

Physics 24 Winter 1998
Lab 1 - Electron Spin Resonance

Theory

The application of an external magnetic field to an atom will split the atomic energy levels due to an interaction between the magnetic moment of the atom and the external magnetic field. If μ is the magnetic moment and \mathbf{B}_0 is the external magnetic field, the interaction potential energy is

$$U = -\mu \cdot \mathbf{B}_0 = -\mu B_0 \cos \theta \quad (1)$$

where θ is the angle between μ and \mathbf{B}_0 . This energy simply adds to, or subtracts from, the unperturbed energy of the atomic energy level.

For the simplified and hypothetical case of a single electron atom with no electron spin, there is a simple relation between the orbital angular momentum of the electron, \mathbf{L} , and the magnetic moment, μ ,

$$\mu = -\frac{e}{2m} \mathbf{L} \quad (2)$$

If we substitute equation (2) into equation (1) and let the external field \mathbf{B}_0 define the Z direction, equation (1) simplifies to

$$U = -\frac{e}{2m} B_0 L_z \quad (3)$$

Figure 1 shows the orientation of \mathbf{B}_0 , \mathbf{L} , μ and L_z .

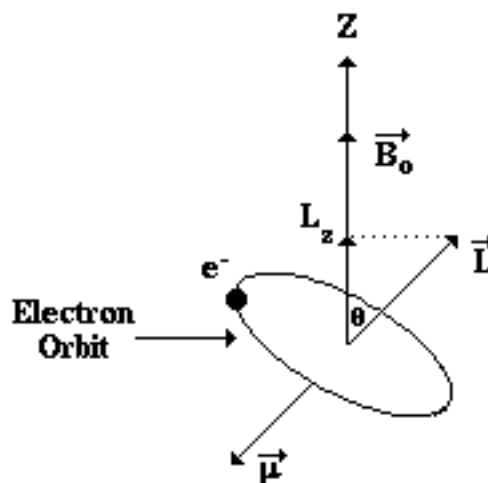


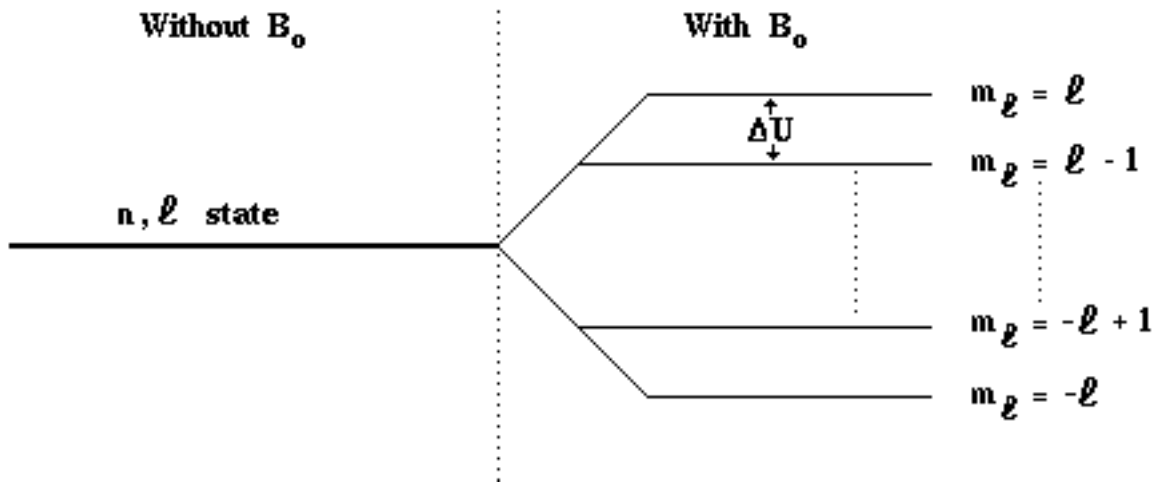
Figure 1

For single electron atoms, however, there is quantization of orientation. If an electron is in a

state denoted by the quantum numbers n and l , then $L_Z = m_l \hbar$ where m_l can have the $2l + 1$ values $l, l - 1, \dots, -l$. Thus, U can only have the values

$$U = \frac{e\hbar}{2m} B_0 m_l \quad . \quad (4)$$

Therefore, when a single electron (no spin) atom is placed in an external field B_0 the energy level n, l is split into $2l + 1$ components, each component separated in energy by an amount $U = \mu_B B_0$ where μ_B is a fundamental constant called the "Bohr magneton" which has the value $e\hbar/2m$.



