Electron Spin Resonance

In this experiment you will detect the “spin” of the electron, and obtain a measure of the electron's magnetic moment, by measuring the energy of interaction of electrons with an external magnetic field. In electron spin resonance, electrons embedded in an external magnetic field change spin states by absorbing energy from an applied oscillating electromagnetic field.

This lab is instructive also because the spin of particles and the resultant interaction with magnetic fields is a commonly used tool for studying assorted aspects of atoms and molecules. Electron spin resonance, also known as electron paramagnetic resonance, uses the spin of electrons. In chemistry and medicine the interaction of the spin of the protons with applied magnetic fields is used in an experimental method known both as nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI).

BACKGROUND

Spin is an intrinsic quantum-mechanical characteristic of particles. The spin of an electron becomes evident when it is placed in a magnetic field. There is a magnetic dipole moment associated with the electron’s spin and so when embedded in an external magnetic field the energy state of the electron will depend on the orientation of its spin relative to the magnetic field. This is analogous to that of a current loop (discussed in Physics 121).

![Figure 1: Energy of current loop in B field](image)

The energy of interaction between a magnetic dipole of moment $\mu$ and a magnetic field $B$ is

\[ E = -\mu B \]

The quantum mechanics requires that there are exactly two spin states for the electron, and hence there are two allowed values of $\mu$. Therefore, for a given value of $B$, there is one possible change of energy that an electron can experience by changing its spin state. In this lab, you will
detect the absorption of electromagnetic energy \((= hf)\) by electrons changing their spin state. This will give you a direct measure of the \(\mu\) of the electron. Since the natural response frequency of the system (the frequency that the electrons absorb) equals the applied frequency (of the oscillating EM field) this is considered a resonance situation (and hence the reason for the name “electron spin resonance”).

**Magnetic Moment and Angular Momentum**

In the classical approach, you might imagine the electron as a spinning charge. In this case you can derive an equation relating its magnetic moment to its spin angular momentum. Keep in mind, however, that the magnetic moment of the electron differs from the classical analogy of a current in a loop in that electron is a really point charge and does not have a finite size to speak of. So, it is not entirely correct to conceptualize the electron's dipole field as due to a spinning charge. This approach, though, leads to a reasonable equation with the right dimensions. One simply puts in a fudge factor at the end, and the quantum mechanic’s goal then is to figure out the reason for the exact value of the fudge factor.

**Prelab exercise:** The magnetic moment of a current in a loop is given by \(\mu=IA\) where \(A\) is the area of the loop. Show that in this case \(\mu=(q/2m)L\). where \(q\) is the charge, \(m\) the mass of the charges, and \(L\) the angular momentum associated with the circling charges.

For the electron, then, we put in the quantum mechanical fudge factor, known as the \(g\)-factor, and so we have \(\mu_e=g(q_e/2m_e)L_e\). The angular momentum of the electron has a magnitude \(L_e=L_z=\pm \frac{1}{2} \hbar\). The component of the angular momentum in the direction of the magnetic field is allowed two values, given by \(L_z=\pm \frac{1}{2} \hbar\). The magnetic moment in the direction of the magnetic field, then, is \(\mu_z=\pm g \frac{e}{2m_e} \frac{1}{2} \hbar = \pm g \frac{1}{2} \mu_B\), where \(\mu_B=\frac{e\hbar}{2m_e}=9.2740 \times 10^{-24} \text{ J/T}\) is known as the Bohr magneton.

When the electron undergoes a transition in its spin-state, then, the change in energy is

\[ \Delta E = -\Delta \mu B = g \mu_B B. \]

For a known \(B\) and \(\Delta E\), you can measure the value of \(g\). The \(g\)-factor for the electron is now known to high accuracy through both experiment and theory to be 2.002319134.

