PHYS3111 Laboratory 1: NMR

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This experiment successfully finds the magnetic moments of the particles 1H in water, 1H in acrylic, 19F and an unpaired electron. The values respectively were 1.41113×10^{-26}, $1.41106 \times 10^{-26}, 1.32751 \times 10^{-26}$ and 947.703×10^{-26} JT^{-1}, with uncertainties respectively of 1.6×10^{-30}, $1.6 \times 10^{-30}, 1.5 \times 10^{-30}$, 35×10^{-26} JT^{-1} and with % difference to their theoretical respectively of 0.0092, $0.0043, 0.022$ and 2.1. This experiment also successfully estimates the earth's magnetic field with value of $0.373 \pm 0.022\ G$.

INTRODUCTION

Classically, a nucleon is seen as a small spinning charge having an angular momentum and a magnetic dipole moment. If a spinning charge is placed into a magnetic field the charge will experience a torque due to its magnetic moment and try to align with the magnetic field. Instead, the charge will precess. This is very similar to what we see quantum mechanically with a nucleon where this angular momentum is called spin and the rate of precession is called the Lamour frequency

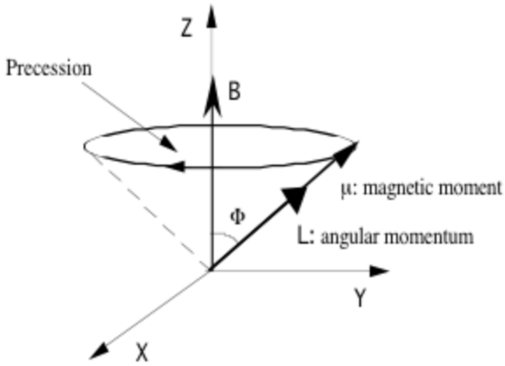


Figure 1: Precession of a nucleon magnetic moment about a magnetic field B.

If an alternating magnetic field is applied perpendicular to the static field *B*, the nucleon can absorb energy from the alternating field. This occurs if the alternating field has the same frequency as the precession of the nucleon, at the Lamour frequency. This is called resonant absorption.

A general wavefunction for the spin of our particle could then be written as;

$$\psi = a|\uparrow\rangle + b|\downarrow\rangle = a\begin{pmatrix}1\\0\end{pmatrix} + b\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}a\\b\end{pmatrix}. \quad [1]$$

The Hamiltonian representing the interaction of the magnetic moment with a magnetic field is;

$$\hat{H} = -\boldsymbol{\mu} \cdot \boldsymbol{B}. \quad [2]$$

where;

$$\boldsymbol{\mu} = gu\hat{\boldsymbol{s}} = gu\left(\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}, \begin{pmatrix}0 & -i\\i & 0\end{pmatrix}, \begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\right). \quad [3]$$

For a static magnetic field $\boldsymbol{B} = B_0\hat{z}$ the Hamiltonian is simple;

$$\hat{H} = -\frac{g\mu B_0}{2}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}, \quad [4]$$

But for an alternating magnetic field described by;

$$\boldsymbol{B} = B_{rf}\cos(\omega t)\hat{x} + B_{rf}\sin(\omega t)\hat{y} + B_0\hat{z}, \quad [5]$$

The Hamiltonian becomes much less trivial, the derivation can be seen in Pre-Work question 3.

The final expressions for $a(t)$ and $b(t)$ are;

$$a(t) = \left[a_0 \cos\frac{\omega' t}{2} + \frac{i}{\omega'}(a_0(\omega - \omega_0) + b_0\Omega) \sin\frac{\omega' t}{2}\right] e^{\frac{i\omega t}{2}}, \quad [6]$$

$$b(t) = \left[b_0 \cos\frac{\omega' t}{2} + \frac{i}{\omega'}(b_0(\omega - \omega_0) + a_0\Omega) \sin\frac{\omega' t}{2}\right] e^{-\frac{i\omega t}{2}}, \quad [7]$$

where;

$$\omega_0 = g\mu B_0, \qquad \Omega = g\mu B_{rf}, \qquad \omega' = \sqrt{(\omega - \omega_0)^2 + \Omega^2}. \quad [8]$$

The received (output) magnetic field needs to be very slowly changing in order to maintain the adiabatic condition thus the DC-like received signal is modulated (seen in Figure 2). This 2^{nd} modulation makes the signal much easier to amplify but it means the received signal is not the actual response but the 1^{st} derivative. The received data still provides enough information to extract the resonant magnetic field but will have to be done carefully.

