Electron Spin Resonance (ESR)

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.

1.1 ESR in Theory

The basic setup for ESR 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 (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:

$$\vec{\mu}_s = -g_s \mu_B \vec{S}/\hbar \tag{1}$$

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.

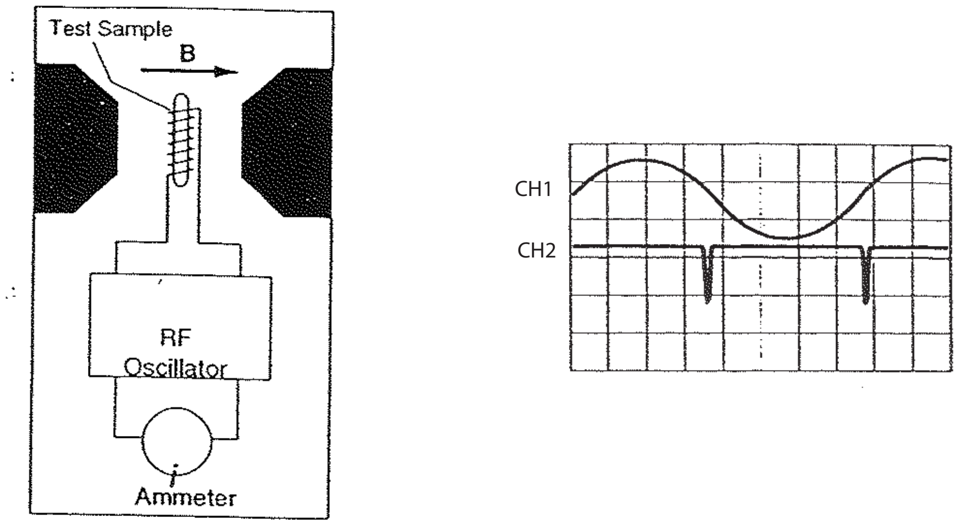

Figure 1: ESR diagram (left), scope display (right)

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 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 magnetic B field, i.e. the energy level has been split. The energy difference between these two possible orientations, and then between the two energy levels, is equal to $g_s \mu_B B$.

The electron can jump from one of these energy levels another by absorbing, or releasing, energy from an external RF field on resonance. Resonance occurs when the RF oscillator is tuned to a frequency ν such that the RF 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 "μ" of the (paramagnetic) test sample, which affects the inductance L of the coil and thereby the oscillations of the RF oscillator. The result is an observable change in the current flowing through the oscillator. As a result, detecting a change in current through the oscillator, coil, is signature that a spin transition has taken place.

The condition for resonance of the external RF field with the spin transition is:

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

1.2 ESR in Practice

In principle, to observe electron spin resonance for an electronic system with only two energy states in a constant magnetic field, it would be necessary to set the RF frequency with high accuracy. In practice, however, this difficulty can be solved by varying the magnitude of the magnetic B field about some constant value B_0 while setting the RF field in a constant value. With our apparatus, having a sinusoidal varying B field around a constant B_0 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 Eq.(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 1 (right). The upper trace ,CH1, is a measure of the current going to the Helmholtz coils, which is proportional to the B field. The lower trace, CH2, shows the envelope of the voltage across the RF oscillator, which is a signature to the modified permeability of the sample. The voltage across (current through) the oscillator dips sharply each time the B field passes through the resonance point.

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. 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.

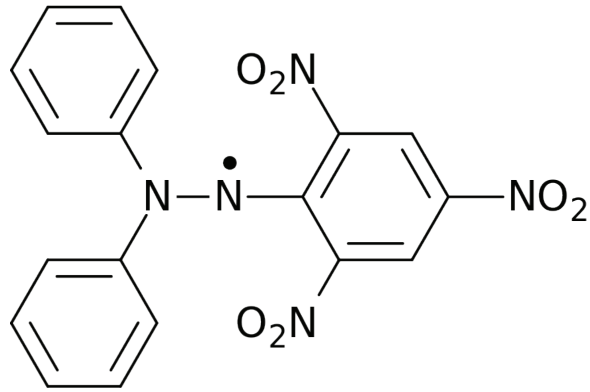

Figure 2: Chemical structure of the paramagnetic sample: DPPH, $(C_6H_5)_2N - NC_6H_2(NO_2)_3$.

