Electron Spin Resonance

Laboratory & Computational Physics 2

Last compiled August 8, 2017

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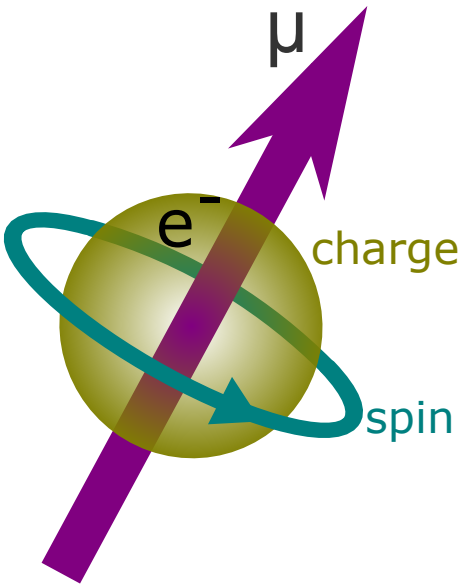


1.1 Introduction

In 1896, Pieter Zeeman observed that atomic spectral lines split when the sample atom was placed in an external magnetic field. In 1922, Stern and Gerlach passed silver atoms through a magnetic field, observing the original beam splitting in two in the presence of the field. Both of these observations were explained in 1925, when Uehlenbeck and Goudsmit postulated that the splitting of atomic spectra was due to an *intrinsic* angular momentum they denoted **spin**. This property *couples* to the orbital angular momentum of the electrons and gives rise to the observed splitting. This *spin-orbit coupling* is a fundamental force in atomic and subatomic physics. While such a feature has been incorporated extensively in the Schrödinger equation to describe phenomena (nuclear physics couldn't work without it), a true understanding of spin-orbit coupling came in 1929 with Dirac and his eponymous equation. Spin was the first quantum observable introduced which has no classical analogue.

In this experiment we will study the Zeeman splitting of spectra from a molecule, diphenyl-picra-hydrazyl (DPPH), which has an unpaired electron on one of the nitrogen atoms. It has features which allow for the spin of the electron to be studied in isolation.

1.2 Prelab questions

1. Use equation 14 to show that when an electron is placed in an external field, its energy changes by
$$\Delta E = \pm\frac{1}{2} g_s \mu_B B \ . \tag{1}$$

2. Calculate the value of the external magnetic field necessary such that a photon, wavelength $\lambda = 450$ nm, has the required energy to flip the spin of the electron. Why then

may we ignore the background light when performing the experiment? You may wish to comment on why this number is so large.

3. Why can't truly free electrons be used in this experiment? Why is a beam of electrons or a metal inappropriate?

4. Let R be the radius of a pair of Helmholtz coils, separated by that same distance R. If x denotes the distance from the centre of the left hand coil to any point along that axis, calculate the magnetic field produced at points $x = 0.2R$ and $x = 0.5R$. Remember that the field produced by one coil with n turns carrying a current I is given by

$$B = \frac{\mu_0 n I R^2}{2\left(x^2 + R^2\right)^{3/2}}. \tag{2}$$

5. Draw a diagram showing the paths of the magnetic fields from the Helmholtz coils, showing that the field is roughly constant in our area of interest.

6. What exactly do the Helmholtz coils produce when in operation for this experiment, in comparison to the RF generator? 'A magnetic field' is only part of the answer.

2 Background theory

2.1 Angular Momentum in quantum mechanics

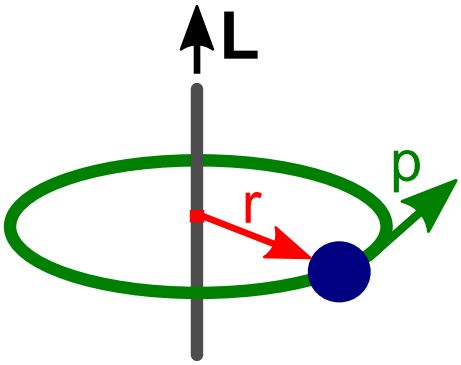


Figure 1: The cross product of the position vector, **r** and the momentum vector, **p** resulting in the angular momentum, **L**.

