

(Dated: May 30th, 2017)

Electron paramagnetic resonance is used to explore different materials, including Copper Sulphate, DPPH, Beryl, and some greentack. The sample is put into a changing magnetic field and light is shot onto it, exciting transitions. Unpaired electrons flip spin, giving the atom a higher energy, but this only happens when the magnetic field sets up the correct energy difference to equal the photons energy. Using lock in amplification and a resonance chamber, noise is overcome and absorption is measured. The spectroscopic splitting factor g and hyperfine parameter A are measured experimentally, g very accurately. Greentack has a surprise contaminant, who invited Oxygen-17?

I. INTRODUCTION

In this lab, we explore properties of Electron Spin Resonance, also called Electron Paramagnetic Resonance, in different material samples. Using a homogeneous magnetic field, induced by a Hemholtz coil¹, we interact with magnetic dipoles within materials. An electron possesses a magnetic dipole moment μ_e related to its spin angular momentum by

$$\mu_e = \frac{-geS}{2m_e} \quad (1)$$

with g being the spectroscopic splitting factor for a free electron, e the charge of an electron, m_e the mass of an electron, and S being the electron's intrinsic spin angular momentum. The Hamiltonian of the system within a magnetic field then becomes

$$H = \frac{geSB}{2m_e} \quad (2)$$

We can say the largest and smallest energies of the electrons in a magnetic field will dictate two eigenstates of the system. This implies that the Z component of an electron's angular momentum will line up parallel and antiparallel to the magnetic field B. With $S_z = \pm \hbar/2$. Most of the electrons will be in the lower energy state, $S_z = -\hbar/2$ due to the Maxwell-Boltzmann distribution² Since most electrons are in a lower energy state, if photons are emitted into a material with unpaired electrons, and the photons have an energy $\hbar\omega$ equalling the energy difference in parallel and anti parallel electrons spin states, absorption will occur.³ By taking the difference in electron spin up energy to spin down energy in a magnetic field, and equating this to the energy of the photons

$$\hbar\omega = (g\beta B)/2 - -(g\beta B/2) = g\beta B \quad (3)$$

With $\beta = \frac{e\hbar}{2m_e} = 927.400 * 10^{-26} \frac{J}{T}$, the Bohr Magneton. Equation (3) gives us the tools to determine the spectroscopic splitting factor in different molecules with an unpaired electron, the first goal of this experiment.

^{a)}Also at Physics Department, Penn State University.

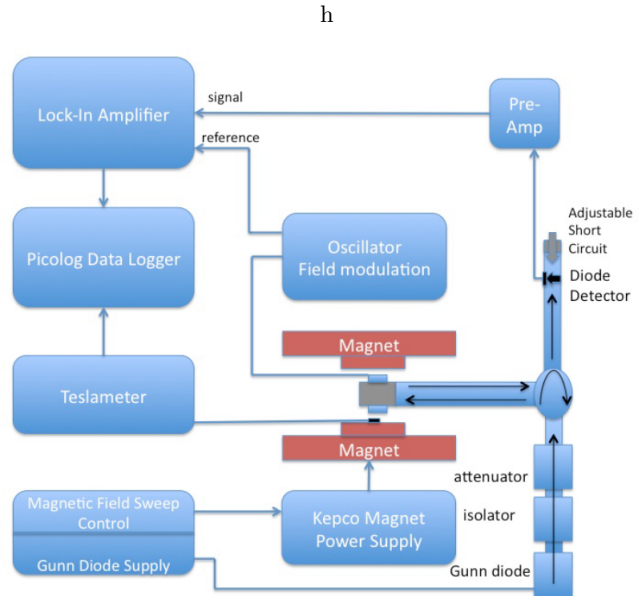


FIG. 1. Lab setup

II. EXPERIMENTAL METHODS

Our experimental setup is described thoroughly in the lab manual and can be referred to for descriptions of different parts. For convenience, a picture of the setup from the lab manual can be found in figure 1 [3]

The sample is located in a chamber called the resonant cavity, which is in the homogeneous field of the Helmholtz coil. It is important to note, that when the sample absorbs photons, the resonance of the cavity will increase by a factor of 3000. This is very beneficial providing us with a much larger signal, helping reduce the impact of system noise. There are a few noise sources in this setup, the microwave attenuator and the detector diode. To remedy this noise we modulate the magnetic field and use a lock in amplifier. After modulation of the magnetic field, and the passing of the signal through the lock-in amplifier, the new AC signal will take the form of the first derivative of the DC, unmodulated signal.

