

Related topics

Zeeman effect, energy quantum, quantum number, resonance, g -factor, Landé factor.

Principle

With electron spin resonance (ESR) spectroscopy compounds having unpaired electrons can be studied. The physical background of ESR is similar to that of nuclear magnetic resonance (NMR), but with this technique electron spins are excited instead of spins of atomic nuclei. The g -factor of a DPPH (Diphenylpicrylhydrazyl) and the halfwidth of the absorption line are determined, using the ESR apparatus.

Equipment

1 ESR resonator with field coils	09050-00	3 Connecting cord, $l = 500$ mm, blue	07361-04
1 ESR power supply	09050-93	2 Connecting cord, $l = 500$ mm, red	07361-01
1 Power supply, universal	13500-93	2 Connecting cord, $l = 500$ mm, yellow	07361-02
1 30 MHz digital storage oscilloscope	11462-99	Options:	
1 DMM, auto range, NiCr-Ni thermocouple	07123-00	1 Teslameter, digital	13610-93
4 Screened cable, BNC, $l = 750$ mm	07542-11	1 Hall probe, tangent., prot. Cap	13610-02
1 Adapter, BNC-socket/4 mm plug pair	07542-27		



Fig. 1: Experimental set-up for determining characteristic curves.

Tasks

This experiment deals with the investigation of the magnetic momentum of the electron spin.

1. Determine the g -factor (Landé-factor) of the DPPH (Diphenylpicrylhydrazyl) specimen
2. Determine the FWHM (Full Width at Half Maximum) of the absorption line

Setup

Set up the experiment according to the following instructions and pictures:

- Connect the ports for alternating voltage of the universal power supply with the two yellow connecting cords to the ESR power supply as shown in Fig. 1 and Fig. 2

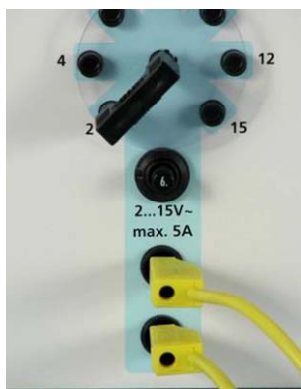


Fig. 1

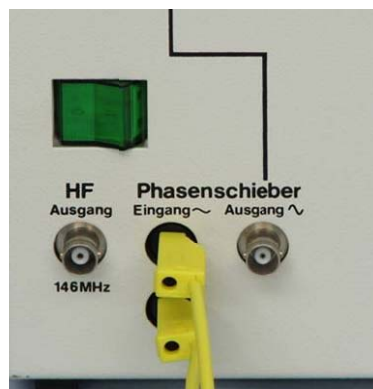


Fig. 2

- Connect the two Helmholtz coils of the ESR resonator in series by connecting a red port to a blue port with a blue connecting cord (Fig. 3)

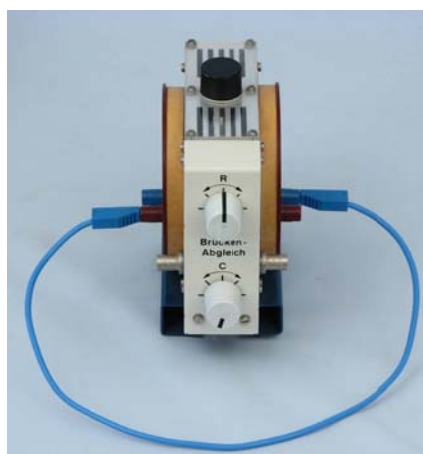


Fig. 3

- Use a blue connecting cord to connect the “minus pole” of the direct voltage ports to the digital multimeter and select the 10 A d.c. setting (Fig. 4 and Fig. 5)

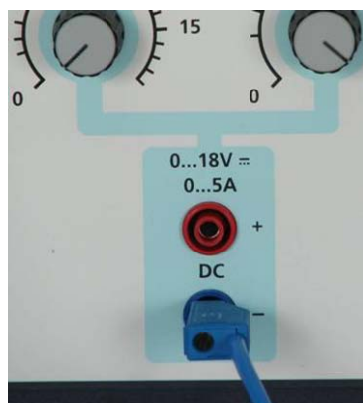


Fig. 4



Fig. 5

- The “10 A” port of the digital multimeter is then connected with a red connecting cord to the ESR resonator according to the following pictures:



Fig. 6

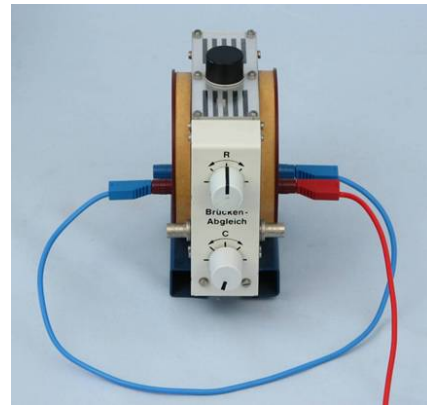


Fig. 7

- After that, connect the resonator to the alternating voltage of the universal power supply with a blue connecting cord (Fig. 8 and Fig. 9)

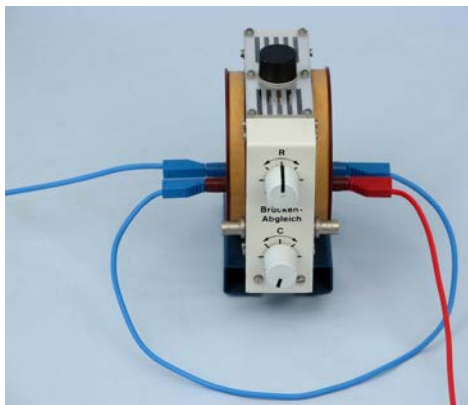


Fig. 8



Fig. 9

- The “plus pole” of the direct voltage is applied to the upper part of the alternating voltage with a red connecting cord as shown in Fig. 10

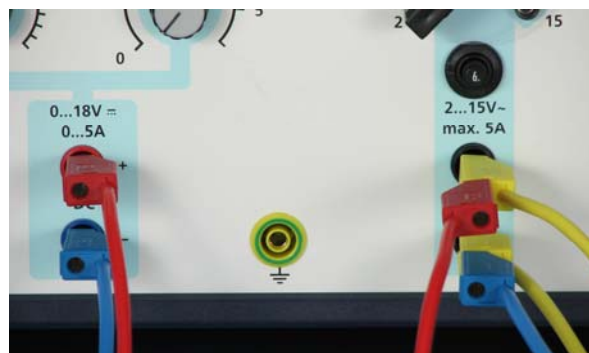


Fig. 10

- Then, the ESR power supply is connected to the ESR resonator with two screened BNC cables. Connect the “HF Ausgang”-port of the power supply to the “HF Eingang”-port of the resonator (Fig. 11 and Fig. 12)

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Fig. 11



Fig. 12

- The “ESR Signal Eingang”-port is connected to the “ESR Ausgang”-port (Fig. 13 and Fig. 14)

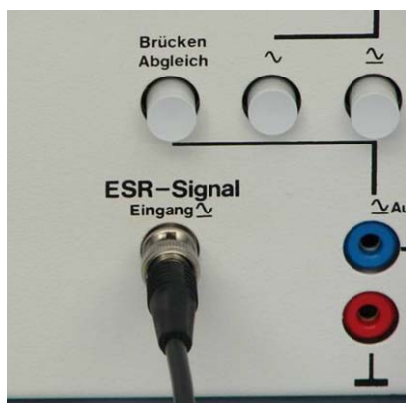


Fig. 13



Fig. 14

- In order to display the ESR-signal on the oscilloscope, connect “Phasenschieber Ausgang” to the “X”-port of the oscilloscope (Fig. 15 and Fig. 17) and the “Y”-port to the ESR-signal amplifier (Fig. 16 and Fig. 17)



Fig. 15



Fig. 16



Fig. 17

- Your setup should now look like the following picture:

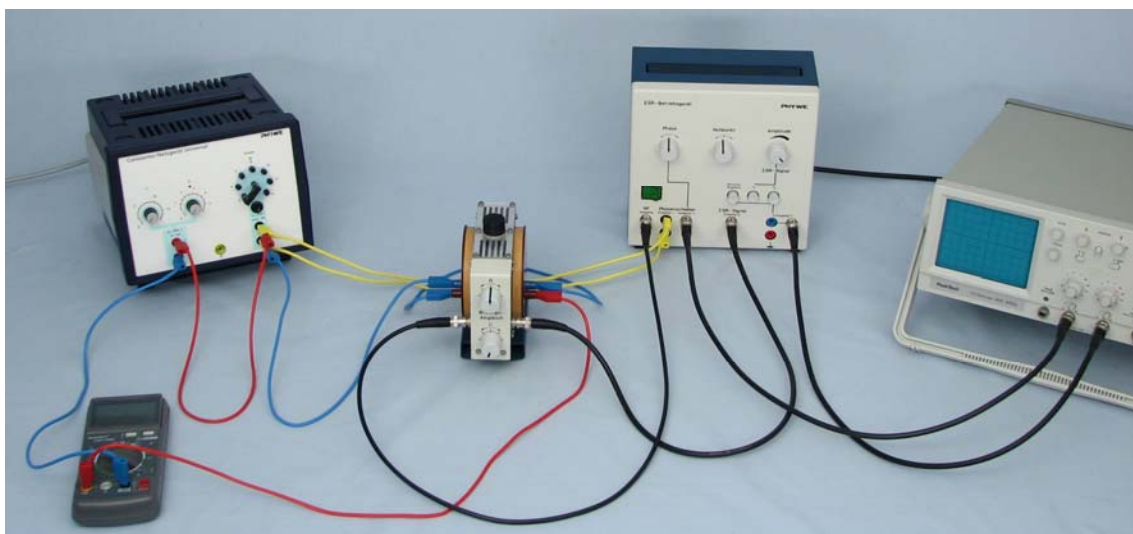


Fig. 18

Procedure

A symmetrically fed bridge circuit (Fig. 2a) contains a variable resistor R in one branch and a high-quality tuned circuit (resonator) in the other. The specimen is located in the coil of the tuned circuit. Normally, the bridge is balanced so that the complex impedance of both branches is the same and consequently there is no voltage between points a and b . If the external magnetic field is now so adjusted that the resonance absorption occurs in the specimen, the bridge becomes unbalanced and the voltage set up between a and b rectified and amplified.

If the magnetic field is modulated with 50 Hz a.c. (voltage 2 V), the resonance point is passed through 100 times a second (Fig. 3), and the absorption signal can be displayed on an oscilloscope, provided the x -deflection is driven with the same a.c. voltage in the correct phase.

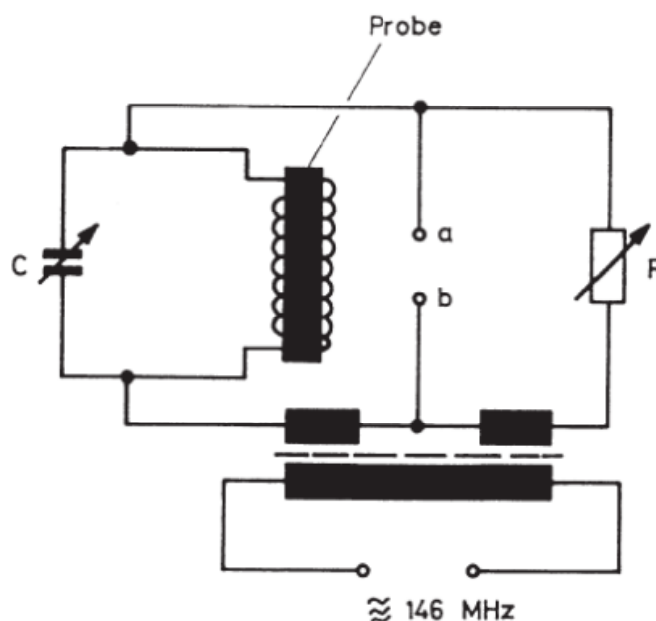


Fig. 2a: Measuring bridge of the ESR apparatus.

1. Determination of the Landé-factor g

- Before switching on the power supply make sure, that the rotating switch for the direct voltage (labelled with "V") on the universal power supply is turned to "0" and the rotating switch for the corresponding current (labelled with "A") is turned to the right-hand stop (5 A)
- The alternating voltage should be set to 2 V
- It is important, that the direct voltage is superimposed by an alternating voltage in order to display the ESR-signal on the oscilloscope (for further information about the functioning of the universal power supply please read its operating instructions)
- Then, switch on the universal power supply, the ESR power supply and the oscilloscope