Energy level splitting of a single electron (no spin) atom placed in an external magnetic field, B_0 .

Figure 2

In an actual atom, we cannot treat the problem as being simply a case of one electron with no spin. In general, for multielectron atoms in an atomic state specified by the quantum numbers s, l, j and assuming that LS coupling is valid (this assumes that B_0 is much less than the internal magnetic field of the atom; the internal field is typically of the order of 10,000 Gauss), we find that

$$U = \mu_B B_0 g m_j \quad (5)$$

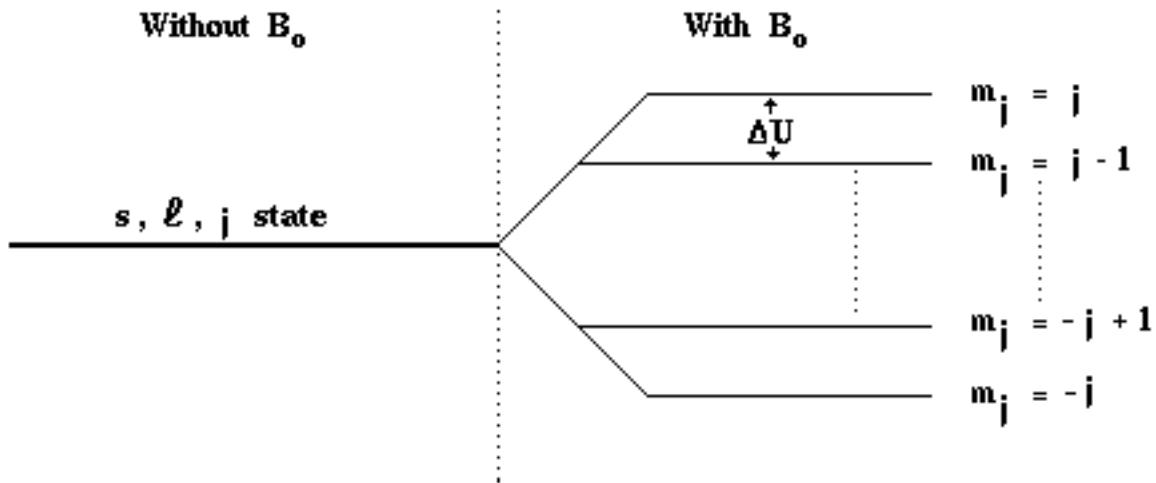
where

$$g = 1 + \frac{j(j + 1) + s(s + 1) - l(l + 1)}{2j(j + 1)} \quad .$$

g is called the Lande g factor. For the case of purely orbital angular momentum such that $s = 0$ and $j = l$, we have $g = 1$. For purely spin angular momentum such that $l = 0$ and $j = s$, we have $g = 2$. The quantity m_j can assume the $2j + 1$ values $j, j - 1, \dots, -j$. An atomic energy level s, l, j is thus split into $2j + 1$ components with each component separated

by an energy

$$U = \mu_B B_0 g \quad . \quad (6)$$



General case. Energy level splitting of a multielectron atom or molecule with electron spin placed in an external magnetic field B_0 .

