ELECTRON SPIN RESONANCE

George Brown
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LABORATORY OBJECTIVES

The objective of this experiment is to learn the fundamentals of microwave theory and instrumentation; to learn the fundamentals of electron spin resonance, and to measure the *g*-factor of an electron in an organic salt known as DPPH.

INTRODUCTION

The fascinating history of the discovery of electron spin has been authoritatively described in the book by Pais.[1] In the mid-1920's, many scientists informally proposed the idea, but the first convincing publication was published by two graduate students, Sam Goudsmidt and George Uhlenbeck.[2] In their seminal article they proposed that the electron had half-integral spin, which qualitatively and quantitatively explained the splitting into doublets of orbital angular momentum states. Today, the electron's spin plays a central role in the magnetism of matter and it is the centerpiece of the modern subject of *spintronics*. At the Stanford Linear Accelerator Center, 50 GeV beams of spin-polarized electrons were once collided with unpolarized positrons at the Z_0 resonance, leading to accurate measurements of an important parameter of the Standard Model.

PHYSICS

Classical treatment: Classical mechanics teaches us that a rigid rotating mass with density function $\rho_m(\mathbf{r})$ may possess a vector spin angular momentum **S**. Likewise, a rotating charge density $\rho_c(\mathbf{r})$ may possess a vector magnetic moment $\boldsymbol{\mu}$. These vector quantities are defined by similar expressions:

$$\begin{aligned} \mathbf{S} &\equiv \int (\mathbf{r}\times\mathbf{v})\,\rho_m(\mathbf{r})\,d^3x \\ \boldsymbol{\mu} &\equiv \frac{1}{2}\int (\mathbf{r}\times\mathbf{v})\,\rho_c(\mathbf{r})\,d^3x \end{aligned} \tag{1}$$

In the special case where the charge density is everywhere proportional to the mass density, it is easy to show that

$$\frac{\rho_c(\mathbf{r})}{\rho_m(\mathbf{r})} = \frac{q}{m} \tag{2}$$

and it follows that

$$\boldsymbol{\mu} = (q/2m)\mathbf{S}\,. \tag{3}$$

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[1] Abraham Pais, **Inward Bound**. Oxford University Press, New York.
[2] G. E. Uhlenbeck and S. Goudsmit, *Naturw.* **13**, 953 (1925).

If, on the other hand, the local ratio of charge density to mass density depends upon position, the magnetic moment will still be proportional to the angular momentum, with the coefficient $q/2m$ scaled by a dimensionless factor known as the *g*-factor:

$$\boldsymbol{\mu} = g(q/2m)\mathbf{S} \tag{4}$$

Empirically, for a free electron the *g* factor is measured to be

$$g_e = 2.002\,319\,304\,362 \tag{5}$$

This is one of the most accurately measured quantities in physics. More remarkably, the theory known as *quantum electrodynamics* predicts this number, within the experimental error (±1) in the final digit.

Quantum treatment: When one properly treats an electron quantum mechanically, the fundamental unit of angular momentum is Planck's constant, $\hbar$. In particular, the electron's spin angular momentum along any axis is given by $\pm\hbar/2$. If we arbitrarily take the axis to be the z-axis, then

$$\mu_z = \pm g_e(e/2m_e)(\hbar/2) = \pm(g_e/2)(e\hbar/2m_e) = \pm(g_e/2)\mu_B \tag{6}$$

where we have defined the Bohr magneton, the natural unit of magnetic moment, as $\mu_B \equiv e\hbar/2m_e$.

