

**ADVANCED UNDERGRADUATE LABORATORY**

**Electron Spin Resonance**

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Original: Joe Vise 1996

## I. INTRODUCTION

### A. Purpose of the Experiment

The first purpose of this experiment is to familiarize a student with the generation and transmission of microwave signals. More than a half of your time, devoted to the ESR experiment, will be spent to study the microwave production and propagation in a resonant cavity.

Secondly, after an understanding of the components of the microwave spectrometer has been obtained, the apparatus is used to measure the magnetic moment of the electron using electron spin resonance techniques.

A strong mathematical theory of different modes of electromagnetic waves and the wave propagation in resonant cavities with different cross-sectional shape can be found in [1]. Some of chapters of this book exist in electronic version and can be found with Google search typing the title of the book in a search box. For the purposes of our experiment, you will need Chapter 9, (9.11; 9.22): “Waveguide Propagation – Bounded Waves”, which also contains some relevant and useful exercises and problems. Actually, you will find a solution of Maxwell’s equations for a waveguide with a rectangular cross section.

To prepare for the first part of the ESR experiment, it would be also useful to recall or get familiar with the 2<sup>nd</sup> year Physics Laboratory experiment “Microwaves in Waveguides”

(see <http://www.physics.utoronto.ca/~phy225h/experiments/microwaves/microwaves.pdf>)

Second part of the ESR experiment demands quantum mechanics background with clear understanding of terms “quantization”, “quantum number”, “spin”([2], pp.115-118), “splitting of energy levels”, etc. as well as good knowledge of Zeeman effect and anomalous Zeeman effect.

As was first suggested by Goudsmit and Uhlenbeck, all electrons have an intrinsic angular momentum which may be attributed to a spin about an internal axis. Associated with this spin is a magnetic dipole moment. In most substances, the orbital angular momenta and the spin angular momenta of the electrons couple together or are “paired” so that the net magnetic moment is zero. These substances are diamagnetic. Other substances have “unpaired” electrons and so can have a net magnetic moment. These are ferromagnetic if exchange forces between the unpaired electrons are strong compared to thermal agitations, or paramagnetic if they are weak.

In chemical free radicals there is one unpaired electron per molecule and these substances are paramagnetic at room temperature. The unpaired electrons in chemical free radicals, although in bound states, are said to be the “most free in captivity” since their magnetic moment is almost entirely uninfluenced by their orbital motion. Thus it is possible to obtain a good value for the free electron gyromagnetic ratio from measurements on a free radical.

### B. Theory of Electron Spin Resonance

The magnetic moment  $\vec{\mu}$  ([3], p.389) is usually written in one of the two forms

$$\vec{\mu} = \gamma \vec{S} \quad (1)$$

or

$$\vec{\mu} = g \left( \frac{e}{2m} \right) \vec{S} \quad (2)$$

where

$$g = \gamma \frac{2m}{e} \quad (3)$$

and

$$|\vec{S}| = \sqrt{s(s+1)} \hbar \quad (4)$$

Here  $\gamma$  is the gyromagnetic ratio ([3], p.386);  $g$  is the Lande factor;  $\vec{S}$  is the spin angular momentum;  $s$  is the spin quantum number; and  $e/2m$  is the gyromagnetic ratio for a classical electron. (An electron considered classically would be a uniform spherical distribution of mass and charge.) If the electron behaved classically,  $g$  would have a value of 1. Spectroscopic observations, such as Zeeman effect or fine structure observations, show that  $g$  must be nearly 2. Quantum electrodynamics shows that  $g$  is slightly greater than 2 (see [3], p.390 and p.574). This phenomenon is called the *Lamb shift*.

