



ALBERT-LUDWIGS-UNIVERSITÄT FREIBURG

PHYSIKALISCHES FORTGESCHRITTENEN-PRAKTIKUM I

Nuclear Magnetic Resonance

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1 Introduction

The goal of this experiment is to research the nuclear magnetic resonance (NMR) at a proton. To do this, we had to check the homogeneity of a permanent magnetic field with a Hall sensor. Afterwards we were to determine the gyromagnetic ratio γ of a proton in hydrogen and glycol respectively. Also, we had to determine the nuclear magneton and the magnetic moment of the ^{19}F – atom in Teflon.

2 Theoretical Background

As our task was to determine nuclear characteristics we put different samples (Teflon, hydrogen and glycol) into a high frequency radiation field located in a homogeneous magnetic field. The nuclear Zeeman-effect, creating energy differences between two spin stances because of the interaction of the nuclear magnetic moment with an external magnetic field, was utilized. When the radiation field's frequency reaches the resonance frequency, the radiation field loses energy because of absorption.

2.1 Nuclear Spin

The spin is an intrinsic property of a quantum-mechanical particle. One can only determine its absolute value and the projection on a particular axis, just as in the case of the angular momentum. The following equations hold:

$$|\vec{S}| = \hbar \cdot \sqrt{S \cdot (S + 1)}, \text{ where } S = 0, 1/2, 1, \dots \text{ and } \hbar \text{ is the reduced Planck constant.}$$

The projection on an axis leads to the following:

$$S_p = m_S \cdot \hbar, \text{ where } -S \leq m_S \leq S$$

As the core is made up of such particles, it has a spin, which we refer to as:

$$|\vec{I}| = \hbar \cdot \sqrt{I \cdot (I + 1)}, \text{ where } I = 0, 1/2, 1, \dots \text{ and}$$

$$I_p = m_I \cdot \hbar, \text{ where } -I \leq m_I \leq I$$

This makes clear that the spin can have $2I + 1$ possible stances.

2.2 Magnetic Moment

The spin of a quantum-mechanical particle causes a magnetic dipole moment interacting with external magnetic fields. It is

$$\vec{\mu} = \gamma \cdot \vec{I}, \text{ where } \gamma = \frac{g_I \cdot \mu_K}{\hbar} \text{ and } \mu_K = \frac{e \cdot \hbar}{2 \cdot m_p}.$$

The variables in the formulas stand for the following:

μ : magnetic dipole moment

γ : gyromagnetic ratio

g_I : nuclear g-factor

e : elementary charge

μ_K : nuclear magneton

m_p : proton mass

Because of the so-called 'Pauli exclusion principle', every orbital is occupied by two protons and neutrons with contrary spin respectively. Thus, the core does only have a spin if there is an odd number of either protons or neutrons or both.

ee: $I = 0$

oo: $I = 1$

eo,oe: $I = \frac{1}{2}$

The first letter stands for the number of protons, the second for the number of neutrons. The letter 'e' stands for an even number, 'o' for an odd number.

Oxygen and carbon are 'ee'-cores, which means that they don't have a spin. Because of this, in the experiment for both glycol ($C_2H_6O_2$) and water (H_2O) a resulting spin of $I = \frac{1}{2}$ for the hydrogen atom is expected. With 9 protons and 10 neutrons, ^{19}F has a resulting spin of $I = \frac{1}{2}$ as well.

2.3 Interaction with Magnetic and Radiation Fields (Nuclear Magnetic Resonance)

A magnetic dipole moment $\vec{\mu}$ in an external magnetic field has the energy

$$E = -\vec{\mu} \cdot \vec{B}$$

which, if again projected on a particular axis, leads to

$$E_p = -g_I \cdot \mu_K \cdot m_I \cdot B$$

This leads to the creation of several energy levels depending on m_I (Zeeman-effect), where

$$\Delta E = g_I \cdot \mu_K \cdot B$$

is the energy difference of two neighboring energy levels.

This is the energy needed or set free when a spin-flip takes place. This energy can be provided by a radiation field (via photons) with resonance frequency

$$\nu = \frac{\Delta E}{h} = \frac{g_I \cdot \mu_K \cdot B}{h} = \frac{\gamma \cdot B}{2\pi}$$

When in thermal equilibrium, the population of two neighboring levels (where $E_{high} > E_{low}$) is Boltzmann-distributed:

$$\frac{n_{high}}{n_{low}} = e^{-\frac{E_{high}-E_{low}}{kT}} = e^{-\frac{\Delta E}{kT}}$$

where k is the Boltzmann-constant and T is the temperature.

There are more particles on the lower level, as can be seen in this formula.

2.4 Relaxation Processes

One would expect the population to be equally distributed after some time. However, there are relaxation processes causing a radiationless fall-back to the lower level. This is the reason why the Boltzmann distribution is maintained. The processes are the following:

2.4.1 Spin-Lattice Relaxation

Excited cores provide the molecule lattice with thermal energy.

2.4.2 Spin-Spin Relaxation

Two particles' magnetic moments interact and thereby cause a line broadening and a small shift of the resonance frequency.

