- In NMR the *FID* $s(t)$ is transformed to the spectrum $S(\omega)$ of cosine and sine waves: $S(\omega) = \int s(t) \exp\{-i\omega t\} dt$
- The *spectrum* $S(\omega) = U(\omega) + i V(\omega)$ consists of a real part $U(\omega)$ and an imaginary part $V(\omega)$
- Often, only the magnitude spectrum $|S(\omega)| = [U(\omega)^2 + V(\omega)^2]^{1/2}$ is employed
- The Fourier transformation corresponds to the transformation of an acoustic signal into the colors of sound when listening to it
- For the discrete Fourier transformation there is a fast algorithm which was rediscovered in 1965 by J. W. Cooley and J. W. Tukey
- The algorithm requires the discrete representation of the time function $s(t)$ and the spectrum $S(\omega)$ in steps Δt and $\Delta\omega$ of the variables t and ω
- The abscissa of the discrete spectrum corresponds to the keys of a piano
- The spectral amplitude corresponds to the volume of a given tone
- In NMR with pulsed excitation the Fourier transformation is part of processing the data
- *Pulsed NMR* is also called *Fourier NMR*
- The product of two Fourier conjugated variables, e. g. t and ω , is always an angle. It is referred to as *phase*

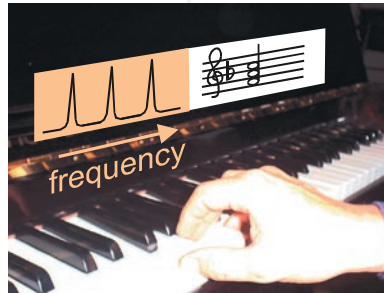
Frequency Analysis



Jean Baptiste
Joseph Fourier
1768 - 1830

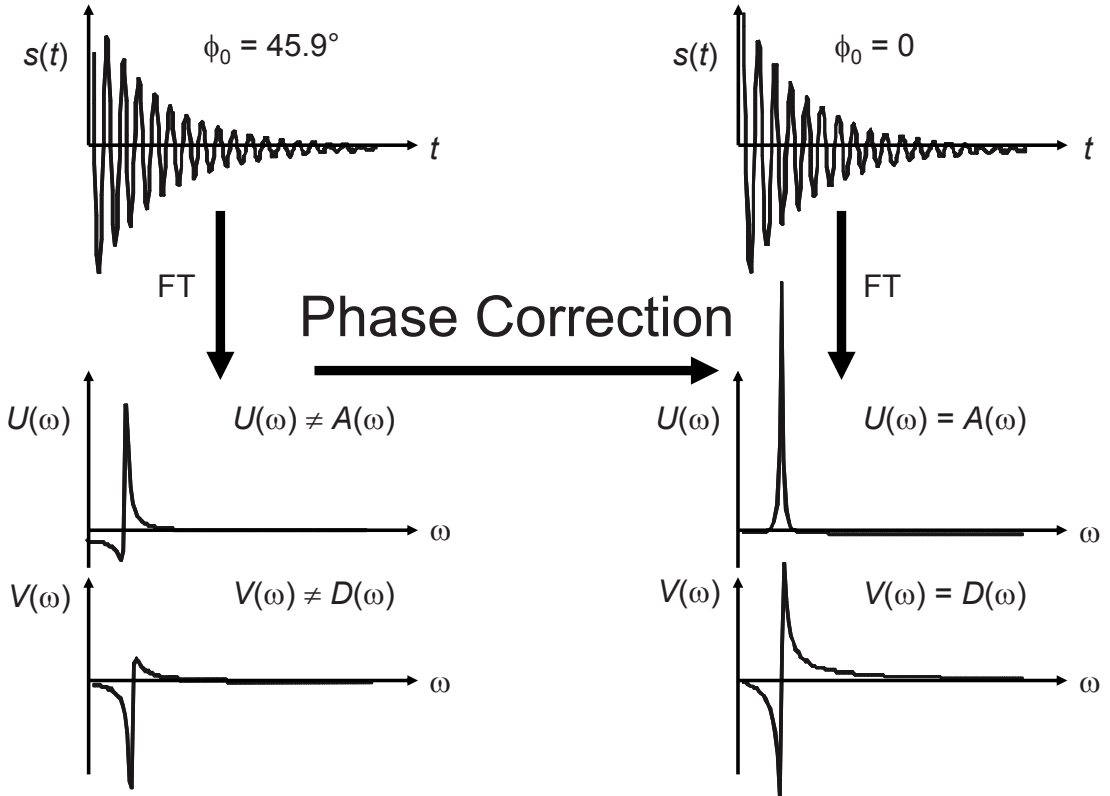


Fourier transformation



Signal Processing

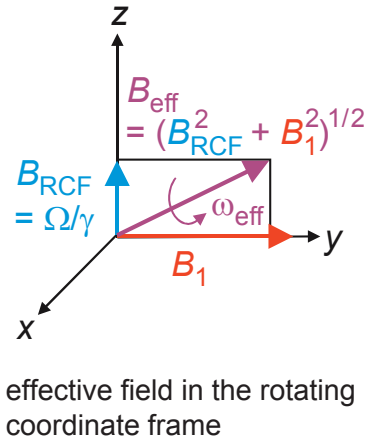
