Electron Spin Resonance

Equipment Electron Spin Resonance apparatus, leads, BK oscilloscope, 15 cm ruler for setting coil separation

Reading Review the "Oscilloscope" lab and bring the lab write-up to this experiment for reference. You will use the BK Precision oscilloscope in this lab. The prepared and interested student might want to consult "Principles of Magnetic Resonance" by Charles P. Slichter (Harper & Row 1963). Most of this will be heavy going, but you will find some worthwhile descriptive material.

1 Introduction

Paramagnetic substances have atoms with unpaired electrons. These atoms have magnetic moments, and if these magnetic moments do not interact strongly enough to produce ferromagnetism (i.e., magnetic domains), the magnetic moments are randomly oriented if no external magnetic field $\vec{B}$ is present. The magnetic moment $\vec{\mu}$ of an electron is the result of adding its orbital and spin magnetic moments in an appropriate way. If a magnetic field is applied the electron's magnetic moment is subjected to a torque given by $\vec{\tau} = \vec{\mu} \times \vec{B}$ which tends to align $\vec{\mu}$ with $\vec{B}$. Opposing this alignment are thermal effects which tend to randomize the directions of the magnetic moments. At modest magnetic fields, it is found that the magnetization $M = C(B/T)$, where C is the Curie constant and T is the temperature. Quantum mechanically, an electron's angular momentum, and hence its magnetic moment, cannot have an arbitrary projection along the magnetic field. Only integer or half integer projections are allowed. As there is a potential energy $U = -\vec{\mu} \cdot \vec{B}$ associated with the interaction between the magnetic moment and the magnetic field, the energy levels take on discrete values, or are quantized. The different energy levels are characterized by different projections of the magnetic moments onto the magnetic field. In electron spin resonance (ESR), an oscillating magnetic field is used to induce transitions between energy levels. For simplicity, assume there are two energy levels in a steady magnetic field. If an oscillating magnetic field is applied with a frequency that corresponds to the energy difference between the two levels, photons will be absorbed as transitions are made from the lower energy level to the upper one, and photons will be emitted as transitions are induced from the upper level to the lower one. In thermal equilibrium, there will be slightly more electrons in the lower state than the upper one, as given by the Boltzmann factor. There will be a net absorption of energy from the oscillating magnetic field. This absorption is what is measured in this experiment. If the electron spins were not coupled to a thermal reservoir, the transition would "saturate" (the population difference between the two energy levels would disappear) and energy absorption would cease. In fact the spins are coupled to the lattice in which the atoms are placed, and the amount of coupling is given by the "spin-lattice" relaxation time. If this time is too long, energy absorption will be hard to see.

Because the ESR signal is perturbed by the fields produced by the surrounding lattice, it is an important method of investigating molecular and crystal structures, chemical reactions, and other problems in physics, chemistry, biology and medicine. Both splittings of the lines (resonances) and line widths provide information.

The substance used in this experiment is 1,1-diphenyl-2-picryl-hydrazyl (DPPH). This organic compound is a relatively stable free radical which has an unpaired valence electron at one atom of the nitrogen bridge which is the source of the paramagnetism of this compound. See Fig. 3. In a free nitrogen atom, 6 electrons pair off and contribute no orbital or spin angular momentum. Nor do these electrons as a whole have a net magnetic moment. The 7th electron is in a 2p state and has one unit of orbital angular momentum with an orbital quantum number of $\ell = 1$. There is a magnetic moment associated with this electron due to both its orbit and spin. When the nitrogen atom is in the DPPH molecule the orbital motion is almost zero and is said to be "quenched." This is brought about by fields produced by the surrounding lattice, which lift the degeneracy of the angular momentum states and block the precession of the magnetic moment. The electron behaves almost like an electron with no orbital angular momentum. It is the energy of this electron in a magnetic field that is investigated in this experiment. The interaction of the electron with the magnetic field is almost entirely due to the spin of the electron.