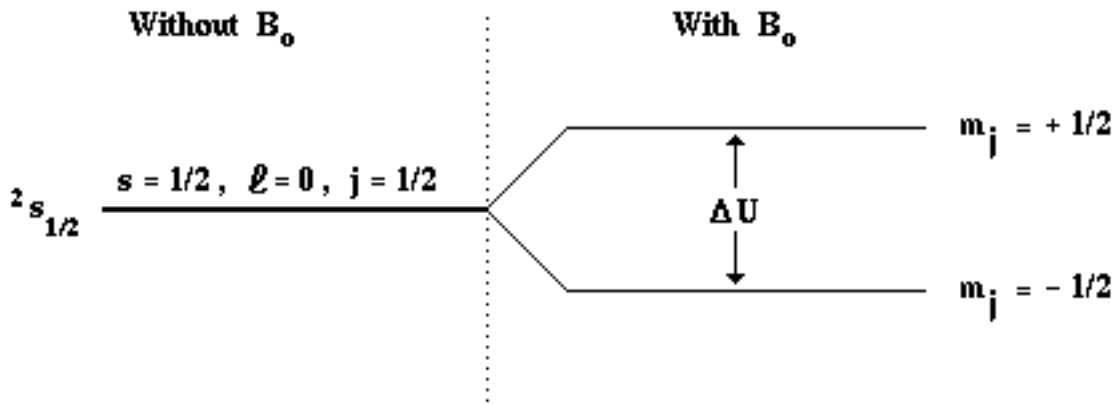
Figure 3

A special case of energy level splitting occurs when a multielectron atom or molecule has one optically active (i.e. unpaired) electron outside a closed subshell. In such a case, we have $s = 1/2$. If, in addition, the ground state is an $l = 0, j = 1/2$ state (a state denoted as $^2S_{1/2}$), then the unperturbed energy state would split into just two energy levels when placed in an external magnetic field B_0 . Under these circumstances, $g = 2$ and the energy difference between the levels, as expressed by equation (6), becomes

$$U = 2 \mu_B B_0 \quad . \quad (7)$$

Since $l = 0$, the $^2S_{1/2}$ state can be considered to be a purely spin angular momentum state. In other words, the energy level splitting is due solely to the interaction between the spin magnetic moment, μ_s , of the electron and the external magnetic field. Therefore, equation (7) can be rewritten as

$$U = 2 \mu_s B_0 \quad . \quad (8)$$



Energy level splitting in an atom or molecule with one optically active electron outside a closed subshell - pure spin angular momentum state: $s = 1/2, \ell = 0, j = 1/2$ - placed in an external magnetic field.

Figure 4

Materials with this atomic structure can be used to experimentally measure the spin magnetic moment of the electron. When the material is placed in an external magnetic field, the energy level of the unpaired electron will split into two levels with the energy level separation proportional to the magnitude of the magnetic field. The spin magnetic moments of those electrons would now have just two possible spatial orientations, either parallel or antiparallel with the external magnetic field. The electrons whose spin magnetic moments become aligned antiparallel to the direction of the external field would have an energy of $+\mu_s B_0$ relative to the unperturbed energy level, the electrons whose spin magnetic moments become aligned parallel to the external field would have a relative energy of $-\mu_s B_0$ and the energy difference between the two levels would be $2\mu_s B_0$.

Consider what would happen if the material were now placed in a region containing an oscillating electromagnetic field, such as a region containing radio waves. The photons in the radio waves would each have an energy equal to $h\nu$ where ν is the frequency of the radio waves. If the frequency were such that the energy $h\nu$ was equal to the energy level separation $2\mu_s B_0$, the photons would induce electron transitions from the lower energy level to the upper and vice versa. The transitions from the lower energy state to the upper state would absorb energy from the electromagnetic field while those transitions from the upper state to the lower state would return energy to the field. Since there are more electrons in the lower energy level, more electrons would absorb energy than emit energy and the net result would be an energy absorption from the field. (One can use the Boltzmann factor $e^{-E/kT}$ to calculate the relative populations of the two states.)

When this condition occurs, the photons are said to be in resonance with ΔU . For this case, the resonance applies to transitions of electrons in a purely spin state ($\ell = 0$). Therefore, we have the term electron spin resonance. From classical arguments, we can show that, to induce the transitions, the magnetic field of the radio waves must be perpendicular to the external magnetic field.

Thus, to measure the spin magnetic moment of the electron in such an atom or molecule, one

applies an external magnetic field \mathbf{B}_0 to a sample to split the ground state energy level in two.

One then places the sample in a region containing small amplitude radio frequency (rf) waves oriented so that the magnetic field of the waves is perpendicular to \mathbf{B}_0 . One then varies either B_0 or ω (it is usually more convenient to vary B_0) until resonance occurs as indicated by a sharp increase in the absorption of energy from the radio wave field. Knowing ω , the energy level separation U can be computed from $h\omega = U$. Knowing U and B_0 , one can then calculate μ_s from equation (8). In this lab, you will use electron spin resonance to measure the spin magnetic moment of the electron.

References

The following are the sections in Tipler's Modern Physics which are pertinent to this lab. They should be read before coming to lab.

1. Chapter 7 sections 7-4 and 7-5
2. Chapter 5 problem 18

Experimental Purpose

The purpose of this lab is to experimentally measure the spin magnetic moment of the electron using the technique of electron spin resonance.

