Investigating electron spin resonance at radio frequencies with dpph

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ABSTRACT

The effects of altering the modulation and lock-in amplifier settings on the ESR graph were investigated to produce a reading with the highest signal to noise ratio and amplitude possible. The ideal settings found were: a modulation amplitude of 6.0V, modulation frequency of 220Hz, lock-in amplifier phase = $(61.1 \pm 0.0)°$, time constant = 300ms. The data was then used to calculate the g-factor for dpph, which had an experimental value of $g = 2.080 \pm 0.068$, within 3.8% of the accepted value of 2.004[1]. The characteristic ESR lineshape was determined to most closely follow a Gaussian distribution.

1 INTRODUCTION

During the early 20th-century physicists discovered that atoms and electrons have discrete energy levels (eigenstates), rather than the classically believed continuous energy distributions[2]. Transitions between these eigenstates can be induced using an oscillating magnetic field. Radio frequencies (RF) are used to observe the magnetic field at which absorption occurs - this practice is commonly referred to as electron spin resonance (ESR), or electron paramagnetic resonance (EPR)[3]. This technique is used to study substances that contain an unpaired electron[4], and is used in a variety of different sectors, from pharmaceuticals to archaeology: tracking catalytic reactions, detecting whether food has been exposed to radiation and determining the age of fossils, to list a few examples[5].

This report outlines the theoretical framework necessary to understand ESR (section 2) and our investigation of the characteristic ESR lineshape for 2,2-diphenyl-1-picrylhydrazyl (dpph). Dpph is being explored due to its well-known characteristics, which allows it to be commonly used as a marker[3]. Analysing how altering various experimental parameters affects the ESR graph is a key component of this report, the culmination of which allowed for optimal settings to be utilised when determining a substance-specific factor, known as the g-factor, for dpph (section7). The effect of modulation is investigated in section 4, and the effect of the lock-in amplifier in section 5. Finding an equation for the ESR line using our optimal settings is investigated in section 8.

2 ELECTRON SPIN RESONANCE THEORY

2.1 Electron transitions

Electrons belong to the group of particles known as fermions. As such, they are said to have spin $\frac{1}{2}$ and can occupy two different energy states. Electrons also possess a magnetic moment μ, and when placed in a magnetic field B_0 will tend to orientate themselves such that the energy of their state is minimised, i.e. the electron will align with the magnetic field[2]. These states are referred to as 'spin up', with energy

$$E_{\uparrow} = \frac{g\mu_B B_0}{2}, \tag{1}$$

and 'spin down', with energy

$$E_{\downarrow} = -\frac{g\mu_B B_0}{2}, \tag{2}$$

where g is the Landé g-factor ($\approx$ 2 for a free electron), and μ_B is the Bohr magneton[1]. These spin states are labelled by the spin quantum numbers $m_s = \pm\frac{1}{2}$.[3]

The difference in energy ΔE is the energy necessary for a transition to occur between the two states.

$$\Delta E = E_{\uparrow} - E_{\downarrow} = g\mu_B B_0. \tag{3}$$

This energy can also be obtained via photon absorption, by applying an external electromagnetic field. From the the Planck-Einstein relation[6], the energy difference ΔE is proportional to the frequency of the electromagnetic radiation ν:

$$\Delta E = h\nu, \tag{4}$$

where h is Planck's constant.

Equating equations (3) and (4) we arrive at the conclusion that

$$h\nu = g\mu_B B_0, \tag{5}$$

The energy required for electron transitions is low enough such that ESR can be observed at radio frequencies. What we can deduce from equation (5) is that, for a given frequency of electromagnetic radiation (EM), there is a specific magnetic field at which a transition can be induced. In practice, this means that we can sweep over a range of magnetic fields to find the exact field at which resonance occurs, and with that knowledge use equation (6) to calculate g, which is unique for a given sample.

$$g = \frac{h\nu}{\mu_B B_0} \tag{6}$$

As we can see from Fig. 1, there is a distribution around the field at which absorption takes place. We can define a quantity known as the half-width ΔB as the width between points with half the maximum amplitude. The difference in energy between these two magnetic fields is similar to equation (3):

$$\Delta E = g\mu_B \Delta B. \tag{7}$$

Rearranging equation (5) for $g\mu_B$ and substituting it into equation (7) we obtain

[1] $\mu_B = \frac{e\hbar}{2m_e}$ [7]

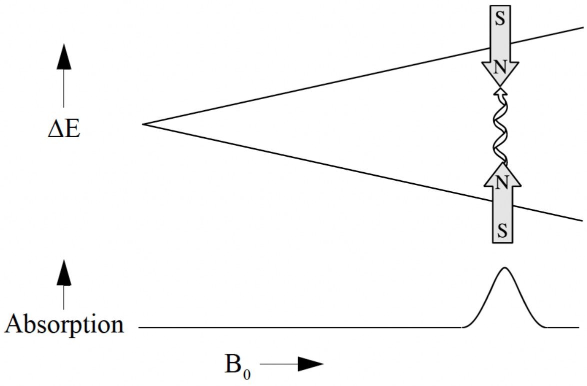

Fig. 1. Visualisation of how electron transitions occurs when $h\nu = g\mu_B B_0$[2].

$$\Delta E = \frac{h\nu}{B_0}\Delta B, \tag{8}$$

where we arrive at the relationship that $\Delta B \propto \Delta E$. The energy width can be increased by increasing the modulation amplitude, the effect of which is investigated in section 4.2.

2.2 Calculating the magnetic field

As outlined in section 3, a solenoid is used to generate the magnetic field necessary for ESR spectroscopy. As the solenoid used is not infinitely long, the magnetic field produced is not uniform, as illustrated in Fig. 2. Non-uniformity in the field can broaden the ESR line, so for best results, a sample should be placed in the centre of the coil, where the field is most uniform. If not, the calculated value for B_0 and g would be incorrect. In practice, this is quite difficult, as the solenoid is opaque, and so one cannot determine how close to the centre the sample is[2].

