Senior Fresh Physics Laboratory Report

Electron Paramagnetic Resonance

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Electron paramagnetic resonance was investigated using a sample of diphenyl pecryl hydrazyl (DPPH) inside an RF coil within a Helmholtz coil arrangement. The Helmholtz coil separation which yielded the most uniform field was the radius of the coil as expected. The resistance, and impedance of the coils were $R = (8.0 \pm 0.1)\Omega$, and $Z = (19.8 \pm 0.9)\Omega$. A graph of the magnetic field at resonance against the AC current through the coil pair was linear [FIG. 3.4], and from the slope we found $B/I = (3.90 \pm 0.15) \times 10^{-3} TA^{-1}$ which agrees with the analytical value of $B/I = (3.83 \pm 0.01) \times 10^{-3} TA^{-1}$. The electron g-factor was found to be $g = 1.9 \pm 0.2$, agreeing with the actual value $g = 2.0023$ [3]. The FWHH of the was found to be more sensitive to changes in the AC voltage more than the DC voltage. Linear relationships were found for the effect of varying RF field amplitude and magnetic field resonance amplitude, on signal height.

Contents

1 Introduction

1.1 Spin and magnetic moments

Spin is an intrinsic quantum property of particles. For electrons, a spin-half particle, the spin angular momentum can take values of $\hbar M_s$ where $M_s = \pm\frac{1}{2}$. As the electron is a charged particle it has a magnetic dipole moment $\vec{\mu}$. Considering the z-component of this moment with respect to a magnetic field $\vec{B}$,

$$\mu_z = \gamma_e \hbar M_S = -g\mu_B M_S. \tag{1.1}$$

Where here $\mu_B = 9.274 \times 10^{-24}\mathrm{JT}^{-1}$ is the Bohr magneton, γ_e is the gyromagnetic ratio (ratio of its magnetic moment to its angular momentum), and $g = 2.00232$ is a dimensionless constant called the electron g-factor (see below). [3].

1.2 Zeeman Splitting

From the quantum mechanical spin effect, we observe the lifting of degenerate energy levels. This is the Zeeman effect. The effect emerges from the energy of a magnetic dipole given by

$$U = -\vec{\mu}.\vec{B}.$$

For an electron, the energy, and the difference in energy between the two states are given by

$$U = g\mu_B M_s B, \quad \text{and} \quad \Delta U = g\mu_B B. \tag{1.2}$$

The difference ΔU is the Zeeman split. The perturbation of the magnetic field B lifts the degeneracy. A photon of frequency f can cause a transition between energy levels if it has energy split ΔU. This is given by

$$hf = g\mu_B B, \tag{1.3}$$

the resonance condition for the electron. Figure 1.1 below illustrates the transition in a Zeeman diagram. For more information on the quantum mechanics involved, consult *Griffiths, Introduction to Quantum Mechanics* [2]

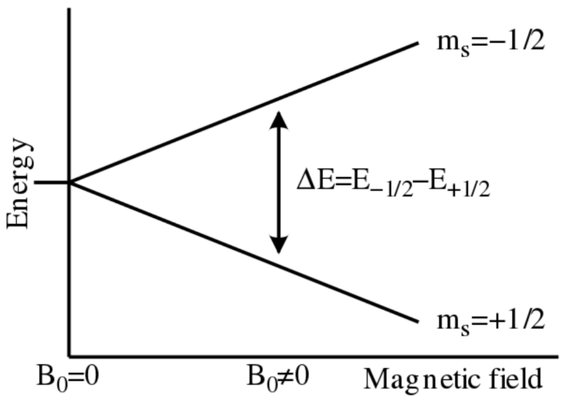

Figure 1.1: Zeeman diagram of the electron spin transition from $M_S^+ \to M_S^-$

1.2.1 Note on the g-factor

Electrons responds not only to a applied magnetic field B_0 but also to local magnetic fields of the system they are in. The effective field is thus parameterized by

$$B_{\text{eff}} = B_0(1 - \sigma),$$

and the resonance condition becomes

$$h\nu = g_e \mu_B B_{\text{eff}} = g_e \mu_{\text{B}} B_0 (1 - \sigma).$$

Where $g = g_e(1 - \sigma)$ is as before the g-factor.