Procedure

The apparatus you will use is shown in figure 5 on the next page. The external magnetic field, \mathbf{B}_0 , is provided by the Helmholtz coils. These coils produce a very uniform magnetic field in the area between the coils which is oriented perpendicularly to the cross sectional area of the coils. The magnitude of the field at the center of the coils is given by

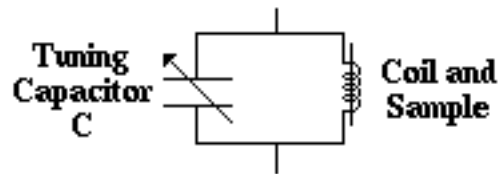
$$B_0 = 0.47 \times 10^{-3} I \quad (9)$$

where I is the current flowing in the coils. If I is in amps, then B_0 is in tesla. The Daedalon ESR power supply has been built in such a way that a voltage of one volt read from the scope display equals one amp of current flowing in the Helmholtz coils. [Note: Equation (9) is not a general result. It is peculiar to the Helmholtz coils used in the lab. In general, the field at the center of a set of Helmholtz coils is given by

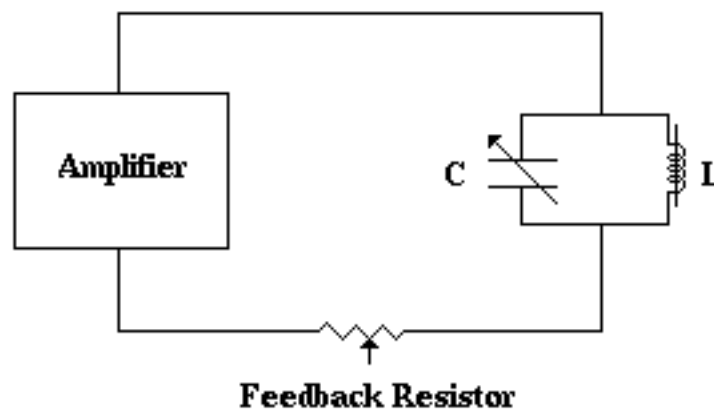
$$B = \frac{8 \mu_0 N I}{a \sqrt{2}}$$

where N is the number of turns of wire in the coils, I is the current in the coils, a is the radius of the coils (and also the intercoil distance), and μ_0 is a constant called the permeability of free space. When the coils you will be using were constructed, N and a were chosen so that this equation simplified to equation (9).]

The material containing the optically active electrons is a red crystalline powder called DPPH (diphenylpicrylhydrazyl). The sample of DPPH is inserted inside a simple helical coil which is located at the tip of the aluminum probe. The coil and sample are used as the inductive portion of an LC "tank circuit" as shown schematically in figure 6a. The tank circuit



(a)



Marginal Oscillator

(b)

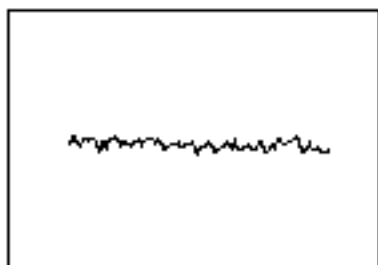
Figure 6

has a resonant frequency $\omega_R = (1 / (2 LC))^{1/2}$. If such a tank circuit is incorporated into an oscillator circuit as shown schematically in figure 6b, the oscillator will have a tendency to oscillate at the frequency ω_R . The current oscillations in the tank circuit will produce a small amplitude (of radio frequency in our case) electromagnetic field inside the coil wrapped around the sample. If the feedback resistor R is adjusted so that the oscillator is barely oscillating (the net gain in the circuit exceeds the net loss by a very small amount), then the amplitude of oscillation will be very sensitive to any changes in absorption of radio frequency energy in the circuit. In particular, the absorption of energy due to electron spin resonance in the sample will give a large change in the amplitude of oscillation. Such a circuit is called a marginal oscillator. The amplitude of the oscillations is displayed on channel A of the oscilloscope. The capacitor C is variable, which

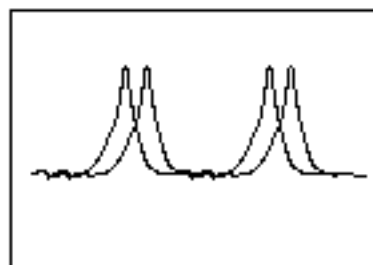
allows us to change ν_R . The frequency of oscillation of the oscillator is measured by the frequency counter. The sample and coil are oriented so that the magnetic field, \mathbf{B}_{rf} , of the electromagnetic waves in the rf field is parallel to the long axis of the sample coil which in turn is parallel to the long axis of the probe. The rf coil and sample are placed between the Helmholtz coils such that \mathbf{B}_{rf} is perpendicular to \mathbf{B}_0 .

