Experiment 7

Electron Spin Resonance (ESR)

7.1 Introduction

Using ESR (Electron Spin Resonance, also known as Electron Paramagnetic Resonance) you will be measuring one of the best known quantities in all of physics, the famous g_s-factor of the electron. This will be achieved by looking for the "spin-flip" transition of a free (unpaired) electron exposed to a magnetic field.

7.1.1 ESR in Theory

The basic setup for ESR is shown in Fig. 7.1. A test sample is placed in a uniform magnetic field. The sample is also wrapped within a coil that is connected to an RF (radio frequency) oscillator. The smaller magnetic field induced in the coil by the oscillator is at right angles to the uniform magnetic field.

Consider, for the moment, a single electron within the test sample. The electron has an intrinsic (not related to any orbital motion!) magnetic dipole moment $\vec{\mu}_s$ that is related to its intrinsic angular momentum, or spin, by the vector equation:

$$\vec{\mu}_s = -g_s \mu_B \vec{S}/\hbar \tag{7.1}$$

where:

g_s = a constant characteristic of the electron, its intrinsic g-factor

μ_B = the Bohr magneton = $e\hbar/2m_e = 5.788 \times 10^{-9} eV/G$

$\vec{S}$ = the spin of the electron

$\hbar$ = Planck's constant/2π = 6.582×10^{-16} eV-sec, or $\hbar c = 197.3$ eV-nm.

The magnetic dipole moment of this electron interacts with the uniform magnetic field, $E = -\vec{\mu}_s \cdot \vec{B}$. Due to its quantum nature, the electron can orient its spin in one

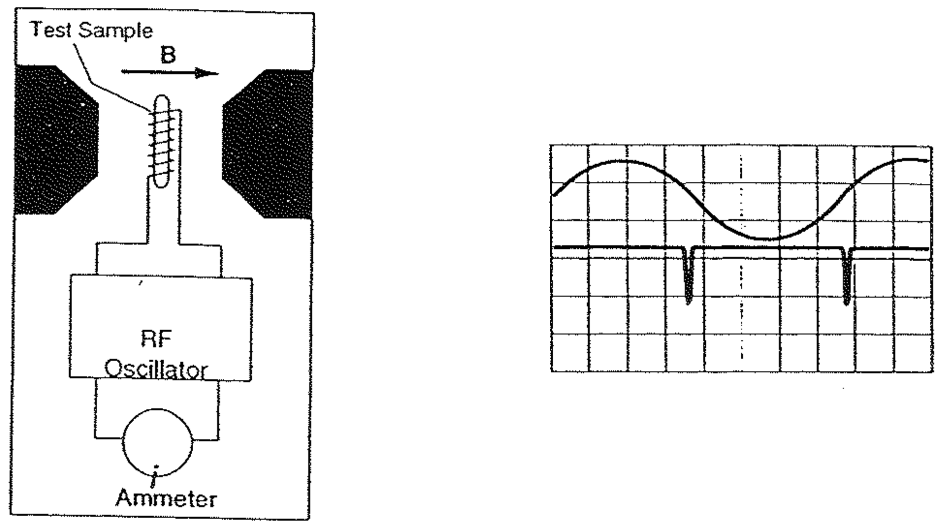


Figure 7.1: ESR diagram (left), scope display (right)

of only two ways ("space quantization"), spin up or spin down, with energies equal to $E_0 \pm g_s \mu_B B/2$; where E_0 is the energy of the electron before the magnetic field was applied. In the language of Quantum Mechanics, the energy degeneracy has been lifted by the B field, i.e. the energy level has been split. The energy difference between these two possible orientations is equal to $g_s \mu_B B$.

Resonance occurs when the RF oscillator is tuned to a frequency ν, such that the photon energy, $h\nu$, 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 of energy affects the permeability of the test sample, which affects 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:

$$h\nu = g_s \mu_B B \quad (2)$$

7.1.2 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 B field about some constant value. With our 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 B 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 B 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 Figure 7.1 (right) . The upper trace is a measure of the current going to the Helmholtz coils, which is proportional to the B field. The lower trace shows the envelope of the voltage across the RF oscillator, which dips sharply each time the B field passes through the resonance point.

