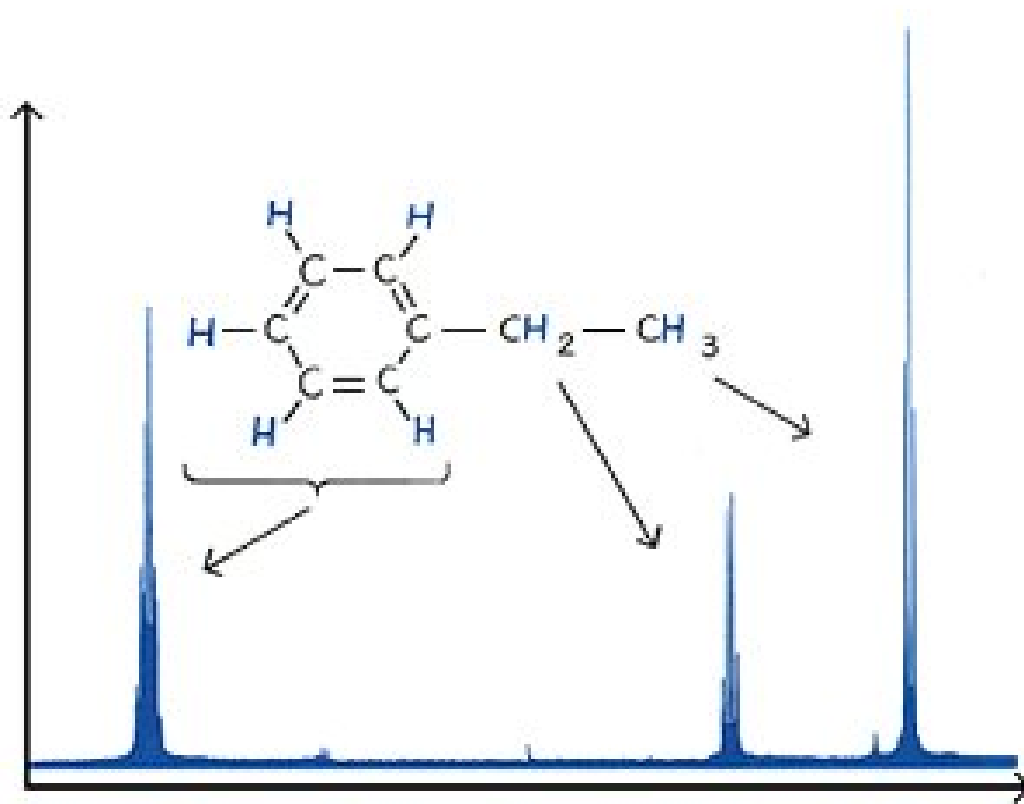


Instruction Manual for the Lab Course:

Nuclear Magnetic Resonance

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Preface

Dear participants of the Advanced Physics Lab Course,

You probably start to prepare yourself right now for the lab course on nuclear magnetic resonance. Please don't be scared off by the extensive manual, it contains everything you need to know for the pre-lab and the successful completion of the lab. You can of course use additional literature, but you will manage well with the following pages.

This manual was conceived during the overhaul of the lab course in 2009. It is based on the previous manual by A. Schwenk, which was a useful resource in preparing this text.

In this manual, first, the foundations of nuclear magnetic resonance are worked out. Then the tasks, which you shall complete, are discussed. Please read everything carefully and try to answer the questions in Part IV to see if you have understood enough.

Ingo Thimig, Tobias Jammer

The cover picture shows a spectrum obtained via Pulsed Fourier NMR. Differently bound Hydrogen atoms can be distinguished by distinct resonance frequencies.

Source: <http://www.stanford.edu/group/pandegroup/folding/education/nmr-b.gif>, last accessed May 7, 2009

Part I

Foundations of NMR spectroscopy

1 Notes on the History of NMR

In 1922, one could for the first time, in the Stern-Gerlach-Experiment, separate the spin components of a beam of silver ions (later a proton beam) by applying a magnetic field. Isidor Isaac Rabi then used modified Stern-Gerlach setups to perform the first NMR experiments. He could show, that one of the beams, i.e. one of the spin components, disappeared, when an electromagnetic wave with matching frequency was applied. Around 1946, Felix Bloch and Edward Mills Purcell performed - independently of each other - first successful NMR experiments with liquid and solid matter. The first patent for a NMR spectrometer followed in 1947 by Felix Bloch and Russell Varian.

In the early days, the sample was illuminated continuously by an electromagnetic wave. This is the so-called continuous wave method, which will not be discussed further in this manual. With this procedure, one can directly obtain a spectrum containing the peaks at the resonance frequencies of the nuclear spins, by scanning the frequency range. However, this method results in a worse signal to noise ratio compared to modern methods based on short electromagnetic pulses and Fourier transform. In these modern methods, one studies how the spin system relaxes after application of a short electromagnetic pulse. The same resonances, that can be measured with the continuous wave method, can then be extracted by applying the Fourier transform. This procedure only became relevant in the mid-1960s, when powerful computers became available. Nowadays, the pulsed Fourier-Transform NMR (FT-NMR) is one of the most important methods to non-destructively identify the chemical ingredients of a sample and to study the structure and interactions of molecules. It is also widely used in medicine in the form of magnetic resonance imaging (MRI) and magnetic resonance spectroscopy (MRS).

2 Which objects are studied in NMR?

Magnetic resonance spectroscopy (MRS) studies transitions between the Zeeman levels of atoms and molecules. The atoms or molecules are present in their ground state. Specifically, one studies the nuclei of the atoms contained in the sample. The following requirements have to be fulfilled:

- The total spin of the electron shell must vanish, i.e. $\mathbf{J} = 0$. Otherwise the electron shell would produce a magnetic field at the location of the nucleus.
- In contrast to this, it is essential, that the studied nucleus has a non-vanishing nuclear spin $\mathbf{I} \neq 0$.

The behavior of the nuclear spin is described by quantum mechanics. Both the magnitude as well as the direction of the nuclear spin are quantized. For the eigenvalues of the operator \mathcal{I} , i.e. the magnitude of the nuclear spin, we get

$$|\mathbf{I}| = \sqrt{I \cdot (I + 1)} \cdot \hbar. \quad (1)$$

Here I is the quantum number for the magnitude of the nuclear spin. This quantum number is a fixed quantity for the ground state of every isotope. I can only be changed by nuclear physics processes, e.g. by exciting the nucleus¹. In all NMR experiments, the nuclei remain in their ground state and thus I is never changed.

A non-zero nuclear spin is associated with a magnetic moment μ :

$$\boldsymbol{\mu} = \gamma \cdot \mathbf{I} \quad (2)$$

The scalar constant γ is the so-called gyromagnetic ratio. The fact that γ is a scalar quantity implies, that the vectors $\boldsymbol{\mu}$ and \mathbf{I} are either parallel ($\gamma > 0$) or anti-parallel ($\gamma < 0$). The magnitude of this magnetic moment can be obtained by applying Eq. (1):

$$|\boldsymbol{\mu}| = |\gamma| \cdot |\mathbf{I}| = |\gamma| \cdot \sqrt{I \cdot (I + 1)} \cdot \hbar. \quad (3)$$

If the requirement $\mathbf{J} = 0$, i.e. a diamagnetic electron shell, is not fulfilled, one mainly studies the alignment of the nuclear magnetic dipole in the magnetic field of the electron shell of the atom or molecule, because the magnetic fields created by the electron shell are usually much higher than the highest fields, that can be created and permanently sustained today (using superconducting magnets) of up to 23 Tesla. Such experiments then belong to the fields of hyperfine structure studies or ENDOR (**E**lectron-**N**ucleon-**D**ouble-**R**eson-ance). They don't belong to NMR.

In NMR, one studies the alignment and energies of the nuclear magnetic moments of a sample in a homogeneous external magnetic field, with a field strength B_0 , that is only slightly modified by the diamagnetic electron shell of the atom or molecule.

3 How can one imagine the spin classically?

A nucleus with non-vanishing nuclear spin has, in the scope of this experiment, two characteristic quantities: the nuclear spin and the associated magnetic moment. Atomic nuclei have to be treated using quantum mechanics. However, as in many other cases, classical considerations can help to develop an idea of the processes involved in NMR. In classical physics, the nuclear spin corresponds to an electrically charged spinning top.

It therefore makes sense to recall the behavior of such a top. We imagine a macroscopic top, which rotates about its axis. This top has an angular momentum \mathbf{I} . If the charge is

¹an example for this is the nucleus ⁵⁷Fe in the lab course Mößbauer effect

distributed evenly over the top, a magnetic moment $\boldsymbol{\mu}$ is associated with the mechanical angular momentum \mathbf{I} , because the charges are moving on a circular path. Since the magnetic moment $\boldsymbol{\mu}$ is created by circular currents, the two vectors \mathbf{I} and $\boldsymbol{\mu}$ are parallel or anti-parallel (depending on the sign of the electric charge).

One thus gets the same relation again

$$\boldsymbol{\mu} = \gamma \cdot \mathbf{I}. \quad (4)$$

The proportionality constant γ is again called gyromagnetic ratio and is also a scalar (since the two vectors are parallel).

If this top is put into an external magnetic field B_0 (the vector B_0 is assumed to point in the z -direction, without loss of generality), it acquires a potential energy due to its magnetic moment $\boldsymbol{\mu}$

$$W_m = -\boldsymbol{\mu} \cdot \mathbf{B}_0 = -\mu_z \cdot B_0. \quad (5)$$

Since the top not only has a magnetic moment, but also an angular momentum, which is well known to be conserved, it does not simply flip in the most energetically favorable state. It rather experiences a torque \mathbf{T} because of the interaction between the magnetic dipole $\boldsymbol{\mu}$ and the external magnetic field

$$\mathbf{T} = \boldsymbol{\mu} \times \mathbf{B}_0 = \gamma \cdot \mathbf{I} \times \mathbf{B}_0. \quad (6)$$

The conservation of angular momentum then yields the relation between torque and change of angular momentum

$$\frac{d\mathbf{I}}{dt} = \mathbf{T}$$

or

$$\frac{d\mathbf{I}}{dt} = \gamma \cdot \mathbf{I} \times \mathbf{B}_0$$

or rather

$$\frac{d\boldsymbol{\mu}}{dt} = \boldsymbol{\mu} \times (\gamma \cdot \mathbf{B}_0). \quad (7)$$

Because of the vector product in these first order differential equations for \mathbf{I} and $\boldsymbol{\mu}$, the time derivative of both these vectors are perpendicular to both the respective vectors \mathbf{I} or $\boldsymbol{\mu}$ as well as the vector of the external magnetic field \mathbf{B}_0 at all times. We now consider the z -component

$$I_z \text{ and } \mu_z$$

and a component perpendicular to the z -direction (in the x, y -plane)

$$\mathbf{I}_\perp \text{ and } \boldsymbol{\mu}_\perp.$$

of \mathbf{I} and $\boldsymbol{\mu}$ separately. The time derivative in (7) is perpendicular to \mathbf{B}_0 . The z -component of the two vectors is therefore constant over time

$$I_z = \text{const.} \quad \text{and} \quad \mu_z = \text{const.}$$

and the x, y -components \mathbf{I}_\perp and $\boldsymbol{\mu}_\perp$, respectively, undergo a circular motion with angular velocity ω_L in the x, y -plane. This results from the fact, that the time derivatives of the two vectors are perpendicular to each other and the magnitude of the two vectors do not change. It is:

$$\left| \frac{d\mathbf{I}_\perp}{dt} \right| = |\mathbf{I}_\perp| \cdot \omega_L \quad \text{or} \quad \left| \frac{d\boldsymbol{\mu}_\perp}{dt} \right| = |\boldsymbol{\mu}_\perp| \cdot \omega_L \quad (8)$$

Comparing these two relations with the differential equations (7) yields the angular frequency of this precession:

$$\omega_L = |\gamma| \cdot B_0 \quad \text{Larmor frequency} \quad (9)$$

It is named after the British physicist Sir Joseph Larmor(1857 - 1942). He was the first to experimentally prove, that the magnetization of a nuclear spin ensemble precesses like a fast heavy top.

The following considerations give a deeper insight than this descriptive derivation of the Larmor precession: Eqs. (7) are transformed in a rotating coordinate system u, v, z , which rotates relative to the laboratory system x, y, z around the z -axis with the angular velocity ω . The rotation vector ω thus points in the direction of the z -axis or negative z -axis. The right hand side of (7) remains unchanged under this change of base vectors. In the time derivative on the left hand side of (7), one has to take into account, that not only the components of a vector, but also the base vectors of the rotating coordinate system are functions of time.