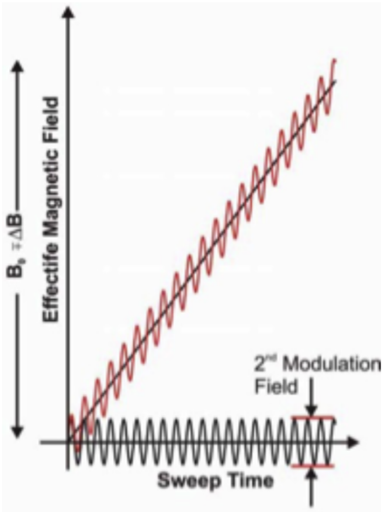


Figure 2: Modulation of the magnetic field: linear sweep as the 1^{st} modulation and sinu- soidal variation as the 2^{nd} modulation.

PRE-WORK

Question 1: Find eigenstates and eigenvalues of matrix $\hat{\boldsymbol{s}}_z$ by solving the equation;

$$\hat{s}_z\psi = s_z\psi, \tag{9}$$

$$\frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} = s_z\begin{pmatrix}a\\ b\end{pmatrix}. \tag{10}$$

Using the formula;

$$\det|\hat{s}_z - \lambda\boldsymbol{I}| = 0, \tag{11}$$

we arrive at the equation;

$$\left(\frac{1}{2} - \lambda\right)\left(-\frac{1}{2} - \lambda\right) = 0, \tag{12}$$

and thus, the eigenvalues for matrix are;

$$\lambda = \pm\frac{1}{2}. \tag{13}$$

For the eigenstates setup the equation;

$$(\hat{s}_z - \lambda\boldsymbol{I})\cdot\psi = 0 \tag{14}$$

which produces two equations for λ_1 and λ_2 respectively;

$$\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} = 0, \qquad \begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} = 0 \tag{15}$$

producing the expected eigenstates;

$$\psi = \begin{pmatrix}1\\ 0\end{pmatrix}, \begin{pmatrix}0\\ 1\end{pmatrix}. \tag{16}$$

Question 2: Solve the matrix form of the Schrödinger equation;

$$\hat{H}\psi = E\psi, \tag{17}$$

with Hamiltonian;

$$\hat{H} = -\boldsymbol{\mu}\cdot\boldsymbol{B} = -\frac{g\mu B}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}. \tag{18}$$

As the matrix is the same from question 1, the eigenstates can be taken from question 1, and the eigenvalues are multiplied through by $-g\mu B$;

$$\psi = \begin{pmatrix}1\\ 0\end{pmatrix}, \begin{pmatrix}0\\ 1\end{pmatrix}, \tag{19}$$

$$\lambda = \frac{-g\mu B}{2}, \frac{g\mu B}{2}. \tag{20}$$

Question 3: Construct the 2×2 Hamiltonian matrix for the same system except now with an oscillating magnetic field in the xy-plane described by;

$$\boldsymbol{B} = \begin{pmatrix}B_{rf}\cos(\omega t)\\ -B_{rf}\sin(\omega t)\\ B_0\end{pmatrix}. \tag{21}$$

The Hamiltonian for this system is;

$$\hat{H} = -\boldsymbol{\mu}\cdot\boldsymbol{B} = -\frac{g\mu}{2}\left(\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z\right)\cdot\begin{pmatrix}B_{rf}\cos(\omega t)\\ -B_{rf}\sin(\omega t)\\ B_0\end{pmatrix}, \tag{22}$$

$$\hat{H} = -\frac{g\mu}{2}\begin{pmatrix} B_o & B_{rf}e^{i\omega t} \\ B_{rf}e^{-i\omega t} & -B_o \end{pmatrix}. \quad [23]$$