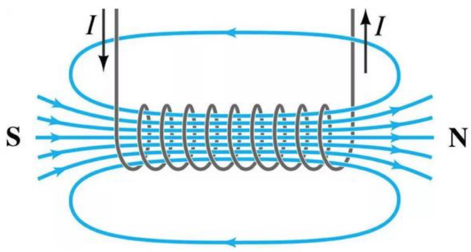

Fig. 2. Diagram of a finite solenoid, showing non-uniformity around the poles.

Knowing the value of the magnetic field requires calculation, as our independent variable is current. A Hall probe could be placed inside the solenoid to find the field strength, however, the problem of positioning the probe exactly in the centre of the solenoid arises again (and ensuring it is exactly parallel to the solenoid).

If the sample is placed in the centre of the solenoid, and we assume the field is therefore uniform, the most accurate method of calculating the magnetic field is to use the infinite solenoid approximation:

$$B = \mu_0 N I, \tag{9}$$

where N is the number of turns per unit length, and I is the current. The solenoid used in this experiment consists of 445 turns, with a length of 15.2 cm.

2.3 Maxwell-Boltzmann distributions and Modulation

For a large sample at thermal equilibrium, there are many electrons, whose spin states are governed by the Maxwell-Boltzmann distribution[8]. This results in the number of electrons in the upper and lower energy levels being approximately equal at room temperature[3]. An electron can only absorb a photon if it is already in the spin-down state, thus there needs to be a greater number of particles in the lower energy state than the higher one[8]. From equation (10) we can deduce that in order for the ratio of spin up to spin down to be as low as possible, the temperature T must also be as low as possible, which is why ESR experiments must be performed at temperatures lower than room temperature.

$$\frac{N_{upper}}{N_{lower}} = exp\left(-\frac{\Delta E}{k_B T}\right) \tag{10}$$

As the absorption ΔE measured in this experiment is very small, to be able to observe it we need to modulate the signal. Modulation involves tuning the signal to a specific frequency and measuring the signal at this specific frequency; this gives the best chance of detecting a signal[3]. The effect that modulation has on the ESR graph is explored in section 4.

2.4 The lock-in amplifier

The lock-in amplifier is a device used to enhance the sensitivity of the ESR signal. The signal generator produces a sinusoidal modulation field, which is passed onto both the modulation coil and the lock-in amplifier. The lock-in amplifier then produces a DC signal proportional to the modulated ESR signal[2]. The phase of the lock-in amplifier ϕ can be used to amplify the ESR signal when $\phi =$ modulation phase. As the signal is sinusoidal, we expect there to be a corresponding sinusoidal relationship between the lock-in amplifier phase and the amplitude of the ESR signal.

As well as the phase, the lock-in amplifier can be used to adjust the time constant; which determines how long it takes to record a data point. The effect that this should have is to reduce the noise of the signal and produce a clear ESR line.

2.5 The ESR line

The absorption peak follows a distribution around B_0, as briefly mentioned in section 2.1; however in practice the absorption isn't what is recorded, rather it is the first derivative of ESR absorption (section 3). As such, the absorption doesn't occur at the maximum point of the graph, but rather the point at which the signal is zero between the maxima and minima, shown in Fig. 3. The ESR data is shown in terms of current rather than magnetic field, so instead of referring to the field at which absorption occurs, B_0, it will instead be the current I_0, and the same principle applies to ΔB and ΔI. When necessary, equation (9) can be used to convert $I \to B$.

The lineshape of the ESR graph is investigated in section 8 by comparing two different possible functions and assessing which produces the best fit. The functions plotted are a Gaussian derivative

$$y = A\frac{exp\left(-\frac{(x-x_0)^2}{2\sigma^2}\right)(x-x_0)}{\sqrt{2\pi}\sigma^3} + c, \tag{11}$$

and Lorentzian derivative

[2] A better method would be to use a Helmholtz coil instead of a solenoid, which would allow for much more precise placement of the sample.

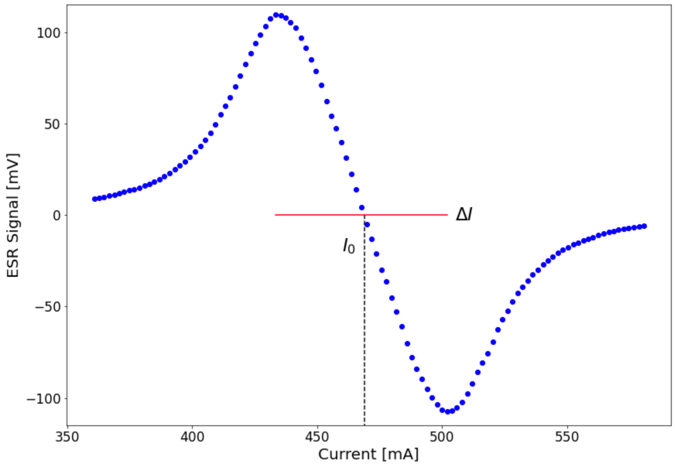

Fig. 3. An example of a first derivative ESR graph, with a dashed black line at current I_0, and red line indicating ΔI.

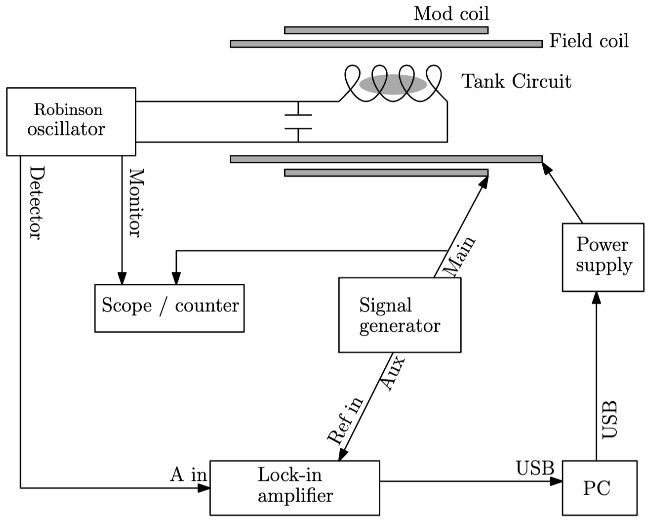

Fig. 4. Diagram of equipment setup and main connections in the experiment[3].

$$y = A\frac{16(x - x_0)\Gamma}{\pi\,(4(x - x_0)^2 + \Gamma^2)} + c, \tag{12}$$

where x is the current, y is ESR signal, and x_0, A, σ and Γ are all constants to be determined.