The time derivative of an arbitrary vector \mathbf{A} can thus be written as

$$\frac{d\mathbf{A}}{dt} = \frac{\partial \mathbf{A}}{\partial t} + \boldsymbol{\omega} \times \mathbf{A}. \quad (10)$$

where $\frac{d\mathbf{A}}{dt}$ is the derivative of the vector \mathbf{A} in the laboratory system and $\frac{\partial \mathbf{A}}{\partial t}$ its derivative in the rotating system. ²

²Eq. (10) is usually first used in theoretical mechanics for the derivation of the centrifugal and Coriolis force and derived there.

With the help of (10), the differential equations (7) can be written in the rotating coordinate system

$$\begin{aligned}\frac{d\mathbf{I}}{dt} &= \mathbf{I} \times (\boldsymbol{\omega} + \gamma \cdot \mathbf{B}_0) \\ \frac{d\boldsymbol{\mu}}{dt} &= \boldsymbol{\mu} \times (\boldsymbol{\omega} + \gamma \cdot \mathbf{B}_0).\end{aligned}\tag{11}$$

If now the angular velocity of the rotating coordinate system is

$$\omega = |\boldsymbol{\omega}| = \omega_L = |\gamma| \cdot \mathbf{B}_0$$

and the vector $\boldsymbol{\omega}$ **anti-parallel** to the vector $\gamma \cdot \mathbf{B}_0$, then in both equations (11) the expression in parenthesis is zero

$$(\boldsymbol{\omega} + \gamma \cdot \mathbf{B}_0) = 0.$$

Thus in both equations (11) the right hand side vanishes and thus also the time derivatives in the rotating coordinate system

$$\frac{d\mathbf{I}}{dt} = \frac{\partial \boldsymbol{\mu}}{\partial t} = 0.$$

In other words: we transformed the time derivative of the angular momentum and the magnetic moment in a rotating coordinate system. We have seen, that the time derivative in this coordinate system is zero exactly when it rotates with the Larmor frequency. This reiterates the fact, that was already the result of the illustrative derivation: if one applies a magnetic field to an electrically charged spinning top, it starts to precess with the Larmor frequency around the direction of the magnetic field.

To obtain the direction of rotation of the Larmor precession one can use the following rule: Watch your hands. Hold your thumb in the direction of the magnetic field \mathbf{B}_0 . Make a fist with the remaining fingers.

For $\gamma > 0$ the fingers of the left hand,

for $\gamma < 0$ the fingers of the right hand show the direction of the precession.

At first glance, the coordinate transform (as is often the case) seems cumbersome and confusing. However, later we will study more complicated movements, where it will simplify the problem a lot, if we can neglect the not very interesting precession about the z -axis.

4 How does an atomic nucleus move in an external magnetic field B_0 ?

The question now is, to what extent can we apply our classical model to the concrete experiment? The motion we derived for the model with the mechanical spinning top cannot readily be applied to an atomic nucleus with spin and magnetic moment, since the atomic nucleus is a particle, which does not obey the classical laws of physics. The operators for the three spatial components of the spin (\mathbf{I}_x , \mathbf{I}_y , and \mathbf{I}_z) do not commute pairwise. Hence, there are no equations of state, that are simultaneously eigenfunctions of the operators of all three spin components. It is thus impossible to simultaneously quote eigenvalues for all three components of the spin (and because of (2) for all three components of the magnetic moment). Each of the three components of the spin commutes individually with the operator \mathcal{I} for the magnitude of the spin. One can therefore find eigenfunctions for the atomic nucleus in an external magnetic field B_0 , that are simultaneously eigenfunctions for the magnitude of the spin \mathbf{I} and to one of its components. It is expedient to ask for eigenfunctions for \mathcal{I} and \mathcal{I}_z , the spin component in the preferred direction. In the following, the preferred direction is always the direction of the external field B_0 , i.e. the z -axis. While one can quote eigenvalues for the magnitude of the spin vector $|\mathbf{I}|$ and for its z -component I_z , one can only give expectation values, i.e. statistical statements, for the transverse components $\langle I_x \rangle$ and $\langle I_y \rangle$. We thus treat the z -component and the transverse components separately.

4.1 The z -component (Zeeman splitting)

Let us consider first the z -component of the spin, or rather the magnetization: it will also not behave like with a classical spinning top. A classical magnetic dipole - one can imagine a compass needle - can take on any direction with respect to the preferred axis. For the spin and the magnetic moment, this does not apply. For the eigenvalues of \mathcal{I}_z we find:

$$I_z = m_I \cdot \hbar \quad \text{and} \quad (12)$$

$$\mu_z = \gamma \cdot I_z = \gamma \cdot m_I \cdot \hbar \quad \text{with} \quad m_I \in \{-I, (-I + 1), \dots, (I - 1), I\} \quad (13)$$

In total, there are $2I + 1$ possible eigenvalues I_z . The spin vector \mathbf{I} (and the magnetic moment μ alike) can thus take on $2I + 1$ configurations with respect to the preferred axis. The largest magnetic dipole moment of the nucleus, which can be observed is:

$$\mu_I = \mu_z(m_I = I) = \gamma \cdot I \cdot \hbar \quad (14)$$

Therefore this value is usually tabulated as the value for the magnetic moment of an atomic nucleus. Besides its SI unit $A \cdot m^2 = J/Tesla$, one frequently uses the special unit nuclear magneton:

$$\mu_K = \frac{e\hbar}{2m_P} = 5.0507866(17) \cdot 10^{-27} \text{A} \cdot \text{m}^2 \quad (15)$$

where m_P is the proton mass. With this one can, analogous to the g_J -factor of the electron, define an nuclear g -factor g_I for the nucleus and express the nuclear magnetic moment as:

$$\mu_I = g_I \cdot \mu_K \cdot I \quad (16)$$

Inserting (14) in (5) yields the interaction energy of the nuclear magnetic dipole in quantum state m_I with the external magnetic field B_0 :

$$W_m(m_I) = -\gamma \cdot m_I \cdot \hbar \cdot B_0 \quad (17)$$

This energy splitting is shown in Fig. 1.

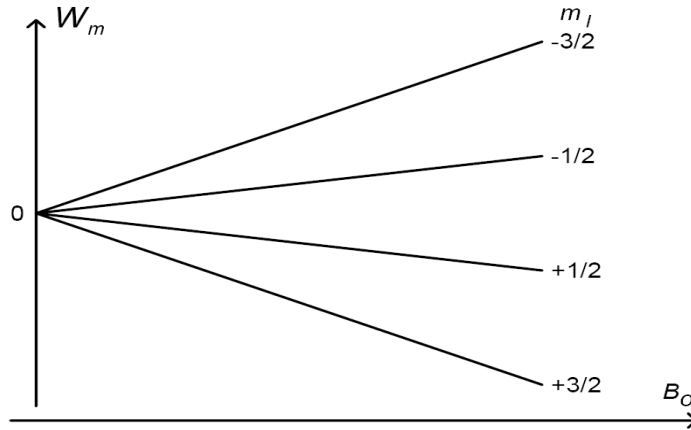


Figure 1: Magnetic interaction energy of a nuclear spin $I = 3/2$ and $\gamma > 0$ with a magnetic field B_0 . This energy splitting is for example valid for the nucleus ${}^7\text{Li}$

4.2 The transverse magnetization

Now we have clarified how the component of the nuclear spin, which is parallel to the external magnetic field, behaves. The other two components can't be observed directly at the same time. One has to take a small detour to make a statement about the total nuclear spin.

According to Ehrenfest's theorem, the quantum mechanical expectation value obeys the laws of classical physics: Eqs. (7) and (11), respectively, derived for the classical spinning top also apply to atomic nuclei, if one replaces the classical vectors \mathbf{I} and $\boldsymbol{\mu}$ with the expectation values of the corresponding operators $\langle \mathbf{I} \rangle$ and $\langle \boldsymbol{\mu} \rangle$. An expectation value can be determined experimentally by repeating the experiment many

times with a single atomic nucleus and averaging over the obtained results. One could of course repeat the experiment with a single device many times one after another or with many identical devices simultaneously. However, both approaches usually are not feasible in practice, either for lack of time or lack of devices.

It seems obvious to perform the experiment once with many nuclear spins simultaneously. This is in fact what will happen during this lab course. This way one can actually study the behavior of the spins. However, the behavior only corresponds to the true average, if the spins don't interact with each other and thus behave as if they were alone in the device. So as long as the spins don't interact with each other, we can assume, that we in fact measure the true expectation value in this way. Only later we will see how to consider this interaction, which in practice cannot be neglected. In the end, it will be exactly this interaction, which is exploited in the various application of NMR.

If we assume there is no interaction between the spins, taking the average over the magnetic moments of the many nuclei in the sample is trivial: the expectation value of the magnetic moment of an atomic nucleus $\langle \boldsymbol{\mu} \rangle$ is

$$\langle \boldsymbol{\mu} \rangle \propto \mathbf{M}$$

where, the magnetization \mathbf{M} is the vector sum over all n_0 magnetic moments per unit volume in the sample. With this we can rewrite the formula for the magnetic moment in the external field \mathbf{B}_0 in the rotating coordinate system (11), neglecting all interactions between the individual nuclei:

$$\frac{d\mathbf{M}}{dt} = \mathbf{M} \times (\boldsymbol{\omega} + \gamma \cdot \mathbf{B}_0) = \mathbf{M} \times \Delta\boldsymbol{\omega} \quad (18)$$

The magnetization can then be measured directly as we will see below.

4.3 Considering the interactions and relaxation

Neglecting the mutual interactions of the nuclei is only valid if the nuclei are spaced far enough apart during the experiment. In an experiment with an atomic beam (like Rabi's), this requirement can be assumed to be fulfilled for the time the nuclei spend in the magnet.

In nuclear and electron resonance experiments with condensed matter (using liquid or solid samples) this mutual interaction can certainly not be neglected. Therefore, nuclear and electron spins will - at least on longer time scales - move differently than expected from the spinning top model. The additional motion of the magnetization \mathbf{M} due to the mutual interactions of the spins are summarized under the term relaxation.

The main interaction of the spins happens through the magnetic dipole moment associated with the spin (dipole-dipole-interaction). Beyond that, there exist a series

of further interaction mechanisms (anisotropic chemical shift, scalar coupling, spin-rotation, etc.), which will not be discussed further. Common to all these interaction mechanisms is, that they lead to a statistically fluctuating magnetic field in all three spatial directions due to the thermal motion within the sample. So there exists a magnetic noise at the location of each nuclear or electron spin, which is superimposed on the static magnetic field \mathbf{B}_0 and any additionally applied magnetic field.

The different frequency components of this magnetic noise give rise to two different relaxation processes:

Spin-Lattice-Relaxation: At the resonance frequency ω_L , the magnetic noise has its full intensity. The transverse component of this statistically fluctuating magnetic field induces transitions between the eigenstates of the spins. Since this "signal", which induces these transitions, is induced by the spins themselves, the induced emission and induced absorption don't have the same transition probability in this case. The probability for emission rather dominates the probability for absorption. If one designates the higher energy level with + and the lower energy level with -, the following holds for the transition probabilities:

$$\frac{W_{+-}}{W_{-+}} = e^{+\Delta/kT} \quad (19)$$

If the sample is in thermal equilibrium, the ratio of the occupation numbers of the two eigenstates can be written according to Boltzmann as:

$$\frac{N_+}{N_-} = e^{-\Delta E/kT} \quad (20)$$

Eqs. (19) and (20) initially apply only for a system with two levels + and -, e.g. for the two possible alignments of a particle with spin $I = 1/2$ (e.g. proton or electron) in a magnetic field. These relations can, however, also be applied to systems with more than two levels (e.g. for nuclei with $I > 1/2$ or for systems with multiple electrons). They hold then for any arbitrarily chosen pair of levels, where the higher energy level is designated with + and the lower energy level is designated with -. In thermal equilibrium (i.e. Eq. (20) is fulfilled), the absolute number of emission transitions and absorption transitions due to relaxation are equal.

The required energy for such an absorption transition or the energy released in such an emission transition is taken from or supplied to the lattice, respectively. In this context, lattice does not refer exclusively to the vibrational energy of a crystal lattice. The term lattice is rather used in a more general sense and refers to all thermodynamic degrees of freedom, i.e. also translational, rotational and vibrational degrees of freedom of the molecules in liquid or solid samples.

