Electron Spin Resonance

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Abstract:

In this paper, for the purpose of better understanding electronic spin resonance, we investigate the organic chemical compound 2,2-diphenyl-1-picrylhydrazyl (DPPH) within a basic RF unit. Using data visualized on an oscilloscope we were able to identify and measure the width of resonance for a given input frequency. Using that information in addition to voltage measurements from our ammeter we calculated an expected magnitude of the magnetic field within the Helmholtz coils. This experimental calculation of B, as well as a magnitude measured with our magnetic field probe, allowed us to determine two analogous values for the ratio between magnetic moment and angular momentum (g). The g-factor determined via calculation was 1.621 ± 0.383 and the value as determined via probe measurements was 1.816 ± 0.131. Both of these results fall short of the accepted value of 2.0023.

I. Introduction

In this experiment we explored the properties of resonance for a single electron. A free electron has spin ½, and when the molecules of a solid exhibit paramagnetism due to its unpaired electron spin, transitions can be induced between the up and down spin states by applying a magnetic field and then supplying electromagnetic energy. When the correct photons of energy interact with the electron the resulting absorption spectrum is described as electron spin resonance (ESR). DPPH is the sample of choice due to its single unpaired electron which acts almost like a free spin.[1] As a result, it only has a single resonant frequency and a very narrow resonance energy which is easy to measure.[2] ESR has been used as a tool for the study of radicals formed in solid materials, since the radicals typically produce an unpaired spin on the molecule from which an electron is removed.[4]

Our goal was firstly to determine the constant of proportionality between the AC amplitude and the modulation amplitude (U_{mod}). This constant would allow us to convert a measurement of the width of resonance into a usable current value which could in turn be used to calculated a predicted value for the magnitude of the magnetic field at the center of the Helmholtz coils. Once this constant is obtained we sought to measure the width of resonance for a variety of input frequencies and, using that conversion factor, identify a range of currents analogous to those frequencies. Next, those resulting currents would be utilized in the calculation of the predicted B values.

For each input frequency, in addition to finding and measuring the width of resonance, we also directly measured the magnitude of the magnetic field using a magnetic field probe. This allowed us compare the values to the calculated predictions, as well as produce a second set of magnetic field data with which we could identify the ratio between magnetic moment and angular momentum. We could then compare the resulting g-factor found through probe measurements as well, as that found via calculation alone, with the well-established expected value.

II. Theory

The effect of a magnetic field on an electron spin depends upon the magnetic moment associated with the spin. For an isolated electron spin, only two orientations are possible: up and down. Applying a magnetic field provides a magnetic potential energy which splits the spin states by an amount proportional to the magnetic field, and then applied radiation of the appropriate frequency can cause a transition between the spin states. The energy associated with the transition is expressed in terms of the applied magnetic field (B), the electron spin g-factor (g), and the Bohr magneton constant (μ_B).[4] From the Plank equation we can also define the energy of a photon as frequency (ν) times the plank constant (h), thus the following relationship can be derived.[5 3]

$$\Delta E = h \cdot \nu = g\mu_B B \tag{1}$$

$$\mu_B = \frac{h \cdot e}{4\pi \cdot m} \tag{2}$$

$$\nu = \frac{g\mu_B B}{h} = \frac{gBe}{4\pi m} = gB(13.99\ GHz/T) \tag{3}$$

Where m is the mass of an electron. This relationship can be utilized in order to determine the g-factor for our sample. To find the value of B necessary to plug into equation 3, we may begin by examining the magnetic field do to a circular current loop of radius R and current I a distance z above the center of the loop.[6]

$$B(z) = \frac{\mu_0 I R^2}{2} \frac{1}{[R^2 + z^2]^{3/2}} \tag{4}$$

Where μ_0 is the constant representing magnetic permeability in a classic vacuum. Taking two such current loops a distance d apart, by principle of superposition:

$$B(z) = \frac{\mu_0 I R^2}{2} \left[\frac{1}{\left[R^2 + \left(z - \frac{d}{2}\right)^2\right]^{3/2}} + \frac{1}{\left[R^2 + \left(z + \frac{d}{2}\right)^2\right]^{3/2}} \right] \tag{5}$$

