Electron Spin Resonance

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Aim: To determine the Landé g-factor using Electron Spin Resonance.

Apparatus: ESR setup which includes Helmholtz coils, R.F. oscillator and the test sample, and in addition, a cathode ray oscilloscope (CRO).

Theory

Background

Suppose a particle having a magnetic moment μ is placed in a uniform magnetic field of intensity B, then the Hamiltonian can be written as

$$\hat{H} = g\left(\frac{e}{2mc}\right)\hat{J} \cdot B,$$

where g is the Landé g-factor, which is 1 for orbital angular momentum, and 2 for spin angular momentum. The factor $\frac{e\hbar}{2mc}$, sometimes written as μ_B, is called *Bohr magneton*, if the particle in question is an electron. If the particle is a nucleon, then the factor is called the *nuclear magneton*. If the angular momentum J results from a combination of an orbital angular momentum and a spin, then g would be given by the Landé formula:

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)},$$

where l, s and j represent the magnitude of the orbital, the spin and the total angular momenta, respectively. Remember that j can go from $l - s$ to $l + s$.

Conventionally, the static magnetic field is assumed to be pointing along the $z-$axis, which modifies the above equation to

$$\hat{H} = g\left(\frac{e}{2mc}\right)\hat{J}_z B.$$

Let us now consider an atom which has an electronic ground state with total angular momentum $j = 1/2$ and an excited state with $j = 3/2$ (see figure 2).There is only a single transition which can be induced by the absorption of radiation of frequency $\omega_{12} = (E_2 - E_1)/\hbar$. As the energy does not depend on the angular momentum states, the ground state is doubly degenerate corresponding to eigenvalues $\pm 1/2$ of $\hat{J}_z$ and the excited state is quadruply degenerate corresponding to eigenvalues $+3/2, 1/2, -1/2, -3/2$ of $\hat{J}_z$.
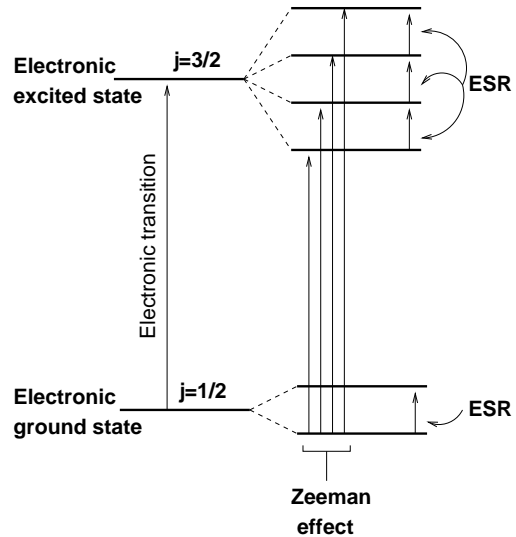
If one now applies a magnetic field B along the z-axis, each of the angular momentum states acquires a different energy. The ground state energy level thus splits into two sublevels and the excited state level into four sublevels. This is called **Zeeman splitting**. Now instead of a single transition of frequency $\omega_{12} = (E_2 - E_1)/\hbar$, many transitions of frequencies close to ω_{12} are possible. Experimentally this is seen as a splitting a single absorption or emission line into several closely spaced lines. This is called **Zeeman effect**.

As one would have noticed, transition should also be possible between the sublevels of the *same* energy level. It is indeed possible and this phenomenon is known as **electron spin resonance (ESR)**.

Electron Spin Resonance

Let us try to understand the phenomenon of ESR in somewhat more detail. As ESR invloves transitions only between the sublevels of one energy level, we will not bother about the Hamiltonian of the atom/molecule which gives us the energy levels. We will only worry about the part of the Hamiltonian which is the result of the applied magnetic field B, which gives us the sublevels.

For simplicity, we will consider one electron with angular momentum j, in a magnetic field B. In addition we have an electromagnetic field of frequency ω in the direction perpendicular to B. The time-dependent Hamiltonian can thus be written as

$$\hat{H} = g\left(\frac{eB}{2mc}\right)\hat{J}_z + \hat{V}_0 e^{i\omega t} + \hat{V}_0^\dagger e^{-i\omega t},$$

where $\hat{V}_0$ represents the interaction of the electromagnetic field with the electron.