The magnetic field is modulated by two coils wound around the resonant cavity. To measure the modulation

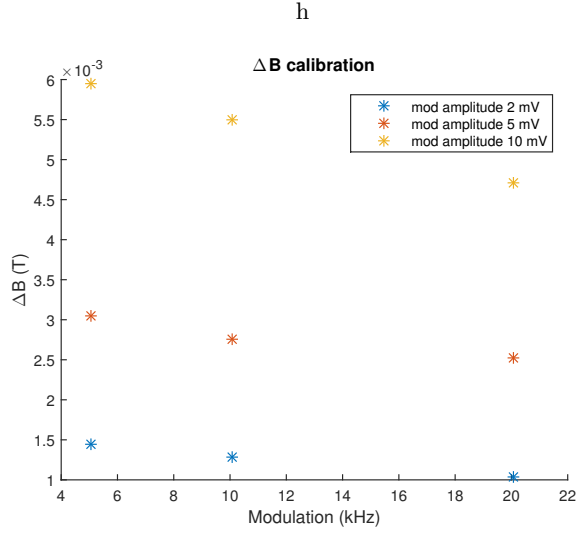


FIG. 2. The dependance of on the frequency of modulation, at 3 different modulation amplitudes; 2, 5, and 10 mV.

amplitude of the magnetic field ΔB we use a search coil. Faraday's law of induction states

$$EMF = N \frac{d\phi}{dt} \quad (4)$$

With N being the number of loops in a coil and ϕ the magnetic flux. We can say $\phi = A_{coil}B$ and $B = \Delta B \cos(\omega t)$. Lastly, $\frac{dB}{dt} = -\omega \Delta B \sin(\omega t)$. Rewriting the equation

$$EMF = -N A_{coil} \omega \Delta B \sin(\omega t) \quad (5)$$

This suggests that as the ω becomes larger, ΔB becomes smaller unless the EMF heavily depends on ω . Next we modulate the signal at an amplitude of 2, 5, and 10 mV and frequencies of 5.07, 10.07, and 20.07 kHz⁴, recording the peak to peak EMF signal from a search coil, conveniently inserted into the setup near the sample. Using (5), we can make graphs of ΔB dependence on ω for different modulation amplitudes as seen in figure II

ΔB tends to decrease as ω is raised and as the modulation amplitude is decreased. More data points would have been preferable to be able to accurately fit the curves, but now we can predict how large the field modulation will be within our range of frequencies. There are two more calibrations needed in our experimental setup.

In the data log, we receive data from our the magnetic field in mV. We must take a few readings of the magnetic field during a sweep in order to find the relationship between mV logged and mT. This has been calculated to be $field(mT) = 0.2002 * signal(mV) + 0.2335 \pm 0.001$ in appendix C. We also need to calibrate the wavemeter. The wavemeter can absorb specific frequencies of

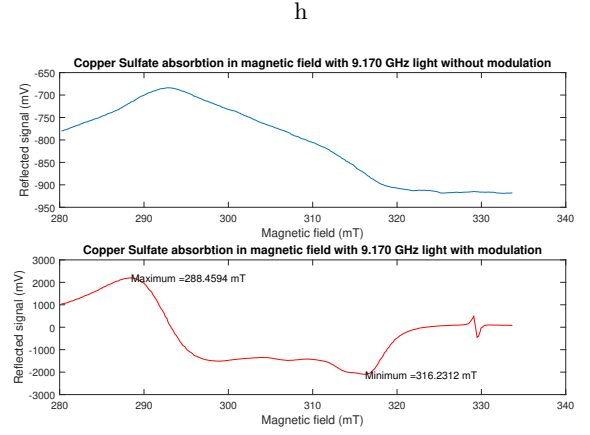


FIG. 3. Copper sulphate absorption spectrum in an increasing magnetic field with 9.170 GHz incident light, with and without modulation. Maximum and minimum are labeled on modulated signal.

