Electron Spin Resonance

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Contents

1 Tasks

1. Determine the electron g factor and ratio $\frac{B}{\nu}$ using the DPPH sample.
2. Estimate the width of the ESR absorption line.

For background theory, see Appendix A. To jump to the analysis, see Section 4.

2 Measurement Instruments and Samples

2.1 Equipment

The main pieces of equipment used in the experiment are:

- A DPPH (2,2-diphenyl-1-picrylhydrazyl) sample and regenerative oscillator used to study the ESR signal.
- A power supply powering the main inductor used to generate the magnetic field B applied to the DPPH sample.
- A function generator controlling the current supplied to the main inductor.
- Secondary inductors used to slightly modulate the magnetic field about the resonance value B_0, which makes it easier to measure the ESR signal.
- A lock-in amplifier to detect the ESR signal. The amplifier is tuned to the modulation frequency of the magnetic field and only detects signals in a small band around the modulation frequency, improving signal-to-noise ratio.
- An oscilloscope to view the regenerative oscillator and lock-in amplifier's signals.

2.2 Overview of Procedure

1. Determine the regenerative oscillator's frequency using an oscilloscope—use the `FREQUENCY` function in `Measure` mode. Expect about 80 MHz.
2. Measure the large inductor's dimensions—you'll need enough information (e.g. number of coils, diagonal distance...) to later calculate the magnetic field inside.
3. Measure the dependence of lock-in amplifier signal U on current I through the large inductor at three different oscillation frequencies.

   Change the current through the large inductor using the function generator using the left-most `Coarse` dial on the `TRIPLE POWER SUPPLY` panel.

   Change oscillator frequency using the oscillator's `Frequency` dial.

   Measure the lock-in amplifier's signal using the oscilloscope's `AVERAGE` function in `MEASURE` mode.

3 Data

An overview of the data in the experiment:

- Independent variable: current I supplied to the main inductor, measured in mA using the function generator.
- Dependent variable: voltage U, measured in mV, of the signal outputted by the lock-in amplifier, which is in turn proportional to the strength of the ESR signal from the DPPH sample. U is measured using the oscilloscope's `MEASURE` mode. I used a four-sample average, and took U to be the difference between the maximum and minimum observed value over an observation period of about twenty seconds.
- Regenerative oscillator frequency ω_0, measured in MHz using the oscilloscope's `MEASURE` mode. The $U(I)$ relationship is measured for three values of ω_0.
- Additional geometric data: inductor length, diameter, and distance between inner and outer radius, measured in cm using a ruler and calipers.

4 Analysis

4.1 Converting from Current to Magnetic Field

I first calculated the inductor's diagonal distance d using

$$d = \sqrt{l^2 + (\Delta y)^2} = \sqrt{(12.2\,\mathrm{cm})^2 + (12.8\,\mathrm{cm})^2} = 17.7\,\mathrm{cm}$$

where l is the inductor's length (along the longitudinal axis) and $\Delta y = D - \Delta a$ is vertical distance between coil's upper and lower midpoints of the coils (measured in a cross-sectional plane perpendicular to the longitudinal axis.)
I then converted current I through the inductor to magnetic field B along the longitudinal axis with

$$B = N\frac{\mu_0 I}{d}$$

where $N = 1557$ is the number of coils and d is the inductor's diagonal length.

4.2 Absorption Line Derivative

Figure 1 shows the $U(B)$ signal, which corresponds to the absorption line's derivative. I estimated the width of the absorption line from the horizontal distance on the B axis between the derivative's extrema, shown in Table 1.

ω_0 [MHz]	B_{min} [mT]	B_{max} [mT]	ΔB [mT]	B_0 [mT]
73.0	2.585	2.720	0.135	2.65
80.5	2.845	2.985	0.140	2.91
86.0	3.070	3.205	0.135	3.13

Table 1: The $U(B)$ signal's extrema for three values of resonance frequency ω_0. ΔB and B_0 denote the width of the absorption line and resonance magnetic field, respectively. The B_{min} and B_{max} points carry an uncertainty of 0.01 mT.