The *energy* of a spinning charge in a magnetic field is given both classically and quantum-mechanically by the simple formula

$$E = -\boldsymbol{\mu}\bullet\mathbf{B}_{local} \tag{7}$$

where $\mathbf{B}_{local}$ is the local microscopic magnetic field at the site of the electron. Therefore, if $\mathbf{B}_{local}$ is directed along the z-axis, formula (6) tells us that there is an energy difference between the state where an electron is aligned parallel with the field, versus the state when it is aligned anti-parallel. The energy difference will simply be

$$\Delta E = g_e \mu_B B_{local} \tag{8}$$

As a consequence, if we shine photons with energy $\hbar\omega = \Delta E$ on to the sample, we can flip the low-energy spin to a high energy state, or alternatively stimulate a transition from the high energy state to a low energy state. Either way, energy will be absorbed from the photon beam by electron. Detecting this absorption is the challenge of electron spin resonance.

Now it gets interesting. The magnetic field at the electron's site will be the sum of the externally applied magnetic field and the induced local magnetic field due to neighboring electrons. If the local magnetic field is equal to the externally applied magnetic field, plus an amount proportional to the applied magnetic field, the material is said to be either paramagnetic or diamagnetic.[3] For this reason, electron spin resonance is sometimes called *electron paramagnetic resonance*, a misnomer since spin resonance occurs perfectly well in nonmagnetic materials. The effective *g*-factor is defined as the coefficient *g* in the formula

$$\Delta E = g\mu_B B_{ext} \tag{9}$$

For most substances, paramagnetism is either weak or absent, and *g* is very close to g_e.[4]

Transitions between the low and high energy states will take place when $\Delta E = \hbar\omega$, where ω is the angular frequency of the incident radiation. Inserting this condition in eq. (9), we get

$$g = \frac{\hbar\omega}{\mu_B B_{ext}} = \frac{2m_e}{e}\frac{\omega}{B_{ext}} = \frac{4\pi m_e}{e}\frac{\nu}{B_{ext}}, \tag{10}$$

where $\nu = \omega/2\pi$ is the frequency of the incident radiation.

EXPERIMENTAL METHOD

The basic method: As previously discussed, microwave energy will be absorbed by a sample when the microwave frequency and the applied magnetic field satisfy the resonance condition. In this experiment we bathe the sample with a known frequency of microwave energy, around 9.7 GHz, and slowly sweep the magnetic field (of order 0.3 T) to observe the absorption profile. Unfortunately, the power absorbed by the sample is only a tiny fraction of the applied power; to achieve high sensitivity, we employ a *bridge* technique where the incident power is effectively subtracted off, so that in the absence of sample absorption, the detector sees little or no microwave power. This method will become clearer in what follows.

Basic Parameters:

1. Nominal microwave frequency: 9.3 GHz
2. Waveguide internal dimensions: 0.400 inches by 0.900 inches
3. Nominal anode voltage: 300 Volts
4. Nominal anode current 30 mA
5. Nominal reflector voltage: 140 Volts
6. Nominal magnet current: 3.4 Amperes
7. Nominal magnetic field 0.33 Tesla

[3] For paramagnets, the local field is increased in magnitude; for diamagnets, the local field is reduced. Paramagnetism in materials is usually far stronger than diamagnetism.

[4] Strictly speaking, *g* is a second-rank tensor, whose principal components can be measured by orienting a single crystal with respect to the external field. We shall neglect this effect.

Magnetic Field: The magnetic field is provided by an electromagnet with water-cooled coils. The power supply is capable of being modulated by an external D.C. coupled input. The approximate calibration of the magnet is 0.1 Tesla/Ampere.

Microwave Source: A klystron *amplifier*, (which we will *not* use) consists of an electron beam that passes through two sequential resonant cavities resonant. Microwave fields introduced into the first cavity modulate the electron speeds, causing the stream of electrons to form bunches. These bunches then induce strong electromagnetic fields in the second cavity, resulting in a large power amplification.

When all that is needed is an oscillator, the two cavities can be cleverly combined into a single cavity; this configuration is known as a *reflex* klystron. Such a klystron can oscillate within plus or minus 10% of the central resonant frequency (because the cavity Q is about 100). The precise microwave frequency is determined by the so-called reflector voltage, which determines the electron bunch spacing.

