Study of Electron Spin Resonance Using DPPH

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Electron Spin Resonance (ESR) was observed in this experiment by subjecting a sample to an alternating magnetic field while applying an RF signal. The resonance conditions were analyzed using an oscilloscope to calculate the g-factor. This measurement offers valuable information about the electronic and magnetic properties of the sample.

I. OBJECTIVE

Study Electron Spin Resonance uding DPPH and calculate the Landé g-factor.

II. THEORY

Electron Spin Resonance (ESR) is a spectroscopic method employed to identify unpaired electrons in substances such as free radicals or transition metals. By applying a magnetic field and electromagnetic radiation (in the microwave or radio wave range), ESR measures transitions between electron spin states, providing insights into the local electronic and magnetic environment. ESR is widely utilized in chemistry, physics, biology, and materials science for investigating molecular structure, magnetic properties, and defects in materials.

The fundamentals of elementary magnetic resonance may be understood in terms of simple classical concepts. When a magnetic moment is placed in external magnetic field it experiences a torque Then the moment μ precess around magnetic field H_0 with and angular Lamor frequency given by,

$$\omega_0 = g\left(\frac{e}{2mc}\right)H_0 \tag{1}$$

where g is Lande's g-factor ($g = 1$ for pure orbital momentum and $g = 2$ for a free electron spin). For the case of anion in a crystal, the behaviour is modified by the environment and the g- factor may differ from the Lande's g-factor. This effective g-factor is known as the spectroscopic splitting factor. We now introduce an additional weak magnetic field that lies in the xy-plane and rotates around the z-axis in the same direction as the Larmor precession, with an angular frequency ω_1. If ω_1 differs from ω_0, the angle between the field H_1 and the magnetic moment μ will continuously change, causing their interaction to average out to zero. However, if $\omega_1 = \omega_0$, the angle between μ and H_1 remains constant, resulting in an effective net interaction.

When viewed in a reference frame rotating around the z-axis with angular velocity ω_0, the spin appears to make an angle $\phi = 90° - \theta$ with H_1, and as a result, begins to precess (in the rotating frame) around H_1. This behavior

is referred to as *nutation* leading to a change in the angle θ, which implies a change in the particle's potential energy in the magnetic field. The change in θ is the classical analogy of a transition between sublevels with different magnetic quantum numbers m. Such transitions can only occur if the rotating field's angular frequency $\omega_1 = \omega_0$.
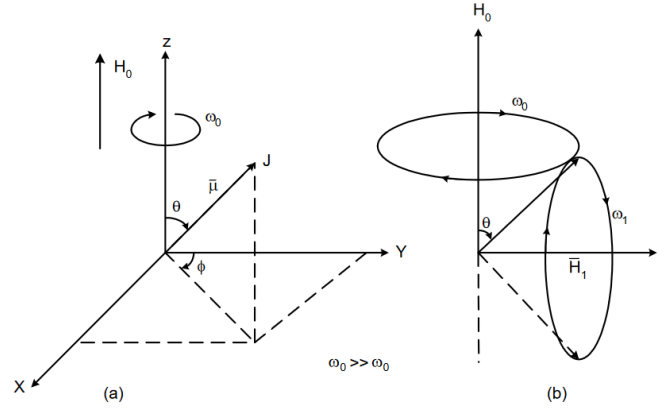

FIG. 1: Precession of magnetic moment μ when placed in magnetic field H_1 (a) Precession of the magnetic moment with frequency ω_0 when no external magnetic field is applied, θ is constant (b) Precession of magnetic moment μ at a frequency ω_1 when H_1 is applied, θ is not constant anymore.

Quantum Mechanical Picture

Now, let's consider the quantum perspective of elementary magnetic resonance. Suppose the intrinsic angular momentum of the electron, S, couples with the orbital angular momentum, L, resulting in a total angular momentum J. The $J+1$ magnetic sub-levels, labeled by the magnetic field H_0, have equal energy differences between adjacent sublevels given by

$$\Delta E = g\mu_B H_0 \tag{2}$$

where μ_B is the Bohr magneton and g is the Lande factor (or g-factor), whose correct quantum mechanical value is

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \qquad (3)$$

If an alternating magnetic field perturbs the particle with a frequency ν, such that the quantum energy $h\nu_1$ exactly matches the energy difference ΔE between the levels, and if the direction of the alternating field is perpendicular to the static magnetic field, transitions will be induced between neighboring sub-levels according to the selection rule $\Delta m = \pm 1$ for magnetic dipole radiation. The condition for resonance is,

$$\Delta E = g\mu_B H_0 = h\nu_0 = h\nu_1 \qquad (4)$$

Here, ν_1 is the resonance frequency in cycles per second, which is identical to the classical condition $\omega_0 = \omega_1$.