light when tuned to the right chamber size. We measure this in mm. This calibration has been done in Appendix D and we find that $freq(GHz) = 11.931 - 0.2779 * length(mm) \pm 0.01$ with $freq(GHz)$: the frequency of our light and $length(mm)$ being the screw distance of our wavemeter.

III. RESULTS AND ANALYSIS

Our first sample was Copper Sulphate mixed with a small amount of DPPH encased in resin. Copper Sulphate will contain Cu^{2+} ions which have an unpaired electron. To record data on this sample we sweep the magnetic field from 0 to 500mT, showering the resonance chamber with $9.170 \pm 0.005 GHz$ light, using modulation frequency of 20.07kHz and amplitude of 5. After a preliminary sweep of the sample, we locate the Copper Sulphate section of the sample between 280mT to 330mT, which we sweep with the same parameters but at a slower rate. We compare the effect of noise on data from this sweep, with and without modulation/lock in amplifier.

It is easy to see that our modulation technique reduces signal noise. However, the new signal seems to be in the form of the first derivative of the unmodulated signal. Since we are looking for the magnetic field at the maximum of our unmodulated signal, we average the max and min magnetic fields of our modulated signal to get $B = 302.3 \pm 0.001 mT$. Next, rearrange equation (3) to find

$$g = \frac{2m_e w}{Be} \quad (6)$$

Plug in B and get $g = 2.167 \pm 0.011$. The uncertainty is from the uncertainty in w + uncertainty in B . $\pm(0.01 + 0.001)[4]$. This is a reasonable result, as the value of g for

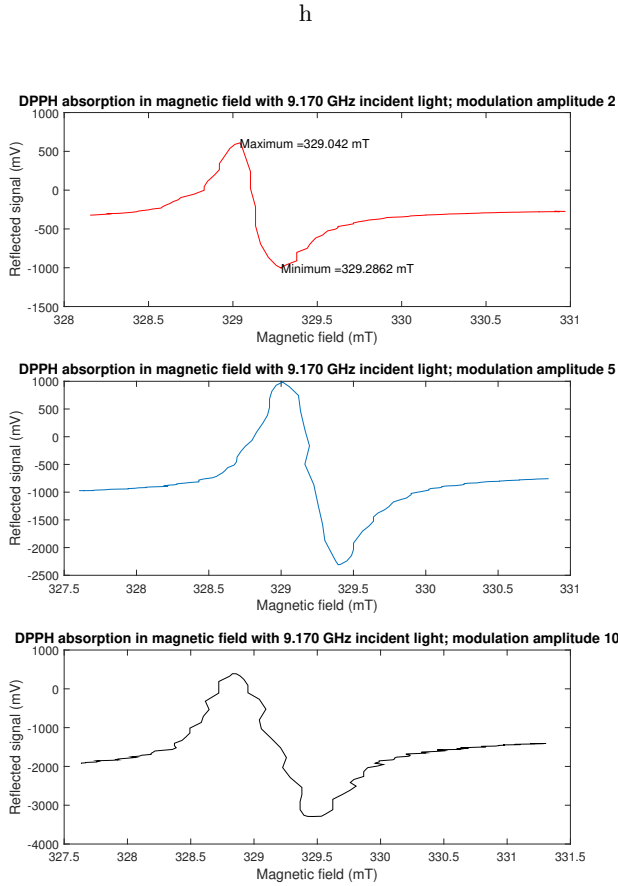


FIG. 4. DPPH absorption spectrum in an increasing magnetic field with 9.170 GHz incident light. Modulated with different modulation amplitudes of 2, 5 and 10 (top to bottom). Maximum and minimum are labeled on the spectrum with modulation amplitude of 2.

