

Electron Spin Resonance (ESR) Lab Report

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1 Introduction

Electrons abide by the quantum mechanical properties; one of their properties is spin, which is related to the magnetic moment. Classical physics suggests continuous rotation of particles, whereas the quantum mechanical interpretation of electrons suggests that momentum is quantized. This idea is represented as the spin quantum number:

$$m = \pm \frac{1}{2} \quad (1)$$

meaning only two eigenstates of spin-up ($+\frac{1}{2}$) and spin-down ($-\frac{1}{2}$) can exist.

Electron Spin Resonance (ESR) is a system of unpaired electrons in an external magnetic field introduced to a radiofrequency wave such that the exact photon energy of ΔE results in the electron transitioning from the spin-down state to the spin-up state. Quantitatively, this idea is achieved using the electron's exhibition of magnetic dipole moment μ , which is related to the spin angular momentum S via the gyromagnetic ratio γ :

$$\mu = \gamma S \quad (2)$$

Electron spin, having only two discrete values,

$$S_z = \pm \frac{\hbar}{2} \quad (3)$$

results in two distinct energy levels:

$$E = \pm \frac{1}{2} \gamma \hbar B_z \quad (4)$$

The unpaired electrons will absorb this quantized amount of energy to change their spin. This energy is produced by electromagnetic waves from an AC coil. Therefore, the energy absorbed can be related to the frequency (ν) of the electromagnetic waves:

$$\nu = \frac{1}{2\pi} \gamma B_z \quad (5)$$

The purpose of this lab is to determine the gyromagnetic ratio γ , which quantifies the response of the electron's magnetic moment to an external magnetic field B , and ultimately compute the Landé g -factor using the equation:

$$g = \frac{\gamma}{e/2m} \quad (6)$$

Physically, γ represents the intrinsic coupling between the magnetic field and the electron's spin, and g captures the deviations from the classical prediction, serving as a correction factor.

2 Materials and Methods

The purpose of this experiment is to measure the Landé g -factor using Electron Spin Resonance (ESR) by finding the resonance condition of the sample with unpaired electrons in a magnetic field. In this lab, only directly measured quantities are current (using an ammeter) and resonance frequency (using a frequency counter). The magnetic field strength B is determined using the measured current and Equation 7. After that, the g factor will be computed using the measured frequency and the resonance condition equation 5 and 6.

2.1 Materials

Refer to Figure 1 in the lab manual for a detailed diagram of the setup. The materials required include:

- **ESR Basic Unit and Adapter:** Controls RF frequency generation and magnetic field application.

- **Diphenylpicrylhydrazyl (DPPH) Sample:** A free radical source placed inside the copper coil.
- **Copper Coils:** Three sizes to adjust the RF frequency range.
- **Helmholtz Coils:** Generate a uniform magnetic field.
- **Oscilloscope and Frequency Counter:** Measure RF signal absorption and resonance frequency.
- **Ammeter:** Monitors current through the Helmholtz coils.
- **Power Supplies:** Provide voltage to the ESR units and Helmholtz coils.

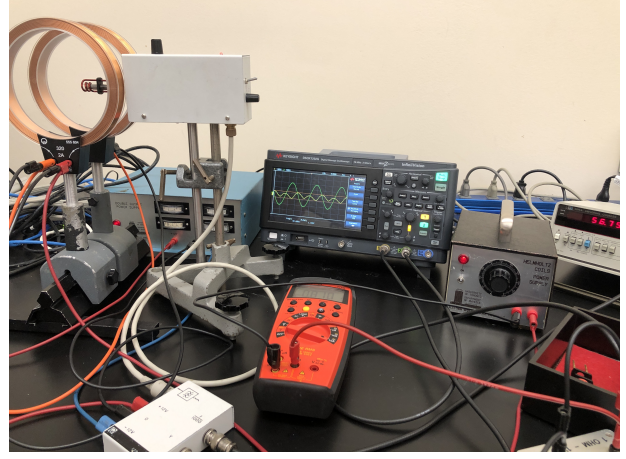


Figure 1: Experimental Setup with periodic dips visible on the oscilloscope.

