

Electron Spin Resonance

1. INTRODUCTION

Since electrons have charge e and are 'spinning' on their axis, they have a magnetic dipole moment $\vec{\mu}$. In the presence of an external magnetic field \vec{B} , a free electron will therefore acquire a potential energy given by:

$$E = -\vec{\mu} \cdot \vec{B} \quad (1)$$

The relationship between magnetic moment $\vec{\mu}$ and the spin angular momentum \vec{S} can be written as:

$$\vec{\mu} = \gamma \vec{S} \quad (2)$$

where γ is the gyromagnetic ratio.

You may show that if an electron is a uniform sphere with homogeneous charge distribution, one expects γ to be $e/2m$. Real electrons have a larger magnetic moment than this simple model predicts, and the discrepancy is often written in terms of the Lande g factor :

$$g = \frac{\gamma}{e/2m} > 1 \quad (3)$$

If we consider the magnetic field \vec{B} to be pointing in the z direction, the potential energy is:

$$E = \mu_z B_z = \gamma S_z B_z \quad (4)$$

We know from quantum mechanics that S_z can only have two values: $S_z = \pm \frac{\hbar}{2}$, therefore the potential energy will have only two values:

$$E = \pm \frac{1}{2} \gamma \hbar B_z \quad (5)$$

The difference in the two energies is then:

$$\Delta E = \gamma \hbar B_z \quad (6)$$

If a photon incident on an electron has an energy corresponding to this energy difference and the electron is in the lower energy state, the photon may be absorbed, inducing the electron to 'flip' its orientation: this phenomenon is *electron spin resonance*. Since the photon energy is just $h\nu$, we can re-write Eqn (6) in terms of the frequency of the incident radiation:

$$\nu = \frac{1}{2\pi} \gamma B_z \quad (7)$$

So far we have only discussed free electrons. However in chemical free radicals there is one unpaired electron per molecule and these substances are paramagnetic. These unpaired electrons are almost entirely uninfluenced by their orbital motion. Thus it is possible to

obtain a good value for the free electron gyromagnetic ratio from measurements on a free radical. This in turn will allow you to calculate the Lande g factor .

2. EXPERIMENT

The free radical you will use in this experiment is diphenylpicryl hydrazyl (*DPPH*); it is contained in the small test tube. Note that it fits neatly inside each of the three small copper coils.

The magnetic field B_z will be supplied by the two Helmholtz coils. Rather than a fixed B_z , you will use an AC current. As the field sweeps through the resonance point you will then see the absorption of the high frequency photons.

Never exceed 1 A current through the coils!

Recall that the field is most uniform when the distance between the coils is equal to their radius. Also, the central field generated by a pair of coils is given by:

$$B = \left(\frac{4}{5}\right)^{3/2} \frac{\mu_o n I}{R} \quad (8)$$

where: $\mu_o = 4\pi \times 10^{-7} (N/A^2)$

R = the radius of the coils

n = the number of turns

I = the current

You should monitor the current going into the coils both with an ammeter and by looking at the voltage drop across the supplied 1Ω resistor with an oscilloscope.

The heart of the apparatus consists of two boxes from Leybold. One, called the *ESR Basic Unit*, contains a socket for mounting one of the small copper coils containing the *DPPH* sample, a *DIN* cable, and two small knobs for controlling the strength and frequency of the high-frequency photons. The unit will generate a *RF* field inside the copper coil. The three different copper coils give you three different ranges of frequencies. Can you predict which of the copper coils will give the maximum frequency?

The other of the Leybold boxes, called an *ESR Adapter*, has:

1. *DIN* socket for connecting the *ESR Basic Unit*.
2. Inputs for +12 V DC, -12 V DC, and 0 V. You will connect these to an appropriate power supply.
3. *BNC* output, labeled *Y*, for looking at the absorption of the high frequency photons. Connect to the other channel of the oscilloscope.
4. *BNC* output, labeled $f/1000$. When connected to a frequency counter it will allow you to determine the frequency of the photons.

3. EXPERIMENTAL TIPS AND FURTHER INVESTIGATIONS

- The axis of the copper coil should be perpendicular to the external field B_z .
- If you can find a combination of frequency and current so that the two peaks have just

merged into one, then the corresponding current at resonance is just the peak current going through the coils.

- Setup the oscilloscope on internal trigger (ignore the connection from the diagram below which seems to connect the external trigger to the resistor and power supply).
- Start with the largest coil (Coil E - see diagram below).

You may also wish to ponder and/or investigate the following:

- The ESR signal may not be exactly symmetric about the maximum current point. Why?
 - Is the relation from Equation (8) true over a wide range of frequencies, i.e.: is the effect truly linear?
 - What is the physical interpretation of the width of the peak?
 - How does the Basic Unit work? What is the knob that adjusts the frequency connected to? What parameter of the circuit is being fed out of the Y socket?
- Python Requirements (PHY224/324 only): Do all the data analysis using Python. Output the gyromagnetic ratio, Lande factor.

This guide sheet has been revised by Ruxandra M. Serbanescu in 2020. Previous versions:dh-1988.