3 EXPERIMENTAL SETUP

The apparatus connections used for this experiment is shown in Fig. 4. The sample being analysed, dpph, is placed inside the tank circuit of a Robinson oscillator, which is connected to a scope (showing the frequency of the electromagnetic field), and also the lock-in amplifier. The radio frequency that the ESR is observed at is around 50 MHz for each experiment (excluding section 6).

The tank circuit itself is inside of a solenoid, which produces a variable sweeping magnetic field using a ramp generator. The solenoid is placed inside of a metal magnetic shield, to stop the contribution of the earth's magnetic field and field from apparatus current on the sample[3]. The earth's field would increase the field on the sample, which would decrease what is recorded as B_0 (as the background field is not taken into account when calculating B). The consequence of this is an increased calculated value for g.

The application Lfser is used to set the current range and step size. A smaller step size increases precision, but also increases the time it takes to obtain data. The most frequently used step size for this experiment was 2.0 mA The modulating coil is driven by the signal generator. The signal generator prompts the lock-in amplifier to search for a signal at the specified modulating frequency. The lock-in amplifier then amplifies this signal, which it sends to the computer and is recorded as data.[3] A capacitor can be attached to the Robinson oscillator to alter the frequency ν. The lock-in amplifier is used to change between the first and second derivative ESR absorption line, by measuring either the fundamental frequency f or the second harmonic $2f$[3]. It is also used to change the phase, time constant and sensitivity.

One of the fundamental aims of this experiment was to investigate the consequences of changing the apparatus parameters. As such, much of the experiment consisted of tinkering with the parameters and then explaining the results, rather than having a theory and testing it.

[3] ≈ 0.05 mT

The end goal of the investigation was to determine the g-factor for dpph and describe its ESR lineshape, which is discussed in section 7 and 8 respectively.

4 HOW MODULATION AFFECTS THE ESR SIGNAL

Without modulation, the signal intensity of the resonance is too weak to differentiate from any background signal, which is why, in combination with the lock-in amplifier, modulation is necessary. The effect of no modulation can be seen in Fig. 5. This section outlines the different effects that modulation has on the ESR signal.

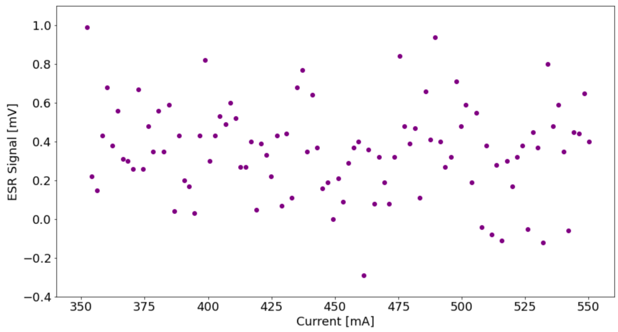

Fig. 5. ESR graph with no modulation, showing how no signal can be detected without modulation.

4.1 Investigating how modulation amplitude affects the ESR intensity and lineshape

An ideal modulation amplitude is needed to obtain the best possible ESR signal. This is achieved when the ESR intensity is largest. The best way to see what effect changing the modulation amplitude has on the ESR signal is to simply take multiple readings at different amplitudes and superimpose each of the graphs. The modulation was increased from 1.5 V to 18.0 V in 1.5 V increments.

Fig. 6 shows the ESR lines for each modulation amplitude. There are three different consequences of increasing the modulation amplitude.

Firstly, as the modulation amplitude increases, the half-width of the ESR line increases (section 4.2). Secondly, as modulation amplitude increases, the ESR signal amplitude increases, before decreasing again past a certain amplitude. Thirdly, as modulation amplitude passes a certain threshold, the lineshape begins to distort.

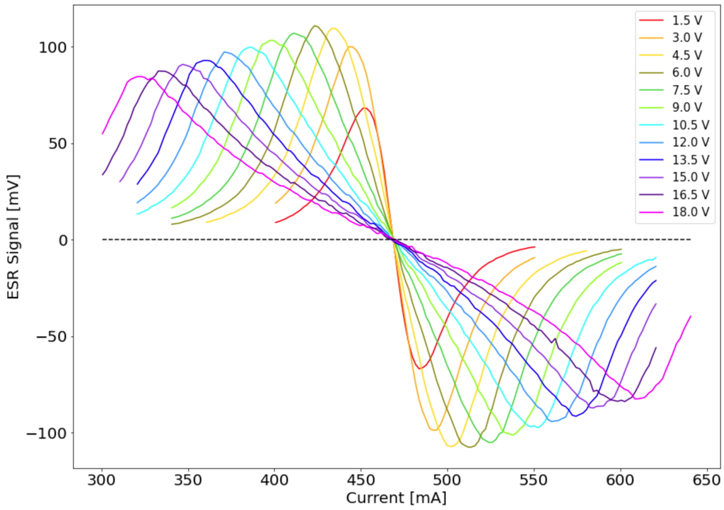

Fig. 6. ESR lineshapes at different modulation amplitudes, showing how ESR amplitude, half-width and lineshape are effected as a result of the modulation amplitude. Modulation frequency 120Hz, time constant 100ms, step 2mA, sensitivity 100mV.

This distortion affects the equation of the line (investigated in section 8), and so it is important to note at which point distortion is too large. It is clear to see that a modulation amplitude of 18.0V is too large, and significantly distorts the graph. Amplitudes of 1.5V to 9.0V don't exhibit much distortion, so would be ideal to use.

