Experiment E112 - Elektronen Spin Resonanz

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Abstrakt

In this experiment, we conducted an Electron Spin Resonance (ESR) analysis on DPPH, aiming to determine the magnetic field strength of a permanent magnet positioned within the coil. Our calculations yielded a Landé factor of 1,55(5) for the DPPH sample, along with a magnetic field strength of 0,59(5) mT created by the permanent magnet at the location of the probe.

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1 Introduction

Electron Spin Resonance (ESR), also known as Electron Paramagnetic Resonance (EPR), is a powerful spectroscopic technique used to study materials with unpaired electrons. Here we used Diphenylpicrylhydrazyl (DPPH), where the unpaired electron is located at the center of the nitrogen atom [1]. This method exploits the magnetic properties of electrons, particularly the fact that electrons have intrinsic angular momentum, or "spin", which gives rise to a magnetic moment. When an external magnetic field is applied, these magnetic moments align themselves in distinct energy states, and transitions between these states can be induced and detected through the absorption of electromagnetic radiation, typically in the microwave frequency range [2]. To generate the external magnetic field, Helmholtz coils are used in this experiment. Helmholtz coils consist of two identical, parallel coils arranged at a specific distance from each other, equal to the radius of the coils. This configuration ensures an almost uniform magnetic field in the region between the coils, which is crucial for the accuracy of the ESR measurements. The foundational principle of ESR rests on the Zeeman-effect, where unpaired electron spins split into different energy levels under an applied magnetic field [3]. The resonance condition occurs when the energy difference between these levels matches the energy of the incident microwave photons. This leads to maximum absorption of the microwave energy, which can be measured by the detection systems. In this case these microwave photons are generated with a variable capacitor (RF oscillator) [1]. This resonance condition is highly sensitive to the local environment of the electron, making ESR an invaluable tool for probing the electronic structure and dynamics of paramagnetic species. Applications of ESR span across various fields of science, including chemistry, physics, biology, and materials science. In chemistry for example, ESR is utilized to investigate the electronic structure of radical species and transition metal complexes. In summary, Electron Spin Resonance is a versatile and essential tool in modern scientific research, offering detailed information about the electronic characteristics of paramagnetic substances [4].

2 Theory

In this section, our focus will be dive deeper into the underlying physics of Electron Spin Resonance (ESR), elucidating how spin interacts with an external magnetic field through the Zeeman effect. We will explore methods to manipulate these spins, particularly through torque resonance, to induce spin flips.

2.1 Zeeman level

In quantum mechanics, the spin of a particle describes its intrinsic quantum angular momentum. This angular momentum can only exist in certain eigenstates, which are described by the relationship 1

$$m_s = \{-s, -s+1, ..., s-1, s\} \tag{1}$$

where m_s describes the magnetic spin quantum number, and s represents the spin of the particle. If the particle carries charge, its self-rotation induces a magnetic moment, given by the equation:2

$$\mu_s = g m_s \mu \tag{2}$$

where g is the Landé Factor of the particle and μ is its magnetic moment. Normally, the energy states of different magnetic moments cannot be distinguished, but in an external magnetic field, they split, appearing with an energy difference 3.

$$\Delta E = \mu_s B \tag{3}$$

For an electron with spin $s = 1/2$, this leads to a split into two different energy levels, as depicted in Figure 1.