The electromagnetic field is supposed to be very *weak* compared to the applied static field B, and so one can use **time-dependent perturbation theory** to study this problem. The states that we will use are the eigenstates of $\hat{J}_z$:

$$\hat{J}_z|m\rangle = \hbar m|m\rangle,$$

where m will take $2j + 1$ values, from $-j$ to $+j$. The energy of these levels is given by

$$g\left(\frac{eB}{2mc}\right)\hat{J}_z|n\rangle = \epsilon_n|n\rangle,$$

where $\epsilon_n = \frac{geB\hbar n}{2mc} = gB\mu_B n$.

In time-dependent perturbation theory, we know that the time-dependent interaction can cause transition between various $|m\rangle$ states. The transition rate per unit time, from $i'th$ level to j'th level is given by:

$$W_{i\rightarrow j} = \frac{2\pi}{\hbar}|\langle j|\hat{V}_0|i\rangle|^2\delta(\epsilon_j - \epsilon_i - \hbar\omega),$$

assuming that $\epsilon_j > \epsilon_i$. This expression says that transition from state $|i\rangle$ to $|j\rangle$ is possible when the frequency of radiation $\omega = (\epsilon_j - \epsilon_i)/\hbar$. This is the condition for resonance, or in our case, *electron spin resonance*.

There is one important point about the form of $\hat{V}_0$. It happens to be such that $\langle j|\hat{V}_0|i\rangle$ is nonzero only when $j = i \pm 1$. This means that transition is possible between, say, $|-3/2\rangle$ and $|-1/2\rangle$, but not between, say, $|-3/2\rangle$ and $|1/2\rangle$. Such restrtictions, imposed by the kind of interaction and the nature of states, are called **selection rules**.

The ESR setup
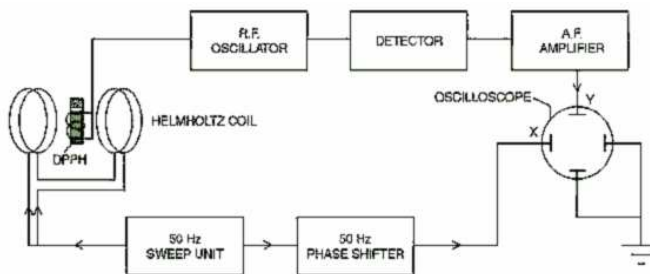
Description of the ESR Spectrometer

A block diagram of the ESR Spectrometer is given in the figure above.

Basic circuit

The first stage of the ESR circuit consists of a critically adjusted radio frequency oscillator. This type of oscillator is required here, so that the slightest increase in its load decreases the amplitude of oscillation to an appreciable extent. The sample is kept inside the tank coil of the oscillator, which in turn, is placed in the 50 Hz magnetic field generated by the Helmholtz coils. At resonance, i.e. when the frequency of oscillation becomes equal to frequency corresponding to the energy splitting of the sublevels, the oscillator amplitude registers a dip due to the absorption of power by the sample. This obviously, occurs periodically four times in each complete cycle of the supply voltage of the magnetic field. The result is an amplitude modulated carrier which is then detected using a diode detector and amplified by a chain of three low noise, high gain audio-frequency amplifiers to suit the input requirement of any oscilloscope.

Highly stabilized and almost ripple free power supply for the above circuit is obtained using an integrated circuit regulator.

Phase shifter

This can compensate the undermined phase difference which may be introduced in the amplification stages of the spectrometer and oscilloscope.

50 Hz sweep unit

A 50 Hz current flows through Helmholtz coils which provides a low frequency magnetic field to the sample. As the resonance is observed at a few gauss only, no static magnetic field is applied.

R.F. Oscillator

It is a transistorised radio frequency oscillator suitable for the determination of resonance frequency.

Frequency range: 10 MHz to 18 MHz
Accuracy: Better than 0.5 %

The Sample

The sample used in our ESR setup is diphenyl-picryl-hydrazyl (DPPH). It is a widely used standard in ESR experiments. The structure of this organic molecule, shown in the figure, contains three benzene rings. Its important feature is that it contains a single unpaired electron, whose orbital angular momentum is
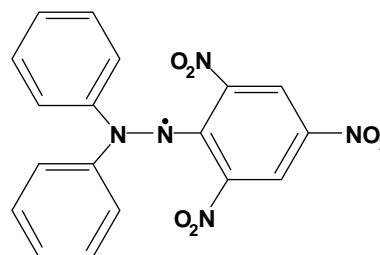
zero. So, the electron has only the spin angular momentum, and the material gives a $g-$factor which is close to 2.0038. One thus has to deal with the simple situation where $j = 1/2$, and only two sublevels are involved.