Following the klystron is an *isolator*, a microwave component that allows power to only flow in one direction, in this case away from the klystron. The isolator protects the klystron from microwave power reflected back from downstream components, power which could damage, or at least disrupt, the action of the klystron.

Microwave Circuit: The full microwave circuit is depicted in Figure 1. The objective of this circuit is to provide a high contrast microwave signal at the detector. By high contrast we mean that variations in the absorption coefficient of the sample with respect to magnetic field (at a constant frequency) appear as a well-defined signal at the detector.

Microwave power is transported to the various components via hollow rectangular waveguides. The power propagating down a waveguide can be resolved into *modes* (m,n); for any given mode there is a minimum propagation frequency, called the cutoff frequency. Power in this mode can only propagate at frequencies higher than the cutoff frequency. The cutoff frequencies for mode *mn* are given by

$$f_{mn}^{(c)} = \frac{c}{2}\left(\frac{m^2}{a^2} + \frac{n^2}{b^2}\right)^{1/2} \tag{11}$$

If a < b, the mode with the lowest cutoff frequency is the (0, 1) mode, with $f_{(0,1)}^{c} = c/2b = 6.562\ \text{GHz}$, which is comfortably less than our working frequency, 9.3 GHz. It is easy to show that all other modes have cutoff frequencies greater than 9.3 GHz, so no other mode can propagate in our waveguide.

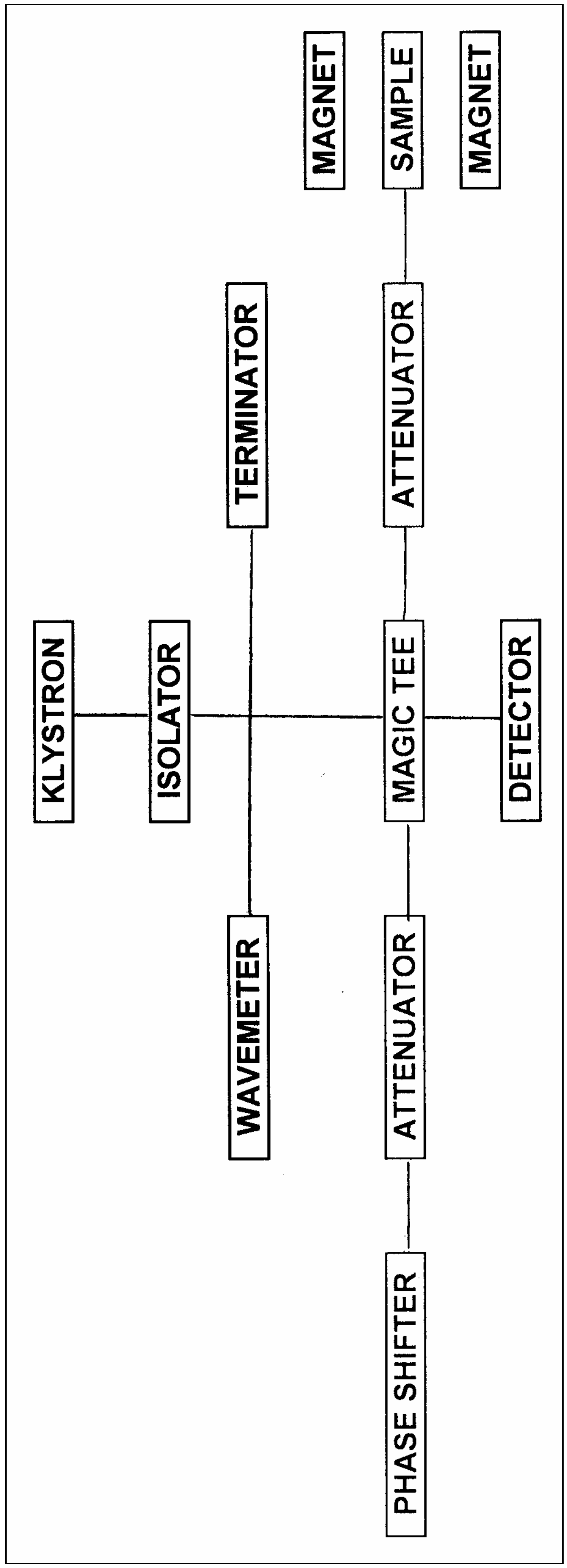

Figure 1. Schematic diagram of the spectrometer circuit.

