EN-35 Electron Spin Resonance Apparatus

Introduction

The application of an external magnetic field to an atom will split the atomic energy level 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:

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

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:

$$\mu = - (e / 2m) \mathbf{L} \qquad (2)$$

If we substitute equation (2) into equation (1) and let the external field $\mathbf{B_0}$ define the Z direction, equation (1) simplifies to:

$$U = - (e / 2m) \mathbf{B_0} \mathbf{L_z} \qquad (3)$$

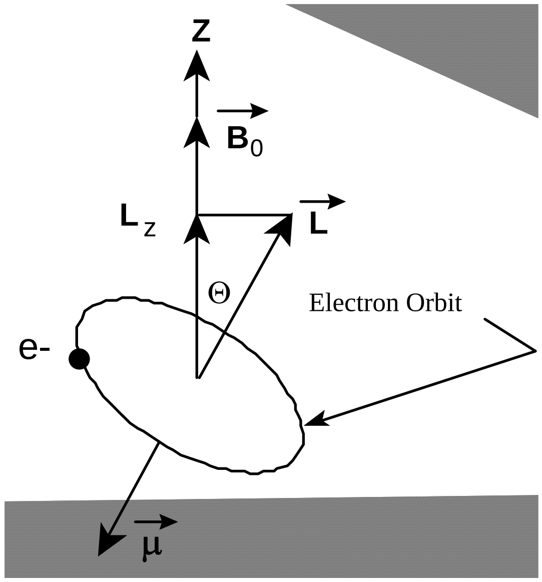


Figure 1. Orientation of $\mathbf{B}_0$, **L**, and $\mathbf{L}_z$

For single electron atoms, however, there is quantization of orientation. If an electron is in a state denoted by quantum numbers n and l, then $L_z = m_l h$ where m_l can have the 2l + 1 values l,l-1,...,-1. Thus, U can only have the values:

$$U = (e\,h / 2\,m)\,\mathbf{B}_0\,m_l \qquad (4)$$

Therefore, when a single electron (no spin) atom is placed in an external field $\mathbf{B}_0$, the energy level n, l is split into 2 l + 1 components, each component separated in energy by an amount $\Delta U = \mu_B B_0$ where μ_B is a fundamental constant called the "Bohr magneton" which has the value e h / 2m.

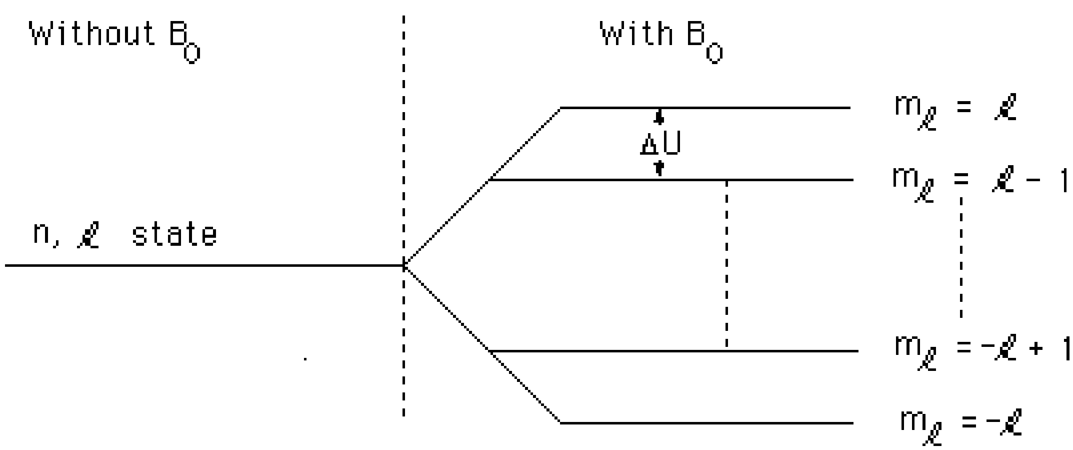


Figure 2. Energy Level splitting of a single electron (no spin) atom placed in an external magnetic field $\mathbf{B}_0$