Spin-Spin-Relaxation: For this relaxation process, the longitudinal component of the magnetic noise is responsible. This longitudinal component enhances or diminishes the static magnetic field \mathbf{B}_0 locally. In locations with enhanced static field, the spins precess faster according to equation (9), whereas in locations of diminished field, they precess slower than the average spin. This means, that due to the local fluctuations of the longitudinal field, the spins diverge (because of the different precession frequencies). Thus the phase coherence of the spins gets disturbed. Luckily, these modifications of the longitudinal field are not constant in time. At every location they fluctuate statistically. In this way the divergence of the spins is compensated partly, however, never completely, since the fluctuations of the longitudinal field happen to be of statistical nature. It is obvious, that the compensation is worse, the longer a certain modification of \mathbf{B}_0 lasts. Thus, for the spin-spin-relaxation, the low-frequency components of the magnetic noise are responsible. The spin-spin-relaxation does not change occupation numbers, so it does not lead to an exchange of energy with other degrees of freedom of the sample.

These two relaxation processes (spin-lattice-relaxation and spin-spin-relaxation) now lead to experimentally observable effects, which modify the motion of the magnetization vector decisively. This implies that (18) must be modified accordingly. Relaxation processes can of course only occur when the spin ensemble was previously taken out of thermal equilibrium. How this can happen in practice will be clarified below. For the time being, let's assume for the following considerations, that the system was influenced in such a way, that the entire magnetization points in the u -direction. In detail, one can then observe the following relaxation effects:

Longitudinal Relaxation: Longitudinal relaxation means the build-up of the longitudinal magnetization M_z until it reaches the value M_0 , which is assumed in thermal equilibrium. M_0 results from the difference of occupation numbers $N_+ - N_-$, since the two levels correspond exactly to the possible alignments of the nuclear magnetic moments. This difference, and thus the equilibrium magnetization, can be calculated according to the Boltzmann equilibrium (Eq. (20) generalized to spin $I > 1/2$) taking into account the total number n_0 of spins per unit volume:

$$M_0 = n_0 \cdot \mu_I \cdot \frac{\mu_I B_0}{kT} \cdot \frac{I + 1}{3I} \quad (21)$$

Here, I is the quantum number of the nuclear or electron spin and μ_I is the largest component of the magnetic moment, which can be measured in the preferred direction.

Only the spin-lattice-relaxation contributes to the restoration of the thermal equilibrium, and thus to the longitudinal relaxation, since for the restoration of thermal equilibrium it is necessary to change the occupation numbers. The rate equations following from the transition probabilities W_{\pm} and W_{\mp} , whose ratio is given in (19), lead to an exponential law for the time to reach the thermal equilibrium:

$$M_z(t) = M_0 \cdot (1 - A \cdot e^{-t/T_1}) \quad (22)$$

Where T_1 is the longitudinal relaxation time. A is an integration constant, which needs to be adapted to the initial conditions, since (22) is the solution of a first order differential equation. It holds, e.g.

$$\begin{aligned} M_z(0) &= 0 && \text{für } A = 1 && \text{oder} \\ M_z(0) &= -M_0 && \text{für } A = 2 && \text{oder} \\ M_z(0) &= +M_0 && \text{für } A = 0 \end{aligned}$$

Transverse Relaxation: Transverse relaxation denotes the decay of any transverse component M_R of the magnetization. Both relaxation processes - spin-lattice-relaxation and spin-spin-relaxation - contribute to this decay. It is obvious, that every transition induced by the magnetic noise changes the phase of the affected spin statistically. Such a spin thus drops out of the ensemble of coherently precessing spins. In this way, the spin-lattice relaxation not only contributes to the longitudinal relaxation but also to the transverse relaxation. Apart from that, the spin-spin relaxation exclusively affects the transverse relaxation. Both relaxation processes finally cause the precessing magnetic moments to dephase, which leads to a canceling of their contributions to the vector sum \mathbf{M} . The decay of the transverse component M_R of the magnetization again ideally follows an exponential law

$$M_R(t) = M_R(0) \cdot e^{-t/T_2}. \quad (23)$$

Where T_2 is the transverse relaxation time. The integration constant $M_R(0)$ represents the transverse magnetization at time $t = 0$.

We modify the equations of motion: To obtain an exact equation of motion for the magnetization vector \mathbf{M} in the laboratory system or the rotating system, one has to supplement the Bloch equations (18) with terms describing the relaxation processes. These terms can be derived by differentiating (22) and (23):

- longitudinal relaxation (z -component):

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \quad (24)$$

- transverse relaxation (x - y - or u - v -component):

$$\frac{dM_R}{dt} = \frac{\partial M_R}{dt} = -\frac{M_R}{T_2} \quad (25)$$

As can be seen, the longitudinal component M_z and the transverse components M_x and M_y or M_u and M_v of the magnetization vector \mathbf{M} obey different laws.

Hence, one has to split the vector equation (18) in the three components before adding the relaxation terms.

$$\begin{aligned}
 \frac{dM_u(t)}{dt} &= -\frac{M_u(t)}{T_2} + \Delta\omega \cdot M_v(t) \\
 \frac{dM_v(t)}{dt} &= -\Delta\omega \cdot M_u(t) - \frac{M_v(t)}{T_2} \\
 \frac{dM_z(t)}{dt} &= \frac{M_0 - M_z(t)}{T_1}
 \end{aligned} \tag{26}$$

The time derivative was taken in the rotating coordinate system as indicated by the indices u and v .

Discussion of the solutions to these differential equations: To simplify the representation, one can define

$$\Delta\omega = \{\boldsymbol{\omega} + \boldsymbol{\gamma} \cdot \mathbf{B}_0\}_z = \omega_z + \boldsymbol{\gamma} \cdot \mathbf{B}_0 \tag{27}$$

\mathbf{B}_0 is always positive, as the quantization axis z is chosen in the direction of the static magnetic field \mathbf{B}_0 . The sign of ω_z can be positive or negative depending on the orientation of the rotating coordinate system according to the above mentioned rule of thumb.

Eqs. (26) represent a system of coupled inhomogeneous linear first-order differential equations. However, only the first two equations are coupled. They form a homogeneous subsystem and describe the transverse component of the magnetization vector. The third inhomogeneous differential equation describes the build-up of the longitudinal component of \mathbf{M} caused by the longitudinal relaxation.

The solutions to the system of differential equations (26) are:

$$\begin{aligned}
 M_u(t) &= \{M_u(0) \cdot \cos(\Delta\omega \cdot t) + M_v(0) \cdot \sin(\Delta\omega \cdot t)\} \cdot e^{-t/T_2} \\
 M_v(t) &= \{M_v(0) \cdot \cos(\Delta\omega \cdot t) - M_u(0) \cdot \sin(\Delta\omega \cdot t)\} \cdot e^{-t/T_2} \\
 M_z(t) &= M_0 - \{M_0 - M_z(0)\} \cdot e^{-t/T_1}
 \end{aligned} \tag{28}$$

with the initial conditions at $t = 0$: $M_u(0), M_v(0)$ and $M_z(0)$.

The solution vector $\mathbf{M}(t)$ in the rotating coordinate system decomposes into a transverse component, rotating with the angular velocity $\Delta\omega$ around the z -axis and, at the same time, decaying exponentially with the time constant T_2 , and a longitudinal component, which approaches the equilibrium value M_0 with a time constant T_1 .

Independently of the initial conditions, for large times the magnetization vector will be

$$\lim_{t \rightarrow \infty} \mathbf{M}(t) = \{0, 0, M_0\} \tag{29}$$

Intermediate Result: We now can predict how the magnetization of an ensemble of nuclear spins will behave over time.³ We can even take into account, that the nuclei interact with each other. We have seen, that after tilting the magnetization vector, it will always return to its initial value parallel to the external magnetic field after sufficient waiting time.

However, it is not yet clear how the tilting of the magnetization vector happens in practice. This will be settled in the next chapter, however, this is a longer story.

5 How can one affect the nuclear spin ensemble experimentally?

In NMR, we deal with a form of spectroscopy, more accurately with high frequency spectroscopy. Let's remember optical spectroscopy, where the electron shell is the focus of interest. The electron shell can be present in different quantum mechanical energy states. If it is irradiated by an electromagnetic wave, whose frequency corresponds exactly to the energy difference between two levels, one can excite a transition. We do exactly the same in NMR: the magnitude of the nuclear spin should stay the same, we only want to change its orientation within the external magnetic field, i.e. the quantum number m_I .

We already know the energy splitting of the Zeeman levels of the nuclear spin from (4.1). It amounts to:

$$W_m(m_I) = -\gamma \cdot m_I \cdot \hbar \cdot B_0 \quad (30)$$

For each individual magnetic field B_0 , the nuclear Zeeman terms are equidistant. The distance between neighboring terms ($\Delta m_I = 1$) is:

$$|\Delta E| = |\gamma| \cdot \hbar \cdot B_0 \quad (31)$$

We have, however, already seen in (9), that $B_0\gamma$ is simply the Larmor frequency of the nuclear spin in the external magnetic field B_0 . By irradiating with a high frequency magnetic field oscillating with the Larmor frequency

$$\nu = \frac{|\Delta E|}{h} = B_0 \cdot \frac{|\gamma|}{2\pi}$$

one can induce magnetic dipole transitions according to the selection rule

$$\Delta m_I = \pm 1$$

This means, that for a nucleus with $I > 1/2$, $2I$ transitions between all the neighboring terms can happen simultaneously.

³Remember, that the magnetization always precesses around the direction of the external magnetic field, however complicated the additional motions may be

Intermediate result: Now we clarified how one can, in principle, affect the nuclear spins: one has to enforce magnetic transitions. This can be achieved by irradiating with an electromagnetic wave with the Larmor frequency. How this looks like exactly will be explained in the chapter concerning pulsed NMR.

6 Chemical Shift

The effect, which is central for spectroscopic studies, is the chemical shift. Up to now we have assumed, that the atomic nucleus under study is basically unaffected by the electron shell or molecular bindings. This is, however, not correct. The nucleus is subjected both to the external field B_0 as well as the shielding field of the shell electrons. The electrons hereby alter the resonance frequency by a few parts per million of the initial value. Through this, one can easily distinguish a sample from a reference. It can also lead to multiple observable resonance frequencies for the same kind of nucleus in a single sample. This can happen if the same type of nucleus occurs in different places in a molecule.

The chemical shift is quoted like this:

$$\delta = \frac{\nu_s - \nu_{ref}}{\nu_{ref}} \cdot 10^6$$

ν_s is the measured resonance frequency, ν_{ref} a reference value. The reference value is usually obtained from an easy to manage species of molecule, whose chemical shift only depends on few external factors.

You will later study the chemical shift qualitatively in an experiment.

7 The Measurement Principle

This chapter should give you an idea how the device, with which you will work during the lab course, is constructed in principle and how it works. It can be split up in three components:

1. We inevitably need an external magnetic field \mathbf{B}_0 . We therefore need a magnet providing a high magnetic flux, whose field is homogeneous and stable enough. The field strength usually lies between 0.5 T and 2 T, but can also be considerably larger in some cases. The permanent magnet we use in the lab course has a field strength of 0.5 T.
2. The nuclear spins are influenced through high frequency electromagnetic waves. A central part of the experiment is therefore a high frequency system, which on the one hand can excite the nuclear spins with a matching frequency and on the other hand register the measured signal. Before this system is described in detailed, first an explanation will be given, how the signal induced by the nuclear spins can be detected.

The data acquisition: The magnetization of a nuclear spin ensemble can not be readily measured. But, as is generally known, every magnetization creates a magnetic field with a characteristic magnetic induction via:

$$\mathbf{B}_M = \mu_0 \cdot \mathbf{M} \quad (32)$$

In a receiver coil, which is exposed to a magnetic flux that varies in time, a voltage is induced according to Faraday's law.

$$U_{ind} = -\frac{d}{dt} \int_A \mathbf{B} \cdot d\mathbf{A} \quad (33)$$

Such a flux is caused by the transverse magnetization, which precesses with the Larmor frequency. If one puts an appropriate coil in the vicinity of the sample, a voltage will be induced, which oscillates sinusoidally between positive and negative values with the same frequency. Its amplitude depends directly on the magnitude of the transverse magnetization. In the end, this yields the following proportional relation between the detected voltage signal S and the magnetization:

$$S(t) \propto \int_V m(\mathbf{x}, t) e^{-i\omega_L t} dV \quad (34)$$

where m is the time and location dependent complex magnitude of the magnetization $m = M_x + iM_y$.

The high frequency system is meant to tilt the magnetization away from thermal equilibrium initially. How this can be done was explained in Chapter 5. Technically this is done via a coil, whose axis is lying in the x - y -plane. In the following we assume the axis of the coil points in the x -direction. When the magnetization is tilted and there is sufficient transverse magnetization, the coil is exposed to the oscillating magnetic field of the nuclear spins. The resulting voltage signal can then be measured.