7.1.3 ESR in Research

In actual ESR research the situation is significantly more complicated than is implied above. With multiple unpaired electrons, finite orbital angular momenta, and shared molecular orbitals the energy level splittings become quite complex. However, the details of the analysis of such systems provide significant insight into the inner structure of the molecules.

The test sample included with our apparatus, DPPH (Diphenyl-Picryl-Hydrazyl, see Fig. 7.2),
is a particularly simple substance for ESR measurements. It has a total orbital angular momentum of zero, and only one unpaired electron. Therefore, for a given value of the external B field, it has only a single resonant frequency. This makes it possible to investigate some of the basic ESR principles without (or before) getting into the more complex world of ESR analysis.

7.2 The ESR Apparatus

7.2.1 The Probe Unit

The ESR Probe Unit (see Fig. 7.3) is the heart of the ESR apparatus. It contains an RF oscillator with a built-in signal amplifier, and 1000:1 frequency divider. The frequency divider allows the RF frequency, which is in the MHz range, to be measured with a standard kHz frequency meter. The frequency and amplitude of the RF signal can be

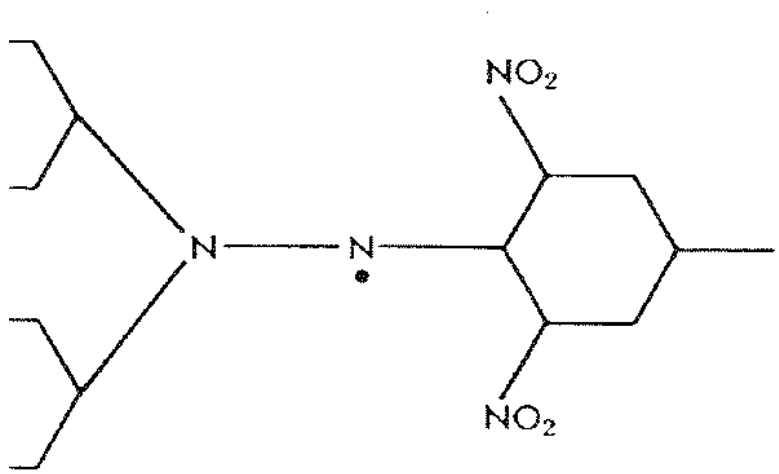
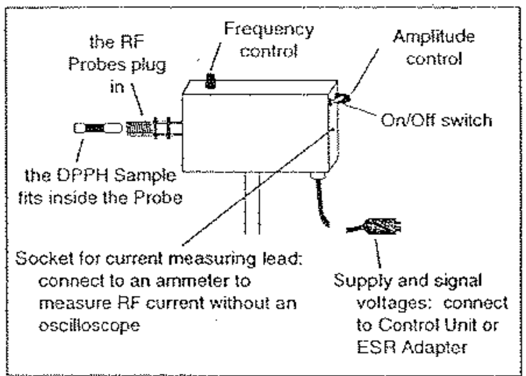


Figure 7.2: Chemical structure of DPPH, $(C_6H_5)_2N - NC_6H_2(NO_2)_3$.

controlled using the knobs shown in the Figure. The range of frequencies provided by the oscillator depends on which RF probe is being used (see Fig. 4). This is because the inductance of the probe determines, in part, the inductance of the oscillator circuit.

The Probe Unit is connected to the ESR Adapter (see Fig. 7.4), which in turn provides the connections to the necessary power supply, frequency meter, and oscilloscope. The Probe Unit requires $\pm 12\ V$, and the frequency output for a digital counter is a TTL signal.