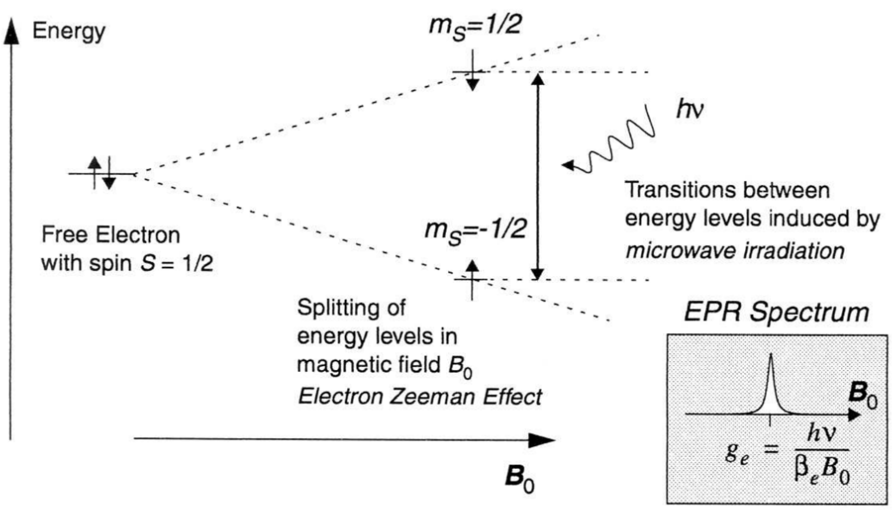

Figure 1: Illustration of the resulting Zeeman levels of a spin $s = 1/2$ particle due to an external magnetic field. Possible transitions between these two levels occur through absorption or emission of photons in the microwave spectrum [5].

To shift the energy level of the electron, it must interact with a photon that possesses this energy.

The energy of a photon is given by $E = h\nu$, where h is the Planck constant and ν is the frequency of the light. For the resonance condition (energy of the photon equal to transition energy), we obtain a relation between the magnetic moment and the frequency of the photon 4.

$$h\nu = g\mu_B B \tag{4}$$

To create photons with this frequency, we apply an alternating magnetic field. This generates photons with the same frequency as the oscillating current.

2.2 Magnetic fields

In this experiment, various magnetic fields are utilized, with the most prevalent being the one created by a Helmholtz coil. A Helmholtz coil is a special arrangement, as illustrated in Figure 2, of coils which generate a homogeneous magnetic field within them. It comprises two coils positioned at a distance R from each other, with both coils having the same radius R. The electrical current flows in the same direction through both coils, resulting in a homogeneous magnetic field given by Equation 5.

$$B_H = \left(\frac{4}{5}\right)^{\frac{3}{2}} \frac{\mu_0 N_H I}{R_H} \tag{5}$$

Where μ_0 is the magnetic field constant, N_H represents the number of turns of the coil, I denotes the current flowing inside the coil, and R_H signifies the radius of the coils. This field is used to

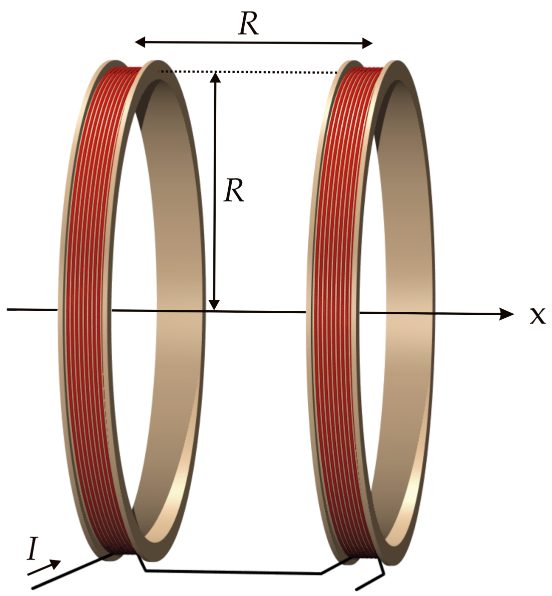

Figure 2: In this setup, two coils with radius R are placed at a distance R from each other, and the same current flows through each coil.

split the energy levels of the electron.
Later in the experiment, a second permanent magnet is placed inside the coil, creating an overlap between these two magnetic fields seen in 6.

$$\vec{B_{tot}} = \vec{B_H} + \vec{B_P} \tag{6}$$

The resulting total magnetic field can be described by Equation 7.

$$B_{tot} = \sqrt{(B_H + B_P cos(\phi))^2 + (B_P sin(\phi))^2} \tag{7}$$

Where B_H is the magnetic field created by the Helmholtz coil, B_P is the magnetic field created by the permanent magnet, and Φ is the angle between both magnetic fields. From this, we can derive Equation 8 to calculate the magnetic field of the permanent magnet.

$$B_P = -B_H cos(\phi) \pm \sqrt{B_{tot}^2 - B_H^2(1 - cos^2(\Phi))} \tag{8}$$

3 Experiment setup and execution

The following text sections illustrate the experimental setup and explain the exact data recording and execution of the experiment.