Question 4: Solve for $\dot{a}$ and $\dot{b}$ using the time-dependent Schrödinger equation;

$$i\frac{\partial\psi}{\partial t} = \hat{H}\psi. \quad [24]$$

$$LHS = i\frac{\partial\psi}{\partial t} = i\begin{pmatrix}\dot{a} \\ \dot{b}\end{pmatrix}. \quad [25]$$

$$RHS = \hat{H}\psi = -\frac{g\mu}{2}\begin{pmatrix} B_o & B_{rf}e^{i\omega t} \\ B_{rf}e^{-i\omega t} & -B_o \end{pmatrix}\cdot\begin{pmatrix}a \\ b\end{pmatrix}, \quad [26]$$

$$= -\frac{g\mu}{2}\begin{pmatrix} B_o a + B_{rf}e^{i\omega t}b \\ B_{rf}e^{-i\omega t}a - B_o b \end{pmatrix}. \quad [27]$$

Substituting [25] and [27] into [24];

$$i\begin{pmatrix}\dot{a} \\ \dot{b}\end{pmatrix} = -\frac{g\mu}{2}\begin{pmatrix} B_o a + B_{rf}e^{i\omega t}b \\ B_{rf}e^{-i\omega t}a - B_o b \end{pmatrix}, \quad [28]$$

$$\begin{pmatrix}\dot{a} \\ \dot{b}\end{pmatrix} = \frac{i}{2}\begin{pmatrix} g\mu B_o a + g\mu B_{rf}e^{i\omega t}b \\ g\mu B_{rf}e^{-i\omega t}a - g\mu B_o b \end{pmatrix}. \quad [29]$$

Thus, expressions for $\dot{a}$ and $\dot{b}$ are found;

$$\dot{a} = \frac{i}{2}\left(g\mu B_o a + g\mu B_{rf}e^{i\omega t}b\right), \quad [30]$$

$$= \frac{i}{2}(\omega_0 a + \Omega e^{i\omega t}b). \quad [31]$$

$$\dot{b} = \frac{i}{2}\left(g\mu B_{rf}e^{-i\omega t}a - g\mu B_o b\right), \quad [32]$$

$$= \frac{i}{2}(\Omega e^{-i\omega t}a - \omega_0 b), \quad [33]$$

where;

$$\Omega = g\mu B_{rf}, \qquad \omega_0 = g\mu B_o. \quad [34]$$

Question 5: If the particle begins with spin up ($a_0 = 1, b_0 = 0$), find the probability of finding the particle in the spin down state as a function of time.

Using equation 10 of the student notes, the full solution of b with initial conditions;

$$b(t) = \left[b_0\cos\frac{\omega' t}{2} + \frac{i}{\omega'}(b_0(\omega - \omega_0) + a_0\Omega)\sin\frac{\omega' t}{2}\right]e^{-\frac{i\omega t}{2}}, \quad [35]$$

where;

$$\omega' = \sqrt{(\omega - \omega_0)^2 + \Omega^2}. \quad [36]$$

Substituting initial conditions $b(t)$ becomes;

$$b(t) = \left[\frac{i\Omega}{\omega'}\sin\frac{\omega' t}{2}\right]e^{-\frac{i\omega t}{2}}, \quad [37]$$

The probability is found by;

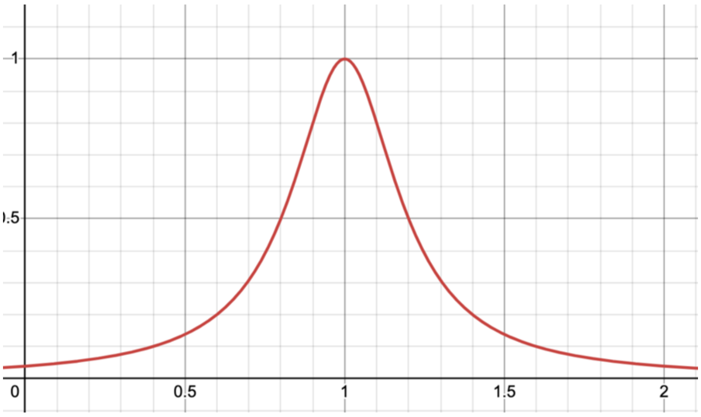
$$b^*b(t) = \left(\left[\frac{i\Omega}{\omega'}\sin\frac{\omega' t}{2}\right]e^{-\frac{i\omega t}{2}}\right)\left(\left[\frac{-i\Omega}{\omega'}\sin\frac{\omega' t}{2}\right]e^{\frac{i\omega t}{2}}\right), \quad [38]$$

$$= \left[\frac{\Omega^2}{(\omega')^2}\sin^2\frac{\omega' t}{2}\right]e^{-i\omega t}. \quad [39]$$