2 The ESR Apparatus

2.1 The Probe Unit

The ESR Probe Unit (see Fig. 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 of the oscillator, 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 controlled using the knobs shown in the Figure. The oscillator can be used with different RF probes (coils), which allow to extend the range of frequencies that can be achieved for the RF photons (see Fig. 4). This is because the inductance L of each probe (coil) determines, in part, the inductance of the oscillator circuit.

The Probe Unit is connected to the ESR Adapter (see Fig. 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.

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. 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. 3.

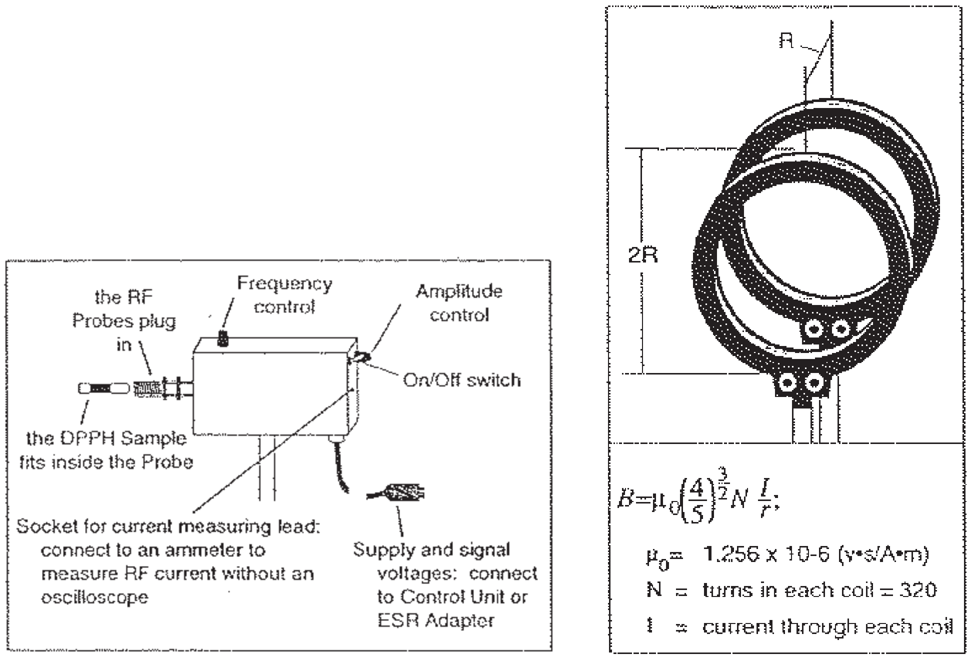

Figure 3: ESR probe unit (left) and Helmholtz coils (right)

• Starting with the Biot-Savart law, derive the expression for the magnetic field B provided by the pair of coils in the Helmholtz configuration.

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

3 Basic ESR Setup

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 4 and 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.