3.1 Experiment setup

Figure 3 shows the experimental setup as it was set up in the practical room, while Figure 4 shows a general sketch of the experimental setup. The Helmholtz coil pair (1 in 3, blue in 4) is operated on a current-regulated laboratory power supply (DC), which is shown in figure 5 and generates a homogeneous magnetic field. The current flowing through the Helmholtz coils is controlled and measured by the DC. Using an autotransformer and two auxiliary coils (2 in 3, green in 4), the homogeneous magnetic field of the Helmholtz coils is combined with a weak low-frequency alternating field. The ampoule containing the sample substance DPPH (4 in 3) is positioned directly within the high-frequency (RF) excitation coil (3 in 3), which forms a tunable resonant circuit with a variable capacitor (RF oscillator, 5 in 3). An electronic system continuously powers the resonant circuit and separately outputs the frequency ν_{HF} and amplitude at the measurement outputs. These measurement outputs are connected to a oscilloscope (see 6), where the RF frequency output is connected to channel 1 on the oscilloscope and the RF amplitude output is connected to channel 2. The display of the oscilloscope in figure 6 shows the amplitude of the RF oscillator exemplary. When the DC current I_{DC} is adjusted so that the high frequency ν_{HF} matches the resonance condition, the magnetic field passes through the sample's resonance twice per period T of the alternating field. In this situation, the resonant circuit loses energy (damping), causing its amplitude to briefly drop. For the second part of the experiment, a permanent magnet is also required, which can be seen in Figure 3 (number 6). However, this is not required for the first part of the experiment. [1]

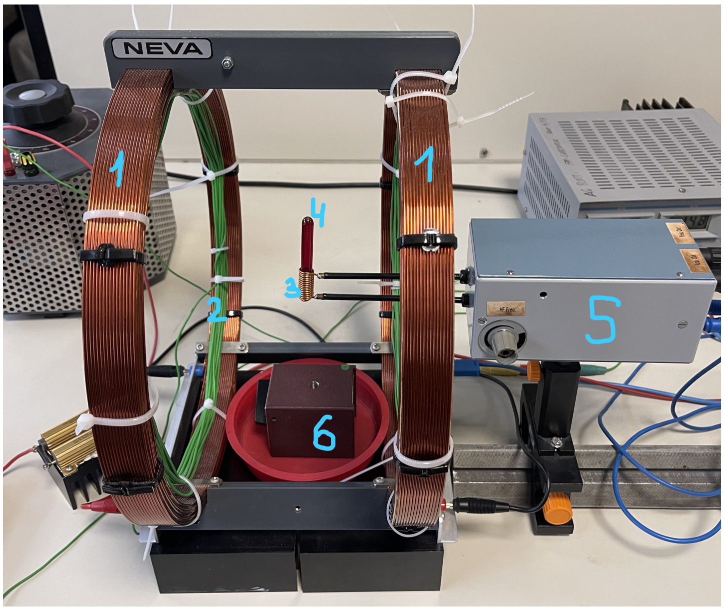

Figure 3: Experimental setup as it was set up in the practical room. (1) Helmholtz coil pair; (2) auxiliary coils; (3) high-frequency (RF) excitation coil; (4) ampoule containing the sample substance DPPH; (5) RF oscillator; (6) permanent magnet.