In general then, one chooses the frequency ν_R by adjusting C . One adjusts R so that the oscillator is barely oscillating. B_0 is varied at a rate of 60 Hz, and whenever B_0 is such that $h\nu_R = 2\mu_s B_0$ there is a decrease in the amplitude of the radio frequency oscillation, as displayed on the oscilloscope, which represents electron spin resonance. B_0 can be computed from the voltage displayed on channel B of the scope and ν_R can be read from the frequency counter. Knowing B_0 and ν_R , μ_s can be computed from equation (8) or from a plot of ν_R vs B_0 .

1. Check to see that the electronic equipment is wired as shown in figure 5.
2. Turn on the oscilloscope and the Daedalon ESR power supply. Press the SETUP button on the scope. A menu will appear at the bottom of the scope display. Press the left most button under the scope display screen until the number 1 is displayed in the left most part of the menu display. Press the third button from the left to recall the scope setup stored in memory location 1. This should set all of the controls on the scope to values that will give you a good display of the data being fed into the scope from the ESR equipment. The display on the oscilloscope will be either a noisy horizontal line or to a line with two or four absorption peaks in it as shown below.



Oscillator not oscillating.
No absorption peaks.



Oscillator oscillating.
Absorption Peaks Displayed.

Figure 7

wired.] If the display is the former, then adjust the feedback resistor until the two or four peaks are displayed. If you adjust the feedback resistor throughout its entire range and cannot obtain the four peaks, then there is a problem with either the marginal oscillator or the probe. See your TA. If you can obtain the four peaks, adjust the feedback resistor to get the largest absorption peaks. The frequency reading displayed on the front of the Daedalon ESR power supply should be somewhere between 20000 and 40000 KHz.

Actually, you should be seeing just two peaks. Consider what theoretically should be

happening. Assume that the scope trace is at the center of the display screen when the current in the Helmholtz coils is zero. As the current in the Helmholtz coils increases from zero, the magnetic field strength increases proportionally and the energy level of the optically active electron splits into two levels with the amount of separation proportional to the strength of the field. The trace starts tracking horizontally to the right (or left) reflecting this increase in the magnetic field strength. There is no vertical deflection of the trace since, initially, the energy level separation, $2\mu_0 B_0$, is less than the energy of the photons in the rf field. Under those conditions, little or no energy absorption can take place. When the magnetic field strength reaches a value such that energy level separation exactly equals the photon energy ($h = 2\mu_0 B_0$), the electrons in the DPPH absorb energy from the rf field and the vertical deflection of the trace becomes large. As the magnetic field continues to grow larger, the energy level separation becomes greater than the energy of the photons in the rf field and absorption stops. The signal amplitude returns to its nonabsorption level. The trace to this point then would be a flat horizontal section followed by an absorption peak followed by another horizontal flat section. As the magnetic field strength reaches its maximum and decreases toward zero, the trace should retrace itself. When $h = 2\mu_0 B_0$ an absorption peak should again occur. It should, however, occur in the same horizontal position as it did when the magnetic field strength was increasing. (Why?) The pattern should then repeat itself on the other side of the zero field position resulting in just two peaks. The reason that you see four peaks is because the electronic circuitry used to monitor the system introduces a phase shift in the signal coming from the 0.1 ohm resistor and from the rf amplitude output on the oscillator. The function of the phase shifter is eliminate this phase shift and thereby make the B_0 measurements easier.

Adjust the PHASE NULL control on the Daedalon ESR power supply until the four peaks merge into just two peaks as shown below.

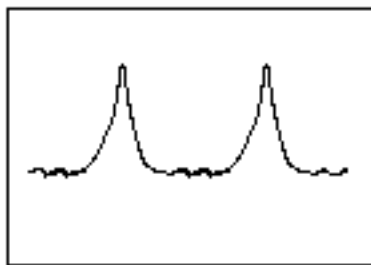


Figure 8

At this point, you should have a scope display similar to figure 8. Adjust the TUNING C control on the oscillator counterclockwise until the two peaks just disappear. Adjust the TUNING C clockwise from that position until the two peaks reappear. Record the frequency of oscillations. This is the lowest value of ν_R which your oscillator can produce. Using a similar procedure, determine the largest value of ν_R which your oscillator can produce.

If all of the equipment functioned as described above, the system is fully operational and you are ready to start taking data.

- Adjust the frequency of the oscillator to its lowest value as determined in step 2 above. Measure the the resonant magnetic field, B_{O-Res} . [Note: As discussed above, there will be two absorption peaks, one on each side of $B_0 = 0$, because we are using an alternating external magnetic field. The distance between the two peaks is thus equal to $2 B_{O-Res}$. To measure B_{O-Res} , measure $2 B_{O-Res}$ directly from the scope and then divide by two to get B_{O-Res} . This is more accurate than trying to measure B_{O-Res} directly. (Why?)]

