Nuclear Magnetic Resonance

Practical Course M
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Abstract

Nuclear magnetic resonance (NMR) techniques are widely used in physics, chemistry, and medicine for a large field of applications such as the study of molecular structures, the investigation of interactions in solids and liquids, as well as medical diagnosis via NMR tomographic image formation. Usually, separate experimental setups are applied to study absorption signals and spin echoes. This experiment is a versatile NMR setup capable of demonstrating resonance transitions, free-induction decay, as well as spin echoes. NMR absorption signals in a sample of glycerol are observed in a small permanent magnet producing a field of approximately 500 Gauss. Observing the beat frequency between the spin detector and the Larmor frequency of the spin system after excitation with short high-frequency pulses, the free-induction decay and spin echoes can be detected.

1 Preparation

Knowledge of the following terms and concepts is important to conduct the experiment.

- Nuclear Zeeman effect
  - Energy splitting in magnetic fields, magnetic quantum number
  - Magnetic moment, spin, Landé factor
  - Dia-/paramagnetism and their temperature dependence
  - Magnetization, susceptibility
  - Polarization
  - Population of energy levels
  - Absorption, spontaneous and induced emission
  - Transition probabilities, selection rules for dipole transitions
- Relaxation processes
  - Spin-lattice relaxation
  - Spin-spin relaxation
- Spin and magnetic moment
  - Spin and magnetic moment in a magnetic field
  - Effect of a time-dependent periodic perturbation caused by high frequency radiation
  - Movement of the magnetization
  - Bloch's equations

Recommended reading:

- The Feynman Lectures on Physics II, 34-1 to 35-12
- The Feynman Lectures on Physics III, 7-10
- Schumacher, *Introduction to Magnetic Resonance* (download on the website)
- Klein, *Nuclear Magnetic Resonance: Free-induction decay and spin echoes in a 0.05 T magnetic field* (download on the website)

2 Principle of operation

2.1 Proton resonance signal

The sample is surrounded by a copper coil and is located between the pole faces of a small permanent magnet. With a modulation of the magnetic field and the tuning capacitor set to the Larmor frequency of protons in the permanent magnetic field, a wiggle signal can be observed. The signal starts with a strong absorption, which is followed by a damped oscillation with increasing frequency when the Larmor frequency is increased or decreased. The frequency ω_0 of the spin detector is kept constant while the Larmor frequency ω_L, i.e. the Zeeman splitting of energy states, is varied periodically in time by a slowly modulated (15 – 30 Hz) magnetic field. The magnetic field strength of the NMR magnet changes through the periodic modulation as follows:

$$B(t) = B_0 + B_{\text{mod}} \sin(\omega_{\text{mod}} t)$$

Resonance is reached at $\omega_0 = \gamma \cdot B(t)$, i.e. at magnetic field strengths, for which the Larmor frequency coincides with the frequency of the spin detector. Under this condition the magnetic susceptibility of the sample changes

$$\chi = \chi' + i\chi'' \ .$$

With χ'' the damping of the resonant circuit coils changes and with χ' its inductance is altered. Thus at resonance, the amplitude of the resonant circuit changes due to the damping. At the same time the frequency of the resonant circuit slightly varies. At the output of the spin detector a high-frequency signal occurs with changing amplitude at the resonance. For this, the frequency of the spin detector is set to the Larmor frequency in the field B_0 as accurate as possible.

2.2 Free-induction decay

The free-induction decay (FID) is the simplest form of an NMR signal. To observe the FID, the magnetization is tilted by 90° compared to B_0 using a 90°-pulse with the Larmor frequency determined by the preceding absorption experiment. This causes the magnetization of the coil in the spin detector to precess. This movement decays with the transverse relaxation time T_2. The precession induces a voltage in the coil with the Larmor frequency $\omega_L = \gamma B_0$, which superposes the voltage of the spin detector oscillating as well with the Larmor frequency at almost constant amplitude. By tuning the spin detector to a frequency differing by a few kilohertz (2 – 4 kHz) from the transition frequency in the permanent magnetic field, a beat-frequency signal of a few kilohertz follows the high-frequency wave train and can easily be observed.