In atomic spectroscopy, transitions between sub-levels with different m (labeled by m with selection rules $\Delta Lm = \pm 1$) are not directly observed. Instead, the splitting of a level is detected as a small change in the frequency of radiation emitted during transitions between widely separated energy levels. If we could directly measure the frequency corresponding to transitions between sublevels of the same state, we would gain much more precise information about the energy splitting.

Electron Paramagnetic Resonance and Spectroscopy

Paramagnetic resonance is a crucial aspect of spectroscopy, offering a way to determine the energy levels of magnetic particles. It has unique characteristics that distinguish it from optical spectroscopy:

- **Frequency Range:** Magnetic resonance experiments use frequencies ranging from 10^9 to 10^{11} cycles per second. These frequencies, located below the infrared part of the spectrum, allow for highly precise investigation of small energy level splittings that are otherwise inaccessible or nearly inaccessible by optical methods.

- **Transition Probability:** The probability of spontaneous transitions in the radio-frequency range is very low, as it is proportional to ν^3. Therefore, paramagnetic resonance studies rely solely on induced absorption and emission.

- **Transition Type:** While optical spectra typically result from electric dipole transitions between energy levels, paramagnetic resonance absorption lines arise exclusively from magnetic dipole transitions. Consequently, the Einstein coefficients for induced absorption and emission in paramagnetic resonance are smaller by approximately four orders of magnitude compared to optical transitions.

- **Detection Sensitivity:** The effect of paramagnetic resonance is extremely small. Its observation is possible due to the high sensitivity of electronic detection methods and the vast number of photons involved (1 mW corresponds to about $\approx 10^{20}$ photons per second at a frequency of 10^{10} cps).

- **Line Width:** In the optical frequency range, the line width is generally much smaller than fundamental frequency. However, in paramagnetic resonance, interactions that broaden the lines can be of the same magnitude as the energy splitting that determines the resonance frequency. As a result, the width of paramagnetic resonance lines is often comparable to the fundamental frequency and can be measured with high precision. This allows for a detailed investigation of various interactions in paramagnetic substances by analyzing the shape and width of the paramagnetic resonance line and how it depends on different factors.

- **Monochromatic Radiation:** Unlike optical experiments, radio-frequency spectroscopy typically uses radiation that is so monochromatic that the generated frequency band is much narrower than the absorption line width.

- **Line Broadening Factors:** The key factors influencing line width include magnetic dipole interactions, exchange forces, local electric fields created by nearby magnetic particles, and thermal motion. The natural line widths of radio frequency spectra are negligible.

- **Spectral Study Method:** In paramagnetic resonance, spectra are not studied by varying the frequency of the incident radiation but by altering the characteristic frequencies of the absorbing systems. This is done by varying the static magnetic field.

In this experiment we are using Helmhlotz coil to generate alternating magnetic field and Radio Frequency (RF) signal is provided to the sample.

The observed peaks appear as absorption dips because the sample absorbs power from the induction coil. These peaks result from the presence of an odd number of inverting amplification stages in the circuit. The electron spin precesses at the Larmor frequency $\omega = eH_0/2mc$ and this frequency varies in both magnitude and direction due to the alternating magnetic field H_0 generated by the Helmholtz coils. Resonance occurs when the radio frequency field ω_1 falls within the range of ω_0, The positions of the four peaks can be understood by referring to Fig. 2. If the X plate signal (50 Hz) and the Y plate signal (ESR output) are in phase, then peaks I and II, as well as peaks III and IV, will align. When $\omega_1 = \omega_0$ both in magnitude and direction, the peaks are seen. Here we
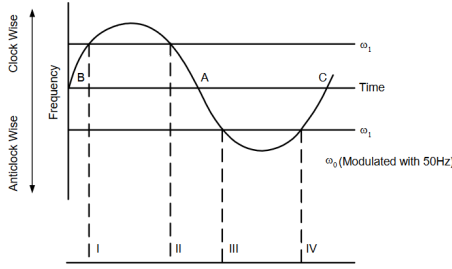
FIG. 2: The radio frequency is linear by polarised, which can be regarded as two circularly polarised fields of opposite direction (say clockwise and anti- clockwise). Further magnetic field H_0 also changes direction. Thus resonance occurs when the two frequencies (ω_1 and ω_0) becomes equal in magnitude as well as direction i.e. four times in one full cycle of H_0.

