

Electron spin resonance at radio frequencies

Aims and Objectives

- Understand the phenomenon of electron spin resonance (ESR).
- Determine the g -factor for unpaired electrons in the free-radical compound *dpph*.
- Determine the width and lineshape of the ESR line and the relaxation time associated with the transition.
- Use a lock-in amplifier to measure a small AC signal in the presence of noise and to understand how it works.

Introduction

An electron spin in a magnetic field has two energy eigenstates: ‘spin up’ and ‘spin down’, relative to the field. Transitions between these two states can be brought about by an oscillating magnetic field - this is called electron spin resonance (ESR). It can be observed at radio frequencies (RF) by placing a sample inside the coil of an L-C tuned circuit (the ‘tank’ circuit). A Robinson oscillator makes the tank circuit oscillate with an amplitude that decreases as the energy losses in the sample increase. Hence, ESR may be detected as a decrease in the oscillator signal level when the ESR frequency of the sample matches the RF frequency of the oscillator. The oscillator circuit is described in the appendix.

Background

In a magnetic field, B , a free electron has two spin states, labelled by the spin quantum numbers $m_s = \pm 1/2$, which are separated in energy by an amount $\pm g\mu_B B/2$, where μ_B is the Bohr magneton (the constant that describes the magnetic moment of a free electron), and g is the Landé g -factor. A g -factor is a dimensionless number that links the observed magnetic moment of a particle to its angular momentum quantum number and the appropriate fundamental unit of magnetism (in our case the Bohr magneton).

An external electromagnetic field can induce transitions between these two states (electron spin resonance) when the frequency of the external electromagnetic field satisfies the resonance condition:

$$h\nu = g\mu_B B. \quad (1)$$

The resonance is characterised by two parameters: (i) the magnitude of the field at resonance, B_0 , and the half width, ΔB . The half-width ΔB of the ESR line corresponds to an energy width (or relaxation time)

$$\Delta E = \frac{h\nu}{B} \Delta B \quad (2)$$

Can you derive this?

for the transition. With these two pieces of information, you can obtain the g -factor and the relaxation time of the system. The ESR linewidth is mainly due to spin-spin interactions between electrons, which are independent of the magnetic field B . Therefore, at radio frequencies, the ESR line is quite broad.

Dirac showed that $g = 2$ for a free electron. (In fact, the precise value including a small correction to Dirac's theory due to quantum electrodynamics, is 2.002319304386, and this difference from 2 has been measured.) However, for an unpaired electron confined in a solid, g may vary, because the effective magnetic field acting on the electron is altered by the local environment. In fact, the changes in g are used as a probe of the material in question, in typical ESR experiments. The half-width ΔB may also vary from specimen to specimen, due to interactions with electrons on neighbouring ions of molecules, and so the electronic structure of a given material can be probed.

What is ESR used for today?

In this experiment, you will investigate ESR in 2,2-diphenyl-1-picrylhydrazyl (*dpph*), $(C_6H_5)_2N-NC_6H_2(NO_2)_3$. This compound has a free radical that behaves very much like a free electron. It has a sharp ESR line, whose g -factor is accurately known. It is therefore commonly used as a g -marker to calibrate ESR spectrometers. You will investigate the width and detailed lineshape of the ESR line, and determine the g -factor for *dpph*.

Experimental Method

The main connections are shown in Fig. 1. The sample is placed inside the coil of the tank circuit of a Robinson oscillator, whose output signal is sensitive to tank-circuit losses. ESR is detected as a decrease in the RF level when the ESR frequency matches the frequency of the oscillator (see Fig. 2a). The oscillator frequency is about 50 MHz. You can monitor the RF signal and measure its exact frequency using an oscilloscope and frequency counter.

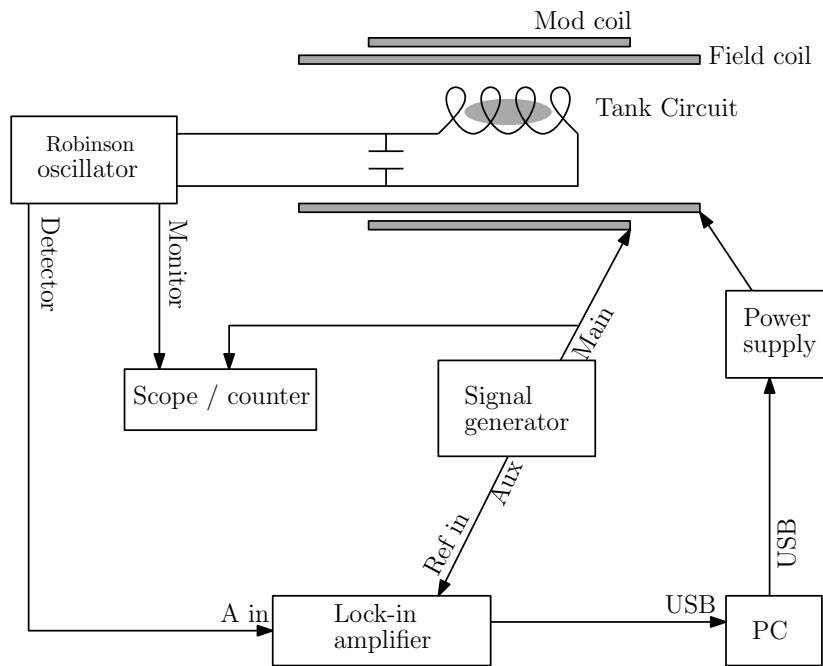


Figure 1: Main connections in the experiment. The tank circuit contains the *dpph* sample