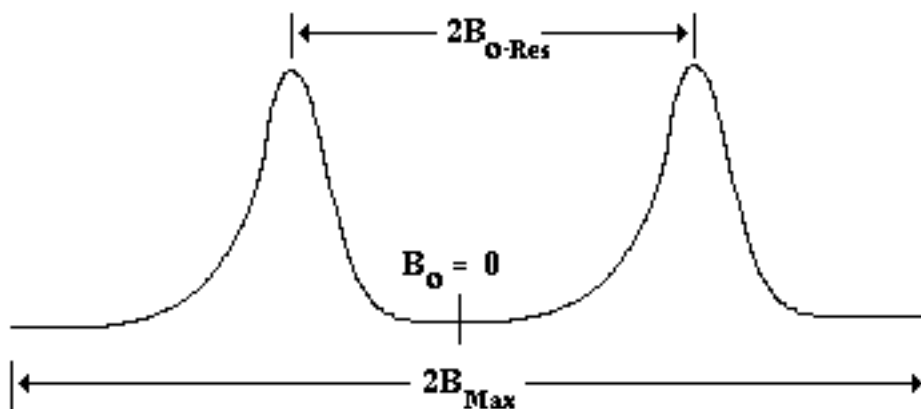


Figure 9

Repeat this step for ten more oscillator frequencies spread uniformly over the entire range of the oscillator frequencies.

- As noted in the introduction, the electron transitions are induced only by perpendicular oscillating magnetic fields. Since only the component of the field B_{rf} of the sample coil perpendicular to the external field is effective in causing transitions, the observed signal height should be proportional to \sin^2 where ϕ is the angle between the axis of the oscillator coil (the probe) and the direction of the external magnetic field B_0 as shown in figure 10.

Choose an oscillator frequency somewhere near its midrange and adjust the feedback resistor to get the largest peaks possible. Using the provided angle apparatus, make signal height vs measurements for a minimum of five different angles.

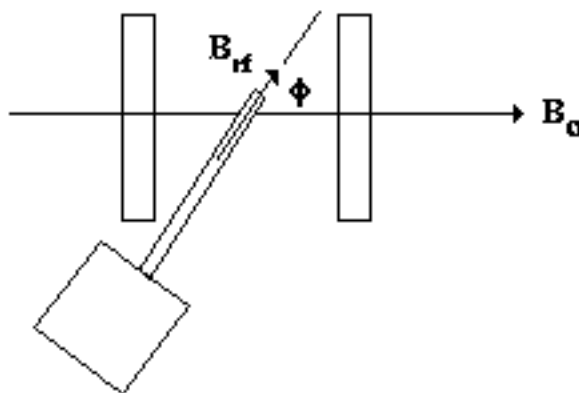


Figure 10

5. Observe the effect on the positions and signal heights of the absorption peaks when a small fixed magnetic field is superimposed on the alternating external magnetic field B_0 . This may be done by bringing up a small permanent magnet. Describe the effect on the absorption peaks as the permanent magnet is brought up from every possible perpendicular direction x, y, z with every possible orientation x, y, z. Reverse the polarity of the magnet and repeat this step.

Lab Report

Follow the usual lab notebook format. Your lab report should include the answers to all of the questions asked in the introduction or procedure, all raw and derived data, and an estimate of the magnitude and sources of error in any data recorded. When answering any question or when giving any comparison or explanation, always refer to specific data to support your statements. For this lab, also do the following.

1. Plot the oscillator frequency versus resonant magnetic field data. From the plot, obtain an experimental value for the spin magnetic moment of the electron and for the Lande g factor. Compare these experimental values with their accepted values.
2. Plot the signal height vs data taken in step 4 of the procedure and verify the \sin^2 dependence.
3. Explain why the addition of the small fixed magnetic field to the external alternating magnetic field changed the position and signal height of the absorption peaks as observed in step 5 of the procedure. [Hint: Vectorially combine the various magnetic fields to explain the overall effect.]
4. Given that the probability of a molecule at temperature T having energy E is proportional to $e^{-E/kT}$ and that there are N_0 molecules in the sample, calculate the difference N in populations between the $m_j = -1/2$ state and the $m_j = +1/2$ state. Assume $\mu_B B_0 \ll kT$.