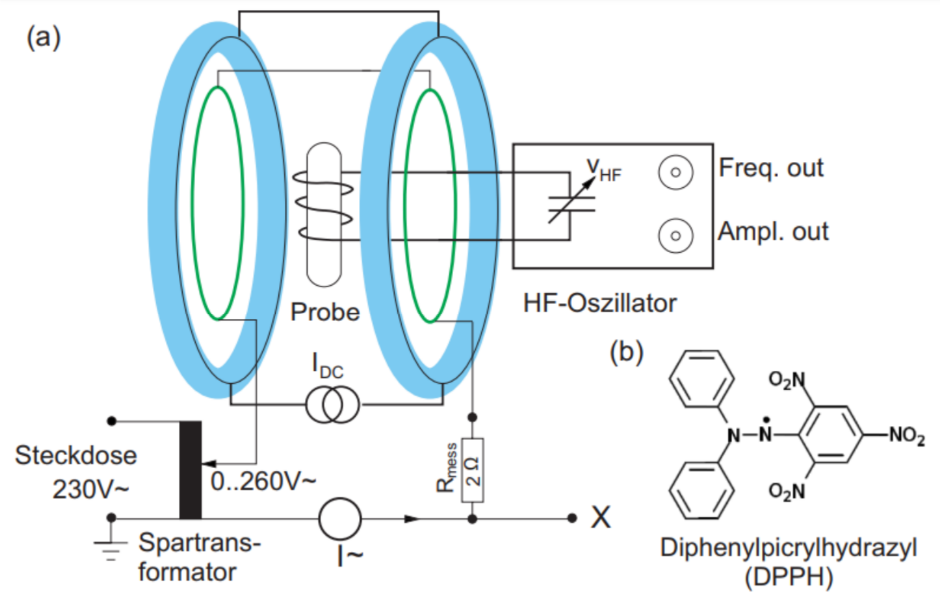

Figure 4: (a) General sketch of the experimental setup. Here is the Helmholtz coil pair in blue and the auxiliary coils in green. (b) Chemical composition of the sample. Here, the free, unpaired electron is marked as a black dot. Image source [1]

3.2 Execution

The experiment can be divided into two parts. In the first part we want to calculate the g-factor and the magnetic moment μ, which is necessary for the calculation of the magnetic field strength in order to calculate the g-factor. To do this, after setting up all devices, the current I_{DC} was varied from 1,52(3) A to 2,02(3) A in steps of a few hundredths of an ampere. The resonance frequency then had to be determined for each current. This was done by bringing the peaks

Figure 5: Current-regulated laboratory power supply (DC), which operates the Helmholtz coil pair. The current flowing through the Helmholtz coils can be controlled and measured this DC

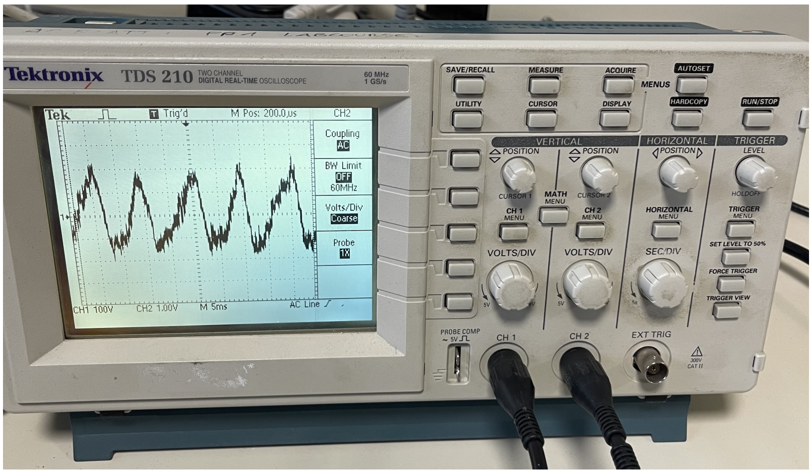

Figure 6: Oscilloscope to display the measurement. Here the RF frequency output is connected to channel 1 on the oscilloscope and the RF amplitude output is connected to channel 2.

of the RF amplitudes in channel two always to the same level to ensure that we were at the resonance frequency. Then it was possible to switch to the RF frequency on channel 1. Here, the frequency spacing between several frequency peaks was measured and then multiplied by the number of peaks to obtain the actual resonance frequency. This procedure was done for at least 11 value pairs (I_{DC}, ν_{HF}). By plotting the different frequencies as a function of the magnetic field strength, we can then calculate the g-factor. The aim of the second part of the experiment was to measure how strong the field generated by the permanent magnet is at the location of the sample. For this, the current without the permanent magnet inside the set up was set to 1,48(3) A and the resonance frequency was fixed again ($\nu_{HF} = 30{,}975\,\text{MHz}$). This frequency was always maintained. Now the permanent magnet was inserted in the center under the sample (see 3) and the current was adjusted so that resonance occurred again. This was carried out for four different positions of the permanent magnet, whereby the magnet was rotated by $\frac{\pi}{2}$ in each case. For each case the current was recorded. With this dataset we were able to calculate the magnetic field strength of the permanent magnet [1]. This calculation is shown in 4.2.

