Electron spin resonance

Physics	Modern Physics	Quantum physics
Physics	Modern Physics	Atomic & Molecular Physics

Difficulty level	Group size	Preparation time	Execution time
medium	2	45+ minutes	45+ minutes

General information

Application

Continuous wave spectrometer (CW-ESR)

Electron spin resonance (ESR) spectroscopy is used in various branches of science, such as in medicine, biology, pharmacy, cosmetology, and biotechnology. It is the method of examination of free radicals in the solid, liquid, or gaseous state, and in paramagnetic centers.

For examle, ESR spectrometers are applied in detection of foodstuffs that exposed to radiation, measurement of the age of geological features using lattice defects, tracking of catalytic reactions and many more.

Other information (1/2)

Prior knowledge

The analyzed specimen DPPH (Diphenylpicrylhydrazyl) is an organic, paramagnetic material with one stable radical. It has an unpaired electron and its orbital contribution to the magnetic moment is negligible because the molecule moves on a highly delocalized orbit. Since the electron is free, the magnetic moment of the molecule is determined only by the spin moment of the valence in the “N”-bridge.

Scientific 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 (Diphenylpikrylhydrazyl) and the halfwidth of the absorption line are determined, using the ESR apparatus.

Other information (2/2)

Learning objective

To allow students to understand further the theoretical principles and experimental techniques used in ESR and the concept of quantum physics concept.

Tasks

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

Safety instructions

For this experiment the general instructions for safe experimentation in science lessons apply.

Before cleaning the equipment, disconnect it from its power supply.

Use a soft, damp cloth to clean it.

Theory (1/17)

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.

Theory (2/17)

The magnetic momentum of a circular current is defined as:

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

where $\vec{A} = A \cdot \vec{e} = \pi \cdot R^2 \cdot \vec{e}$ is 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:

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

where m_e is the mass of an electron.

Theory (3/17)

It follows

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

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:

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

In general, one can imagine the spin of an electron as a self-rotation with a spin angular momentum $\vec{S}$.

Theory (4/17)

The magnetic momentum of the electron spin is proportional to this spin angular momentum $\vec{S}$, so that the following is valid:

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

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 γ_{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.

Theory (5/17)

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:

$$L_z = m\hbar \qquad (m = l, l-1, l-2, \ldots, 1-l, l) \qquad (6)$$

where L_z is the z-component of the orbital angular momentum, $h = 6.626\text{x}10^{-34} Js$ is Planck's quantum of action with $\hbar = \frac{h}{2\pi}$, and $l = 0, 1, 2, \ldots$ 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:

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

Theory (6/17)

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

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

It follows:

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

and

$$\mu_{z,spin} = \gamma_{spin} \cdot S_z = g_{spin} \cdot \gamma_{orbital} \cdot S_z = (\pm\tfrac{1}{2}) \cdot g_{spin} \cdot \mu_B \qquad (10)$$

Theory (7/17)

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:

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

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

The corresponding magnetic momentum is then:

$$\vec{\mu}_j = \vec{\mu}_{orbital} + \vec{\mu}_{spin}$$

Theory (8/17)

$$\vec{\mu}_j = -\frac{e}{2m_e} \text{ x } \vec{L} - \frac{e}{2m_e} \cdot g_{spin} \cdot \vec{S} \qquad (11)$$

$$\vec{\mu}_j = -\frac{\mu_B}{\hbar} \cdot (\vec{L} + g_{spin} \cdot \vec{S})$$

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

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

Theory (9/17)

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.**

Theory (10/17)

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 $g_{spin} = g_j$ 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*.

Theory (11/17)

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:

$$E = \mu \cdot B \qquad (13)$$

Theory (12/17)

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:

$$\Delta E = -\Delta \mu_{orbital} \cdot B$$

$$\Delta E = \frac{e}{2m_e} \cdot \Delta L_z \cdot B \qquad (14)$$

$$\Delta E = \mu_B \cdot \Delta m \cdot B$$

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

Theory (13/17)

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

$$\Delta E = \mu_B \cdot g_j \cdot B \cdot \Delta \mu_j \qquad (15)$$

The selection rule for magnetic transitions is:

$$\Delta \mu_j = \pm 1$$

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

$$\Delta E = \mu_B \cdot g_j \cdot B \qquad (16)$$

Theory (14/17)

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:

$$E = h \cdot f \qquad (17)$$

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:

$$\mu_B \cdot g_j \cdot B_r = h \cdot f$$

Theory (15/17)

$$g_j = \frac{hf}{\mu_B B_r} \qquad (18)$$

where $h = 6.626 \cdot 10^{-34} Js\,,\ f = 146 \cdot 10^6 Hz = 146 MHz,\, \mu_B = 9.27 \cdot 10^{-24} Am^2$. After inserting these values one gets:

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

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

$$g = 10.43 \cdot 10^{-3} [\frac{Js\,Hz}{Am^2}] \cdot \frac{1}{B_r} = 10.43 \cdot 10^{-3} [\frac{Js\,\frac{1}{s}}{Am^2}] \cdot \frac{1}{B_r} = 10.43 \cdot 10^{-3} [\frac{Nm}{Am^2}] \cdot \frac{1}{B_r}$$

$$g = 10.43 \cdot 10^{-3} [\frac{N}{Am}] \cdot \frac{1}{B_r} = 10.43 \cdot 10^{-3} [T] \cdot \frac{1}{B_r} \qquad (20)$$