see that this happens 4 times in a full cycle of H_0. We are able to witness EPR since DPPH is a paramagnetic compound and thus have a net non zero magnetization. The magnetic field due to Helmholtz coil is gven by

$$H = \frac{8\mu_0 N}{\sqrt{125}a}I \tag{5}$$

where a is the radius of the coil and N is the number of turns. The peak to peak value of magnetic field is $H_{pp} = 2\sqrt{2}H$. And the relation between the H_0 and H_{pp} is given by

$$H_0 = H_{pp}\frac{Q}{P} \tag{6}$$

Thus if we plot a graph between $1/Q$ and H_{pp} the slope is $1/(H_0P)$.
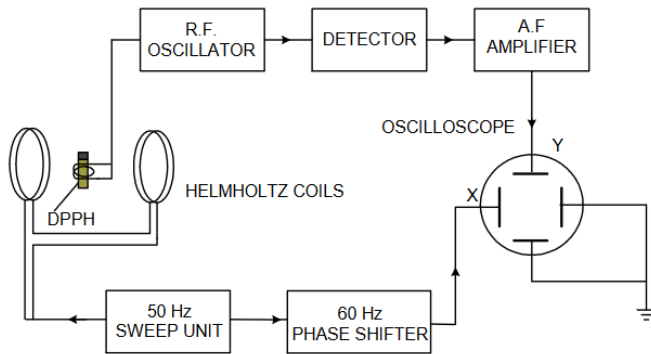
III. EXPERIMENTAL SETUP

Apparatus

FIG. 3: Block Set Diagram of ESR

1. ESR Spectrometer
2. AC Gauss meter
3. Cathode Ray oscilloscope
4. Helmholtz Coil
5. Paramagnetic substance (DPPH)

The number of turns in each coil of Helmholtz coil is 500 and the coils have a radius of 15.4 cm. The separation between the two coils is 7.7cm. A test sample, Diphenyl Picryl Hydrazyl (DPPH) is placed in a plastic tube, which itself is in the induction coils. This increases the filling factor to the maximum. DPPH is a free radical and widely used as a standard for ESR measurements.
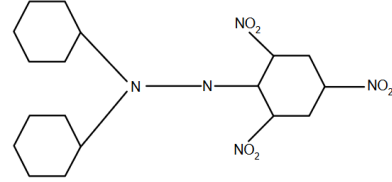

FIG. 4: Chemical structure of DPPH

IV. PROCEDURE

1. Turn on the Helmoltz Coil power supply and set the current to 150 mA.
2. Configure the ESR Spectrometer front panel controls as follows – Frequency: Centered, Phase: Centered.
3. On the CRO (Cathode Ray Oscilloscope) screen, operating in XY mode, observe four peaks. Adjust the FREQUENCY of the Spectrometer and the SENSITIVITY of the CRO to achieve optimal results, ensuring sharp peaks and a good signal-to-noise ratio.
4. Use the PHASE knob to align the two pairs of peaks as closely as possible.
5. Adjust the orientation of the Helmholtz coils relative to the main unit to achieve the best overlap of the baselines.
6. Adjust the horizontal sensitivity of the oscilloscope to the maximum. The X-axis of the oscilloscope represents the constant AC voltage supplied by the ESR spectrometer for measurement purposes.
7. Measure the total display on the X-axis, denoted as 'P' divisions of the CRO X plate. Note that the zero field is located at the middle point of the X-axis.
8. Adjust the frequency, detection level, and vertical sensitivity of the oscilloscope to obtain the best possible resonance peaks, while keeping the current fixed at 150 mA.
9. Fix the frequency and vary the current flowing through the coils. Measure the corresponding horizontal separation between the two resonance peaks ($2Q$) after adjusting the phase. Take five to six sets

of observations by varying the current.

10. Use the provided A.C. Gauss meter to measure the A.C. r.m.s magnetic field (H) corresponding to the currents used in the previous step.

11. Measure the gap between the positions of the two peaks (2Q). Ensure that these peaks are equidistant from the middle point (denoted as Q divi- sions). Calculate Q from the measured value of 2Q by dividing 2Q by 2.