There are devices, which use two different coils for sending and receiving. Nowadays, usually a single coil is used for both tasks. The PS2-A, you will be working with, is equipped with a single sender-receiver-coil.

3. Finally one usually needs a computer to control the measurement and save and analyse the data. For the experiments in this lab course, a simple storage oscilloscope is sufficient. The settings will be adjusted on the devices themselves. All further steps of the analysis can be done with a computer at home.

The measurement principle: The permanent magnet provides the homogeneous stable magnetic field \mathbf{B}_0 . The sample to be studied is located in this field. The individual nuclear magnetic moments interact with \mathbf{B}_0 . There is a small excess of magnetic moments aligned in parallel to the magnetic field. The Larmor precession of each individual spin leads, in the end, to a magnetization \mathbf{M}_0 in thermal equilibrium

pointing in the direction of the magnetic field, which results from the vector sum over all magnetic moments. This direction defines the z -axis.

The coil to create the high frequency resonant electromagnetic wave and detect the induction signal is oriented in the plane perpendicular to the z -axis. We define without loss of generality, that the axis of the coil points in the x -direction. The coil is a central piece of the so-called sender and receiver chains.

- The sender chain starts with a frequency generator providing the high frequency voltage, with which the coil is operated. The frequency generator, called synthesizer in the PS2-A, is connected to the pulse programmer, which can modulate the oscillating voltage in time, so that the above mentioned pulses can be generated. Finally, the voltage pulses are supplied to the coil irradiating the sample with the high frequency signal.

If the coil serves both for sending and receiving, there is a so-called sender-receiver-switch in the receiver between the coil and the following devices. It guarantees that the sender and receiver paths of the signal don't interfere with each other. Therefore the synthesizer is not directly connected to the coil but with the receiver, which is in turn connected to the sender-receiver-switch.

- The receiver chain starts with the coil, where the precessing magnetization induces a high frequency alternating voltage. After passing through the sender-receiver-switch, this alternating voltage is fed into an amplifier (or rather a pre-amplifier). The amplified signal is further processed by a so-called demodulator, which knows the frequency of the sender. The magnetization results from the spin precessions happening in a narrow frequency band around the sender frequency. In the end one can remove the sender frequency from the signal without loss of information. The high frequency induction signal oscillating in the MHz regime becomes a signal in the kHz range. There are different outputs for the voltage signal: one for the original signal, one for its envelope and one for the just mentioned low frequency signal. These signals can be further processed with the oscilloscope.

Part II

Pulsed NMR

8 Tilting the Magnetization with the Help of B-fields

8.1 Revision: How does a constant homogeneous magnetic field affect the magnetization?

We consider the well-known system of nuclear spins, whose magnetization we want to study. The external magnetic field is pointing again in z -direction. The equations of

motion have already been derived, the interaction between nuclei should once more be neglected to begin with. We can therefore proceed like this:

Both in the laboratory system as well as in the coordinate system u, v, z , that rotates with angular velocity ω , one can write this magnetic field as $\mathbf{B} = \{0, 0, B_0\}$. We now choose the direction of rotation and the angular velocity of the rotating system as follows:

- ω and $(\gamma\mathbf{B})$ anti-parallel,
- as well as $\omega = |\omega| = \gamma \cdot B_0$

Then the term in parenthesis on the right hand side of (18) vanishes. This means the entire right hand side of the equation vanishes, i.e. $\frac{\partial \mathbf{M}}{\partial t} \equiv 0$ in the rotating system. In other words: the magnetization vector is spatially fixed in this rotating coordinate system.

Viewed from the laboratory system, the magnetization vector precesses with the Larmor frequency

$$\omega_L := \gamma \cdot B_0 \tag{35}$$

The precession motion of the magnetization vector in the laboratory system x, y, z is shown in Fig. 2.

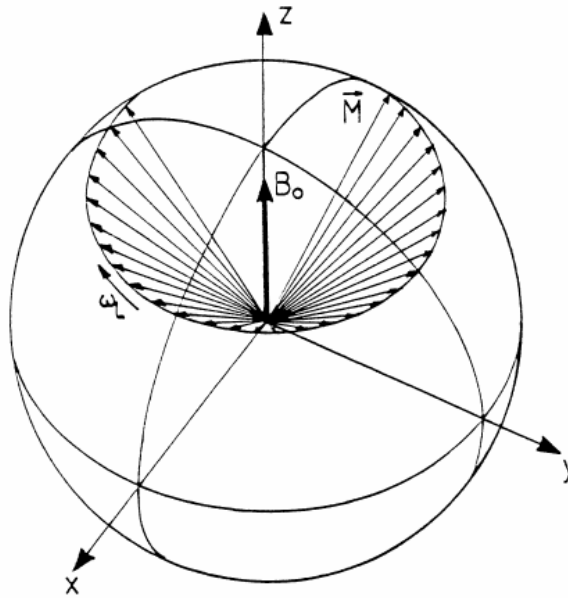


Figure 2: Motion of the magnetization vector \mathbf{M} in the static magnetic field B_0 shown in the laboratory system.

8.2 What is the impact of an additional high frequency magnetic field pointing in x -direction?

We use the same assumptions as in Section 8.1. Additionally, now an electromagnetic wave is applied, whose \mathbf{B} -field component oscillates in x -direction. The magnetic field oscillating in x -direction of the laboratory system with angular frequency ω_S and amplitude $2B_1$ can be split in two oppositely rotating components with amplitude B_1 . Since for any NMR experiment the sender frequency ω_S has to lie in the vicinity of the Larmor frequency ω_L , one of these field components is rotating in the same direction and almost synchronous with the precession of the magnetization. The interaction of this field component with the nuclear or electron dipole is large, as it keeps its direction with respect to the transverse component of the magnetization for a rather long time. In contrast, the other component of the oscillating field rotates with approximately twice the Larmor frequency in the opposite direction compared to the nuclear or electron dipoles. The effects on \mathbf{M} cancel in good approximation, one can therefore neglect this component.

From now on we assume, that the magnetic field rotates exactly with the angular frequency of the sender in the correct direction:

$$\omega = \omega_S \quad (36)$$

Then one of the two rotating components of the oscillating magnetic field, the one rotating in the correct direction, is spatially fixed in the rotating coordinate system u, v, z . Without loss of generality this spatially fixed component shall point in the u -direction. With this, the total magnetic field can be written in this rotating coordinate system as

$$B = \{B_1, 0, B_0\} \quad \text{with respect to the coordinates } u, v, z.$$

If one adjusts the sender frequency ω_S or the magnetic field \mathbf{B}_0 such, that the condition

$$\omega_S = \omega_L = \gamma \cdot B_0 \quad \text{resonance condition} \quad (37)$$

is fulfilled, inserting the total magnetic field \mathbf{B} in the Bloch equations for the rotating coordinate system (Eq. (18)) yields:

$$\frac{\partial \mathbf{M}}{\partial t} = \mathbf{M} \times (\gamma \cdot \{B_1, 0, 0\}) \quad (38)$$

The solution for the differential equation can be obtained by transferring the result of the previous chapter: Instead of the static field \mathbf{B}_0 in z -direction of the laboratory system, now there is a static field \mathbf{B}_1 in u -direction of the rotating coordinate system. In the rotating coordinate system u, v, z , the magnetization vector \mathbf{M} will now precess around the u -direction with the angular velocity

$$\omega_1 := \gamma \cdot B_1 \quad (39)$$

If one chooses $\mathbf{M}_a = \{0, 0, M_0\}$ as the initial condition for the magnetization vector in the rotating coordinate system (i.e. the thermal equilibrium according to Boltzmann), the magnetization vector precesses in the rotating system in the v - z -plane with the frequency ω_1 under the influence of the oscillating magnetic field from the $+z$ -direction to the $+v$ -direction, $-z$ -direction, $-v$ -direction, $+z$ -direction and so forth (assuming a nucleus with $\gamma > 0$). This motion is shown in Fig. 3.

If one considers this motion of the magnetization vector in the laboratory system x, y, z , the rotation of the coordinate system with the angular velocity $\omega = \omega_S = \omega_L$ around the z -axis is added to the precession with ω_1 around the u -axis. \mathbf{B}_0 has a much larger magnitude than \mathbf{B}_1 . The precession around \mathbf{B}_0 is therefore much faster than the one around \mathbf{B}_1 . The magnetization vector thus moves on a helical curve as shown in Fig. 4. Here the huge advantage of introducing the rotating coordinate system becomes obvious: the relatively complex motion of \mathbf{M} on the helical curve is decomposed into two simple precession motions with ω_L around the z -axis and ω_1 around the u -axis of the rotating coordinate system.

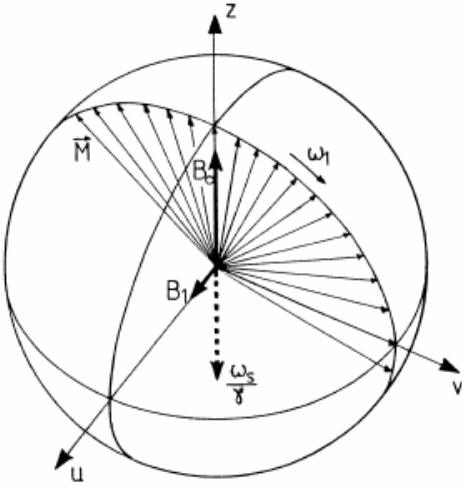


Figure 3: Motion of the magnetization vector \mathbf{M} in the rotating coordinate system. Acting here are the static field component B_0 and the, in this system, spatially fixed component B_1 of the oscillating magnetic field with $\omega_S = \omega_L$.

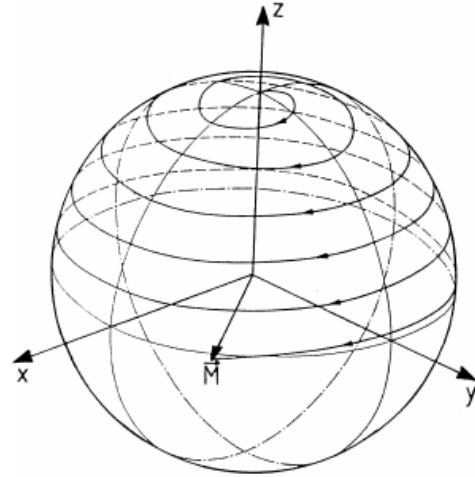


Figure 4: Motion of the magnetization vector \mathbf{M} in the laboratory system. Acting here are the static field component B_0 and the in x -direction oscillating magnetic field with amplitude $2B_1$.

If the resonance condition (37) is not fulfilled exactly, the z -component of the magnetic field in (38) does not vanish. This equation is now rather written as

$$\frac{\partial \mathbf{M}}{\partial t} = \mathbf{M} \times (\gamma \cdot \mathbf{B}_{eff}) \quad (40)$$

with $\mathbf{B}_{eff} = \{B_1, 0, (B_0 - \omega_s/\gamma)\}$

Now, the magnetization vector no longer precesses around the u -axis in the rotating

coordinate system, but around the direction of the effective magnetic field B_{eff} . This precession proceeds with the angular velocity

$$\omega_{eff} = \gamma \cdot |\mathbf{B}_{eff}| = \gamma \cdot \sqrt{B_1^2 + (B_0 - \omega_s/\gamma)^2} \quad (41)$$

If one starts again from the magnetization vector $\mathbf{M}_a = \{0, 0, M_0\}$ as an initial condition, \mathbf{M} now precesses (in the rotating coordinate system!) on a cone around the effective magnetic field \mathbf{B}_{eff} . The opening angle of this cone is given by the fact, that the initial magnetization vector \mathbf{M}_i has to lie on this cone, i.e. the z -axis has to be a surface line of the cone. The circumstances in the rotating system are illustrated in Fig. 5.

By now it must be clear, why it is convenient and advantageous for the purpose of illustration to transform in a suitable rotating coordinate system before studying the additional motions of the magnetization further.