The intensity of the ESR signal increases very rapidly up to the maximum amplitude, before falling steadily back down. This is shown in Fig. 7. An increase in ESR intensity was expected, but once the modulation amplitude becomes larger than the linewidth of the ESR signal, the signal broadens and becomes distorted[2]. From this graph, we can deduce that the optimal modulation amplitude to use is 6.0V.

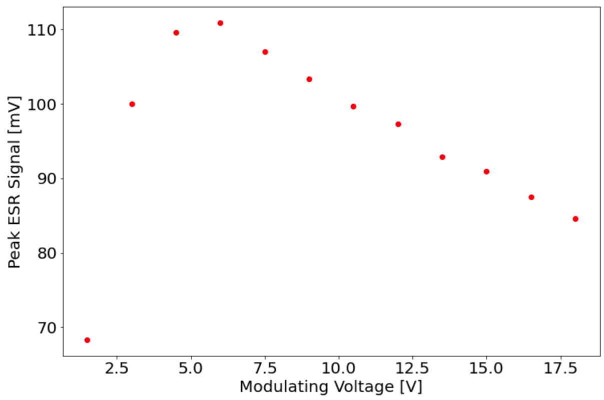

Fig. 7. How modulation amplitude affects the ESR signal amplitude. Modulation frequency 120Hz, time constant 100ms, step 2mA, sensitivity 100mV.

4.2 Finding a relationship between modulation amplitude and ESR half-width

In section 2.1 the linear proportionality between ΔB and ΔE was theorised. This proportionality has been investigated by taking ESR readings at different modulation amplitudes and measuring the half-width ΔI, which is defined in section 2.5.

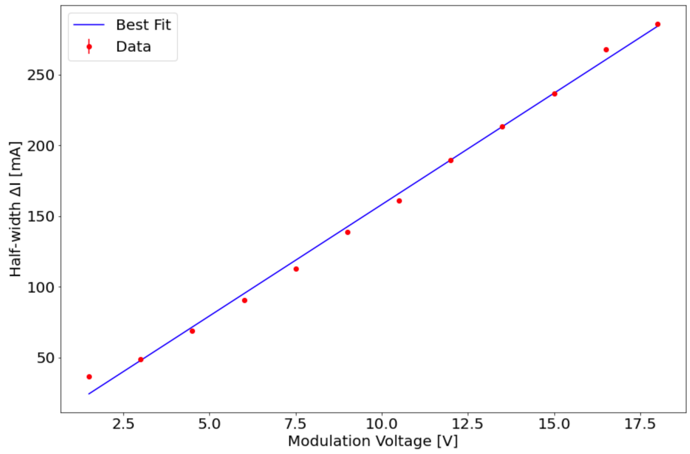

Fig. 8. Relationship between half-width ΔI and modulation voltage, with an optimised linear fit (blue). Modulation frequency 120Hz, time constant 100ms, step 2mA, sensitivity 100mV.

As seen in Fig. 8, there is a clear linear relationship between the modulation amplitude and ΔI. A best-fit line was plotted using an optimisation function to produce a linear fit. The optimisation works by fitting a function with parameters such that it produces the least amount of deviation from the data (Appendix A).

The equation for the best fit line is given by

$$\Delta I = (15.75 \pm 0.31)x + (0.72 \pm 3.38), \tag{13}$$

where ΔI is in mA, and x is the modulation voltage. Errors are given from the code. From this equation, at zero modulation ($x = 0$), $\Delta I = 0.72 \pm 3.38$ mA. The error is so large because our resolution for current is 2 mA. This can be seen when looking at Fig. 5, where no half-width is even discernible.

The data shows a superficially good fit with the best fit line, but a chi-squared test is required to quantitatively analyse this fit (Appendix B). $\chi^2_v = 1.57$, which suggests a good fit to the data.

4.3 Finding a relationship between modulation frequency and ESR amplitude

The modulation frequency is the frequency at which the lock-in amplifier 'looks' for the ESR signal. To investigate its effect on ESR the modulation frequency was set between 20Hz and 260Hz, and the peak ESR signal was recorded. The results can be seen in Fig. 9.

This relationship does not follow a simple sinusoidal function and hasn't been properly characterised. However, the important thing to be noted is that the maximum (absolute) ESR intensity occurs at a modulation frequency of 220Hz.

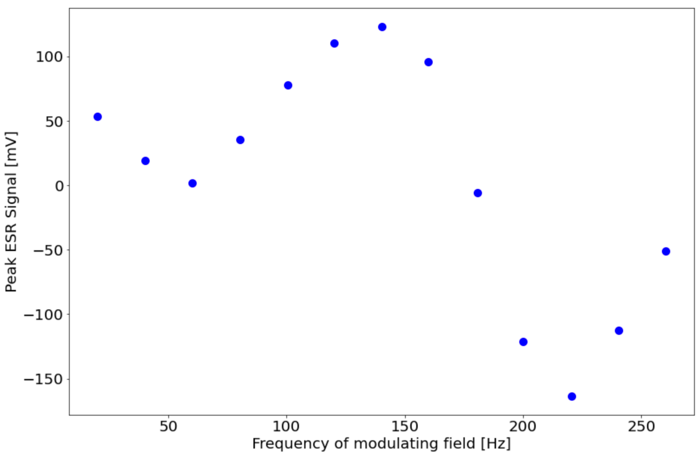

Fig. 9. How modulation frequency affects the maximum ESR signal intensity. Modulation amplitude 6.0V, time constant 100ms, step 2ma, sensitivity 100mV.

5 HOW THE LOCK-IN AMPLIFIER AFFECTS THE ESR SIGNAL

5.1 Finding a relationship between lock-in amplifier phase and ESR amplitude

As discussed in section 2.4, a sinusoidal relationship is expected between the lock-in amplifier phase and ESR amplitude. To investigate this, ESR readings between -180° and 180° in 15° intervals were taken, and the maximum signal intensity for each angle was determined. The signals were then plotted in a graph, and fitted with an optimised sine curve using Python (see Appendix A), the results of which can be seen in Fig. 10.