12. Calculate H_{pp} (Peak-to-peak magnetic field), H_0 (static magnetic field), and g (Lande factor).

13. Repeat the experiment using different frequencies, following the same procedure for each frequency

TABLE II: Table for measurement of g at $\nu = 14.01$ MHz

Current (I) (mA)	2Q (V)	Q (V)	Magnetic Field H (mT)	H_{pp} (Gauss)
99	3.4	1.70	0.51	14.42
127	2.6	1.30	0.72	20.36
154	2.0	1.00	0.86	24.32
184	1.7	0.85	0.99	28.00
209	1.5	0.75	1.14	32.24
233	1.3	0.65	1.27	35.92
258	1.1	0.55	1.44	40.73
282	1.0	0.50	1.51	42.71
307	0.9	0.45	1.63	46.10

V.   OBSERVATION AND CALCULATIONS

Least Count of oscilloscope $= 0.2$ V, $P = 5$ V

TABLE I: Table for measurement of g at $\nu = 13.03$ MHz

Current (I) (mA)	2Q (V)	Q (V)	Magnetic Field H (mT)	H_{pp} (Gauss)
99	3.2	1.60	0.51	14.42
126	2.4	1.20	0.72	20.36
153	1.8	0.90	0.86	24.32
180	1.6	0.80	0.99	28.00
207	1.4	0.70	1.14	32.24
230	1.2	0.60	1.27	35.92
257	1.1	0.55	1.44	40.73
282	1.0	0.50	1.51	42.71
307	0.9	0.45	1.63	46.10

FIG. 6: Plot of 1/Q vs. H_{pp} at $\nu = 14.01$ MHz

From Fig. 6, slope $= 0.0517$. Putting $P = 5$ V, we get $H_0 = 3.87$ Gauss and hence, $g = 2.59$.

TABLE III: Table for measurement of g at $\nu = 15.02$ MHz

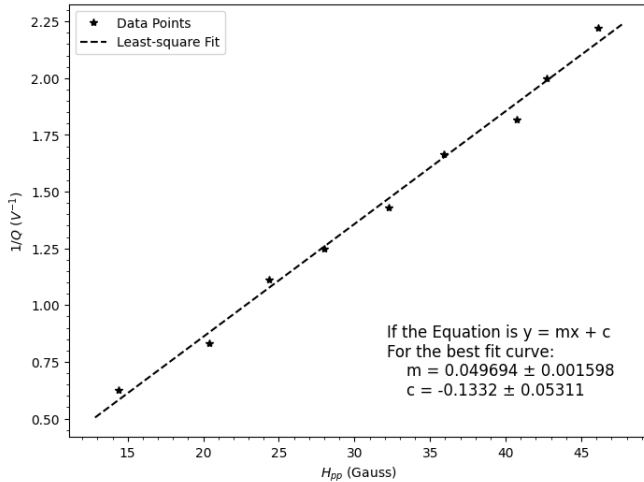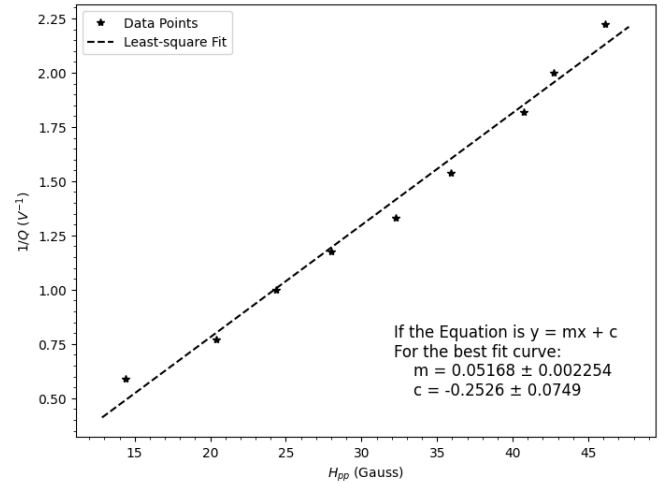| Current (I) (mA)	2Q (V)	Q (V)	Magnetic Field H (mT)	H_{pp} (Gauss)
99	3.4	1.70	0.51	14.42
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154	2.0	1.00	0.86	24.32
184	1.7	0.85	0.99	28.00
209	1.5	0.75	1.14	32.24
233	1.3	0.65	1.27	35.92
258	1.1	0.55	1.44	40.73
282	1.0	0.50	1.51	42.71
307	0.9	0.45	1.63	46.10