2.3 Spin echo

Spin echoes are observed when the initial high-frequency pulse is followed after a time delay ΔT by a second pulse, which tilts all contributions of the magnetization. The spin echo appears after this second pulse. The first spin echo signal was observed by Hahn with a sequence of two 90° pulses. The maximum spin echo signal is obtained with a 90°–180° sequence. If an initial 90° pulse is followed by a sequence of 180° pulses (this is called a

Carr-Purcell sequence), a series of spin echoes appears. The echo amplitude decreases with $\exp(-t/T_2)$, where T_2 is the transverse relaxation time of the spin system.
In all spin echo experiments, the duration of the first pulse must be chosen to reach a tilt of the magnetization of 90° to give a maximum FID signal. The second pulse is adjusted for zero FID, i.e. at a tilt of 180°.

2.4 Inversion recovery

An initial 180° pulse inverts the magnetization, which recovers at a rate proportional to $[1-2\exp(-t/T_1)]$. A second 90° pulse generates a FID. The FID signal starts with an amplitude, which is proportional to the (partially recovered) magnetization at the delay time ΔT between the two pulses. Hence, by changing the delay time between the inverting 180° pulse and the 90° pulse causing the FID, the longitudinal relaxation time T_1 can be measured.

3 Experimental setup

The experimental setup consists of a magnet, a sample head, and a spin detector. In addition, there are peripheral devices for field modulation, a high-frequency generator, a pulse generator, and an oscillograph. Figure 1 shows a bock diagram of the NMR setup.

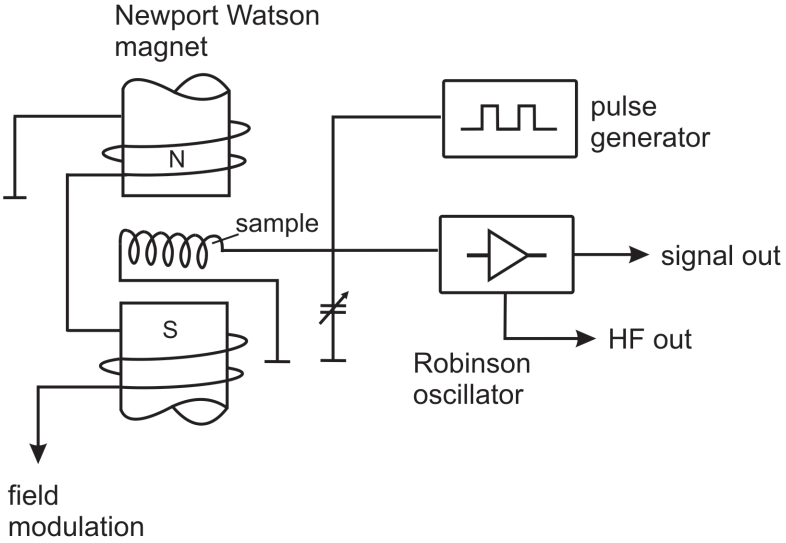

Figure 1: Block diagram of the NMR setup (from Klein, Am. J. Phys. 58 (1990))

3.1 NMR magnet

The NMR magnet used in this setup is a so-called Newport-Watson magnet consisting of two permanent magnet bars mounted between rectangular steel plates. Such a design offers a homogeneous field (with only small deviations of about 0.1%) in the open space between the pole faces over a relatively large volume (about 2 cm^3). The permanent magnetic field is about 500 Gauss. Modulation coils are wound on the permanent magnets and allow a field modulation of ± 5 Gauss with a maximum modulation voltage of 1.5 V.

Take care! The magnet is extremely sensitive to percussion and to contact with ferromagnetic materials.

The modulation of the magnetic field is given by a function generator (see Fig. 2), which is set to a modulation frequency of about 15 – 30 Hz.