4 Experimental results

In this section, we will calculate the Landé factor of DPPH and determine the magnetic field strength that the permanent magnet exerts at the probe position.

4.1 Calculation of the Landé faktor

In the first part of the experiment, we varied the current of the Helmholtz coil to find the corresponding resonance frequency of the second coil. The current inside the coil was increased from 1,5 A to 2 A, resulting in 11 data points. Inside the Helmholtz coil, there is a secondary coil with a varying magnetic field. This causes the secondary coil to switch between resonance and non-resonance, creating two peaks in the current profile of the secondary coil. When these peaks are of equal height and equidistant from each other, we know that the magnetic field of the Helmholtz coil is in resonance. It is not easy to find a position where both peaks are of the same height, and we found that the peaks stay at the same height for a range of 0,06 A. This gives our error for the current inside the coil as 0,03 A. After finding the resonance, we can read the frequency in the oscillator by calculating the time it takes for a number of oscillations. The error describes how accurately the peaks can be determined.

After conducting the experiments, we obtained the following values (see Figure 7).
From the slope of the graph, we can calculate the Landé factor of the DPPH using Equation 4, which should be similar to that of a single electron. From this, we calculate a Landé factor of $g = 1{,}55(5)$ wich results in a magnatic moment of $\mu = 1{,}43(5) \cdot 10^{-23}$ J/T. This value is not very close to the expected value of 2 for a single electron, which is similar to DPPH, known to have a single unpaired electron at its center.

The main source of error for this value is the difficulty in precisely locating the resonance position, although this alone doesn't entirely explain the discrepancy. One possibility for the deviation in the Landé factor could be the age of the Helmholtz coil, which may not generate the expected magnetic field at a given current. Alternatively, there could have been a different material inside the probe, affecting the observed results.

4.2 Strength of a permanent magnet

In the second part of the experiment, we placed a permanent magnet inside the Helmholtz coil at different positions to determine its strength. First, we set the current to 1,48(3) A and found the resonance frequency again. This resonance frequency remained unchanged for the rest of the experiment, and we determined that the DPPH would experience a total magnetic field of $B_{\text{tot}} = 1{,}33(3)$ mT whenever it was in resonance.