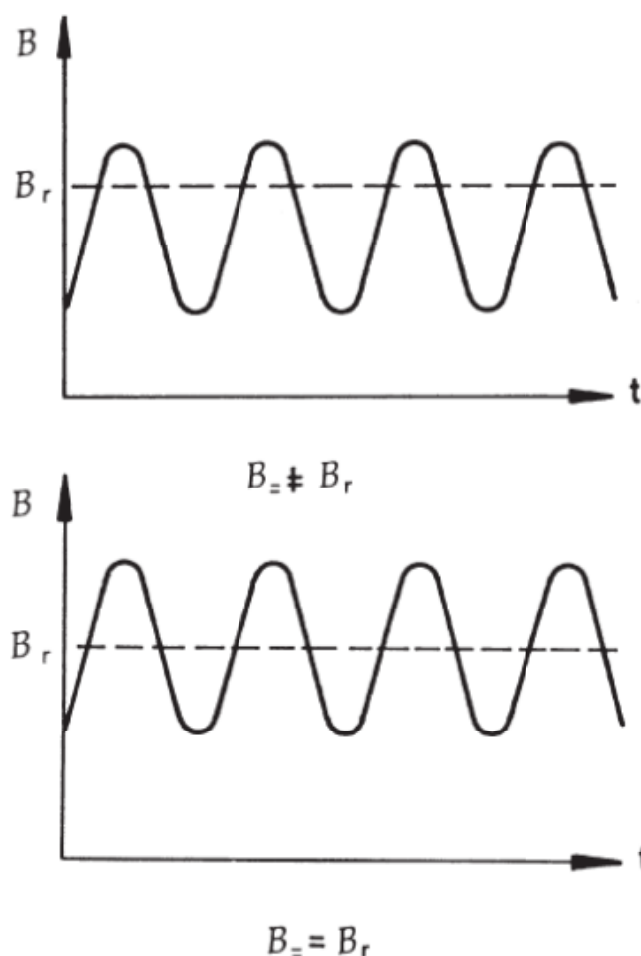


Fig. 3: The magnetic field B is compounded from a d.c. field B_{\pm} and an alternating field B_{\sim} , so that $B = B_{\pm} + B_{\sim}$. Through I_{\pm} , B_{\pm} is to be adjusted so that $B_{\pm} = B_r$.

In the following, one has to do several settings on the ESR power supply. Therefore, we will just refer to the numbers given in the following picture (these numbers correspond to the numbers that you can find in its operating instructions):

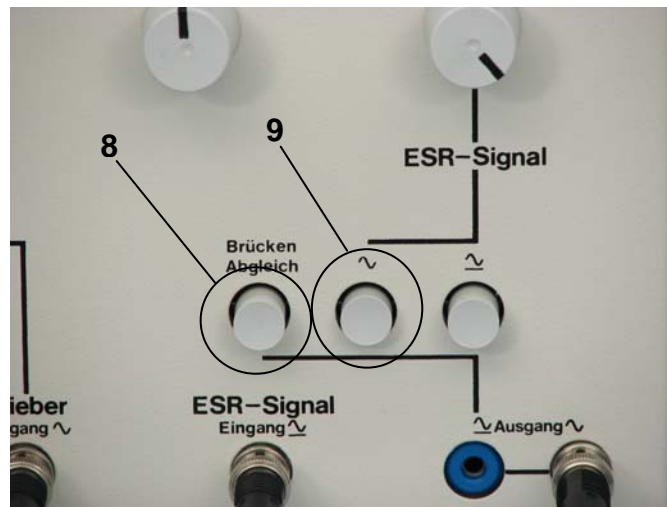


Fig. 19

- Push the “Bridge balancing” (“Brücken Abgleich”) button on the ESR power supply (number “8”)
- The “R” rotating switch of the ESR resonator should be in its middle position and the “C” rotating switch should be brought to its left-hand stop
- At the oscilloscope, select the X-Y-mode (Fig. 20)



Fig. 20

- Select the “GND” mode for the “X”-channel and the “d.c.” mode for the “Y”-channel
- The signal sensitivity for both channels should be 1 V/cm (for further information about the settings please read the operating instructions of the oscilloscope)
- You should see a single point on the oscilloscope
- Use the rotating switches “Position” to centre the displayed point exactly in the middle of the coordinate system
- After that, push button “9” on the ESR power supply (Fig. 19) and select the “d.c.” mode for the “X”-channel at the oscilloscope
- You should see a horizontal line on the oscilloscope
- Increase the direct voltage on the universal power supply until the digital multimeter shows about 1.3 A
- Now, carefully turn “C” on the resonator to the right until you see a signal appearing on the oscilloscope (it might be useful to increase the intensities of the “X”- and “Y”-channels to 0.5 V/cm or more to get a stronger signal displayed)