Wavemeter: Downstream of the isolator, a "tee" diverts[5] a small fraction of the klystron power into a high-Q resonant cavity with an adjustable and accurately calibrated piston. A crystal detector downstream of the wavemeter will show a dip in power when the klystron frequency is at resonance. The wavemeter is accordingly used to calibrate the klystron frequency.

Magic Tee: Downstream of the wavemeter circuit, the klystron power encounters a "magic tee." This magic tee is a four-port device with the following remarkable property: all of the power entering the tee from the klystron is evenly split to the two side ports, but none flows to the output port (connected to the final detector). However, power returning from the two side ports *coherently* combines at the tee but only flows to the output port.

Sample Chamber: One of the two symmetric ports of the magic tee, the *sample arm*, provides power to the sample chamber; the other port provides power to a variable reactance. (See below).

The sample chamber is a short piece of waveguide (a=0.400 inches, b=0.900 inches) of internal length d = 1.543 inches, soldered to the sample arm. Signal enters the sample cavity via a small hole drilled in the upper face of the sample arm waveguide. The sample is contained in a miniature test tube which slips into a hole in the upper part of the sample chamber. By suspending the sample in a resonant cavity, one substantially increases the electromagnetic fields at the sample over the fields in the waveguide proper.[6] Since the sample is close to the conducting boundary of the cavity, the oscillating electric field **E** is small, but the oscillating magnetic field **B** is large.

A perfectly conducting rectangular cavity with no apertures has an infinite Q and an infinite spectrum of resonances, given by the formula

$$f_{lmn} = \frac{c}{2}\left[\left(\frac{l}{a}\right)^2 + \left(\frac{m}{b}\right)^2 + \left(\frac{n}{d}\right)^2\right]^{1/2}. \tag{12}$$

Because our chamber has finite conductivity and a large hole to admit the sample, the resonant frequency is significantly shifted downward, and the Q is substantially reduced.[7]

The ideal configuration of the sample arm occurs when most of the power traveling down the sample arm is absorbed by the resonant cavity walls, and by the sample itself. This is called a "matched" configuration. It occurs when the aperture admitting the power to the chamber is exactly the right size, and when the fields are at a maximum at the aperture.

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[5] Half the diverted power goes to the wavemeter and half to a dummy matched load. An equivalent approach would have been to use a *directional coupler* connected only to the wavemeter, instead of a tee to two arms.

[6] The spectrometer described in Mellisinos has the sample suspended in the standing wave field of the waveguide, rather than in a high-Q resonator. The signal in such a spectrometer is much smaller.

[7] A closed copper cavity at these frequencies typically has a Q of about 10,000. The apertures in our sample chamber reduce the Q to of order 100, which is still a huge improvement over the Mellisinos method.

Maximizing the fields at the aperture is accomplished by terminating the sample arm in an adjustable short, which sets up standing waves in the sample arm, with maxima separated by λ_g. When the aperture is adjusted to be a distance $(p+½)\lambda_g$ from the aperture, the coupling will be optimal. In practice, this adjustment is made empirically. (See below).

Variable reactance: The other symmetric port of the magic tee is connected to a calibrated variable attenuator, followed by a variable reactance. The variable attenuator is a masterpiece in engineering: It reduces the power transmitted to the downstream components, yet it always presents a matched impedance to the waveguide, so no power is reflected back by the attenuator. It is also symmetric in this regard.