We shall assume that there is a constant external magnetic field  $B_0$  in the  $z$  direction. The energy of interaction of the magnetic moments with the magnetic field is given by

$$E = -\vec{\mu} \cdot \vec{B}_0 = -\mu_z B_0 \quad (5)$$

Equation (1) gives

$$\mu_z = \gamma S_z \quad (6)$$

Since the spin quantum number for a single electron is  $s = 1/2$ , the quantum mechanically allowed projections along the  $z$  axis of  $\vec{S}$  which has magnitude  $\sqrt{s(s+1)} \hbar = \frac{\sqrt{3}\hbar}{2}$  are

$$S_z = \pm \frac{\hbar}{2} \quad (7)$$

Equations (7) and (6) give

$$\mu_z = \pm \gamma \frac{\hbar}{2} \quad (8)$$

Substituting  $\mu_z$  in Eqn. (5) by its value from Eqn. (8) gives for the energy of interaction

$$E = \pm \frac{1}{2} \gamma \hbar B_0 \quad (9)$$

The difference in energies of the two levels is then given by

$$\Delta E = \gamma \hbar B_0 \quad (10)$$

Resonance occurs when the energy of the microwave photons,  $h\nu_0$ , is equal to the energy separation of the levels given by Eqn. (10).

$$h\nu_0 = \gamma \hbar B_0 \quad (11)$$

or

$$\omega_0 = \gamma B_0 \quad (12)$$

This is known as the Larmor frequency<sup>1</sup> because it is the Larmor precessional frequency of a classical magnetic moment  $\mu$  in a magnetic field  $B_0$ .

One may calculate the gyromagnetic ratio  $\gamma$  from Eqn. (12) or equivalently the Lande  $g$  factor from Eqn. (3) or the magnetic moment  $\mu_z$  from Eqn. (8). It must be remembered that values, quoted in handbooks and other sources for the magnetic dipole moment of the electron, are measured quantities.  $|\mu|$  cannot be measured directly, but only  $\mu_z$ , its projection onto some axis.

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<sup>1</sup>For a development of the Larmor frequency condition see Appendix I.

When the resonance condition is satisfied, the radiation will induce transitions between the energy levels and thus tend to destroy the thermal difference in population. There is a resulting loss of power from the radiation field which can be detected electronically.

The most effective means of inducing transitions between these levels separated by  $\Delta E$  is to provide a magnetic field  $B_1$  rotating at the Larmor frequency and in the correct sense, in the plane perpendicular to the static field. The production of such a rotating field, although not impossible, is difficult. To overcome this difficulty, one merely needs to note, as is demonstrated in figure 1, that a sinusoidally varying field in a fixed direction (linearly polarized), is equivalent to the sum of two constant fields of half the amplitude rotating in opposite directions (circularly polarized). Experimentally,  $B_1$ , the sinusoidally varying field in a fixed direction, is obtained by orienting the waveguide cavity containing the sample such that the magnetic field of the microwaves is always perpendicular to the direction of the external magnetic field  $B_0$ . As is pointed out in Appendices I and II, in a frame of reference, rotating at the Larmor frequency, the only field seen is the field  $B_1$ , which is constant in the rotating frame. In other words, the transformation from the laboratory frame to a frame, rotating at the Larmor frequency, causes the static field to disappear from the equations of motion of the magnetization. The magnetic moment  $\mu$  will then precess about  $B_0$  so that  $\mu$ , which had originally pointed in the direction of  $B_0$  in the laboratory frame (lower energy state), will change so that it points in the direction opposite to  $B_0$  (higher energy state). In this way, the rotating component of the sinusoidally varying field in the correct sense and at the Larmor frequency will induce transitions between the electron spin levels. The other rotating component will be  $2\omega_0$  away from the resonance frequency and will have a negligible effect.<sup>2</sup>