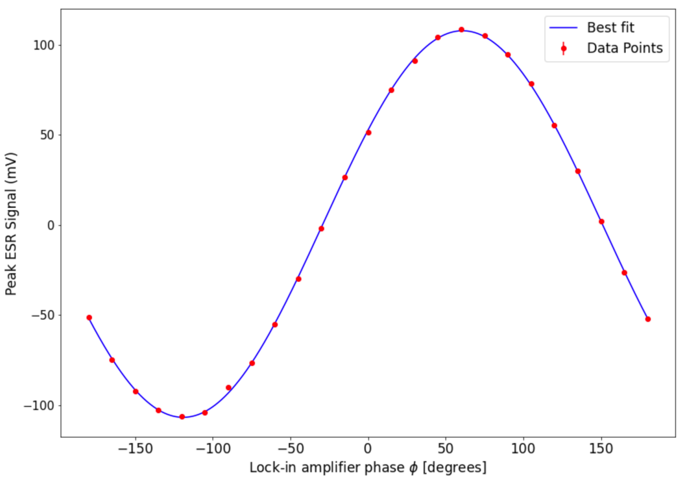

Fig. 10. Graph showing how ESR absorption amplitude varies with the lock-in amplifier phase, using: modulation frequency 120Hz, modulation amplitude 5.0V, time constant 100ms, step 2mA, sensitivity 100mV.

The equation of the best fit curve is

$$y = 107\sin(\phi + 28.9), \tag{14}$$

where y is the Peak ESR signal in mV. The errors in the constants are neglected, as the only error which matters when deciding the optimal phase is $\delta(\phi) = \pm 0.00$. Maximisation of equation (14) occurs when $\phi + 28.9 = 90$, i.e. when $\phi = 61.1°$, or $\phi = -118.9°$ in the negative direction. This value has no significant meaning, except for the fact that it allows us to set an optimal value for our lock-in amplifier phase, to give us the maximum possible signal intensity.

The chi-squared result for this fit is $\chi^2_v = 2.86$. As $\chi^2_v > 1$, we can conclude that the model is a good fit[9], but some of the variables in the sine curve may need adjusting. If we omit the data point for $\phi = -90°$ from our chi-squared test then we obtain a result of $\chi^2_v = 1.39$, suggesting an even better fit with the data. As the crucial aspect of this fit is to determine the phase at which the ESR signal is maximised, leaving out this data point is acceptable.

5.2 How different time constants affect the ESR lineshape

The time constant is used to reduce the amount of noise and improve the signal to noise ratio of the ESR graph[2]. An example of this can be seen in Fig. 11. However, if the time constant is excessively high then this leads to distortion of the lineshape and absorption position.

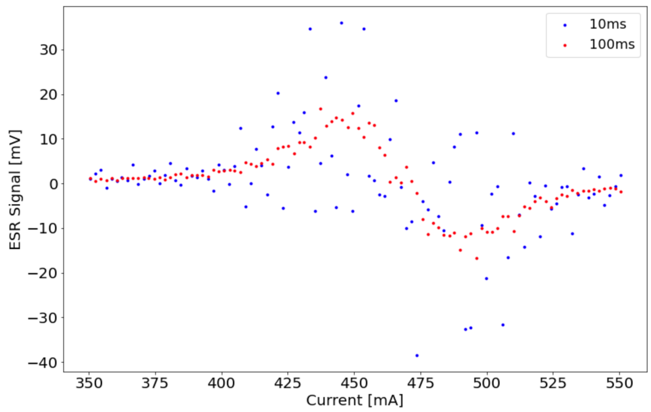

Fig. 11. ESR plot using 10ms and 100ms time constants, illustrating the improved signal to noise ratio. Modulation frequency 10Hz, modulation amplitude 5.0V, step 2mA, sensitivity 100mV.

To investigate this, nine different time constants were used to produce an ESR signal. The results are shown in Fig. 12.

The graph once again illustrates how the signal to noise ratio improves as the time constant increases (most notable between 10ms and 1s). Plotting the whole lineshape allows for the comparison of how the line shifts and distorts. As the time constant increases, the position of the peak shifts towards the right. The black line in Fig. 12 is used as a marker to determine at which point the line has noticeably shifted, which occurs around a time constant of one to three seconds.

The line is 'smoothed out' so much at higher time constants that the entire shape of the graph is distorted. This is most notable when looking at the red line in Fig. 12, which has distorted to a completely flat line. Distortion occurs because the lock-in amplifier assumes that the signals we are recording is nothing more than noise, and so it reduces how much signal we detect. This is useful at low time constants for improving our SNR ratio but detrimental at higher ones. Thus a balance must be met when choosing which time constant to use. In this case, the best time constant for smoothing out the data without loss of lineshape or line position is 300ms.

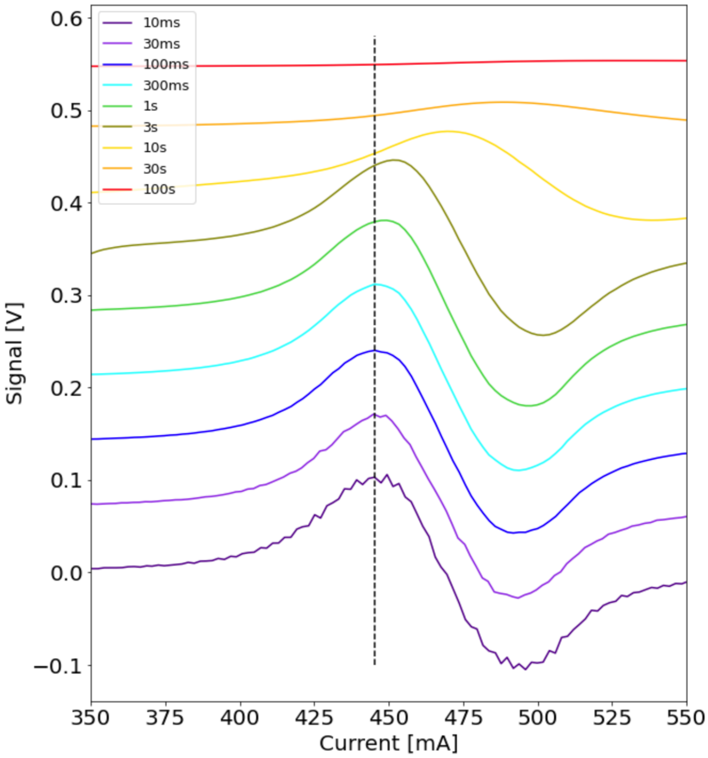

Fig. 12. ESR plot using nine different time constants, showing both how the ESR lineshape distorts with excessive time constant, and how it shifts the absorption point. A dashed black line is plotted to mark the peak position for the 100ms time constant. Modulation frequency 140Hz, modulation amplitude 3.0V, $\phi = 61.1°$, step 2mA, sensitivity 100mV.

