Electron Spin Resonance v2.0

Background. This experiment measures the dimensionless g-factor (g_s) of an unpaired electron using the technique of Electron Spin Resonance, also known as Electron Paramagnetic Resonance. This will be achieved by probing the spin-flip transition of a free (unpaired) electron exposed to a magnetic field.

Each electron has an angular momentum arising from orbital motion and spin. The former is classical and the latter is quantum mechanical. Because of spin, the magnetic moment of an electron is approximately twice that of a classical, elementary charged particle. The intrinsic or spin magnetic moment of an electron is given by the following vector equation:

$$\boldsymbol{\mu_s} = -g_s \mu_B \boldsymbol{S}/\hbar \tag{1}$$

where
$g_s \approx 2$ is an intrinsic constant of the electron
$\mu_B = e\hbar/2m_e = 5.788 \times 10^{-9}$ eV/G is the Bohr magnetron
$\boldsymbol{S}$ is the spin of the electron
$\hbar = h/2\pi = 6.582 \times 10^{-16}$ eV-sec is Planck's constant.

When an electron of energy E_0 interacts with a magnetic field B, it will exist in one of two new energy states: $E_0 \pm g_s\mu_B B/2$ corresponding to an energy difference $\Delta E = g_s\mu_B B$. The magnetic field acts to lift the two-state spin degeneracy of the electron. ΔE can be varied over a continuum, depending on the magnitude of B.

In an electron ensemble, this energy difference can be probed with an external electromagnetic wave. The energy of a coherent electromagnetic wave of frequency ν is also quantized: $h\nu = \hbar\omega$. When the photon energy equals the B-field splitting, i.e. when

$$h\nu = g_s\mu_B B \tag{2}$$

a resonance condition exists and photons will be *absorbed* by the material. At resonance, the permeability of the sample changes dramatically and can be detected. The photons used here are at radio frequencies (RF) on the order of MHz.

A test sample is placed in a uniform magnetic field B that is present between two Helmholtz coils. The probing photons at frequency ν are coupled into the sample in a direction perpendicular to B. Efficient coupling is accomplished by inserting the sample into a series of solenoid probes having different RF responses, depending on how they are wound. In this way, Equation (2) can be mapped out over a range of frequencies and magnetic fields.

In practical ESR experiments the situation is significantly more complicated than descrined by Equation (2). Multiple unpaired electrons, finite orbital angular momenta, and shared molecular orbitals make the energy splitting difficult to interpret. The test sample used here is Diphenyl-Picryl-Hydrazyl. It has zero total orbital angular momentum and only one unpaired electron. For a given value of the B-field, there is only one resonant frequency.

Experiment. The goal of the experiment is to identify the spin resonance frequency of DPPH as a function of magnetic field. The coupling of RF energy into the sample is very sensitive to its permeability. By monitoring the RF drive current, a distinct change (sharp drop) can be observed at the resonance point.

For an electron with only two energy states, it is difficult to identify the exact resonance condition. This is solved by slowly varying (at the AC line frequency of 60 Hz) the magnitude of the B-field about a constant value, i.e. the magnetic field is generated by an AC current with a DC offset. Absorption can be observed, but associating it with a value of B is still a problem because it is time-varying. The phase of the driving current is therefore adjusted to put the DC component exactly on resonance. When this is established, only the DC B-field contributes in Equation (2).

The Helmholtz coils of radius R are separated by a distance R. The on-axis magnetic field at the midway point between them is found from elementary physics:

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

where I is the current and $N = 320$ is the number of turns in each coil. When phase is correctly set as described in the following section, the magnetic field in Equation (2) is exclusively from the DC current.

The probe unit (Figure 2) contains an RF oscillator with a built-in signal amplifier, and 1000:1 frequency divider. The frequency divider produces TTL pulses and allows MHz frequency RF signals to be measured with a standard frequency counter.

There are 3 different solenoid plug-ins available. These probes cover the approximate frequency ranges: 13–30 MHz, 30–75 MHz, and 75–130 MHz, as the number of turns decreases. The RF oscillator frequency is determined in part by the inductance of these plug-ins.

Setup. Collect the following equipment:

- Pair of 13.5 cm diameter Helmholtz coils
- Probe module
- 3 RF probe plug-ins
- Test sample: DPPH (Diphenyl-Picryl-Hydrazil)
- Adapter module
- 2-channel oscilloscope
- Frequency counter
- DC power supply; 10V, 4A
- Split-mode ±12V DC power supply
- 6.3 VAC stepdown transformer
- Variac
- Phase-shifter box

- Cord with 1000 μF blocking capacitor
- 2 digital multi-meters
- BNC cables and hookup wires

Construct the experimental setup shown in Figures 1 and 2. Connect the Helmholtz coils in parallel (terminals A to A and Z to Z), position them as parallel as possible, and separate them by their radius where $2R = 13.5$ cm. The separation distance R is very close to the physical width of the probe box that is placed between them.