2.1.1 Quantum angular momentum

The quantum mechanical analogue of classical angular momentum is orbital angular momentum. For a particle moving in a circular path around a fixed point in space, its angular momentum is defined as in the orbital classical case:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \, . \tag{3}$$

Where **L** is the angular momentum, **r** is the position vector of the particle, and **p** is the momentum vector of the particle, as shown in figure 1.

2.1.2 Quantum orbital momentum

Quantum mechanical orbital angular momentum is quite different from the classical case.

We will start with noting some quantum numbers required to describe atomic states. The *principal* quantum number, n corresponds to the 'shell' an electron occupies in an atom. As electron shells are themselves quantised, the principal quantum number is similarly quantised and may take positive integer values beginning at one. That is,

$$n = 1, 2, 3, \ldots \tag{4}$$

The next quantum number of interest is the *orbital angular momentum* quantum number, l. This number is the value of the electron's orbital angular momentum. It can take values of zero and positive integers, up to a maximum value of $n - 1$. That is,

$$l = 0, 1, 2, \ldots, n - 1. \tag{5}$$

To give some more physical insight, $l = 0$ corresponds to an s-orbital, $l = 1$ corresponds to a p-orbital, $l = 2$ corresponds to a d-orbital, and so on...

We also need to consider the *projection* (sometimes called *magnetic*) quantum number, m_l. This describes the direction in space the orbital angular momentum vector of an electron may point. Or, more specifically, m_l is the value of the projection of the vector onto some quantisation axis. This number can take values from $-l$ to $+l$ in integer steps, with negatives included as our projection can also be negative. For example, if $l = 2$, then $m_l = -2, -1, 0, 1, 2$ (and these would correspond to the five different types of d-orbitals that exist). That is,

$$-l \leq m_l \leq l \tag{6}$$

So for any given value of l, there exist $2l + 1$ projections.

2.1.3 Energy states

The above picture, however, is incomplete. We only observe the above projections in the presence of a magnetic field. For a particle moving in a magnetic field, the splitting is due to an induced magnetic moment:

$$\boldsymbol{\mu} = \frac{e\hbar}{2m_e}. \tag{7}$$

For an atom, comprising of (an even number of) electrons, Z, the **total** magnetic moment is the **sum** of the magnetic moments induced by each orbiting electron. This amounts to the splitting into $2l + 1$, or m_l, levels, with the energy levels defined by:

$$E = m_l B \mu_B, \tag{8}$$

So for *even-Z* atoms, there are an *odd* number of energy states, arising from the $2l + 1$ dependence.

In the above equation, B is magnetic field strength and μ_B is the Bohr magneton:

$$\mu_B = \frac{e\hbar}{2m_e}\ . \tag{9}$$

2.2 Empirical observations and spin

So for an even-Z atom, we have an odd number of energy levels. Conversely, for odd-Z atoms, the number of split levels is observed to be *even*. This was observed most strikingly in 1922 by Stern and Gerlach. They passed a beam of silver atoms through a magnetic field and observed that the beam split into two.. Remember that silver has $Z = 47$ which means that there is one odd electron in its configuration.

An even number of energy levels must lead to the conclusion that l is *half*-integer! If there are $2l + 1 = 2$ levels, then l cannot be a whole number, but rather *half*-integer. Specifically, $l = \frac{1}{2}$.

In 1925 Uehlenbeck and Goudsmit postulated that the electron therefore must contain an *intrinsic* angular momentum, which they called *spin*, with a value of $\frac{1}{2}$ for the electron. This additional intrinsic angular momentum then induces an additional magnetic moment in the presence of a magnetic field, which is given by

$$\boldsymbol{\mu}_s = g_s \frac{e\hbar}{2m_e}\mathbf{s} \tag{10}$$

where $\mathbf{s}$ is the spin of the electron. $g_s = 2$ is called the g-factor.