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 1T), we find that

$$U = \mu_B \mathbf{B_0} g \, m_j \qquad (5)$$

where

$$g = 1 + (j(j+1) + s(s+l) - l(l+1))/2j(j+1)$$

g is called the Lande g factor. For the case of purely orbital angular momentum such that s = 0 and j = 1, 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 2 j + 1 values j, j - 1, ..., -j. An atomic energy level s, l, j is thus split into 2 j + 1 components with each component separated by an energy

$$\Delta U = \mu_B \mathbf{B_0} g \qquad (6)$$

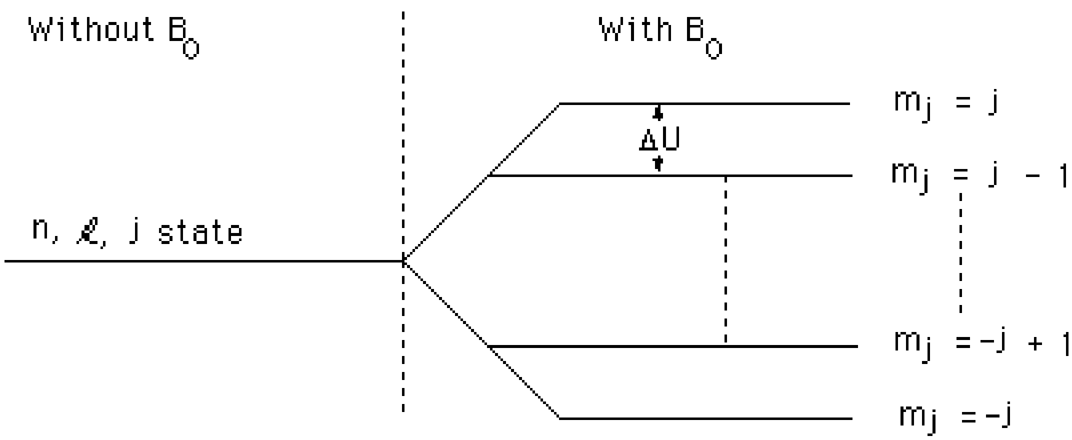


Figure 3. Energy level splitting of a multielectron atom or molecule with electron spin placed in an external magnetic field $\mathbf{B_0}$

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

$$\Delta U = 2 \mu_B \mathbf{B_0} \qquad (7)$$

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, m_S, of the electron and the external magnetic field. Therefore, equation (7) can be rewritten as

$$\Delta U = 2\ \mu_S\ \mathbf{B}_0 \qquad (8)$$

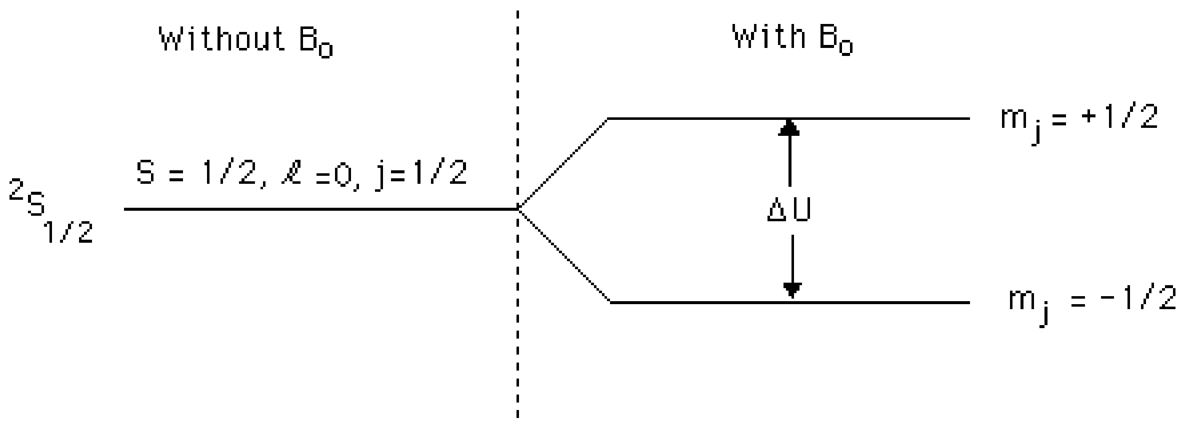


Figure 4. Energy level splitting in an atom or molecule with one optically active electron outside a closed subshell- pure spin angular momentum state: s =1/2, l =0,j =1/2 placed in an external magnetic field.