FIG. 5: Plot of 1/Q vs. H_{pp} at $\nu = 13.03$ MHz

From Fig. 5, slope $= 0.0497$. Putting $P = 5$ V, we get $H_0 = 4.02$ Gauss and hence, $g = 2.31$.
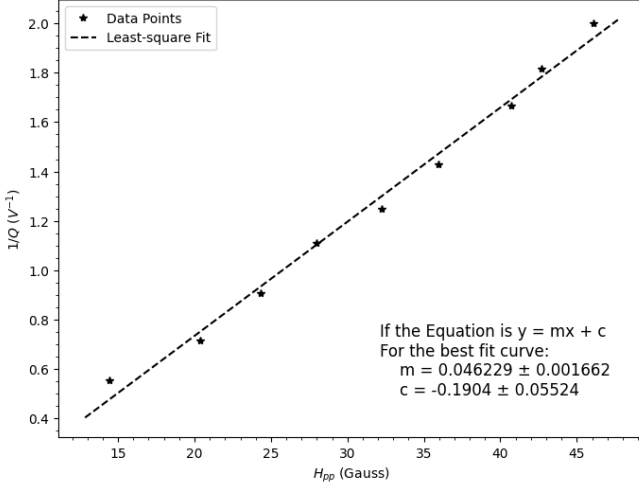
FIG. 7: Plot of $1/Q$ vs. H_{pp} at $\nu = 15.02$ MHz

From Fig. 7, slope $= 0.0462$. Putting $P = 5$ V, we get $H_0 = 4.33$ Gauss and hence, $g = 2.48$. And hence average value of $H_0 = 4.07$ Gauss and $g = 2.46$.

VI. ERROR ANALYSIS

Error in H_0 will be given by,

$$\frac{\Delta H_0}{H_0} = \sqrt{\left(\frac{\Delta P}{P}\right)^2 + \left(\frac{\Delta \text{slope}}{\text{slope}}\right)^2} \qquad (7)$$

And error in g will be given by,

$$\frac{\Delta g}{g} = \sqrt{\left(\frac{\Delta \nu}{\nu}\right)^2 + \left(\frac{\Delta H_0}{H_0}\right)^2} \qquad (8)$$

Using $\Delta P = 0.2$ V and $\Delta \nu = 0.01$ MHz, plugging in the values:

- For $\nu = 13.03$ MHz,

$$\Delta H_{0_1} = 0.21 \text{ Gauss}, \Delta g_1 = 0.12$$

- For $\nu = 14.01$ MHz,

$$\Delta H_{0_2} = 0.23 \text{ Gauss}, \Delta g_2 = 0.15$$

- For $\nu = 15.02$ MHz,

$$\Delta H_{0_3} = 0.23 \text{ Gauss}, \Delta g_3 = 0.13$$

Avg. error in H_0,

$$\Delta H_{0_{\text{avg}}} = \frac{1}{3}\sqrt{(\Delta H_{0_1})^2 + (\Delta H_{0_2})^2 + (\Delta H_{0_2})^2}$$
$$= 0.13 \text{ Gauss}$$

Avg. error in g,

$$\Delta g_{\text{avg}} = \frac{1}{3}\sqrt{(\Delta g_1)^2 + (\Delta g_2)^2 + (\Delta g_3)^2} = 0.08$$

VII. DISCUSSION AND CONCLUSION

The static magnetic field was measured as,

$$H_0 = (4.07 \pm 0.13) \text{ Gauss}$$

And the Lande's factor was measured as,

$$g = (2.46 \pm 0.08)$$

This is quite close to the literature value of $g = 2.0$. The error is due to the precision in the measurement of Q and P. Very small changes in Q at very high current is also not properly resolved leading to errors. Also, the phase matching of the four peaks is done by eye approximation. Errors may also come from the incorrect phase matching.

VIII. PRECAUTIONS

1. Set up the experiment in a quiet location free from mechanical and electrical disturbances.
2. Adjust the sensitivities of the X and Y plates of the oscilloscope so that the measurements remain within the linear range.
3. Use a shielded cable to connect the Y-output from the ESR Spectrometer to minimize external noise and interference.
4. Do not allow high currents (around 200 mA) to flow through the Helmholtz coils for a prolonged time. This can cause unnecessary heating of the coils, potentially damaging them.
5. Do not use an AC stabilizer, as it may distort the sinusoidal waveform. If necessary, use a variac to regulate the voltage.
6. If the peaks do not align on the x-scale, check the sinusoidal waveform of the mains voltage. Distortion may occur due to overloading of the main line by other heavy devices operating on the same circuit.

[1] SPS, *ELECTRON SPIN RESONANCE USING DPPH*, NISER (2023).