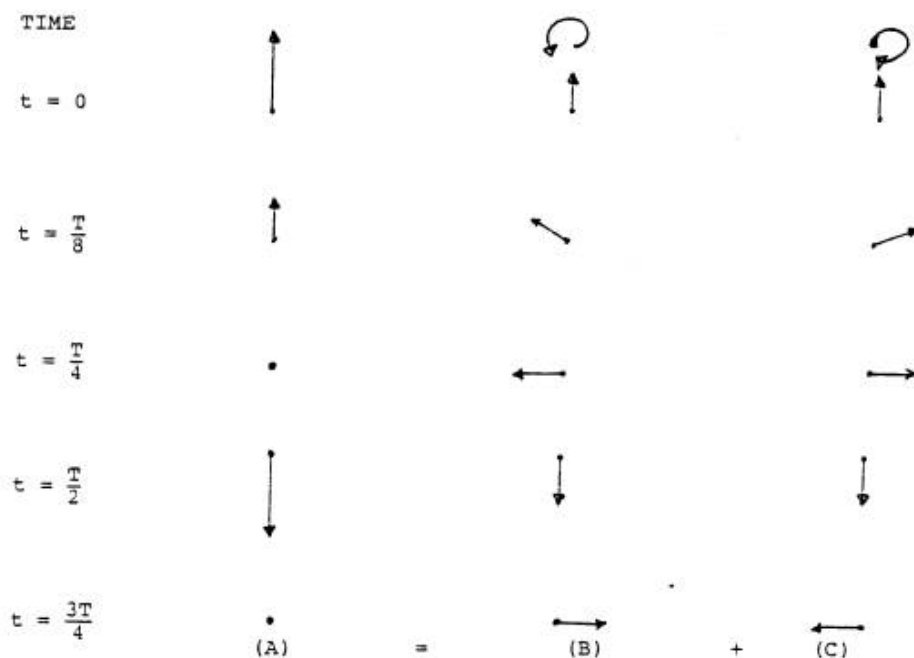


Figure 1: A linearly polarized field (A) is the sum of two counter-rotating circularly polarized fields (B) and (C)

<sup>2</sup>For a rigorous proof of these statements see Appendix II.

## C. Apparatus

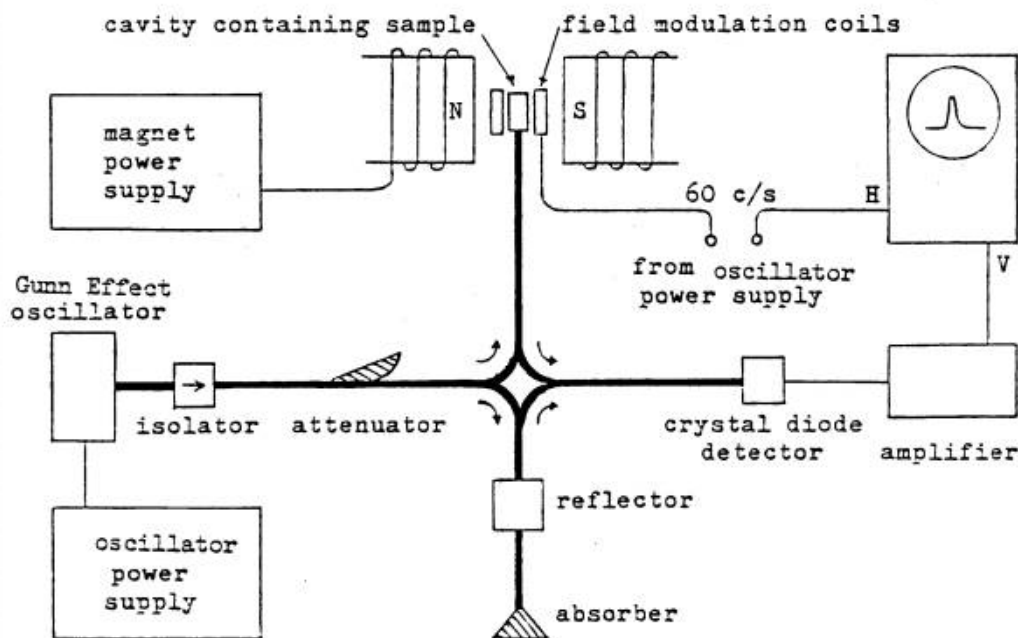


Figure 2: Schematic diagram of the apparatus

A schematic diagram of the apparatus is shown in Figure 2.

In a typical laboratory magnetic field of a few kilogausses, the spin resonance frequency lies midway between the radiofrequency region of the electromagnetic spectrum and the infrared. Wavelengths in this region are of the order of a few centimeters.

