Electron Spin Resonance

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Abstract
The purpose of this experiment was to determine the spectroscopic splitting factor by observing electron spin resonance following Zavoisky's technique. We obtained three distinct data sets for calculating the g-factor. The values were 1.65, 1.72, and 1.83 the latter being closest to the theoretical value of 2.002319 with an 8.26% of error.

1 Introduction

Electron spin resonance (ESR) is a technique that can directly detect and quantify unpaired or odd electrons in atomic or molecular systems. These are often seen in paramagnetic materials because they exhibit a net magnetic moment when an external magnetic field is applied. For this reason, the technique is also known as electron paramagnetic resonance. The ESR technique is analogous to nuclear magnetic resonance (NMR) with the difference that the electron spins are exited instead of the spins of atomic nuclei. Free electrons are often short lived, but still play important roles in processes such as photosynthesis, oxidation, catalysis, and polymerization. Electron spin resonance was observed by Russian physicist Yevgeny Zavoisky in 1944 and the technique was developed independently by Brebis Bleaney. In this experiment we follow Zavoisky's ESR technique to obtain the g-factor which has a theoretical value of 2.002319.

2 Experimental Theory

There are three magnetic moments associated with an electron: one from its spin, another from its orbital, and the last from its total angular momentum. Electron spin g-factor is the most studied with a theoretical value roughly equal to 2.002319. Furthermore, the total angular momentum is known as the Landé g-factor named after Alfred Landé who described it in 1921. If a particle having magnetic moment is placed in a uniform magnetic field, then the moment will precess around the field with an angular Larmor frequency ***(fig. 1)***.

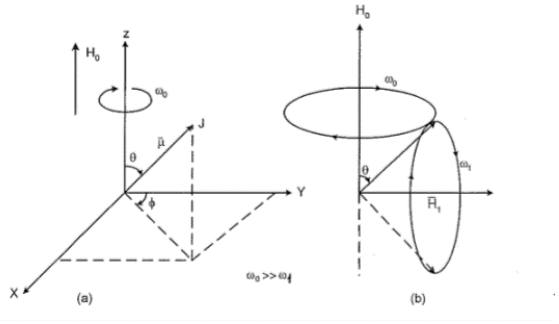

Figure 1. Precession of a magnetic moment when placed in a magnetic field. The spin precesses with angular frequency w=g(e/2mc) H.

The property of magnetic moment is observed in electrons because they have "spin". This property makes the electron behave like a bar magnet. If an external magnetic field is applied, the paramagnetic electrons can orient in a direction parallel or antiparallel to the direction of this field. This creates two distinct energy levels for the unpaired electrons and allows for measuring as they are driven between the two levels. Initially, there will be more electrons in the lower energy level (parallel) than in the upper level (antiparallel). Each alignment has a specific energy due to the Zeeman effect ***(fig. 3)***

$$E = m_s g_e \mu_B B_0, \qquad (1)$$

where g_e is the electron's g-factor, μ_B is the Bohr magneton, m_s the magnetic component, and B_0 the magnetic field strength. The separation between lower and upper state is ΔE with the splitting of the energy levels being directly proportional to the magnetic field strength ***(fig. 2)***. An unpaired electron can transition between the energy levels by absorbing or emitting a photon of energy hv,

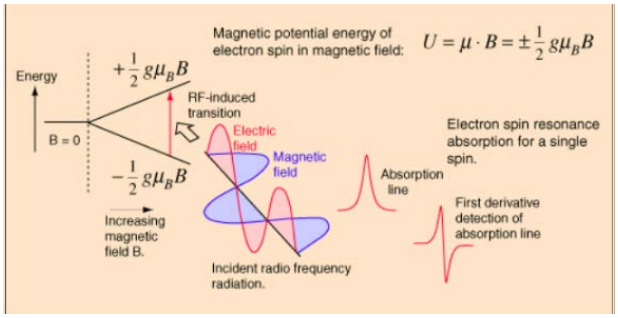

Figure 2. Separation between lower and upper states corresponding to an energy ΔE.

such that the resonance condition $h\nu = \Delta E$ is satisfied. A fixed frequency of microwave irradiation is used to excite some of the electrons in the lower energy level to the upper energy level. For a transition to occur the external magnetic field must be at a strength, such that the energy level separation between the lower and upper states is exactly matched by the microwave frequency. The condition where the magnetic field and the microwave frequency are right to produce an ESR resonance (or absorption) is known as the resonance condition. The Zeeman Effect is the splitting of a spectral line into several components in the presence of a static magnetic field ***(fig. 3)***. Zeeman observed in 1896 that sodium's spectral pair of D-lines would split when placed in an intense magnetic field. Zeeman effect is the breaking of degeneracy in atomic energy levels due to the interaction between the magnetic moment of an atom and an external magnetic field. The magnetic field interacts with an electron spin magnetic moment, but this was not yet discovered. Therefore, the term anomalous was used in cases where electron spin contributes, and more spectral patterns are observed.