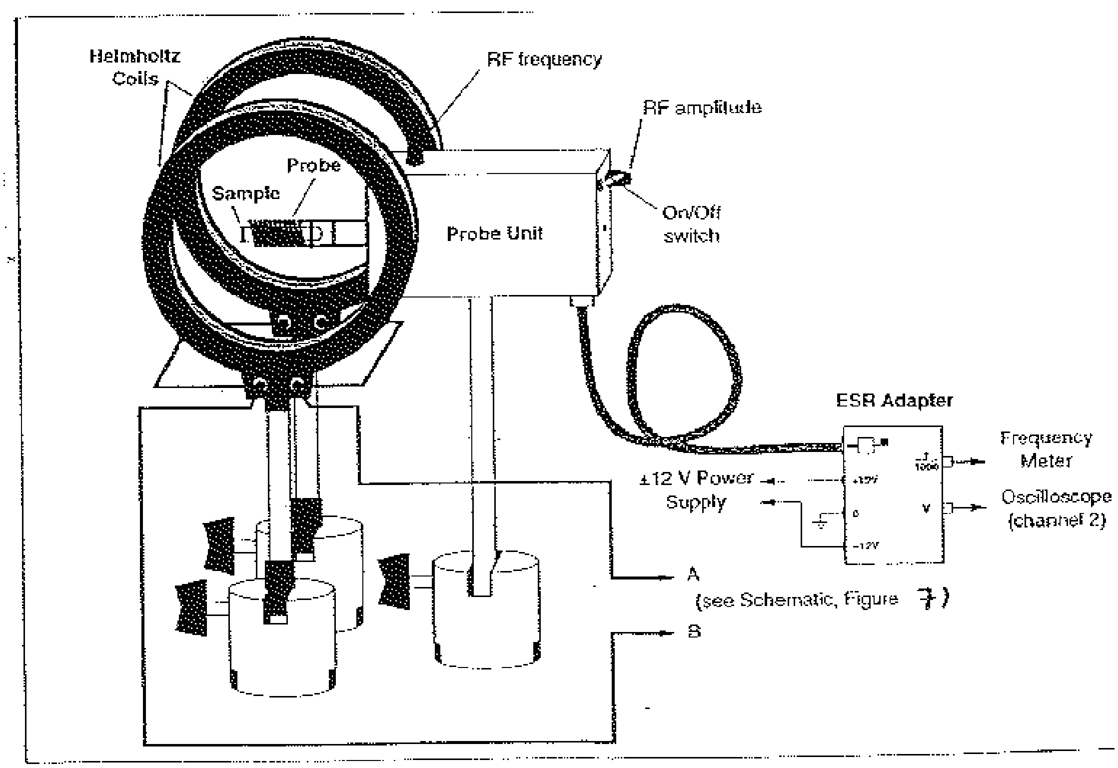

Figure 4: ESR setup

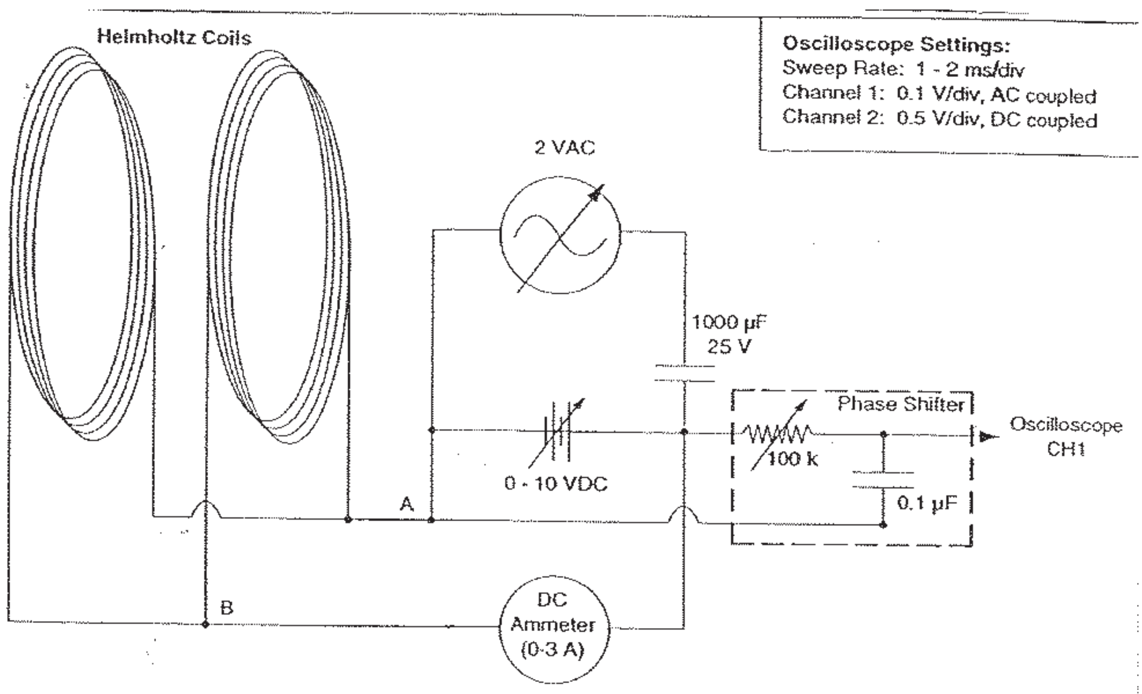

Figure 5: Schematic for Helmholtz coil connections

3.2 Setup

Connect the Helmholtz coils in parallel (A to A, Z to Z, see Fig. 4) and position them appropriately. Connect the power supplies, ammeter, oscilloscope, and circuit components to the Helmholtz coils as shown in Figures 4 and 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 (this is a polar capacitor. Make sure to connect the capacitor with the correct polarity.). 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. 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 signal (voltage deeps) 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 (CH1) of the oscilloscope will show a signal proportional to 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

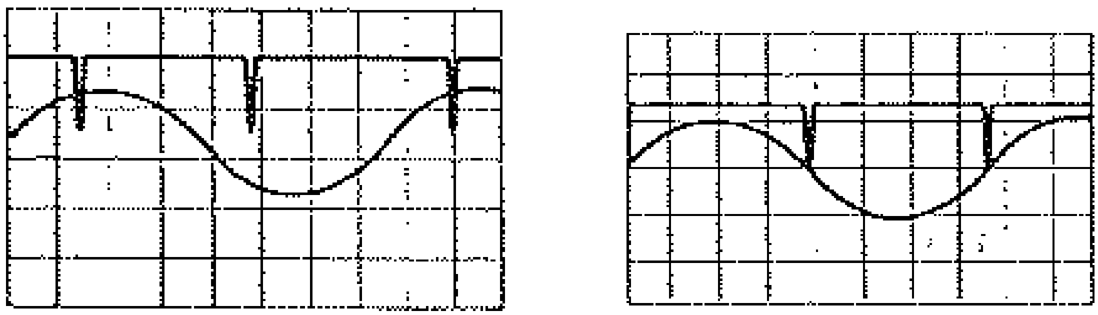

Figure 6: Scope displays

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 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 6. If you don't see the resonance signals, 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 DC. power supply, keep this limit relatively high and only adjust the current to the coils (otherwise the AC sine wave may get distorted).

4 Taking ESR Data

Adjust the phase shifter so that the resonance deeps lses 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 deep occur when the AC component of the current to the Helmholtz coils is zero. (i.e., the resonance pulses occur at the crossover points on thesine wave (CH1)). Phase misalignment is due to the inductance of the coils but this can becompensated by taking the following steps:

To do this:

a. Make sure that channel 1 (CH1) is AC coupled.

b. The baseline of the sign wave can be seen by switching the channel 1 coupling to GROUND.You can then move the baseline to a convenient place on the display and switch back to AC coupling.

c. Adjust the DC current. As you do, notice how the resonance signal move closer together or farther apart. Adjust the DC current, and the phase shifter if necessary, until the deep signal 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 CH2 so that the bottom of the resonance signal are just at the zero level of channel 1 CH1. This ensures that resonance is established at the point where AC magnetic field is zero.

After these adjustments, the scope traces should appear as in Fig. 6. Everything is set for making ESR measurements. Since the current has been adjusted so that the resonance signals 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 of the oscillator 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.

5 Analysis

• Calculate g_s for each data point, then mean, the uncertainty σ, and the error in the mean σ_{mean} and compare with the accepted value.

• As a second step, determine g_s from a linear least squares fit for data from each probe and the combined data. Comment on your results relative to the accepted value.

• Explain the physics of ESR.

• Explain how the experiment works.

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.

6 References

[1] Melissinos and Napolitano, Chapters 7.

[3] Data Reduction and Error Analysis for Physical Sciences, 3rd ed. Philip R. Bevington, D. Keith Robinson.