a free electron is 2.0023 [3]. Our Cu^{2+} electron magnetic dipoles μ_e can be affected by other magnetic dipoles in the material that have aligned with the magnetic field from the Helmholtz coil. This increases the magnetic field in the copper sulphate which means compared to the field the electrons experience to excite a spin flip, we will actually measure a lower magnetic field, which would account for the increased value of g in copper sulphate.

In Figure 3 one can see another peak around 330 mT. This is the DPPH encased in resin. DPPH contains a better approximation to a free unpaired electron when measured with Electron Paramagnetic Resonance thus we will get a more approximate spectroscopic splitting factor g . See the DPPH peak graphed with 2, 5, and 10mV modulation amplitudes in figure 4

The first thing we see is how messy increasing the modulation amplitude makes our graph. The modulation amplitude of 2 gives the best results, and by averaging the maximum and minimum we find our signal peak at 329.12

mT. Using equation (6) we find $g = 1.991 \pm 0.011$. This is a very good result as it is incredibly close to the spectroscopic splitting factor of a free electron 2.0023. It is fascinating how well DPPH approximates a free electron. This suggests DPPH's structure barely interacts with its free electron.

A. Hyperfine Interactions

When an electron occupies the ground state, the S orbital, the wavefunction does not go to zero at the nucleus. This means in hydrogen, an s state electron interacts with the proton when near the nucleus. This interaction, also called Fermi contact [3], adds another term to the Hamiltonian.

$$H = g\beta B \cdot S + AI \cdot S \quad (7)$$

with I being the spin of the nucleus and A being the hyperfine parameter. We run a program called spinhalf on Matlab, which graphs eigenstates of hydrogen vs a magnetic field. The Hamiltonian is built up from the spin matrices of a proton and an electron and eigenstates of this Hamiltonian are calculated with an increasing magnetic field parallel to the z axis. We see the Hamiltonian is almost diagonal, $H =$

0.2398	0	0	0
0	0.2272	0.125	0
0	0.125	-0.2398	0
0	0	0	-0.2272

[3]

...suggesting the Hamiltonian would only depend on the eigenstate that is parallel to the magnetic field, ie: the eigenstate along the z axis (S_z). An easier way to picture it is that the x and y components of the hyperfine interaction are nearly perpendicular to the magnetic field, thus they do not affect the Hamiltonian much other than at low magnetic field strengths. One can see their increased importance to determine an eigenstate at low magnetic field values in figure 5

Thus we can rewrite (7) only taking into account the Z component of spin,

$$H = g\beta B_z S_z + AI_z S_z \quad (8)$$

Equation (9) is interesting because it shows existence of 4 eigenstates in a Hydrogen atom with a fixed magnetic field and this suggests 6 different energy transitions. However, there are only two allowed transitions because the nucleus will not switch spin, thus the only transitions are $|e_+, p_- \rangle$ to $|e_-, p_- \rangle$ and $|e_+, p_+ \rangle$ to $|e_-, p_+ \rangle$ We can plug in spin values for the electron and proton and find the difference in energies for $g=2$

$$|H_{++} - H_{+-}| = |H_{-+} - H_{--}| \quad (9)$$

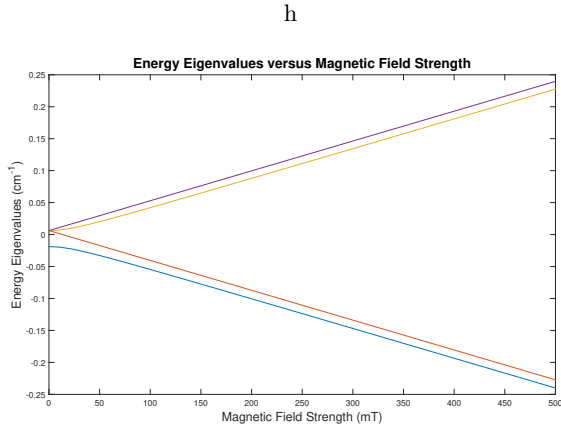


FIG. 5. The energy eigenvalues of a Hydrogen atom in a homogeneous magnetic field vs increasing magnetic field strength. The x and y components of spin affect the linearity of the eigenvalues near $T=0$, but they are negligible above 0.1T.