Question 6: Sketch the strength of the oscillation seen in question (5) as a function of ω seen by the equation;

$$P(\omega) = \frac{\Omega^2}{(\omega - \omega_0)^2 + \Omega^2}, \quad [40]$$

What parameter determines the width of the resonance?



The Ω term determines the width of the curve.

Question 7: Google the values of the proton and electron magnetic moments.

$$\mu_P = 1.411 \times 10^{-26}\ \mathrm{JT^{-1}}, \quad [41]$$
$$\mu_e = 928.5 \times 10^{-26}\ \mathrm{JT^{-1}}. \quad [42]$$

Question 8: Using these values, calculate magnetic fields which would cause precession of a) protons at $f_0 = 14\ MHz$ and b) electrons at $f_0 = 50\ MHz$.

From derivation in question 4 (adding a $\hbar$ in the numerator due to wrong derivation);

$$B_0 = \frac{2\pi\hbar f_0}{g\mu} = \frac{hf_0}{g\mu}. \quad [43]$$

For the proton; ($g = 2$ given in Student Notes)

$$B_0 = \frac{(6.626 \times 10^{-34})(14 \times 10^6)}{(2)(1.411 \times 10^{-26})} = 0.32872\ T = 3287.2\ G. \quad [44]$$

For the electron;

$$B_0 = \frac{(6.626 \times 10^{-34})(50 \times 10^6)}{(2)(928.5 \times 10^{-26})} = 0.001784\ T = 17.84\ G. \quad [45]$$

Question 9: Calculate $\frac{n_H}{n_L}$, the ratio of particles in the high to low energy states, for protons to 6 decimal places at $25°C$, $B = 0.3$ Tesla, and ΔE from question 2 using the formula;

$$\frac{n_H}{n_L} = e^{-\frac{\Delta E}{k_B T}}, \quad [46]$$
$$= e^{-\frac{(g\mu B_0)}{(1.381\times10^{-23})(25+273.15)}}, \quad [47]$$
$$= 0.9999979. \quad [48]$$

Essentially all protons are in the high energy state.

Question 10:

a) **Google the value of the 19F nuclear magnetic moment and hence;**

$$\mu_{19F} = 1.3278 \times 10^{-26}\ \mathrm{JT}^{-1}. \quad [49]$$

b) calculate the field in which 19F nuclei would process at 14 MHz.

$$B_0 = \frac{(6.626 \times 10^{-34})(14 \times 10^6)}{(2)(1.3278 \times 10^{-26})} = 0.34931\,T = 3493.1\,G. \quad [50]$$

The maximum field strength of the electromagnet is $0.34\,T$ which is lower than that of the resonance of 19F at 14 MHz.

c) Calculate the resonant frequency of 19F in the field found for protons in Question 8.

$$f_0 = \frac{B_0 \mu g}{h} = \frac{(0.32872)(2)(1.3278 \times 10^{-26})}{(6.626 \times 10^{-34})} = 13.175\,MHz. \quad [51]$$

To measure the resonance of 19F, this frequency will be used as the field strength is within the capabilities of the electromagnet.

METHOD

Experiment 1: NMRH1

1. Place the electromagnet and spectrometer in position detailed in Figure 2 of the operating instructions.
2. Turn on the electromagnet and spectrometer and ensure connection to the computer software.
3. Input the values for NMRH1 for water detailed on the printed sheet into the software.
4. Place the water sample into the nozzle of the spectrometer.
5. Run the field sweep.
6. Adjust the sweep and 2^{nd} modulation amplitude to ensure full resonance curve is on screen.
7. Screen shot the curve and record input values.
8. Repeat steps 2-7 for both Acrylic and Teflon.