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 2 μ_S $\mathbf{B}_0$ 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 + $\mu_S\mathbf{B}_0$, and the energy difference between the two levels would be $2\mu_S\mathbf{B}_0$. 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 hυ where υ is the frequency of the radio waves. If the frequency υ were such that the energy hυ was equal to the energy level separation 2 μ_S $\mathbf{B}_0$, 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 (l= 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 $\mathbf{B}_0$ or υ (it is usually more convenient to vary $\mathbf{B}_0$) until resonance occurs as indicated by a sharp increase in the absorption of energy from the radio wave field. Knowing υ, the energy level separation ΔU can be computed from $h\upsilon = \Delta U$. Knowing ΔU and $\mathbf{B}_0$, one can then calculate μ_s from equation (8). In this experiment, you will use electron spin resonance to measure the spin magnetic moment of the electron.

References

The following are the sections on Eisenberg and Resnick's *Fundamentals of Physics* (3rd ed.) which are pertinent to this experiment. They should be read before coming to lab.

1. Chapter 8 sections 8-1 and 8-2

2. Chapter 10 section 10-6

Daedalon EN-35 ESR Apparatus

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. In general, the field at the center of a set of Helmholtz coils is given by

$$\mathbf{B} = (4/5)^{3/2} (\mu_0 \, N \, \mathbf{I})/ a \qquad (9)$$

where N is the number of turns of wire in the coils, **I** is the current in each coil, a is the radius of the coils, and μ_0 is a constant called the permeability of free space. For these coils, N=60 and a=.056m. In a Helmholtz coil the intercoil distance is the same as the radius of the coils. However, in this apparatus the two coils are connected in parallel, so that the current through them is only half of the measured value. The magnitude of the field at the center of the coils is given by

$$\mathbf{B}_0 = 0.48 \, \mathbf{I} \, \mathrm{mT} \qquad (10)$$

where **I** is the measured current flowing in both coils. If **I** is in amperes, then $\mathbf{B}_0$ is in milliTeslas. {Note: Equation (10) is not a general result, it merely describes the set of coils supplied with this apparatus}. The Helmholtz coil current sense output on the EN-35 base unit provides a voltage scaled such that one volt is equal to one amp of current flowing through the coils.