The ESR frequency, ν , is tuned by varying the external magnetic field B . This is done using a solenoid connected to a ramp generator, which sweeps the current applied to the solenoid at a steady rate. The solenoid field coil has 445 turns and is 15.2 cm long. Approximately what current is needed to generate the desired field?

The solenoid is not infinitely long, and non-uniformity of the magnetic field can broaden the ESR line, and so the sample should be placed where the field is most uniform. You should also consider whether the magnetic field of the Earth, and mains-frequency magnetic interference are important. A Hall probe and magnetic shield are available.

How does non-uniformity broaden it?

The power absorption we are trying to measure is very small. One reason for this is that, at room temperature, the Boltzmann distribution causes the occupation of the high- and low energy spin states to be nearly equal, while absorption relies on there being more electrons in the lower state than the upper state. The electronics amplifies the small changes in the RF level, but cannot avoid also amplifying intrinsic electrical noise and any interference. The usual solution to this problem is to modulate the signal of interest at a known low (“audio”) frequency (e.g. 120 Hz), and use a lock-in amplifier to measure signals at just this frequency; noise at other frequencies is effectively filtered out by the lock-in amplifier.

Calculate $N_{\text{upper}}/N_{\text{lower}}$

In the complete experiment, the main, steady magnetic field is swept slowly up through resonance by a software-controlled power supply that supplies current to the solenoid.

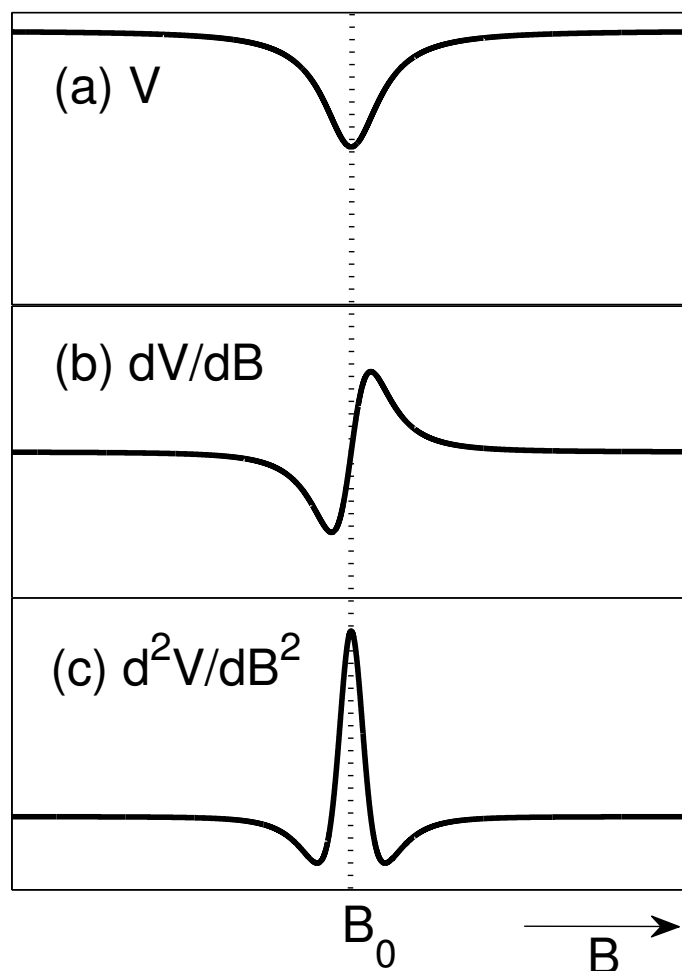


Figure 2: (a) The variation of RF output level V with magnetic field B . (b) The first derivative of the absorption line as a function of magnetic field B . (c) The second derivative of the absorption line as a function of magnetic field B .

At the same time, a smaller audio frequency field is superimposed by a second solenoid (the “modulation coil”) that is wound on top of the main solenoid. The modulation coil is driven by an audio signal generator. The signal generator also supplies a reference signal to the lock-in amplifier, which effectively tells it what frequency to look for at its input. The application **Lfesr** controls the field sweep and records the output from the lock-in amplifier. You will need to set the audio signal generator and lock-in amplifier controls appropriately.