1.3 Electron Paramagnetic Resonance

Electron spin resonance is the transition between magnetic states, ie: the spin 'flip'. Electron Paramagnetic Resonance (EPR) occurs due to the orbital effect of the magnetic moment of the electron $\vec{\mu}$. EPR spectra corresponding to $M_S^{\pm}$) can be generated by either varying the photon frequency incident holding the magnetic field constant or doing the reverse. We usually vary the magnetic field keeping the frequency fixed, altering the energy gap ΔU until the resonance condition (1.3) is met. The unpaired electrons can move between their spin states at this point.

Appropriate samples for EPR must contain large amounts of unpaired electrons, as paired electrons spin in opposite directions with cancelling magnetic moments. The ratio of electrons obeying the Boltzmann distribution, in upper to lower states at equilibrium is given by

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \exp\left(-\frac{U_{\text{upper}} - U_{\text{lower}}}{kT}\right) = \exp\left(-\frac{\Delta U}{kT}\right) = \exp\left(-\frac{hf}{kT}\right) \leq 1, \tag{1.4}$$

where f is the resonance frequency, T is the temperature, and k is the Boltzman constant. Thus, from the lower to the higher level transitions are more likely than the reverse and due to this we will observe a power absorption by the sample from the electromagnetic field. For example, at room temperature and radio resonance frequencies $\frac{n_{\text{upper}}}{n_{\text{lower}}} \approx 0.95$.

2 Methodology

2.1 Experimental Setup

Figure 2.1 illustrates the experimental setup. Below is the apparatus used.

- **EPR module:** Contains a variable capacitor C, in parallel with a radio frequency (RF) coil, of inductance L. The frequency of this circuit can be changed using the frequency adjustment knob which alters C. The field of the RF coil (B_1) is given by a reading of the current on the microammeter.
- **Control Unit:** Displays the frequency of f, and supplies the voltages for the EPR module and Helmholtz coils. It also outputs voltage reading to the oscilloscope
- **Sample:** We used a sample of diphenyl pecryl hydrazyl (DPPH), an organic radical (a molecule with many unpaired electrons) whose EPR spectrum is a single line.
- **Oscilloscope:** Dual output. One output is the voltage in the RF coil and is used to view the resonance pulses. The other is the voltage supplied to the Helmholtz coils and indicates the magnitude of the magnetic field.
- **Helmholtz Coils:** For EPR a stable magnetic field must be used, as variations in B lead to variations in ΔU [equation 1.2]. The coils provide a uniform magnetic field in which to place the sample. The magnetic field for the Helmholtz coils is most uniform for the spacing between the coils equal to the radius of the coils. The magnetic field is given by

$$B = \mu_0 \left(\frac{4}{5}\right)^{\frac{3}{2}} N\frac{I}{r} \tag{2.1}$$

  where: $\mu_0 = 1.256 \times 10^{-6}$Vs/Am
  N = number of turns in each coil (320)
  r = the radius of the Helmholtz coils
  I = current passing through the coils.
  A derivation of this formula is included in the appendix.
- **Hall Probe:** This was used to check the uniformity of the field.

2.2 Method

A test sample is placed in a uniform magnetic field supplied by the Helmholtz coils. The sample is also wrapped within a coil that is connected to an RF oscillator. The smaller magnetic field induced in the coil by the oscillations of the oscillator is orthogonal to the uniform field.