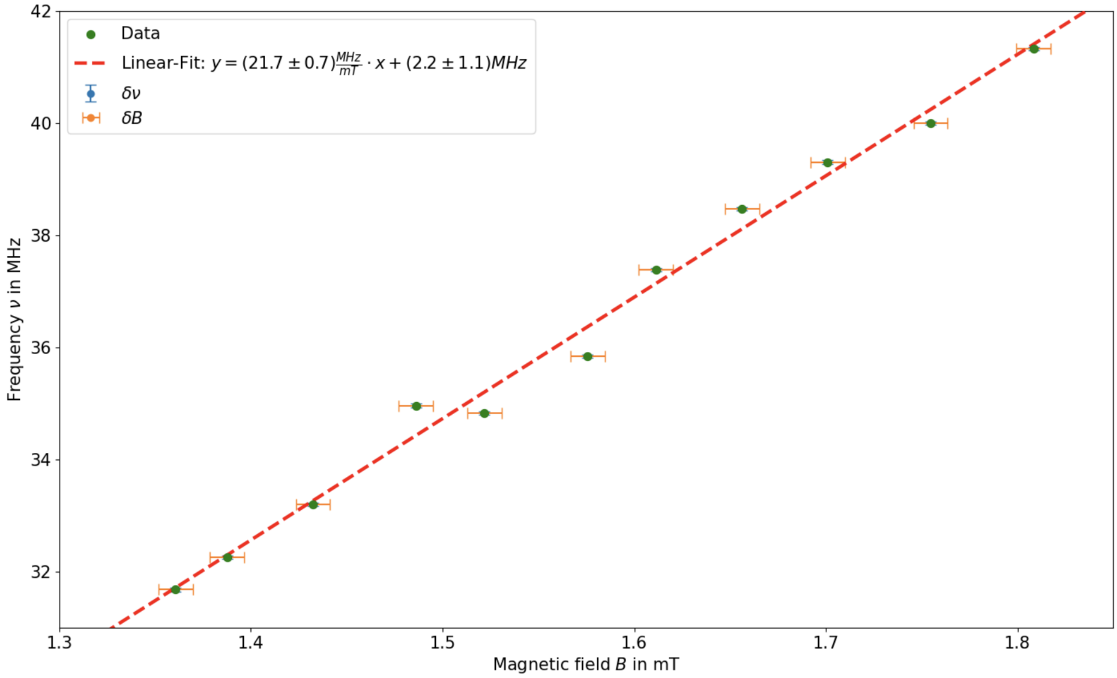

Figure 7: The graph depicts frequency ν plotted against the strength of the magnetic field B, with errors indicated by error bars, where the errors associated with the frequency $\delta\nu$ are negligibly small. A linear fit is applied to the data, characterized by the function $y = 21{,}7(7)\,\mathrm{MHz/mT} \cdot x + 2{,}2(11)\,\mathrm{MHz}$

After placing the magnet inside the coils, we observed that the magnetic field at the position of the probe changed. By adjusting the current inside the coils, we found the resonance again. This process was repeated for four different positions at the following angles to the Helmholtz coil: 0(3) °,90(3) °,180(3) °,270(3) °. The error in the placement was due to only rough alignment, where we couldn't check the exact angle of the permanent magnet and had to align them by eye. After finding the resonance of the system again in every position, we obtained the following values as shown in Table 4.2. Using Equation 8, we can calculate the strength of the magnetic field created by the permanent magnet at the position of the probe.

Table 1: The magnetic field dependency at various orientations ϕ of a permanent magnet is investigated.

I (A)	B_{Helm} (mT)	ϕ (°)	B_{perm} (mT)
0,81(3)	0,73(3)	0(3)	0,60(4)
1,33(3)	1,19(3)	90(3)	0,58(10)
2,23(3)	2,00(3)	180(3)	0,67(4)
1.37(3)	1,23(3)	270(3)	0,50(12)

Averaging over all four positions, we obtain $B_P = 0{,}59(5)\,\mathrm{mT}$ as the strength of the magnetic field created by the permanent magnet. The strength of the magnetic field of a permanent magnet is dependent on the distance to the magnet, meaning a position farther away from the magnet would result in a smaller magnetic field. It was not verified if the distance between the probe and the magnet is exactly the same for every position. This could have caused a change in the strength of the magnetic field, affecting our results.

5 Discussion

In this experiment, we delved into Electron Spin Resonance (ESR) and acquainted ourselves with its intricacies. In our initial series of measurements (chapter 4.1), we were able to ascertain the Landé factor of our sample material (DPPH) to be $g = 1.55(5)$ by varying the current and identifying the resonance frequency. This determination, however, deviates significantly from the expected value for a single electron, $g_e = 2.00231930436092(36)$[6]. Consequently, we can conclude that the assumption that DPPH closely mimics such a system does not hold. Thus, our hypothesis of comparing DPPH to a single electron in this experimental context was not validated. Moving to our subsequent series of measurements (chapter 4.2), a permanent magnet was positioned within the magnetic field generated by the Helmholtz coils and systematically oriented. This allowed us to calculate the magnetic field strength at the location of the sample to be $B_P = 0{,}59(5)\,\mathrm{mT}$.

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Erklärung

Hereby we confirm that the present report was written independently and that all necessary sources and references have been provided.

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Arbeitsaufwand

Arik Bürkle	02.05.2024
Vorbereitung:3,5h	
Versuch:2h	
Bericht:8h	
Robin Hoffmann	02.05.2024
Vorbereitung:2,5h	
Versuch:2h	
Bericht:8h	
Valentin Ertl	02.05.2024
Vorbereitung:3,5h	
Versuch:2h	
Bericht:10h	