2 Theory

Due to quenching, the role of the orbital angular momentum of the paramagnetic electron in a DPPH molecule is very small. To begin with, we assume it is zero, and then will modify our expressions slightly at the end. The electron has a spin angular momentum $\vec{S}$ whose magnitude is given by $S = \sqrt{s(s+1)}\hbar$ where $s = \frac{1}{2}$ is the spin quantum number. Associated with $\vec{S}$ is a spin magnetic moment given by $\vec{\mu} = -(g_s\mu_B\vec{S})/\hbar$, where g_s is the g factor for the electron's spin and μ_B is the Bohr magneton. From this relation it is seen that g_s, which is dimensionless, is the ratio of the electron's magnetic moment in units of the Bohr magneton to its angular momentum in units of $\hbar$. We will take $g_s = 2$ although if Q.E.D. corrections are included it is equal to about 2.0023. It is twice g_ℓ, the g factor for the orbital motion. In a magnetic field that points in the z direction the spin angular momentum can only have projections onto the z-axis of $S_z = \hbar m_s$, where m_s is the magnetic spin quantum number with values of only $\pm\frac{1}{2}$. As a result the spin magnetic moment can only have projections onto the magnetic field of $\mu_z = -g_s\mu_B m_s$. As the potential energy of a dipole $\vec{\mu}$ in a magnetic field $\vec{B}$ is $U = -\vec{\mu}\cdot\vec{B}$, there are two possible energy levels whose values are $\pm\frac{1}{2}g_s\mu_B B$. The energy of these levels is plotted as a function of the magnetic field in Fig. 1. The energy difference $\triangle E$ between these two levels at a given magnetic field is

$$\triangle E = h\nu = g\mu_B B, \tag{1}$$

where ν is the frequency of the radiation necessary to induce a transition and the subscript s has been removed from the g to account for the fact that there are still small effects due to the electron's orbital motion and that we do not expect g to be exactly equal to 2. The value of g is measured in this experiment.

In an ESR experiment the line width can supply information about many properties. Contributions to the line width can come from

1. dipole-dipole interactions between the electron magnetic moments (spin-spin relaxation),

2. interactions between the magnetic moments and the fluctuating fields of the lattice (spin-lattice relaxation),

3. electron exchange interactions, which make can make the line width much smaller than expected, and
4. spin-orbit coupling which produces a path for spin-latttice relaxation.

In DPPH it is electron exchange which is important. The full width at half height of the resonance in terms of the magnetic field will be called δB and will be measured.

3 Classical Analog of Spin Flip

The kind of transition involved in ESR is often referred to as a spin flip, as the spin of the electron is flipped from one direction to another. There is a useful classical analog of this kind of transition which you are familiar with if you have done the Magnetic Torque experiment. We review the salient ideas. Consider a classical spinning ball with angular momentum $\vec{L}$ and a parallel or anti parallel magnetic moment $\vec{\mu}$ which is supplied by a small permanent magnet buried at the center of the ball. Define the gyromagnetic ratio $\gamma = \mu/L$. The quantity γ is similar to g but has dimensions. If the spinning ball is placed in a uniform steady magnetic field $\vec{B}$ the angular momentum and magnetic moment will precess about the field $\vec{B}$ with the Larmor angular frequency ω_L. The precession frequency w_L can be obtained from the equation of motion which is

$$\vec{\mu} \times \vec{B} = \omega_L \times \vec{L}. \tag{2}$$

This gives $\omega_L = \gamma B$. Assume that a rotating magnetic field B_{rot} of angular frequency ω_L is applied perpendicularly to the steady magnetic field and that the sense of rotation is the same as that of the precession. In a non-inertial reference frame rotating at the angular frequency ω_L the steady magnetic field B is transformed to zero and the rotating magnetic field B_{rot} is seen as a time independent magnetic field. The spinning ball will now precess about B_{rot} and will flip. Referring to Eq. **??** it is seen that the Larmor precession frequency is identical to the frequency that induces the transition.