Figure 5

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

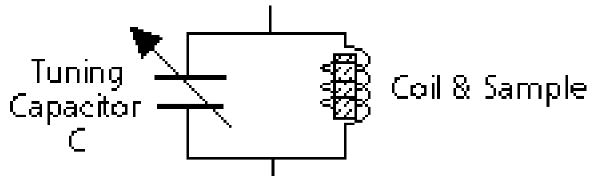


Figure 6a

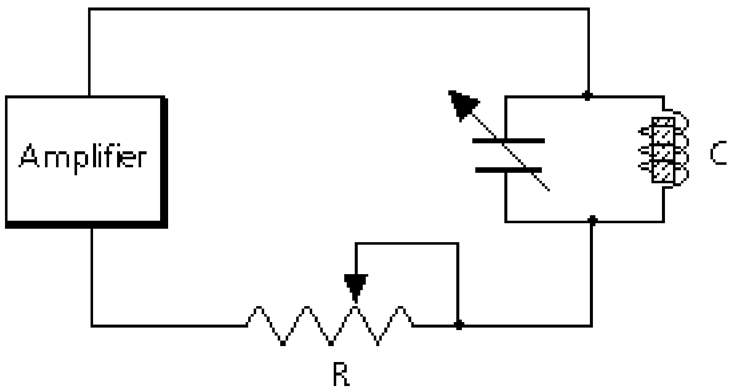


Figure 6b

The tank circuit has a resonant frequency $\upsilon_R = (1/(2\pi LC))^{1/2}$. If such a circuit is incorporated into an oscillator circuit, as shown schematically in Figure 6b, the oscillator will have a tendency to oscillate at the frequency υ_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 the Y channel of the oscilloscope. The capacitor C is variable, which allows us to change υ_R. The frequency of oscillation of the oscillator is measured by the frequency counter built in to the base unit. 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 υ_R by adjusting C. One adjusts R so that the oscillator is barely oscillating. $\mathbf{B}_0$ is varied at a rate of 60 Hz, and whenever $\mathbf{B}_0$ is such that $h\,\upsilon_R = 2\,\mu_S\,\mathbf{B}_0$ there is a decrease in the amplitude of the radio frequency oscillation, as displayed on the oscilloscope, which represents electron spin resonance. $\mathbf{B}_0$ can be computed from the voltage displayed on the X channel of the scope and υ_R can be read from the frequency counter. Knowing $\mathbf{B}_0$ and υ_R, μ_S can be computed from Equation (8) or from a plot of υ_R versus $\mathbf{B}_0$.

Setup

1. Connect the Helmholtz coils to the banana jacks labelled *SUPPLY*, located on back of the base unit.

2. The small box, labelled *ESR HEAD* is designed to mount on a ring stand. Fasten this box to a ring stand with a rod diameter of .5",and tighten the adjustment knob.

3. Connect the head to the base unit with the five pin DIN cable. Also connect a BNC cable from the jack labelled *FREQUENCY/ 100* to the *FREQUENCY* jack on the base unit.

4. Connect a BNC cable from the *VIDEO* output of the ESR Head to the Y input of an oscilloscope. Connect another BNC cable between the Helmholtz coil sense jack, on the back of the base unit, and the Oscilloscope's X channel.

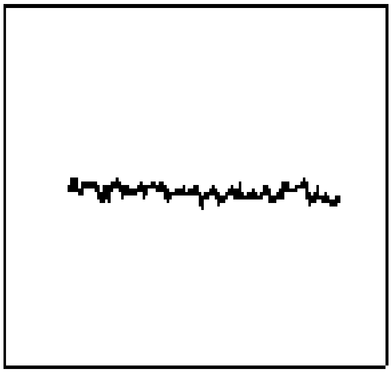
5. Plug the probe into the head, and position it through one of the openings through the side of the Helmholtz coil.

6. Turn on the base unit and the head. The *OSCILLATOR ON* LED should be lit. If not, check the connections.

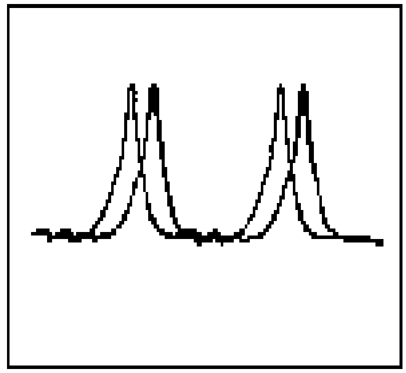
7. Turn on the Oscilloscope, and set it to X-Y mode. The X scale should be approximately 2 v/cm, the Y scale should be between 50mV/cm and 1V/cm. The coupling for both inputs should be set to DC.

Operation

8. If the frequency meter reads "0000", the head is not oscillating. It may be necessary to turn the *FEEDBACK* control higher (clockwise). The frequency readout on the base unit should read between 25 and 40Mhz.



Oscillator not oscillating
No absorption peaks



Oscillator oscillating
Absorption peaks displayed

Figure Seven

9. Turn the *COIL CURRENT ADJUST* control to its maximum setting. Two or four peaks should be visible. The X axis on the display represents the current flowing through the coil, and the voltage displayed on this channel is scaled such that one volt is present for one amp of current through the coils, which are wired in parallel. The Y axis represents the envelope of the oscillator signal. To increase the amplitude of the peaks, turn down the feedback control (counterclockwise). Turning the feedback control too far down will cause the head to stop oscillating. At this point, you should have a scope display similar to Figure 8.

10. Determine the largest value of υ_r that your oscillator can produce. Adjust the *FEEDBACK* control fully clockwise. Adjust the *TUNING* control on the oscillator clockwise until the display reads all zeros. The head may oscillate over the entire range of this tuning pot, and the display may never read zeros. Adjust the *TUNING* counterclockwise and determine the lowest frequency which your oscillator can produce. If all of the equipment functions as described above, the system is fully operational and you are ready to start taking data.

