

Study of Electron Spin Resonance

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October 17, 2022

1 Abstract

When the molecules of a solid are paramagnetic and have unpaired electrons then splitting can be induced between spin states by applying a magnetic field and then the transition of electrons between layers by supplying electromagnetic energy (usually in the microwave range of frequencies). The resulting absorption spectra are described as electron spin resonance (ESR).

2 Apparatus

- ESR setup
- Paramagnetic sample, Diphenyl Picryl Hydrazyl (DPPH)
- Microwave generator
- Helmholtz coil
- Oscilloscope
- Power supply

3 Theory

3.1 Electron Spin Resonance

Electron Spin Resonance can be understood from classical concepts. A particle having a magnetic moment μ is placed in a uniform magnetic field of intensity H_0 , and the moment precesses about the field at a frequency called Larmor frequency is given by:

$$\omega_0 = \frac{geH_0}{2mc}$$

where g is the Lande g -factor ($g = 1$ for pure orbital momentum and $g = 2$ for a free electron spin). In the case of an ion in a crystal, the behaviour is modified by the environment and the g factor may differ from the Lande g -factor. This effective g -factor is known as the spectroscopic splitting factor.

If now an additional weak magnetic field H_1 oriented in the x - y plane and rotating about the z axis (in the same direction as the "Larmor processing") with an angular frequency ω_1 is introduced, there is a change in energy of the system.

1. For $\omega_1 \neq \omega_0$, the angle between the field H_1 and the magnetic moment μ will continuously change. Thus their average interaction will be zero.
2. For $\omega_1 = \omega_0$, the angle between the field H_1 and the magnetic moment μ will be constant. Thus their net interaction is effective.

This implies a change in the potential energy of the particle in the magnetic field. The change in θ is the classical analogy to a transition between sublevels with different m .

Now considering the quantum picture, suppose the intrinsic angular momentum of the electron S couples with the orbital angular momentum of electron L to give a resultant J . We know, that $J + 1$ magnetic sublevels are labelled by the magnetic field H_0 by equal energy difference. Now if we introduce a perturbation of the alternating magnetic field H_1 with a frequency corresponding to the energy difference between the levels ($h\nu$), then there will be induced transitions between neighbouring sublevels according to the selection rules $\Delta m = \pm 1$ for magnetic dipolar radiation. Therefore, the condition for resonance is

$$\Delta D = g\mu_0 H_0 = h\nu_0 = h\nu_1$$

Where ν_1 is the resonance frequency in cycles per second.

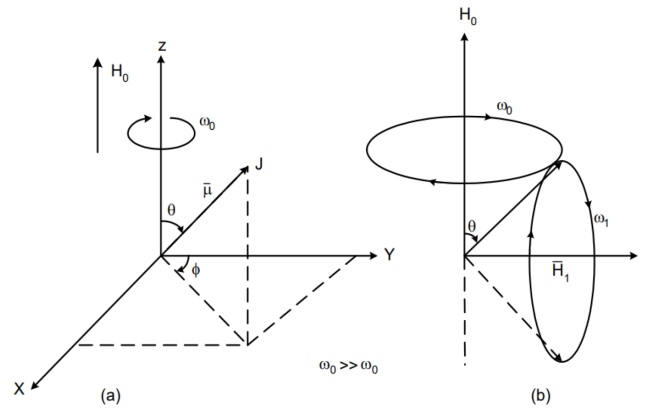


Figure 1: (a) Precession of a magnetic moment μ_1 when placed in a magnetic field H_0 where in (b) a weak field H_1 is applied.

3.2 Experimental Setup

The experimental setup consists of four parts:

- **Basic Circuit:** It consists of a critically adjusted (marginal) radio frequency oscillator having a frequency range of approximately 12-16 MHz, which is required for the decrease in the amplitude of oscillation to an appreciable extent for the slightest increase in its load. There is a Helmholtz coil for the production of a magnetic field in and around the DPPH sample kept inside the tank coil. At resonance, an amplitude-modulated carrier is produced which is then detected using a diode detector and amplified by a chain of three low-noise, high-gain audio-frequency amplifiers (with sensitivity controls) of excellent stability.