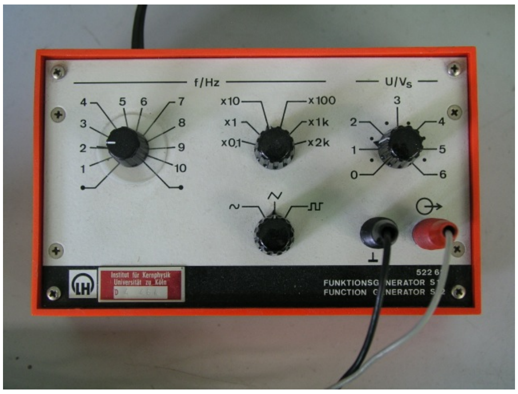

Figure 2: Overview of the control elements of the function generator used to modulate the field of the NMR-magnet.

3.2 Sample head

Located between the two pole faces of the NMR magnet is the sample head consisting of a copper coil and a capacitor (see Fig. 3), which form the resonant circuit of the spin detector. Connected in parallel is a variable capacitor, which allows to fine-tune the frequency. It is located in the housing of the spin detector. Inside the sample head, surrounded by the coil, resides a 2 cm^3 sample of glycerol.

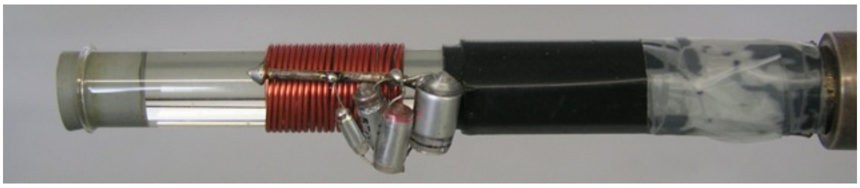

Figure 3: Sample head consisting of a tube filled with glycerol, which is surrounded by a copper coil and a capacitor forming a resonant circuit.

3.3 Spin detector/Robinson Oscillator

The resonant circuit of the sample head is connected to a low-noise feedback amplifier, called Robinson Oscillator, which is the heart of the spin detector (see Fig. 4). The coupling is conducted in such a way, that the resonant circuit oscillates with small amplitude (typically 500 mV). At the proton resonance signal, the damping of the resonant circuit changes, which causes a change of the oscillation amplitude (typically 50 μV). For detection, the high-frequency signal, which is modulated in amplitude by the resonance signal, is rectified and is weakly integrated by an RC-element. This corresponds to amplitude demodulation, with which the envelope of the high-frequency signal is obtained as a mean value. The low-frequency envelope corresponds to the amplitude signal and is disengaged from the DC component using a coupling capacitor. The signal is observed with an oscillograph and it is recorded with an analog-to-digital converter (ADC) attached to a computer. Fig. 5 shows an overview of the control elements of the spin detector.

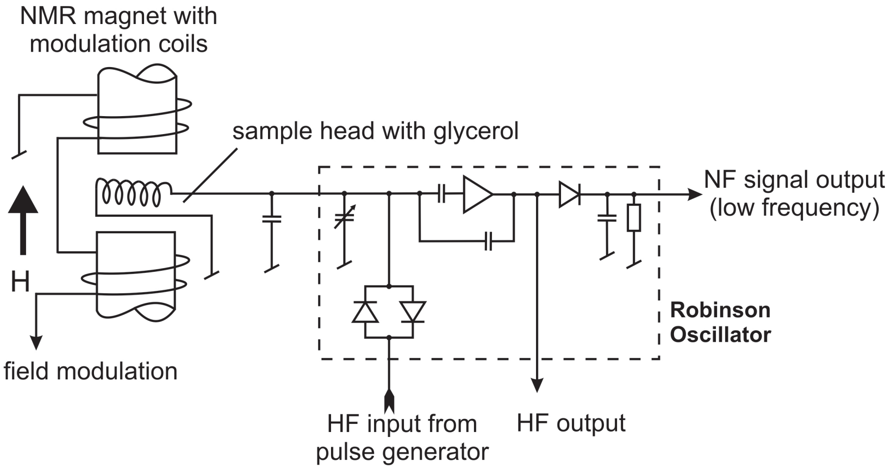

Figure 4: Schematic diagram of the spin detector (Robinson-Oscillator)