- As soon as a signal appears, the two lines are made to coincide with the “Phase” rotating switch of the ESR power supply
- Adjust the signal with “C” until you see a symmetrical figure with a minimum (try to adjust the signal as symmetrical as possible)
- By lowering the direct voltage on the universal power supply, the minimum of the figure should be brought exactly onto the y-axis of the oscilloscope (again use “C” to get a symmetrical figure)
- You have found a good resonance signal when your figure looks like the following picture:

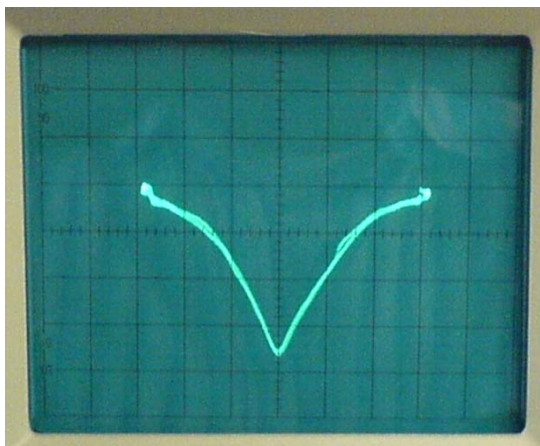


Fig. 21

- The current that is now flowing and that is displayed on the digital multimeter, is the resonance current I_r
- Note this value

2. Determination of the FWHM

- Then move the signal with the help of the “Position” rotating switches of the oscilloscope in such a way, that the x-axis goes exactly through the half of the signal’s height
 - Count the scale divisions from the zero point to the positions, where the signal and the x-axis intersect (the more symmetrical the signal, the more accurate this measurement)
 - The number of scale divisions is dependent on the sensitivity that you have selected; therefore, ensure that you do not change the signal sensitivity during the rest of the experiment
 - Note your results
- In order to determine the FWHM, one has to measure the distance between the two points of intersection in amperes
- Therefore, one has to switch off the alternating voltage and connect the resonator directly to the direct voltage (i.e. remove the red connecting cord that connected a direct voltage port with an alternating voltage port and connect the blue connecting cord of the resonator to the now free direct voltage port (Fig. 22))

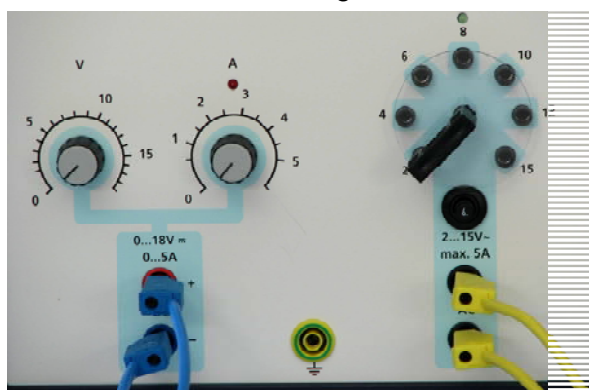


Fig. 22

- Remove the BNC cable from the ESR power supply that is connected to the “X”-channel of the oscilloscope
- Connect the end of this BNC cable to the corresponding adapter as shown in Fig. 24



Fig. 24

- Connect the adapter to the direct voltage ports of the universal power supply (Fig. 24)



Fig. 24

- Pay attention to the fact, that you do not change the sensitivity of the “X”- and “Y”-channels during this measurement
- Vary the direct voltage as long as a single point appears on the oscilloscope
- When the point appears, you can change its position with the “Position” rotating switches of the oscilloscope until it lies on the x-axis
- Move the point by varying the direct voltage on the universal power supply to one of the two points of intersection that you determined before
- Note the current I that is now displayed on the digital multimeter
- Then, move the point to the other point of intersection and note the value of the current.

Theory and evaluation

In general, the phenomena in this experiment can be explained with the Zeeman effect and the transitions between Zeeman-levels. Therefore, we will have to shortly discuss the Zeeman-effect itself and also have to talk about the basics of the atomic physics and quantum mechanics.

First of all, there are two different atomic magnetic dipoles: on the one hand the circular currents that represent the electrons on their revolution around the atomic nucleus, and on the other hand the magnetic momentums that are dependent on the electron spin.