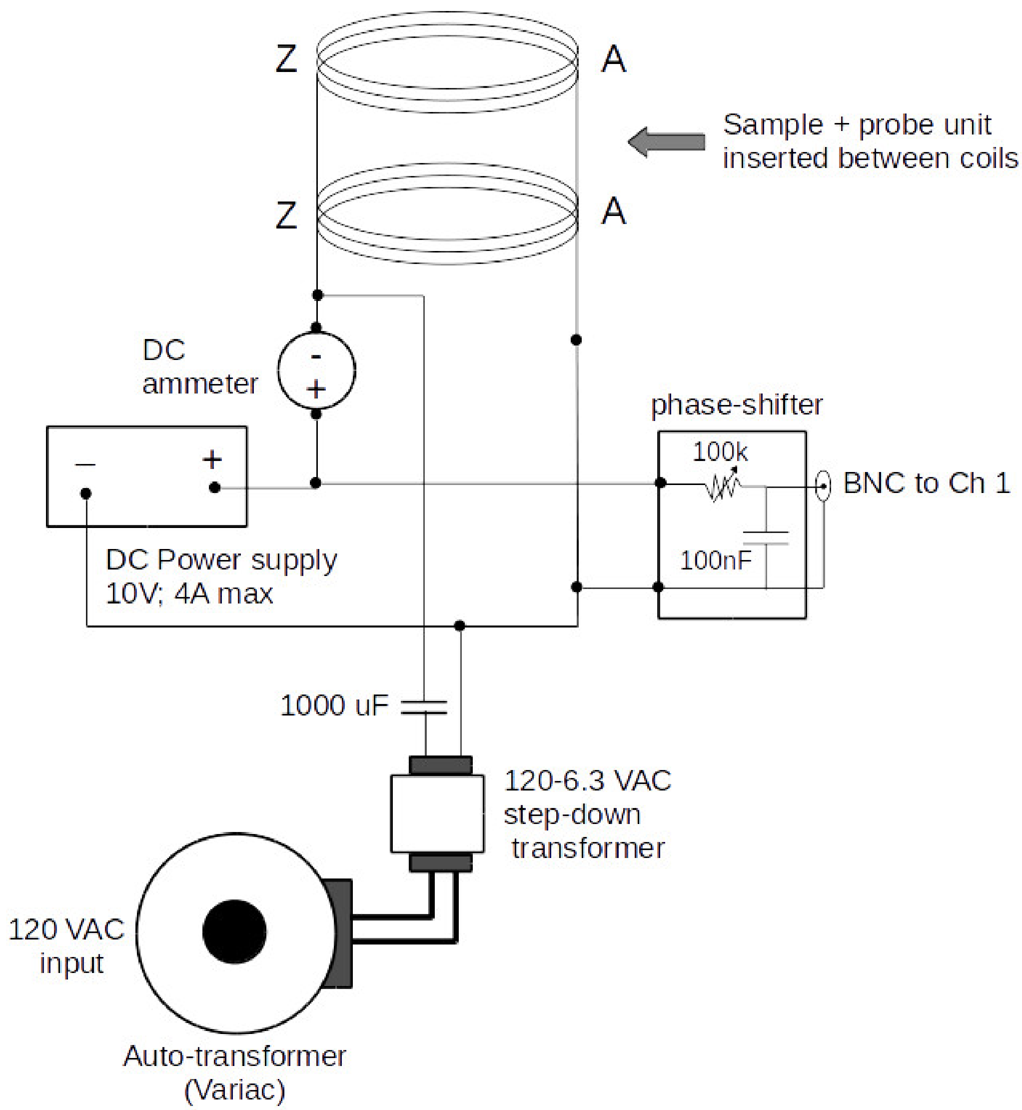

Figure 1: Connect the Helmholtz coils ($2R = 13.5$ cm) in parallel and separate them by a distance R. The probe unit (see Figure 2) should fit snugly between the two coils. Set the AC voltage on the secondary winding of the step-down transformer to ~ 2 Vrms. Do not exceed 2A DC into the individual coils, or 4A total.

The current through the coils has both DC and AC components, supplied by two separate sources.

The DC current is monitored by a digital multi-meter inserted in series. Because the coils are connected in parallel, the current is divided between them. Note: Different terminals on the meter must be connected depending on whether it is being used as an ammeter or a voltmeter, ohm-meter, etc. The 1000 μF capacitor blocks DC current from getting to the transformer. Recall that the impedance of a capacitor is $Z = 1/j\omega C$, which makes it appear as an open circuit to DC ($\omega = 0$). A large capacitance allows the AC voltage at $\omega/2\pi = 60$ Hz to pass through.

Use an auto-transformer (often called a Variac) on the primary side of the step-down transformer to set the secondary AC voltage at $\sim$ 2V rms. Measure this with the second multimeter. The adapter unit requires $\pm$12V DC bias voltage that must be correctly referenced to ground potential. Use the second multimeter to check voltages. Follow the wiring diagram shown in Figure 2. When making BNC connections to the oscilloscope, use the default 1 MΩ input impedance, i.e. do not use 50 Ω terminators.