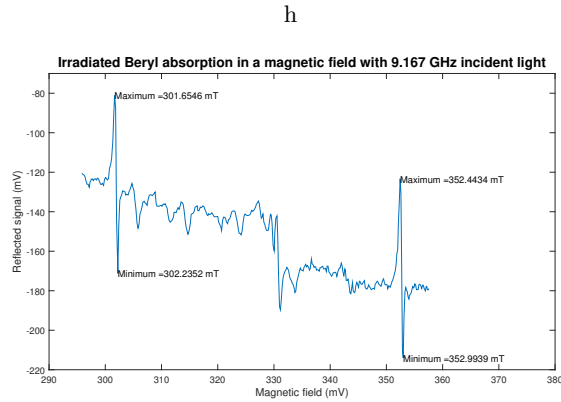


FIG. 6. Irradiated Beryl absorption in a magnetic field with 9.167 GHz incident light. Two major transitions are observed near 300mT and 350mT, the maximums and minimums are provided.

$$|B_+ - B_-| = \Delta B = \frac{A\hbar}{g\beta} \quad (10)$$

So now we are confident that we will see two transition with a free hydrogen atom. A material called irradiated Beryl is the perfect candidate to search for these two transitions. With irradiated Beryl in the sample chamber we sweep the magnetic field while showering Beryl with 9.167 GHz light. Our spectrum is shown in figure 6.

After averaging the two peaks we find the magnetic field difference between them to be 50.729 mT. We also find the magnetic field right between these peaks to be 327.21 mT. Using equation (3) at this point we find $g = 2.004 \pm 0.011$, a very accurate approximation. Using equation (10) we find $A = 1.008 * 10^{10} s^{-1}$. With some

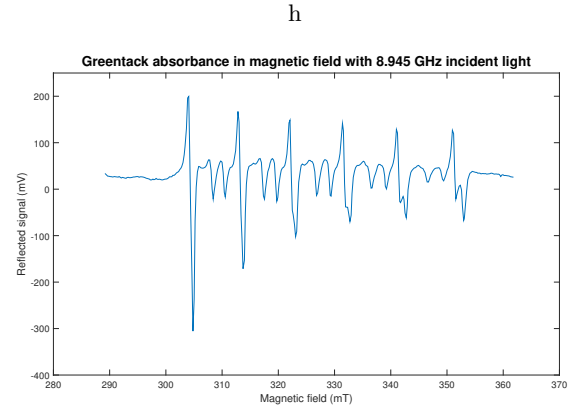


FIG. 7. Greentack absorbance in a magnetic field with 8.94 GHz incident light. One can see 6 absorption peaks and that they decrease with larger magnetic field values

quick dimensional analysis this can be compared to the value given in the lab notebook of 0.025 . First A can be divided by the speed of light to get m^{-1} then converted to cm^{-1} to yield $A = 0.3359 \pm .011 cm^{-1}$. Although not what expected, this answer is within one order of magnitude of the given value[3].

Our last sample material, greentack, is a mix of calcium silicate, oil, and small concentrations of paramagnetic ions.[3] Since it has such a rich platter of possible unpaired electron transitions, we put it in our resonance chamber under 8.995 GHz light and swept the magnetic field from 280 to 350mT, seen in figure 7.