The purpose of this circuit is to reflect power back to the magic tee with a phase and amplitude that nearly cancels the power reflected from the sample chamber when the spin resonance condition (B, ω) is *not* met. Then, when the spin resonance condition is met (in our case by varying B at fixed ω) the bridge will be unbalanced and a net signal will flow to the output detector.

Detector: The microwave detector is a simple semiconductor diode placed in the waveguide at the point of maximum electric field. The diode rectifies the applied electric field, producing a D.C. signal whose amplitude increases with the applied electric field.

It turns out that the DC signal output is proportional to the square of the electric field at the diode, by the following argument. A well-made pn junction diode has a current-voltage relationship given by the Ebers-Moll formula:

$$i(t) = i_0[\exp(ev(t)/kT) - 1] \tag{13}$$

where k is the Boltzmann constant,[8] i_0 is the asymptotic reverse current in the diode, and $v(t) = v_0 \cos(\omega t)$ is the voltage across the diode, which is oscillating at the microwave frequency. Ordinarily the argument of the exponential is small compared to 1, so we may expand this expression in a power series:

$$i(t) = i_0[(ev(t)/kT) + (1/2)(ev(t)/kT)^2 + \cdots] \tag{14}$$

Recalling that $v(t)$ is oscillating at roughly 10 GHz, and that our detector is measuring the DC, or average value of i, the first term vanishes, and, using $<\cos^2 \omega t> = 1/2$,

$$< i(t) > \approx (i_0/2) < (ev(t)/kT)^2 > = (i_0/4)(ev_0/kT)^2 . \tag{15}$$

Thus the diode current is proportional to the average of the square of the incident microwave voltage, hence proportional to the incident power.

[8] At room temperature, kT/e = 0.025 volts.

PROCEDURE

Preliminaries: The first step is to turn on the power strip on the desktop. This supplies power to a cooling fan for the klystron.

CAUTION: THE HIGH VOLTAGE LEADS OF THE KLYSTRON ARE PARTIALLY EXPOSED AT THE KLYSTRON. BE CAREFUL TO NOT TOUCH THE EXPOSED LEADS WITH YOUR HAND OR WITH A CONDUCTING TOOL.

Klystron tuning: The goal of this section is to tune the klystron oscillator so that it oscillates at the resonant frequency of the sample chamber. First, the klystron *cavity* must be mechanically tuned so that its resonant frequency is centered at the frequency of the sample chamber. Then, the precise klystron frequency is determined by the *reflector voltage*, which should be in the neighborhood of 150 volts.

1. Turn on the anode voltage and set to 300 volts.
2. Turn on the reflector voltage and set to about 150 volts.
3. Hook up channel 1 of the oscilloscope to the crystal detector.
4. Set the modulation to 60~.
5. Hook up the filament output of the Heathkit power supply to channel 2 of the oscilloscope.
6. Set the attenuator to maximum attenuation; *i.e.* 50 dB. The attenuator will then absorb virtually all of the incident power in that arm.
7. Observe the crystal output in tandem with the reflector voltage. The crystal output, when the klystron cavity, the reflector voltage, the modulation amplitude, and the sample tuning short are properly set, should look like Figure 2. This will be accomplished by the procedure given below.

