

Physics 4D Lab: Electron Spin Resonance

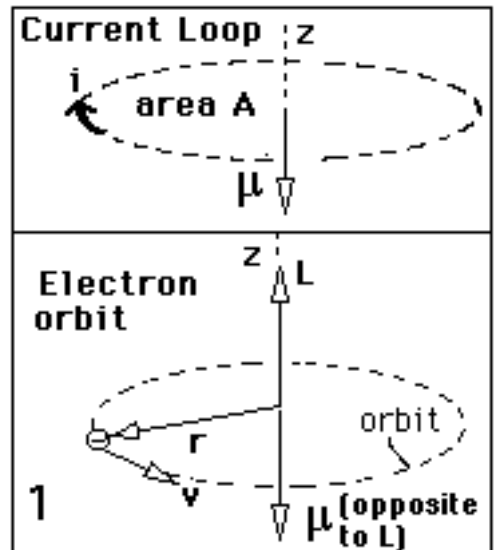
The objective of this experiment is to determine the g factor of the electron using the experimental technique called electron spin resonance.

Introduction:

**A . Review of Classical Ideas:**

(Note: when **vector notation** is desirable vectors are in **bold**)

According to classical physics, the magnetic dipole moment  $\mu$  of a circular current loop with current  $i$  and cross-section area  $A$  is defined by  $\mu = i A$  with a direction normal to the area in the same sense as that indicated by the right hand rule for conventional current. We can apply this definition to the planetary model of an electron of mass  $m$ , charge  $q = -e$ , orbit radius  $r$ , orbit period  $T$  and velocity  $v$  orbiting about a positively charged nucleus. The current associated with the orbit will be  $q/T$  and the velocity will be  $v = 2\pi r/T$ . The magnitude of the angular momentum  $L$  of the electron in its orbit is  $L = mvr$  as shown in the diagram to the right. The magnitude of the magnetic moment  $\mu$  of the electron of charge  $q = -e$  would then be:

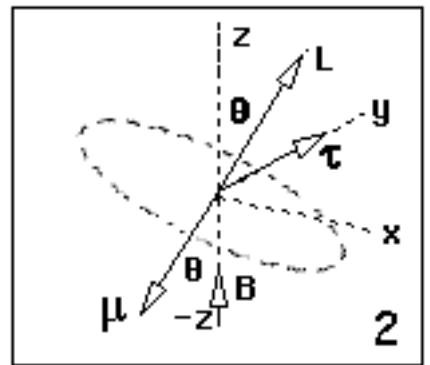


$$\mu = i A = (q/T)(\pi r^2) = q / (2\pi r/v) (\pi r^2) = (q/2m)(m v r)$$

$$\text{or } \mu = (q / 2m) L \quad (\text{Eq.1})$$

$$\text{or in terms of vectors: } \mu = (-e / 2m) L \quad (\text{Eq.2})$$

The negative charge would mean the direction of electron magnetic moment  $\mu$  is opposite to its angular momentum  $L$  as depicted in the diagram. In general, the classical orbit of an electron will be directed in an arbitrary direction in space. The effect of an external magnetic field  $B$  on an arbitrarily oriented orbit will be to exert a torque  $\tau$  on the system given by  $\tau = \mu B \sin\theta$  with a direction perpendicular to the plane of  $\mu$  and  $B$  vector as shown in the diagram to the right.



Since the direction of the torque is perpendicular to the angular momentum vector, there will be no change in the magnitude of the angular momentum and but only be changes the direction of the angular momentum. As we know from classical mechanics torques produce infinitesimal changes in angular momentum  $dL$  of a rotating system according to :

$$| dL | = | \tau | dt = | \mu \times B | dt = \mu B \sin \theta dt .$$

Referring to the diagram to the right, the result is a precession of the angular momentum vector  $L$  about an axis defined by the direction of the magnetic field with an angular velocity  $\omega_L = d\alpha / dt$  where  $d\alpha$  is given by

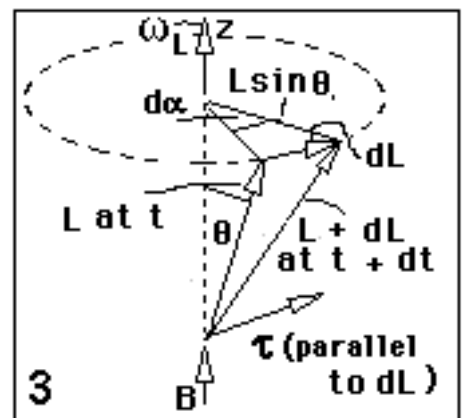
$$d\alpha = dL / L \sin \theta = (\mu B \sin \theta dt) / L \sin \theta$$

$$= (\mu B / L) dt.$$

The precessional angular velocity would then be given by:

$$\omega_L = d\alpha / dt = \mu B / L. \quad (\text{Eq.3})$$

This example is analogous to the precession of a gyroscope in



a gravitational field.