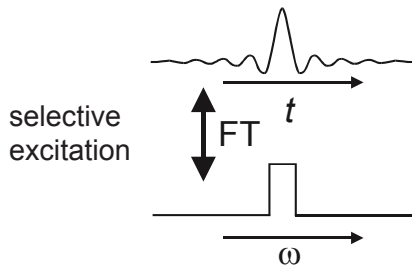
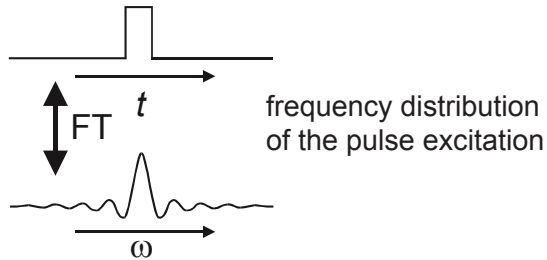
- Depending on the phase ϕ_0 of the *rotating coordinate frame*, the *FID* is measured as the sum of impulse responses $s(t) = s(0) \exp\{-[1/T_2 - i\Omega] t + i \phi_0\}$ for each magnetization component with different Ω in the RCF
- For $\phi_0 = 0$ the real part $U(\omega)$ of the *Fourier transform* $S(\omega)$ is an *absorption signal* $A(\omega)$ and the imaginary part $V(\omega)$ a *dispersion signal* $D(\omega)$
- For $\phi_0 \neq 0$ the absorptive and dispersive components are mixed in $U(\omega)$ and $V(\omega)$, and the associated complex *spectrum* $S(\omega) = U(\omega) + i V(\omega) = [A(\omega) + i D(\omega)] \exp\{i \phi_0\}$ has to be corrected in phase by multiplication with $\exp\{-i \phi_0\}$
- The correction phase ϕ_0 consists of a frequency dependent and a frequency independent part
- The frequency-independent part can be adjusted by software before data acquisition via the rf reference phase of the spectrometer
- The frequency dependent part is determined by time the signals take to pass through the spectrometer and by the receiver *deadtime* following an excitation pulse
- For optimum resolution the spectrum is needed in pure absorptive mode
- A frequency dependent *phase correction* of the spectrum is a routine step in data processing of high-resolution NMR spectroscopy