The magnetic momentum of a circular current is defined as:

$$\vec{\mu}_{orbital} = I \cdot \vec{A} = -\frac{e}{T} \cdot \pi \cdot R^2 \cdot \vec{e} = -\frac{e \cdot \omega}{2} \cdot R^2 \cdot \vec{e} \quad (1)$$

where $\vec{A} = A \cdot \vec{e} = \pi \cdot R^2 \cdot \vec{e}$ the area around which the electron moves, R the radius of the orbit, and \vec{e} the unit vector, which is perpendicular to the area A ; $T = \frac{2\pi}{\omega}$ is the revolution time and ω the angular velocity.

This magnetic momentum is proportional to the orbital angular momentum \vec{L} , which is defined as:

$$\vec{L} = m_e \cdot \vec{r} \cdot \vec{v} = m_e \cdot \omega \cdot R^2 \cdot \vec{e} \quad (2)$$

where m_e the mass of an electron.

It follows:

$$\vec{\mu}_{orbital} = -\frac{e}{2m_e} \cdot g_{orbital} \cdot \vec{L} = \gamma_{orbital} \cdot g_{orbital} \cdot \vec{L} \quad (3)$$

where $g_{orbital}$ the Landé-factor and $\gamma_{orbital} = -\frac{e}{2m_e}$ the so called gyro magnetic ratio. As you can conclude from the comparison of equations (1) and (2), the Landé-factor for a pure orbital momentum is $g_{orbital} = 1$. Therefore:

$$\vec{\mu}_{orbital} = \gamma_{orbital} \cdot \vec{L}. \quad (4)$$

In general, one can imagine the spin of an electron as a self-rotation with a spin angular momentum \vec{S} . The magnetic momentum of the electron spin is proportional to this spin angular momentum \vec{S} , so that the following is valid:

$$\vec{\mu}_{spin} = -\frac{e}{2m_e} \cdot g_{spin} \cdot \vec{S} = \gamma_{spin} \cdot \vec{S} \quad (5)$$

where $\gamma_{spin} = -g_{spin} \cdot \frac{e}{2m_e} = g_{spin} \cdot \gamma_{orbital}$.

One aim of this experiment is the determination of the Landé-factor g_{spin} for the electron spin.

In addition, the atomic nuclei also have a spin, but since the mass of a nucleus is much larger than the mass of an electron, the corresponding gyro magnetic ratio $\gamma_{nucleus}$ is very small. That is the reason why one can disregard the magnetic momentum of the atomic nuclei.

By the laws of the quantum mechanics, the angular momentums are quantised, i.e. they can only reach certain values. Therefore, the following values are possible for the orbital angular momentum:

$$L_z = m\hbar \quad (m = l, l-1, l-2, \dots, 1-l, l) \quad (6)$$

where L_z is the z-component of the orbital angular momentum, $h = 6.626 \times 10^{-34}$ Js is Planck's quantum of action with $\hbar \equiv \frac{h}{2\pi}$, and $l = 0, 1, 2, \dots$ a quantum number; m is called the magnetic quantum number.

The spin angular momentum of an electron only has the magnetic quantum number $\frac{1}{2}$. Therefore, the following is valid:

$$S_z = \pm \frac{1}{2} \hbar. \quad (7)$$

From this, it is reasonable, that the magnetic momentums are also quantised. They are expressed in units of the Bohr magneton μ_B :

$$\mu_B = \frac{e}{2m_e} \hbar = 9.27 \cdot 10^{-24} \text{ Am}^2. \quad (8)$$

It follows:

$$\mu_{z, \text{orbital}} = \gamma_{\text{orbital}} \cdot L_z = -m \cdot \mu_B \quad (m = l, l-1, l-2, \dots, 1-l, l) \quad (9)$$

and

$$\mu_{z, \text{spin}} = \gamma_{\text{spin}} \cdot S_z = g_{\text{spin}} \cdot \gamma_{\text{orbital}} \cdot S_z = \left(\pm \frac{1}{2}\right) \cdot g_{\text{spin}} \cdot \mu_B. \quad (10)$$

If an electron has an orbital angular momentum \vec{L} as well as a spin angular momentum \vec{S} , the resulting total angular momentum \vec{J} will be:

$$\vec{J} = \vec{L} + \vec{S}$$

$$|J| = |L-S|, |L-S+1|, |L-S+2|, \dots, |L+S|.$$

The corresponding magnetic momentum is then:

$$\begin{aligned}
 \vec{\mu}_j &= \vec{\mu}_{\text{orbital}} + \vec{\mu}_{\text{spin}} \\
 &= -\frac{e}{2m_e} \times \vec{L} - \frac{e}{2m_e} \cdot g_{\text{spin}} \cdot \vec{S} \\
 &= -\frac{\mu_B}{\hbar} \cdot (\vec{L} + g_{\text{spin}} \cdot \vec{S})
 \end{aligned}
 \tag{11}$$