The number of energy transitions corresponding to electron spin flips is equal to $2I + 1$ with I the nuclear spin.[3] In the absorption spectrum for greentack, there are clearly 6 peaks which lead to $I = \frac{5}{2}$. Oxygen-17 has a nuclear spin of $\frac{5}{2}$ [6]. I think this is the most likely ion producing this graph, since greentack would be exposed to it any time it comes in contact with water which may be frequent during the manufacturing or processing processes. Some down-steps in absorbance can be observed in greentack's absorbance spectrum, and they seem to be consistent, two in between every large peak. I believe this is the result of nuclear spin interacting with the magnetic field. As the magnetic field increases, the absorption peaks become smaller because nuclear spin values are lower, accounting for less change in the Hamiltonian. These steps down could be re-orientations of the nuclear spin polarization that are brought on by increasing the magnetic field. They also suggest the existence of another contaminate with a much higher nuclear spin than Oxygen-17.

IV. CONCLUSION

The electron paramagnetic resonance lab was one of the most intricate and theoretically dense labs I have ever

done, and definitely my favorite. The lab gives physical context to something unavoidably abstract that I believe many students learning quantum physics will struggle with. Error is introduced immediately in our experiment with the calibration of our measurement of frequency of light and calibration of our magnetic field reading from mV to mT, but small enough error to still let us be successful. The setup was complex and required some fine tuning before each run, setting the modulation amplitude and frequency and finding our light frequency. The lock in amplifier did a good job of isolating our signal and seemed to work better at higher modulation frequencies and lower modulation amplitudes for some runs. Our experiment was a success for measuring the spectroscopic splitting factor g of a few materials. Although our experimental g value in copper sulphate was not equal to the actual g , this was because copper sulphate is not the best approximation of a free electron. DPPH gave a much better approximation and, within error estimation, our value was equal to the theoretical value of 2.0023. Lucky enough to get a beautiful absorption spectrum for Beryl, our experimental g was again equal to the theoretical g value within error estimation. The experimental value for the hyperfine parameter A was not an acceptable value and this was probably due to the dimensional analysis step during my analysis. The value in the lab manual has different units than the equation that is derived from the hyperfine Hamiltonian. Pesky oxygen-17 is identified as the contaminate in the greentack sample, and possibilities of another contaminate exist in the absorption spectrum. These take the form of downsteps with increasing magnetic field, 2 between each absorption peak. Overall this lab was a success, increasing theoretical knowledge on spin and getting some reasonable results for the spectroscopic splitting factor of a free electron.

V. REFERENCES

- [1] S. A. Wolf, *Science* Spintronics: A Spin-Based Electronics Vision for the Future, 1488-1495, 2001.
- [2] Griffiths, David J. (2007) *Introduction to Electrodynamics, 3rd Edition*, World Publishing Company, 1998.
- [3] Uli Zuehlke, Phys 307 Electron Spin Resonance Lab Manual, 2017.
- [4] J. Alexander. *Basic Rules for Uncertainty Calculations* [Online].
<http://web.uvic.ca/~jalexndr/192UncertRules.pdf>
- [5] Griffiths, David Jeffrey. *Introduction to Quantum Mechanics*. Cambridge: Cambridge UP, 2017.
- [6] Blinder, Seyour. *Nuclear Magnetic Resonance* [Online].
https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Physical_Chemistry/Chapter_14._Nuclear_Magnetic_Resonance

Appendix A: Helmholtz Coil [2]

Magnetic field of current I in loop of radius R at a distance z above the center of the loop along its axis.

$$B = \frac{\mu_0 I R^2}{2(R^2 + z^2)^{3/2}} \quad (A1)$$

Now two coils a distance d apart along the center axis with $z=0$ as the midpoint between them.

$$B = \frac{\mu_0 I R^2}{2} \left(\frac{1}{(R^2 + (z - \frac{d}{2})^2)^{3/2}} + \frac{1}{(R^2 + (z + \frac{d}{2})^2)^{3/2}} \right) \quad (A2)$$

The first derivative of this equation with respect to z will always be zero when setting $z=0$. However, by taking the second derivative and setting this to zero at $z=0$, one gets

$$d = R \quad (A3)$$

The criteria for a Helmholtz coil is now found. A Helmholtz coil creates a very good approximation to a homogeneous magnetic field near the center of the two coils.