6 HOW CHANGING RADIO FREQUENCY ALTERS THE ESR LINE

From equation 5 we expect that as ν increases so will B_0. However, as we see from this investigation, other effects occur as a result of changing the frequency.

A capacitor is used to change the frequency, which can be increased by reducing the plate width. Increasing the capacitance has the effect of decreasing the frequency ν, which is observed on the scope. The frequency is very sensitive to slight changes in capacitance, and we noticed that during the experiments the frequency would change by up to 0.2 MHz, completely on its own. For this reason, the data in this section is considered to be less accurate than others in this report.

Ten different frequencies were used to obtain what we see in Fig. 13, with ν between 39.87 MHz and 44.45 MHz.

From Fig. 13 we can see how I_0 shifts to higher values as ν increases. These different values for I_0 were recorded and plotted as a function of frequency, seen in Fig 14. As we can see, there is a very strong linear relationship between ν and I_0, as was expected ($I_0 \propto B_0$).

The second effect we notice from Fig. 13 is that as the frequency increases, the amplitude of the ESR signal also increases. The relationship seems to be linear, but this is by no means conclusive due to the very poor linear fit. Fig. 15 shows the upwards trend in amplitude.

This result was surprising, as there doesn't seem to be a reason why the radio frequencies used should have any effect on the amplitude. A possible explanation behind this could be to do with the fact that up until now, we have been using a frequency of 50 MHz for all other experiments. These investigations have been to find the 'ideal settings' to produce the largest signal intensity for $\nu = 50$ MHz. It may be that,

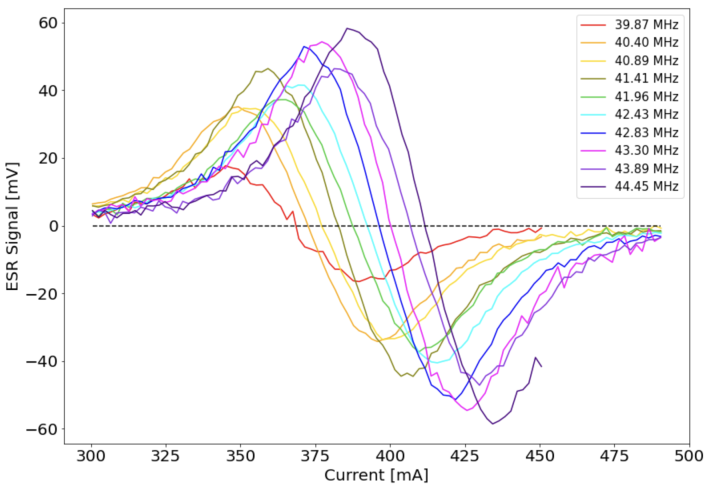

Fig. 13. The lineshape of the ESR at different frequencies. Modulation amplitude 220Hz, modulation amplitude 6.0V, phase $\phi = -118.9$, time constant 300ms, step 1mA, sensitivity 100mV.

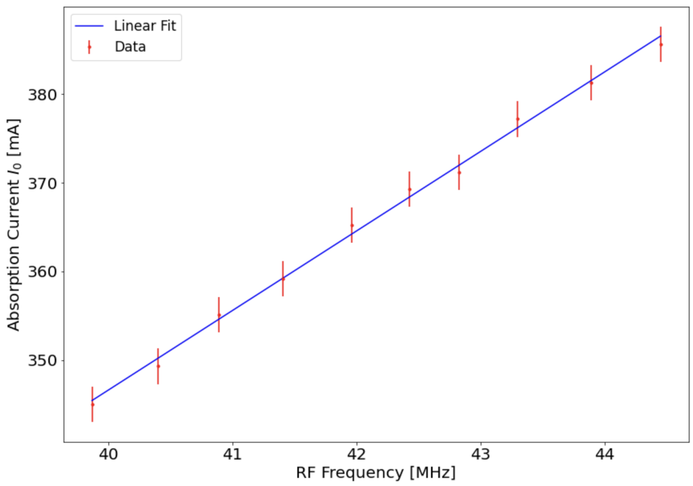

Fig. 14. The linear relationship between the frequency ν and absorption current I_0.

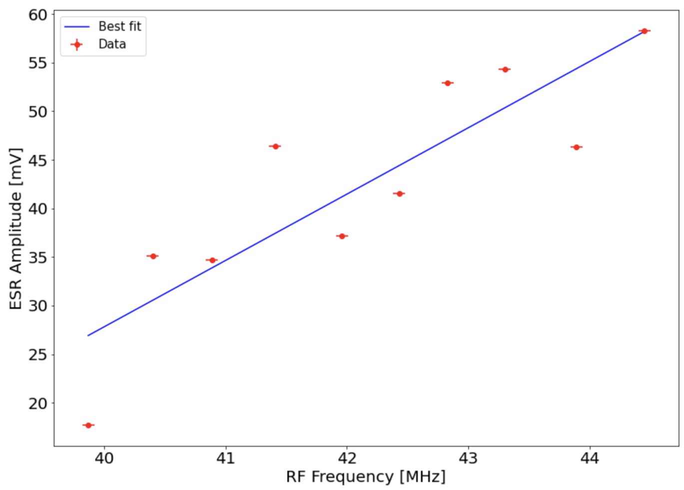

Fig. 15. How increasing radio frequency increases the intensity of the ESR signal.

as ν tends towards 50 MHz, the signal amplitude increases. To test this theory, we would need to increase the frequency past 50 MHz and see if there is a drop in amplitude. Unfortunately, the capacitor can only be used to decrease the frequency from 50 MHz, so another method would have to be used to increase ν.

