Physics 338 Advanced Physics Laboratory

Electron Spin Resonance
Report: **Due Friday, October 4, 2024**

Safety:

- Chemical safety of powder sample (DPPH)
  - Find and read through the Safety Data Sheet (SDS) for the DPPH sample. The DPPH sample is completely enclosed in glass and therefore there should be no exposure. Should the sample break and an accidental spill occur, leave a note for your fellow students on the door, and let me know ASAP so we can work to clean it up together! (This seems very unlikely).
- Magnetic field safety
  - In laboratories with magnetic fields, it is typical to delineate a "5 Gauss line" (or 0.5 mT line) so that people sensitive to magnetic fields can avoid these fields. Medical devices such as pacemakers, which are relatively common, typically have a $\sim$5 Gauss magnetic field exposure limit, beyond which they may be come miscalibrated. Use the magnetic field sensor near the entrance to the laboratory to get a sense for how close to the magnet you need to be to get to 5 Gauss. Then avoid placing your medical devices, credit cards, hard drives, or pocket magnets in that area.
- Electrical/fire safety
  - Do not leave the current through the Helmholtz coils on for longer than a few minutes at a time. The coils can heat up and cause damage.
- If you have any other safety concerns I have not mentioned, please bring them to me!

Timeline:

- Sign up for a 2-hour lab time slot.
- Read through the attached information BEFORE you start lab work.
- First lab time slot - take first data! Plan for more lab time in a few days.
- Analyze data and compare to expected values.
- More lab time to take additional data and resolve any problems you had.
- Iterate as needed.
- Write report.

1 Introduction

One of the intrinsic quantum-mechanical characteristics of fundamental particles is that they have "spin," or intrinsic angular momentum. As with many quantities in the quantum mechanical realm, the energy states associated with the spin are quantized. A charged particle with a spin has an associated magnetic dipole moment and, when placed in an external magnetic field, the energy of the particle will depend on the orientation of its spin relative to the magnetic field.

In electron spin resonance, electrons in an external magnetic field absorb energy from an applied oscillating electromagnetic field and change from one spin orientation to another. The spins of particles and their interactions with magnetic fields provide a useful modern-day experimental tool for studying their environment. Electron spin resonance (ESR), also known as electron paramagnetic resonance, uses the spin of electrons. The resonant frequency is sensitive to the local environment of the electrons. In chemistry and medicine, the resonant frequency of a proton gives information about the local magnetic field of the proton. This is the key to nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI). In this experiment, you will produce electron spin resonance and show that the electron has two discrete spin energy states. Additionally, you will determine the value of the Landé g factor for a sample.[1]

2 Theory

The behavior of a classical spinning magnetic dipole in an external magnetic field can be studied classically in terms of magnetic torque. For electron spin resonance, a quantum mechanical treatment is required, but much of the language carries over.

2.1 The Zeeman Effect

The basic theory of an atomic electron in an external magnetic field is covered in most *Modern Physics* texts in the discussion of the Zeeman effect.[2] Only a brief summary will be given here.

[1] For useful references, see Griffiths, *Introduction to Quantum Mechanics*, 4.4 (pp. 171 on), Thornton and Rex, *Modern Physics for Scientists and Engineers*, section 7.4, and Eisberg and Resnick, *Quantum Physics of Atoms, Molecules*, Solids, Nuclei and Particles, Sec. 8.1 to 8.3.

[2] Another good summary is given at http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/zeeman.html.

A magnetic dipole moment $\vec{\mu}$ placed in an external magnetic field $\vec{B}$ will tend to align with the external field. The torque is

$$\vec{\tau} = \vec{\mu} \times \vec{B}\,,$$

and the corresponding potential energy is

$$V = -\vec{\mu} \cdot \vec{B}\,.$$

The direction of the external magnetic field $\vec{B}$ is conventionally taken to define the z direction.

Problem: The magnetic moment of a current I caused by a charge circulating in a loop is given by $\mu = IA$, where A is the area of the loop. Show that for a charge q of mass m in a circular orbit, the magnetic moment is given by

$$\mu = \frac{q}{2m} L\,,$$

where L is the angular momentum associated with the circling charge.