Experiment 2: ESR

1. Place the Helmholtz coils and spectrometer in position detailed in Figure 2 of the operating instructions.
2. Turn on the Helmholtz coils and spectrometer and ensure connection to the computer software.
3. Input the values for ESR for TCNQ detailed on the printed sheet into the software.
4. Place the TCNQ sample into the nozzle of the spectrometer.
5. Run the field sweep.
6. Adjust the sweep and 2^{nd} modulation amplitude to ensure full resonance curve is on screen.
7. Screen shot the curve and record input values.
8. Align the magnetic field in the coil to earth's magnetic field (north).
9. Repeat steps 5-7.
10. Rotate the magnetic field such it is perpendicular to earth's magnetic field.
11. Repeat steps 5-7.

RESULTS & ANALYSIS

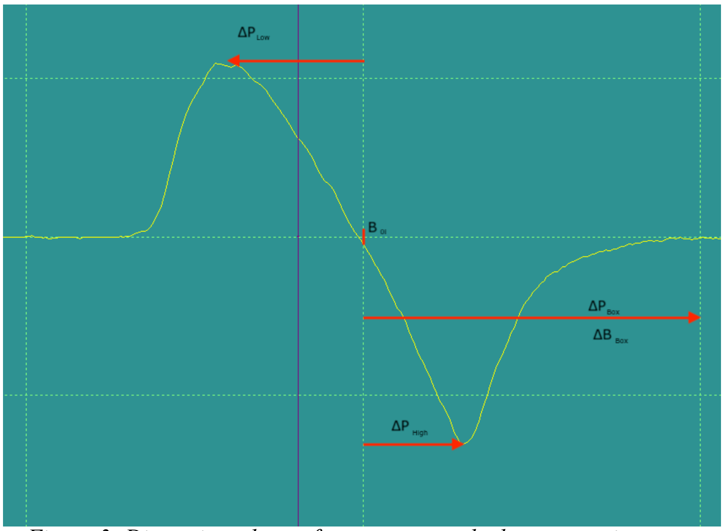


Figure 3: Dimensions drawn from curve to calculate magnetic moment.

The values for magnetic field at resonant frequency was calculated by finding the average between peak and trough of the curve in Figure 3. This was read by pixel and transformed by the unit box to give the final value of magnetic field.

Table 1: Results and pixel analysis for magnetic field at resonance.

B_{0i} (G)	f_0 (MHz)	ΔB_{Box} (G)	ΔP_{Box} (pixel)	ΔP_{High} (pixel)	ΔP_{Low} (pixel)	ΔB_{High} (G)	ΔB_{Low} (G)	B_0 (G)
NRM1H								
Water								
3286.92	14	2.5	399	118	−162	0.29573935	−0.406015	3286.86486
Acrylic								
3286.92	14	12.5	399	115	−28	0.28822055	−0.0701754	3287.02902
Teflon								
3286.92	13.171	12.5	399	83	0	0.20802005	0	3287.02401
ESR								
TCNQ								
17.84	50	0.75	399	−84	−204	−0.2105263	−0.5112782	17.4790977
ECR TCNQ Earths Field								
Anti-Parallel								
17.84	50	0.75	399	−85	−205	−0.2130326	−0.5137845	17.4765915
Perpendicular								
17.84	50	0.75	399	55	−65	0.13784461	−0.1629073	17.8274687
Perpendicular								
17.84	50	0.75	399	54	−62	0.13533835	−0.1553885	17.8299749
Parallel								
17.84	50	0.75	399	206	84	0.51629073	0.21052632	18.2034085

To calculate the magnetic moments of the particles, solve the equation for resonant frequency for μ;

$$\mu_i = \frac{hf_o}{g\left(B_{0i} + \frac{\Delta B_{Box}\frac{(\Delta P_{High} + \Delta P_{Low})}{\Delta P_{Box}}}{2}\right) \times 10^{-4}} = \frac{hf_o}{gB_0}. \qquad [52]$$