In practice, a linearly polarized oscillating magnetic field is applied to the sample in a direction perpendicular to the steady magnetic field. A linearly polarized oscillating field can be view as the sum of two circularly polarized fields rotating in opposite directions. This is the procedure used in this experiment. The component of the field rotating in the wrong direction does not affect the experiment, i.e., it does not produce the conditions for resonance.

4 Experimental Set-Up

Fig. 4 shows the experimental set-up. Helmholtz coils, which are wired in parallel, are connected to a power supply. A multimeter measures the current to the coils. The power supply provides a DC voltage U_0 to the coils plus a 60 Hz modulation voltage U_{mod}. Two controls on the power supply vary these voltage. The DC voltage U_0 produces a DC current I_0 in each wire of the coils, and a sinusoidal voltage U_{mod} produces the AC current I_{mod}. In addition, there is a 3rd control that changes the phase φ of the modulation voltage with respect to the demodulated radio frequency (RF) signal. From the power supply the voltage to the Helmholtz coils is also connected to the x-axis or channel 1 of an oscilloscope. The oscilloscope, not identical to the one shown in the Fig. 4, can be used either as a two trace scope or as an x-y scope.

The RF unit has the oscillator circuit in it. Part of the oscillator circuit is a plug-in coil into which the DPPH sample is inserted. A cable from the RF unit is connected to the power supply and serves not only to provide the oscillator with the power it needs, but to carry the demodulated RF signal to the power supply. From the power supply the signal goes to y-axis or channel 2 of the oscilloscope. The top of the RF unit has a knob that the controls the frequency of the RF. The frequency can be read out on the power supply. Three plug-in coils cover the range of frequencies used in this experiment. The largest coil is for the lowest frequencies and the smallest coil for the highest frequencies. On the back of the RF unit is an off-on switch for the unit and a knob that adjusts the amplitude of the RF. This knob should be fully clockwise for maximum amplitude. Fig. 5 is a top view of the RF unit with the coil inserted into the Helmholtz coils.

4.1 Helmholtz Coils

Two coaxial circular coils of radius R that are separated by R are known as Helmholtz coils. Such coils are often used to create a relatively uniform magnetic field. At the center of the coils the first and second derivatives of the magnetic field in the axial direction are zero. The choice of coil separation leads to this result. If N is the number of turns in each coil and I_0 is the current in each wire, the magnetic field at the center of the coils is given by

$$\frac{\mu_0 N}{2R}\left(\frac{4}{5}\right)^{3/2}(2I_0)\ T = 2.115(2I_0)\ mT, \qquad (3)$$

where $\mu_0 = 4\pi \times 10^{-7}\ N/A^2$. This expression is written in terms of $2I_0$ as that is the quantity actually measured.

5 Overview of the Experiment

There are two parts to the experiment. One is obtaining the effective g value for the electron and the other is obtaining a line width for one of the resonances. For both parts resonance curves must be obtained. A resonant curve is obtained by setting the RF frequency at a fixed value and sweeping the magnetic field so that the energy difference $\triangle E$ between the two energy levels of the electron correspond to the RF frequency. See Fig. 1. At the resonant frequency a maximum amount of power is being absorbed by the sample and the RF current in the oscillator circuit is a minimum. Off resonance, the RF current in the circuit is a maximum. The resonance is an absorption curve. The RF current in the oscillator circuit is demodulated or rectified in the RF unit giving a DC current that is proportional to the RF amplitude in the oscillator circuit. This "DC signal" or signal, which actually varies as the magntic field is varied, is displayed on channel 2 of the scope. The magnetic field modulation voltage U_{mod} is displayed on channel 1 of the scope.

The electronics inserts a phase difference between the signal and U_{mod}. The phase φ is adjustable and allows this phase difference to be cancelled out so that a proper looking resonance curve can be obtained. Conceptually, the most difficult part of this experiment is understanding how the traces on the scope are affected by the three parameters U_0, U_{mod}, and φ. Refer to Fig. 2. The four scope patterns on the left have been taken with the scope in the two trace mode. The lower trace is U_{mod}. U_0 is blocked by a scope input capacitor. The upper trace is the signal. The four scope patterns on the right are with the scope in the x-y mode and are Lissajous figures. The desired trace is the lowest one on the right.

