EXP 11 ESR (Electron Spin Resonance)

Introduction

ESR in Theory

The basic setup for electron spin resonance is shown in Fig 1. A test sample is placed in a uniform magnetic field. The sample is also wrapped within a coil that is connected to an rf oscillator. The smaller magnetic field induced in the coil by the oscillations of the oscillator is at right angles to the uniform magnetic field.

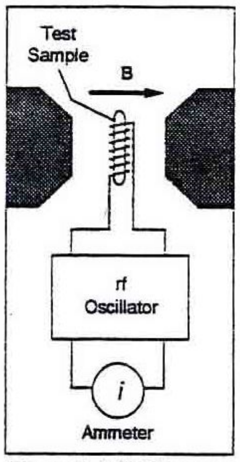


Figure 1 ESR Diagram

Consider, for the moment, a single electron within the test sample. The electron has a magnetic dipole moment (μ_s) that is related to its intrinsic angular momentum, or spin, by the vector equation:

$$\mu_s = g_s \mu_B s / \eta \qquad (1)$$

where:

g_s = a constant characteristic of the electron, the g-facotr

μ_B = the Bohr magneton

$= \dfrac{eh}{2m_e} = 5.788 \times 10^{-9} eV/G$

s = the spin of the electron

η = Planck's constant $= 6.582 \times 10^{-16} eV - \sec$.

The magnetic dipole moment of this electron interacts with the uniform magnetic field. Due to its quantum nature, the electron can orient itself in one of only two ways, with energies equal to $E_0 \pm g_s \mu_B / 2$; where E_0 is the energy of the electron before the magnetic field was applied. The energy difference between these two possible orientations is equal to $g_s \mu_B B$; where *B* is the magnitude of the magnetic field.

Resonance occurs when the rf oscillator is tuned to a frequency *f*, such that the energy of the irradiated photons, hf , is equal to the difference between the two possible energy states of the electron. Electrons in the lower energy state can then absorb a photon and jump to the higher energy state. This absorption on energy effects the permeability of the test sample, which effects the inductance of the coil and thereby the oscillations of the rf oscillator. The result is an observable change in the current flowing through the oscillator.

The condition for resonance, therefore, is that the energy of the photons emitted by the oscillator match the energy difference between the spin states of the electrons in the test sample. Stated mathematically:

$$hf = g_s \mu_B B \qquad (2)$$

ESR in Practice

For an electron with only two energy states, in a magnetic field of a given magnitude, it would be necessary to set the rf frequency with considerable accuracy in order to observe resonance. In practice, this difficulty is solved by varying the magnitude of the magnetic field about some constant value. With the PASCO ESR Apparatus, this is done by supplying a small ac current, superimposed on a larger dc current, to a pair of Helmholtz coils. The result is a magnetic field that varies sinusoidally about a constant value.

If the rf frequency is such that equation 2 is satisfied at some point between the minimum and maximum values of the sinusoidally varying magnetic field, then resonance will occur twice during each cycle of the field.

Resonance is normally observed using a dual trace oscilloscope. The oscilloscope traces, during resonance, appear as in Fig. 2. The upper trace is a measure of the current going to the Helmholtz coils, which is proportional to the magnetic field. The lower trace shows the envelope of the voltage across the rf oscillator, which dips sharply each time the magnetic field passes through the resonance point.

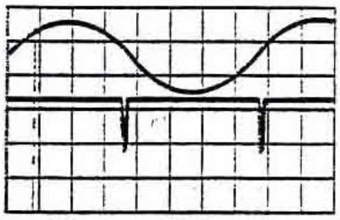


Figure 2 ESR on the Oscilloscope

ESR in Research

In research, ESR measurements are considerably more complicated that equation 2 would indicate. The electrons and protons in an atom or molecule form a complicated electromagnetic environment, which is affected by the externally applied magnetic field. The various energy splitting and shifts that show up in ESR measurements can therefore provide sensitive information about the internal structure of the atoms and molecules.

The test sample included with the PASCO ESR Apparatus DPPH, is a particularly simple substance for ESR measurements. It has an orbital angular momentum of zero, and only one unpaired electron. Therefore, for a given value of the external magnetic field, it has only a single resonant frequency. This makes it possible to investigate some of the basic principles of electron spin resonance, without (or before) getting into the more complex world of ESR analysis.