**THE EXPERIMENT**

**EQUIPMENT:** (see Figures 2 & 3)

(a) rf probes: 3 small plug-in coils (inductors), labelled E,F, and G in Figure 3

(b) rf oscillator (white box on stand)
(c) Frequency adapter
(d) LC circuit (we don’t use this in our set-up)
(e) Helmholtz coils: 2 coils of diameter 13.6 cm
(f) DPPH sample (in small test tube)

You’ll also need two 12-V DC power supplies, frequency meter, oscilloscope, 120-to-25 V AC transformer, and DMM.

The DPPH contains the electrons whose spin will produce the desired resonance. DPPH is a molecule, called diphenylpeirylhydrazil (in case you like big terms), that contains an electron that is unpaired and has 0 orbital angular momentum and therefore behaves like an isolated electron.

Figure 2: ESR equipment

SET-UP and PROCEDURE:

To measure the magnetic moment of the electron you need to create a B field and provide the electrons with an oscillating EM field (i.e. a photon) of known frequency. You will create the known magnetic field with a set of Helmholtz coils. The oscillating EM field of known frequency will be created by embedding the electrons inside a small solenoid with an oscillating current. Then, by placing the solenoid with electrons inside the Helmholtz coils, you will provide the electrons with the necessary conditions.

To explore the range of possibilities and find the resonance condition, while monitoring the voltage across the solenoid, you will put an AC current through the Helmholtz coils, thereby
exploring a range of B values at a rate of 60 Hz. When the electrons undergo a spin transition by absorbing the energy of the oscillating EM field, there will be a sudden drop in the voltage across the solenoid. You will see this as a small dip in the trace of \( V_{\text{solenoid}} \) vs. \( t \). The dip results because the absorption of the energy of the electromagnetic field created by the current alters the impedance of the solenoid. To facilitate the reading, a DC offset is applied to the oscillating current of the small coil. Then, you'll only need to read a drop in the DC offset.

**Creating the oscillating electromagnetic field:**

The three small plug-in coils are capable of producing EM fields of the following frequencies: E (biggest coil): \( f \approx 13–30 \text{ MHz} \); F: \( f \approx 30–75 \text{ MHz} \); G (smallest): \( f \approx 75–130 \text{ MHz} \).

To start, insert coil F into the oscillator and set up the circuit shown in Figure 3. (Do not insert the DPPH sample yet.) The adapter ports are labelled and should be connected as follows:

- "f/1000" attaches to the frequency meter;
- "Y" attaches to channel 1 of the oscilloscope;
- "+12 V", "0", and "-12 V" attach to the DC supplies as shown.

![Oscillator set-up](image)

Note that the frequency adapter mixes down the frequency by a factor of 1000, as indicated by the "f/1000" on the port connecting to the frequency meter. This is needed because, as indicated in the chart above, you're going to need to attain frequencies of 10's of MHz, which is not readable with an inexpensive frequency meter.

To avoid damaging the oscillator, please adhere to the following operating rules:
1. DO NOT ALLOW THE APPLIED VOLTAGE TO EXCEED 12 V,
2. BE SURE THAT THE VOLTAGE IS AT 0 BEFORE TURNING THE OSCILLATOR SWITCH ON OR OFF, and
3. DO NOT UNPLUG A COIL WITH THE OSCILLATOR ON.

Steps:
1. Plug in and turn on the DC supply, the oscilloscope, and the frequency meter.
2. Turn on the oscillator, and bring the voltage up to 12 V.
3. Watch the frequency meter and turn up the gain on the oscillator (knob on the back with curved wedge label indicating strength) until a reasonable frequency reading appears on the meter. The meter should see frequencies from 30 to 75 kHz (remember that the frequency is reduced by a factor of 1000).
4. Set the oscilloscope to trigger from channel 1.

   The signal you have on the oscilloscope now is a display of the voltage across the oscillator versus time. When you achieve resonance, it is this signal that will show an absorption. Since the magnetic field will be varied at 60 Hz and you want to know at what value of the magnetic field this signal will be absorbed, adjust the oscilloscope so that it sweeps at 60 Hz (set the time scale to ~ 1 ms/cm). Since the scope is sweeping too slow for the oscillator signal, the display should appear as a straight line. When you get electron spin resonance later this straight line will show a dip.