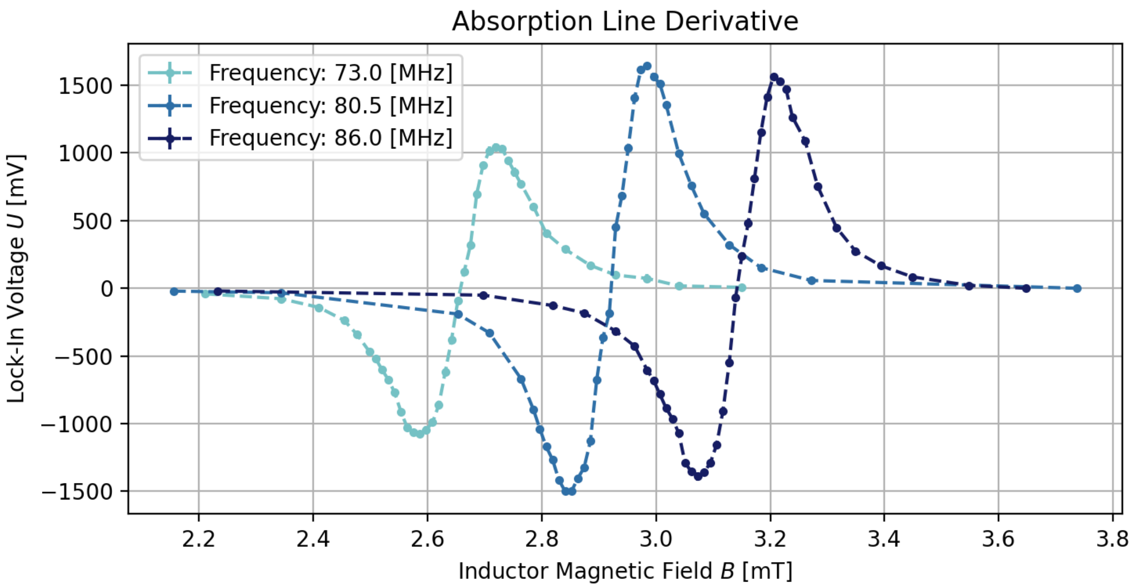

Figure 1: Lock-in amplifier voltage U versus inductor magnetic field B for three different resonance frequencies. The $U(B)$ signal corresponds to the absorption line's derivative, and $U(B)$'s intersection with the B axis is the resonance field B_0.

4.3 Electron g Factor

I first found the resonance magnetic field value B_0 by interpolating a line between the $B(U)$ signal's extrema and finding the line's intersection with the B axis according to

$$B_0 = B_{\max} - \frac{U_{\max}}{k} \qquad \text{where} \qquad k = \frac{B_{\max} - B_{\min}}{U_{\max} - U_{\min}}$$

The interpolation approach seemed more thorough than just visually estimating the $U(B)$ signal's intersection with the B axis. I then found the electron g factor using

$$g = \frac{h\omega_0}{\mu_B B_0}$$

where B_0 is the resonance magnetic field and ω_0 is the resonance frequency.

Frequency ω_0 [MHz]	Ratio ω_0/B_0 [GHz T^{-1}]	Electron g factor
73.0	27.51 ± 0.28	1.97 ± 0.02
80.5	27.64 ± 0.27	1.98 ± 0.02
86.0	27.44 ± 0.24	1.96 ± 0.02

Table 2: Resonance ratio ω_0/B_0 and electron g factor for three resonance frequencies.

5 Error Analysis

5.1 Error in Inductor Diagonal Distance

The input data is $l = (13.2 \pm 0.2)\,\text{cm}$ and $\Delta y = (12.8 \pm 0.4)\,\text{cm}$, from which I found d with

$$d = \sqrt{l^2 + (\Delta y)^2}$$

The associated sensitivity coefficients are

$$c_l = \frac{\partial d}{\partial l} = \frac{l}{\sqrt{l^2 + (\Delta y)^2}} = 0.72 \qquad \text{and} \qquad c_y = \frac{\partial d}{\partial [\Delta y]} = \frac{\Delta y}{\sqrt{l^2 + (\Delta y)^2}} = 0.70$$