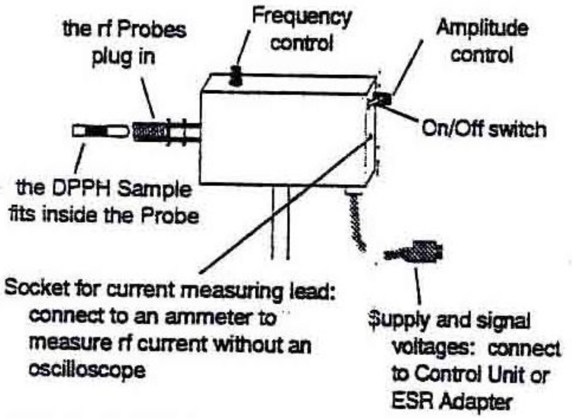
The ESR Equipment

Included Equipment

The ESR Apparatus is available in three separate packages (see Fig. 3):

- The ESR Probe Unit (SE-9634) includes:
  - The probe Unit with base
  - Three rf Probes and a DPPH sample in a vial
  - The passive Resonant Circuit
  - The current Measuring Lead for the Probe Unit
- The ESR Basic System (SE-9635) includes:
  - The ESR Probe Unit (se-9634)
  - A pair of Helmholtz Coils with bases
  - The ESR Adapter (SE-9637)
- The Complete ESR System (SE-9636) includes:
  - The ESR Probe Unit (SE-9634)
  - A pair of Helmholtz Coils with bases
  - The Control Unit

- **SE-9637 ESR Adapter** (or a junction box of your own making—see Appendix)
- **a pair of Helmholtz coils.**