2.5 Hall Effect and Hall Sensor

An external magnetic field distracts moving charge in a conductor. The resulting force is given by

$$\vec{F}_L = e \cdot (\vec{v} \times \vec{B})$$

with \vec{v} being the electron drift velocity. Due to this force a separation of charge is taking place, leading to the generation of an electric field. After some time, the force caused by the electric field equals the Lorentz force. As it is $v \perp B$, this leads to

$$F_L = F_E$$

$$\leftrightarrow e \cdot v \cdot B = e \cdot E$$

$$\leftrightarrow v \cdot B = \frac{U_H}{d}$$

$$\leftrightarrow U_H = v \cdot B \cdot d = \frac{I}{n \cdot e}$$

where it is

U_H : Hall voltage

d : conductor width

n : charge carrier density

$I = n \cdot e \cdot v \cdot B \cdot d$ is the current flowing through the conductor. For Hall sensors often semiconductors are used as those have a much smaller charge carrier density than conductors, making the Hall voltage much larger.

2.6 Lock-In Method

This method is used as it is capable of visualizing weak signals with a large background noise. The signal is multiplied with a reference signal in the synchron detector, which has a frequency close to the one of the expected signal. To improve our result for the resonance frequency, the magnetic field gets modulated with a saw tooth voltage superimposed by a sine voltage. This way, we get the differentiated absorption curve, in which - for us - the position of the zero is of interest, as that's the position where the absorption curve has its minimum.

3 Realization

3.1 Experimental Setups

The permanent magnetic field is provided by a large electromagnet connected to a power supply. The modulation of the magnetic field is created by two coils on the left and the right side of the sample holder. Those are connected to a sine voltage firstly and an adder at the end. There's an electromagnetic oscillating circuit between the respective ends of the iron cores of the electromagnet. There is a hole in the middle of it where the Hall sensor or the samples can be introduced. It's also connected to a frequency generator. An oscilloscope is connected to the modulating voltage to show its course just as to the oscillating circuit to show resonances.

3.2 Experimental Approach

Firstly, the homogeneity of the magnetic field inside the sample holder had to be proven using a Hall sensor. With this measurement, a working point was determined. The setup was the following:

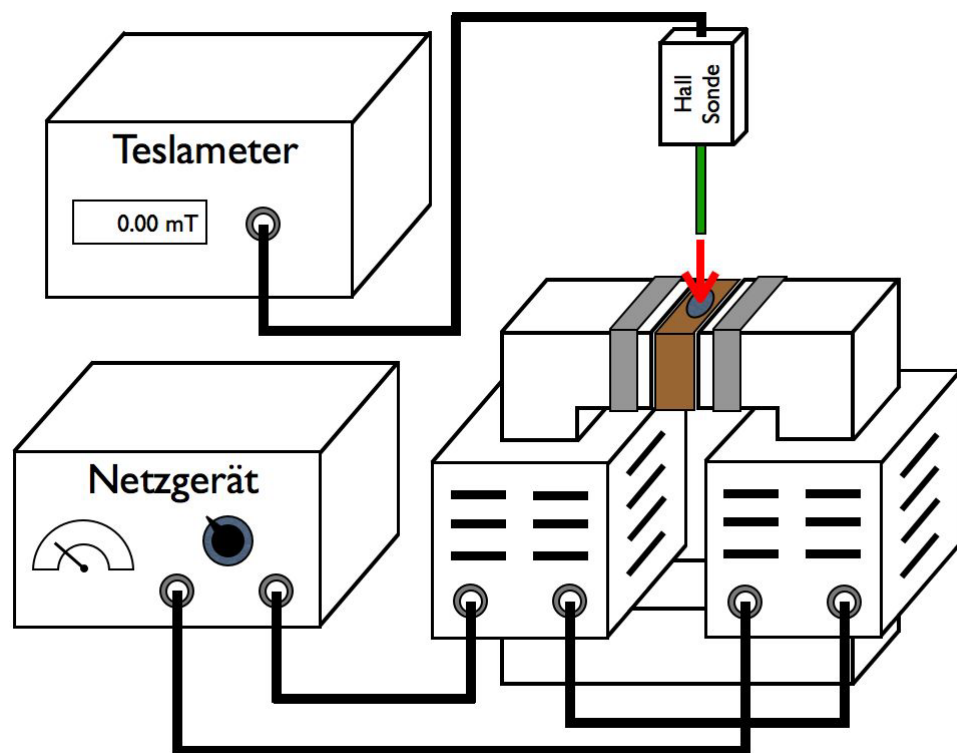


Figure 1: Experimental setup for the determination of the homogeneity of the magnetic field (source: [ver])

Afterwards, hydrogen, glycol and Teflon samples were put inside the field one after the other with the intention to find their resonance frequency. A sine modulation was used to facilitate the realization of this part of the experiment: The resonance is passed by twice per sine period. Thus in the resulting absorption curve, one gets two absorption minima. To find the resonance frequency, the minima need to be equidistant, because that way they are at the zero of the modulation, which is at the appointed frequency of the radiation field. The setup and the expected curves can be seen below:

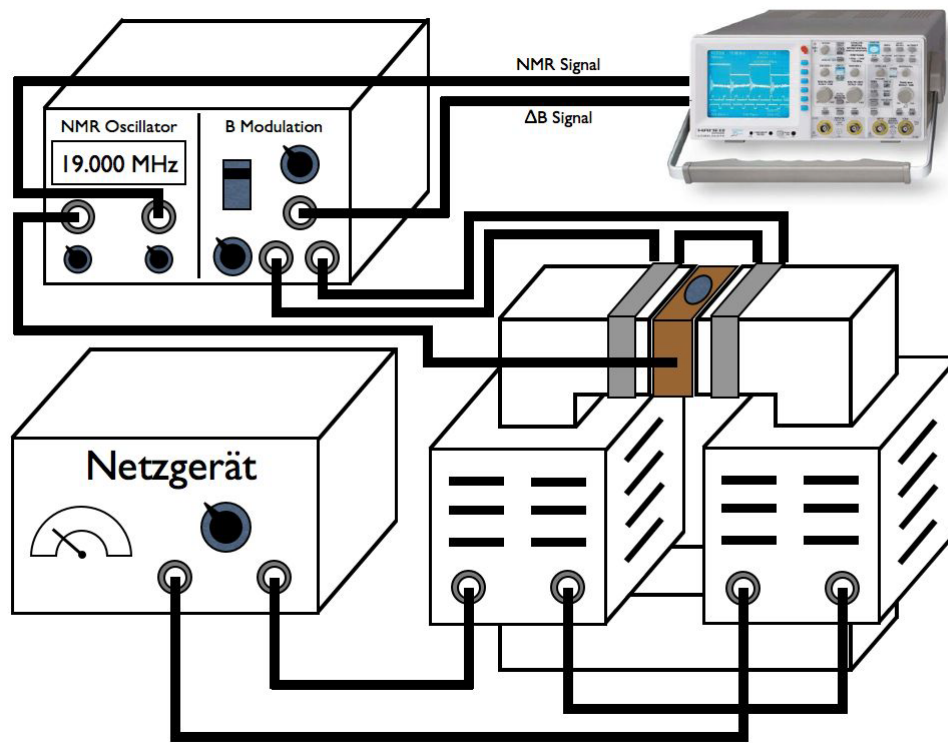


Figure 2: Experimental setup for the determination of the resonance frequency with the sine-modulation (source: [ver])

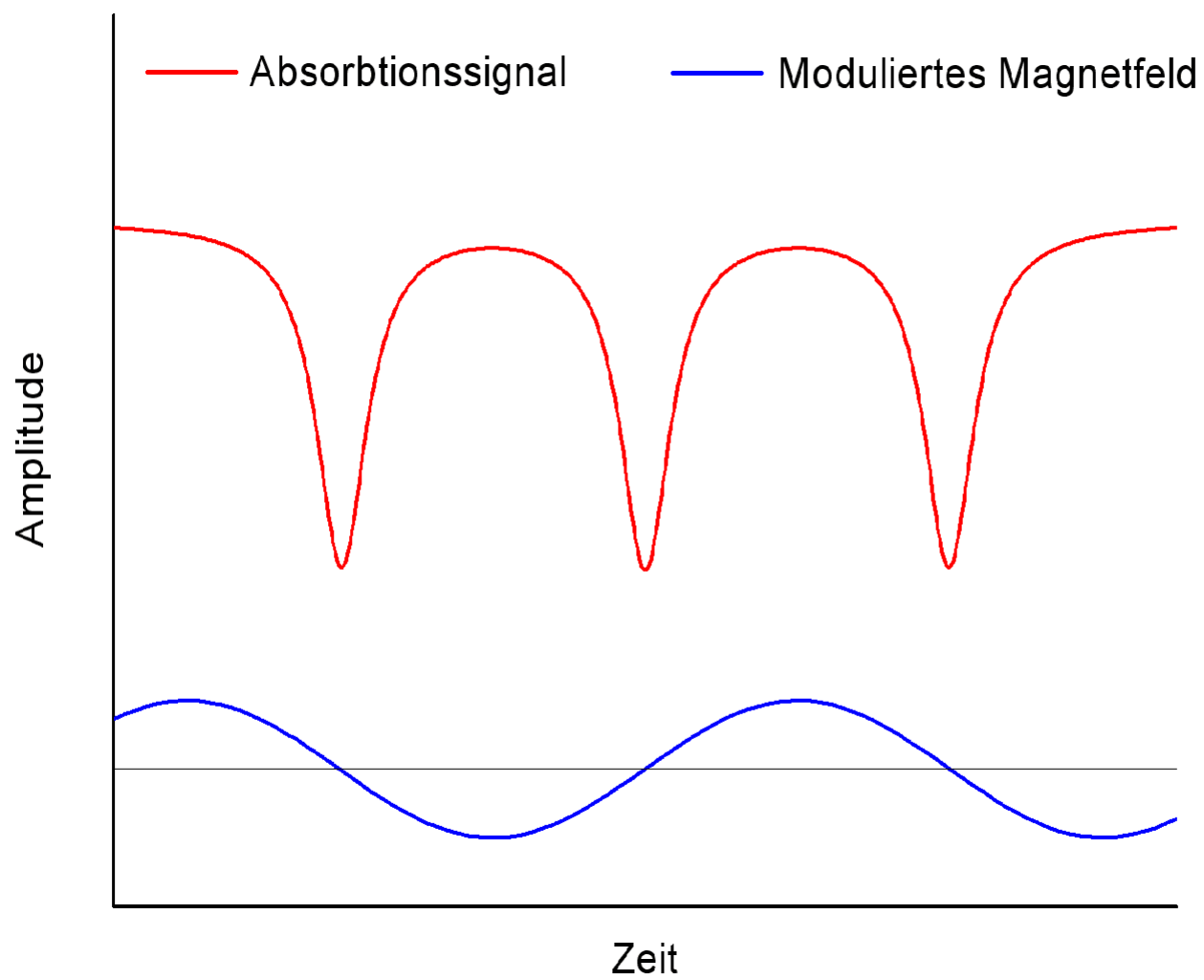


Figure 3: Expected curves (source: [ver])

To get a better result for hydrogen, we use the lock-in method: a sawtooth voltage is applied as modulation, overlapped by a sine voltage with much lower amplitude and much higher frequency. The differences between the zero of the derived absorption curve and the sine-modulated sawtooth signal in time Δt were measured for different frequencies. By using a linear fit, the resonance frequency could be determined (that's the frequency at $\Delta t = 0s$). The setup and the expected curves look the following:

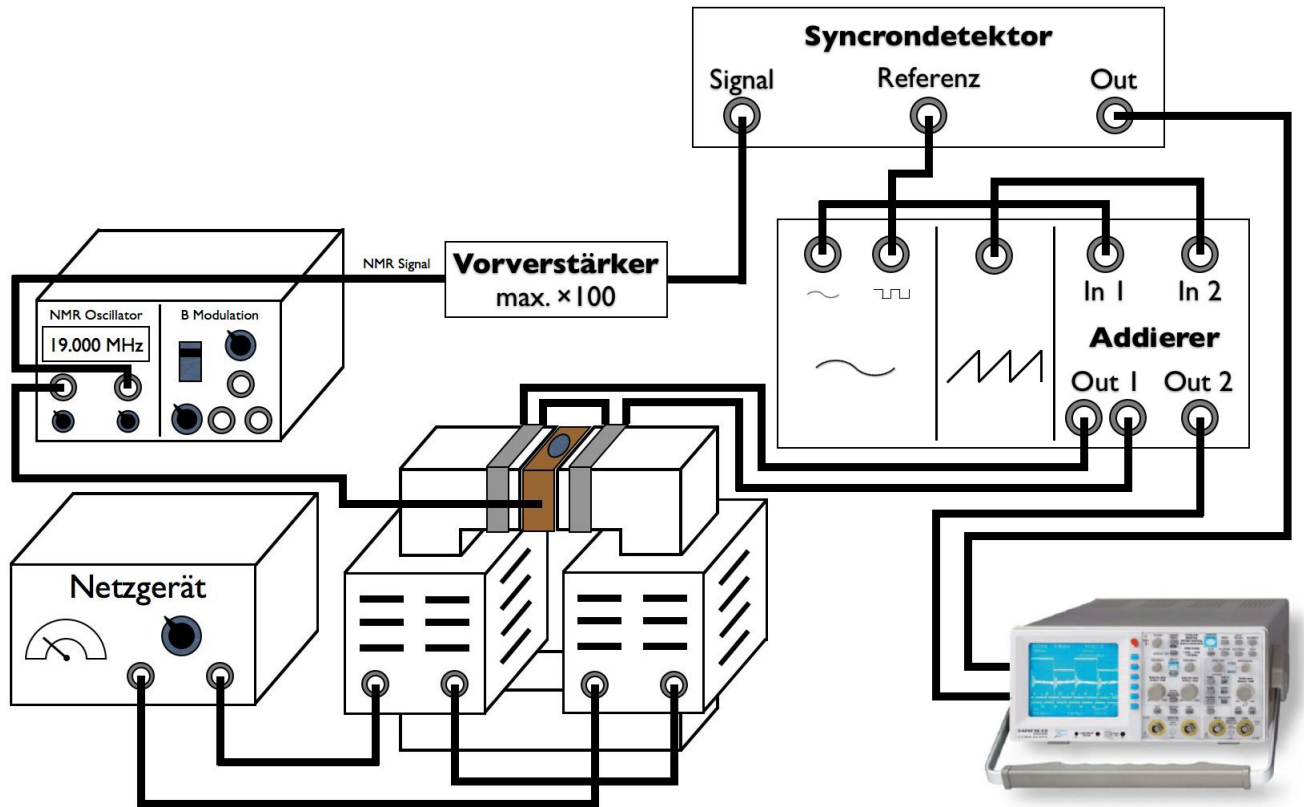


Figure 4: Lock-in method (source: [ver])