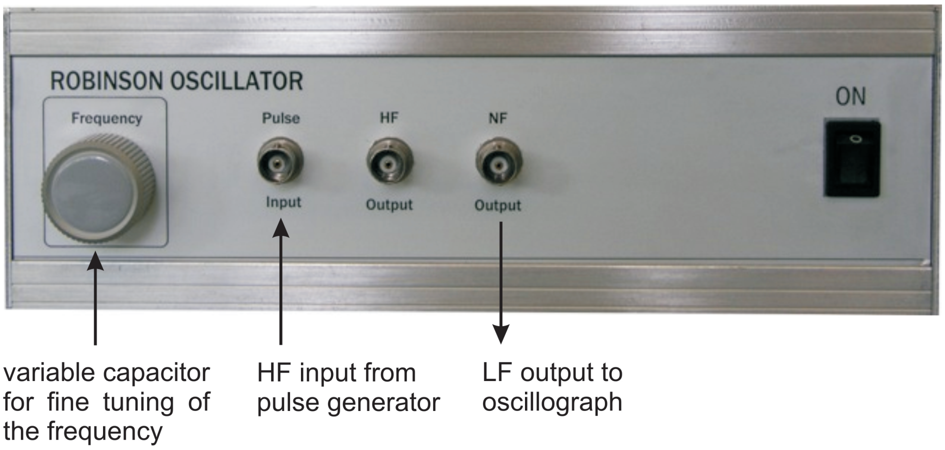

Figure 5: Overview of the control elements of the spin detector

3.4 HF-generator and pulse generator

To observe the free induction decay and spin echo signals, high-frequency pulses are needed, which are generated by a sine generator (see Fig. 6). The trigger output of the pulser is used to synchronize the oscillograph. The oscillograph is triggered with the first pulse of each pulse sequence. The following pulse sequences can be selected at the pulse generator (see Fig. 7)

- Carr-Purcell Sequence (CPS) generates a pulse with duration T_1 followed by a sequence of up to nine pulses with duration T_2. The number of T_2-pulses can be chosen with a rotary switch at the back of the housing.

- Continuous Wave (CW) generates a continuous signal output (needed to adjust the frequency of the HF-generator)

- Single Pulse (⎍) generates a single pulse (not needed in this experiment)

- Double Pulse (⎍_⎍) generates a double-pulse sequence (needed to observe spin echo signals). T_1 and T_2 define the duration of the first and the second pulse, and ΔT gives the time interval between the two pulses.

Since the output resistance of the HF-generator, which is connected to the pulse generator, would heavily attenuate the resonant circuit, the pulser has to be decoupled from the resonant circuit during the pulse pauses, in which the signal is observed. This is realized by a switch consisting of two parallel connected diodes (see Fig. 5). The low-resistant generator output is adapted to the high-resistant (R > 1 kΩ) resonant circuit of the spin detector using a matching network. In the pulse pauses, only the voltage of 500 mV of the resonant circuit reaches the diodes, and the diodes are blocking. During an HF-pulse, a voltage of up to 30 V_{ss} occurs, and each diode is passed by the respective half-wave of the HF-signal. This way, the HF-generator is connected to the resonant circuit. To prevent the sensitive amplifier connected to the resonant circuit to reach full saturation during an HF-pulse, there are two further diodes limiting the input voltage to the amplifier to 400 mV_{ss}. In spite of this limitation, the down time of the spin detector is in the order of a few milliseconds.