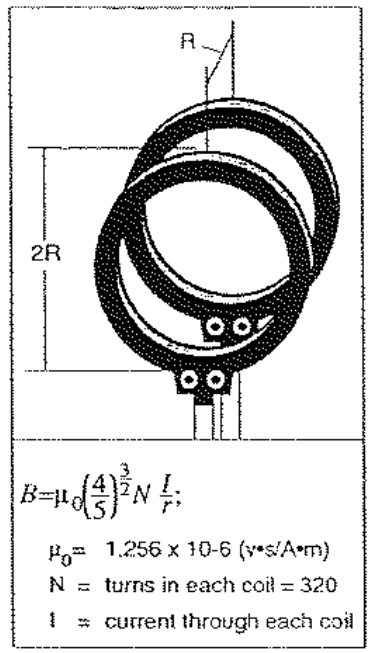


Figure 7.3: ESR probe unit (left) and Helmholtz coils (right)

7.2.2 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. 7.3). Their diameter is 13.5 cm, and it turns out that the correct separation is achieved by positioning them essentially flush against the ESR Probe Unit. Make sure the two coils are as parallel as possible. When all this is the case, the B field in the central region between the two coils is highly uniform, and is given in Fig. 7.3. You should be able to derive the expression for B yourself, starting with the Biot-Savart law. It can also be found in most introductory physics textbooks.

→ IMPORTANT: The current to *each* of the coils should never exceed 2A, i.e. the total current should never exceed 4A!

7.3 Basic ESR Setup

7.3.1 Required Equipment

In addition to the Probe Unit, the ESR Adapter, and the Helmholtz coils, you will need the following additional equipment: Frequency Meter, DC Power Supply (10V, 3-4A), Power supplies providing ±12 VDC to the ESR Adapter, a Variac plus a 6.3 V transformer to provide approx. 2 VAC, DC Ammeter, Oscilloscope, a 1000 μF capacitor, and our home-made phase shifter box.

Figures 7.4 and 7.5 show the setup and the required connections. Please be careful not to short out anything! The +12 V draws considerably more current than the -12 V, make sure your power supply doesn't limit the current too much.

7.3.2 Setup

Connect the Helmholtz coils in parallel (A to A, Z to Z, see Fig. 7.4) and position them appropriately.
Connect the power supplies, ammeter, oscilloscope, and circuit components to the Helmholtz coils as shown in Figures 7.4 and 7.5. Do not terminate the scope in 50 Ω.
Circuit Explanation:

The Helmholtz coils require a small AC current superimposed on a larger DC current. This is supplied by the Variac/small transformer and DC power supply, respectively. They are connected in parallel, with the 1000 μF capacitor isolating the AC from the DC to prevent wave distortion. Because of the inductance of the Helmholtz coils, the current in the coils is out of phase with the voltage that is observed on the oscilloscope. To correct this, a 100 $k\Omega$ variable resistor and a 0.1

μF capacitor are used to shift the phase of the voltage that is displayed on the oscilloscope, see Fig. 7.5. This allows the experimenter to adjust the phase between the oscilloscope traces, so that the AC current to the Helmholtz coils and the ESR resonance pulses appear symmetrical, which in reality they are.

Turn on the power supplies. Adjust the DC to approximately 1 A and the AC to about 2 V. Channel 1 of the oscilloscope will show the current to the Helmholtz coils, except for the phase shift caused by the induction of the coils. The trace should be a simple sine wave. If you switch channel 1 to DC coupling, it should show an AC voltage superimposed on a DC voltage.

Insert the medium-sized RF probe into the Probe Unit, and turn on the Probe Unit. Make sure the two green LEDs on the side of the ESR Adapter are on. Adjust the frequency to about 50 MHz (50 kHz on your frequency meter) and the amplitude to a