Then, taking the derivative twice we find:

$$\frac{\partial B}{\partial z} = \frac{\mu_0 I R^2}{2} \left[-\frac{3}{2} \frac{2z - d}{\left[R^2 + \left(z - \frac{d}{2}\right)^2\right]^{5/2}} - \frac{3}{2} \frac{2z + d}{\left[R^2 + \left(z + \frac{d}{2}\right)^2\right]^{5/2}} \right] \tag{6}$$

$$\frac{2}{\mu_0 I R^2}\frac{\partial^2 B}{\partial z^2} = \frac{15}{4}\frac{(2z-d)^2}{\left[R^2+\left(z-\frac{d}{2}\right)^2\right]^{7/2}} - \frac{3}{\left[R^2+\left(z-\frac{d}{2}\right)^2\right]^{5/2}} + \frac{15}{4}\frac{(2z+d)^2}{\left[R^2+\left(z+\frac{d}{2}\right)^2\right]^{7/2}} - \frac{3}{\left[R^2+\left(z+\frac{d}{2}\right)^2\right]^{5/2}} \quad (7)$$

Since we intend to measure the magnetic field at the center of the coils we can set z = 0, which yields the following:

$$\frac{\partial^2 B}{\partial z^2} = \frac{\mu_0 I R^2}{2}\left[\frac{15}{2}\frac{d^2}{\left(R^2+\frac{d^2}{4}\right)^{7/2}} - \frac{6}{\left(R^2+\frac{d^2}{4}\right)^{5/2}}\right] \quad (8)$$

Because we chose to separate our coils by a distance equivalent to their radii, we can set d = R. And since our apparatus is comprised of two coils, each with multiple loops, we multiple this final relation by a factor of N/2, where N is the number of loops. This yields the following equation, which will become our tool for predicting the magnitude of the magnetic field at the direct center of our two coils.

$$B = \mu_0 \left(\frac{4}{5}\right)^{3/2}\frac{I}{r}\cdot\left(\frac{\mathrm{N}}{2}\right) = \frac{4IN\mu_0}{5\sqrt{5}R} \quad (9)$$

In order to utilize equation 9, we must first determine a constant of proportionality between the AC amplitude and the modulation amplitude (U_{mod}). This constant can be multiplied by our resonance width to yield a modulation current in amps which can then be entered into equation 4 and return a magnitude of the magnetic field.

III. Materials and Methods

For each part of our experiment we analyzed the data produced by our setup depicted in Figure 1 and assembled according to the lab manual.[3] The system is comprised of a PASCO SE-9634 ESR apparatus which is situated with a coiled RF probe housing our DPPH sample in a vial and situated between two Helmholtz coils. The coils were manipulated by a control unit which also fed data to our Tektronix TDS 2002C oscilloscope. Frequency was adjusted with a dial on the top of the ESR unit. The control unit had three primary functions used in finding resonance: adjusting the modulation amplitude U_{mod}, adjusting the direct voltage U_0, and shifting the phase by angle φ. We measured the current using a FLUKE 175 True RMS Multimeter situated along the connection between the coils and the control unit. We probed the magnetic field using a 5180 Gauss/Tesla Meter, with the flat end of the probe positioned parallel to the coils and the tip positioned precisely at the center, just beyond the tip of the RF probe.