7 DETERMINING THE G-FACTOR FOR DPPH

After investigating the different effects that modulation and the lock-in amplifier have on the ESR signal (section 4 and 5), it was possible to choose settings that give the largest amplitude with minimum distortion and the best signal to noise ratio. The 'optimal' ESR graph can be seen in Fig. 16

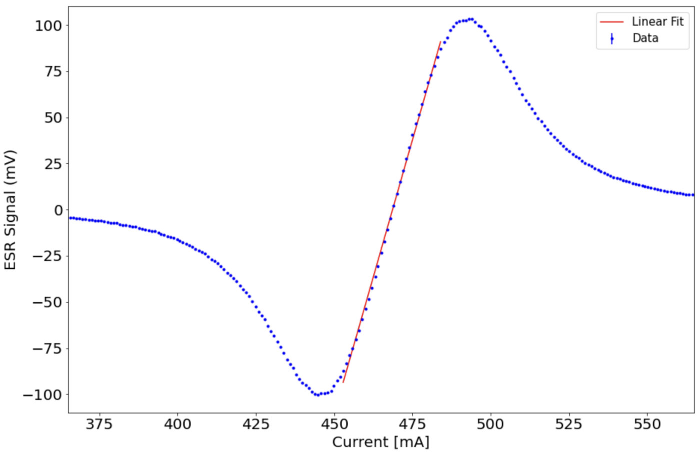

Fig. 16. Optimal ESR graph, fitted with the ideal experimental parameters calculated in sections 4 5, which include: modulation amplitude 220Hz, modulation amplitude 6.0V, phase $\phi = -118.9$, time constant 300ms, step 1mA, sensitivity 100mV. An optimised linear fit is plotted between the maxima and minima.

The ESR line is roughly linear between the maxima and minima, and so an optimised linear fit between these two points was plotted. This fit produced parameters for the equation of a straight line.

$$y = (5.93 \pm 0.05)x - (2780 \pm 22), \tag{15}$$

where x is current, and y is ESR signal, and the errors were determined from the code. From this equation, it was possible to determine the current at which absorption occurs, by setting $y = 0$. We obtain a value of $I_0 = 468.67$ mA. Using equation 9 this correlates to a magnetic field $B_0 = 1.72 \pm 0.07$ mT.

From the residuals of the linear fit, we can see that there is a systematic error, hinting that the graph isn't as linear between these two points as it appears, as the residuals are not completely random. However, we can see in Fig. 17 that the residuals at I_0 are (close to) zero, and therefore it is still possible to obtain a reasonably accurate value of I_0 using the straight-line approximation.

Noting the scope reading for frequency as $\nu = 50.20 \pm 0.02$ MHz, the value of g we obtained was $g = 2.080 \pm 0.068$. This is within 3.8% of the accepted value of g for dpph (2.004)[1], and as such can be considered to be a reasonably good experimental value, even though it doesn't exactly agree within the error parameters.

As mentioned in section 2, the position of the sample inside the solenoid drastically affects the recorded absorption position, and thus the g-factor. Although we aimed to position the sample as close to the

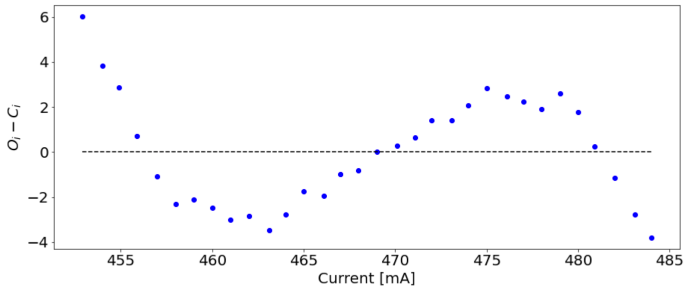

Fig. 17. The residuals of the best fit curve and data shown in Fig. 16, where we can see a systematic error when trying to approximate this as a linear line.

centre of the solenoid as possible, in practice it is not that easy; any slight deviation shifts the value of I_0, which is why our value for g is not as accurate as it otherwise could have been. A solution to this problem in future experiments would be to use a Helmholtz coil instead of a solenoid. This would allow the sample to be accurately placed in the centre of the two coils, rather than just guessing at how deep in the solenoid it should go.

8 CHARACTERISING THE LINESHAPE OF THE ESR SIGNAL

Using the same data from section 7 we were able to determine what function best described the resonance line.

A similar optimisation code to the ones used in sections 4.2 and 5.1 was used. This particular piece of code was created by Dr Mark Colclough[3]. The data was plotted with the optimised Gaussian and Lorentzian derivatives, described by equation (11) and (12) respectively.

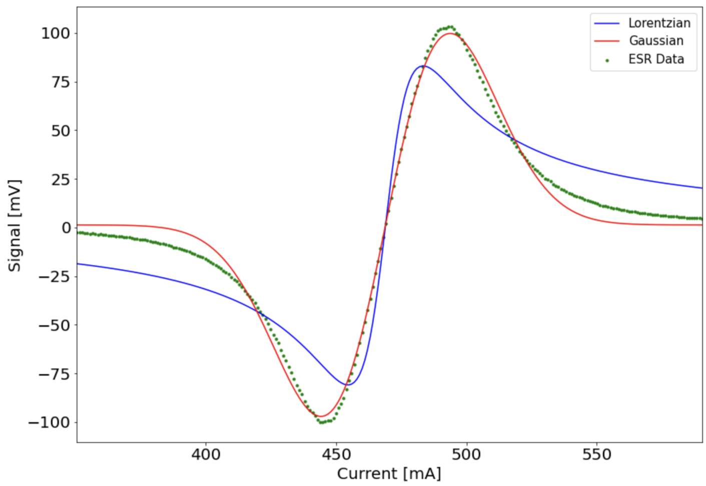

Fig. 18. Graph comparing ESR data with a Gaussian and Lorentzian lines, showing how the Gaussian line is the best fit. Experimental settings: modulation amplitude 6.0V, modulation frequency 220Hz, $\phi = -118.9°$, time constant 300ms, step 1mA, sensitivity 100mV. Gaussian optimisation constants produced: $x_0 = 468.9$, $\sigma = 24.8$, $A = 249.8$, $c = 1.3 \times 10^{-3}$

