Introduction

Electron spin resonance (ESR) (or electron paramagnetic resonance (EPR) as it is sometimes called) is a phenomenon whereby the intrinsic spin of an electron interacts with an external magnetic field and gives up energy to or takes energy from its surroundings. The energy of interaction between the spin and the field is quantized giving rise to two energy levels, sometimes referred to as "spin up" and "spin down." When the spin makes a transition from one state to the other, a photon of a specific frequency is emitted or absorbed. The goal of this experiment is to investigate the technique of electron spin resonance and in doing so learn about the physics of "spin." We can measure the magnetic moment of the electron to the accuracy we can measure or calculate the magnetic fields used. The physics of spin may be new to you. There is an extensive theory section presented later in this write-up. The degree to which you immerse yourself in it should be dependent on what courses you have and have not had and what you wish to get out of this particular experiment. You should discuss these matters with the instructor.

Theory: An Extremely Brief Primer

A quantum mechanical spin $\frac{1}{2}$ particle like the unpaired electrons in the material you will be using interacts with a magnetic field $B$. There are two energy levels differing by $\Delta E = 2\mu B$ where $\mu$ is the magnetic moment of the electron. When you provide photons of energy $E = hf$ there will be a resonance when $hf = 2\mu B$. In this experiment you will set the frequency $f$ as the independent variable and measure the value of $B$ that produces resonance. The slope of your data will give you the magnetic moment $\mu$ of the electron. As outlined in the extensive theory section, $\mu$ can be related to other good stuff.
**Apparatus** (see figures 1, 2, and 5)

1. Leybold radio frequency oscillator/detector (A)
2. ESR adapter (B)  {Seems to be lost. We don't need it.}
3. 3 insert coils: 13-30 MHz (E), 30-75 MHz (F) and 75-130 MHz (G)
4. resonant LC circuit (C)
5. DPPH sample (D)
6. frequency counter (to 150 kHz) (H)
7. +12/−12 V supply with common ground (J)
8. oscilloscope (K)
9. 120 V mains variable transformer (L)
10. fixed 120 to about 25 V transformer (M)
11. One ohm resistor (N)
12. Pair of Leybold Helmholtz coils (P)
13. Leybold ESR adapter (Q)
14. Two digital voltmeters

**Experiment: General Considerations**

A general discussion is given here. It is followed by two specific experiments. The unpaired electron used in this study is in a molecule called diphenylpicrylhydrazil which, fortunately for physicists, is abbreviated DPPH. It is shown in figure 3. All we are concerned about for this introductory study is that one of the electrons in this molecule behaves like an isolated electron. We note, however, that one of the uses of ESR as a research technique is learning about the complicated electrostatic and magnetic interactions in molecules like DPPH.

The sample will be placed in a coil which acts as an inductor in an LRC resonant circuit. The coil (E, F or G in figure 1) plugs into an oscillator/detector (A) which contains the rest of the resonance circuit. The first experiment is simply to investigate the sharpness or the "Q" of this resonant circuit as a function of frequency.
The second experiment is the ESR experiment. A magnetic field $B$ is produced by a set of Helmholtz coils. This determines the energy difference $\Delta E = hf = 2\mu B$ which, in turn, determines the frequency of photons which must be provided to produce resonance (i.e., to "flip" spins from $E = -\mu B$ to $+\mu B$ and vice-versa). There are a variety of ways to view how the sample (because of its unpaired electrons) leads to an observed electrical signal. From one point of view, the inductance $L$ of the coil is changed if the sample absorbs (and simultaneously contributes to) the magnetic energy created by the current in the coil. The voltage across the coil changes when $L$ does and this is detected. From another point of view, the alternating current in the coil is producing an ac magnetic field in the inductor. This alternating field can be thought of as a photon field and when the resonant condition is satisfied, the spins will absorb the photons and go from $E = -\mu B$ to $E = +\mu B$. They will also use these photons for stimulated emission and go from $+\mu B$ to $-\mu B$. Thus the electron spins are a constantly changing state. Since they behave like magnetic dipoles (i.e., like bar magnets) flipping back and forth, they give rise to an oscillating magnetic field of their own and this induces a current (really a change in current) in the coil via Faraday's Law. In any event, an appropriately measured current or voltage is measured and when the resonance condition is satisfied, this signal changes.

**Setting up the Spectrometer**

The upper case letters refer to letters in the accompanying figures. Insert the 30-75 MHz coil (coil F) in the oscillator/adapter (A). Do not use the DPPH sample in the coil. The cable from the Leybold oscillator/detector (A) to the Leybold connector box (Q) should always be left connected.

The ESR adapter box requires $+12V$ and $-12V$ supplied to it as shown in figure 2. Make sure both the $+12$ and $-12V$ supplies are off and have the voltage control knobs set to zero. One supply should have minus and ground connected together with the plus going to $+12V$ on the adapter box. The other supply should have the plus and the ground connected together with the minus going to the $-12V$ on the adapter box. The grounds on the two supplies and the "0" on the adapter box should then be connected. See the accompanying figure (although our power supplies may be quite different from that
shown in the figure). Two digital multimeters are provided to monitor the plus and minus 12 volts since you can only monitor one voltage at a time with the power supply. Connect the two digital multimeters in such a way that one is going to measure +12V and the other is going to measure −12V. There will be many leads coming from the power supply.