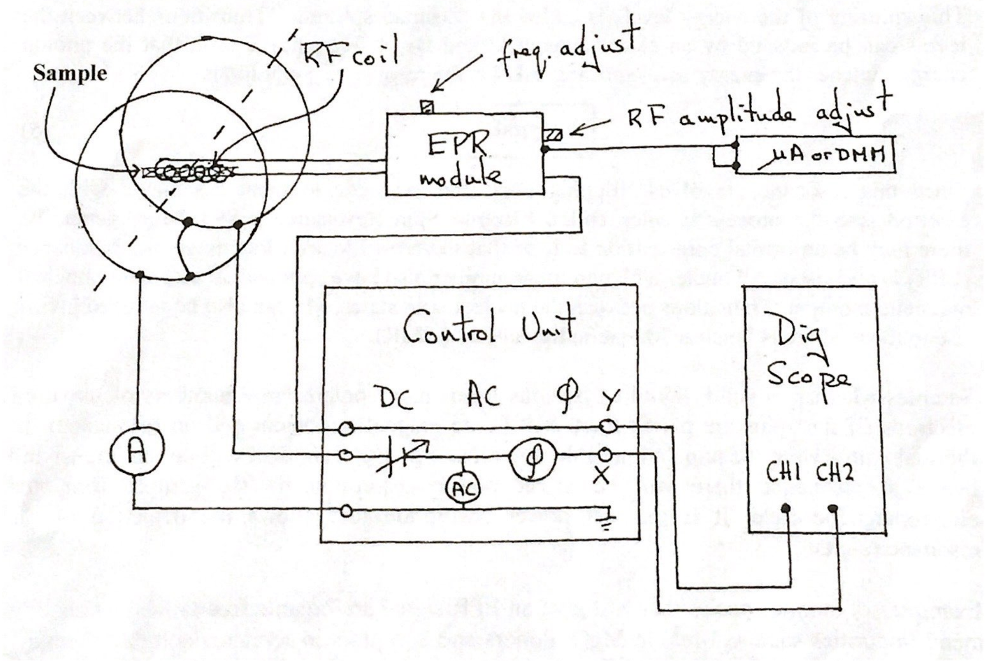

Figure 2.1: Diagram of the experimental setup used

EPR materialises when at resonance, electrons in the lower energy state can absorb a photon and jump to the higher energy state. This absorption of energy affects the permeability of the test sample which affects the inductance of the coil and thus the oscillations of the RF coil. This results in a change in the current flowing through the coil.

For an electron in a magnetic field, it would be necessary to set the RF frequency with pinpoint accuracy to observe resonance. This difficulty is solved by varying the magnitude of the magnetic field about some constant value. This is done by supplying a small AC current, superimposed on a larger DC current, to a pair of Helmholtz coils. This results in a sinusoidal magnetic field. The form of this magnetic field is given by

$$B = B_{dc} + B_{ac}\sin[(50Hz)t], \tag{2.2}$$

where 50Hz is the frequency of the AC mains current in Ireland. When the resonance condition defined by 1.3 we observe absorption of the electromagnetic field. In order to actually see the absorption peaks, the electrons need to be disturbed from equilibrium due to spin lattice relaxation. The AC magnetic field repeatedly crosses the resonance point with the electrons returning to equilibrium, meaning absorption occurs each cycle of the field. The figure below illustrates this magnetic field and the resonance point.

The experiment was split into various parts detailed below.

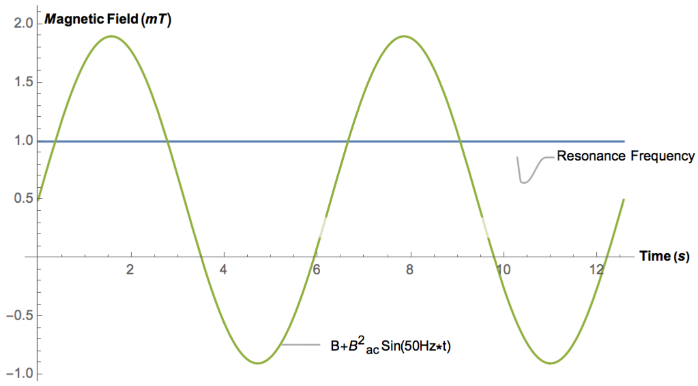

Figure 2.2: Magnetic field as a function of time

2.3 Determining the uniformity of the field

Setting up the apparatus as in figure 2.1 and fixing the current to $I = 0.5A$, we took values of the magnetic field for three values of the coil spacing, $\delta = r, < r$, and $> r$. A plot of B against the position along the central axis was made using the Hall probe. For the value of $\delta = r$, a plot of B against I was made.