Appendix B: Maxwell-Boltzmann distribution

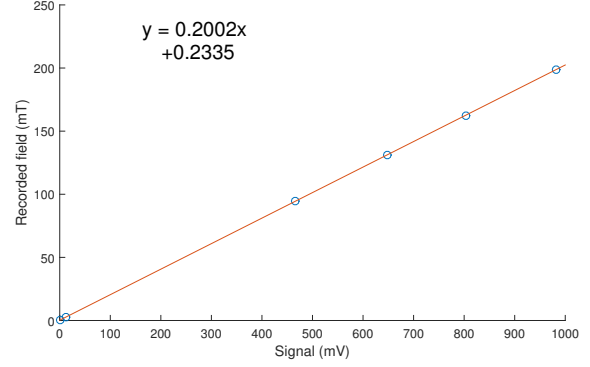
Evidence of the Maxwell-Boltzmann distribution can be shown with statistics. Consider a system of n harmonic oscillators that can contain energy in the form of quanta. Now give the system m quanta with $m \geq n$. If a condition is made that all of the oscillators have no more than one quanta each, there are $\binom{n}{m}$ states of the system, $\binom{n}{m}$ being the choose function. If a new condition says all oscillators has 2 quanta, there are $\binom{n}{m/2}$ states of the system. Three quanta per oscillator, $\binom{n}{m/3}$. If one continues this they can see that as the condition changes and oscillators occupy higher energy states, the total number of states of the system decreases. Since the number of states of a system is proportional to the probability of a system with that condition existing, one can see that the oscillators are more likely to occupy a lower energy state.

An exact derivation using the partition function can be found from the Grand Canonical Ensemble.

Appendix C: mV to mT relation

While sweeping the magnetic field, readings of the magnetic field in mT were recorded along with the data logged in mV

Magnetic Field signal in mV relation to Tesla



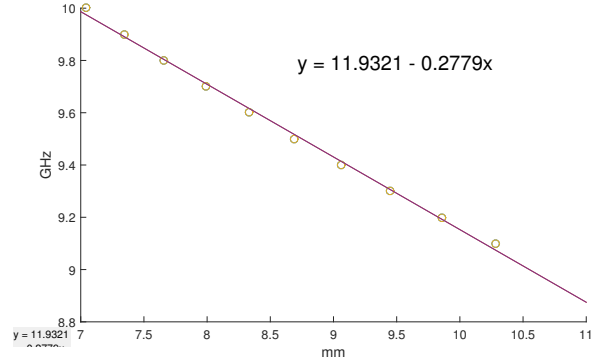
Logged data value of field in mV versus manually recorded Tesla reading, plotted and linearly fit to find an accurate relation equation.

$field(mT) = 0.2002 * signal(mV) + 0.2335 \pm 0.001$ for all recorded data in this lab.

Appendix D: Wavemeter Calibration

We were given a list of data to calibrate our wavemeter in the back of our lab manual. [3]

Wavemeter Calibration



Ghz of light from Gunn Diode versus manually recorded wavemeter mm measurements, linearly fit to find an accurate relation equation.

We now have a relation between mm on the wavemeter and the frequency of our light. $freq(GHz) = 11.931 - 0.2779 * length(mm) \pm 0.01$

¹A Helmholtz coil, invented by Herman von Helmholtz of course, is a setup of coils used to create a homogeneous magnetic field. See appendix A.

²The Maxwell-Boltzmann distribution is a distribution of particles' probability density vs particle energy of particles in an isolated system of multiple particle states. It shows that particles are most likely to occupy a low energy state. See appendix B.

³Time independent permutation theory states that the magnetic field of the photon must be aligned parallel to the magnetic field for absorption to occur[5].

⁴We have these specific frequencies because they are not a multiple of the national electricity frequency in New Zealand of 50Hz.