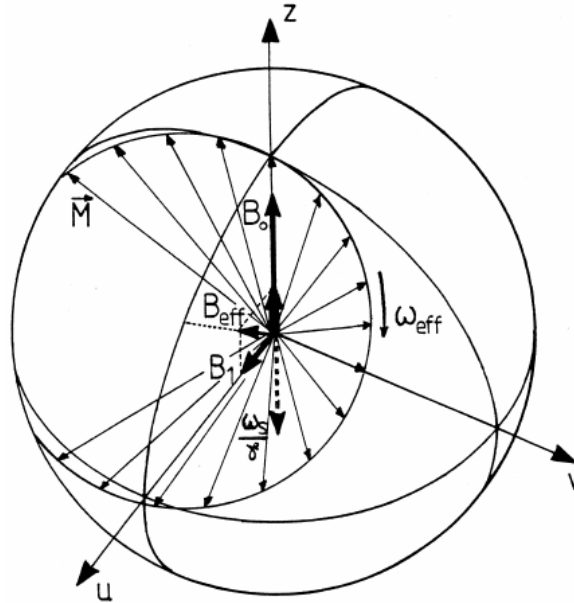


Figure 5: Motion of the magnetization vector \mathbf{M} in the rotating coordinate system under the influence of the static field \mathbf{B}_0 and the oscillating field with frequency $\omega_s \neq \omega_L$. The static field \mathbf{B}_0 is not fully compensated here. The remainder $(B_0 - \omega_s/\gamma)$ forms together with the spatially fixed component B_1 of the oscillating field the effective field \mathbf{B}_{eff} . \mathbf{M} precesses on a cone around this spatially fixed magnetic field \mathbf{B}_{eff} with an angular velocity ω_{eff} .

Intermediate Result: We have shown in this chapter, that the magnetization vector can not only be rotated around the z -axis. One can, in addition to the anyway given precession in the external homogeneous magnetic field \mathbf{B}_0 , force rotations around vectors in the u - v -plane. This happens by applying a field, whose B-field oscillates in the x - y -plane. The frequency of this oscillation has to be exactly the Larmor frequency of the atomic nuclei. The phase fixes the vector in the u - v -plane around which

the rotation takes place. Usually one assumes, that the rotation happens around the u -axis.

If the frequency of the B_1 -field component is slightly shifted with respect to the Larmor frequency, one obtains a rotation around an axis of the rotating coordinate system, lying in the u - z -plane.

That way one can arbitrarily rotate the magnetization by applying an electromagnetic wave with matching frequency and phase. We will exploit exactly this effect in the pulsed NMR experiments.

9 Pulsed NMR and Relaxation

We have learned, that the magnetization only obeys the equations of motion (18), if there are no interactions between the nuclei, i.e. if one can neglect relaxation processes. In deriving these equations in the previous chapter, we didn't consider relaxation processes. On longer time scales, i.e. for times $t \gg T_1$ or T_2 , the measured magnetization will show a different behavior. One will therefore not observe these precessions about arbitrarily chosen axes.

This would only be possible if one could suppress the relaxation processes, which, however, is impossible. On the other hand, one can observe the system on shorter time scales, where these relaxation processes don't have a significant influence on the system, simply because the spins don't have enough time to interact with each other. This is exactly what is done in pulsed NMR: one doesn't apply the electromagnetic wave continuously, but one rather limits the irradiation time on times $\Delta t \ll T_1$ or T_2 , which usually corresponds to a few μs . With these short pulses it is then actually possible to perform defined rotations of the magnetization vector.

9.1 Pulsed HF-Excitation

So in pulsed NMR, the sample is not permanently exposed to an oscillating magnetic field. On the contrary, only short but intense pulses with angular frequency ω_S are applied. Thus, in the rotating coordinate system, the magnetic field

$$\mathbf{B} = \{B_1, 0, B_0\}$$

is applied only during the duration τ of the pulse. If the resonance condition (37) is fulfilled, the magnetization vector will precess in the rotating coordinate system around the u -direction with angular velocity

$$\omega_1 = \gamma \cdot B_1$$

Overall, the magnetization will precess during the time τ by the flipping angle

$$\Theta = \omega_1 \cdot \tau = \gamma \cdot B_1 \cdot \tau \quad (42)$$

Special values for the flipping angle, which are of practical relevance, are:

- $\Theta = \pi/2 \Rightarrow 90^\circ$ pulse or $\pi/2$ pulse, e.g. flipping the magnetization from the z -direction to the transverse plane (u - v -plane).
- $\Theta = \pi \Rightarrow 180^\circ$ pulse or π pulse, e.g. flipping the magnetization from the $+z$ -direction to the $-z$ -direction and vice versa or flipping the magnetization in the transverse plane from the $+v$ -direction to the $-v$ -direction (the u -component stays the same).

Equ (42) shows, that the product of B_1 and τ alone defines the flipping angle Θ . In practice, B_1 is chosen as large as technically feasible (limited by the power output of the sender). This leads to pulse durations in the range of $\tau_{\pi/2} \approx 1...2 \mu s$ for a 90° pulse. This means for us, that even in the case where the resonance condition (37) is only fulfilled approximately or not for all the spins simultaneously

$$B_1 \gg |(\omega_L - \omega_s)/\gamma| \quad (43)$$

still holds and therefore it remains a good approximation, that

$$B_{eff} \approx B_1. \quad (44)$$

The effective magnetic field thus points in the u -direction and we have

$$\omega_{eff} \approx \omega_1. \quad (45)$$

Hence, the resonance condition is fulfilled during the short duration of the pulse, so we can neglect the relaxation processes during the duration of the pulse in good approximation.

9.2 Free precession with relaxation

We have now seen what happens with the magnetization during a pulse. This chapter describes how the magnetization behaves after the application of the pulse. Usually, the sample will be exposed to a defined series of electromagnetic pulses. Between these pulses, one always waits for a certain amount of time and leaves the spin ensemble to itself. So only the static magnetic field \mathbf{B}_0 is applied, the total magnetic field hence is $\mathbf{B} = \{0, 0, B_0\}$. The magnetization vector \mathbf{M} then precesses, as you already know, around the direction of this field with the Larmor frequency $\omega_L = \gamma \cdot B_0$ (cf. Eq. (35)). Besides this free precession, we now have to consider the relaxation processes according to (22) and (23) for the longitudinal and transverse relaxation respectively, as the times

between pulses are generally on the order of the relaxation times T_1 and T_2 or sometimes even considerably longer.

If the spin ensemble is in thermal equilibrium ($\mathbf{M} = \{0, 0, M_0\}$), only longitudinal magnetization is present. This can be turned into transverse magnetization either partly or entirely (using a 90° pulse). As soon as there is a transverse component of the magnetization, it will start precessing around the direction of the \mathbf{B} -field. This transverse component of the magnetization vector M_R , which precesses with ω_L , induces a voltage signal in a coil, which is mounted in a fixed orientation in the laboratory system (e.g. pointing in x -direction). According to (23), this transverse component decays exponentially with the time constant T_2 , due to the transverse relaxation process. Accordingly, also the signal picked up in the induction coil decays exponentially with the same time constant. This assumes a completely homogeneous static magnetic field (i.e. \mathbf{B}_0 , independently of the location). This exponentially decaying signal is called

Free Induction Decay=**FID**

The voltage signal induced in the receiver coil by the precessing transverse component of the magnetization vector \mathbf{M} can be described by

$$U_S(t) = C \cdot M_R \cdot e^{-t/T_2} \cdot \cos(\omega_L t + \phi) \quad (46)$$

where C is a constant given by the device and ϕ is the initial phase of the induced signal. It also depends on the equipment used.

Intermediate Result: In the last two chapters we have seen how the magnetization, which we can pick up as a signal from the sample, behaves,

- when an electromagnetic pulse is applied.
- and also after a pulse.

This is sufficient to adjust the settings for pulsed NMR, because, in principle, one does nothing else but apply a suitable series of pulses to the sample and wait for appropriate times in between. The durations are on the order of a few microseconds. The pulse sequences can be programmed and executed by the device. At given times, the induced voltage signal will be recorded.

10 Pulse Sequences

We are now facing the question, what constitutes a suitable pulse sequence. We are pursuing three goals with the measurements:

1. Determining the longitudinal relaxation time T_1 .
2. Determining the transverse relaxation time T_2 .
3. Acquire a spectrum.

In the following, the different measurement techniques will be explained step by step.

10.1 Inversion-Recovery Technique to Determine T_1

Here we will discuss the most precise method to determine the longitudinal relaxation time T_1 . It is at the same time the method, which is easiest to understand. However, it is also the one with the longest measurement time.

We assume, that the sample is in thermal equilibrium at the beginning of the measurement, i.e. Eq. (20) holds for each pair of eigenstates (designated with + and -). This means, that the magnetization M_0 has been built up in z -direction according to (21) (Fig. 6a). By means of a 180° pulse, the magnetization, which was pointing in $+z$ -direction initially, is inverted and now points in the $-z$ -direction (Fig. 6b). With this, the alignment of the spin system is maximally perturbed (i.e. the occupation numbers of all energy levels with magnetic quantum numbers of opposite sign are exchanged):

$$N_m \Leftrightarrow N_{-m}$$

After this perturbation of the thermal equilibrium, the longitudinal relaxation - as described in (22) - sets in. The magnetization in $-z$ -direction decreases further and further until it vanishes and starts to build up in $+z$ -direction again. Different stages of this process are depicted in Figs. 6c, 6d and 6e.

Unfortunately, it is impossible to detect the longitudinal magnetization M_z directly, as it doesn't precess and therefore can't induce a signal in the receiver coil. Hence, the longitudinal component of the magnetization M_z has to be converted in a transverse component M_R , whose induction signal can then be detected. For this, a 90° pulse is applied after a waiting time t (after the 180° pulse). If, during this pulse, the oscillating magnetic field B_1 is pointing in u -direction (in the rotating coordinate system), the z -component of the magnetization will be converted in a v -component (regarding the sign):

$$M_z \Rightarrow M_v \quad \text{via a } 90^\circ \text{ pulse in } u\text{-direction}$$

Figs. 6c', 6d' and 6e' show the magnetization at the end of the 90° pulses (time t_+), which result from the longitudinal magnetizations (immediately before this pulse at time t_-), depicted in Figs. 6c, 6d und 6e.

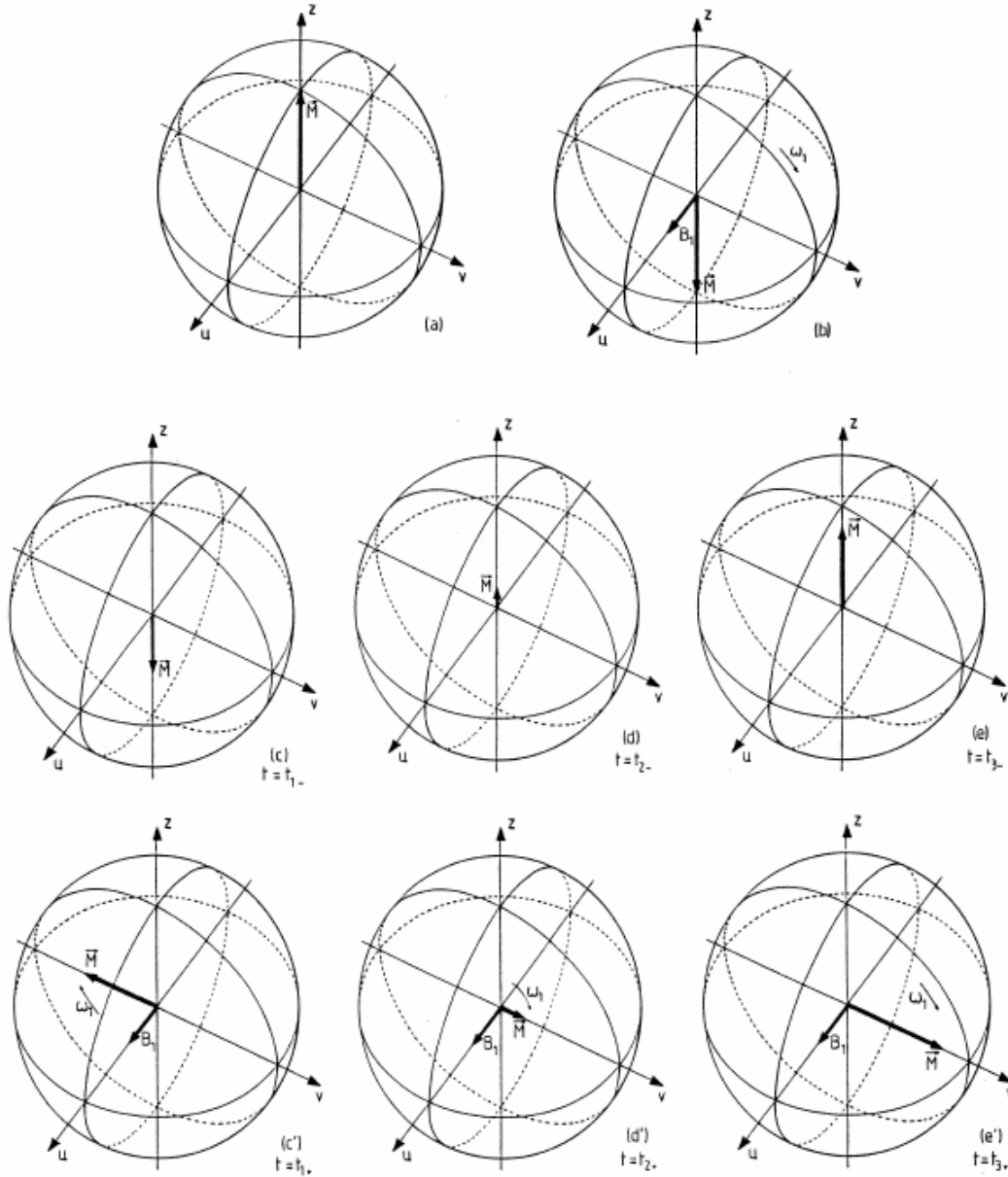


Figure 6: Illustration of the inversion-recovery-technique to determine the longitudinal relaxation time T_1 , shown in the rotating coordinate system. The sphere with radius M_0 drawn around the origin in all sub-figures indicates the maximum length of the magnetization vector. In sub-figures (a) and (b), the magnetization is shown in thermal equilibrium and after inversion by a 180° pulse, respectively. Sub-figures (c), (d) and (e) show the magnetization at times $t_1 \leq t_2 \leq t_3$ immediately before the application of the 90° pulse needed to detect the magnetization. Sub-figures (c'), (d') and (e') show the magnetization at the end of these pulses (immediately before turning off the sender). The magnetization vector has assumed its final position. As the duration of the pulse is $t \ll T_1$, the point in time just before and after the pulse are designated using the indices $-$ and $+$, respectively.