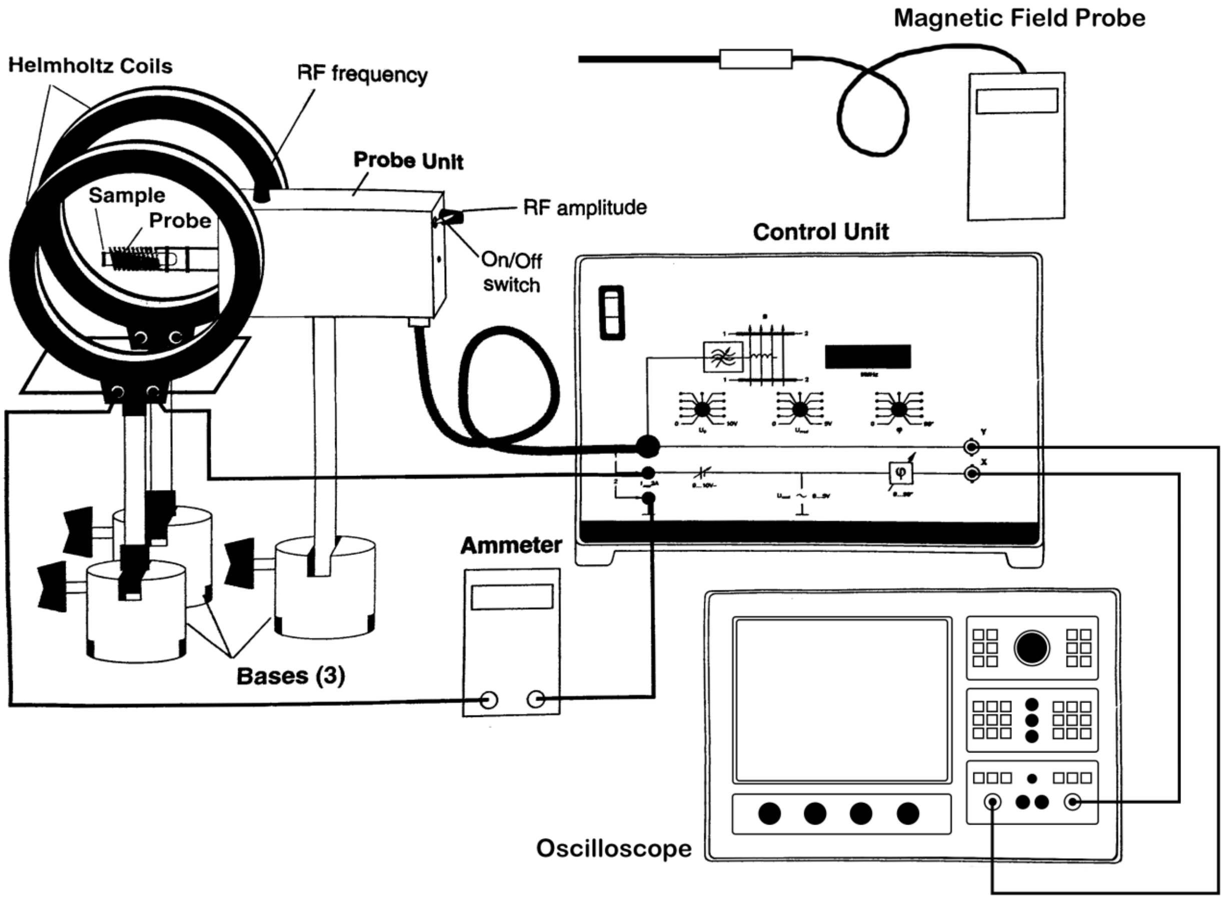

Figure 1 - System setup comprised of RF apparatus, control unit, and oscilloscope

For each of our experiments we utilized a pair of Helmholtz coils which each had a radius of 62.0 ± 0.1 mm, and they were separated by a distance (and uncertainty) exactly equal to that radius. Each coil was comprised of 320 copper wire loops (N).

For the first part of our experiment we sought to identify the constant of proportionality between the AC amplitude and the modulation amplitude. This was achieved by recording the AC amplitude for incrementing values of U_{mod} and fitting the resulting relationship. We were able to measure current with our ammeter within a certainty of ±0.001 A due to minor fluctuations in the readings. The slope of that fit was identified as the constant of proportionality. This number could then be multiplied by our measurements for the width of resonance (ΔV), which were determined on our oscilloscope within a certainty of ±0.7 V, to determine a usable current for equation 9.

Once the constant of proportionality had been determined we began to record data for resonance at incrementing values of frequency. Resonance was achieved at each frequency by tweaking the three dials on our control unit. The two values of interest were ΔV as measured on the oscilloscope and the B field as measured with the magnetic field probe. Once a value of B was determined via equation 9 as well as with the probe for an acceptable number of frequencies, a relationship was plotted for each and a value of g was extracted according to equation 3.

IV. Results, Analysis and Data

The determined relationship between AC amplitude and modulation amplitude is plotted in Figure 2 below, where the error bars are too small to be visible. The constant of proportionality was determined to be 0.1693 ± 0.0003.