2.4 Determining the resistance and impedance of the Helmholtz coils

A multimeter was connected in series with the coils, and the resistance was measured. Values of V_{ac} and I_{ac} were taken which are the AC potential difference across the coils, and the AC current through the coils respectively. The impedance was found using the following formula,

$$Z = \frac{V_{\text{ac}}}{I_{\text{ac}}}. \tag{2.3}$$

2.5 Measuring B vs f at resonance to determine g for DPPH

The sample was placed in the small coil, between the two Helmholtz coils. The frequency $f = (\omega_0 C)^{-1/2}$ of the circuit was changed on the EPR module by altering the capacitance C. B_{ac} and B_{dc} were changed on the control unit until resonance was reached. A plot of B vs f was then made. Figure 2.3 shows the oscilloscope at resonance frequency. We see two dips as the resonance condition is satisfied twice in one period of the AC voltage.

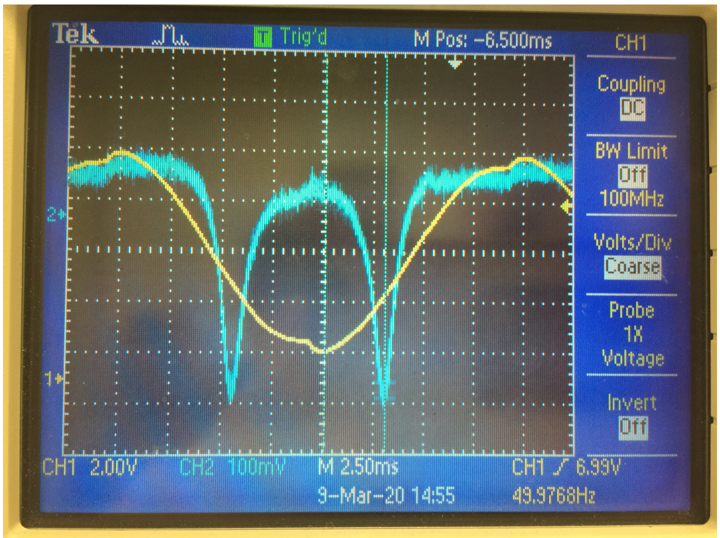

Figure 2.3: Oscilloscope showing the two resonance dips in the RF coil voltage.

2.6 Measuring the FWHH of the signal for (a) various amplitudes of the 50H alternating magnetic field, and (b) various values of the resonance field

The phase shift was adjusted on the control unit so the zeros of the AC current coincide with the resonance dips.

$a)$ f and B_{dc} were fixed and the FWHH of the signal was measured for different values of the amplitude of the 50Hz field.

(b) B_{ac} was fixed and values of FWHH were taken for values of B_{dc} at resonance.

2.7 Measuring the signal height h for (a) a fixed point of magnetic field resonance B_{res} on the RF field amplitude (A), and $b)$ fixed RF field amplitude, on a varied B_{res}

$a)$ Using the oscilloscope values of the signal height, h, at resonance were taken as the RF field was varied on the EPR module. A plot of h vs A was produced.

$b)$ Height of the resonance signal (h) was then measured as a function of the resonance field (B_{res}). A plot of h vs B_{res} was produced.

3 Results

3.1 Determining the uniformity of the field

The radius of the Helmholtz coil was measured with a ruler to be $r = (7.5 \pm 0.1)cm$. The graphs below show the magnetic field strength as a function of position along the axis perpendicular to the faces of the Helmholtz coils for 3 different values of coil spacing, at a constant current of $I = 0.5A$.

From figures 3.1,2,3 we see that when the spacing of the coils is equal to the radius of the coils, $r = \delta$, observe a uniform magnetic field as expected.

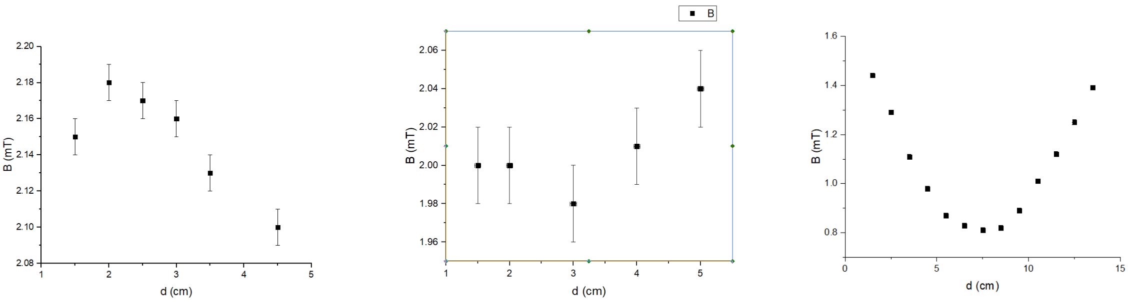

Figure 3.1: Graphs illustrating the field uniformity for $\delta \leq r$, $\delta = r$, and $\delta \geq r$