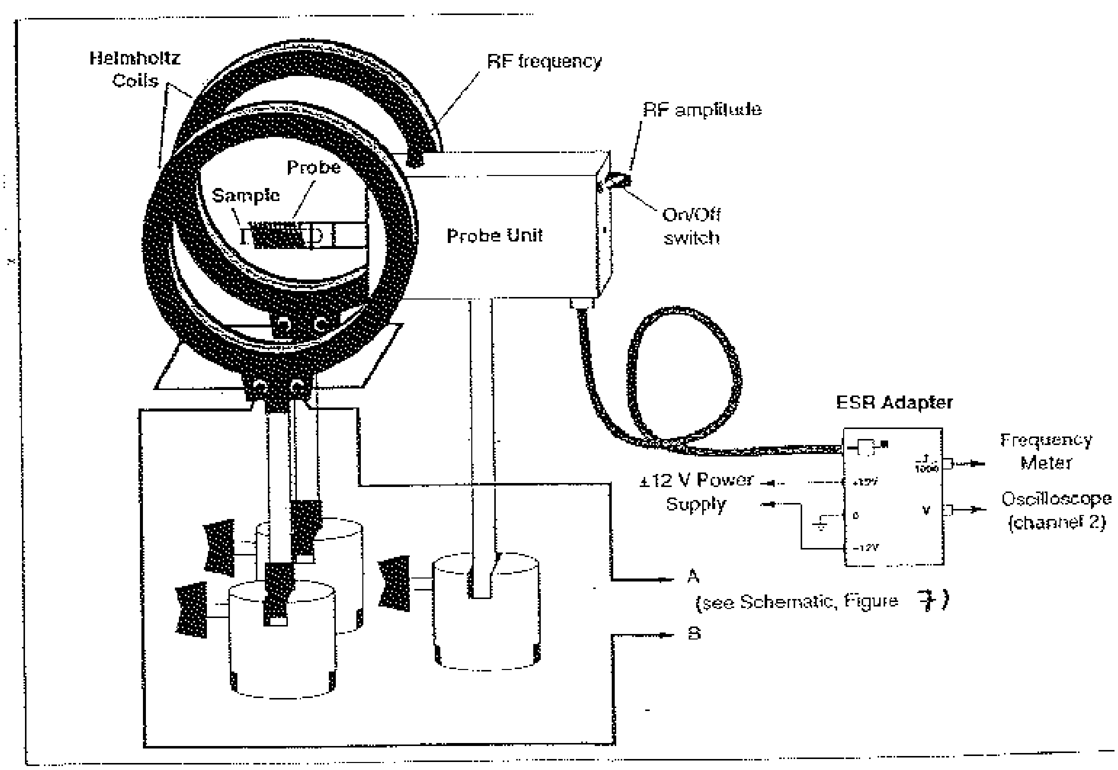


Figure 7.4: ESR setup

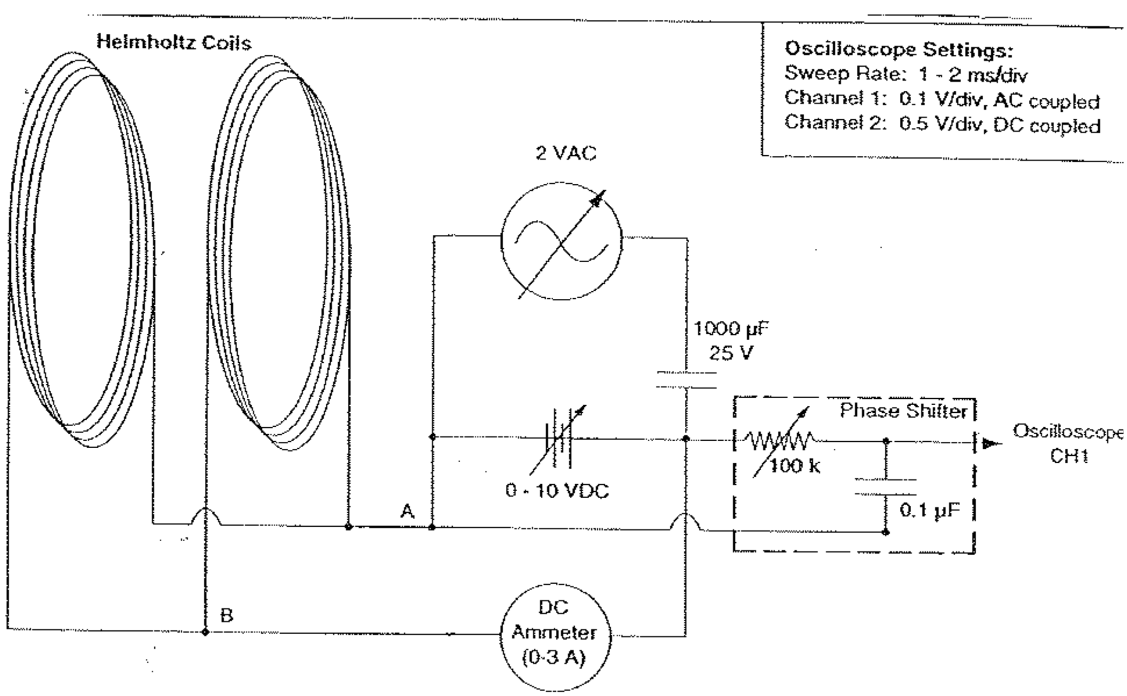


Figure 7.5: Schematic for Helmholtz coil connections

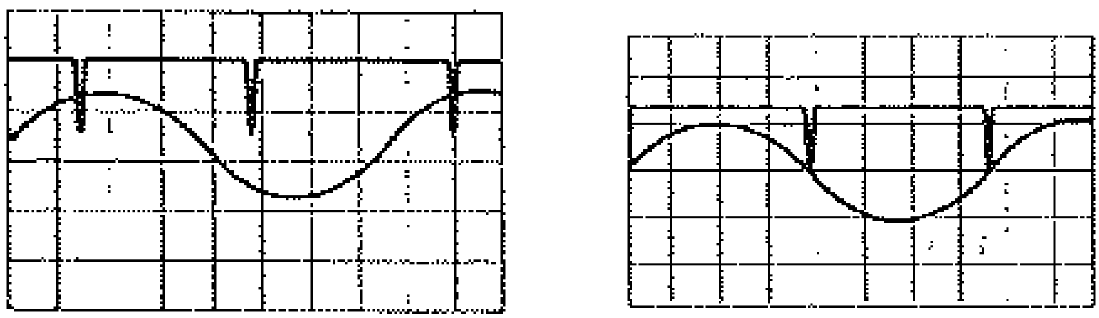


Figure 7.6: Scope displays

midrange value. Then insert the test sample into the RF probe and place the probe and sample in the center of the Helmholtz coils, with the Helmholtz coil axis perpendicular to the sample. The oscilloscope traces should now appear as in Figure 7.6. If you don't see the resonance pulses, slowly vary the DC current to the Helmholtz coils, or vary the RF frequency, until you do.
Note: do not limit the voltage on the coils d.c. power supply, keep this limit relatively high and only adjust the current to the coils (otherwise the a.c. sine wave may get distorted).

7.4 Taking ESR Data

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. 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. Make sure that channel 1 is AC coupled.
b. Using the scope 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 channel 2 so that the bottom of the resonance pulses are just at the zero level of channel 1.

After these adjustments, the scope traces should appear as in Fig. 7.6. 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.

Measure the RF frequency and the DC current. Then vary the current and find the new resonance frequency, or the other way around. For each of the three RF probes take at least five different data points, covering as large a frequency range as possible. In order of decreasing number of turns the three RF probes cover approximate frequency ranges of 13-30 MHz, 30-75 MHz, and 75-130 MHz, respectively.

7.5 Analysis

Calculate g_s for each data point, then mean, σ, σ_{mean} and compare with the accepted value. You should also determine g_s from a linear least squares fit. Comment on your results relative to the accepted value.

What systematic error do you think results from the fact that the ESR Probe Unit (metal!) protrudes into the region between the Helmholtz coils? Explain whether your results show evidence for such a systematic effect.

7.6 References

[1] Melissinos and Napolitano, Chapter 7.