frequency tuning

connection to Spin-Echo pulser

Figure 6: Overview of the control elements of the HF-generator

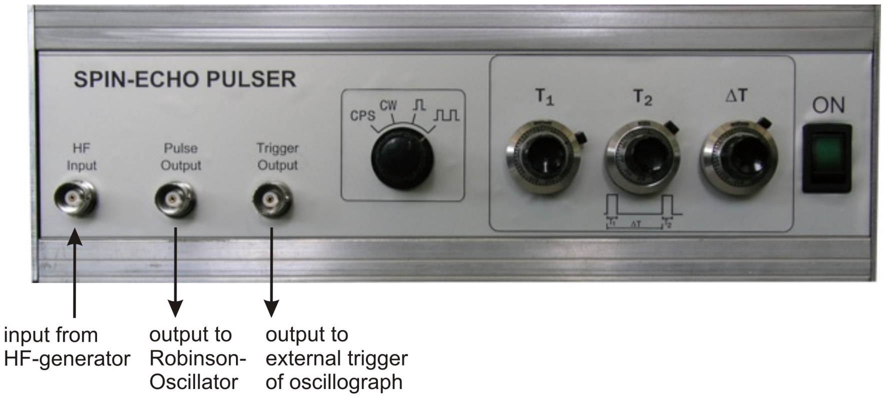

Figure 7: Overview of the control elements of the pulse generator

4 Apparatus settings for measurements

4.1 Proton resonance signal and determination of the Larmor frequency

Position the sample head as precisely as possible in the middle of the magnetic field. In order to do so, the magnet can be moved on the table relative to the sample head. You do not need to adjust the height. Set the modulation frequency of the magnetic field to about 20 Hz and the modulation amplitude to 1 V. Adjust the sensitivity of the oscillograph so that the noise of the spin detector is visible. Now vary the frequency of the spin detector to find the spin resonance signal (wiggle). Now you can fine adjust the magnet to the position, at which the resonance signal is maximal. Fine adjust the frequency to observe three equidistant wiggles. For higher resolution, you can also decrease the modulation amplitude of the magnetic field to 500 mV. The Robinson Oscillator is now set to the Larmor frequency and should not be changed for the following measurement of the FID. The modulation of the magnetic field can be turned off.

4.2 Free induction decay

In the previous section, the Robinson Oscillator was set to the Larmor frequency. Now we want to transfer this frequency to the HF-generator. To do so, set the function selector of the pulse generator to CW (continuous wave) and disconnect the connection to the pulse generator. Even without a direct connection between the pulse generator and the pulse input of the spin detector, already enough HF signal can couple over so that a beat signal can be measured at the NF output of the spin detector. Now adjust the HF-generator to give a beat signal of zero; in this case it is also oscillating with the Larmor frequency. Select the pulse duration T_1 to tilt the magnetization by 90° and observe the FID.

4.3 Spin echo

When 5 – 10 ms after the 90° pulse another pulse twice as long irradiates the spin system, then a spin echo occurs after the second pulse with the same time delay. To observe a spin echo, set the Spin-Echo Pulser to generate double pulse sequences. To optimize the spin echo signal, you should adjust the pulse duration and their frequency iteratively until the amplitude of the echo signal reaches its maximum. Due to the spin-spin relaxation the amplitude of the

spin echo signal decreases with increasing time delay ΔT.
Now select the Carr-Purcell sequence to observe the transverse relaxation time.

4.4 Inversion recovery

In contrast to the spin echo experiments, the pulse sequence used to observe inversion recovery is 180° – 90°. Set the function selector of the pulse generator to generate a double pulse and choose the pulse duration accordingly. With the first 180° pulse the magnetization is tilted by π. After the second 90° pulse the FID signal is observed. The initial amplitude of this signal is proportional to the magnetization after the delay time ΔT between the first and the second pulse, and thus it is a measure for the longitudinal relaxation time T_1.

5 Tasks

- **Proton resonance signal**
  - Observe and explain the change of the signal shape when
    - changing the position of the sample head in the magnetic field
    - changing the modulation frequency and amplitude of the magnetic field
- Calculate the polarization P of the proton spin system in a magnetic field of 500 Gauss at 20°C. What is the number of protons $n_1 - n_2$ in 2 cm^3 glycerol contributing to the signal generation?

$$P = \frac{n_1 - n_2}{n_1 + n_2}$$

- **FID**
  - Observe the free induction decay. Which parameters determine the envelope of the signal?
- **Spin echo and inversion recovery**
  - Determine the transverse relaxation time of the glycerol sample by measuring at least six double pulse sequences and two CPS for different delay times.
  - Determine the longitudinal relaxation time with eight to nine measurements for different delay times.
  - Which is the fastest method to determine T_1?