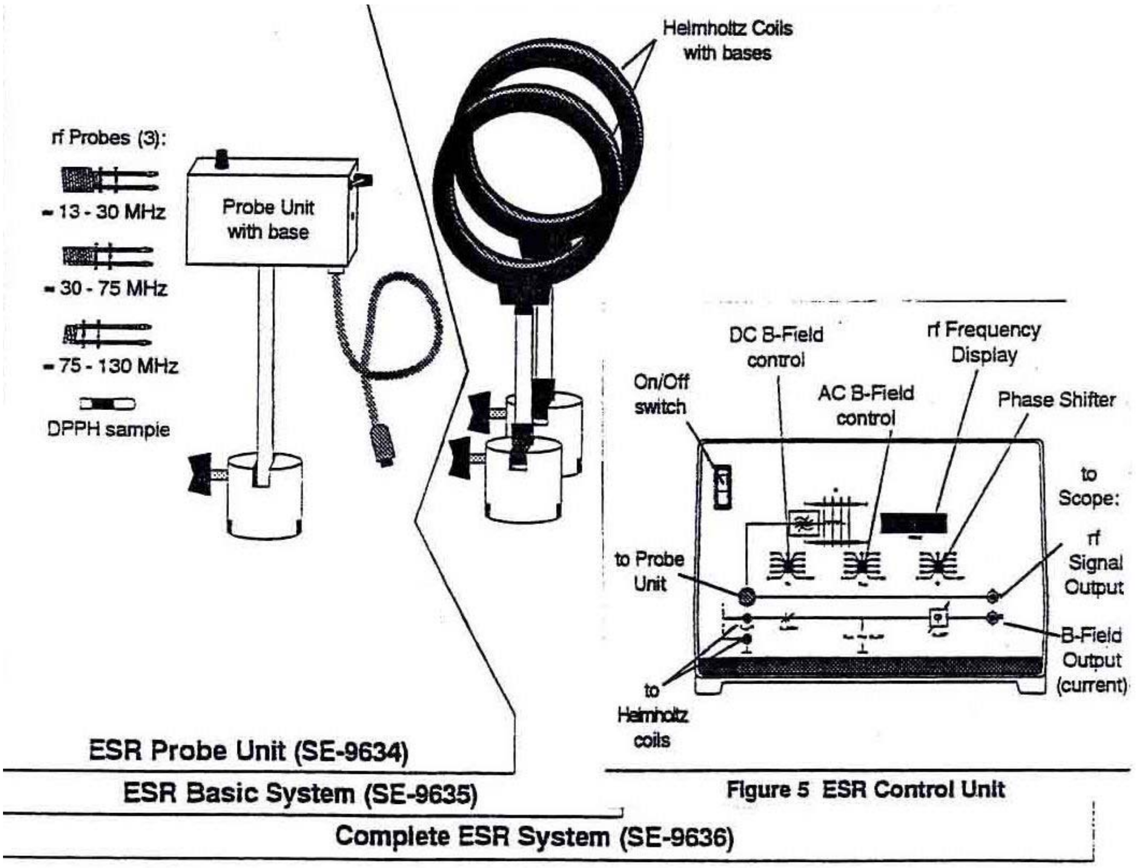


Figure 5 ESR Control Unit

Figure 3 The ESR Apparatus

If you're using the SE-9634 ESR Probe Unit, you'll need the same equipment as is required with the Basic ESR System, except that you will also need:

- SE-9637 ESR Adapter (or a junction box of your own making)
- A pair of Helmholtz coils.

The Control Unit operates on a line voltage of 110, 130, 220 or 240VAC, 60Hz.

Control Unit Technical Data:

Power Requirement: 120 or 240 VAC; 60Hz

Fuse: 1.6A, 220V (sil-bio) for 120VAC; 0.8A, 220V (sil-bio) for 120VAC

Magnetic Field Supply: 0-10 VDC; 0-5 VAC; maximum current 3A (not overload protected)

Phase Shifter: 0-90˚ Digital Frequency Display: 4 digits

ESR Adapter

If you are not using the Control Unit, the ESR Adapter can bs used to connect the probe Unit to the necessary power supply, frequency meter, and oscilloscope. See the section, Setup with the Basic ESR System, for details of the connections. See the Appendix if you would like details for building your own adapter.

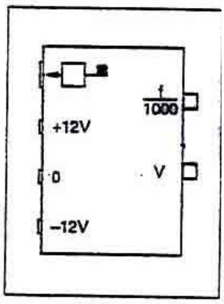


Figure 6 ESR Adapter

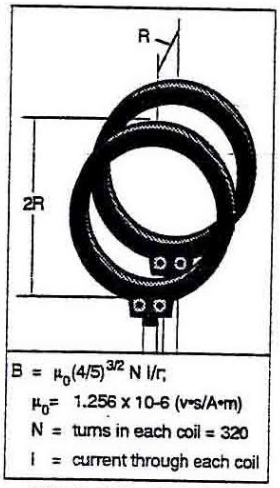


Figure 7 The Helmholtz Coils

Helmholtz Coils

The Helmholtz coils provide a highly uniform magnetic field in which to place the sample material for the ESR measurement. They should be connected in parallel and placed so that the separation between them is equal to the radius (see Fig. 7). When this is the case, the magnetic field in the central area between the two ciols is highly uniform, and is equal to the value shown in Fig. 7.

> Important: Current to each of the Helmholtz Coils should never exceed 3A. Therefore, if they are connected in parallel, the total current to them should never exceed 6A.

The Passive Resonant Circuit

The Passive Resonant Circuit can be used to demonstrate resonant energy absorption in a non-quantum system. It is just an LC circuit with an adjustable capacitance. It replaces the test sample and the Helmholtz coils in the ESR experiment.

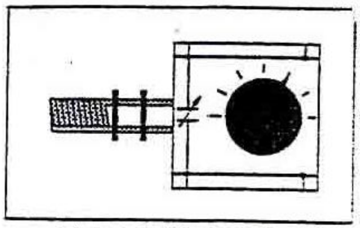


Figure 8 The Passive Resonant Circuit

Required Equipment

To perform ESR experiments with the Complete ESR System, you'll need the following additional equipment:

- A DC ammeter capable of measuring up to 3A
- A dual trace oscilloscope
- Connecting wires with banana plug connectors.