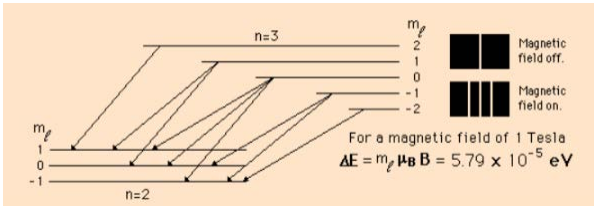

Figure 3. Representation of the Zeeman effect for hydrogen.

The g-factor can give information about a paramagnet's electronic structure. An unpaired electron responds not only to a spectrometer's applied magnetic field but also to any local magnetic fields of atoms or molecules. The effective field experienced by an electron is thus written

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

where σ includes the effects of local fields (σ can be positive or negative). Therefore, the resonance condition is rewritten as

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

The quantity g(1- σ) is denoted g and called simply the g-factor, so that the final resonance equation becomes

$$h\nu = g\mu_B B_0.$$

3 Equipment & Procedure

The equipment consisted of the Tektronix Oscilloscope, an R.F. Oscillator to determine resonance frequency, Helmholtz coils with 500 turns and a separation of 7.7cm, a Diphenyl Picryl Hydrazyl (DPPH) sample, a power supply, and the Scientific Equipment Electron Spin Resonance apparatus ***(fig. 4)***. The equipment was already connected except for the oscilloscope which was replaced by the one specified.

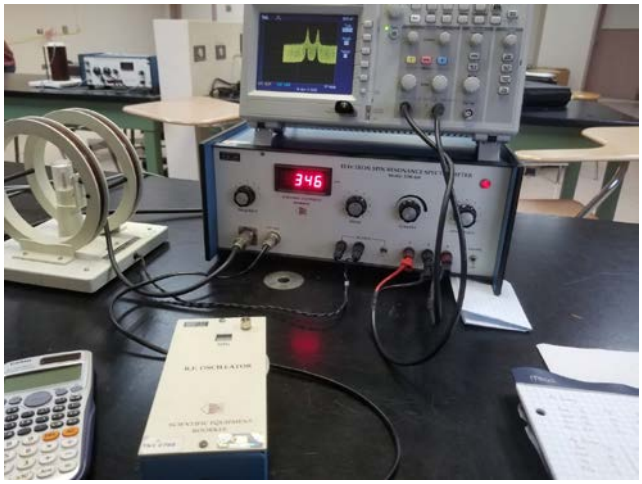

Figure 4. Representation of the Zeeman effect for hydrogen.

Following the instruction manual we calibrated the equipment and searched for the resonance frequency using the R.F. Oscillator. Keeping the frequency of the apparatus fixed we varied the current in the Helmholtz coils from 100mA to 150, 200, 250, 300, and 350mA obtaining a graph like ***(fig. 5)*** in the Oscilloscope after phase adjustments. The

data in the oscilloscope was saved and used to remake the graphs with Microsoft Excel. We changed the frequency of the ESR apparatus three times to obtain the lowest, medium, and highest frequency available. The R.F. Oscillator and the phase knob of the apparatus were adjusted to observe resonance. From these three fixed frequencies we obtained our three data sets. For the six different currents per frequency, six graphs were created to determine the 2Q values corresponding to the peak distances ***(fig. 5)***. Afterwards, we made a graph of inverse currents and Q values obtaining a straight line and its slope which was needed to calculate the g-factor ***(fig. 8, 9)***.

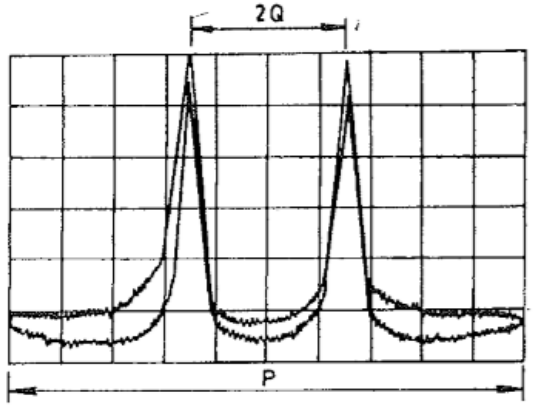

Figure 5. Sketch of the resonance peaks.