For an orbital electron (ignoring spin for the moment) the orbital angular momentum is $m_l \hbar$, where m_l is the orbital angular momentum quantum number, so

$$\mu_z = \frac{e\hbar}{2m} m_l = \mu_B m_l$$

where μ_B is the Bohr magneton, defined by[3]

$$\mu_B = \frac{e\hbar}{2m} = 9.274\,010\,0783(28) \times 10^{-24}\,\mathrm{J/T}\,.$$

Since m_l is quantized, only discrete energies are allowed. The energy spacing between different states is given by

$$\Delta E = \mu_B B$$

[3]Values for fundamental constants are taken from the National Institutes of Standards and Technology (NIST) Reference on Constants, Units, and Uncertainty: http://physics.nist.gov/cuu/index.html.

This energy difference corresponds to the emission or absorption of a photon of frequency f, where

$$hf = \Delta E = \mu_B B\,. \tag{1}$$

It may also be helpful to think of this classically. Recall that a magnetic dipole with an intrinsic angular momentum will precess about the direction of the external magnetic field. The angular precessional frequency is given by

$$\omega = \frac{\mu B}{L}\,,$$

where $L = 2m\mu/e$. The result (see Example 7.3 in Thornton & Rex) is

$$\begin{aligned} \omega &= \frac{eB}{2m} \\ \hbar\omega &= \frac{e\hbar}{2m}B \\ hf &= \frac{e\hbar}{2m}B \\ hf &= \mu_B B\,, \end{aligned} \tag{2}$$

which is the same result as Eq. 1.

This is analogous to resonance in classical physics because the natural response frequency of the system (the frequency of radiation that the electrons will absorb) equals the applied frequency (of the oscillating EM field).

2.2 Electron Spin and the Anomalous Zeeman Effect

If you include the electron spin, the calculations become more complex, but the essential ideas remain. The result is written in the same form as Eq. 1, but with an additional "Landé g factor":

$$hf = g\mu_B B\,. \tag{3}$$

For a free electron, the value of the g factor is known to quite high precision. The current best value is is $g_e = 2.002\ 319\ 304\ 362\ 56(35)$.

For an electron in an atom, both orbital and spin angular momentum must be considered, and the interaction is known as the "Anomalous Zeeman Effect." The result is that

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

(see Eq. 8.23 in Thornton & Rex).

2.3 Atoms and Molecules

Lastly, for electrons in multi-electron atoms and in molecules, the calculation is even more complicated. Still, it is common to express the result as in Eq. 3, but to now consider g to be an effective value. In this context, measurements of the g value can give information about the local environment of an electron. For the DPPH sample used in this experiment, for example, $g = 2.0036$, which is quite close to the free electron value, indicating that at least one electron in the molecule is very loosely bound.

3 Experiment

In this experiment, the oscillating EM field is created by a sinusoidally-varying current in a small solenoid. This frequency f is in the radio frequency range. Each photon in this oscillating EM field has energy hf. The sample is placed inside this solenoid, which is located inside a set of Helmholtz coils that provide B, the constant external magnetic field. When $hf = g\mu_B B$ the electrons can absorb energy from the oscillating EM field.

The equipment used in this experiment is shown in Fig. 1. It includes:

1. Three small radio frequency (RF) coils
2. RF probe unit
3. Helmholtz coils: 2 coils (the source of the external magnetic field)
4. Diphenyl-picryl-hydrazil (DPPH) sample in small ampule.
5. Power supply
6. Oscilloscope

The sample is diphenyl-picryl-hydrazil (DPPH), an organic salt with the chemical formula $(C_6H_5)_2N{-}NC_6H_2(NO_2)_3$. DPPH contains an unpaired electron with zero