11. Adjust the frequency of the oscillator to its lowest value, as described in Step 10. Measure the resonant magnetic field, $B_{o\text{ - Res}}$. The distance between the two peaks is equal to 2 $B_{o\text{ - Res}}$.

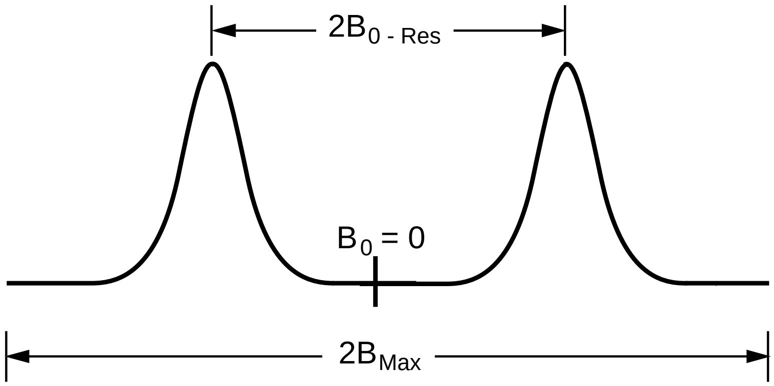


Figure 8

To measure $B_{0\text{ - Res}}$, measure 2 $B_{o\text{ - Res}}$ directly from the scope and then divide by 2. This is more accurate than trying to measure $B_{0\text{ - Res}}$ directly.

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

12. 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 $\cos\theta^2$ where θ is the angle between the axis of the oscillator coil (the probe) and the direction of the external magnetic field B_0 shown in Figure Nine.

Choose an oscillator frequency somewhere near its midrange and adjust the feedback to get the largest peaks possible. Make signal height vs θ measurements for a minimum of five different angles.

13. 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 $\mathbf{B_0}$. 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.

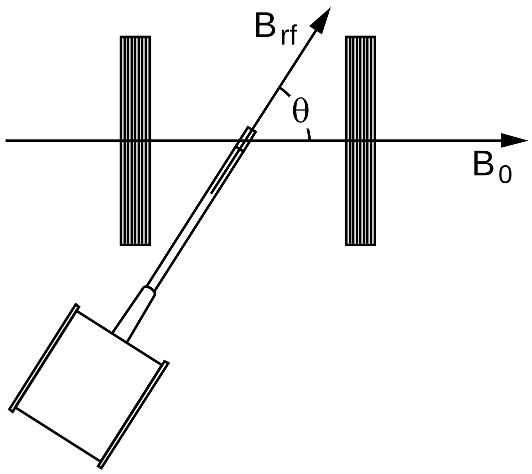


Figure 9

Since the Electron Spin Resonance occurs at a frequency proportional to the external applied field, adjusting the frequency control will vary the distance between the two peaks.

Note: The feedback and tuning controls will interact with one another slightly; adjustment of the feedback control will alter the oscillator frequency slightly, and adjusting the tuning control will have some effect on the size of the absorption peaks. Make these adjustments slowly, and do not take frequency readings until all adjustments have been made.

If the display contains four peaks, there is a phase difference between the X and Y channels. Try adjusting the *PHASE NULL* control on the base unit. When the phase difference has been properly nulled, there will only be two peaks visible. If there is still a phase error, be sure that the coupling is set to DC at both oscilloscope inputs.

Measuring Oscillator frequency with the Oscilloscope directly

The frequency of the oscillator signal is displayed on the front of the base unit, with four-digit accuracy. If desired, it is possible to also measure the signal directly with an oscilloscope if its band width is sufficiently high.

Turn the *COIL CURRENT ADJUST* control down to minimum. Turn the *FEEDBACK* control to its maximum position. Set the scope to single channel time base mode, and connect the *VIDEO* output to the scope's input channel. Turn the gain of this channel up to its maximum position. A sine wave should appear on the scope. You are now viewing the oscillator signal directly.

Example Problems for Students

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 $\cos^2 \theta$ 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: Combine the vectors of the various magnetic fields to explain the overall effect.]

Given that the probability of a molecule at temperature T having energy E is proportional to $e^{-E/kT}$ and that there are N_o 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 $\mu_B B_0 << kT$.

Acknowledgements

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