Setup

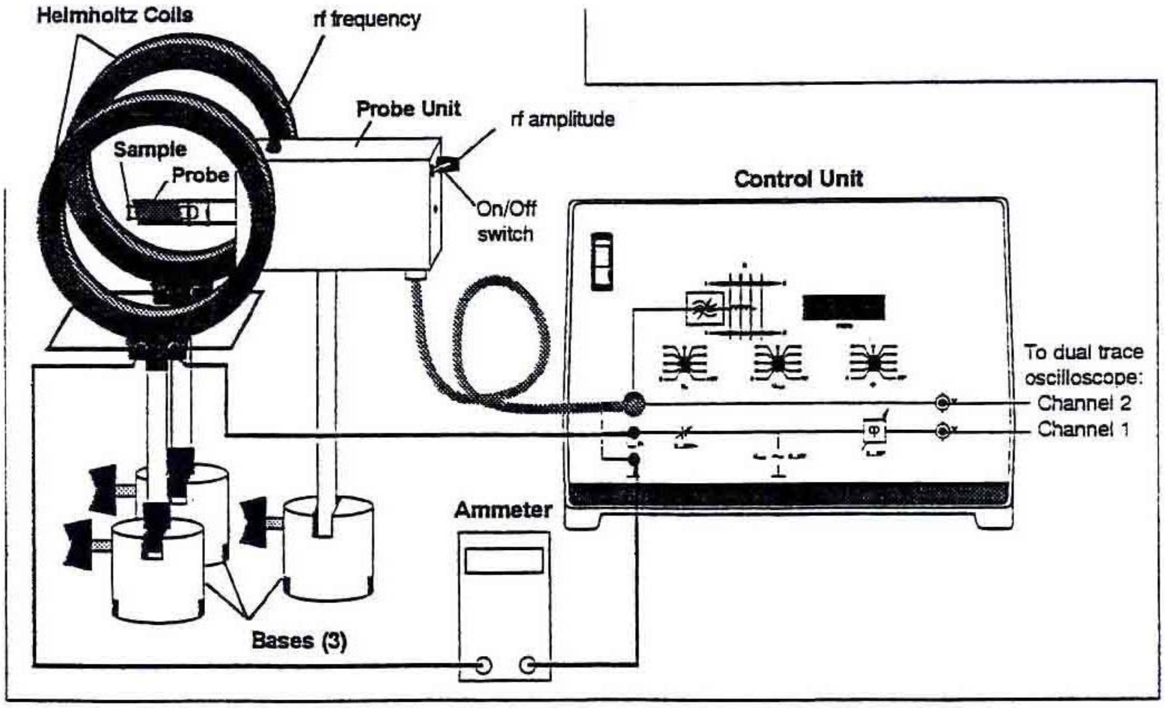


Figure 9 Setup using the Control Unit

1. Connect the Helmholtz coils to the Control Unit, as shown in Fig. 9. (The coils should be connected in parallel-terminal A to terminal A, and Z to Z.) Connect an ammeter in series, as shown, to monitor

the current to the coils.

> Important: the DC current supply in the Control Unit is not overload protected. Do not let the current to the Helmholtz coils exceed 3A.

2. Position the Helmholtz coils so that they are parallel and facing in the same direction, and their separation is equal to approximately one half their diameter.
3. Connect the X output of the Control Unit to channel 1 of a dual trace oscilloscope. Set the oscilloscope controls as follws:
   Sensitivity: 1 or 2 V/div
   Sweep Rate: 2 or 5 ms/div
   Coupling: DC
4. Set U_{mod} the center knob on the Control Unit, to zero, then slowly vary U_0, the left knob, from 0 to 10V and observe the trace on the oscilloscope. It should be a clean, straight line, showing that the DC component of the current to the Helmholtz coils is constant. (U_0 controls the DC current going to the Helmholtz coils.)

> Note: If the oscilloscope trace is not straight your Control Unit is probably not set for the proper line voltage.

5. Set U_0 at approximately midscale, then turn U_{mod} clockwise, to increase the AC component of the current to the Helmholtz coils. The trace on the oscilloscope should now show a smooth sine wave, as in Fig. 10, corresponding to an AC magnetic field that is superimposed upon a constant DC field.