2.2 Methods

1. **Setup:** Connect the Helmholtz coils in parallel, then place the copper coil of the DPPH sample's perpendicular to the external field B_z . Link the ESR Basic Unit and Adapter like Figure 1.
2. **Power Connection:** Connect power supplies to the Helmholtz coils and ESR unit, keeping current under 1A.
3. **Frequency and Field Adjustment:** Use the knob on the ESR Basic Unit to adjust RF field strength and frequency.
4. **Data Collection:** Find the combination of the frequency and current that gives clean, periodic resonance dip signal on the oscilloscope.
5. **Measurement:** Record the resonance frequency using the frequency counter and the current from the ammeter. Compute B_z using:

$$B = \left(\frac{4}{5}\right)^{3/2} \frac{\mu_0 n I}{R} \quad (7)$$

and compute γ using:

$$\gamma = \frac{2\pi\nu}{B_z} \quad (8)$$

6. **Repetition:** Repeat for different copper coils, collecting at least five data points per coil to ensure statistical reliability.

It is important to keep Helmholtz coil parallel, and ensure the current does not exceed 1 A to prevent equipment damage.

3 Data and Analysis

For each copper coil, the associated frequency and current that resulted in resonance dips were recorded. The raw data is given in the appendix. Only the low and middle frequency coils were measured because even after lab assistance, the high frequency coil produced no resonance. For each current, the associated magnetic field B was calculated using (7). The magnetic field was then plotted against the frequency.

The fit in from Figure 2 has a $R^2 = 0.985$ and $\chi_v^2 = 1.46$. The R^2 value is approximately 1, and therefore the data variation is well described by the best-fit line. The χ_v^2 value is larger than the ideal value of 1. There is an outlier in the data, which results in the linear model not fully explaining the relationship and therefore resulting in a higher χ_v^2 value.

The fit in from Figure 3 has a $R^2 = 0.913$ and $\chi_v^2 = 2.14$. The R^2 value is approximately 1, and therefore the data variation is well described by the best-fit line. The χ_v^2 value is larger than the ideal value of 1. This likely suggests additional experimental or systematic errors.

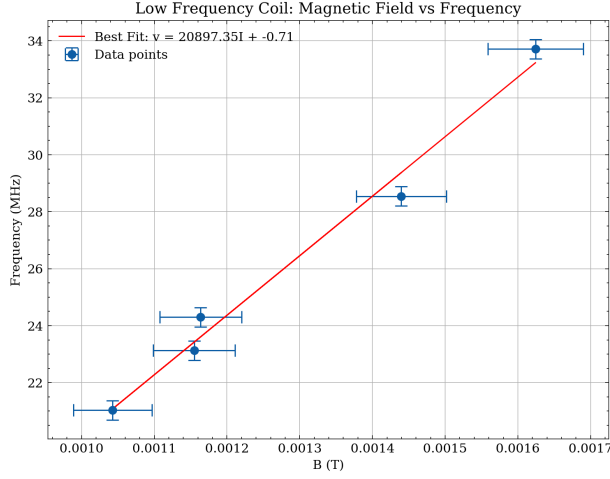


Figure 2: Plot of magnetic field (T) and frequency (MHz) for the low frequency 20-30 MHz coil. Uncertainty is indicated by the blue bars. The line of best fit from Scipy's curve_fit function [x] is given by $\nu = (20897.35 \pm 1473.78) \frac{\text{MHz}}{\text{T}} \times B + (-0.71 \pm 1.92) \text{ MHz}$.

