The University of Hong Kong
Department of Physics

Physics Laboratory
PHYS3760 Physics Laboratory
Experiment No. 3760-2: Electron Spin Resonance

Name:
University No:

Aim:

To demonstrate the quantized energy of a spin in magnetic field. To determine the g-factor for DPPH (diphenyl-picryl-hydrazil).

Background:

Electron-spin resonance (ESR; synonymous with electron paramagnetic resonance EPR) is a spectroscopic method concerned with microwave-induced transitions between quantized energy levels of electron spin. The spin of an unpaired electron is associated with a magnetic dipole, which is coupled to the magnetic field. Therefore, in an applied external magnetic field, the electron spin has two energy eigenstates, i.e. spin aligned itself in one of two ways (parallel or antiparallel) with the magnetic field. These two eigenstates correspond to different eigenenergies, with the difference ΔE proportional to the magnetic field. By applying microwave radiation with frequency of ω to the sample, a transition from the lower energy state to the higher energy state can be achieved ($\Delta E=\hbar\omega$). The precise dependence of ΔE on the magnetic field, characterized by the g-factor (see Eqt. 1), depends on the surrounding electrons in the atom or molecule. In this way the position of unpaired electrons can be investigated. The obtained ESR spectra provide information regarding the bonds and structure of investigated material. The technique is used for studying free radicals and paramagnetic substances such as inorganic complexes, as well as investigation of defects in semiconductor materials.

An electron of mass m_e, with charge $-e$ and spin **J** has a magnetic moment

$$\boldsymbol{\mu} = -g_j \frac{e}{2m_e}\mathbf{J}, \qquad (1)$$

where g_j is the g-factor (Landé factor). In an external magnetic field $\mathbf{B} = B_z\hat{\mathbf{z}}$, energy levels corresponding to the different quantised orientations of **J**, $J_z = m_j\hbar$, is

$$\left.\begin{aligned}
E_j &= -\boldsymbol{\mu}\cdot\mathbf{B} \\
&= g_j \frac{e}{2m_\mathbf{e}} \boldsymbol{J}\cdot\mathbf{B} && \textbf{(from Eqt. 1)} \\
&= g_j \frac{e}{2m_\mathbf{e}} J_z B_z \\
&= g_j \frac{e}{2m_\mathbf{e}} m_j \hbar B_z . \\
\left|\Delta E_j\right| &= g_j \frac{e}{2m_\mathbf{e}} \left|\Delta m_j\right| \hbar B_z \\
&= g_j \frac{e\hbar}{2m_\mathbf{e}} B_z && (\textbf{as } \Delta m_j = \pm 1) \\
&= g_j \mu_\mathbf{B} B_z ,
\end{aligned}\right\} \qquad (2)$$

where $\mu_B = 9.274 \times 10^{-24}$ Am^2 is the Bohr magneton. In the classical point of view, the magnetic moment processes in the external field with the Larmor frequency ω_L given by

$$\hbar\omega_\mathrm{L} = \left|\Delta E_j\right|. \qquad (3)$$

EPR signal can be generated by resonant energy absorption measurements made at different electromagnetic radiation frequencies ν in a constant external magnetic field (*i.e.* you scan with a range of different frequency radiation whilst holding the field constant). Conversely, measurements can be provided by changing the magnetic field *B* and using a constant frequency radiation, which is common method in practice. Thus, the EPR spectrum is usually plotted against magnetic field or g-factor as x axis. A free electron (on its own) has a *g* value of 2.002319304386. This means that for radiation at frequency of 9.5 GHz, resonance occurs at a magnetic field of about 0.34 tesla (3400 gauss).