The spectrometer provided operates at frequencies around 9 GHz, which correspond to wavelengths of about 3.3 cm.

Power is generated by a continuous wave Gunn Effect oscillator operating at frequencies between 8.5 and 9.6 GHz depending on the bias and varactor voltage settings. A description of Gunn Effect oscillators plus a test performance sheet for the oscillator in the apparatus is provided in appendix III.

The electromagnetic waves must be confined within and propagated down a carefully machined hollow tube known as a waveguide if excessive losses through radiation are to be avoided. An inspection of the power flow in the circuit, as indicated in figure 2 shows that it is a simple two-arm bridge. Both arms send a signal to the crystal detector where they are added. One arm contains the sample in a resonant cavity while the other can be adjusted to provide a reference signal of the desired magnitude and phase.

The magnetic field is provided by an electromagnet powered by a variable D.C. supply, which can be adjusted for resonance. In order to display this resonance, the magnetic field is swept back and forth in synchronism with the oscilloscope time base by means of a 60 Hz sinusoidal current supplied to small field modulation coils in the magnet gap.

The free radical is a small amount of toxic black powder, Diphenylpicryl Hydrazyl (DPPH), contained in a small glass vial. The microwave frequency is measured with a Hewlett Packard Model X532B micrometer controlled cavity wavemeter for which specifications are given in appendix IV. A description of the operating procedures and specifications for the Bell 620 Gaussmeter are given in

## II EXPERIMENTAL

This section is broken up into four parts:

- A. Familiarization with the Apparatus
- B. The Gunn Oscillator
- C. Cavity Resonance and Tuning in the Absence of Magnetic Field
- D. The Magnetic Moment of the Electron

At the end of each part there are sections called "Questions" and "Supplementary Questions". Every student should know all the answers to the "Questions". A student's knowledge of answers to the "Supplementary Questions" will be a determining factor in deciding how high above average a student's grade will be.

### A. FAMILIARIZATION WITH THE APPARATUS

While proceeding through items 1 to 7 you should be referring to the questions at the end of this part.

#### 1. Gunn Effect Oscillator

*Do not unscrew the oscillator from the isolator to examine it.*

#### 2. Resonant Isolator

Remove the isolator together with the attached Gunn Effect oscillator (section **a** in Fig.3) and carefully examine it. Measure the inside dimensions of the waveguide. Using the Hall Effect gaussmeter, (see appendix V for operating instructions), measure the approximate strength of the magnetic field inside the isolator. By comparison with a magnet of known polarity, determine which of the poles of the permanent magnet on the isolator a north pole is and hence determine the direction of the magnetic field lines inside the isolator.

#### 3. Wavemeter and Attenuator

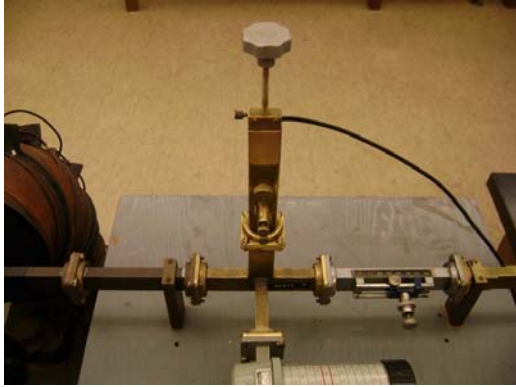
Do not take the wavemeter apart. Remove the wavemeter and attenuator together, being careful not to subject the apparatus to any excessive torques. Examine the attenuator and note the position of the iris leading to the cavity wavemeter.