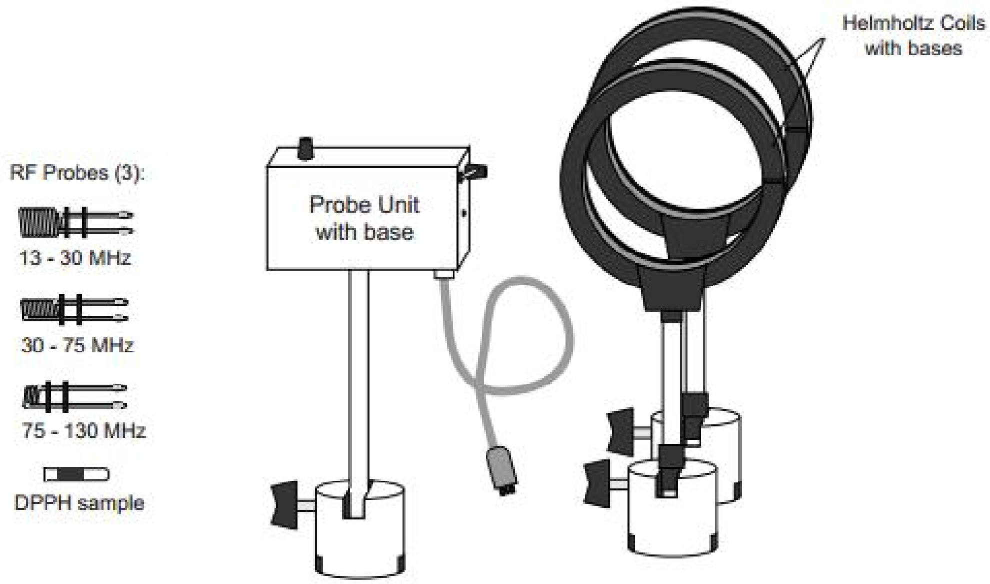

Figure 1: ESR equipment

orbital angular momentum. Since this electron is in an s orbital, its orbital angular momentum quantum number l must equal zero, leaving only its spin angular momentum to interact with the oscillating EM field. This nearly-free electron results in a very strong and narrow absorption line, with a g-factor (2.0036) that is very close to that for free electrons.

4 Procedure

The goal in this experiment is to measure the Landé g factor for electron spin resonance in DPPH. You will place the sample in an oscillating RF field of known frequency f. By placing the sample between the Helmholtz coils and varying B, you can provide the electrons with the necessary condition for spin flip transitions given in Eq. 3. When this condition is satisfied, the electrons will absorb RF energy from the small coil. This causes the voltage across the small RF coil to drop because the electrons absorb energy $E = hf$ from the RF coil's electromagnetic field, thereby effectively altering its impedance. (With different equipment, you could instead fix B and vary f, to take an ESR spectrum.)

4.1 Creating the external magnetic field B (Helmholtz coils)

Caution: Do not leave the Helmholtz coils with more than 0.5 A RMS for periods of longer than five minutes, or they could overheat.

Use the two larger coils to make a set of Helmholtz coils. The ideal requirement for Helmholtz coils is that the coils be placed along the same axis with a separation equal to 1/2 their diameter, as in Fig. 2. (Solenoids would give a more uniform field, but they are harder to use in the sample geometry we need to employ here.) However, with this apparatus, it is difficult to exactly meet these criteria while keeping the DPPH sample centered between the Helmholtz coils.

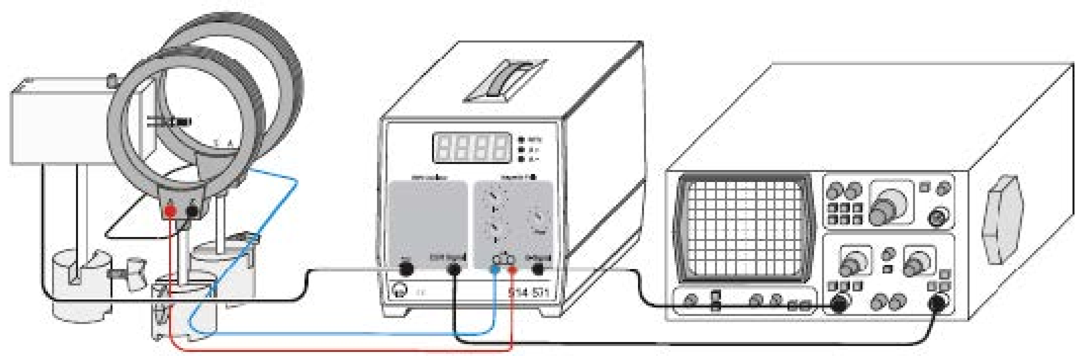

Figure 2: The final setup: the DPPH sample and oscillator inside Helmholtz coils.