Frequency Distributions

- The rotating coordinate frame rotates with the rf frequency ω_{rf}
- In the laboratory frame the magnetization components M_i rotate with frequencies ω_{L_i}
- The *rf pulse* with frequency ω_{rf} has to couple to several frequencies ω_{L_i}
- The *bandwidth of the excitation* pulse is determined in approximation by the inverse of the pulse width t_p
- A better measure for the frequency dependence of the excitation is the *Fourier transform* of the excitation pulse
- For a rectangular pulse the Fourier transform is the *sinc function*
- Vice versa, the excitation can be made frequency selective by excitation with a rf pulse having a sinc shape in the time domain
- This simple Fourier relationship is a convenient approximation valid for small flip angles only
- In the RCF the magnetization components rotate with frequencies $\Omega_i = \omega_{L_i} - \omega_{\text{rf}}$
- For a given component the offset frequency Ω corresponds to a magnetic *off-set field* Ω/γ along the z axis of the RCF
- The magnetization always rotates around the *effective field* \mathbf{B}_{eff} , which is the vector sum of the offset field Ω/γ and the rf field \mathbf{B}_1
- The *rotation angle of a pulse* is then given by $\gamma B_{\text{eff}} t_p = \omega_{\text{eff}} t_p$
- The rotation axis is in the xy plane if $|B_1| \gg |\Omega/\gamma|$
- If $|B_1| \ll |\Omega/\gamma|$, longitudinal magnetization cannot be rotated into the xy plane

RF Excitation and Effective Field

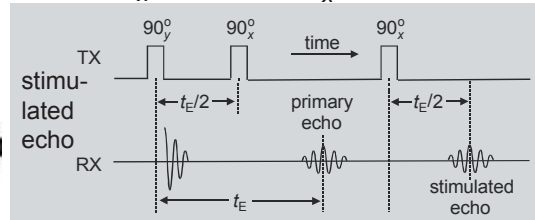
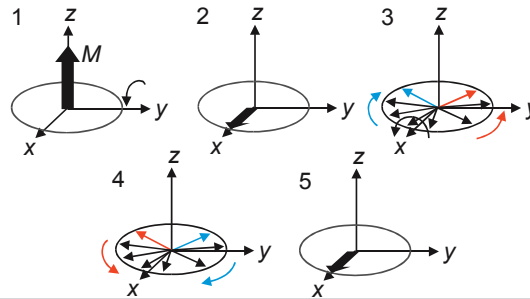
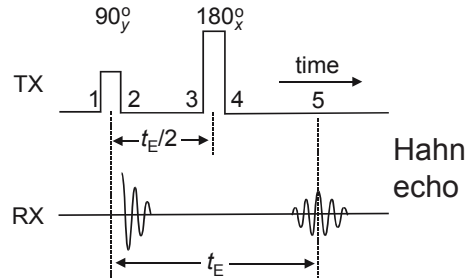
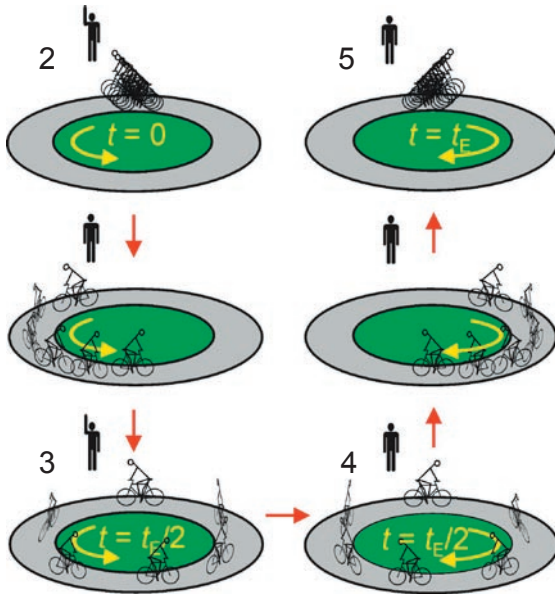