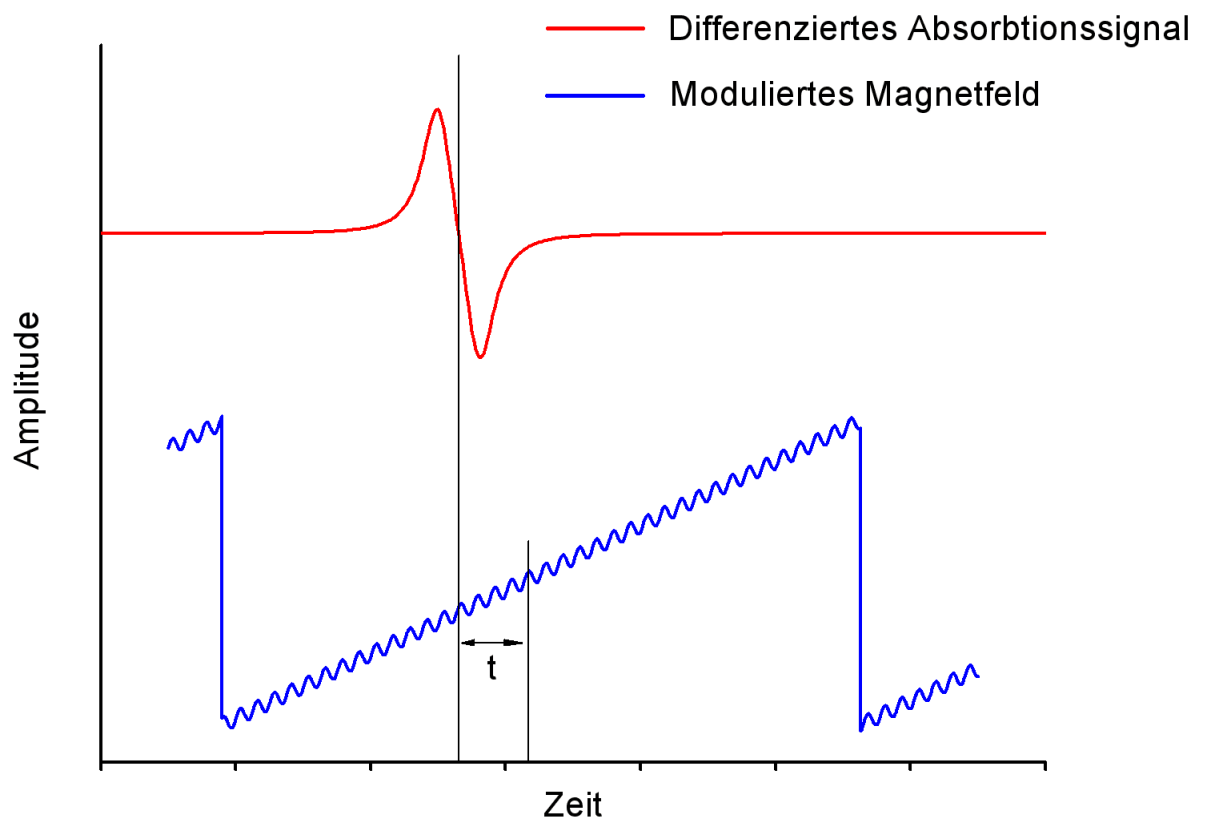


Figure 5: Expected curves for the lock-in method (source: [ver])

4 Analysis

4.1 Homogeneity-measurement of the magnetic field

To determine the homogeneity of the magnetic field we used a Hall-sensor. As you can see in the diagram below (figure 6), a homogeneous field is determined between the two coils which were used to modulate the magnetic field. The error of the depth depends on our accuracy to read the scale attached to the Hall-sensor.

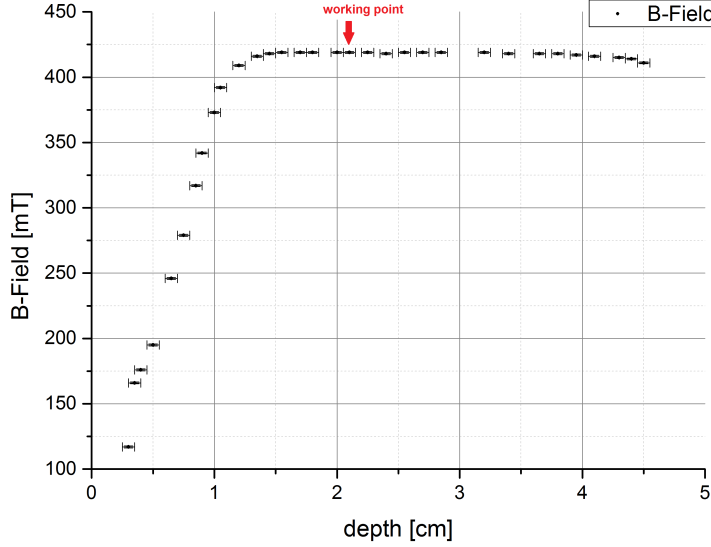


Figure 6: Diagram of the homogeneity measurement of the magnetic field

To determine our uncertainty of the B-field we did an extra measurement. The B-field depends on the voltage on the big coils (as can be seen in the realization section above), so we measured the B-field at the same position and the same voltage multiple times by readjusting the voltage again every time. That measurement is shown in the appendix. Out of the statistics of that measurement, we got a standard deviation for the B-field of $s_B = 0,8mT$.

We decided to use a depth of $d = 2,10cm$ as our working point so we can guarantee that the samples are in the homogeneous magnetic field.

4.2 Nuclear magnetic moment of ^{19}F

We measured the resonance frequency as it is described in the 'realization' section. To the given time the signal looked as can be seen in figure 7. With that settings we measured a frequency for ^{19}F of:

$$\nu_F = 16,61 \pm 0,01 \text{ MHz}$$

To estimate the uncertainty s_{ν_F} we varied the frequency to see where we can see a difference on the oscilloscope.

The nuclear g factor can be calculated by:

$$\nu = \frac{\gamma B}{2\pi} \Rightarrow \gamma = \frac{2\pi\nu}{B}$$

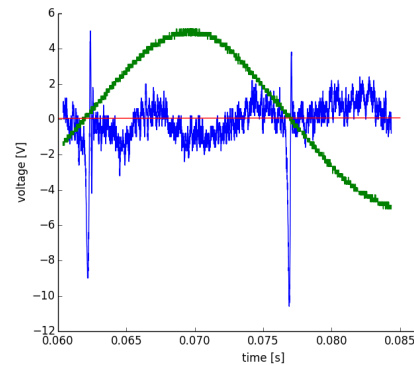


Figure 7: Signal at our measured resonance frequency with ^{19}F . To see the peaks in the absorption curve we amplified it by a 100 times.

$$\frac{g_F \mu_K}{\hbar} = \frac{2\pi\nu}{b}$$

$$\Leftrightarrow g_F = \frac{h\nu}{\mu_K B} = \frac{4\pi\nu m_p}{eB}.$$

Its uncertainty can be calculated as follows:

$$s_{g_F} = \sqrt{\left(\frac{\partial g_F}{\partial B}\right)^2 s_B^2 + \left(\frac{\partial g_F}{\partial \nu}\right)^2 s_\nu^2}$$

So with:

$m_p = 1,67262158 \cdot 10^{-27} kg$ as the mass of the proton and

$e = 1,602176462 \cdot 10^{-19} C$ as the elementary charge,

we get with our magnetic field of $B = 419,0 \pm 0,8 mT$:

$$g_F = 5,20 \pm 0,01$$

With that result, we can calculate the magnetic moment of ^{19}F . By using the formula which is given in the description:

$$\mu_K = \frac{h\nu}{g_F B}$$

To calculate the uncertainty of our magnetic moment we use Gaussian propagation:

$$s_{\mu_K} = \sqrt{\left(\frac{\partial \mu_K}{\partial B}\right)^2 s_B^2 + \left(\frac{\partial \mu_K}{\partial \nu}\right)^2 s_\nu^2}$$

This leads to a value of:

$$\Rightarrow \mu_K = (5,05 \pm 0,01) \cdot 10^{-27} \frac{J}{T}$$

Our measured value involves the literature value, which is given by

$$\mu_{K,Lit} = \frac{e \cdot \hbar}{2m_p} = 5,05 \cdot 10^{-27} \frac{J}{T}$$

4.3 Determination of the gyromagnetic ratios

Hydrogen

For hydrogen, we measured the frequency and its error the same way as described for fluorine. Here we got a resonance frequency of:

$$\nu_H = (17,62 \pm 0,01) MHz$$

We could now calculate the gyromagnetic ratio with that frequency:

$$\gamma_1 = \frac{2\pi\nu_R}{B}$$

and the uncertainty using

$$s_{\gamma_H} = \sqrt{\left(\frac{\partial \gamma_1}{\partial B}\right)^2 s_B^2 + \left(\frac{\partial \gamma_H}{\partial \nu}\right)^2 s_\nu^2}$$

$$\Rightarrow \gamma_H = (2,643 \pm 0,005) \cdot 10^8 s^{-1} \cdot T^{-1}$$

The literature value for hydrogen is $\gamma_{H,Lit} = 2,675 \cdot 10^8 s^{-1} \cdot T^{-1}$ (source: [NIST]). As one can see our value does not fit the literature value within its limits of accuracy. Further discussion can be found in the part 'Conclusion'.

Glycol

The calculation for the gyromagnetic ratio of glycol is analogue to the calculation for hydrogen. Our resonance frequency here is:

$$\nu_{glycol} = (17,65 \pm 0,01) MHz$$

So we get a gyromagnetic ratio of:

$$\gamma_{glycol} = (2,647 \pm 0,005) \cdot 10^8 \text{ s}^{-1} \cdot T^{-1}$$

Again, this does not equal the literature value $\gamma_{Gl,Lit} = 2,675 \cdot 10^8 \text{ s}^{-1} \cdot T^{-1}$. Further discussion can be found in the chapter "Conclusion".

4.4 Determination of the Proton Resonance Frequency Using the Lock-in Method

As already discussed in the "Theoretical Background" chapter, to determine the resonance frequency of a proton in hydrogen using the lock-in method, the zero passages of the sine-overlapped sawtooth voltage and the derived absorption curve had to be measured. The time difference of these had to be determined for different frequencies in order to be able to do a linear fit, with which it was possible to determine the resonance frequency (that's the frequency at $\Delta t = 0s$). The frequencies for which we did a measurement can be found in the appendix: as one can see, we decided to neglect the second and third measurement as the chosen frequencies were above the resonance frequency determined in part 2 of the experiment.

We determined the zero passage of the derived absorption curve by looking at the two values around the passage. We took the time attached to the closer one and an uncertainty of $s_{t_{abs}} = 0,002s$ as there is a measurement every 0,002 seconds and there might be a deviation for the voltage measured, making it hard to determine the point neighboring the zero passage which is actually closer to 0: this is why we decided to take this uncertainty, the time between two measurements. As for the sine-overlapped sawtooth voltage it was quite hard to determine a zero passage, we decided to determine the period of the signal and add half of it onto the lower end (the start) of the signal.

The period was determined as can be seen below:

$$T = t_{top} - t_{bottom}$$

where t_{top} stands for the time attached to the maximum voltage and t_{bottom} for the time attached to the minimum voltage reached by the sine-modulated sawtooth signal. Again, we decided to use an uncertainty of $s_{t_{top}} = s_{t_{bottom}} = 0,002s$ because we don't know about what is happening between the minimum and the maximum of the signal and therefore can't decide, where the actual starting and ending points are. Therefore, the resulting uncertainty can be calculated the following way:

$$s_T = \sqrt{s_{t_{top}}^2 + s_{t_{bottom}}^2}$$

The period was determined 6 times: we would get $T = 5,251s$ in every measurement. The resulting uncertainty reduces to

$$s_{\bar{T}} = \frac{\sqrt{s_{t_{top}}^2 + s_{t_{bottom}}^2}}{\sqrt{6}},$$

whereas the period is

$$\bar{T} = \frac{1}{6} \sum_{i=1}^6 T_i = 5,251s.$$

As the uncertainty on t_{bottom} , $s_{t_{bottom}} = 0,2s$ is not independent of the uncertainty on \bar{T} and that uncertainty is smaller, we decided to neglect $s_{\bar{T}}$, when determining the uncertainty on

$$t_{0_{sawtooth}} = t_{bottom} + \bar{T},$$

making the resulting uncertainty look like the following:

$$s_{t_{0_{sawtooth}}} \approx s_{t_{bottom}}$$

A measurement can be seen below:

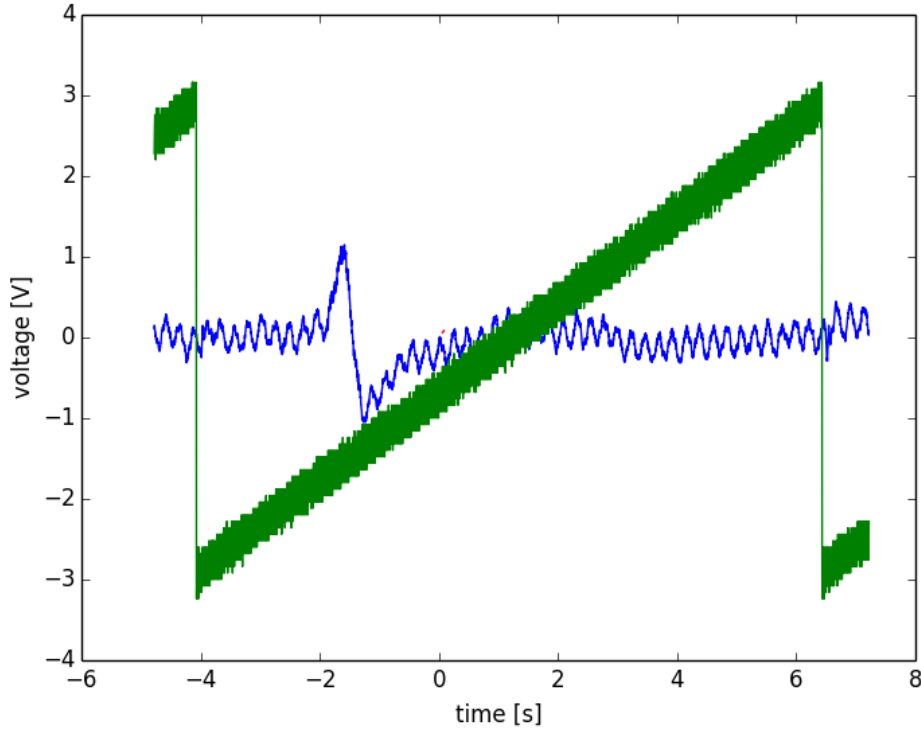


Figure 8: Sine-overlapped sawtooth signal (green) and resulting derived absorption curve (blue)

This fits the theoretical expectation, which can be found in the "Theoretical Background" chapter, well.

To determine Δt , we have to calculate the difference between the zero passages of the sine-overlapped sawtooth and the derived absorption signal:

$$\Delta t = t_{0_{sawtooth}} - t_{0_{abs}}$$

with

$$s_{\delta t} = \sqrt{s_{t_{0_{sawtooth}}}^2 + s_{t_{0_{abs}}}^2}$$

With the formula and the method explained above we got the following results:

f in MHz	s_f in MHz	Δt in s	$s_{\Delta t}$ in s
17,624	0,01	0,271	0,00283
17,618	0,01	0,285	0,00283
17,6042	0,01	2,219	0,00283
17,5998	0,01	4,195	0,00283
17,5797	0,01	4,315	0,00283
17,6019	0,01	3,475	0,00283
17,5892	0,01	4,017	0,00283

We used the displayed values to do our linear fit. The uncertainty we attach to the frequency has already been discussed. Using this values, we did the linear fit mentioned. It can be seen below:

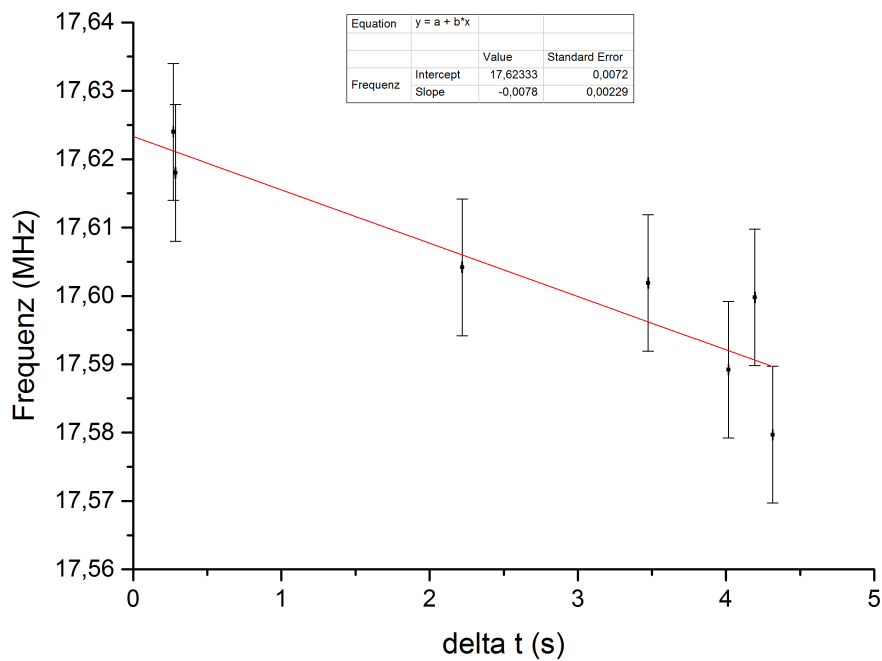


Figure 9: Linear fit used for the determination of the resonance frequency

The scattering of the measured values is quite large due to the fact that the frequency couldn't be determined very accurately.