Measure the average diameter of the coils, as well as the spacing D between the centers of the coils. The results are sensitive to D, so be sure to measure it carefully and check often in case you bump things. Recall that the Earth has a constant (DC) magnetic field. If you aren't careful with the direction in which you align your Helmholtz coils, the Earth's field could add to the external DC B-field in an uncontrolled way. With the power supply switched off and the knobs marked: `I=` (DC current) and `I~` (AC current) OFF (in their fully counterclockwise positions), connect the Helmholtz coils in series and then connect them to the **coil output** of the power supply. Since it is imperative for the current to go in the same direction in both coils, ensure that the coils are oriented the same way (use the A and E labels on the coils for orientation). You may find it convenient to turn one of the coils around so the wires don't get in the way. Use a small compass to verify everything is hooked up in the correct direction. Check with your instructor if you are not sure about this last part.

Connect channel 1 of your oscilloscope to the B (magnetic field) output. To analyze the electron spin resonance, you need to determine for which value of B your system absorbs RF energy. To create the B-field, you provide a current with both DC and AC components through the Helmholtz coils. The resulting magnetic field will have an AC component superimposed on a DC offset. You can vary both components' magnitudes in order to produce electron spin resonance. Turn the knobs marked `I=` (DC) and `I~` (AC) and watch the display on the oscilloscope. Make sure you understand how these controls influence the resulting current (and hence B-field). If you don't understand what you're seeing, consult your instructor.

The magnetic field inside a pair of parallel (Helmholtz) coils is given by:

$$B = \mu_0 N I \frac{R^2}{(R^2 + (D/2)^2)^{3/2}}$$

where R is the average coil radius, D is the average coil separation, I is the current, and N is the number of turns in each coil. The Helmholtz coils each have $N = 320$. You can read both the AC and DC components of the current through the coils directly from the LED screen on the front of the power supply. Turn the Helmholtz coils off and proceed to the next part of the experiment.

4.2 Creating the oscillating RF field

The three small plug-in coils are capable of producing RF fields of the following frequencies: $13 - 30$ MHz for the biggest coil; $30 - 75$ MHz for the medium-sized coil; and $75 - 130$ MHz for the smallest coil. For now, insert the medium-sized coil into the oscillator and insert the DPPH sample. You will first create an oscillating RF field in the small coil so you can understand its behavior before you insert it into the Helmholtz coils. You do not want a current in the Helmholtz coils at this point.

Turn on the oscilloscope and verify that Channel 1 and Channel 2 are both set to the Probe `1X` setting.

With the power supply turned off and the switch on the side of the probe unit in the off (lower) position, plug the probe unit into the power supply. Connect the ESR output to channel 2 of the oscilloscope. Turn on the power supply and probe unit. Press the button on the front of the power supply until the meter is reading the probe frequency. Turn the RF power up with a clockwise turn of the knob on the back with curved wedge label. Continue doing so until the meter on the front of the power supply shows a frequency reading between 30 and 75 MHz. If the RF signal is too small, the frequency counter will read zero. The signal you should now see on Channel 2 of the oscilloscope is a display of the ESR RF oscillator voltage versus time. This RF signal will be quite noisy, so you can't do any measurements yet. When you achieve resonance in the next step, this RF oscillator voltage is the signal that will show absorption.

4.3 Measuring electron spin resonance

Now you will actually perform an ESR experiment! Ensuring that the power supply is switched off, place the DPPH sample inside the medium-sized RF coil (which should still be plugged into the oscillator). Check that the part of the ampule containing the black powder is centered in the RF coil. Place the RF coil and sample inside the Helmholtz coil setup, as shown in Fig. 3.

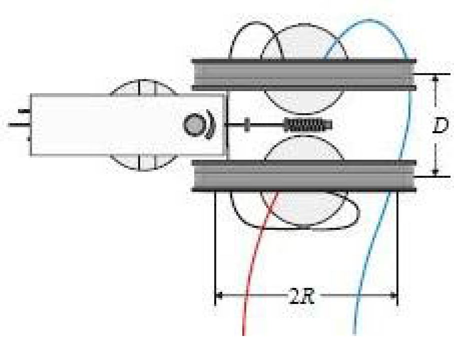

Figure 3: Top View of Helmholtz Coils Set-up.

Turn on the power supply and the oscillator power switch, and turn up the gain on the oscillator, as before. Set the frequency to around 50 MHz. Increase the AC current through the Helmholtz coils to about 0.200 A and press the autoset button on the oscilloscope—you should be able to observe this signal in real time on Channel 1 of the oscilloscope. If it doesn't appear, consult your instructor for help. The maximum amplitude of the AC magnetic field is not large enough to induce spin flips, so this should not affect your ESR signal yet, but the coil will pick up a signal from the AC field.