Relaxation

- *Relaxation* denotes the loss of *transverse magnetization* with the time constant T_2 and build-up of *longitudinal magnetization* with T_1
- The loss of transverse magnetization due to different time-invariant local magnetic fields can stroboscopically be reversed by formation of *echoes*
- For formation of a *racetrack echo* all bicyclists start at the same time but ride with different speeds. At a certain time all go back and meet at the starting line forming the *echo* after twice that time
- Their total riding time is the *echo time* t_E
- The NMR *echo* has accidentally been discovered in 1949 by Erwin Hahn
- For formation of a *Hahn echo* all transverse magnetization components are rotated by 180° around an axis in the xy plane
- The direction of precession is maintained with this change of positions on the circle, and all magnetization components refocus at time t_E
- If some components randomly change their precession frequencies, the *echo amplitude* is irreversibly reduced
- Random frequency changes arise from fluctuating local magnetic fields associated with molecules in motion
- T_2 relaxation denotes the irreversible loss of the echo amplitude
- Both *relaxation times* T_1 and T_2 are determined by the type and time scale of molecular motion
- By splitting the 180° pulse of the Hahn echo sequence into two 90° pulses separated by a time delay, one obtains the *stimulated echo* sequence

Echoes

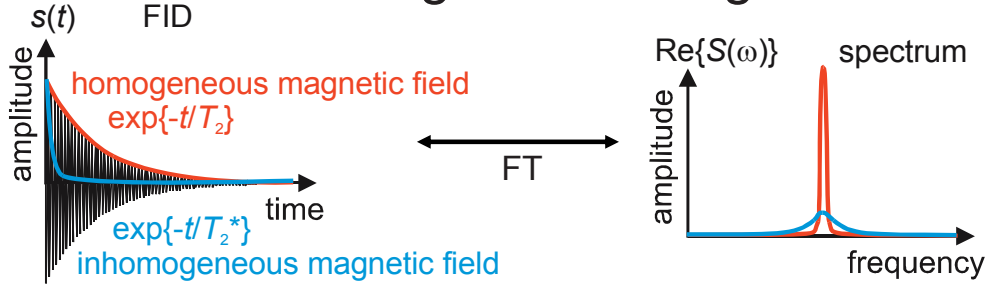
racetrack echo



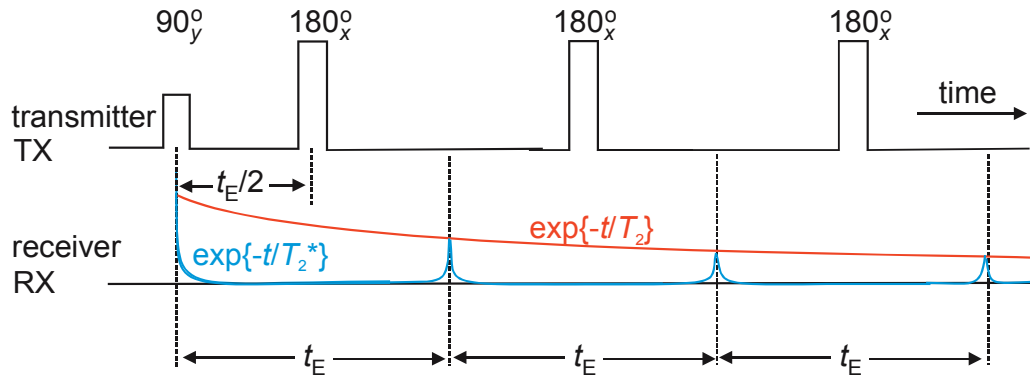
Multiple Echoes

- Transverse relaxation is often exponential with the time constant T_2
- In *inhomogeneous magnetic fields*, the FID decays faster with $T_2^* < T_2$
- The resonance signal in inhomogeneous magnetic fields is broad and small
- The envelope of the *FID* in homogeneous fields can be observed stroboscopically in inhomogeneous fields via the amplitude of many time shifted echoes
- Instead of many Hahn echoes with different echo times the echo envelope can be observed by a single train of multiple Hahn echoes