The resonance frequency we determined using this method is $\nu = (17,623 \pm 0,007)MHz$. Using $B = (419 \pm 0,8)mT$, for the gyromagnetic ratio we get:

$$\begin{aligned}\nu &= \frac{\gamma \cdot B}{2\pi} \\ \Leftrightarrow \gamma &= \frac{\nu \cdot 2\pi}{B} \\ \Rightarrow s_\gamma &= \sqrt{\left(\frac{\partial \gamma}{\partial B}\right)^2 \cdot s_B^2 + \left(\frac{\partial \gamma}{\partial \nu}\right)^2 \cdot s_\nu^2} = \sqrt{\frac{4\pi^2 \cdot \nu^2}{B^4} \cdot s_B^2 + \frac{4\pi^2}{B^2} \cdot s_\nu^2}\end{aligned}$$

With this formula, using the lock-in method we get the following for the gyromagnetic ratio:

$$\gamma = (2,643 \pm 0,005) \cdot 10^8 \frac{1}{s \cdot T}$$

A discussion of this result can be found in the chapter "Conclusion".

5 Conclusion

5.1 Homogeneity measurement of the magnetic field

The magnetic field was found to have a zone in which the magnetic field was homogeneous with $B = (419, 0 \pm 0, 8)mT$.

5.2 Nuclear magnetic moment of ^{19}F

For the nuclear magnetic moment, we got a result of $\mu_K = (5,05 \pm 0,01) \cdot 10^{-27} \frac{J}{T}$, which equals within its limits of accuracy the literature value of $\mu_{K,Lit} = 5,05 \cdot 10^{-27} \frac{J}{T}$.

5.3 Determination of the gyromagnetic ratios

5.3.1 Hydrogen

For hydrogen, the gyromagnetic ratio was determined to be $\gamma_H = (2,643 \pm 0,005) \cdot 10^8 s^{-1} \cdot T^{-1}$

5.3.2 Glycol

For glycol, the gyromagnetic ratio was determined to be $\gamma_{glycol} = (2,647 \pm 0,005) \cdot 10^8 s^{-1} \cdot T^{-1}$.

5.4 Determination of the Proton Resonance Frequency Using the Lock-in Method

In this part of the experiment, the hydrogen sample was used once again.

With this method, the proton resonance frequency was determined to be $\nu = (17,623 \pm 0,007)MHz$.

Using this result, we got $\gamma = (2,643 \pm 0,005) \cdot 10^8 s^{-1} \cdot T^{-1}$ for the gyromagnetic ratio.

5.5 Discussion of the results

The gyromagnetic ratios we determined for hydrogen with both methods and for glycol are equal within their limits of accuracy. This means, that our measurements are consistent. Still, they do not equal within their limits of accuracy the literature value $\gamma_{H,Lit} \approx \gamma_{Gl,Lit} = 2,675 \cdot 10^8 s^{-1} \cdot T^{-1}$ (source: [NIST]; theoretically, the values should be the same, but because of the different structure there is a minor difference, which is not of any interest in this experiment, as we cannot measure that accurately). Because of this, most probably there was a systematic error in this experiment. It is possible, that there were impurities in both samples, which is unlikely as we used two different samples and get the same value within the limits of accuracy. Another possibility would be a weakening of the B-field which we doubt as we checked it between all parts of the measurement and didn't notice any change. As we touched the samples our fingerprints might have been the cause for a minor spin, causing a systematic error. This could be a possible reason as we touched both samples and the values we received are consistent.

6 References

[ver] : Experiment instruction

[NIST] : National Institute of Standards and Technology,
<http://physics.nist.gov/cgi-bin/cuu/Category?view=pdf&All+values.x=88&All+values.y=16>

7 Appendix

① gemessen ab der Kante!	Tiefe / cm	B-Feld / mT	Tiefe / cm	B-Feld / mT
	0,30 0,30	117	3,95	417
	0,40 0,40	176	4,10	416
	0,35	166	4,30	415
	0,50	195	4,40	414
	0,65	246	4,50	411
	0,75	279	$\Delta \text{Tiefe} = 0,05 \text{ cm}$	
	0,85	317	5,10	
	0,90	342	<u>Fehler</u>	
	1,00	373	Tiefe = $(2,10 \pm 0,05) \text{ cm}$	
	1,05	392	U = 8,0 V	
	1,20	409	<u>B / mT</u>	
	1,35	416	419	
	1,45	418	419	
	1,55	419	419	
	1,70	419	418	
	1,80	419	419	
	2,00	419	420	
	2,10	419	418	
	2,25	419		
	2,40	418		
	2,55	419		
	2,70	419		
	2,85	419		
	3,20	419		
	3,40	418		
	3,65	418		
	3,80	418		

Figure 10: Homogeneity-measurement of the magnetic field.

② Wasserstoff

$$f = 17,6260 \text{ MHz}$$

Fluor

$$f = 16,6106 \text{ MHz}$$

Glykol

$$f = 17,6538 \text{ MHz}$$

⑤ Lock-in

$$f = 17,6240 \text{ MHz}$$

TRC 01, 02, SCR 01

$$f = 17,6664 \text{ MHz}$$

03, 04

$$f = 17,7012 \text{ MHz}$$

05, 06

$$f = 17,6180 \text{ MHz}$$

07, 08

$$f = 17,6042 \text{ MHz}$$

09, 10

$$f = 17,5998 \text{ MHz}$$

11, 12

$$f = 17,5797 \text{ MHz}$$

13, 14

$$f = 17,5888 \text{ MHz}$$

$$f = 17,6111 \text{ MHz}$$

$$(17,6019) \text{ MHz}$$

15, 16

$$f = 17,5892 \text{ MHz}$$

17, 18

Figure 11: Measurement to determine the resonance frequency.