This transverse magnetization will now decay because of the transversal relaxation according to (23), but even more so due to the inhomogeneity of the static field \mathbf{B}_0 . As long as there is a finite transverse magnetization, it will induce a **FID** in the receiver coil. The initial amplitude of this **FID**, considering also its phase, is a measure for the longitudinal component of the magnetization $M_z(t)$ after the partial relaxation during the time t , which we want to determine. In Fig. 7, this longitudinal component $M_z(t)$, which has been converted to a transverse component, is plotted as a function of the waiting time t between the 180° pulse and the 90° pulse, during which the partial relaxation takes place. A least squares fit of a curve as described in (22) is drawn through the measured points. In this fit, the three quantities

$$\begin{aligned} M_0 &= \text{thermal equilibrium magnetization} \\ T_1 &= \text{longitudinal relaxation time and} \\ A &= \text{integration constant to account for the initial conditions} \end{aligned}$$

are determined such, that the sum of the squared differences between the measured points and the predicted values according to equation (22) is minimized.

This procedure is called inversion-recovery-method. Keep in mind, that before the described pulse sequence can be repeated with the same or a different waiting time t , one has to wait until the sample has reached thermal equilibrium again, which is the case after 4 to $5 \cdot T_1$.

Intermediate Result: We know how the longitudinal magnetization is restored after a perturbation (cf. Eq. (22)). In order to determine the time constant of this process, one uses a pulse sequence of the form

$$\pi \rightarrow \text{waiting time} \rightarrow \frac{\pi}{2} \rightarrow \text{acquisition of the induction signal}$$

The amplitude at the beginning of each measurement yields one point of the curve representing the build up of the longitudinal magnetization. After many measurements with different waiting times, one obtains the full curve and from that one can determine T_1 .

10.2 Spin echo to determine the transverse relaxation time T_2

According to (23), one should be able to obtain the transverse relaxation time T_2 from the **FID** after a 90° pulse. This, however, requires a sufficiently homogeneous magnetic field \mathbf{B}_0 , so the decay of the **FID** is caused almost exclusively by the transverse relaxation and not by other effects.

The observed decay of the transverse magnetization without any special precautions, however, is not solely caused by the transverse relaxation. Inhomogeneities in the \mathbf{B}_0 -field of the device have an effect, that adds to the transverse relaxation and results in

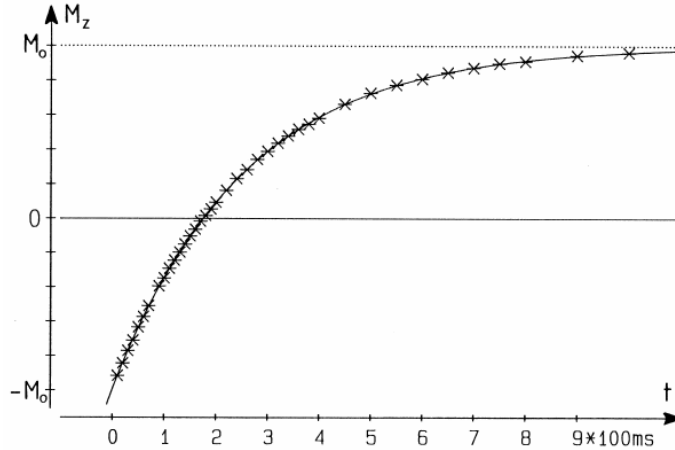


Figure 7: Initial amplitudes of the **FID** taking into account the phase after different waiting times t , during which a partial relaxation takes place. If the magnetization vector points in the $+v$ -direction after the 90° pulse, the initial amplitude of the **FID** is plotted with a positive sign ($M_z > 0$ before the 90° pulse); if the magnetization vector points in the $-v$ -direction after the 90° pulse, the initial amplitude of the **FID** is plotted with a negative sign ($M_z < 0$).

a shorter decay time. If the nuclei in the sample are exposed to different z -components of the static magnetic field, they precess with different velocities. This effect can be decreased with clever adjustments, but is difficult to remove entirely.

For relaxation times T_2 larger than a few milliseconds, the different Larmor frequencies $\omega_L(\mathbf{r})$ at different locations \mathbf{r} in the sample have a noticeable effect. To describe this theoretically, we consider spin packets, so-called spin isochromates. These are classes of spins precessing with the same Larmor frequency. In contrast, spins of different spin isochromates precess with different Larmor frequencies $\omega_L(\mathbf{r})$. This means of course, that the adjustment of the resonance condition, i.e. the sender or the Larmor frequency, respectively, (and with this the magnetic field \mathbf{B}_0) according to (37) is not possible for all spin isochromates at the same time. Only the spin packet with the average Larmor frequency ω_{av} fulfills the resonance conditions. The magnetization vectors of all other spin isochromates $\mathbf{M}(\mathbf{r})$ are then not spatially fixed anymore with respect to the coordinate system, that rotates with the sender frequency ω_S .

Let M_{av} , M_{max} and M_{min} be the transverse components of the magnetization vectors precessing with the average, the maximum and the minimum Larmor frequency ω_{av} , ω_{max} and ω_{L-} , respectively. If the spin system is in thermal equilibrium

$$\mathbf{M} = \{0, 0, M_0\} \quad (\text{Fig. 8a})$$

the magnetization of all spin isochromates points in v -direction immediately after a 90° pulse (assuming B_1 in u -direction). The total magnetization in the rotating coordinate system immediately after the pulse is then given by

$$\mathbf{M} = \{0, M_0, 0\} \quad (\text{Fig. 8b})$$

If the spins are allowed to precess freely after this pulse, each spin isochromate will precess with its own Larmor frequency $\omega(\mathbf{r})$. In the rotating coordinate system, this precession occurs with the angular velocity

$$\omega(\mathbf{r}) - \omega_S$$

- i.e. M_{av} remains spatially fixed in v -direction
 M_{max} precesses in the transverse plane towards the $+u$ -direction
 and M_{min} precesses in the transverse plane towards the $-u$ -direction.

Fig. 8c shows M_{av} , M_{max} and M_{min} after a certain free precession time t_e . Recall that M_{max} and M_{min} are the transverse magnetizations of the spin packets with the largest and smallest Larmor frequency. The precession frequencies of all other spin packets lie in between. Then it becomes clear, that the transverse magnetization resulting from all these spin isochromates decreases over time, even without any transverse relaxation. Approximately when M_{min} and M_{max} cross each other near the $-v$ -axis, the magnetization vectors of all spin packets are homogeneously distributed across all directions in the u - v -plane. The resulting magnetization therefore vanishes and no signal will be induced any more.

This effect can, however, be reversed. The question now is, which method best measures the true transverse relaxation. We will discuss the spin echo method introduced by Carr and Purcell and the improvements suggested by Gill and Meiboom: After flipping the magnetization at time $t = 0$ from the z -direction (Fig. 8a, thermal equilibrium) with a 90° pulse (assuming B_1 in u -direction) to the v -direction (Fig. 8b), the individual spin isochromates are precessing in the rotating coordinate system with their specific Larmor frequency $\omega_L(\mathbf{r}) - \omega_S$.

After precessing freely for a time t_e , these spin packets have diverged, as illustrated in Fig. 8c. Now, a 180° pulse is applied with B_1 pointing in v -direction (this is achieved by shifting the phase of the applied pulse by 90°). This pulse does not affect M_{av} , however, the spin isochromates M_{max} and M_{min} will change their direction. Fig. 8d shows the magnetization vectors of these spin packets at the end of this pulse, i.e. immediately before switching off the oscillating field B_1 . Still, M_{max} precesses with the larger Larmor frequency ω_{max} and M_{min} with the smaller Larmor frequency ω_{min} .

If one now lets the spin isochromates M_{av} , M_{max} and M_{min} precess freely for a time t_e once more, all three spin isochromates will point in the same direction again at the end of this interval (i.e. after a total time of $2 \cdot t_e$ following the 90° pulse). This is depicted in Fig. 8e. The 180° pulse at time t_e causes the diverging spin isochromates M_{av} , M_{max} and M_{min} to refocus in the v -direction after time $2 \cdot t_e$. The resulting transverse component $M_R = M_{av} + M_{max} + M_{min}$ at time $2 \cdot t_e$ (the spin-echo time) now corresponds exactly to the transverse component M_R , which one would observe in a perfectly homogeneous magnetic field B_0 . What is discussed here exemplary for the three spin isochromates M_{av} , M_{max} and M_{min} , can of course be generalized for an arbitrary number of spin packets having all Larmor frequencies between ω_{max} and ω_{min} .

The refocusing of the spin isochromates can be repeated any number of times. For this, a 180° pulse with B_1 pointing in v -direction is applied always at times $(2n - 1) \cdot t_e$. Then one can observe a spin-echo at times $2n \cdot t_e$ (where $n = 1, 2, 3, \dots$). This can be seen in Fig. 9.

Figure 8: Presentation of the Carr-Purcell spin-echo to determine the transverse relaxation time T_2 in the rotating coordinate system. The sphere drawn around the origin with radius M_0 in all sub-figures illustrates the maximum length of the magnetization vector. The magnetization M_0 shown in sub-figure (a) is flipped to the v -direction by a 90° pulse (b). During the time interval $0 \leq t \leq t_{e-}$, the transverse magnetization of the three spin packets diverges (c). Applying a 180° pulse at time t_e rotates all magnetization vectors by 180° around the v -axis, i.e. M_{max} and M_{min} change their positions, but remain precessing in the same direction with the same Larmor frequency (d). Hence, at time $2t_e$, all spin packets meet again in v -direction (e) and begin to diverge again afterwards (f). As the duration of all pulses is short compared to t_e , the times immediately before and after the pulses are denoted with indices - and +, respectively.

Since, at the times of a spin-echo $2n \cdot t_e$, the transverse component of the magnetization in the not perfectly homogeneous static magnetic field \mathbf{B}_0 equals the one in the ideal, perfectly homogeneous case, the spin-echos shown in Fig. 9 lie on the decaying curve described by (23) for the transverse relaxation.

