ELECTRON SPIN RESONANCE

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:

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

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

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

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* :

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

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

$$E = \mu_z B_z \qquad (4a)$$
$$= \gamma S_z B_z \qquad (4b)$$

Since we know from quantum mechanics that S_z can only have two values:

$$S_z = \pm \frac{\hbar}{2} \qquad (5)$$

the potential energy will only have two values:

$$E = \pm \tfrac{1}{2} \gamma \hbar B_z \qquad (6)$$

The difference in the two energies is then:

$$\Delta E = \gamma \hbar B_z \qquad (7)$$

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 hν, we can re-write Eqn (7) in terms of the frequency of the incident radiation:

$$\nu = \frac{1}{2\pi}\gamma B_z \qquad (8)$$

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 .

THE 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 3 small copper coils.

The magnetic :field B_z will be supplied by the 2 Helmholtz coils. Rather than a fixed B_z, you will use an AC current[1] 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:

$$B = \left(\frac{4}{5}\right)^{3/2} \frac{\mu_o n I}{R} \text{Tesla} \qquad (9)$$

where:

$\mu_o = 47\pi \times 10^{-7}$ Wb $A^{-1}m^{-1}$
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 1 Ω resistor with a scope.

The heart of the apparatus are the 2 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 3 different copper coils give you 3 different ranges of frequencies. Can you predict which of the copper coils will give the maximum frequency?

---

[1] 1. 60 Hz is very slow compared to atomic times, so the fact that the field is varying doesn't matter.

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

1. a DIN socket for connecting to 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. a BNC output, labelled Y, for looking at the absorption of the high frequency photons. Connect to the other channel of the scope.

4. a BNC output, labelled f/l000. When connected to a frequency counter it will allow you to determine the frequency of the photons.

Finally, a couple of experimental tips:

- the axis of the copper coil should be perpendicular to the extern 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.

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 Eqn (8) true over a wide range of frequencies, ie: 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?

REFERENCES

Advanced Undergraduate Laboratory Experiment 15: Electron Spin Resonance, rev. John Pitre (U of T Physics, 1988).

Leybold-Heraeus, *Instruction Sheet: ESR Basic Unit, ESR Adapter, ESR Control Unit* (Koln, 1986).

D.J .E. Ingram, *Free Radicals as Studied by Electron Spin Resonance* (Butterworth, London, 1958). QC 471 I 5

D. Harrison, Aug. 1988.

10/86 – kr – brs –

Instruction Sheet **514 55/56/57**

ESR Basic Unit
ESR Adapter

Measuring Principle:

A paramagnetic electron spin system – probe consisting of DIPHENYL-PICRYL-HYDRAZYL (DPPH) – placed between the coils of an r-f oscillatory circuit and applying a constant field, will absorb r-f energy thus measurably changing the impedance of the oscillatory circuit. The impedance change of the constant magnetic field as produced by the modulation can be displayed on an oscilloscope.

Examples of experiments:

- Verification of electron spin resonance
- Magnetic field as a function of resonant frequency (linearity of Zeeman interaction)
- Measurement of the gyromagnetic ratio and factor of g
- ESR line width
- Signal amplitude as a function of resonant frequency

1 Safety

□ Output ⑲ of the ESR control unit (magnet supply) is not overload-protected! Max. current 3 A!

2 Parts, Description, Technical Data

2.1 514 55 ESR basic unit

The basic unit consists of the following parts:

Ⓐ ESR probe holder with frequency divider 1000 : 1 and signal amplifier

Ⓑ Measuring lead to use the apparatus as a resonance meter

Ⓒ Electric resonant circuit, passive (for investigating the relationship between resonant frequency and magnetic field)