The uncertainty u_d is

$$u_d = \sqrt{(c_l u_l)^2 + (c_y u_y)^2} \approx 0.3\,\mathrm{cm}$$

5.2 Error in Magnetic Field Data Points

Input values carrying uncertainty are inductor diagonal distance $d = (17.7 \pm 0.3)\,\mathrm{cm}$ and inductor current I, with uncertainty $u_I = 0.5\,\mathrm{mA}$. I estimated u_I as half of function generator's smallest displayed decimal value, which was $1\,\mathrm{mA}$. Ideally, I would estimate current error as a percent of the full-scale reading, but I did not know the function generator's accuracy. From I and d, I found B using

$$B = N\frac{\mu_0 I}{d}$$

The associated sensitivity coefficients are

$$c_I = \frac{\partial B}{\partial I} = \frac{N\mu_0}{d} \qquad \text{and} \qquad c_d = \frac{\partial B}{\partial d} = -N\frac{\mu_0 I}{d^2}$$

and the propagated error in magnetic field u_B is

$$u_B = \sqrt{(c_I u_I)^2 + (c_d u_d)^2}$$

I implemented this expression programmatically and calculated the uncertainty of each B point individually when plotting the $U(B)$ signal in Figure 1—the values are of order $0.005\,\mathrm{mT}$.

5.3 Error In Extrema Positions and Resonance Field

- First, I estimated the error in the B positions of $U(B)$ signal's extrema $B_{\max}$ and $B_{\min}$ as $0.01\,\mathrm{mT}$—this is the B spacing between two (B, U) points near the extrema (see Figure 1) and is roughly twice the uncertainty on a standard B data point.
- I then estimated the error of the absorption line width ΔB as $0.02\,\mathrm{mT}$. This is twice the error of a single extrema point; ΔB is the difference of $B_{\max}$ and $B_{\min}$ and error adds during subtraction.
- Along similar lines, I estimated the error of the resonance field B_0 as $0.02\,\mathrm{mT}$. My reasoning is that the information of B_0's position is encoded in the positions of the two extrema points $B_{\max}$ and $B_{\min}$. As an estimate, I thus combined the uncertainty of $B_{\max}$ and $B_{\min}$ to get $0.02\,\mathrm{mT} = 2 \cdot 0.01\,\mathrm{mT}$.

5.4 Error in Resonance Ratio and Electron g Factor

Resonance Ratio: The input quantities are ω_0, with uncertainty $0.5\,\mathrm{MHz}$, and B_0, with uncertainty $0.02\,\mathrm{mT}$. I found the resonance ratio with

$$\mathcal{R} = \frac{\omega_0}{B_0}$$

The sensitivity coefficients are

$$c_\omega = \frac{\partial \mathcal{R}}{\partial \omega_0} = \frac{1}{B_0} \qquad \text{and} \qquad c_B = \frac{\partial \mathcal{R}}{\partial B_0} = -\frac{\omega_0}{B_0^2}$$

and the error is

$$u_{\mathcal{R}} = \sqrt{(c_\omega u_\omega)^2 + (c_B u_B)^2}$$

The value of $u_{\mathcal{R}}$ for each value of ω_0 is shown in the second column of Table 2.

***g*-Factor** The input quantities are the same as for $\mathcal{R}$. The g factor is found with

$$g = \frac{h\omega_0}{\mu_B B_0} = \frac{\hbar}{\mu_B}\mathcal{R}$$

where B_0 is the resonance magnetic field and ω_0 is the resonance frequency. Using the above results for $\mathcal{R}$, the error is

$$u_g = \frac{h}{\mu_B} u_{\mathcal{R}} = \frac{h}{\mu_B}\sqrt{(c_\omega u_\omega)^2 + (c_B u_B)^2}$$

The value of u_g for each value of ω_0 is shown in the third column of Table 2.