Substitution of  $\mu$  from (Eq.1) into (Eq.3) gives

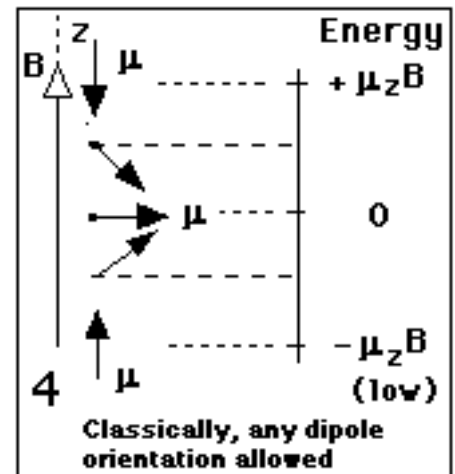
$$\omega_L = e B / 2 m \quad (\text{Eq.4})$$

The frequency  $\omega_L$  (in radian/sec here) is called the Larmor precession frequency  $\omega_L$ . It is independent of  $\theta$  and  $L$

The magnetic potential energy  $U_m$  of a magnetic dipole in a magnetic field is given by :

$$U_{\text{mag}} = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu B \cos \theta = \mu_z B \quad (\text{Eq.5})$$

where  $\theta = \pi/2$  is chosen as the zero of energy. This suggests that the lowest energy is  $-\mu_z B$  (when  $\theta = 0$  and  $\mu$  and  $B$  are parallel) and the highest energy is  $+\mu_z B$  (when  $\theta = \pi$  and  $\mu$  and  $B$  are anti-parallel). Classical physics allows any possible energy between these two extremes. The diagram to the right shows the orientation for various dipoles in relation to the  $B$  field with the zero and the two extremes of energy  $+\mu_z B$  and  $-\mu_z B$  indicated.



### B. Modifications to Classical Ideas due to Quantum Physics

(1) The vector model of the atom resulting from Schroedinger's model of Hydrogen necessitated changes in the classical relationships given above.

(a) According to the vector model the angular momentum of the atom is restricted to values for which  $L = [l(l+1)]^{1/2} h$  with  $l = 0, 1, 2, 3, \dots, (n-1)$  where  $n$  is Bohr quantum number for total energy  $E_n$ .

(b) Spacial quantization also required so that the  $z$ -components of angular momentum could only have the values  $L_z = m_l h$ . where  $m_l = 0, 1, 2, 3, \dots, l$ .

(c) This would require the  $z$  component of orbital magnetic moment to be limited to the values:  $\mu_{Lz} = (e/2m)L_z = (e/2m)(m_l h) = (eh/2m) (m_l) = \mu_B m_l$  (Eq.7)

where  $\mu_B$  is called the Bohr magneton and is the natural unit for atomic magnetic moments.

(d) The allowed energies of the electron in a magnetic field would now be limited to

$$E = E_n + U_{\text{mag,orb}} = E_n + (\mu_{Lz} B) = E_n + (\mu_B m_l B) \quad (\text{Eq.8})$$

(2) In 1925 Uhlenbeck and Goudsmit introduced electron spin angular momentum as an intrinsic property of the electron in order to explain the results of the Stern-Gerlach experiment . It was necessary to modify the Schroedinger equation. As a result:

(a) the electron also has a spin angular momentum  $S = [s(s+1)]^{1/2} h$  where  $s = 1/2$  .