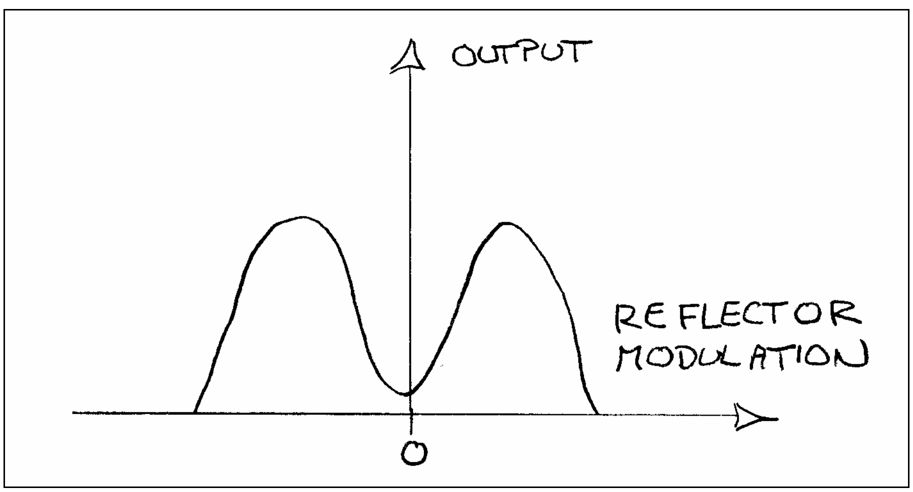

Figure 2. Crystal output as a function of reflector modulation when the klystron cavity and the reflector voltage are set properly. The klystron cavity is first tuned to put the sample dip into the center of the output peak; and the klystron voltage is then set so that the dip occurs at 0 reflector modulation.

Here is what is happening: As the reflector voltage sweeps over its full range, the klystron oscillator comes to life and oscillates with a frequency that increases as the magnitude of the reflector voltage increases. This is because the bunch spacing in the klystron beam becomes progressively shorter as the reflector voltage is increased. However, the klystron will only oscillate when the electron bunch frequency is near the resonant frequency of the klystron cavity, which in turn is determined by the internal dimensions of the cavity, tunable with the tuning screw on the klystron.

The dip in the klystron peak is the resonant absorption of the sample cavity. Since the Q of the sample cavity is somewhat higher than the Q of the klystron, the dip is fairly well resolved within the positive peak.

To achieve the proper tuning, perform the following steps:

1. Mechanically adjust the klystron cavity resonant frequency to the center of the sample chamber fixed resonant frequency. This is accomplished by adjusting the tuning screw on the klystron until the sample chamber "dip" is centered on the klystron peak.
2. Now adjust the reflector voltage until the center of the preceding "dipped peak" falls at 0 reflector modulation voltage (as observed on channel 2, the 60 Hz signal which is proportional to the modulation voltage. You are now very close to the final tuning.
3. Now reduce the modulation voltage by about a factor of two, and repeat steps 1 and 2.
4. Keep repeating steps 1-3 until the sweep amplitude is zero. The reflector voltage, the klystron cavity, and the sample cavity are now tuned to the same frequency.

To measure the resonant frequency of the sample cavity, repeat steps 1 and 2 above. Then connect channel 2 of the oscilloscope to the wavemeter crystal. The wavemeter is an accurately calibrated, adjustable resonant cavity). Adjust the knob of the wavemeter until a sharp dip appears at the center of the "dipped peak." You may now read out the resonant frequency to high precision.

Now adjust the phase and the amplitude of the signal reflected from the bridge circuit (the attenuator and the phase shifter) so that the reflected signal exactly cancels the residual signal from the sample chamber. Once you have tuned the bridge to exactly null the sample signal you need to "spoil" the tune by detuning the attenuator by about 3 dB away from its null setting. This is because the detector is sensitive to the *curvature* of the diode response curve at the operating point.

You are now ready to turn on the magnet. To do this, turn on the magnet power supply, and simultaneously adjust the coarse and fine current control knobs to a current of about 3.4 Amperes.

Meanwhile, you may turn on the Hall probe power supply, and measure, with both the analog panel meter and a digital voltmeter, the magnetic field.

If you slowly by hand adjust the current in the magnet, you will see the resonance! By carefully sweeping the current by hand, you may set the field to maximum absorption, and thus calculate g using equation (10).