#### 4. Load and Slide Screw Tuner

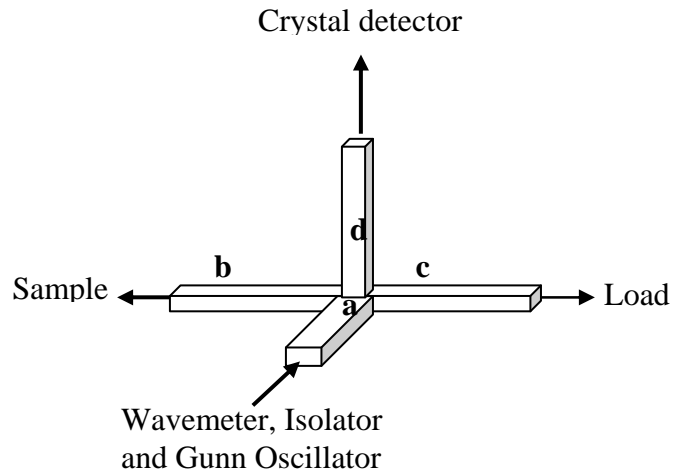
Slide the black resistive wedge out of the load (arm **c** in Fig.3) and use a light to look down the length of the waveguide toward the cavity. Move the slide screw in the tuner and observe how it enters and exits the waveguide. Turn the screw so that it is entirely out of the waveguide for the first parts of this experiment.

#### 5. Magic T

Examine the Magic T (Fig.3) by using a desk lamp and looking down the arms from the oscillator and the load. Note the positions of the post and the iris. The position of the iris may also be determined by examining the top of the waveguide section. One can see where the brass plate was inserted to form the iris. Now replace the wavemeter, attenuator and isolator section. Put the black wedge back into the load.



(a)



(b)

Fig.3. Magic T; (a) photo; (b) arrangement of principal sections.

6. **Resonant Cavity**

Remove the cavity (**b**) and examine it noting the position and size of the iris. Measure the length of the cavity and note where the sample will be if placed about 1 cm from the bottom. Replace the cavity.

7. **Detector**

Remove and examine the detector section and unscrew the detector from the waveguide section (**d**). Locate the tuning plunger and tuning screws. Adjust the screws so that they are not sticking into the waveguide. Knowing the length of the resonant cavity you should be able to estimate the wavelength for resonance. Knowing this wavelength, adjust the plunger until the face of the plunger is one-quarter wavelength from the detector. Replace the detector section.

**Questions - Part A**

1. What is meant by the term "transferred electron mechanism"? See appendix III.
2. What are Gunn domains and how do they form and propagate? See appendix III.
3. What is the band designation of this apparatus and what range of wavelengths and frequencies can propagate in waveguides of these dimensions? What is the relationship between wavelength in free space and wavelength in the waveguide? See [4], pp. 97-100.
4. For the  $TE_{10}$  mode of propagation, be able to describe the orientation of the E and H vectors in the waveguide and how they propagate. See [4], pp. 97-100.
5. How does the isolator work? Since you have determined the direction of the lines of the permanent magnetic field in the isolator, show that the precession of the spins of the electrons in the ferrite and also the rotation of the microwave magnetic field are such that the isolator works as it should. See appendix VI; [5], pp. 158 and 196; and [4], p.220.

6. How does the attenuator work? Could the waveguide flap attenuator be inserted into the waveguide with the flap parallel to the longer dimension and still work well? See [4], p. 217.
7. Knowing:
  - a) the approximate range of wavelengths permissible from a knowledge of the dimensions of the waveguide,
  - b) the physical dimensions of the cavity,
  - c) that the rf magnetic field  $B_1$  must be perpendicular to the applied steady magnetic field  $B_0$  as outlined in the theory section at the beginning of this manual,
  - d) that the sample must be located at a point of maximum  $B_1$  for maximum power absorption in the sample, and
  - e) that the sample must be placed at a position of minimum  $E$  to minimize dielectric power loss,
 determine the resonant mode of the cavity that will be used in this experiment. See [4], p. 263. What do the subscripts on the mode designation  $TE_{mnp}$  mean in terms of the wavelength that you are using?
8. What kind of electrical component is the detector? How does it work? See [6], p.75, or [4], p. 430 for more detail. Is the positive or negative end of the detector in contact with the central conductor of the UHF connector? Does the electric or magnetic field excite the detector?