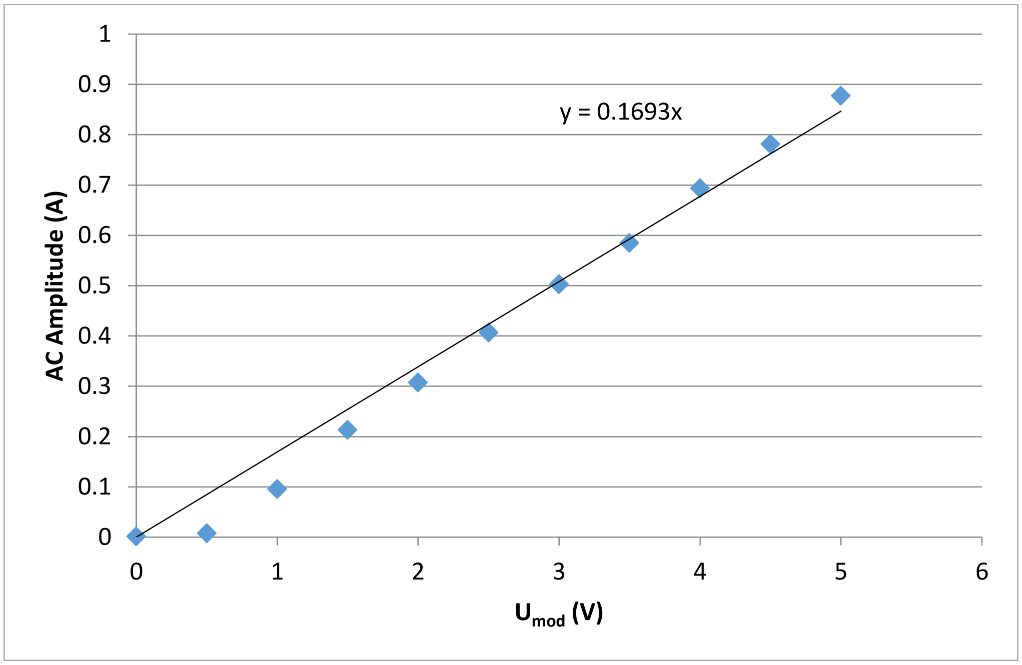

Figure 2 - AC amplitude vs U_{mod}, where the slope is the constant of proportionality

Using the above conversion factor we translated the widths of resonance for each tested frequency into a set of values for current to be plugged into equation 9. The result relationship identified between the calculated B field at resonance and the corresponding frequency is plotted in Figure 3, where the error bars are again too small to be made visible. According to equation 3 the slope of this plot is equal to 13.99g. The resulting value g-factor found via calculation was 1.621 ± 0.383.

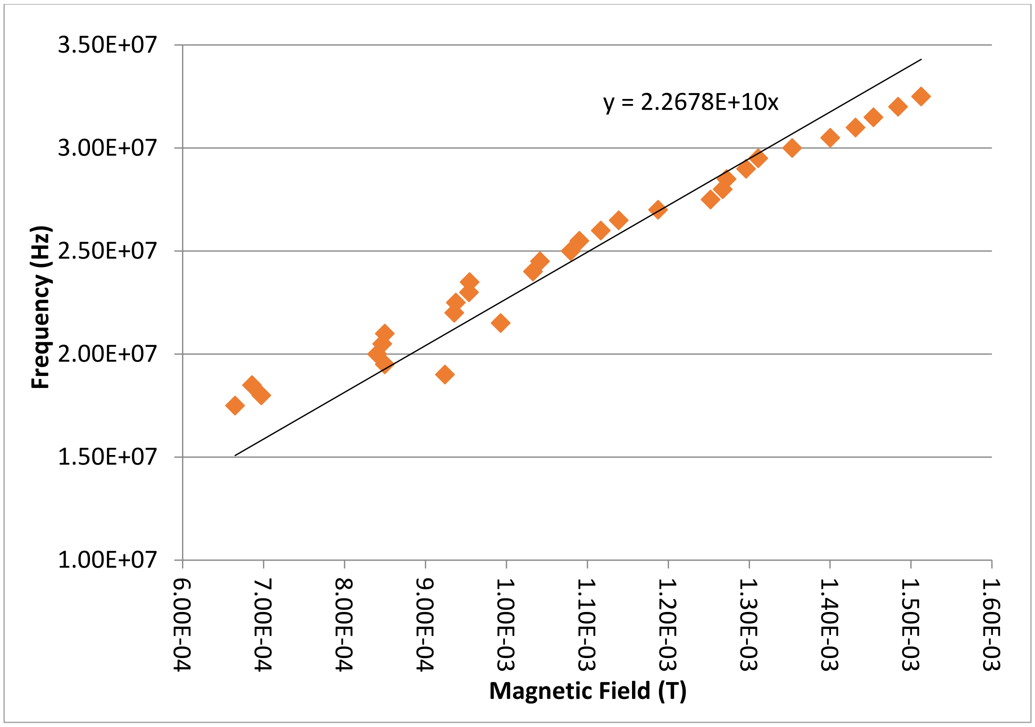

Figure 3 - Frequency vs magnetic field as calculated via equation 9

For each of the same tested frequencies we measured the magnetic field with our magnetic field probe. However, during our first run of data collection we failed to drop the alternating current component prior to probing the B field, and as a result the measurements fluctuated wildly. We returned to few of those tested frequencies in what time we had available and properly tested the magnetic field, this time with much more stable results. But as a result the data is much thinner than that presented in Figure 3. The resulting relationship between B at resonance, as found with the probe, and frequency is plotted in Figure 4 below, where once again the error bars are too small to display. Using the same relationship from equation 3 we identified the g-factor as 1.816 ± 0.131.