In conventional spectroscopy, absorption intensity is plotted against the frequency of radiation to get the absorption spectrum. In the present case, one should obtain a single abosorption peak at frequency $\omega = (\epsilon_j - \epsilon_i)/\hbar$, which is nothing but $\omega = \frac{geB}{2mc}$. However, in this setup it is difficult to vary the frequency of radiation. So, what is done is that the frequency of radiation is fixed at some ω_0, and the normally static, magnetic field is swept between the positive and negative extremes of a maximum field value. This is done by supplying an alternating current to the Helmholts coils which are supposed to generate the magnetic field. During the AC cycle, whenever the strength of the magnetic field (+ve or -ve) becomes equal to $B_0 = \frac{\omega_0 2mc}{ge}$, there is a resonance condition, and radiation is absorbed.

Origin of four peaks

In this experiment, the CRO is used in the x-y mode. The signal from the AC source, which supplies current for the magnetic field, is fed to the X plates of the CRO, and the absorption signal is fed to the Y plates. The point on the extreme right on the CRO screen represents the maximum positive value of the field, and the point on the extreme left represents the maximum negative value of the field. The point at the center represents zero field. Without the Y-plates, the point on the CRO screen goes from maximum negative value to zero, and the maximum positive value, and then back again to the mimimum value. As one can see from the figure, the field strength becomes B_0 four times in one single sweep cycle.
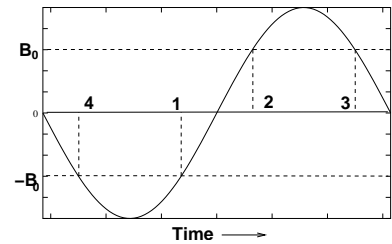
Now if the absorption signal is fed to the Y-plates, whenever the field strength becomes B_0, the Y-axis will show a peak. So, one should see **four peaks** corresponding to points 1,2,3,4 in the figure. But one can see that on the X-axis of the CRO screen, points 2 and 3 are the same, because they correspond to the same value of the field B_0, and points 1 and 4 are the same because they correspond to the field $-B_0$. So, the **four peaks should overlap such that only two are visible**. However, the absorption signal passes through some electronic circuitry before being fed to the Y-plates of the CRO, so it very difficult to make sure that no phase change occurs in the process. If there is a small phase difference between the AC signal on the X plates and the signal on the Y plates, when points 3 and 4 are traced, the peaks do not overlap with those at 1 and 2. So, **in practice one would see four peaks**. If one has a way of changing the phase of, say, the Y signal, one can adjust the phase manually so that the four peaks merge into two.

Getting the numbers

We have the control over the current that is passing through the Helmholtz coils, and this can also be measured. But what we actually need for our calculation is, the magnetic field B applied to the sample.

Let us first calculate the magnetic field through the Helmholtz coils. This can be done easily

using the *Biot-Savart law.*

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

where:

μ_0 = $4\pi \times 10^{-1}$ (cgs units)

N = number of turns in each coil.

r = the radius of the Helmholtz coils in cm (which is equal to their separation when they are properly arranged).

I = current passing through the coils.

The value of B is obtained in gauss. As the current is measured by an AC ammeter, the value of the current, and thus the field, is the r.m.s. value. The peak value of the field will be given by

$$B_{max} = \sqrt{2}B = \mu_0 \frac{8\sqrt{2}}{\sqrt{125}} N\frac{I}{r}.$$

Suppose the peak value of the field ($= B_{max}$) corresponds to P divisions from the center on the x-axis of the CRO screen. Then if Q be the distance of the observed resonances from the center (in the units of divisions), the field corresponding to the resonance will be given by:

$$B_0 = Q\frac{B_{max}}{P}$$

But the resonance condition is given by:

$$B_0 = \frac{\hbar\omega_0}{g\mu_B},$$

which can be used to determine the value of g, once B_0 is known.

Now, for a fixed ω_0, B_0 is fixed, although one can vary the current I and get various position of the absorption peaks. Let us write the expression for B_0 and see what is most accurate way to calculate it:

$$B_0 = \left(\frac{N\mu_0 8\sqrt{2}}{rP\sqrt{125}}\right) I \cdot Q.$$

The ESR spectrometer is such that P does not vary as one varies I. So, the best way to evaluate the above expression will be to plot a graph between $1/I$ and Q, and find out the slope, which will give the average value of $I \cdot Q$. The field at the absorption peaks can be calulated as:

$$B_0 = \left(\frac{N\mu_0 8\sqrt{2}}{rP\sqrt{125}}\right) \times slope\ of\ graph\ between\ 1/I\ and\ Q.$$

Procedure

Connections

Connections are done as follows:

- ESR spectrometer and power supply are connected with connecting cables.