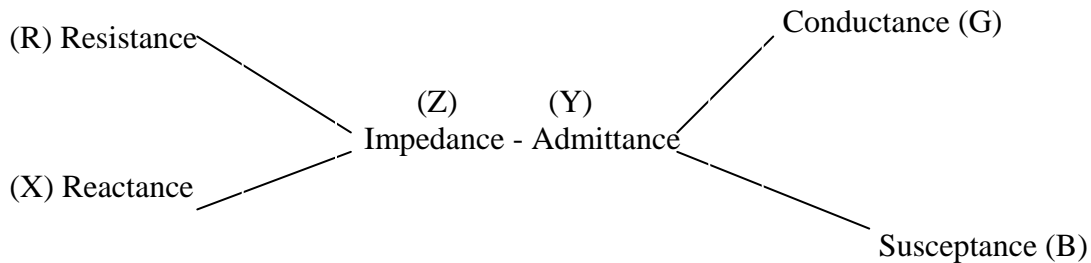
### Supplementary Questions - Part A

1. Give some rough explanation of how a Gunn effect device can produce microwave power. See appendix III.
2. The forward loss of this isolator is 0.5 db and the reverse loss is between 40 and 70 db. What does this mean?
3. The model X532B frequency meter consists of a  $TE_{111}$  mode resonant cavity coupled to a waveguide section. The high  $Q$  cavity is tuned by a choke plunger. What do the subscripts on the designation for the mode mean? Be able to describe this in terms of the shape of the cavity. For help see [6], p. 189; [4], pp. 270, 275; and [7], p. 297. A picture can be found in [4], p. 277. In trying to understand the picture on p. 277 it is useful to know that the  $TE_{111}$  mode corresponds to half of the  $TE_{112}$  mode. It is analogous to the  $TE_{101}$  rectangular cavity mode, and the two may be derived from one another by deforming the cylinder into a rectangular parallelepiped and vice versa.
4. What is the purpose of the load? What are the electrical properties of the black wedge and what function does it perform as a microwave component? How does this compare to matched loads for coaxial cables? See [4], p. 240, for help.
5. What changes as you insert the screw of the tuner into the cavity? What changes as you slide the screw along the length of the cavity? See [4], p. 239, or [8], p. 485 for more detail.
6. What function does the Magic T perform? Does the post extend into the arm coming from the Gunn oscillator or its height is equal to a dimension of the waveguide? What is the purpose of the post and the iris? Which arms are the E arm, the H arm and the side



arms? Why are they called the E arm and the H arm? See [7], p. 525; [4], p. 229; and [9], p. 345.

7. What is the function of the tuning plunger? See [10], p. 60; [4], p. 240; and [9], p. 343.
8. What is the function of the double screw tuner? Is the separation of the screws consistent with your estimation of the wavelength obtained from measurement of the cavity length? See [4], pp. 131-133 for a picture and explanation.
9. What do the terms resistance, reactance, impedance, conductance, susceptance and admittance mean and how are they related to one another? The following diagram may be useful.



## B. THE GUNN OSCILLATOR

**NOTE: Do not make any mechanical tuning adjustments to the Gunn diode.**

1. With a varactor voltage of 4 volts, make a plot of BIAS current as a function of BIAS voltage. Do your results agree with the specifications on the test performance sheet in appendix III?
2. Remove the quartz tube from the cavity if it is in the cavity. Put the attenuator flap fully in for maximum attenuation and connect the output from the crystal detector to the preamplifier. Set the bias and varactor voltages to 9.5 V.
3. Determine the operating frequency for the bias voltage you have chosen. It should be somewhere near 9.15 GHz. One finds the operating frequency by slowly turning the wavemeter dial. There will be a sharp dip in the signal to the preamplifier when the wavemeter is set to the operating frequency. This corresponds to absorption of power by the resonant cavity wavemeter.
4. Make a plot of frequency versus tuning voltage for a bias voltage of 11 V. It is true that different bias voltages from the recommended one could be used, but, for lower bias voltages, a frequency versus tuning voltage curve tends to have rapid changes.

## C. CAVITY RESONANCE AND TUNING IN THE ABSENCE OF MAGNETIC FIELD

There should be no sample in the cavity. The attenuator flap should be completely in and

the detector should be connected to the preamplifier.