6 Results

The width of the absorption line for resonance frequencies of 73.0 MHz, 80.5 MHz and 86.0 MHz where 0.135 mT, 0.140 mT and 0.135 mT, respectively. Since the uncertainty in ΔB is 0.02 mT, it is unreasonable to give ΔB to more than two decimal places, and we can round the above values to 0.14 mT. The result is then

$$\boxed{\Delta B = (0.14 \pm 0.02)\,\mathrm{mT}}$$

The values of the ratio ω_0/B_0 and electron g-factor are shown in Table 2, which, I'm reprinting below for convenience.

ω_0 [MHz]	ω_0/B_0 [GHz T^{-1}]	g factor
73.0	27.51 ± 0.28	1.97 ± 0.02
80.5	27.64 ± 0.27	1.98 ± 0.02
86.0	27.44 ± 0.24	1.96 ± 0.02

The average values—rounded to a reasonable three significant digits—are

$$\boxed{\frac{\omega_0}{B_0} = (26.5 \pm 0.3)\,\mathrm{GHz\,T^{-1}}} \qquad \text{and} \qquad \boxed{g = 1.97 \pm 0.02}$$

For reference, the correct values are $\omega_0/B_0 \approx 28.0\,\mathrm{GHz\,T^{-1}}$ and $g \approx 2.00$.
The fact the three values of both ω_0/B_0 and g are quite precise, but not perfectly accurate, suggests the presence of a systematic error. I may be wrong, but I believe the value of the inductor's diagonal distance d is at fault here. If found d only indirectly with a rough calculation, and wouldn't be surprised if my result is systematically off. A fault value of d would skew the value of magnetic field B, which would then propagate to ω_0/B_0 and g view the resonance field B_0.

A Theory

- An electron has spin $S = \frac{1}{2}$ and a magnetic moment with magnitude of one Bohr magneton
$$\mu_B = \frac{e\hbar}{2m_e c} \approx 9.27 \times 10^{-24}\,\mathrm{J\,T^{-1}}.$$
In an external magnetic field B_0 there are two possible spin states: $m_s = \frac{1}{2}$, corresponding to spin up (parallel to the external field) and $m_s = -\frac{1}{2}$, corresponding to spin down (anti-parallel to the external field). The energy between the spin-up and spin-down states is
$$\Delta E = E_\uparrow - E_\downarrow = g\mu_B B_0$$
where $g \approx 2$ is the Landé g factor for an electron.

- We can excite a transition between the up and down states with electromagnetic radiation with frequency ν satisfying the condition
$$\Delta E = g\mu_B B_0 = h\nu$$
This relationships connects the frequency of the radiation with the resonance value of the magnetic field B_0. The resonance frequency ν is thus a function of the magnetic field B_0. For a free electron, the ratio $\frac{\nu}{B_0}$ is roughly
$$\frac{\nu}{B_0} = \frac{g\mu_B}{h} \approx 28.026\,\mathrm{GHz\,T^{-1}}$$
Typical energies differences ΔE are quite low compared to photon energies in the infrared and visible range, so ESR signals are typically quite weak.

- The relative population of the spin-up and spin-down energy levels in an ESR sample is distributed according to the Boltzmann distribution
$$\frac{n_\uparrow}{n_\downarrow} = \exp\left(-\frac{\Delta E}{k_B T}\right) = \exp\left(-\frac{h\nu}{k_B T}\right)$$
As an example, at room temperature and frequency $\nu = 100\,\mathrm{MHz}$ the relative population difference is
$$\frac{n_\uparrow - n_\downarrow}{n_\downarrow} = \frac{n_\uparrow}{n_\downarrow} - 1 \approx 2 \times 10^{-5} \qquad \text{at } T = 300\,\mathrm{K} \text{ and } \nu = 100\,\mathrm{MHz}$$
The net absorption of radiation, and thus ESR's sensitivity, depends on the population difference $n_\uparrow - n_\downarrow$, which depends on radiation frequency ν, which in turn depends on the resonance field B_0. The higher the frequency, the smaller the ratio $\frac{n_\uparrow}{n_\downarrow}$, the larger the difference $n_\uparrow - n_\downarrow$, and the larger the ESR sensitivity. Because of electron interactions (e.g. with the sample's crystal lattice, with other electrons, with nuclei, etc...) the ESR resonance lines are not perfectly sharp, but are somewhat spread out.