Figure 3.4 is the magnetic field strength plotted as a function of current. It shows a linear relationship predicted by the theory. Using equation 2.1, the slope is predicted to be

$$\frac{B}{I} = \left(\frac{4}{5}\right)^{\frac{3}{2}} \frac{(4\pi \times 10^{-7})(320)}{((7.5 \pm 0.1) \times 10^{-2})} = (3.83 \pm 0.01) \times 10^{-3} TA^{-1}.$$

The slope of the graph was found to be $m = \frac{B}{I} = (3.925 \pm 0.150) \times 10^{-3} TA^{-1}$. These values agree within error.

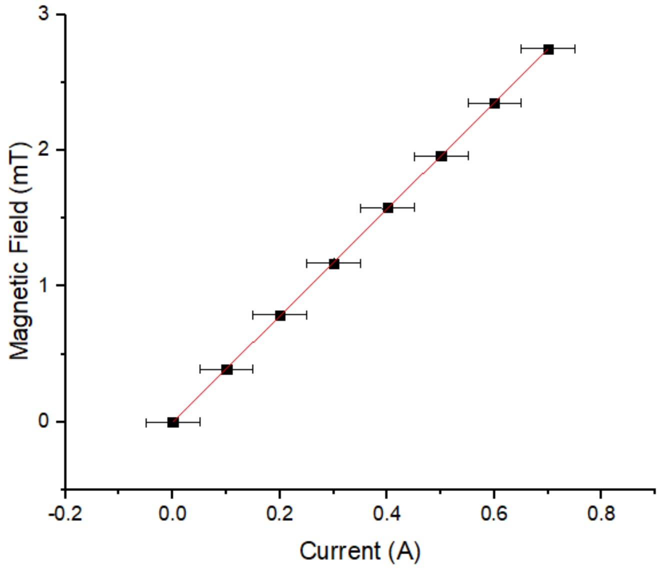

Figure 3.2: Graphs illustrating the field uniformity for $\delta \leq r$, $\delta = r$, and $\delta \geq r$

3.2 Determining the resistance and impedance of the Helmholtz coils

The findings for this section are displayed in the table below. Note, the impedance is a complex number with its real component being the resistance. They are related by a phase difference $R = |Z| \cos \phi$. This phase difference is due to the current in the coils being of phase with the voltage on the oscilloscope due to the inductance of the coils.

Quantity	Value
R	$8.0 \pm 0.1\Omega$
V_{ac}	$4.8 \pm 0.1\text{V}$
I_{ac}	$0.24 \pm 0.01\text{A}$
Z	$19.8 \pm 0.9\Omega$
ϕ	$66 \pm 1°$

3.3 Measuring B vs f at resonance to determine g for DPPH

The figure below illustrates the magnetic field as a function of the resonance frequency. The magnetic field strength was converted from current using the ratio B/I from the previous section.

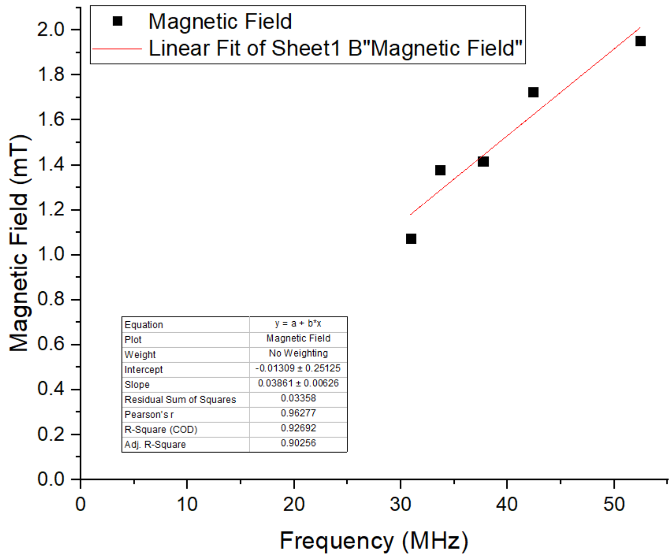

Figure 3.3: Graph of magnetic field strength against resonance frequency.