Let us focus on the left hand pictures of Fig 2, all two trace patterns. Consider Fig. 2a. The voltage U_0 has been adjusted so that the resonance occurs at a value of the magnetic field near the maximum of U_{mod}. Dotted lines indicate the magnetic field for which the resonance is occurring. Due to a phase shift, the actual resonances are displaced from these magnetic field values. Note that the four resonances shown are not equally spaced. In Fig. 2b U_0 and U_{mod} are the same as in Fig. 2a but the phase φ has been adjusted so that the resonance dips occur at the appropriate value of U_{mod}. Fig. 2c shows a pattern in which U_0 has been adjusted so that the resonances are equally spaced and occur when $U_{mod} = 0$. The phase φ is 90 deg off. Finally, Fig. 2d shows the desired pattern. The resonances are equally spaced, indicating that the resonances are occurring when $U_{mod} = 0$ and the phase has been adjusted so that the resonances are at the right magnetic field. When this pattern is obtained and the scope is switched to the x-y mode, the right pattern in Fig. 2d is obtained. Once a pattern like this is seen, it can be optimized by adjusting U_0, U_{mod}, and φ. In optimizing the pattern, be sure the minimum of the resonance is exactly in the middle of the sweep and that the amplitude of U_{mod} is large enough to display the full resonance but no larger.

6 Measuring g

1. Check that the RF unit, power supply and scope are off.
2. Plug the largest RF coil into the RF unit. Please do this carefully so as not to bend any part of the coil. Insert the DPPH sample all the way into the coil and arrange the components as shown in Fig. 4 and Fig. 5. The average separation of the coils should be should the average radius of the coils which is $R = 6.8\ cm$.
3. Set the DC coil voltage control U_0 to zero and the modulation amplitude U_{mod} to the 2nd scale marking.
4. Check the wiring. The coils should be connected in parallel and then to the power supply through a multimeter. The 10 A and COM terminals of the multimeter should be used. There is a single cable that goes from the RF unit to the power supply. From the power supply, the coil voltage goes to the x-axis or channel 1 of the scope, and the signal goes to the y axis or channel 2 of the scope.
5. Turn on the scope, power supply, the RF unit, and the multimeter at DC amperes.
6. Adjust the scope for two channel operation with triggering on channel 1. Set the time base at a calibrated 2 ms/div and the vertical amplification for both channels at a calibrated 0.5V/div. Set the input for channel 1 at AC and the input for channel 2 at DC.
7. Set the frequency ν at 15 MHz and the RF amplitude at maximum.
8. With the scope in the two trace mode, increase U_0 until resonances are seen. Adjust the controls until the traces look like the left trace in Fig. 2d. (The control for the phase shift φ is a ten turn potentiometer and the markings do not mean anything.) Then switch the scope to the x-y mode and optimize the traces. See the previous section.

9. Prepare a table with three columns and twenty rows. Label the columns "Resonant Frequency (MHz)," "$2I_0$ (A)", and "Magnetic Field (mT)". Record the resonant frequency and the current $2I_0$, where I_0 is the current through one of the coils. Use Eq. **??** to calculate the magnetic field.
10. Increase the frequency in steps of 5 MHz up to 30 MHz, obtaining the current $2I_0$ and calculating the magnetic field in each case.
11. Turn the power on the RF unit off and remove the sample. Replace the large coil with the medium coil and reinsert the sample. Turn the power on the RF unit back on.
12. Obtain frequencies and measurements of $2I_0$ from 30 MHz to 75 MHz in steps of 5 MHz
13. Using the small coil, repeat for frequencies from 75 MHz to 100 MHz in steps of 5 MHz.