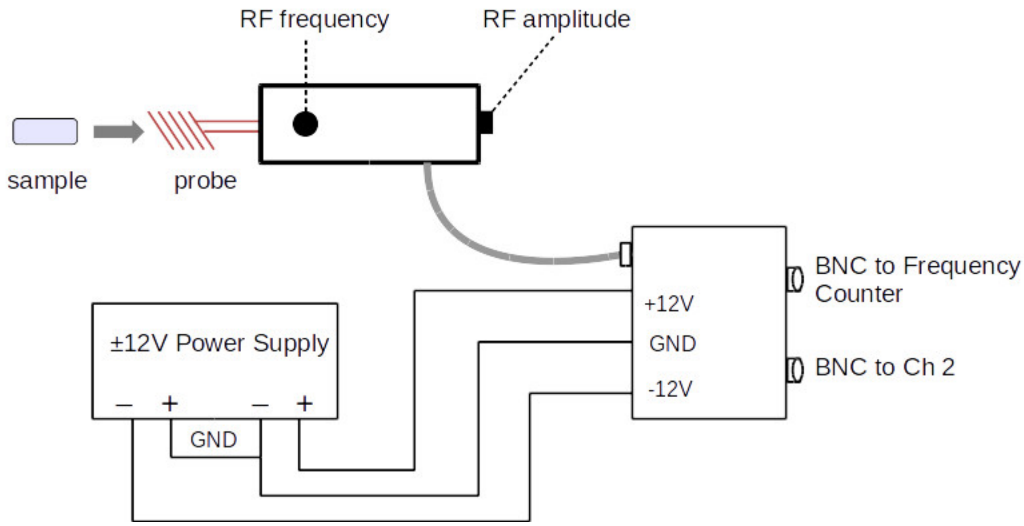

Figure 2: Connections of the probe unit, adapter, and split-mode power supply. The sample is inserted into one of three different probe solenoids. Drawing not to scale.

Now turn on the DC power supply to the Helmholtz coils and set the current to about 1A. You should see the sinusoidal current waveform on Channel 1 of the oscilloscope with and without the DC offset current, depending on the input coupling of Channel 1. Set the scope to trigger on Channel 1. Never exceed 2A in the coils, or 4A total as read on the ammeter.

Connect a solenoid sample holder to the probe unit; the middle-size unit is a good place to start. Turn on the probe unit and confirm the two green LEDs on the adapter are illuminated. Set the RF amplitude to about mid-range (not critical) and the frequency to 50 MHz; this is read as 50 kHz on the counter.

The goal is to get a scope display resembling Figure 3. The resonance spikes are made visible by changing the RF frequency and DC current. The amplitude of the spikes may be slightly adjusted by re-positioning the probe in B-field. It is very important to center the spikes exactly at the crossover points on the sine wave. Phase misalignment is due to the inductance of the coils, but this can be compensated with the phase shifter box.

The baseline of the sine wave can be seen by switching the Channel 1 input coupling to GROUND.

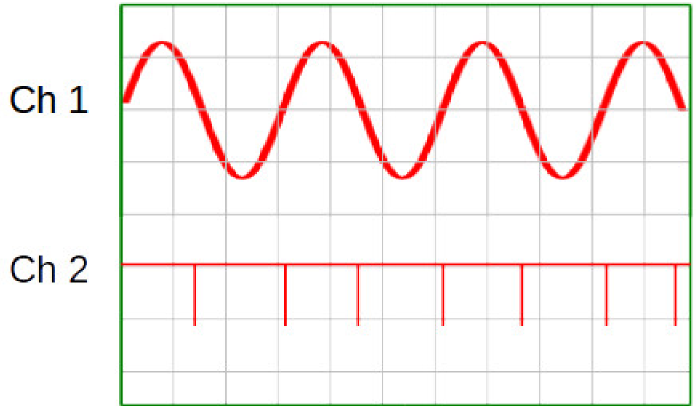

Figure 3: Representative oscilloscope waveforms. The top trace shows the current in the Helmholtz coils. The lower trace is the RF probe signal; distinct spikes identify resonance. DC current, RF frequency, and phase should be carefully adjusted to put the resonance points exactly at the crossovers of the sine wave.

You can then move the baseline to a convenient place on the display and switch back to AC coupling. Adjust until the resonance spikes are perfectly periodic and positioned at the sine wave crossovers. This ensures that resonance is established at the point where the AC magnetic field is zero.

Record the DC current and RF frequency for a variety of resonance conditions. The three available probes allow the frequency range to be mapped in the range 13–130 MHz.

Analysis. You will have a table of data showing the current and frequency associated with many resonance conditions. Equations (2) and (3) allow the extraction of g_s at each entry in the table. Use care with dimensional analysis and units. Calculate the mean and standard deviation of the data set. Since the equations describe a linear relationship, plot your data in any convenient form (eg. ν vs B). Obtain a slope and its uncertainty using least-square-fit. Compare your experimental results for g_s with the accepted value.

Insertion of the metal probe box between the Helmholtz coils can introduce a systematic error. Does your data provide evidence for such an error?