The errors for magnetic moment were calculated through the equation;

$$\Delta\mu_i = \Delta\mu_i\left(f_0, B_{0i}, \Delta B_{Box}, \Delta P_{Box}, \Delta P_{High}, \Delta P_{Low}\right), \quad [53]$$

$$= \sqrt{\left(\Delta f_0 \frac{\partial \mu_i}{\partial f_0}\right)^2 + \left(\Delta B_{0i} \frac{\partial \mu_i}{\partial B_{0i}}\right)^2 + \left(\Delta(\Delta B_{Box}) \frac{\partial \mu_i}{\partial(\Delta B_{Box})}\right)^2 + \left(\Delta(\Delta P_{Box}) \frac{\partial \mu_i}{\partial(\Delta P_{Box})}\right)^2 + \cdots}\,\Bigg|_{f_0, B_{0i}, \dots}, \quad [54]$$

where the error for pixel measurements are $\pm 0.5\ pixel$, frequency is to 5.s.f. and magnetic field measurements are to $\pm 0.373\ G$ which is determined from the maximum of earth's magnetic field measured in the later part of analysis.

Repeated for all cases, the calculated values for μ are;

Table 2: Experimental and theoretical values for Magnetic Moment.

Material	Particle	$\mu_{exp}\ (JT^{-1})$	$\Delta\mu_{exp}(JT^{-1})$	$\mu_{theo}(JT^{-1})$	% accuracy to theoretical
Water	1H	1.41113×10^{-26}	1.6×10^{-30}	1.411×10^{-26}	0.0092
Acrylic	1H	1.41106×10^{-26}	1.6×10^{-30}	1.411×10^{-26}	0.0043
Teflon	19F	1.32751×10^{-26}	1.5×10^{-30}	1.3278×10^{-26}	0.022
TCNQ	e	947.703×10^{-26}	35×10^{-26}	928.5×10^{-26}	2.1

To calculate earths magnetic field at the location of the experiment, find the difference between the values of the magnetic field when parallel and perpendicular. The perpendicular component of the earth's magnetic field is zero thus the resonant magnetic field when perpendicular is unchanged. When parallel/anti-parallel the component is maximum. Taking their difference should provide the parallel component of the earth' magnetic field.

$$B_{earth} = B_{\parallel} - B_{\perp} = 18.203 - 17.830 = 0.373 \pm 0.022\ G. \quad [55]$$

The errors for earth's magnetic field were calculated through the equation;

$$\Delta B_{earth} = \Delta B_{earth}(B_{\parallel}, B_{\perp}) = \sqrt{\left(\Delta B_{\parallel} \frac{\partial B_{earth}}{\partial B_{\parallel}}\right)^2 + \left(\Delta B_{\perp} \frac{\partial B_{earth}}{\partial B_{\perp}}\right)^2}\,\Bigg|_{B_{\parallel}, B_{\perp}}. \quad [56]$$

DISCUSSION

The experimental values of magnetic moment were impressively accurate. The data extraction method of pixel analysis was accurate, but the introduction of error is mainly due to the inaccuracy of finding the exact peak/trough of the curve. The data has noise thus a more accurate way of determining the centre of the peak/trough would be to curve fit the data and read off the stationary point. Even with the inaccurate method, the uncertainties of all values remained small.

The other main error source would be that of the arbitrary alignment to the earth's magnetic field for most of the measurements. In reality, the magnetic fields of both the NMR and ESR were relatively aligned thus the error should be constant for all but the error was none the less propagated which increased the uncertainty of the values. The values were still extremely accurate and the % difference to the theoretical was small.

CONCLUSION

The experiment was highly successful in finding the magnetic moments of the particles 1H in water, 1H in acrylic, 19F and an unpaired electron. The values respectively were 1.41113×10^{-26}, 1.41106×10^{-26}, 1.32751×10^{-26} and $947.703 \times 10^{-26}\ JT^{-1}$, with uncertainties respectively of 1.6×10^{-30}, 1.6×10^{-30}, 1.5×10^{-30}, $35 \times 10^{-26}\ JT^{-1}$ and with % difference to their theoretical respectively of 0.0092, 0.0043, 0.022 and 2.1. The experiment was successful in estimating the earth's magnetic field with value of $0.373 \pm 0.022\ G$.

REFERENCES

[1] UNSW, "Magnetic Resonance Student Notes".

[2] UNSW, "Magnetic Resonance Operating Instructions".