Magnetic Sweep: The final step is to sweep the magnet current with a slow triangular waveform. This is accomplished by connecting the Krohn-Hite sweep generator to the magnet power supply and to channel 2 of the oscilloscope. (A good choice of frequency would be about 2 Hz.) You should be able to observe the resonance waveform. To improve the signal and suppress the noise, you might try the signal averaging capability of the oscilloscope, by setting Average in the Acquire menu. Why does the resonance appear at a different current going up, as compared to going down? Once you have a nice waveform you should download it to a flash drive for further analysis.

Phase-sensitive detection: You will notice that the signal appears on top of a background. There is a very clever and well-established method for dramatically reducing the background noise, known variously as *phase-sensitive* detection, *synchronous* detection, and *lock-in* detection. With this technique, one superimposes a tiny sinusoidal current at, say, 1,000 Hz, on top of the normal sweep current.[9] One then observes the variation of the output signal at the same frequency (*e.g.* 1 kHz) within a narrow bandwidth, determined by the averaging time. (When you do the complete analysis, you discover that the output signal is proportional to the derivative, with respect to the magnet current, of the original signal). This method rejects all noise not falling within this narrow bandwidth.

The setup is relatively straightforward.

1. Connect the 1 kHz sinusoidal output of the lock-in amplifier to the Radio Shack audio amplifier, and connect the output of the audio amplifier to the sweep coils of the magnet.
2. Connect the crystal detector to the input of the lock-in amplifier.
3. Connect the output of the lock-in amplifier to channel 1 of the oscilloscope.
4. The settings of the lock-in amplifier should be: Time constant, 30 ms.; sensitivity, 10 mV.

Presto! You will see a dramatic improvement in the signal-to-noise ratio, at the expense of outputting the derivative of the signal.

ANALYSIS

From your measurements of the resonant frequency and of the magnetic field, determine the g-factor of the electron for the DPPH signal. Compare to the established value, $g = 2.0036$. You should include in your report the plots of signal versus magnet current, with an estimate of the hysteresis effects in the magnet.

[9] By "tiny," we mean small enough so that the resulting sinusoidal magnetic field variation is small in comparison to the "width" of the signal.

FURTHER QUESTIONS AND MEASUREMENTS

1. In your own words, briefly describe how the following microwave components work, and their properties: a) reflex klystron, b) isolator, c) wavemeter, d) magic tee, e) attenuator, f) diode detector.

2. With the wavemeter, measure the range of frequencies over which the klystron oscillates. From this, estimate the *Q* of the wavemeter and of the Klystron cavity.

3. The waveguide internal dimensions are 0.400″ x 0.900″. Calculate the five lowest cut-off frequencies.

4. The internal dimensions of the sample resonant cavity are 0.400″ x 0.900″ x 1.543″. What are the six lowest resonant frequencies of the cavity, assuming one can neglect the sample opening?

APPENDIX

At first glance, one might expect that the instrument would be most sensitive when, off resonance, the microwave bridge is perfectly balanced. This way, one can amplify the signal as much as one pleases, since the "background" signal has been eliminated. This is almost, but not quite, correct. Recall from equation (15) that the D.C. signal that one measures, for an incident microwave voltage across the detector diode, is

$$< i(t) > \approx (i_0/2) < (ev(t)/kT)^2 > = (i_0/4)(ev_0/kT)^2 \quad (16)$$

If we take Δv to be the change in voltage amplitude at the detector caused by absorption, and Δi to be the corresponding change in detector current, it follows that

$$\begin{aligned} &< i + \Delta i > \approx (i_0/4)(e(v_0 + \Delta v)/kT)^2 \\ &< i + \Delta i > - < i > \approx (i_0/4)(e^2(2v_0\Delta v + (\Delta v)^2)/k^2T^2) \end{aligned} \quad (17)$$

To first order, the change in current is proportional to v_0, the "unbalanced" voltage! Thus, to the extent that we can electronically subtract the baseline average current, we gain in signal by deliberately unbalancing the bridge.

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