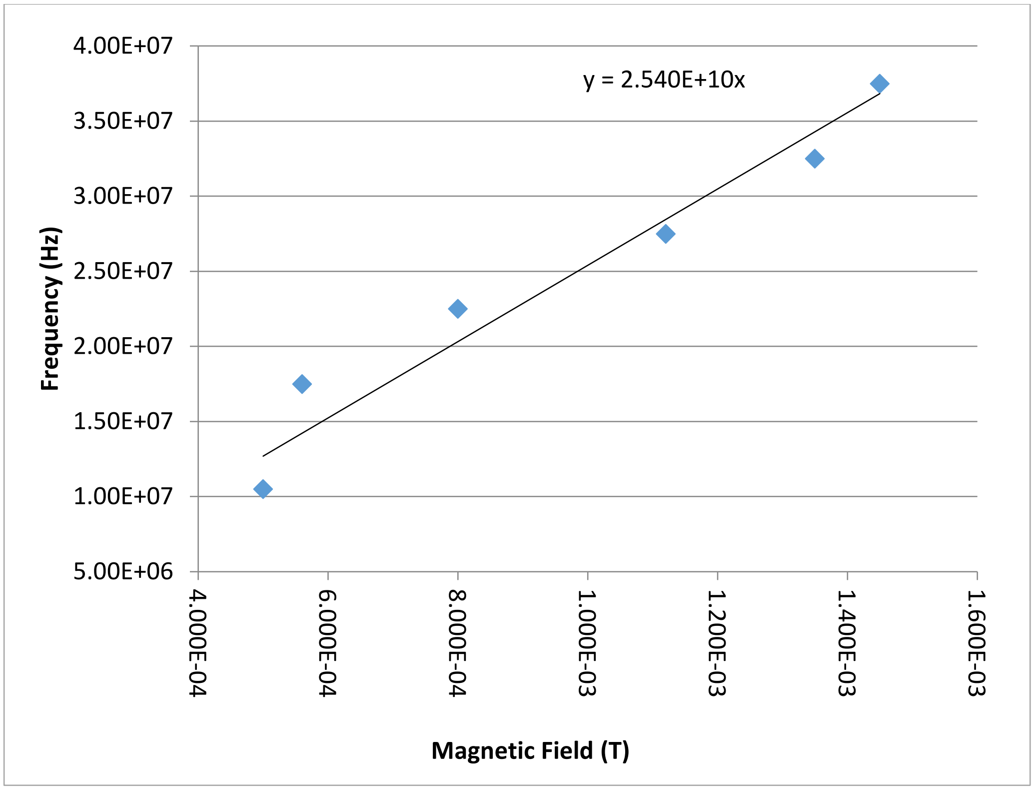

Figure 4 - Frequency vs magnetic field as determined via probe measurements

These two values for the g-factor of an electron are in agreement but fall short of the accepted value 2.0023. Potential sources of error for the g-factor determined with the calculated B field values include a potentially erroneous radius measurement, as well as perhaps faulting wiring leading to incorrect readings of the current, which may also explain the fluctuations in our readings. As for the g-factor determined with the probed values of B field, potential sources of error include slight variations in the location of measurement as well as the efficacy of the magnetic field probe itself. We noticed fairly drastic differences in measurements depending on where the probe was zeroed, and the probe seemed to fluctuate in measured values increasingly over time, even while simply sitting motionless in an isolated area.

V. Conclusion

The g-factor of the free electron in our sample, as determined via two different methods, failed to meet expectations in terms of accuracy. I would have at least expected the value of g determined with the calculated B field values to be closer to the accepted value than that of the g-factor determined with probed B field values, as it seemed there was greater room for error in the probe measurements. The dependence of a consistent and steady measurement of the B field at the exact center of the two Helmholtz coils appeared to have a much greater potential for error. However, this was not the case, and in fact the B field as calculated via equation 9 had both a larger error bar and a resulting g-factor which was further from the accepted value than that determined with the probed B field. It seems this experiment had too many opportunities for error which compiled into a poor final result. That said, the shape of the trend relating frequency and magnetic field did formulate roughly as predicted, as did the relationship between AC amplitude and modulation amplitude.

VI. References

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