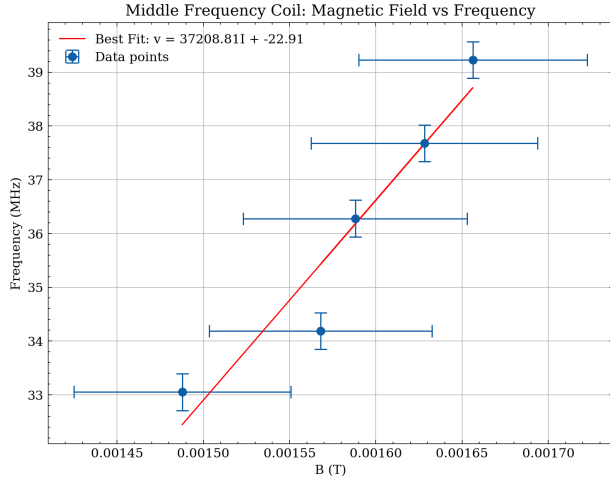


Figure 3: Plot of magnetic field (T) and frequency (MHz) for the middle frequency 30-40 MHz coil. The line of best fit from Scipy's curve_fit function [3] is given by $\nu = (37208.81 \pm 6602.24) \frac{\text{MHz}}{\text{T}} \times B + (-22.91 \pm 10.48) \text{ MHz}$.

4 Discussion

To find the g from the given plots, the following relationship can be used by combining 6 and 8:

$$g = \frac{4\pi sm}{e} \quad (9)$$

where $s = \frac{\nu}{B}$ is the slope from the magnetic field and frequency plot. The error is propagated from the slope uncertainty:

$$\Delta g = \frac{\partial}{\partial s} g \Delta s = \frac{4\pi m \Delta s}{e} \quad (10)$$

For the low frequency coil, $g = 1.49 \pm 0.11$. For the high frequency coil $g = 2.66 \pm 0.47$. These values fail to agree with each other within uncertainty and the expected g factor of 2 [4]. Disturbances to the assumed uniform magnetic field can also have affects. An overestimated B will result in a smaller g , while an underestimated B results in a larger g . Interference from other magnetic materials or EM waves, or accurate distancing of the Helmholtz coils to achieve a uniform field can explain this. The fact one g is overestimated and the other is underestimated suggests other experimental design errors. If the sample is contaminated in any way with magnetic impurities. In addition, the frequency observed fluctuated very easily, reaching nearly 1000 MHz from a 20-30 MHz coil, suggesting damaged equipment and potentially inaccurate frequency values.

Uncertainties

The uncertainty in the magnetic field strength comes from measurable uncertainty in the current and radius of the coils. The uncertainty in the current is given from two factors: firstly the accuracy of the multimeter (2% of the reading as per [2], and secondly half the range of current values where one dip is observed on the oscilloscope at a fixed frequency. This range was found by adjusting the voltage on the Helmholtz power supply and finding the maximum and minimum current where one dip in voltage was measurable. The uncertainty in current for both coils is $\pm 0.00825 \text{ MHz}$. These uncertainties are propagated according to:

$$\Delta B_i = \sqrt{\left(\frac{B_i}{\Delta R} \cdot R\right)^2 + \left(\frac{B_i}{i} \cdot \Delta i\right)^2} \quad (11)$$

where B_i is the magnetic field given a current value i , and R is the radius of the Helmholtz coils, with error given by ± 0.01 , the precision of the ruler used. The uncertainties in current are quite large, as seen by the error bars in Figure 3. Using more precise equipment to reduce uncertainty in ammeter reading could reduce this uncertainty.

4.1 Uncertainty in Merging Resonance Dips

The uncertainty in the frequency is also given by the half the range of frequency values where a single dip is visible on the oscilloscope, at a given current. For the low frequency coil, this was found to be ± 0.34 MHz and ± 0.35 MHz for the middle frequency coil.

4.2 Qualitative Analysis of Resonance Dips

There is uncertainty in when the resonant dip occurs on the oscilloscope since it is visible for a range of current and frequency values as described above. Ideally, the resonance is a very sharp peak, but is found to be more gaussian.

The width of resonant peak, is related to the uniformity of the magnetic field B . With a perfect setup of the Helmholtz coils, and sample concentrated at one point, the electrons all experience the same B_z , and are therefore excited by the same frequency by (4). Rather, different electrons absorb different frequencies, which result in a variety a range of magnetic fields where resonance is measured. Other inconsistencies that result in varying frequencies exciting electrons can also explain the width of the dip.

Reducing the width of the resonant peak would also help reduce the uncertainty in the current and therefore the magnetic field, which as stated before, is significantly large.