(b) Spacial quantization also required that the  $z$ -components of angular momentum  $S$  could only have the values  $S_z = m_s h$ . where  $m_s = \pm 1/2$

(c) This would require the  $z$  component of spin magnetic moment to be limited to the values:  $\mu_{Sz} = (e/2m)S_z = (e/2m)(m_s h) = (eh/2m) (m_s) = \mu_B m_l$  (Eq.9)

(d) The allowed energies of the electron in a magnetic field would now be extended (Eq.8) to  $E = E_n + U_{\text{mag,orb}} + U_{\text{mag,spin}} = E_n + (\mu_{Lz} B) + (\mu_{Sz} B) = E_n + (\mu_B m_l) B + (\mu_B m_s) B$  (Eq.10)

(3) In order to explain the unequal splitting that occurs in the fine structure of spectral lines of atoms in a magnetic field in the Anomalous Zeeman Effect , Lande found it necessary to modify (Eq.7) and (Eq.9) for the orbital and spin magnetic moments by introducing an ad hoc "g factor".

(Eq.7) is rewritten as:  $\mu_{L,z} = g_{\text{orb}} \mu_B B m_l$  (where  $g_{\text{orb}} = 1.00$ )

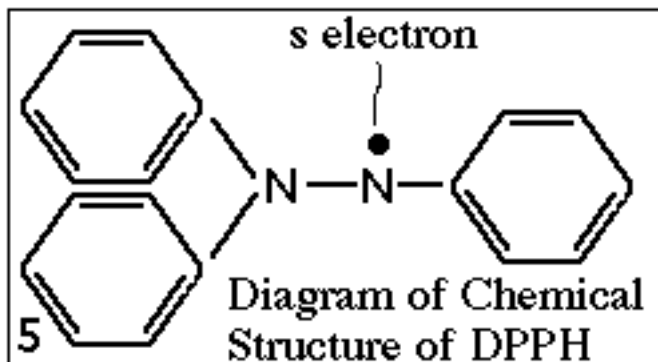
and (Eq.9) is rewritten as:  $\mu_{S,z} = g_{\text{spin}} \mu_B B m_s$ . (where  $g_{\text{spin}} = 2.00$ ) . (Eq.10)

for the electrons energy in the  $B$  field is now rewritten as:

$$E = E_n + U_{\text{mag}} = E_n + (g_{\text{orb}} \mu_B m_l) B + (g_{\text{spin}} \mu_B m_s) B \quad (\text{Eq.11})$$

(It should be mentioned here that Dirac extended the Schroedinger Equation to a relativistic formulation. He calculated the magnetic moment of the electron to be  $2.0023 \mu_B$  by considering the interaction of the electron with its own radiation field justifying Lande's ad hoc assumption).

(4) Our observations in this experiment is going to involve an organic compound called Diphenyl-picryl-hydrazine (DPPH). The chemical structure of DPPH is depicted to the right. It is a closed shell free radical with a an unpaired s electron ( $m_l = 0$ ) which is associated with a Nitrogen atom. Therefore (Eq.11) may be rewritten as:



$$E = E_n + U_{mag} = E_n + g_{spin} \mu_B m_s B \quad (\text{Eq.12})$$

The allowed values of  $m_s$  are  $\pm 1/2$  and selection rules for spin angular momentum give  $\Delta m_s = 0, 1$ .

Therefore the allowed energies for the s electron are  $E_{high} = E_n + U_{mag,high} = E_n + g_{spin} \mu_B (1/2)B$  (Eq.13) and

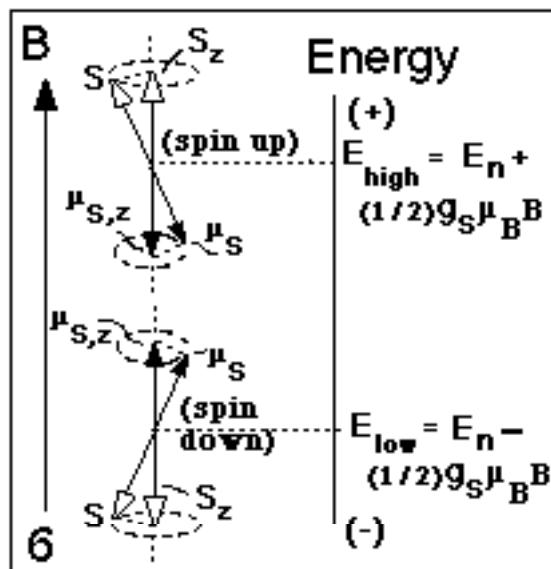
$$E_{low} = E_n + U_{mag,low} = E_n - g_{spin} \mu_B (1/2)B \quad (\text{Eq.14})$$

The allowable difference in energy between these two states is then:

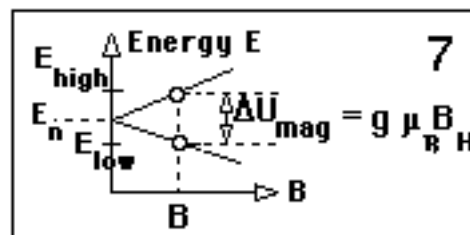
$$E_{high} - E_{low} = U_{mag,high} - U_{mag,low}$$

$$\text{or} \quad \Delta U_{mag} = g_{spin} \mu_B B \quad (\text{Eq.15})$$

The diagram above shows the two spin states (one up and one down) and the two energies associated with (Eq.13) and (Eq.14)b

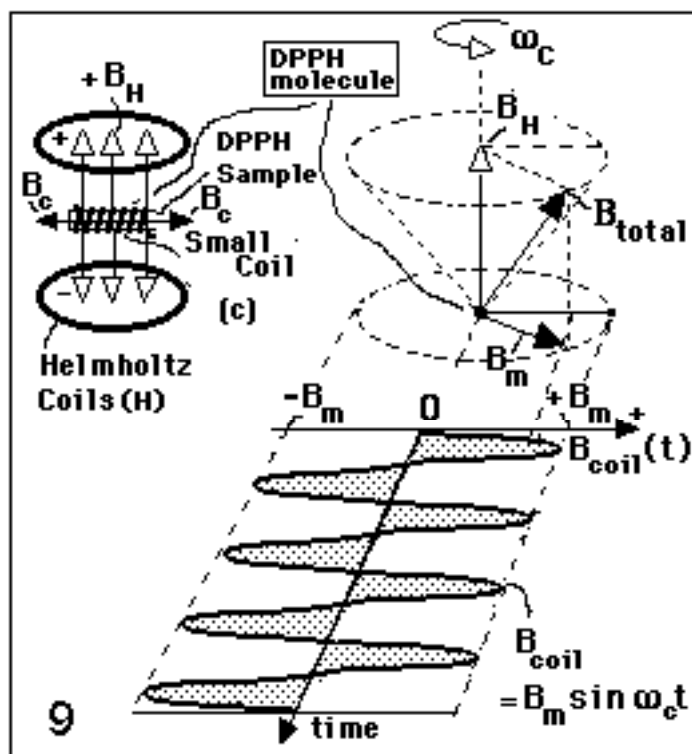


Graphs of (Eq.13) and (Eq.14) are show in the graph Energy E versus B to the right The slopes are  $\pm g_{spin} \mu_B B$ . Clearly the separation in energy is directly proportional to the static magnetic field B.



**C. The Electron Spin Resonance Method:**

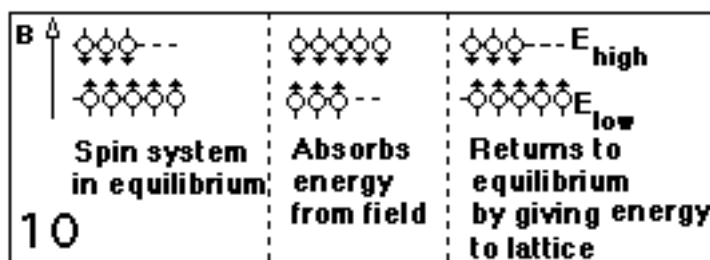
The energy difference  $\Delta U_{\text{mag}}$  given by (Eq.15) can be observed and the  $g_{\text{spin}}$  value of the electron can be determined by using the Electron Spin Resonance technique first used by the Russian physicist Zavoisky in 1945. A time varying magnetic field  $B = B_c \sin \omega_c t$  in a small coil is set up perpendicular to a constant magnetic field  $B_H$  provided by a pair of Helmholtz coils. The coil system and an exploded view of the total field acting on a given electron is shown to the right. The total field  $B_{\text{total}}$  is precessing with frequency  $\omega_c$ .



Classically, if the angular velocity the precessing field  $B_{\text{total}}$  is the same as the Larmor precessional angular of the electron in the field, we should expect a resonance and energy absorption from the field. This classical argument is valid to a point but, unfortunately, actual observed resonant frequencies are not the expected Larmor frequency (Eq.4).