From the resonance condition, we are able to determine g from our slope using

$$\frac{B}{f} = \text{slope} = \frac{h}{g\mu_B},$$

leading to a value of $g = (1.9 \pm 0.2)$. This is within error of the actual value of $g = 2.0023$ [3].

3.4 Measuring the FWHH of the signal for (a) various amplitudes of the 50H alternating magnetic field, and (b) various values of the resonance field

$V_{ac}(\pm 0.2V)$	FWHH $(\pm 0.2ms)$	FWHH $(\pm 2nT)$
4.0	1.1	32
4.5	0.8	44
5.0	0.7	51

Table 3.1: Results for a)

The values for the magnetic field of the FWHH were calculated using equation 1.3. These results are in the order of nT which is incredibly small. Approximating the distribution of the voltage about the resonance point as Gaussian, with a standard deviation of $FWHH \approx 2.355\sigma$ [1] we see that the standard deviation is similarly on the order of nano-Teslas. This means if we

$V_{dc}(\pm 0.02V)$	FWHM ($\pm 0.2ms$)	FWHH ($\pm 2nT$)
7.2	1.8	20
8.0	1.6	22
9.0	1.7	21

Table 3.2: Results for part b)

were using only a DC current, we would have needed nano-Tesla precision in order to observe resonance peaks, but the AC current sweeps over a range which makes it much easier to pick up on resonance peaks.

From table 3.1, the FWHH increases with the application of AC voltage. Table 3.2 shows the FWHH is less sensitive to changes in the DC voltage.

3.5 Measuring the signal height h for (a) a fixed point of magnetic field resonance B_{res}, on the RF field amplitude (A), and b) fixed RF field amplitude, on a varied B_{res}

From equation 1.4, the higher value of the resonance frequency or the lower the temperature should increase the number of electrons in lower energy and thus increasing the amount of absorbed magnetic field, increasing the dip height h.

a) Shown below in figure 3.4 is a graph of the results obtained. A strong linear relationship is evident. As RF field amplitude increases, more photons are emitted from the RF coil that can be absorbed by the electrons in the DPPH, which leads to the larger signal height.

b) Figure 3.5 shows a linear relationship between V_{ac} and signal height. V_{ac} is proportional to I_{ac} from equation 2.3 and thus to B_{ac}.

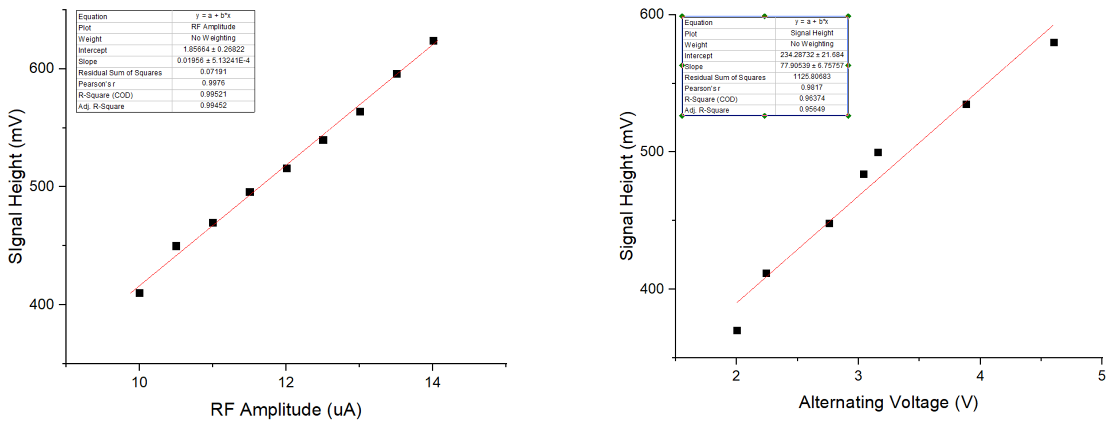

Figure 3.4: Graphs for (a) and (b)