You should be able to show that the change in the RF level V due to the oscillating magnetic field is

$$\delta V(t) = \frac{dV}{dB}(\delta B) \cos(\omega t) + \frac{1}{2} \frac{d^2V}{dB^2}(\delta B)^2 \cos^2(\omega t) \quad (3)$$

Hint: use Taylor's theorem.

where δB is the amplitude of the field modulation at angular frequency ω , and higher order terms are neglected.

The first term of the expansion oscillates at the audio frequency, $f = \omega/(2\pi)$. Its amplitude is proportional to the first derivative, dV/dB , of the RF level with respect to magnetic field (see Fig. 2b).

The second term of the expansion is proportional to the second derivative d^2V/dB^2 . This term oscillates at frequency $2f$. Fig. 2c shows how this second derivative varies with magnetic field.

Can you show this?

The lock-in amplifier can measure the signal at either the fundamental frequency f or the second harmonic $2f$, and so it can measure both the first and second derivatives of the ESR line. The derivatives show the line shape more clearly than the line itself, so it is usual to leave the data in derivative form when reporting it.

Possible investigations

Examine how the XY-plots depend on the following parameters:

- the amplitude of the modulating field,
- the frequency of the modulation,
- the phase setting of the lock-in amplifier,
- the time constant used to smooth the output of the lock-in amplifier,
- the position of the *dpph* in the coils.

Explain your observations, and use them to obtain the clearest picture of the ESR signal. Determine the g -factor and linewidth, and compare with published values for $dpph$. What is the lineshape of the electron spin resonance? The linewidth of the resonance can be related to a relaxation time. What is the physical meaning of this, and how does it relate to the electron spin in the magnetic field?

Hint:
Lorentzian?
Gaussian?
Voigt?

Appendix: The Robinson oscillator

An obvious way to measure the losses in a parallel LCR tuned circuit is to drive it with a current of constant amplitude at its resonant frequency $\omega : i_{RF} \sin \omega t$. At resonance, the inductive and capacitive reactances cancel, and the circuit behaves like the resistor R that represents its losses. Thus the voltage across the tuned circuit is $R i_{RF} \sin \omega t$, which can be amplified and its amplitude measured, giving a result proportional to R .

This arrangement is known as a Q meter (from the quality factor, Q). Its drawback is that any deviation of the driving frequency from the resonant frequency will have a large unwanted effect on the measured amplitude. The Robinson oscillator solves this problem by making the current source part of an oscillator whose frequency is determined by the LCR circuit. Thus the tuned circuit is always driven on resonance. This clever arrangement was invented by FNH Robinson, a British physicist who specialised in NMR.

Appendix: The lock-in amplifier

It is worth finding out in detail how a lock-in amplifier works, because the technique is very powerful for measuring small signals in the presence of noise. Here is a quick mathematical model. The input we wish to measure is $S \cos(\omega_s t + \phi_s)$, a signal of known frequency ω_s , whose amplitude S we wish to know. We know ω because we have modulated the source of the signal at that frequency, by modulating a field, chopping a light beam, or a similar trick. We will also be able to find out the phase of the signal ϕ_s , with respect to the modulation. This signal arrives accompanied by the noise of many interfering signals, represented as $N \cos(\omega_n t + \phi_n)$. N may be much larger than S , but crucially, $\omega_s \neq \omega_n$. Thus the input is

$$S \cos(\omega_s t + \phi_s) + N \cos(\omega_n t + \phi_n) + \text{many other noise terms.} \quad (4)$$

The lock-in uses its reference input to form a reference signal of unit amplitude and fixed phase, $\cos(\omega_s t + \theta)$. It then multiplies the whole input signal this by this reference. The trigonometric identity $\cos A \cos B = \frac{1}{2}(\cos(A + B) + \cos(A - B))$ implies

that there will be only one zero-frequency term in the resulting product, $\frac{1}{2}S \cos(\phi - \theta)$, which gives us the desired value S . All the other terms will be at frequencies of $2\omega_s$ and $\omega_s \pm \omega_n$. The lock-in follows the multiplication by averaging the result over a time τ , using an electronic integrator or low-pass filter. This does not affect the zero-frequency component, but the average over a large number of cycles of any of the other, oscillating, terms is zero, so they vanish from the output. It is necessary to set τ to be shorter than the time scale over which the signal size is expected to vary, but long enough to integrate away the $\omega_s - \omega_n$ terms. There is therefore a tradeoff between the speed with which the signal can be allowed to vary, and how far ω_n needs to be from ω_s before it is rejected.

In practice, one adjusts the reference phase θ to maximise the output signal, which occurs when $\theta = \phi$. Many lock-ins have a second channel with a reference 90° away from the first channel, so that both in-phase and quadrature components of the signal can be captured at once.

Recommended Reading

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R. P. Feynman, *Lectures on Physics, Vol. II*, Chapters 34 & 35, Addison-Wesley, Reading, Massachusetts (1964).

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EB 2009-08-06
MSC 2016-09-15