A more sophisticated quantum mechanical argument is required to explain observed results. Quantum mechanically, the time varying field  $B_c$  represents a flux of photons of energy  $\Delta E = h \omega_c = h \nu_c$  incident on the magnetic spin system(s). If the energy of the photons is varied until equals the difference of energy such that  $\Delta E = \Delta U_m$  accessible to the electron spin system, then electron dipoles in the low energy spin state will absorb energy and "flip over" to the high energy state and electron dipoles in the high energy state will flip over and de-excite to the low energy state.

Statistically, for a large number of electrons, at equilibrium the number of electron in the high energy spin state will be less than the number in lower energy state. The effect of the field is to reverse this briefly with the net result will be a maximum in absorption of energy from the coil. The spin will quickly go back to equilibrium by transferring its absorbed energy back to the lattice. The rate at which the spins relax in going to equilibrium will determine the width of the resonance.



The resonant frequency  $\nu_{\text{res}} = \nu_{\text{coil}}$  will be given by :

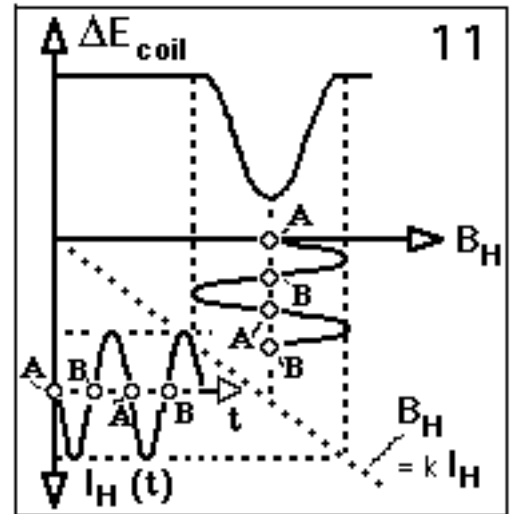
$$h \nu_{\text{res}} = g \mu_B B_H = g \mu_B k I_H \quad (\text{Eq.16})$$

where  $k$  is the proportionality constant  $\mu_0 N / [(5/4)^{3/2} a]$  between  $B_H$  and  $I_H$  in the Helmholtz Coils. ( $N$  is number of turns on coil and  $a$  is radius and separation of coils).

The absorption of energy will be observed as a drop in impedance of the coil. In order to convert the impedance to a voltage change that can be observed with an oscilloscope it will be necessary to have repeated traversals of the resonant point. This is achieved by using a low frequency field in the Helmholtz coils

$$B_H(t) = B_H \sin \omega_H t \text{ where } \nu_H = \omega_H / 2\pi = 50 \text{ Hz.}$$