Fig. 18 shows how well these two models fit the curve. The Gaussian derivative is a much better fit with the data than the Lorentzian, however, the fit is still not perfect. From other publications, it seems as though the ESR line does follow a Gaussian distribution[10], which is what we found. However, the fact that the optimised graph very clearly has noticeable deviations from the data suggests that there may be some missing parameters from the optimisation code, which would help form a better fit.

9 CONCLUSION

This experiment aimed to determine the g-factor for dpph, by understanding how each of the different apparatus affected the electron spin resonance and using these findings to produce the most accurate data possible.

The need for modulation and the effect that modulation had on the ESR signal was investigated; we saw how excessive modulation distorted the lineshape and found the optimal values for modulation amplitude and frequency to use, which produces the largest amplitude graphs: 6.0V and 220Hz respectively.

The effect of the lock-in amplifier was investigated, where it was possible to determine the best phase and time constant to use. A sinusoidal relationship between phase and signal intensity was found, with a maximum intensity at $\phi = 61.1°$ or $-118.9°$. The time constant was found to improve the signal to noise ratio, but at excessively high time constants the line's shape and position were distorted. The optimum time constant to use was 300ms.

When we altered the frequency of radio waves we noticed the shift in the ESR line, as a result of the proportionality between ν and B_0. It was also noted that there was a weak linear relationship between an increase in ν and an increase in signal intensity, which may have been because of how the apparatus was tuned to a frequency of 50 MHz, but could not be further investigated.

With the best apparatus settings known, an optimal ESR line was recorded and the g-factor for dpph was found to be 2.080 ± 0.068, which was within 3.8% of the accepted value 2.004 [1]. We also noted how placing the sample at different positions inside the solenoid produced very different g values, and so in future, to ensure that the sample is in the optimal position, a Helmholtz coil should be used.

The equation of the ESR line was also investigated using a curve fitting code, where we concluded that the line most closely followed a Gaussian distribution, which agreed with the findings from other sources [10].

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APPENDIX A CURVE FITTING CODE

```
''' Defining linear fit '''
def linear_fit(x, a, b):
    return a*x + b

''' Optimisation of linear fit '''
popt, pcov = curve_fit(linear_fit, modulating_amplitude, half_width, sigma=errors)
perr = np.sqrt(np.diag(pcov))

''' Plotting the optimised linear fit'''
modulation_amplitude = np.arange(1.5,19,1.5)
plt.plot(modulating_amplitude, linear_fit(modulating_amplitude, popt[0], popt[1]))
```

Fig. 19. Code used to produce the best fit line in Fig. 8 section 4.2.

```
''' Defining sine curve '''
def my_sin(x, freq, amplitude, phase, offset):
    return np.sin(x*(np.pi/180) * freq + phase) * amplitude + offset

''' Optimisation of sine curve '''
popt, pcov = curve_fit(my_sin, phi, amplitude, sigma=errors)
perr = np.sqrt(np.diag(pcov))

''' Plotting the optimised sine curve'''
angle = np.linspace(-180,180,1000)
plt.plot(angle, my_sin(angle, popt[0], popt[1], popt[2], popt[3]),
         label = 'Best fit', color = 'blue')
```

Fig. 20. Code used to produce an optimised sine graph for Fig. 10 section 5.1

```
from scipy import optimize

def lorentz_deriv(x, x0, gamma, ampl, offset):
    return ampl * 16 * (x-x0) * gamma / (np.pi *(4*(x-x0)**2
                                          + gamma**2)) + offset
guess = [480, 50, 1e-3, 0]
params, covariances = optimize.curve_fit(lorentz_deriv, xdat, ydat, guess)

def gauss_deriv(x, x0, sigma, ampl, offset):
    return  ampl * np.exp(-(x-x0)**2 / (2 * sigma**2)) * (x-x0)
                           /(np.sqrt(2*np.pi)*sigma**3) + offset

guess = [480, 2.88, 1e-3, -1e-3]
params2, cov2 = optimize.curve_fit(gauss_deriv, xdat, ydat, guess)
```

Fig. 21. Code used to produce the Lorentzian and Gaussian best-fit curves in Fig. 18.

APPENDIX B REDUCED CHI-SQUARED

The chi-squared value χ^2 can be calculated using the following equation:

$$\chi^2 = \sum_i \frac{(O_i - C_i)^2}{\sigma_i^2}, \tag{16}$$

where $O_i - C_i$ is the difference between the data points and best-fit points (residuals), and σ_i is the error for each point.

The reduced chi-squared normalises this value based on the number of data points:

$$\chi_\upsilon^2 = \frac{\chi^2}{\upsilon}, \tag{17}$$

where υ is the number of data points.

APPENDIX C ERROR IN G

The error in g is calculated as:

$$\delta(g) = g\sqrt{\left(\frac{\delta(\nu)}{\nu}\right)^2 + \left(\frac{\delta(B_0)}{B_0}\right)^2} \tag{18}$$

where $\delta(\nu) = \pm 0.015$ MHz, based on the amount that ν fluctuated during the experiment. $\delta(B_0)$ has two main contributions, an error from our value for the current and an error from our best-fit line.

The error due to the current is $\delta(B_0) = \mu_0 N \delta(I_0) = \pm 0.00184$ mT. $\delta(I_0) = \pm 0.5$mA is half the step size.

The error from the best fit line, which is given in the code, is $\delta(B_0) \pm 0.057$ mT, therefore the total error $\delta(B_0) = \pm 0.068$ mT.