- The rf pulse scheme for excitation of multiple Hahn echoes is the *CPMG sequence* named after their discoverers Carr, Purcell, Meiboom, and Gill
- The repetition times of $5T_1$ for regeneration of longitudinal magnetization between generation of different Hahn echoes are eliminated
- $5T_1$ are needed to regain 99% of the thermodynamic equilibrium magnetization, because $\exp\{-5\} = 0.007$
- Besides the Hahn echo and the CPMG echo train there are many more echoes and multiple-echo schemes to partially recover signal loss caused by the influence of different nuclear spin interactions on the resonance frequencies
- In the *Hahn echo* maximum, inhomogeneities in the B_0 field and the spread in chemical shifts do not affect the NMR signal

Echoes and Inhomogeneous Magnetic Fields



multiple Hahn echoes following Carr, Purcell, Meiboom, and Gill (CPMG):

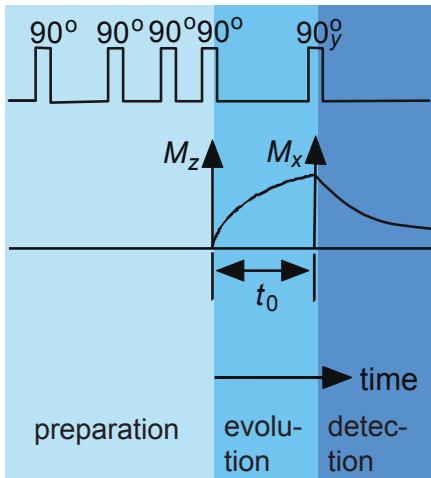


Determination of T_1

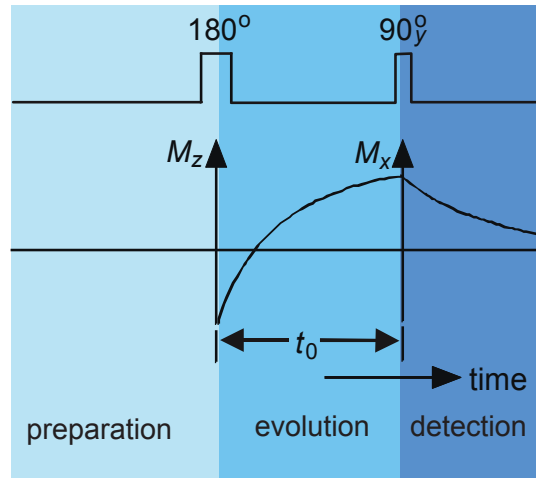
- *Longitudinal magnetization* cannot be directly observed
- Its momentary value can be interrogated via the amplitude of the FID following a 90° pulse
- There are two methods to measure the build-up of longitudinal magnetization: the recovery following saturation (*saturation recovery*) and the recovery following inversion of the magnetization (*inversion recovery*)
- For saturation, the spin system is irradiated with an aperiodic sequence of 90° pulses which destroys all magnetization
- Inversion of longitudinal magnetization is achieved by a 180° pulse following the establishment of equilibrium magnetization after a waiting time of $5T_1$
- After such preparation of the initial magnetization a variable evolution time t_0 follows for partial recovery of the *thermodynamic equilibrium* state
- Following the waiting time t_0 , the momentary value of the longitudinal magnetization is converted into the amplitude of the *transverse magnetization* by a 90° pulse
- The transverse magnetization is measured and evaluated for different values of t_0
- In homogeneous spin systems, the longitudinal relaxation follows an exponential law