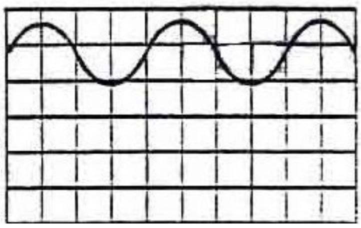


Fig 10 Oscilloscope – current to the Helmholtz coils

6. Connect the Y output of the Control Unit to channel 2 of the oscilloscope. Set the oscilloscope controls for channel 2 as follow:
   Sensitivity: 0.5 or 1 V/div
   Coupling: DC
7. Connect the Probe Unit to the Control Unit, as shown in Fig. 9.
8. Plug the medium sized rf Probe into the Probe Unit, and insert the sample of DPPH into the coil of the probe.
9. Turn on the Probe Unit by flipping the On/Off switch to the up (I) position. Then turn the Amplitude knob on the Probe Unit to a medium setting.
10. The Frequency meter on the Control Unit should now indicate the frequency of the rf oscillations. Adjust the Frequency control knob on the Probe Unit to produce an output of approximately 50MHz.
11. Set U_{mod} to about the 4th position above zero (at about the 11 o'clock position).
12. Increase U_0 from zero to a medium value, so the Helmholtz coil current is about 1.0 A. The oscilloscope traces should now look as in Fig. 11. Then channel 1 trace shows the current to the Helmholtz coils, which is proportional to the magnetic field produced by the coils. The channel 2 trace shows the envelope of the voltage across the rf oscillator, with the pulses showing the points of resonance absorption. If you see no resonance pulses, slowly vary U_{mod} or the rf frequency, until you do.

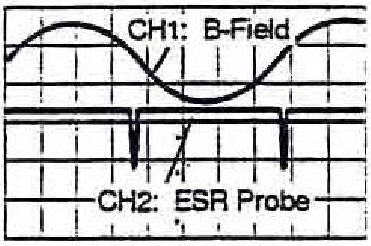


Fig. 11 the Oscilloscope Display

13. Your traces may not be symmetrical, as they are in Fig. 11. This is because of the inductance of the Helmholtz coils, which causes the current through them, and therefore the magnetic field they produce, to lag the voltage that drives them. You can compensate for this delay by adjusting φ, the Phase Shifter control knob, until the traces are symmetrical. When symmetrical, the traces properly reflect the relationship between the modulating magnetic field and the resonant pulses.

ESR in the X-Y Mode

14. ESR is often observed with the oscilloscope in the X-Y mode. For this mode of observation, connect the X and Y outputs of the Control Unit to the X and Y inputs of the oscilloscope, respectively. In this mode, the horizontal displacement of the trace indicates the magnitude of the magnetic field between the Helmholtz coils. The vertical displacement indicates the signal from the Prob Unit. As before, two resonance pulses can be observed since the magnetic field passes through the correct value twice each cycle. By adjusting the Phase Shifter, the two peaks can be brought into coincidence. The resulting trace will appear as in Fig. 12.