Now, slowly turn up the DC magnetic field. As the DC offset of your time-varying B-field increases, the voltage proportional to the magnetic field will increase beyond the oscilloscope's default trigger level. To allay this problem, set the Channel 1 coupling to AC. Alternatively, you can increase the trigger level on the oscilloscope by pressing the trigger button, choosing source 1, then slowly turning the trigger knob clockwise.

As you continue to increase the DC offset, the maximum value of the magnetic field (AC plus DC) eventually becomes large enough to induce a spin flip when $B(t)$ matches the applied f. You should see a significant decrease in the ESR coil voltage amplitude at that point. Ask your instructor if you do not see anything like this. As you continue to increase the DC component of the magnetic field beyond this point, the dip will first bifurcate (split in two), as shown in Fig. 4(a), then the two dips will begin to move apart. If you adjust the DC offset too much, you will end up where you started—with no resonance. Make sure you understand why!

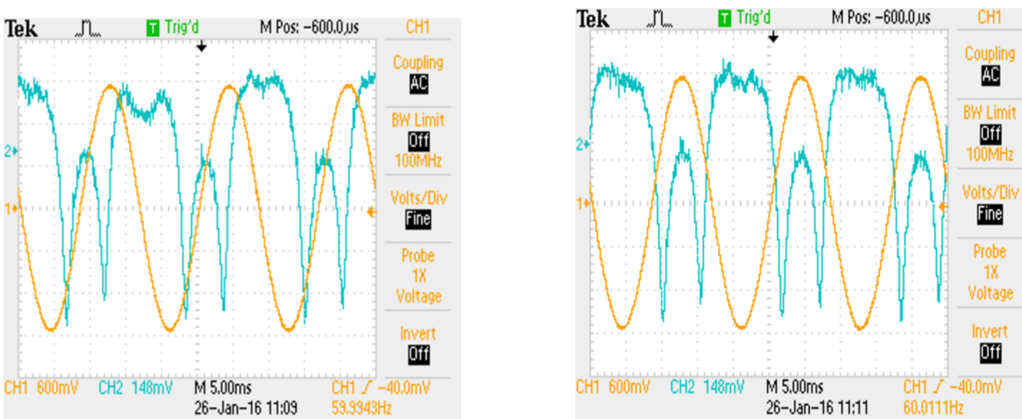

Figure 4: Typical oscilloscope display of ESR signal (blue, top curve) and Helmholtz coil voltage (gold, bottom curve) (a) with a phase offset and (b) after correction for electronic delay.

The two dips in the ESR signal in Fig. 4(a) should correspond to two equal values for B at which Eq. 3 is satisfied and resonance occurs. However, since there are electronic delays in processing the signals, there is a phase shift. Use the phase adjustment knob on the front of the power supply to align the signals so each dip corresponds approximately to the same value of B, as in Fig. 4(b).

Adjust the DC offset (the `I=` knob) until you have (a) two ESR absorption dips per cycle of the magnetic field and (b) the spacing between *all* absorption dips is approximately equal. Use your knowledge of sine waves to determine the Helmholtz coil current that corresponds to these two equally-spaced absorptions. Record this value to use later.

In the steps above, you've used your eyes to coarsely estimate the point at which the two dips are equally-spaced. In order to do a finer adjustment, switch the oscilloscope to `XY` mode by pressing `Display`, then pressing `Format` till you get `XY`. If you have selected the phase correctly in the coarse alignment described above, the plot should look like the one in Fig. 5(b) below: one symmetrical dip. Think about the values for `X` and `Y` to convince yourself why this is the case.