On a piece of graph paper, plot the resonant frequencies in MHz on the vertical axis and the magnetic field in mT on the horizontal axis. Draw a straight line which goes through the origin. Calculate the slope of the line from the graph. Double check using the linear regression function of your calculator. Use Eq. **??** to calculate the value of g. Compare your value to 2.0036 which is what appears in the literature.

7 Measuring δB

Define δB as the full width at half minimum for the resonance. Determine δB at 50 MHz as follows. Using the medium sized coil, set the frequency to 50 MHz and obtain a resonance curve in the x-y mode of the scope. The graticule of the scope is 10 cm wide and 8 cm high. Consider the graticule to be an x-y coordinate system with the origin at the center of the graticule. Adjust the parameters of the ESR experiment and the scope controls so that the minimum of the resonance is at (0, -4), off resonance the signal is at y=+4, and the horizontal extent of the trace is from $x = -5$ to $x = +5$. The calibration features of the scope are of no consequence and you should use the variable gain controls and the position controls of the scope to get the desired pattern. U_{mod} should be adjusted so that the resonance curve is as wide as possible under the constraint that the resonance curve has a well defined off resonance base line. Using the graticule of the scope, measure the width δW of the resonance trace at y=0 in cm. Switch the multimeter to AC amperes and record the rms value of the modulation current $I_{mod,rms}$. Convert this to a p-p value $I_{mod,p-p}$ by multiplying by $2\sqrt{2}$. Multiply this p-p value of the current by $\delta W/10$ to obtain $\delta(2I_0)$, which is the current change that corresponds to δB. Use Eq. **??** to calculate the line width δB. The line widths quoted in the literature vary from 0.15 to .81 mT. The line width depends strongly on the solvent in which the sample has recrystallized.

8 Questions

1. The manufacturer designed this experiment with the coils connected in parallel. A series connection would be better. Why?
2. The p-p modulation current $\delta(2I_0)$ for the half-width δB is obtained from

$$\delta(2I_0) = I_{mod,p-p}\frac{\delta W}{10}. \quad (4)$$

Where does the divisor 10 come from?

3. In the method given for measuring δB, the scope controls are not used in a calibrated mode. Why is this OK?
4. Why is the multimeter set for DC amperes for measuring g and for AC amperes for measuring the line width?
5. Is there an RF electric field associated with the RF coil? If so, make a sketch of what the fields look like.

9 Finishing Up

Please leave the bench as you found it. Thank you.

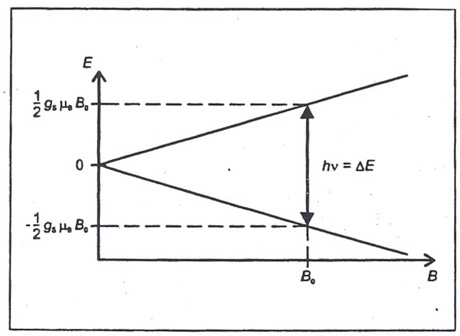

Figure 1: Energy splitting of a free electron in a magnetic field and resonance condition for electron spin resonance