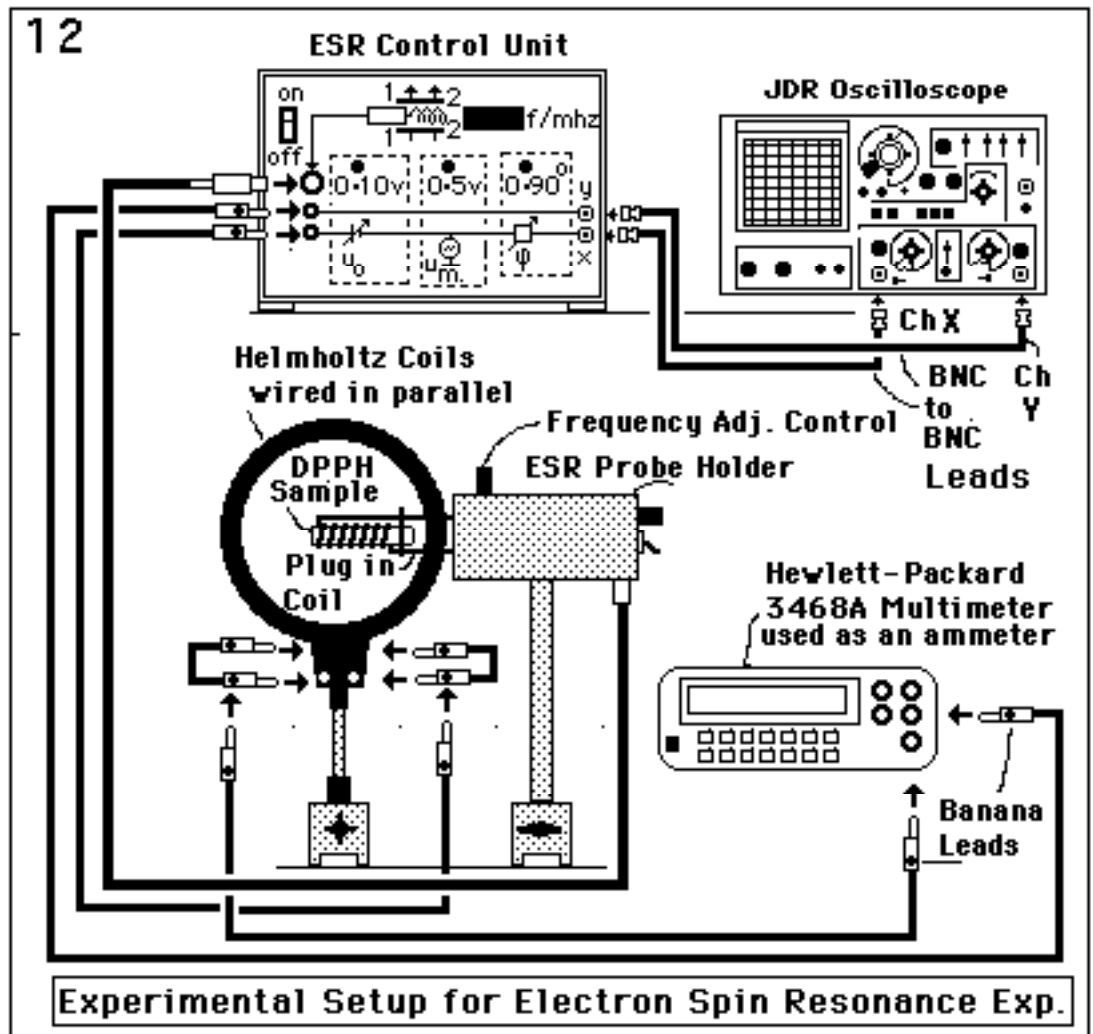
The graph to the right shows a graph of  $\Delta E_{\text{coil}}$  versus  $B_H$  near resonance. Also shown is the sinusoidal variation of  $B_H(t)$  as a linear function of the current  $I_H(t)$ . The resonant point will be swept through twice (points A and B on  $I_H(t)$  and  $B_H(t)$ ) each cycle and result in two resonant points per cycle.



**Experiment :**

**A. Equipment:**

- (1) ESR Control Unit, with Power Cord
- (2) ESR Probe Holder
- (3) JDR 3500 Oscilloscope with Power Cord
- (4) Two Helmholtz (HH) Coils,
- (5) HP 3468A Multimeter with Power Cord
- (6) DPPH sample in very small test tube
- (7) 3 small plug in coils
- (8) Special cable to connect ESR Control Unit to the Sample and Probe Holder
- (9) 2 shielded cables with BNC to BNC connectors
- (10) 6 leads with banana connectors.



**B. Experimental Setup:**

Setup the Equipment as shown in the diagram above with the following special considerations:

(1) Connect the HH Coils in parallel. (Caution : current in HH Coils should not exceed a maximum of 1.5 amperes) The HPDMM is limited to 3 amperes. When wired in parallel, this limits current in each coil to 1.5 amperes.

(2) Set the coils parallel and coaxially with a separation equal to their radius  $a$ . Measure the separation in cm with a metric scale.

(3) Select one of the interchangeable small plug in coils.

(i) Coil E (largest) for  $\nu_{\text{res}}$  in range 13 to 30 MHz for low currents

(ii) Coil F (middle size) for  $\nu_{\text{res}}$  in range 30 to 75 MHz for intermediate currents

(iii) Coil G (smallest) for  $\nu_{\text{res}}$  in range 75 to 130 MHz for high currents (less than 3 amperes)

tho)

(4) Carefully Place the DPPH sample in the coil and carefully insert the coil in the Coil holder Unit.

(5) Position the DPPH sample, Coil and Probe Holder between the HH Coils with the sample in the center of HH Coils. Be sure the test tube axis is perpendicular to the common axis of the HH Coils.