Make sure there is a coil in the oscillator/detector (coil F in figure 1) and that the switch (1 in figure 1) on the unit is off (the zero position). Turn on the supplies and raise the two voltages to +12V and −12V. Monitor the two digital voltmeters and make sure they are reading the appropriate sign. Within reason don't exceed 12 volts and remember to lower the voltages to zero before turning the supplies off. ("Within reason," here means to within 0.3 volts.) During the experiment, glance at these voltages from time to time to make sure they are in the vicinity of +12V and −12V.

Connect the "Y" output of the ESR adapter (Q) to channel one of the oscilloscope (K). This is the signal channel. This connector is labeled Y1 in figure 2.

Connect the "f/1000" output of the ESR adapter (Q) to channel one of the frequency counter (H) as shown the figure 2. One of the very useful features of the adapter is that it divides the frequency of the oscillator by 1000 so it an be measured with a relatively inexpensive frequency counter like the one we are using.

Turn on the scope (L), the oscillator (switch 1 on unit A in figure 1) and the frequency counter (H). Turn the frequency range (knob 7 in figure 1) until you register a frequency of about 30 kHz on the frequency counter (H). (Knob 7 turns three full turns from one end to the other and there are some places in the three turns where the resistance to turning is high. That's okay.) Note that the actual frequency is 30 MHz (or so). Make sure the scope is on dc. Look at the noise on the scope and note what happens when you vary the gain on the oscillator (knob 2 in figure 1). Every time you change the gain it takes a moment (sometimes several moments) to settle down. This is the basic spectrometer set-up.
The Resonant Circuit
With the spectrometer set-up, add the passive LC circuit (in a clamp on a stand) shown in figure 4. Inspect the passive circuit. Note it is just an inductor \(L\) (the coil) and a variable capacitor \(C\). When you add a coaxial cable there will be an effective resistance \(R\) so its just a passive LRC circuit. (What does passive mean?) If the frequency response of an LRC circuit is unknown to you, you can ask an instructor. Using the clip-to-BNC adapter, display the output of the passive circuit on the (other channel of) the scope. Set the scope time per division to its most sensitive scale. This will probably be about 25 ns per division. You have to be careful when observing a high frequency signal (tens of MHz) on a digital oscilloscope since it can play tricks on you. You can ask an instructor about this. Measure the period on the scope and make sure it corresponds to the frequency indicated on the frequency counter (times 1000). You are seeing a signal from a passive circuit. Why is there any signal at all? Where does it come from? The coil (inductor) on the passive unit is not touching the coil on the oscillator. Adjust the variable capacitor on the passive circuit and the frequency of the oscillator. Investigate the frequency dependence of the peak-to-peak amplitude of the induced signal. As an aside, this is how a transformer works. If the input to a transformer is \(V_0 \sin(\omega t + \phi)\), what is changed and what is not changed by a transformer?

The Magnetic Field for the ESR Experiment
The resonance condition we want to investigate is \(2\mu B = hf\) where \(f\) is the frequency of the oscillator and \(B\) is the strength of the magnetic field where the ESR signal occurs. By measuring \(B(f)\) or \(f(B)\), we can determine \(\mu\). The signal from the oscillator is a dc level. We could use a constant field \(B\) and slowly change \(f\), noting where the dc level changed (\(i.e.,\) where resonance occurred). Then we would reset \(B\) and repeat. Alternately, we could fix \(f\) and slowly change \(B\), note where resonance occurred, reset \(f\) and so on. We will do the latter but rather than change \(B\) slowly, we will cycle it at 60 Hz between a particular \(+B_{\text{max}}\) and \(-B_{\text{max}}\) and note, where in the cycle (that is, at which precise value of \(B\)), the ESR signal occurs. Note that the spins are interacting with their environment at 10-100 MHz (\(10^7-10^8\) Hz). A field changing at 60 Hz can be considered a \textit{very} slow change in a "fixed" field.
Remove the passive circuit and set-up the Helmholtz coils in series with the high-power 1 Ω (one ohm) resistor to the output of a 120-to-25V (or so) transformer as indicated in figure 5. (Do not hook up the resistor in parallel as shown in figure 2!). You want the current going in the same sense in both coils. The wiring in figure 5, which looks down from above, assumes the writing on both coils is facing the same direction (that is, not facing each other or facing away from each other). The reducing transformer should, in turn, be hooked up to the output of a variable 120V transformer (figure 5). Thus you can vary the voltage to the coils and 0 to 25 volts (or so) when the variac is moved from 0 to 120V or from 0 to 100% depending on the type of variable transformer is being used. If the variable transformer is of the 0-100% type, use the 140V position.