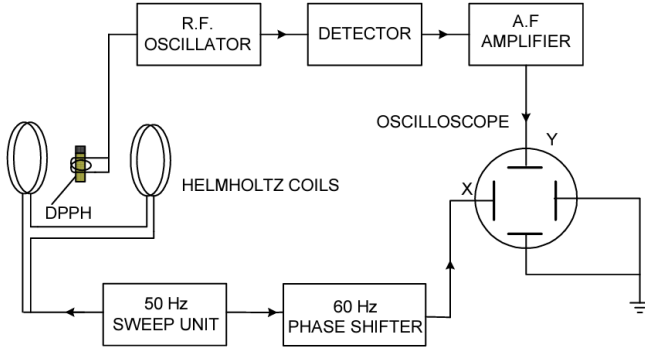


Figure 2: Block diagram of ESR Circuit Setup

- **Phase Shifter:** To make it possible to use an ordinary displaying type oscilloscope, instead of a measuring oscilloscope which preserves the phase between X and plate signals, a phase shifter is provided. This can compensate for the phase difference which is introduced in the amplification stage of the ordinary oscilloscope as shown in Figure 3.

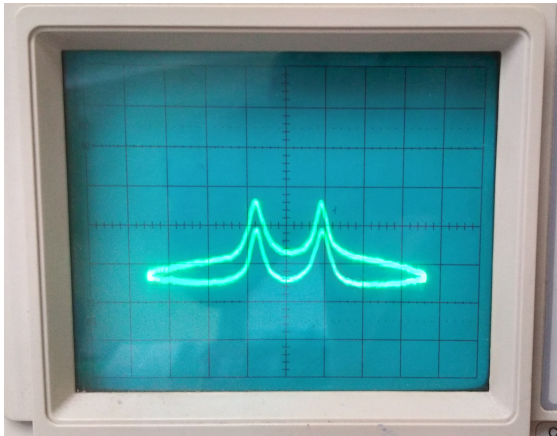


Figure 3: Oscilloscope

- **50Hz Sweep Unit:** For modulation with a low-frequency magnetic field, a 50 Hz current flows through the Helmholtz coils.

- **Power Supplies:** DC Power supply for ESR circuit and the Helmholtz coils power supply consisting of a step-down transformer (220V to 35V AC).
- **Helmholtz Coil** of radius 7.5cm and 500 turns.

3.3 Origin of Four Peaks

Observing the output in the oscilloscope, peaks can be found which are in fact absorption dips, because the sample absorbs power from the induction coil. The reason for getting peaks is due to an odd number of amplifying stages in the circuitry. The spin precesses with Larmor frequency ω_0 vary in magnitude and direction due to variation of magnetic field H_0 which is due to an alternating current in the Helmholtz coils. Now if the radio frequency field, $\omega_1 \approx \omega_0$ then resonance occurs. If the X plate signal (50Hz) and Y plate signal (ESR output) are in phase the I and II peaks and III and IV peaks will coincide. The coincidence of peaks on the x-scale needs to be calibrated for magnetic field measurements. The coincidence ensures that the magnetic field is zero at the centre and has peak values at the two ends. A complete merger of the peaks on the y-scale may not occur due to many reasons such as 50Hz pickups, ripples in the power supply etc.

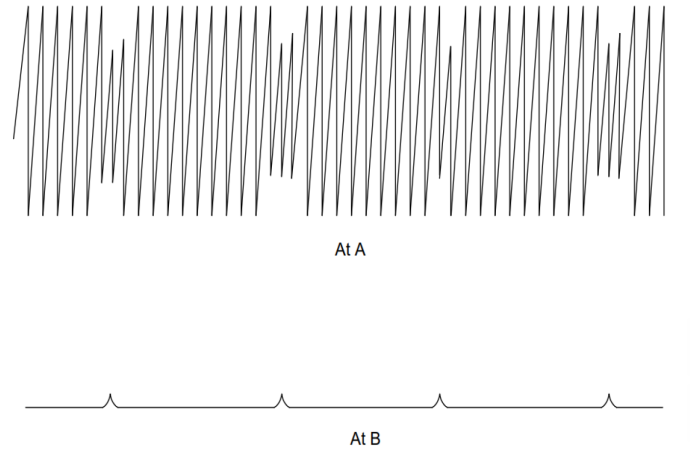


Figure 4: Occurrence of Peaks

Therefore g can be calculated by the following equation:

$$g = \frac{h\nu_0}{\mu_0 H_0}$$

here h ($= 6.625 \times 10^{-27} \text{ erg sec}$) is the Plack's constant and μ_0 ($= 0.927 \times 10^{-20} \text{ erg/Gauss}$) is the permeability of free space.

$$H_0 = H_{pp} \frac{Q}{P}$$

Where H_{pp} is the peak-to-peak value of the magnetic field, Q is half the distance between the two peaks and P is the maximum X deflection. A magnetic field defined for RMS field H as:

$$H_{pp} = 2\sqrt{2}H$$

H, the RMS magnetic field between the Helmholtz coils is given by:

$$H = \frac{32\pi n I}{10a\sqrt{125}}$$

Putting appropriate values in the above equations, we get:

$$g = c \times \frac{\nu_0}{IQ} = 3.375 \times 10^{-8} \times \frac{\nu_0}{m} \quad (1)$$

where $c = \frac{5a\sqrt{125}}{32\pi n\sqrt{2}} \times \frac{Ph}{\mu_0} = 3.375 \times 10^{-8}$ and m is the slope of Q vs $\frac{1}{I}$ graph.

4 Observations and Calculations

Least Count of the Oscilloscope Reading (for measuring Q and P) is 0.2 cm. P (=maximum X deflection) = 7.8cm.

Frequency (ν)(MHz)	I (mA)	2Q (mm)	$1/I$ (A^{-1})	Q (cm)
13.42	98	46	10.204	2.3
	125	36	8.000	1.8
	152	28	6.579	1.4
	178	24	5.618	1.2
	203	22	4.926	1.1
	228	18	4.386	0.9
	255	16	3.922	0.8
	279	16	3.584	0.8
14.34	301	14	3.322	0.7
	96	50	10.417	2.5
	123	38	8.130	1.9
	150	30	6.667	1.5
	176	26	5.682	1.3
	201	22	4.975	1.1
	226	20	4.425	1
	252	18	3.968	0.9
15.44	276	18	3.623	0.9
	301	16	3.322	0.8
	96	52	10.417	2.6
	123	42	8.130	2.1
	150	32	6.667	1.6
	176	28	5.682	1.4
	203	24	4.926	1.2
	228	22	4.386	1.1
15.44	254	20	3.937	1
	279	18	3.584	0.9
	303	16	3.300	0.8

Table 1: Observation Table

From Table 1 we can see that:

- For $\nu_0 = 13.42MHz$ the value of slope (m) = $IQ = 0.233$.

$$g = c \times \frac{13.42 \times 10^6}{0.233} = 1.944$$

- For $\nu_0 = 14.34MHz$ the value of slope (m) = $IQ = 0.239$.

$$g = c \times \frac{14.34 \times 10^6}{0.239} = 2.025$$

- For $\nu_0 = 15.44MHz$ the value of slope (m) = $IQ = 0.239$.