Ⓓ DPPH probe

Ⓔ, Ⓕ, Ⓖ Plug-in coils for different frequency ranges

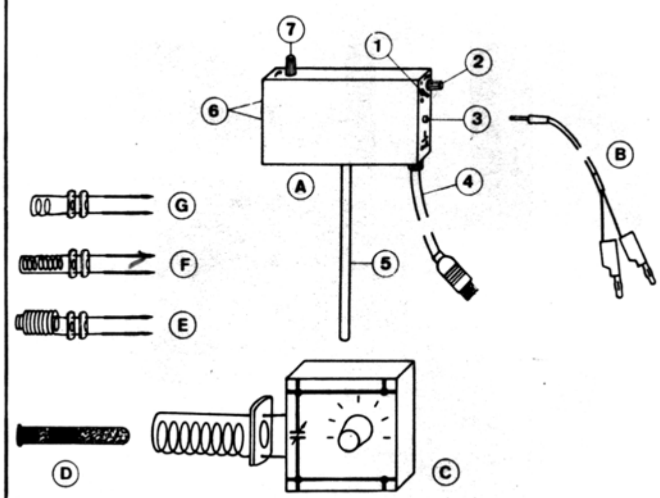

Fig. 1

Control elements:

① On/off switch
② Potentiometer for r-f amplitude adjustment
③ Socket for measuring cable Ⓑ
④ Multi-core lead for supply and signal voltages
⑤ Stand rod
⑥ Sockets for connecting the r-f plug-in coils
⑦ Variable capacitor for frequency adjustment

Technical Data:

Supply voltage and current:	±12 V/175 mA
Frequency ranges:	with plug-in coil Ⓔ: 13 to 30 MHz approx.
	with plug-in coil Ⓕ: 30 to 75 MHz approx.
	with plug-in coil Ⓖ: 75 to 130 MHz approx.
Voltage across the r-f coil: (with ref. to ground)	6 V_{pp} approx. at 13 MHz amplitude adjusted to maximum
ESR signal:	1 to 6 V approx. (depending on frequency)
Frequency divider:	1000 : 1
Frequency output for digital counter:	TTL
D. C. current (at output ③):	100 μA approx.
Test substance:	Diphenyl-Picryl-Hydrazyl (DPPH)
Frequency range of the passive resonant circuit Ⓒ:	10 to 50 MHz

2.2 514 56 ESR adapter

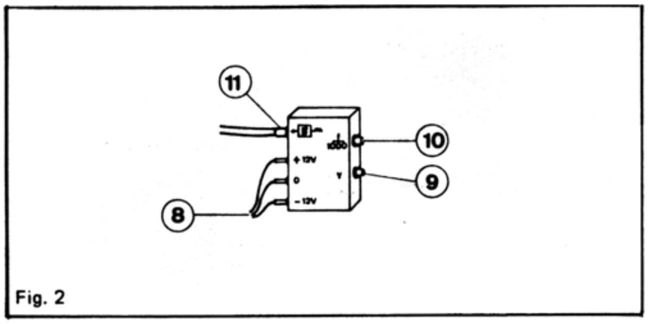

Fig. 2

Control elements:

⑧ Supply voltage connection
⑨ Signal output Y
⑩ Frequency output
⑪ Connection for the ESR basic unit (probe holder)

Technical Data:

Signal output Y:	BNC socket
Frequency output $\frac{f}{1000}$:	BNC socket
Supply voltage input +12 V, 0, −12 V:	4-mm sockets
Socket for ESR basic unit:	for 5-pin connector

3 Experiment Assemblies, Operation

3.1 Assembly for demonstrating the operating principle of the ESR basic unit (514 55)

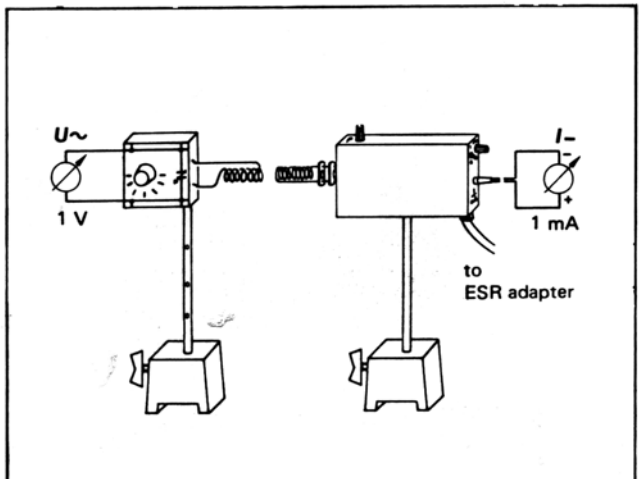

Fig. 4 U_{min} with resonance