- Connect the coaxial cable of the induction coil to the oscillator through the socket marked "*input*".

- Connect the Helmoltz coils to the power supply terminal marked "H" coil.

- Connect the "*Out-put*" terminal marked X, Y, E on the ESR spectrometer to the X plate, Y plate input and ground of the oscilloscope respectively and switch on the oscilloscope.

- Connect the power supply with AC mains.

Adjustments

Adjust the current in the Helmholtz coils at 150 mA. The front panel controls of the ESR spectrometer are adjusted as follows: frequency, detector and phase, all centered.

Experimental procedure

The X plate of the CRO is callibrated in terms of magentic field as follows:

1. X amplifier of the CRO is adjusted to obtain the maximum X deflection (e.g. P divisions.

2. Note the current flowing in the Helmholtz coils. The magnetic field can then be calculated from the formula for B given before. Number of turn in the coils $N = 500$ and the radius $r = 7.7cm$.

The positions of the two peaks of the ESR signal at resonance is measured. Let this be Q divisions from the center.

The best possible resonance peaks are obtained by varying the frequency in the range of 12 to 14 MHz and the Y sensitivity of the oscilloscope. The pahse knob is adjusted to coincide one pair of peaks with the other. The current through the coils is then varied, keeping the frequency fixed, and the corresponding position of the peaks from the center noted. A graph between $1/I$ and Q is then plotted and can be used in calculating the g-factor, as described earlier.

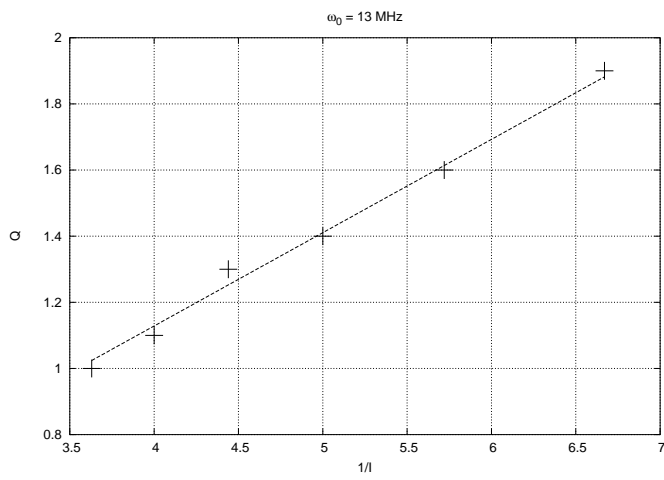Repeat the above procedure for different values of frequency.

Observations and calculation

S.No.	I(mA)	I(A)	1/I	Distance of peaks from center (Q)			
				10 MHz	13 MHz	15 MHz	17 MHz
1.	150	0.150	6.667	2.4	1.9	1.9	1.9
2.	175	0.175	5.714	2.0	1.6	1.6	1.5
3.	200	0.200	5.00	1.4	1.4	1.4	1.4
4.	225	0.225	4.44	1.2	1.3	1.2	1.2
5.	250	0.250	4.00	1.1	1.1	1.1	1.0
6.	275	0.275	2.636	1.0	1.0	1.0	1.0

Slope of the graph $(= I \cdot Q) = 0.282$, $P = 5$, $N = 500$
$r = 7.7cm$, $\mu_0 = 0.1 \times 4\pi$, $\mu_B = 9.2741 \times 10^{-21}$, $h = 6.626 \times 10^{-27}$.

$$
\begin{aligned}
B_0 &= \left(\frac{N\mu_0 8\sqrt{2}}{rP\sqrt{125}}\right) I \cdot Q \\
&= \left(\frac{500 \times 0.1 \times 4\pi 8\sqrt{2}}{7.7 \times 5\sqrt{125}}\right) \times 0.282 \\
&= 4.657
\end{aligned}
$$

$$g = \frac{h\nu_0}{\mu_B B_0}$$
$$= \frac{6.626 \times 10^{-27} \times 13 \times 10^6}{9.2741 \times 10^{-21} 4.657}$$
$$= 1.9944$$

Precautions

1. The direction of the Helmholtz coils should be preferable adjusted so that the field is perpendicular to earth's magnetic field, which is about 0.3 Gauss.

2. Setup the experiment at a place free from electric and magnetic fields and mechanical disturbances.

3. Y-output from the ESR spectrometer should be through a good shielded cable.