4.3 Asymmetry of the ESR Signal

The asymmetry of the ESR signal about the maximum current point, which is the resonance dip, can be attributed to several factors, including experimental errors. However, based on substantial research, the most likely reason for asymmetry is related to spin relaxation dynamics. Since the x-axis of the oscilloscope represents time, the process of electrons

absorbing and releasing energy is time-dependent. It is characterized by two different relaxation times: T_1 (Spin-Lattice Relaxation Time), which describes how quickly the system transfers energy from the spins to the surrounding lattice, and T_2 (Spin-Spin Relaxation Time), which captures how long the spin system maintains phase coherence before interactions cause dephasing [5]. The asymmetry in the ESR signal can arise from differing rates of energy absorption (T_1) and energy loss due to dephasing (T_2).

Experimentally, asymmetry, as well as the general noise in the signal, can be caused by misalignment of the Helmholtz coils, improper sample positioning, and instability in the frequency counter, all of which were observed to be very sensitive during the lab.

4.4 Linearity Across Different Frequencies

Equation (7) predicts that the resonance frequency ν and magnetic field B have a linear relationship. Figures 2 and 3, which plot ν vs B , show a reasonably linear trend, but the precision of linearity differs across different frequency ranges.

For the low-frequency coil (20–30 MHz), $R^2 = 0.985$, suggesting that the data points follow the linear trend. The value of $\chi_v^2 = 1.46$, which is slightly above the ideal value of 1, indicates a small deviation. Overall, the equation holds linearity well in this range. One notable thing is the data point at 33.71 MHz, which is above the suggested 20–30 MHz range, yet still follows the linear trend.

On the other hand, for the middle-frequency coil (30–40 MHz), $R^2 = 0.913$, which is lower than that of the low-frequency coil, indicates a greater deviation from linearity. Additionally, $\chi_v^2 = 2.14$, which is more than twice the ideal value of 1, suggests increasing errors in resonance. Overall, the graph still demonstrates a linear relationship, with all error bars touching the best-fit line, but it starts to deviate slightly.

For the high-frequency range (40–60 MHz), no measurable data was obtained, as discussed earlier. This is likely due to significant distortion in the signal, confirming that the relationship between ν and B is certainly not linear in this range.

4.5 Equipment Design

The frequency knob attach to the AC coil is likely a variable LC circuit. By increasing capacitance, more charge can be stored, resulting in slower oscillations and therefore lower frequency. Similarly, an inductor opposes sudden changes in current, again lowering the frequency. The basic unit as a wholes adjust the electromagnetic field created, likely with the help of a circuit connected to the AC coil.

The basic unit needs to output some measurable value related to the amount of energy absorbed by the sample as electrons change their spin. The output of y converts this absorbed energy in a measurable voltage that can be viewed on the oscilloscope.

5 Appendix

Current (A)	Frequency (MHz)
0.405	33.71
0.2902	24.30
0.260	21.03
0.288	23.13
0.359	28.54

Table 1: Measured Current and Frequency Data for the Low Frequency Coil

Current (A)	Frequency (MHz)
0.406	37.68
0.396	36.28
0.391	34.19
0.413	39.23
0.371	33.05

Table 2: Measured Current and Frequency Data for the Middle Frequency Coil

References

- [1] Electron Spin Resonance Manual https://www.physics.utoronto.ca/~phy224_324/LabManuals/ElectronSpinResonance.pdf#page=4.73

- [2] Multimeter Spec Sheet https://res.cloudinary.com/iwh/image/upload/q_auto,g_center/assets/1/26/Documents/Wavetek/38xrdatasheet.pdf
- [3] Scipy curve_fit https://docs.scipy.org/doc/scipy/reference/generated/scipy.optimize.curve_fit.html#curve-fit
- [4] Electron Paramagnetic Resonance https://en.wikipedia.org/wiki/Electron_paramagnetic_resonance
- [5] Spin Relaxation and ESR Signal Asymmetry <https://pmc.ncbi.nlm.nih.gov/articles/PMC9318273/>