4 Data & Results

To obtain the value of the g-factor we used the formulas in ***(fig. 6)*** provided by the instruction manual. The new variables that appear here are *v* which is the resonance frequency in megahertz, *h* is Plank's constant, and *H* which corresponds to the magnetic field at the centre of the Helmholtz coils ***(fig. 7)***. To calculate the magnetic field *H* for resonance, we used the total x-deflection in the oscilloscope with zero field at the centre denoted by H_{pp} with a value of 165.25G/amp. This value was provided by the instruction manual. The magnetic field per millimetre of the x-deflection is H_{pp} / *P*, where *P* is the range of the graph in the x-axis. The magnetic field for the resonance is then the formula obtained in ***(fig.6)*** where IQ is the slope of the plotted graphs ***(fig. 9, 10, 11)***.

$$g = \frac{h\nu_0}{\mu_0 H_0}, \qquad H_0 = \frac{H_{pp}}{P} IQ$$

Figure 6. Formulas used to calculate the g-factor specific to our experimental setup.

variable	value
H_{pp}	165.25 gauss
h	6.625×10^{-27} erg sec
μ_0	0.927×10^{-20} erg/gauss
g (theoretic)	2.00

Figure 7. Variables used to calculate the g-factor.

	Data Set 1	Data Set 2	Data Set 3
slope	4.937	5.680	6.493
P	145	145	145
H_0	5.626	6.473	7.400
ν_0	13×10^6	15.6×10^6	19×10^6
g	1.651	1.722	1.835

Figure 8. Obtained data and g-factor values.

The data of the obtained graphs is summarized in ***(fig. 8)***. Data set #1 corresponds to the lowest frequency in the ESR apparatus while Data set #3 to the highest. The corresponding slopes are presented in ***(fig. 8)*** along with the *P*, *H*, *v*, and the g-factor values.

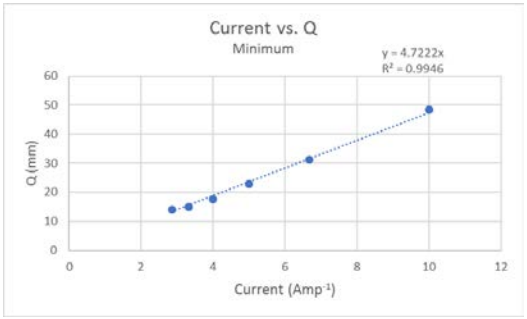

Figure 9. Graph of current in amperes vs. Q values of data set #1.

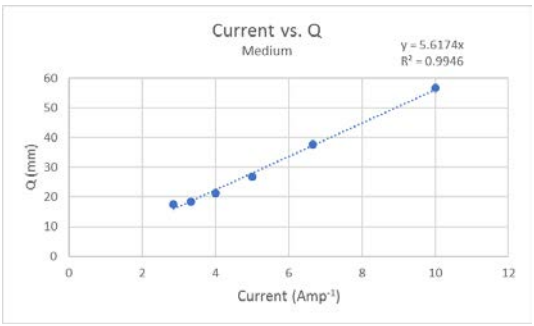

Figure 10. Graph of current in amperes vs. Q values of data set #2.

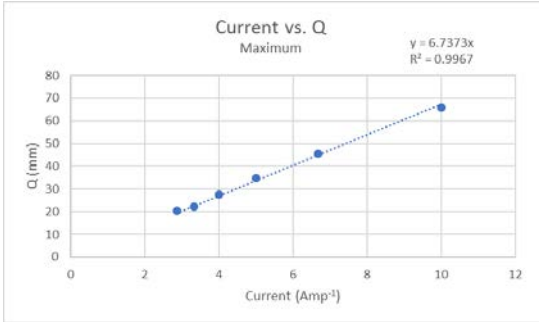

Figure 11. Graph of current in amperes vs. Q values of data set #3.

5 Conclusions

The obtained values for the g-factor did not fall within the 5% of error. However, closer values to the theoretical can be obtained given that other experimenters did obtained them utilizing a different oscilloscope. The g-factor value calculated from data set #1 was 1.651 with a 17.43% of error. For data set #2 we obtained a value of 1.722 with an error of 13.88%. Lastly, for data set #3 the value was of 1.835 with an 8.26% error being the closest to the theoretical value of 2.0023.

6 References

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