$$g = c \times \frac{15.44 \times 10^6}{0.253} = 2.060$$

$$\text{So, } g_{av} = 2.0098$$

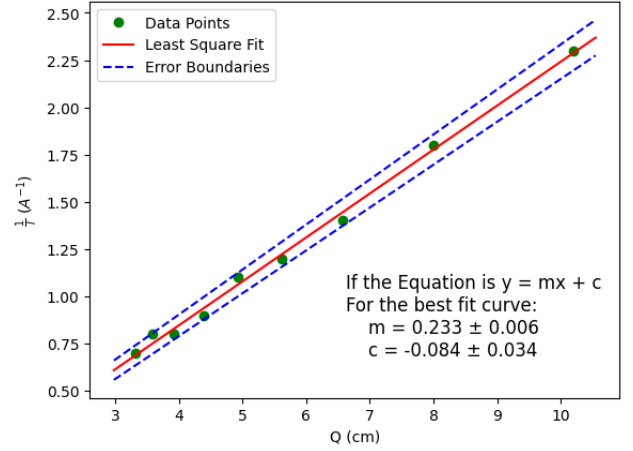


Figure 5: Q vs. $1/I$ for $\nu = 13.42MHz$

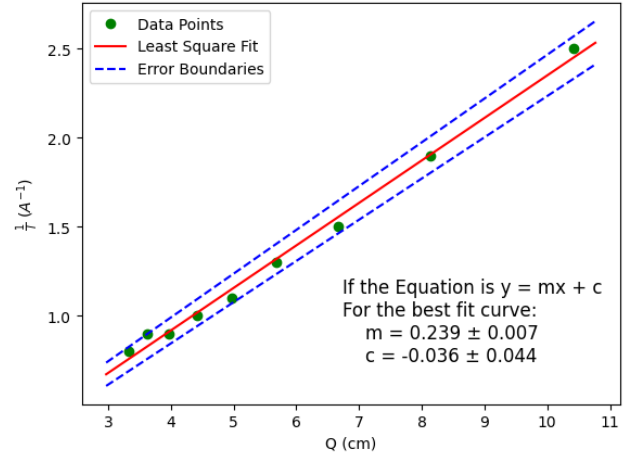


Figure 6: Q vs. $1/I$ for $\nu = 14.34MHz$

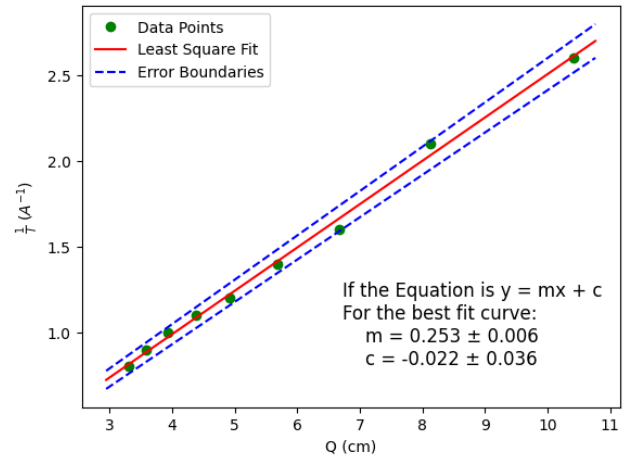


Figure 7: Q vs. $1/I$ for $\nu = 15.44MHz$

5 Error Analysis

$$\frac{\Delta g}{g} = \frac{\Delta P}{P^2} + \frac{\Delta \nu_0}{\nu_0^2} - \frac{\Delta m}{m}$$

$$\therefore \Delta g_{\nu=13.42MHz} = -0.049$$

$$\therefore \Delta g_{\nu=14.34MHz} = -0.058$$

$$\therefore \Delta g_{\nu=15.44MHz} = -0.048$$

$$\therefore \Delta g_{av} = -0.052$$

$$g = 2.0098 \mp 0.052$$

6 Conclusions

Compared to the literature value ($g=2$), the relative error in the value of g is 0.5%.

6.1 Sources of Error

- Low precision due to large least count value of the oscilloscope. It can easily be reduced to 0.1cm by putting more graduations on both the x and y scales.
- Oscilloscope line is thick; leads to ambiguity while taking readings.
- Flowing of large currents through the helmholtz coil may heat it up, changing the resistance and hence the the value of the magnetic field.
- Incomplete merger of the peaks on y-scale due to many reasons such as 50Hz pick-ups, ripples in the power supply, noise, etc. However since measurement is made in the X scale only, its effect is minimal

References

[SPS, 2022] SPS (2022). Lab manual. *Website*.
https://www.niser.ac.in/sps/sites/default/files/basic_page/ESR_manual.pdf.