(6) Set up the Oscilloscope with the following initial settings:

(i) SWEEP TIME/DIV:  $\underline{X Y}$

(ii) MODE: Dual

(iii) X VOLTS/DIV: AC, 0.5 volts/div(cm)

(iv) Y VOLTS/DIV: AC, 0.2 volts/div(cm)

(7) With ESR Control Unit power cord not plugged in yet start with the following settings:

(i) Set On-Off Switch on Off

(ii) Set  $U_0$  counter-clockwise to 0 volts. This control determines the current  $I_H$  to the Helmholtz coils (and hence the field  $B_0$  in the coils). When you increase this control you should always be observing the ammeter also so that you don't inadvertently exceed the 3 ampere limit for coils (and ammeter).

(iii) Set  $U_{\text{mod}}$  counter-clockwise to 0 volts. This control determines the amplitude with which the current in the Helmholtz coils is modulated with a frequency of 50 Hz.

**C. Experiment and Data:**

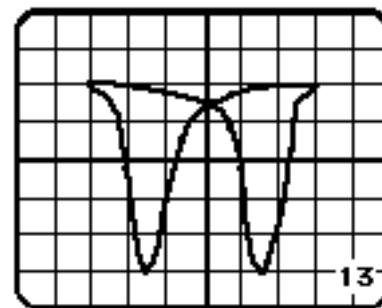
The goal of this part of the experiment is collect data which satisfies (Eq.16). Resonances will be observed on the oscilloscope and corresponding resonant frequencies  $\nu_{\text{res}}$  and Helmholtz currents  $I_H$  measured.

(1) With the equipment setup as indicated above, plug in all power cords and turn power to the ESR Control Unit, HP DMM and oscilloscope to ON. Set the HP Multimeter for DC Current (the ESR control unit will provide the 50 Hz modulation about this DC current)

(2) Center the CRT spot at the center on the upper Y axes (2 or 3 div above above X axis) with the ChA and Ch B position control. This horizontal centering is important since all adjustments will be relative to this vertical line. Increase  $U_{\text{mod}}$  to about 1.0 volts. You should now get a horizontal line approximately 2 divisions left and right of center on the scope trace.

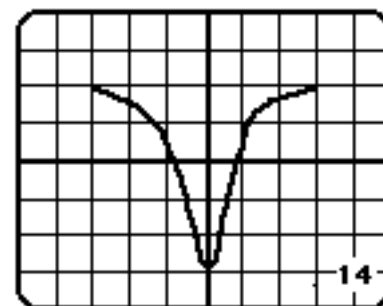
(3) Flip the small ON-OFF toggle switch on the ESR Probe Holder from 0 to 1. Turn the control knob to the right of the toggle switch fully clock-wise. You will probably see noise showup on your scope trace.

(4) Now, while watching the ammeter(don't exceed 3 amps) , slowly increase  $U_0$  on the ESR Control Unit until see a scope trace similar to that drawn to the right. The two inverted peaks are the resonances for the repeated traversals of the 50 cycle Helmholtz current discussed above. If changing  $U_0$  doesn't produce the trace , vary the frequency control on the top of the ESR Probe Holder until you get it.



Scope Trace

(5) Adjust the phase control ( $\phi$ ) on the ESR Control Unit until the the two inverted peaks are aligned with each other. Readjust  $U_0$  until the tips of the aligned peaks line up with the Y axis of the scope. The resulting trace should similar to the trace drawn to the right. The system is now adjusted for resonance and the current  $I_H$  in amperes on the HP-DMM and the resonant frequency  $\nu_{res}$  , in MHz, indicated on the ESR Control Unit should now be recorded.



Scope Trace

(6) To obtain more data for  $I_H$  and  $\nu_{res}$  change the frequency by adjusting the control on the ESR Probe Holder. This should cause the aligned peaks to move off the left or right of the Y axis.  $U_0$  may be then adjusted to realign the peaks with the Y-axis. The new values of  $I_H$  and  $\nu_{res}$  may be recorded. This process may be repeated until observations of resonance span the frequency range for the probe.

The other two probes should be also be used. Data ranging from approximately 25 to 120 MHz is obtainable from the three probes provided with this apparatus.

#### D. Analysis of Data:

(Eq.16) suggests that a graph of  $\nu_{res}$  (vertical) versus  $I_H$  (horizontal) should be linear. Plot the graph and determine the slope of the best fit line. Don't forget that the current divides equally between the two coils when they are wired in parallel. Compute the proportionality constant  $k$  for your Helmholtz coils. Use the slope, your value for  $k$  and the value for  $\mu_B$  to compute the  $g_{spin}$  value for your data. Compare your value with the theoretical value of 2.0023 determined by Dirac.