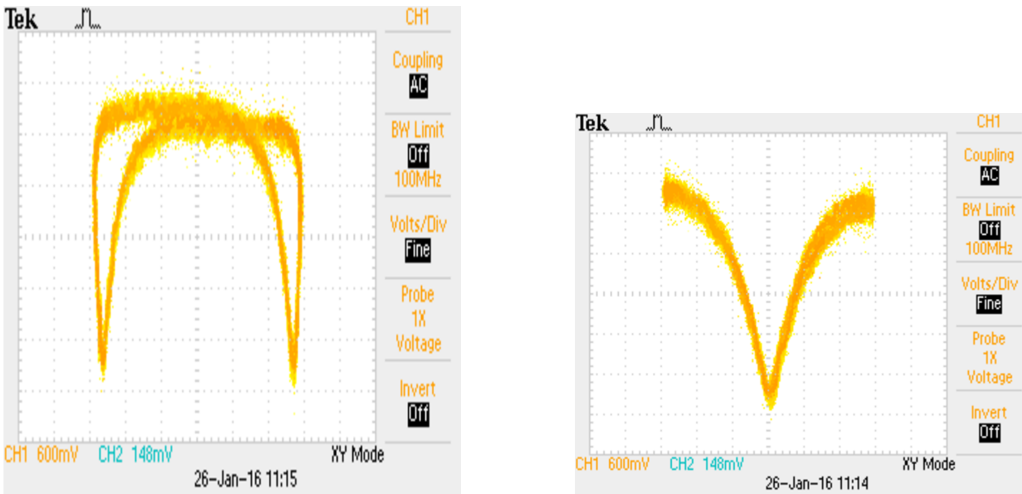

Figure 5: (a) `XY` Oscilloscope display when Helmholtz coil signal (X) and ESR signal (Y) are out of phase. (b) `XY` Oscilloscope display when phase has been set correctly.

As you perform this experiment, you may find it convenient to switch between `YT` and `XY` modes. If the image is too jittery to measure, you can use the `Single` button to acquire a single sweep of data, or you may save your data and analyze it on a computer (see below).

Note that the dips are not narrow spikes, but have significant widths. Measure the widths of the dips. Be sure to be clear about the units you are using to describe any width. Consider physical factors that would contribute to the broadening of the dips, and make any measurements you will need to characterize the magnitude of these effects in the analysis section. *Hint*: Use the `Cursor` button. Expand the horizontal scale so that the peaks are easier to see. The term "width" is rather vague. Come up with a concrete, specific measurement. Recall that the full-width at half-maximum (FWHM) is one common way to characterize the width of a resonance peak.

At any time, if you want to save an image of the screen, you may insert a USB flash drive in the front of the oscilloscope and press the `Save` button. (It can also save the raw data files. See the manual under "Data Logging.") Alternatively, you can use the `OpenChoice Desktop` software on the lab computer to store screenshots or to download data from the oscilloscope.

> At this point, the Helmholtz coils have been carrying current for a while, and may have warmed up significantly. Turn down both the AC and DC coil current knobs to let the coils cool off. Use this opportunity to check that everything is still properly aligned in your set-up and check your value for D.

4.4 Measurements

Find electron spin resonance for at least 12 different frequencies, using all three RF coils. Record the frequency and current for each resonance, along with an estimate of the uncertainty in the current. *Hint: Try 6 different frequencies with the medium coil and 3 each for the low and high frequency coils. The data for the extreme frequencies may not end up being reliable, so you may have to drop a few if they don't work well. This is fine, but do state what frequencies you had to drop in your lab report and why you dropped them.* Measure the widths of the dips for several cases to determine if they depend on any measurable parameter (see Analysis). *Hint: It is sufficient to just try with the medium and high frequency coils. The widths for the low frequency coil are usually hard to measure.*

When you change the RF coil, be careful not to disturb the spacing or alignment of the Helmholtz coils. You will likely find that the signals are much noisier for the low and high frequency coils. Since f and I are linearly related, you can use your existing results to *predict* a good starting guess for the necessary currents. For the lower-frequency coil, you may find it helpful to decrease the AC component to 0.150 A. You may also find it helpful to switch back and forth between `YT` and `XY` display modes.

5 Analysis

Calculate the magnetic field for each ESR case you observe and make a plot of B *vs.* f, including error bars[4]. Compute the theoretical slope of this curve from the

[4] In *Mathematica*, the command `ErrorListPlot` will make plots with errorbars. To incorporate uncertainties (and hence weights) into `LinearModelFit`, look at the online help under `Options`, `Weights`.

discussion above, being careful about units. From the slope of the best-fit line to your actual data, determine the Landé g factor for DPPH, and its uncertainty. Compare to the expected value.

In your report, discuss the effect of the Earth's magnetic field (about $5 \times 10^{-5}\,\mathrm{T}$) and any other source of experimental uncertainty.

Consider what might determine the observed widths of the resonant dips. Use your measurements to estimate the magnitude of various possible explanations. Is it the inhomogeneity of the magnetic field, or the lifetime of the excited spin flip state, or something else? Try to make estimates to test your ideas.