Pulse Sequences for Measurement of T_1

build-up of longitudinal magnetization following saturation



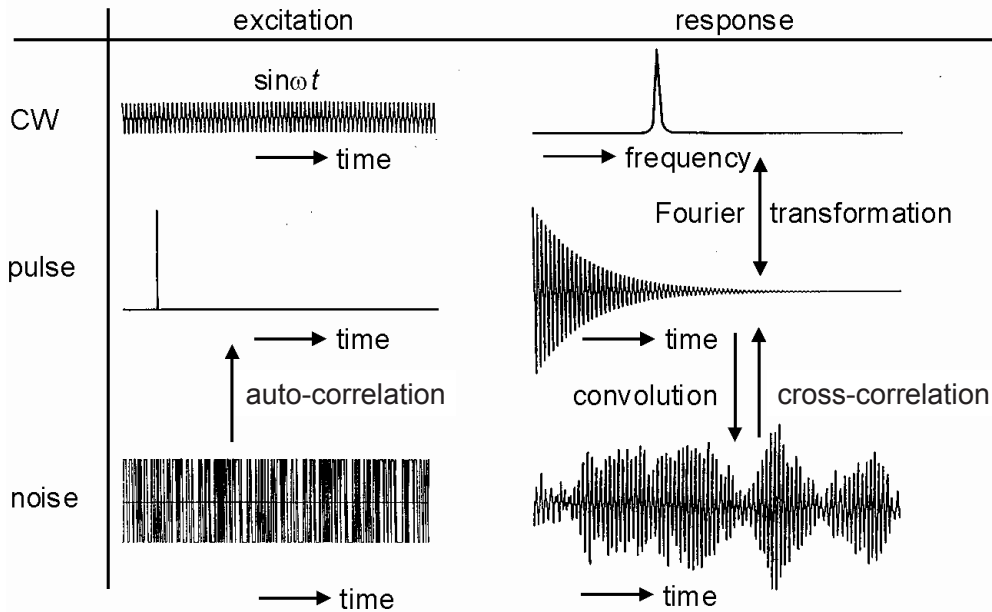
build-up of longitudinal magnetization following inversion



Measuring Methods

- *Pulsed excitation* and acquisition of an impulse response or an echo constitute the most successful class of methods to acquire NMR data
- In pulsed NMR, the signal measured can be conditioned by manipulating the initial magnetization in preceding preparation and evolution periods
- Pulsed NMR is uniquely suited for extension to *multi-dimensional NMR*
- With short pulses large spectral widths can be excited, and many frequency components can be simultaneously measured (*multiplex advantage*)
- When exciting the spins with *continuous waves (CW)*, the frequency of the excitation wave is slowly scanned through the spectrum
- CW NMR is slow, because the frequency components of the spectrum are measured successively
- With *noise excitation* large bandwidths are excited and can be measured simultaneously (*stochastic NMR*)
- A division of the experiment into different periods such as preparation, evolution, and detection is not possible
- Such a partitioning of the time axis can be achieved during data processing by means of *cross-correlation* of excitation and response signals
- The *excitation power* in CW NMR and stochastic NMR is several orders of magnitude lower compared to that of pulsed NMR

CW-, Fourier, and Stochastic NMR



B. Blümich, *Prog. Nucl. Magn. Reson. Spectr.* 19 (1987) 331 - 417

Spatial Resolution

- By exploring the proportionality of the NMR frequency ω and the applied magnetic field B , signals from different positions in the sample can be discriminated if the magnetic field changes with position
- For a linear change of B with position, the NMR frequency ω is directly proportional to position
- Then, the magnetic field B is characterized by a space-invariant *gradient* G
- In such a gradient field, the linear frequency axis of an NMR spectrum can be directly replaced by a linear space axis
- The signal amplitude is determined by the number of nuclear spins at a particular position along the gradient direction
- This number is obtained by summation over all nuclei in the other two space directions
- Due to the large number of nuclei, the sum is written as an integral
- This integral over the spatially resolved magnetization $M_z(x,y,z)$ is called a *projection*
- $M_z(x,y,z)$ is also referred to as *spin density*
- From a set of projections acquired for different gradient directions an image of the object can be reconstructed in analogy to X-ray tomography

Space Encoding