If one knows the values for L and S , one can directly calculate the theoretically Landé-factor according to the following equation:

$$g_j = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \tag{12}$$

Since the aim of this experiment is the determination of the magnetic momentum of the electron spin, and therefore the Landé-factor g , one considers an unpaired electron:

In order to discuss the characteristics of an atom or molecule respectively, one has to consider all its electrons, i.e. the electrons in the shells of the several nuclei as well as the electrons, which cause a chemical bond. The total orbital angular momentum of the electrons in filled shells is zero. Since the spins of two electrons that cause a chemical bond are always anti-parallel to each other, the total spin angular momentum is zero, too. In this case, the molecule is diamagnetic.

But there are also substances, which have electrons that do not have a corresponding spin-compensating partner. These electrons are called unpaired electrons. Substances that have such an electron are paramagnetic.

Our DPPH specimen has exactly one unpaired electron. Its orbital magnetic momentum is razed (i.e. $L = 0$) and that is the reason why its total magnetic momentum is only given by its spin. Therefore, its Landé-factor $g_{\text{spin}} = g_j$ is nearly the same as the Landé-factor of a free electron. The theoretically expected value for the Landé-factor of the DPPH specimen can be obtained when inserting the values for L ($L = 0$) and S ($S = \frac{1}{2}$) in equation (12). One gets:

$$g_j = 2.$$

However, the “real” value for g is be slightly higher than 2 because of other interactions, which depend on the magnetic displacement B .

Zeeman effect and magnetic resonance

In order to understand the principle and the functioning of this experiment, we now have to talk about the Zeeman effect and have to realise what magnetic resonance is.

At first, the Zeeman effect describes the splitting of an atomic spectral line into several lines when applying an external magnetic field to an atom or molecule respectively. This effect is attributed to the interaction between the external magnetic field and the magnetic moments of the atom or molecule respectively. For the potential energy in the magnetic field is valid:

$$E = -\mu \cdot B. \tag{13}$$

One differs between two different Zeeman effects: the “normal” (without electron spin: $S = 0$) and the “anomalous” (with electron spin: $S \neq 0$). When dealing with the normal Zeeman effect, only the orbital angular momentum is existent and therefore the external magnetic field only interacts with the orbital magnetic momentum. When the external magnetic field is applied, the energy levels within the atom are split into equally spaced energy levels:

$$\begin{aligned}\Delta E &= -\Delta\mu_{\text{orbital}} \cdot B \\ &= \frac{e}{2m_e} \cdot \Delta L_z \cdot B \\ &= \mu_B \cdot \Delta m \cdot B.\end{aligned}\tag{14}$$

This splitting into several energy levels is called the Zeeman effect.

But normally, one has to consider the electron spin as well, as it is the case in our experiment. Then, the external magnetic field also interacts with the spin magnetic momentum and the Zeeman interaction takes the form

$$\Delta E = \mu_B \cdot g_j \cdot B \cdot \Delta m_j.\tag{15}$$

The selection rule for magnetic transitions is:

$$\Delta m_j = \pm 1.$$

So the distance between the two Zeeman-levels is then:

$$\Delta E = \mu_B \cdot g_j \cdot B.\tag{16}$$

A transition from a lower to an higher energy level is achieved by absorbing a radiant quantum whose absolute value is equal to the energy difference between the two energy levels. This radiant energy comes from the applied electromagnetic wave of frequency f within the ESR-resonator. The absolute value of the energy then results in:

$$E = h \cdot f.\tag{17}$$

This process is called magnetic resonance.

From this we get the condition of resonance that one has to adjust during the experiment by varying the magnetic resonance displacement B_r (by varying the direct voltage) and then one can calculate the Landé-factor according to the following equation:

$$\begin{aligned}\mu_B \cdot g_j \cdot B_r &= h \cdot f \\ \Leftrightarrow g_j &= \frac{h \cdot f}{\mu_B \cdot B_r}\end{aligned}\tag{18}$$

where $h = 6.626 \cdot 10^{-34}$ Js, $f = 146 \cdot 10^6$ Hz = 146 MHz, $\mu_B = 9.27 \cdot 10^{-24}$ Am². After inserting these values one gets:

$$g = 10.43 \cdot 10^{-3} \text{ T} \cdot \frac{1}{B_r} \quad (19)$$

When inserting the values and calculating the Landé-factor, one has to pay attention to the units:

$$\begin{aligned} g &= 10.43 \cdot 10^{-3} \left[\frac{\text{Js Hz}}{\text{Am}^2} \right] \cdot \frac{1}{B_r} \\ &= 10.43 \cdot 10^{-3} \left[\frac{\text{Js } \frac{1}{\text{s}}}{\text{Am}^2} \right] \cdot \frac{1}{B_r} \\ &= 10.43 \cdot 10^{-3} \left[\frac{\text{Nm}}{\text{Am}^2} \right] \cdot \frac{1}{B_r} \\ &= 10.43 \cdot 10^{-3} \left[\frac{\text{N}}{\text{Am}} \right] \cdot \frac{1}{B_r} = 10.43 \cdot 10^{-3} [\text{T}] \cdot \frac{1}{B_r}. \end{aligned} \quad (20)$$

Within the ESR-apparatus the magnetic field is produced by a pair of Helmholtz coils with the winding number $w = 241$ and the radius $R = 0.048 \text{ m}$. For the magnetic displacement B is then valid:

$$\begin{aligned} B &= \mu_0 \cdot \frac{8 \cdot I \cdot w}{\sqrt{125} \cdot R} \\ &= 0.7155 \cdot \mu_0 \cdot \frac{I \cdot w}{R} \end{aligned} \quad (21)$$

where $\mu_0 = 4 \pi \cdot 10^{-7} \frac{\text{Tm}}{\text{A}}$ and I the current flowing through the coils. For geometrical reasons, however, the coils within the ESR-resonator are no ideal Helmholtz coils. If one measures the real magnetic displacement between the two coils, one will get the following equation:

$$B = 0.6445 \cdot \mu_0 \cdot \frac{I \cdot w}{R} \quad (22)$$

After inserting the respective values, one gets:

$$B = 4.07 \cdot 10^{-3} \frac{\text{T}}{\text{A}} \cdot I. \quad (23)$$

Now, one can express the Landé-factor g with the help of the resonance current I_r by inserting equation (23) in equation (20) as B_r :

$$g = \frac{2.565 \text{ A}}{I_r}. \quad (24)$$

Evaluation

1. Determination of the Landé-factor g

The Landé-factor g can be expressed with the help of the resonance current I_r (see appendix):

$$g = \frac{2.565 \text{ A}}{I_r}.$$

In our sample measurement, we got the following result ($I_r = 1.24 \text{ A}$):

$$g = 2.0685.$$

The literature value is given as:

$$g = 2.0037.$$

2. Determination of the FWHM

In our sample measurement, we selected a sensitivity for the "X"-channel of 0.5 V/cm and for the "Y"-channel of 20 mV/cm .

In order to determine the full width at half maximum use your measurement results for the currents I_1 and I_2 and calculate the difference. Note your result below:

$$\Delta I = |I_1 - I_2| =$$

Then, calculate the resulting magnetic displacement ΔB by inserting ΔI following equation (formula 23 in the appendix):

$$\Delta B = 4.07 \cdot 10^{-3} \frac{\text{T}}{\text{A}} \cdot \Delta I$$

This ΔB corresponds to the FWHM that was sought.

In our sample measurement, we got the following results:

$$\Delta I = 0.1 \text{ A}$$

$$\Rightarrow \Delta B = 4.07 \cdot 10^{-4} \text{ T}.$$

The literature value is given by:

$$\Delta B = 2.8 \cdot 10^{-4} \text{ T.}$$

This experimental result is not very accurate compared to the literature value. The reason for this is the geometrical setup of the ESR-resonator. The two coils do not function as ideal Helmholtz coils. For a more accurate result one must use much larger coils in order to get an almost ideal pair of Helmholtz coils, which would lead to an unreasonable large increase in costs of the experiment, which set-up is already very good for determining the Landé-factor g . Nevertheless, this will be topic during a redesign. A resonance current of 1.245 A was measured, corresponding to a g -factor of 2.02, and a half-width value of $2.7 \cdot 10^{-4} \text{ T}$.

(Literature values for DPPH: $g = 2.0037$, half-width $2.8 \cdot 10^{-4} \text{ T}$).

Note

The analyzed specimen DPPH (Diphenylpicrylhydrazyl) is a organic, paramagnetic material with one stable radical. The magnetic moment of the molecule is determined only by the spin moment of the valence in the "N"-bridge.