Theory (16/17)

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 m. For the magnetic displacement B is then valid:

$$B = \mu_0 \cdot \frac{8 \cdot I \cdot w}{\sqrt{125} \cdot R} = 0.7155 \cdot \mu_0 \cdot \frac{I \cdot w}{R} \qquad (21)$$

where $\mu_0 = 4\pi \cdot 10^{-7} \frac{Tm}{A}$ and I the current flowing through the coils. For geometrically 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:

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

Theory (17/17)

After inserting the respective values, one gets:

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

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

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

Equipment

Position	Material	Item No.	Quantity
1	ESR / NMR Basic unit	09051-93	1
2	ESR extension set	09051-00	1
3	Digital storage oscilloscope, 20 MHz, 2 channels, 100 MS/s	EAK-P-1335	1
4	Screened cable, BNC, l = 750 mm	07542-11	2

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Setup and procedure

Setup (1/2)

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Connection to the control unit

- Insert the probe into the chamber in the basic unit so that it touches the housing.
- Plug the lead from the probe into the socket “Probe In” on the control unit. Take note of the slot in the connector socket.
- Note! Always be careful when connecting and disconnecting the measuring head cable. The red dot on the connector must point in the direction of the "Sensitivity" LED. When disconnecting the plug, only pull on its housing, the plug unlocks automatically. Never pull on the cable!

Base with coils and NMR probe

Setup (2/2)

Calibration and settings

- Connect the output “SIGNAL OUT” on the control console to channel 1 of the oscilloscope and the output “FIELD OUT” to channel 2.
- Set the oscilloscope as follows:
- Channel 1: 1 V DC (0.5 V DC)
- Channel 2: 1 V DC (0.5 V DC)
- Time base: 5 ms
- Trigger settings: Channel 2

Base with coils and NMR probe

Procedure (1/3)

Note!

Mobile phones interfere with the measurement, therefore no mobile phones should be near the device during the measurement.

Use only high-quality HF cables for the measurement.

Procedure (2/3)

- Insert the glycerine sample (yellow top) into the sample chamber.
- Set the specified frequency on the control panel from the measurement report supplied (since the frequency controller is a 10-turn potentiometer, several turns may be necessary to do this).
- Set the sensitivity to medium and adjust if necessary.

At the optimum setting, the LED can be seen to flicker slightly. If the LED lights up fully, the signal is overloaded.

- Carefully adjust the fine setting using the frequency

Base unit with glycerine sample inserted

Procedure (3/3)

Note!

- A further adjustment of the signal quality is not necessary, since the NMR module is delivered factory calibrated. For the polystyrene sample (green top) the frequency will be in the same range as for the glycerine sample. For the Teflon sample (blue top) the frequency will be lower. Another experiment can be carried out in which the stalk of a plant can be inserted into the sample chamber for its resonant frequency to be determined.

Evaluation (1/3)

Evaluation

Resonant frequencies of material samples

- Glycerine (^1H) 42.58 MHz/T
- Polystyrene (^1H) 42.58 MHz/T
- Teflon (^{19}F) 40.06 MHz/T
- Plant stalk (^1H) 42.58 MHz/T

Therefore, in a constant magnetic field:

- $\nu_{Glycerin} = \nu_{Polystrol} \cdot \frac{\nu_{Teflon}}{\nu_{Glycerin}} = 0,941$
- Glycerine = 12.854 MHz
- Polystyrene = 12.854 MHz
- Teflon = 12.100 MHz

Evaluation (2/3)

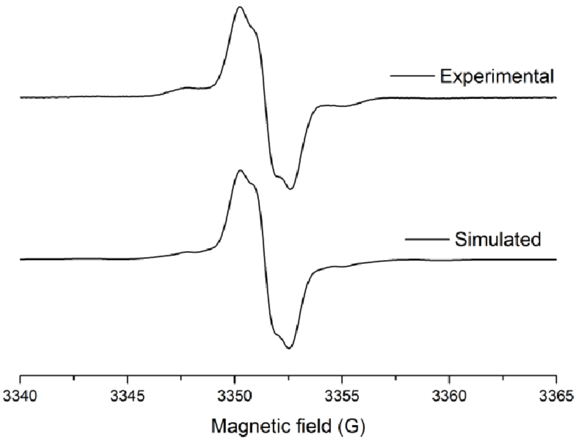
What are the factors that contribute to the inaccuracy in the measurement?

☐ An unpaired electron gains or loses angular momentum

☐ The size of the coils of the ESR-resonator.

☐ The applied voltage

Check



An example of experimental and simulated ESR spectrum

Evaluation (3/3)

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The ESR sensitivity can be increased by:

- ☐ Decreasing temperature
- ☐ Increasing magnetic field strength
- ☐ Increasing the size of coils
- ☐ Decreasing magnetic field strength

Check

What will happen, if a strong magnetic field is applied to the unpaired spins of an electron?

- ○ The electrons will be split into two groups.
- ○ An unpaired electron gains angular momentum

Check

Slide	Score / Total
Slide 31: Inaccuracy in measurement	**0/2**
Slide 32: Multiple tasks	**0/4**

Total Score ☆ **0/6**

Show solutions Retry