Creating the external magnetic field (Helmholtz coils):

Use the two larger coils to make a set of Helmholtz coils. The requirement for Helmholtz coils is that the coils be placed along the same axis with a separation equal to 1/2 their diameter. The diameter of these coils is 13.6 cm. Connect the coils in series and to the transformer and variac as shown in Figure 4. Make sure that the coils face the same way (use the writing on the coils for orientation) so that the current goes the same direction in both coils.
The magnetic field inside a set of Helmholtz coils is given by

\[ B = \frac{\mu_0 NI}{R} (\frac{4}{5})^{1/2} \]

where \( R \) is the radius = 6.8 cm, \( I \) the current, and \( N \) the number of turns in each coil = 320. To measure the current, insert an ammeter, in series.

**Prelab exercise:** What is the magnetic field between the coils if the resistance across the coils is 20 ohms and the applied voltage is 5 volts?

Since it is an AC current, the ammeter (which must be set on AC) will read the r.m.s. current, not the amplitude. The coils are reported to be safe for currents up to 2 Amps, so don’t let your rms current get larger than \((2/1.4)\). You also should be careful about leaving smaller voltages on the coils for long periods of time. The coils get quite hot and will slowly degrade over time. So, as a general rule of thumb, do not leave the coils with more than 10 V or so for periods of longer than five minutes.

With the variac set at 0, turn on the power. Turn the variac up until the ammeter shows some reasonable current—e.g., 0.5 amps.

**Electron Spin Resonance:**
1. Making sure, first, that the DC power supply is off and the variac is turned to 0, place the DPPH sample inside coil F (which should still be plugged into the oscillator) and place the coil, with DPPH, inside the Helmholtz coils set-up, as shown in Figure 5.
2. Turn on the DC power supply and the oscillator switch, bring the voltage up to 12 V, and turn up the gain on the oscillator, as before.

3. Set the frequency to around 40 MHz (40 kHz on meter) using the knob on the top of the oscillator.

4. Set the oscilloscope to trigger from channel 1 and be sure that you see a signal (flat line) before continuing.

5. Watch the reading on the ammeter and slowly turn up the variac.

6. Continue raising the voltage until you see strong dips in the oscilloscope signal appear. When they do you have found electron spin resonance! Raise the voltage a little higher and note that you see four dips per cycle of the magnetic field. You get four dips per cycle at a high voltage because the absolute value of the magnetic field reaches the appropriate value for resonance four times per cycle. You get two dips when the appropriate value of the magnetic field occurs at the extrema of the sine wave, which occurs twice per cycle.

7. Now you need to determine at exactly what current going through the Helmholtz coils enables the electrons to absorb the oscillating EM fields. You can use your knowledge of a sine wave. For example, you can adjust the voltage until you see exactly two dips, in which case the absorption occurs when the current is at the extrema of the AC sine wave. Since there is a range over which two dips occur, a more precise method would be to set the current so that you have four equally spaced dips. This happens when the appropriate value of the current occurs 90° apart in phase...which means at phases of 45°, 135°, 225° and 315°, i.e. at the rms values. Therefore, the correct value of the current corresponds exactly to the reading on the ammeter.
When you go to higher oscillator frequencies, you may find that you can’t go to high enough voltages to get four equally spaced dips. In this case, the two dips approach (occurring at the maximum value of I) will have to do.

8. Record the currents and oscillator frequencies for electron spin resonance at 9 to 10 different frequencies, using about 3 frequency settings per plug-in coil. **Take care when changing the small coils--remember to turn off the oscillator first.**

ANALYSIS

Calculate the magnetic field for each ESR case you observe and make a plot of f vs B. From the slope of the best fit line, determine the magnetic moment of the electron. Show that the classical relation between angular momentum and magnetic moment of a dipole disagrees with your results for the electron. Calculate the g factor of the electron.

In your discussion, also address the issue of space quantization. If you had put the DPPH in the coils in a different orientation, would that change your results?