Intermediate Result: We know how the transverse magnetization decays. To determine the time constant of this process, one would naively think, that it is enough to simply record a FID, which is precisely caused by the decaying transverse magnetization. Unfortunately, inhomogeneities of the B_0 -field speed up the decay of the transverse magnetization. To study the decay of the transverse magnetization caused by relaxation processes alone, one employs pulse sequences of the form:

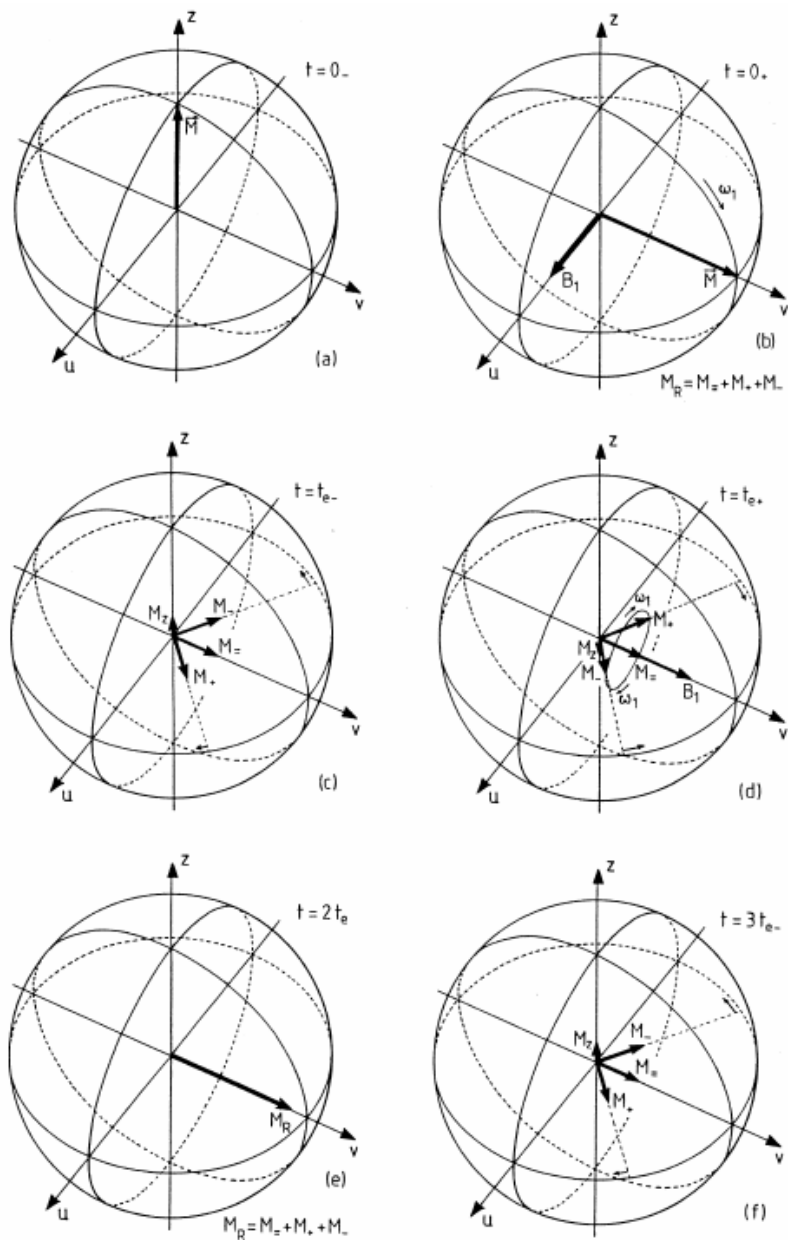
$$\frac{\pi}{2} \rightarrow \text{waiting time } t_1 \rightarrow \pi \rightarrow t_1 \rightarrow \text{measure} \rightarrow t_1 \rightarrow \pi \rightarrow t_1 \rightarrow \text{measure} \rightarrow \dots$$

10.3 Fourier spectroscopy and recording a spectrum

Applying the Fourier transform (FT) to the signal induced by a pure **FID** (described by Eq. (46)) results in the same absorption and dispersion curves, that can be obtained with cw-spectroscopy by scanning the resonance frequency.

This means, one gets exactly the same information about a system, that shows a resonance, either by

1. recording the resonance curve (intensity and phase or real and imaginary part) as a function of excitation frequency, i.e. scanning the resonance curve as a function of frequency slowly, point by point, or
2. perturbing the system with a short excitation and recording the signal, following this perturbation, as a function of time.



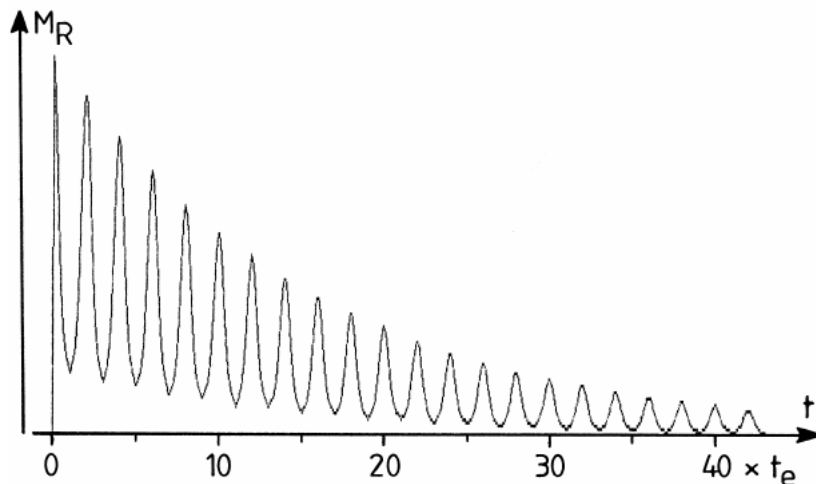


Figure 9: Amplitude of the NMR signal of a Carr-Purcell spin-echo sequence. At time $t = 0$, the 90° is applied. For each time $(2n - 1) \cdot t_e$ ($n = 1, 2, 3, \dots$), a 180° pulse (B_1 pointing in v -direction) is applied to refocus the spin packets. At times $2n \cdot t_e$, the spins are refocused and match exactly the amplitudes one would observe in a perfectly homogeneous field B_0 . The resulting spin-echo amplitudes decay from each echo to the next due to the transverse relaxation.

Both sets of information form a pair of Fourier transforms: time domain signal of the free unperturbed resonance system on the one hand, and complex resonance curve in the frequency domain on the other hand. Depending on which of the two equivalent sets of information (resonance frequency or time domain signal) is more readily accessible, one will record one or the other. Ever since powerful computers and the fast Fourier transform algorithm by Cooley and Tukey are available, this form of Fourier transform spectroscopy has seen a dramatic rise. Today, pulsed FT spectroscopy is almost exclusively used in magnetic resonance spectroscopy. The use of cw-methods is reserved for a few special use cases (e.g. broad lines due to very short relaxation times T_2).

Intermediate Result: The time domain signal induced by the transverse magnetization contains all spectral information. One merely has to apply a Fourier transform.

Part III

Experiment

11 Overview of all Tasks

This chapter contains a short description of all tasks you are expected to complete during the lab course. More detailed explanations can be found in the following chapter.

1. Prepare the device for pulsed measurements. Make all necessary connections, choose suitable settings for all modules and calibrate the device.
2. Experiments with Mineral Oil Light (MOL):
 - Record a free induction decay (FID).
 - Determine the longitudinal relaxation time using the inversion-recovery technique. Read the relevant data from the screen of the oscilloscope.
 - Determine transverse relaxation time. First use a Carr-Purcell sequence and then a Meiboom-Gill sequence. Save the data on the oscilloscope.
3. Spatial resolution using a Teflon sample:
 - Apply a gradient in y -direction and record a FFT spectrum.
4. Experiments with FC-43:
 - Record a FID.
 - Choose suitable settings and record a FFT spectrum.

12 Explanations of the Tasks

12.1 Preparation for pulsed measurements

For experiments in pulsed mode, besides the permanent magnet and the gradient fields, the receiver, the synthesizer and the pulse programmer are needed. First one has to start the temperature control of the magnet. Ideally this is done at least 45 minutes before the start of the measurement. Otherwise the optimal stability of the magnetic field can not be guaranteed. If the magnetic field is not stable over time, also the Larmor frequency is not constant and one needs to adjust the resonance condition constantly. With open feedback loops in the PS2 controller, the potentiometers are adjusted such, that the corresponding control is off. This sets the goal temperature of the temperature control to the current ambient temperature (green/red LED means the goal temperature is lower/higher than the current ambient temperature.). If one now closes the feedback loops, the magnet temperature will be stabilized to the desired goal temperature.

On the pulse programmer, the outputs I Out and Q Out are connected with the inputs I In and Q In of the synthesizer. Through this, beginning and end of a high frequency pulse are transmitted to the synthesizer. The output Blanking Out is connected with the input Blanking In of the receiver. With this, the receiver chain of the device gets the information, when a pulse begins and when it ends. During the duration of the pulse, the amplifier, which processes the induced signal, will be turned off to prevent saturation of the capacitors in the receiver. Finally, the output Sync Out is connected to the external trigger input of the oscilloscope. The switches MG and B are turned off at first, A is turned on and sync is set to A.

On the synthesizer, the output Pulsed RF Out has to be connected to the corresponding input on the receiver. Thereby, the sinusoidal high frequency signal formed by the pulse programmer is transmitted to the receiver, who passes it on to the coil surrounding the sample inside the permanent magnet. The amplitude of this signals can not be changed in pulsed mode. Frequency and pulse duration can be adjusted with the pulse programmer and the synthesizer. Finally, the output REF Out is connected to the corresponding input on the receiver. This transmits a reference signal to the receiver, which is multiplied with the induced signal in a special circuit in the receiver. This allows to isolate different components of the transverse magnetization. This signal is turned on with the corresponding switch above the output REF Out. The switch CW is turned off.

Finally, on the receiver, the sample coil inside the permanent magnet has to be connected with the output Sample using the blue BNC cable coming out from the top of the magnet. The output Env. Out is connected to channel 1 of the oscilloscope, output Q Out or I Out to channel 2. Setting the built-in amplifier to 0.75 amplifies the induced signal sufficiently without saturating the amplifier. Depending on the kind of nucleus to be studied, the band pass, which filters noise from the induced signal, has to be set to p for protons or f for Fluorine. In the beginning, the switch thus has to be set to p. Finally, the time constant of the built-in lock-in-module of the receiver has to be adjusted. By default 0.01 ms are used. Later one can try to reduce the noise in a signal, e.g. a FID, by increasing the time constant. For too large values of Filter TC, the signal gets washed out and becomes unusable.

The signal outputs on the receiver: On the receiver, four different signals can be picked up and e.g. viewed on the oscilloscope. All of them originate from the voltage signal induced in the sample coil. They reflect, however, different aspects of this signal, since they are processed differently in the receiver.

- RF Out outputs the induced signal directly.
- Env. Out yields the envelope of the RF Out signal.
- The receiver contains a form of lock-in. Its reference frequency is simply the sender frequency, transmitted from the synthesizer to the receiver via Ref. Out or Ref. In,

respectively. The induced signal is of course not modulated with the sender frequency. It rather automatically contains approximately this frequency, due to the precession of the spins. If the reference frequency and the precession frequency don't match, i.e. if the resonance condition is not fulfilled, one will not get a constant signal, but rather a beat signal. This has to be considered when adjusting the device. All other interfering signals usually have a much different frequency and are thus filtered out. The phase-sensitive induced signal is then multiplied with the reference signal. This output signal is only different from zero, if the input signal oscillates with the reference frequency. It furthermore depends on the phase shift between input and reference signal and is proportional to the cosine of this angle. Of course, both the u - and the v -component of the magnetization (in the rotating coordinate system) precess with the corresponding frequency. Only if the phase is adjusted correctly, one can observe exactly one of the two signals and thus the absorption or dispersion curve, respectively, without any interferences. In all other cases one gets a superposition of the two signals. The phase shift can be adjusted with the control labeled P on the synthesizer.

The output I Out yields the output of this lock-in amplifier.

- Q Out basically outputs the same signal. The only difference is, that the phase shift compared to the reference signal is larger by 90° , than the one adjusted for I Out. This means if one has found one of the signals (absorption or dispersion curve) at I Out, Q Out automatically yields the other signal (or its inverse).

The oscilloscope is set to Y-t-mode and external triggering.

Fig. 10 gives a schematic overview of the pulsed NMR setup.

12.2 Calibrating the device

There are three frequencies, that have to be synchronized, in order to only record the spin-induced signals: The Larmor frequency of the nuclear magnetic moments in the sample is fixed. It depends only on the gyromagnetic ratio and the fixed strength of the permanent magnetic field (as shown in Chapter 3). The frequency of the applied electromagnetic wave can be chosen with the synthesizer. The third frequency comes from the sender-receiver-circuit: According to the manufacturer of the device, one can imagine the sender coil as a part of a resonant electric circuit, which has a specific eigenfrequency, which can be tuned by adjusting variable capacitors.