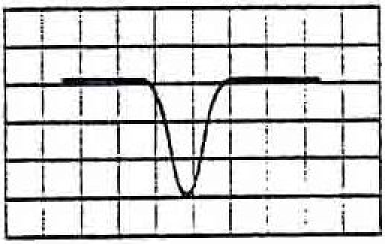


Fig. 12 the Oscilloscope Display

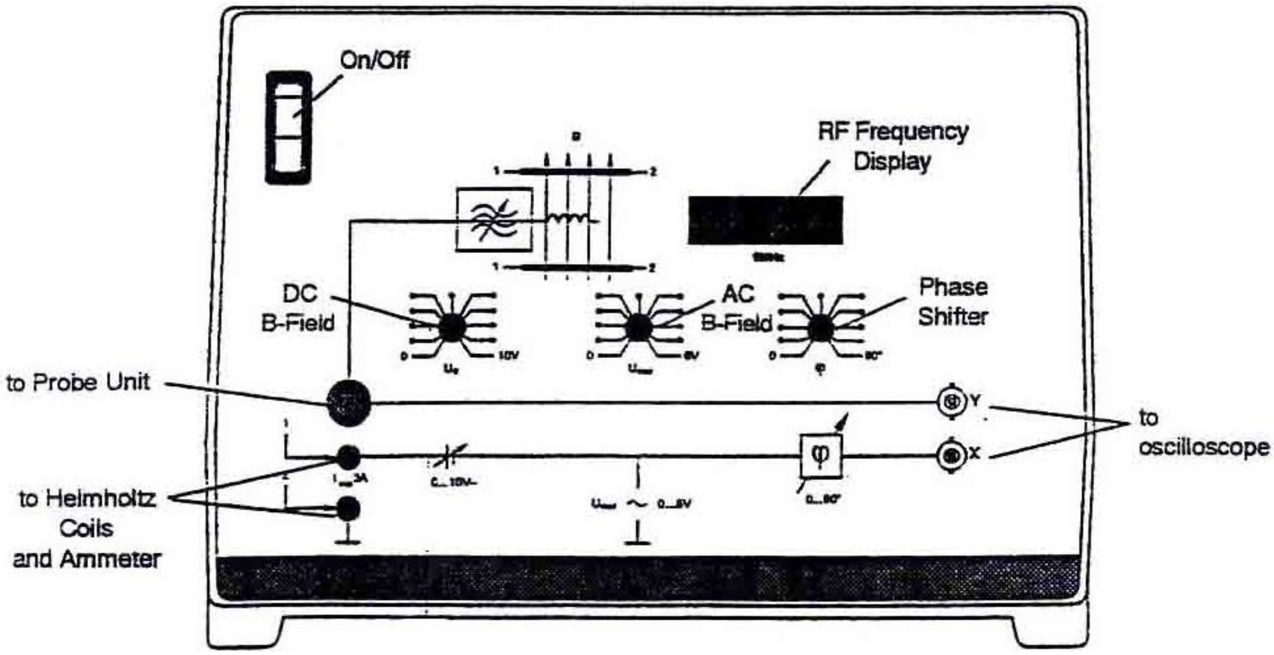


Fig. 13 Using the Control Unit

Making ESR Measurements

Whether you are using the Complete ESR System of the ESR Basic System, the same technique is used for making measurements.

1. Setup the apparatus as described in the appropriate section.
2. Adjust the rf frequency and the DC current to the Helmholtz coils until you locate the resonance pulses.
3. Adjust the phase shifter so that the resonance pulses are symmetric with respect to the oscilloscope trace that shows the current to the Helmholtz coils.
4. Refine the adjustment of the DC current until the resonance pulses occur when the AC component of the current to the Helmholtz coils is zero.

   To do this:

   a. Making sure that channel 1 of the oscilloscope (the trace showing the current to the Helmholtz coils) is in the AC coupled mode.

   b. Using the oscilloscope controls, ground the input to channel 1, zero the trace, and then unground the input.

   c. Adjust the DC current. As you do, notice how the resonance pulses move closer together or farther apart. Adjust the DC current, and the phase shifter if necessary, until the pulses occur just when the AC current to the Helmholtz coils is zero. (This is most accurately accomplished if you adjust the vertical position of the channel 2 trace so that the bottom of the resonance pulses are just at the zero level of the channel 1 trace.)

   With these adjustments, the oscilloscope traces should appear as in Figure 17. Everything is set for making ESR measurements. Since the current has been adjusted so that the resonance pulses occur when the AC current to the coils is zero, the current to the Helmholtz coils at resonance is just the DC value indicated by the ammeter. The resonant frequency is equal to the value on the Control Unit display (or the value indicated by your frequency meter multiplied by 1,000).

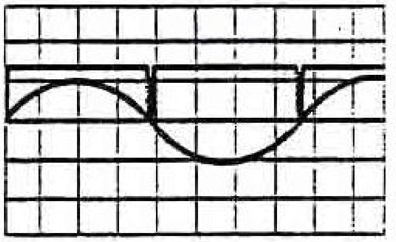


Fig. 17 Scope Display

5. Measure the rf frequency and the DC current. Then vary the current and find the new resonance frequency. Do this for several values of the frequency.
6. The magnitude of the magnetic field between the Helmholtz coils is directly proportional to the current supplied to the coils. You can determine the magnitude of the field using the following equation (easily derived from the Biot-Savart Law):

$$B = \mu_0 \left(\frac{4}{5}\right)^{3/2} NI / R$$

where:

$$\mu_0 \quad = \quad 1.256 \times 10^{-6} Vs/Am$$

N = number of turns in each coil

R = the radius of the Helmholtz coils (which is equal to their separation when they are properly arranged)

I = current passing through the coil

7. If you are using the test sample of DPPH, you can now determine the g-factor for the electron using the equation $hf = g_s \mu_B B$