Experiment:

Apparatus

- A radio-frequency (RF) oscillator
- A plug-in coil (frequency range: 20–80 MHz)
- A DPPH sample

- A pair of Helmholtz coils
- A Hall probe
- A multimeter
- An ESR control unit
- A 2-channel oscilloscope

Set-up

(see Fig. 1)

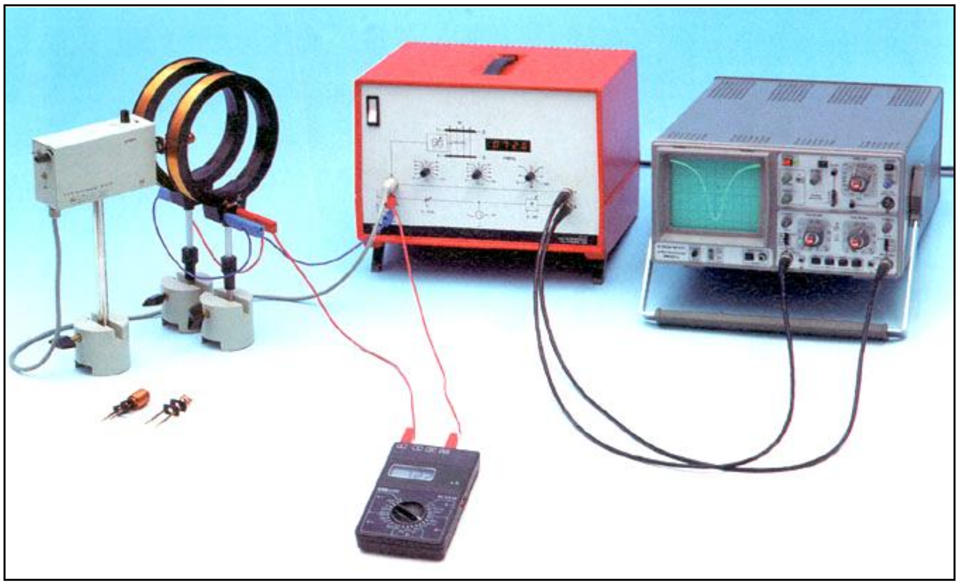

Figure 1. Set-up.

Procedure:

With g_j of the order of unity the resonance condition can be fulfilled in a field of about 1 mT at a radio frequency of about 20 MHz, or in a much stronger field of about 1 T at a microwave frequency of about 20 GHz. In this experiment we adopt the radio frequency region.

1. Separate the two Helmholtz coils by their mean radius. Connect them in serial so that they carry current in the same direction. Use the magnet supply in the ESR control unit to pass a current I from 0 to 1.5 A through the coils. With the modulation voltage off (the "I~" knob at its zero position), use the Hall probe to calibrate the field at the center of the configuration. Calibrate the magnetic field by plotting the magnetic flux density B against the current I.
2. Connect the RF oscillator to the ESR control unit and insert the plug-in coil (with the DPPH sample placed inside it) into the oscillator. Position the plug-in coil at the centre of the Helmholtz configuration so that the axis of the plug-in coil is

perpendicular to the applied field. Use the B Signal and the ESR Signal of the control unit as the inputs to the X- and the Y-channels of the oscilloscope. Set the oscilloscope to the "X-Y" Mode. With the supply voltage for the Helmholtz coils set to zero, adjust "I~" (which is a 50 Hz signal) to give a peak-to-peak amplitude *Maximum* on the X-channel. Do not readjust this setting of "I~" for the rest of the experiment.

3. For some values of the frequency, adjust the magnetic field current to reveal an absorption dip on the oscilloscope. Fine adjust this current so that the minimum of the dip lies at the centre of the oscilloscope screen (in symmetry). This then corresponds to the maximum absorption, or in other words resonance is taking place. As there will probably be two such dips observed, adjust the "PHASE" knob on the control unit until these two dips coincide. Plot the resonance frequency f_r (note $\omega_r = 2\pi f_r$) against the magnetic flux density B. Hence determine the g-factor g_j for the DPPH sample from the slope of the plot.

   Note that error analysis should be included in the calculations.

References:

1. A.C. Melissinos, *Experiments in Modern Physics* (Academic Press, New York, 1966).
2. A. Yariv, *Theory and Applications of Quantum Mechanics* (Wiley, New York, 1982).