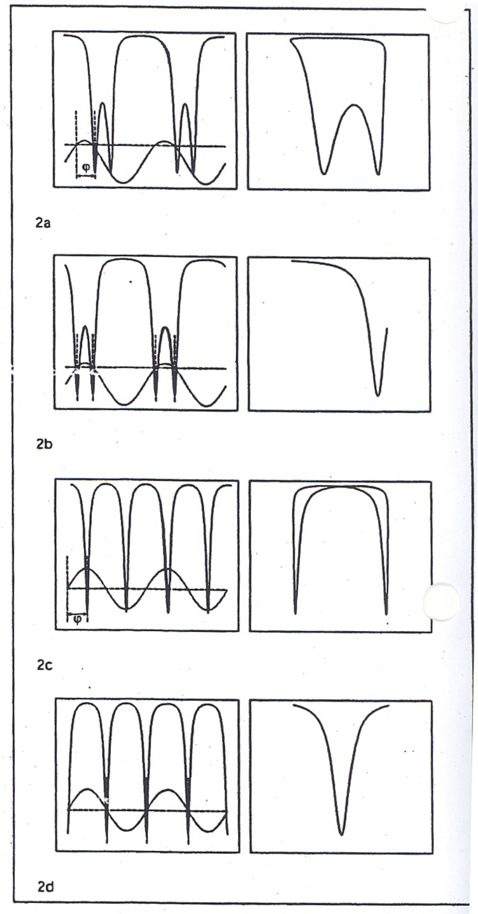

Figure 2: Oscilloscope display of the measuring signal (Y or I, respectively) and the modulated magnetic field (X or II, respectively). Left: two-channel display with DC coupled channel II. Right: XY display with AC coupled channel II.

2a phase shift ϕ not compensated, equidirectional field B_0 too weak

2b phase shift ϕ compensated, equidirectional field $B0$ too weak

2c phase shift ϕ not compensated, appropriate equidirectional field B_0

2d phase shift ϕ compensated, appropriate equidirectional field B_0

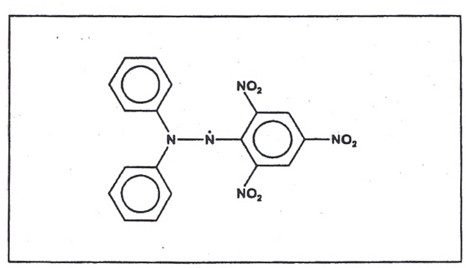

Figure 3: Chemical structure of 1,1-diphenyl-2-picryl-hydrazyl (DPPH)

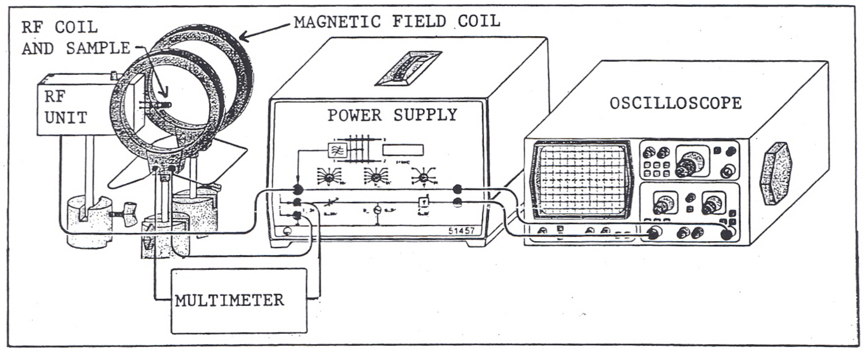

Figure 4: Experimental Setup for electron spin resonance at DPPH

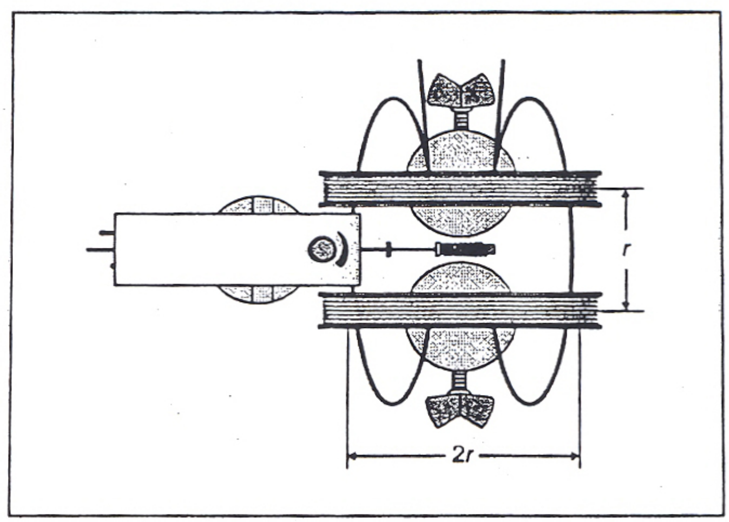

Figure 5: Arrangement of the Helmholtz coils and the ESR basic unit, viewed from above