1. Determine the cavity resonance by varying the tuning voltage until you pass through a very sharp dip in the signal from the detector. The reading should go to zero. This is the cavity resonance.
2. Adjust the tuning screws and the plunger near the detector so that they are all the way out. Now insert the screw in the slide screw tuner until enough power is reflected to the detector to give a one third scale reading on the preamplifier meter. (There may be one to three maxima depending on the amount of power being sent into the system. Choose the maximum near the centre of the slide range.)
3. Adjust the plunger for maximum signal. As you can see, this adjustment is not critical. Adjust the tuning screws near the detector. In this arrangement these screws have little effect and in fact the tuning screws near the detector may be left all the way out. The system is now adjusted for maximum efficiency.
4. Measure the cavity resonance frequency with the wavemeter by adjusting it until a sharp dip is observed. Now, remove the screw in the slide screw tuner from the waveguide and check to see if the frequency has drifted. The preamplifier reading should go to zero, or a minimum near zero.
5. Place a small amount (size of a large pin head) of DPPH in the bottom of a clean dry quartz tube and place the tube in the cavity so that its bottom is 1 cm above the lower surface. It may be held up with a rubber band. Note the change in cavity resonance frequency. Adjust the frequency until complete absorption in the cavity is observed. Insert the tuner screw and measure the cavity resonance as at step 4. Now, move the wavemeter absorption well away from the cavity absorption.

### **Questions - Part B and Part C**

1. Find the iris, which defines the end of the resonant cavity. Determine the length of the resonant cavity by measuring the distance from the iris to the end wall. Compare the cavity length with  $\lambda_g$  at the cavity resonance wavelength. Is this what you expected knowing the resonant mode of the cavity?
2. How far is the plunger from the centre of the diode? Why is this distance to be expected?
3. Does the frequency increase or decrease when the quartz tube is placed in the resonant cavity? Is this what you expected? See [4], p. 313.

### **D THE MAGNETIC MOMENT OF THE ELECTRON**

1. The detector is a diode and the diode current is most sensitive to changes in voltage when the operating point is chosen to be on the steep portion of the current versus voltage curve of the diode. In order that there will be a small steady current in the diode, insert the tuner screw until the preamplifier indicates about 0.5 mA.
2. Connect the output from the preamplifier to the vertical input of the oscilloscope. Connect the SCOPE HORIZ. AND PHASE ADJUST to the horizontal input of the

oscilloscope. Connect the MODULATION COILS and AMPLITUDE to the small modulation coils around the cavity. These coils provide a small sinusoidal magnetic field at the sample.

- Turn on the main magnet power supply and adjust the current until two sharp peaks are seen on the oscilloscope. Adjust the SCOPE HORIZ. AND PHASE ADJUST until the two peaks coincide and adjust the current until the peaks are exactly in the centre of the oscilloscope trace (Fig.4).



Fig.4. Two peaks coincide in the centre of the oscilloscope image

- Remove the quartz tube with the sample and measure the magnetic field at the position of the sample using the Bell 620 gaussmeter.
- Calculate the magnetic moment of the electron and the Lande  $g$  factor. What is the experimental error in your measurement of the magnetic moment?

### Questions - Part D

- Explain the physical meaning of the traces on the oscilloscope.
- Why did you ignore the sinusoidal modulation magnetic field, or did you? Was it too small to measure?
- Removing the quartz tube changes the resonant frequency by a small amount. Does it change the magnetic field by the same amount?

### Supplementary Questions - Part D

- What does it mean to say that the Lande  $g$  factor is two instead of one?
- Starting from  $\mu = \gamma \mathcal{S}$  and  $S_z = \pm \frac{1}{2} \hbar$ , show that  $\gamma = \omega / B$ .
- Why is the energy of interaction of magnetic moments with magnetic fields given by  $-\mu \cdot B$  instead of  $\mu \cdot B$ ? Give a simple explanation using current loops. Does the field, created by a current loop, line up with or against the external magnetic field? Explain your answer using simple arguments from forces on current loops in magnetic fields.

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## Other Useful Materials

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