To tune these three frequencies, one proceeds as follows:

1. First one calculates the Larmor frequency of the respective kind of nuclei in the field of the permanent magnet theoretically. The strength of the magnet is 0.5 T. The manufacturer provides the following formulas:

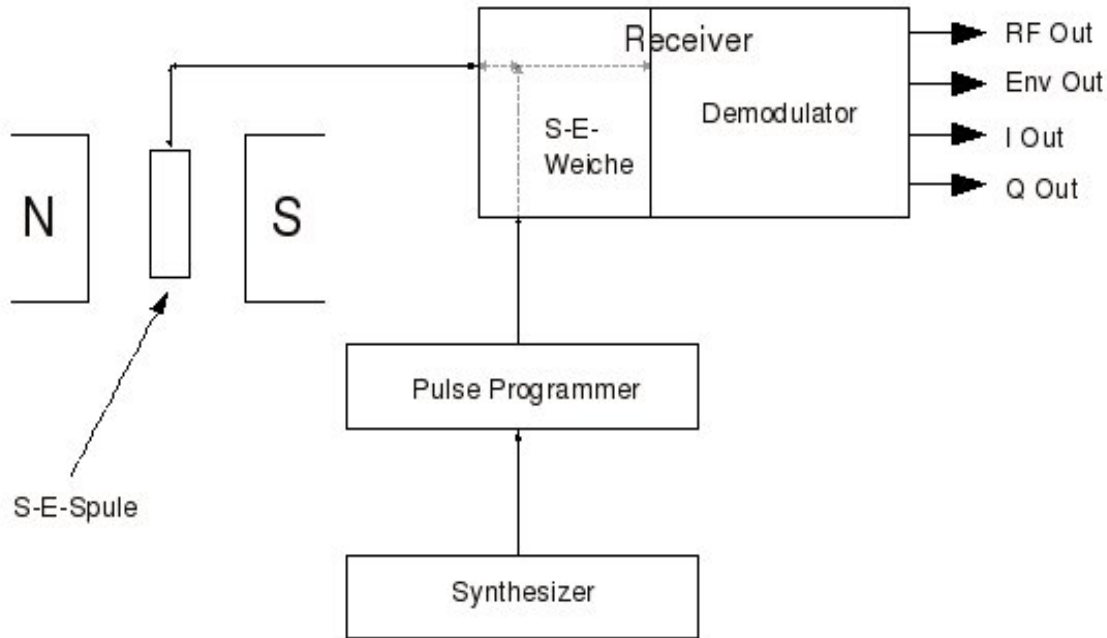


Figure 10: Schematic setup for pulsed NMR

$$\omega_H = 42.576 \frac{\text{MHz}}{\text{T}} \cdot 0.5\text{T} = 21.288\text{MHz} \quad (47)$$

$$\omega_F = 40.044 \frac{\text{MHz}}{\text{T}} \cdot 0.5\text{T} = 20.022\text{MHz} \quad (48)$$

One then sets the frequency of the synthesizer to the calculated Larmor frequency under the menu option F. Keep in mind, that these are theoretical values, which can sometimes be rather far from the actual resonance frequencies of the nuclei in the sample, e.g. due to the chemical shift. Experience shows, that the following values for the two different sample materials are good starting values:

$$\omega_{MOL} = 21.55\text{MHz} \quad (49)$$

$$\omega_{FC-43} = 20.20\text{MHz} \quad (50)$$

- Then, the resonant circuit containing the sender coil has to be tuned to this frequency. This ensures, that the fraction of the power of the high frequency electromagnetic wave actually acting on the sample is as high as possible. To tune this circuit there are four variable capacitors, which can be adjusted with screws. There are two screws, respectively, in recesses on each side of the sample holder in the magnet. The two outer ones are for coarse adjustments and the two inner ones are for fine adjustments. Since these screws are very close to

the magnet, one has to use a ceramic screw driver to turn the screws. For the time being, only the two capacitors to the left of the sample holder (the so-called tuning capacitors) need to be adjusted.

Instead of a sample vial, a coil with three turns, the so-called rf-pickup-probe, is put inside the sample holder. As long as the sender coil emits an electromagnetic wave, a corresponding signal will be induced in the pickup probe. One has to ensure, that the pickup probe is in the center of the sender coil, which at a depth of 3.9 cm. This can be done by adjusting the position of the rubber O-ring. The pickup probe is then connected directly to channel 1 of the oscilloscope. The vertical scale of the oscilloscope is set to 5V per division and the time period to $2.5 \mu\text{s}$.

Afterwards one turns on the A pulse on the pulse programmer. Under the menu option A, one sets its length to $2.5 \mu\text{s}$. The period, with which the pulse is repeated, can be set under the option P. A period of 100 ms is long enough, so that the induced signals of two consecutive pulses don't interfere with each other, and short enough, that the signal displayed on the oscilloscope quickly follows the adjustments of the capacitors. Then one carefully adjusts the tuning capacitors, until the signal has a peak-to-peak amplitude of roughly 40 V.

3. Then the sender frequency has to be matched to the Larmor frequency of the nuclei on the synthesizer. For this, the sample vial filled with MOL is put in the sample holder (watch again for the correct depth, see above). One simultaneously observes the signals of the outputs Env Out and Q Out (or I Out) on the oscilloscope. On the pulse programmer, a 90° pulse is set. How this is done is explained in Chapter 12.3. The closer the two frequencies are, the lower the beat frequency visible in the signal of Q Out (or I Out). Now we vary the frequency of the synthesizer until the beat signal disappears. There should be no visible beat signal in the output of Q Out (or I Out) - the two signals on the oscilloscope should be almost identical. The signal itself should not disappear! On the contrary, one should simultaneously observe an increase in signal intensity, as the resonance condition is now fulfilled better.
4. Following this, one tries to improve the homogeneity of the magnetic field by varying the settings of the four gradient fields X, Y, Z and Z^2 on the magnet control. The switches for the sign should be set to +, -, + and - respectively. Afterwards the gradients are varied until the decay constant of the signal is as large as possible. This means that the additional decay of the transverse magnetization due to inhomogeneities in the field are minimized.
5. Finally, the tuning capacitors are tuned to the resonance frequency. This can be done by setting a 180° pulse in the pulse programmer. In the ideal case one observes no signal after such a pulse, i.e. the Env Out signal is zero. However, as long as the eigenfrequency of the sender circuit is not matched to the sender frequency (which is set to the resonance frequency), a signal can be observed, because the electromagnetic wave created in the sender coil does not exactly follow the pulse from the pulse programmer. It rather builds up slowly and decays

again after the end of the pulse. As long as the frequency is given by the synthesizer, the coils emits with exactly this frequency. However, as soon as the sender circuit is decoupled from the synthesizer, it emits with its own eigenfrequency, which doesn't fulfill the resonance condition of the nuclei anymore. In general it is then no longer possible to find an exact 180° pulse by adjusting the length of the pulse.

To fine tune the sender circuit, one sets the best possible 180° pulse. One then carefully turns the right tuning capacitor in one direction and readjusts the pulse duration. If the smallest possible signal is smaller than before, one continues adjusting in the same direction. Otherwise one tries to adjust in the other direction. These steps are repeated until the signal can't be made smaller anymore. In the end one can also carefully adjust the matching capacitors (to the right of the sample holder) to achieve a better 180° pulse.

12.3 Adjusting the pulses

If the device is calibrated and the sample is placed in the magnet, one can start to adjust the pulses. The only parameter, that can still be changed, is the pulse duration, which can be set with \underline{A} . According to (42), the flipping angle is proportional to the pulse duration. Depending on the kind of nucleus and the molecular bindings, the magnetization takes different amounts of time to relax from a pulse. You can vary the period between pulses to optimize the signal.

12.4 Settings for the measurement of the longitudinal and the transverse relaxation time

Which pulse sequence you need for each of the measurements can be found in Chapter 10. The settings are performed with the pulse programmer. The first pulse is always called A pulse. Its duration is set with \underline{A} . All following pulses are called B pulses and have the same length, which is set with \underline{B} . How many such B pulses are sent in each sequence is specified with \underline{N} . The waiting time between pulses is set with $\underline{\tau}$. The waiting time between the A pulse and the first B pulse is τ , between two consecutive B pulses, there is a waiting time of 2τ . If the MG switch is off, the axes around which the A and B pulse rotate the magnetization are the same. If it is turned on, the two axes lie in the transverse plane and are perpendicular to each other.

To determine the longitudinal relaxation time with the inversion-recovery technique, you need to perform multiple two pulse sequences with varying values of τ and record the data by hand. Choose reasonable values for τ , such that the curve is mapped out with sufficient detail without spending too much time on the measurement.

To determine the transverse relaxation time, it is in principle sufficient to record one Carr-Purcell sequence and one Meiboom-Gill-Sequence each.

12.5 Settings to record a FFT spectrum

This measurement is performed with a sample containing Fluorine nuclei (FC-43). Therefore the resonance frequency will be different from the one the system is currently tuned to. So one first has to repeat all the steps to calibrate the device again. It is a good idea to write down the new resonance frequency set in the synthesizer and found by optimizing the FID signal after a 90° pulse. This will be needed later!

Then slightly change the sender frequency in the synthesizer compared to the previously found resonance frequency. Think about how one can recognize a suitable new frequency!

One thereby ensures, that the frequency of the sender is different from the Larmor frequencies and thus does not interfere with the Fourier transform. One then performs a FFT of the Q Out or I Out signals with the oscilloscope. This can be done using the corresponding function in the math mode and selecting the correct channel.

13 Analysis

Make sure that your lab report satisfies the following criteria:

1. Write a short summary of the theory. Arrange details with the tutor.
2. All plots mentioned in the tasks have to be included in the lab report. Also note which settings you made on the different devices.
3. Determine the longitudinal and transverse relaxation times of MOL.
4. Which of the two methods to determine the transverse relaxation time is more precise? Why?
5. Explain the spectra obtained with FFT.

14 Further Remarks to the Analysis

The data you took to determine the relaxation time can be analyzed with a computer at home with a spreadsheet application or more advanced programs like MATLAB. The relevant information can be extracted from the data by fitting the theory curves for the longitudinal and transverse magnetization, respectively:

$$M_{\text{longitudinal}}(t) = M_0 \cdot \left(1 - 2 \exp -\frac{t}{T_2}\right) \quad (51)$$

$$M_{\text{transverse}}(t) = M_0 \cdot \exp -\frac{t}{T_2} \quad (52)$$

If you don't manage to fit the exponential curves to the data, you can take the logarithm of the data and the theory functions to get a linear relation. Then you can simply fit a straight line to the linearized data to extract the relaxation times.

Part IV

Appendix

15 Questions for the Preparation

1. Fundamentals

- What kind of objects are studied and which properties do they need to have?
- How to treat a nuclear spin mathematically?
- Why can a macroscopic electrically charged spinning top be used to simulate a nuclear spin?
- How does such a top behaves in a homogeneous external magnetic field?
- To what extent can the knowledge about such a macroscopic top be transferred to nuclear spins?
- What does Ehrenfest's theorem state?

2. Magnitude and z -component of a single nuclear spin

- Describe and explain the energy splitting due to the different alignments of I_z in a homogeneous external magnetic field.
- How can one stimulate transitions of spins between different energy levels and what is the selection rule?
- How does the magnitude of the nuclear spin behave during a NMR experiment?

3. Magnetization and relaxation

- Which macroscopic quantity of the nuclear spin ensemble will be measured in the end and how is it connected to the individual nuclear spins?
- Does the magnetization, and therefore the expectation value of the magnetic moment, behave exactly as predicted by the model with the top? Explain!
- How do nuclear spins interact and with what?
- What relaxation processes exist, by which spin interaction are they caused and how can they be treated mathematically?

4. Bloch equations and relaxation

- Which differential equations describe a nuclear spin system without interactions? How can one illustrate the behavior of the magnetization of such a sample?

- How does one need to modify these differential equations to take into account the interactions?
- Which components of the magnetization are considered separately and how do they behave as a function of time?

5. Measurement

- Because of which effect can the magnetization be measured?
- Which component of the magnetization is directly accessible by the experiment?

6. Basics of pulsed NMR

- How does one perturb the magnetization from its equilibrium value?
- One can split this perturbation in two precessions. Which ones? Sketch the train of thought of the derivation.
- How can one rotate the magnetization by a defined angle with respect to the z-axis?
- Why can the relaxation be neglected during this?
- What happens to the magnetization after a perturbation? What effects does this have on the observed signal?

7. Pulse sequences

- The amplitude of the induced signal does not only decay due to transverse relaxation. Which other effect plays a role?
- Describe the pulse sequence, with which one can eliminate this effect from the measurement.
- How can one determine T_2 from the pure FID?
- With which pulse sequence can T_1 be determined. Explain!
- How can a spectrum be recorded with pulsed NMR?