DO NOT LEAVE THE COILS WITH HIGH CURRENT RUNNING THROUGH THEM FOR PERIODS LONGER THAN TWENTY MINUTES. THEY GET QUITE HOT AND WILL SLOWLY DEGRADE OVER TIME.

On the Helmholtz pair of coils it says they have 320 turns and that the current should be limited to 2A (2 amps). The coils are of radius 6.8 cm.

Look at the field voltage (across the one ohm resistor) on the scope, turn on the variable transformer (set at zero) and note that the sinusoidal-shaped voltage increases in amplitude when you increase the variable transformer. As $V(t)$ varies from $+V_{\text{max}}$ to $-V_{\text{max}}$, the magnetic field varies from $+B_{\text{max}}$ to $-B_{\text{max}}$.

Place the ESR coil with its sample in the center of the pair of coils. Place the coils as close together as possible. Now you need to determine the magnetic field $B$ you are measuring. The magnetic field at the center of a circular loop of wire of radius $R$ carrying a current $I$ is

$$B = \frac{\mu_0 I}{2R},$$

(1)
where

\[ \mu_0 = 4\pi \times 10^{-7} \text{ tesla - m/amp} \] (2)

exactly. If there are \( N \) turns,

\[ B = \frac{\mu_0 NI}{2R} \] , (3)

If you measure a distance \( z \) from the center of the loop along an axis perpendicular to the plane of the loop of \( N \) turns, then

\[ B = \frac{\mu_0 NI R^2}{2\left(R^2 + z^2\right)^{3/2}} \] . (4)

Notice how this simplifies back to equation 3 when \( z = 0 \) (the center of the loop). The direction of the field is along the axis. Now we have two sets of these loops arranged so the currents flow in the same sense. If the two loops are \( 2z \) apart, then the point along the axis half way between them is \( z \) from each set and the field will be twice the above value.

\[ B = \frac{\mu_0 NI R^2}{\left(R^2 + z^2\right)^{3/2}} \] . (5)

It so happens that the magnetic field in this spot half way between the two loops is quite homogeneous. That is, it is quite constant over a relatively large region of space.

The Helmholtz coils you are using have \( N = 320 \) and \( R = 6.8 \text{ cm} \) (0.068 m). When they are as close together as you can get them, the centers of the two coils are 6.7 cm apart, so \( z = 3.35 \text{ cm} \) (0.0335 m) and everything in the above equation is known except the current \( I \). So,
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\[ B = \left( 4.269 \times 10^{-3} \frac{\text{tesla}}{\text{ampere}} \right) I \]  

(6)

We rewrite the above relationship \( B = DI \) where \( D \) is the constant in equation 6. For this to be valid, you have to make sure the coils are 6.7 cm apart (as measured from the centers of the coils).

**The ESR Signal**

With the 30-75 MHz coil, set the spectrometer to about 40 MHz. Put the DPPH sample in the coil. The DPPH is the black part of the sample, not the white part. Make sure a good portion of the sample is in the coil. This may mean putting it in as far as it can go.

Look at the ESR signal and the field simultaneously on the scope. (Always make sure you see noise on the signal channel. This tells you the spectrometer is on and probably working.) Both channels on the scope can be on ac now if dc settings are inconvenient. Increase the magnetic field (i.e., the variable transformer) until you see resonance. Note that in one complete cycle of the field you see four ESR resonances since the absolute value of the field has the resonant value four times in one period.

You need to figure out (the absolute value of) \( V \) that corresponds to the resonance. There may be a time delay between the ESR signal and the ac field voltage. You can tell this is the case if, on slowly increasing the field amplitude, the ESR signal does not first appear exactly at the maxima and minima of the field cycle. On further increasing the field amplitude, the ESR signal must be exactly centered around the maxima and minima of the ac field sine curve. If this is not observed then you must find a way to correct for it.

Record the frequency \( f \) and the value \( V \) where the resonance occurs. When you go below 30 MHz or above 75 MHz you must change coils. Once you have decided on an appropriate setup, you can do a careful \( V = V(f) \) experiment. Don’t perturb the geometry of the experiment midstream! AS A SAFEGUARD, PLEASE TURN THE
SPECTROMETER OFF (SWITCH 1) WHEN YOU CHANGE COILS. YOU NEEDN’T TURN OFF THE DC VOLTAGES TO THE ADAPTER.

The best way to proceed is to plot $V$ versus $f$ since these are both experimentally determined parameters. Fit your data to a line and determine the slope $G$ in $V = Gf$. Then from $V = IR$ (the resistor says $R = 1$ ohm but measure it carefully!) and $B = DI$ above, we have $IR = Gf$ and then $(B/D)R = Gf$. Since $2\mu B = hf$, $\mu = hf/2B = hR/(2GD)$ and you know everything on the right-hand side. Determine $\mu$, the magnetic moment of the electron. Pay attention to your error analysis. Discuss the sources of error. The accepted value for the electron magnetic moment (February 2008) is $\mu_e = 9.28476377(23) \times 10^{-24}$ Joule/Tesla where the number in parentheses is the uncertainty in the last two figures. There is an accompany theory write-up to help you better understand the underpinnings of this experiment.

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