4 Error handling

- Calipers and rulers were used to measure distances but due to the setup, I found this method was susceptible to measurement errors. This was evident in figure 3.1, where the distances measured were small. If there was a scale on the track for the Helmholtz coils the error would be mitigated.
- I found determining the FWHH was difficult because as the voltage was varied, the FWHH changed by only a few milliseconds.
- All errors were handled using Gaussian error propagation.

5 Conclusion

We have verified that the most uniform field occurred when the spacing of the Helmholtz coil was equal to the radius of the coil [figure 3.1]. A plot of magnetic field strength against the current at this spacing was found to be linear [figure 3.2], and from the slope of this graph, the ratio B/I was found to agree with the theory. For more accurate results, more accurate distance measuring equipment could have been used as the setup was difficult to accurately measure the hall probes position.

The total resistance of the coil pair was found and from this, the impedance and phase shift were determined.

A value for the electron g-factor was found to agree very well with the theoretical value, from a plot of the resonance magnetic field against the frequency of resonance [figure 3.3]. A more accurate result could have been obtained by taking more data points however, we did not have the time available.

The response of the FWHH of the resonance signal was determined for various magnetic AC field components amplitudes and resonance field points. I found difficulty determining the FWHH as the signal was fuzzy and the differences were of the order of nano-Tesla, so I am not entirely confident of the results for this section.

The final part of the experiment yielded linear graphs for both the signal height against the RF and AC voltage amplitudes respectively, in agreement with theory.

6 Appendix

6.1 Derivation of equation 2.1

Start with the formula for the on-axis field due to a single wire loop which is itself derived from the Biot–Savart law:[5]

$$B_1(x) = \frac{\mu_0 I R^2}{2(R^2 + x^2)^{3/2}}.$$

R = coil radius, in meters,
x = coil distance, on axis, to point, in meters.

The Helmholtz coils consists of n turns of wire, so the equivalent current in a one-turn coil is n times the current I in the n-turn coil. Substituting nI for I in the above formula gives the field for an n-turn coil:

$$B_1(x) = \frac{\mu_0 n I R^2}{2(R^2 + x^2)^{3/2}}.$$

In a Helmholtz coil, a point halfway between the two loops has an x value equal to R/2, so calculate the field strength at that point:

$$B_1\left(\frac{R}{2}\right) = \frac{\mu_0 n I R^2}{2\left(R^2 + \left(\frac{R}{2}\right)^2\right)^{3/2}}.$$

There are also two coils instead of one (the coil above is at x=0; there is a second coil at x=R). From symmetry, the field strength at the midpoint will be twice the single coil value:

$$\begin{aligned}
B\left(\frac{R}{2}\right) &= 2B_1\left(\frac{R}{2}\right) \\
&= \frac{2\mu_0 n I R^2}{2\left(R^2 + \left(\frac{R}{2}\right)^2\right)^{3/2}} = \frac{\mu_0 n I R^2}{\left(R^2 + \left(\frac{R}{2}\right)^2\right)^{3/2}} \\
&= \frac{\mu_0 n I R^2}{\left(R^2 + \frac{1}{4}R^2\right)^{3/2}} = \frac{\mu_0 n I R^2}{\left(\frac{5}{4}R^2\right)^{3/2}} \\
&= \left(\frac{4}{5}\right)^{3/2} \frac{\mu_0 n I}{R} \\
&= \left(\frac{8}{5\sqrt{5}}\right) \frac{\mu_0 n I}{R}.
\end{aligned}$$

References

[1] Wolfram Alpha. Gaussian function. URL: `https://mathworld.wolfram.com/GaussianFunction.html`.

[2] David J Griffiths and Darrell F Schroeter. *Introduction to quantum mechanics*. Cambridge University Press, 2018.

[3] NIST. Fundamental physical constants. URL: `https://physics.nist.gov/cuu/Constants/`.