If we consider the spin vector s as we did orbital angular momentum l, we can project the spin vector onto an arbitrary axis and spin magnetic values, m_s, are taken from $-s$ to $+s$ in integer steps. For the electron, $s = \frac{1}{2}$ so its projection values are $m_s = \pm\frac{1}{2}$. We call the positive 'spin-up' and the negative 'spin-down'. Having only two m_s values explains the splitting of the silver atom beam into two in the Stern-Gerlach experiment.

It is important to know that not all particles have half-integer spin. Particles with whole integer spin (0, 1, 2) are called *bosons*, which includes photons, gravitons, the Higgs boson. Particles with half-integer spin (1/2, 3/2, 5/2) are called *fermions*, which includes quarks and leptons (electron, muon, etc).

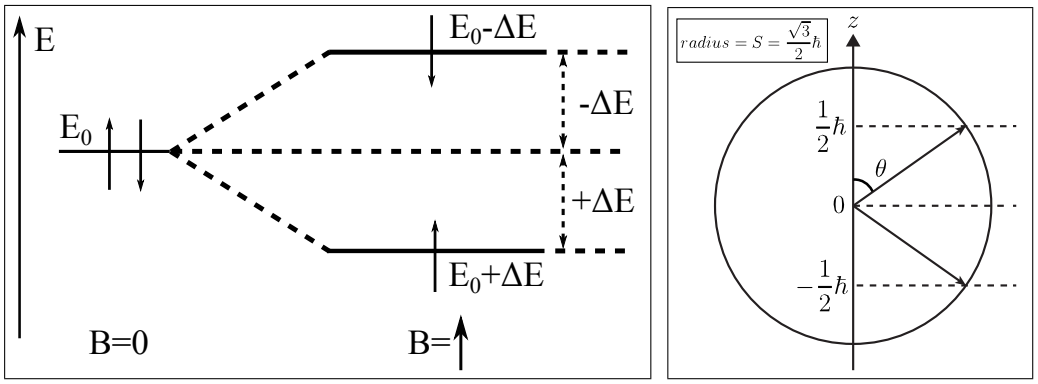
2.2.1 An aside about spin

Two important properties of spin should be noted:

1. It is a fundamental property of particles;
2. **There is no classical analogy for it.**

This second point is particularly important. Don't try to imagine particles actually spinning or a particle with half spin being "half as spinning" as a particle with whole spin. If it helps, call the spin property 'spyn' or 'spinn', whatever takes away the notion of spinning, dizzying particles.

2.3 The Zeeman effect



(a) (b)

Figure 2: (a) Energy splitting for an electron in a uniform magnetic field B, with direction as indicated. Note that, from equation (14), the value of ΔE is *negative*. (b) Depiction of the spin-up and spin-down states, with their projections, against some quantisation axis z. In the presence of a magnetic field, the field would point in the z direction.

For an electron moving in a magnetic field, each of its angular momentum components (orbital, l and spin, s) induces a magnetic moment

$$\boldsymbol{\mu_L} = \frac{-e}{2m_e}\mathbf{L} \qquad \text{and} \qquad \boldsymbol{\mu_S} = g_s\frac{e}{2m_e}\mathbf{S} \tag{11}$$

where $\mathbf{L}$ and $\mathbf{S}$ are given by

$$\mathbf{L} = \hbar\sqrt{l(l+1)} \qquad \text{and} \qquad \mathbf{S} = \hbar\sqrt{s(s+1)} \tag{12}$$

In the presence of a magnetic field, the spin component in the z direction becomes quantised, and remembering that for an electron, $m_s = \pm\frac{1}{2}$, we have

$$S_z = m_s\hbar = \pm\frac{1}{2}\hbar \tag{13}$$

In the case of this experiment, we will be examining the single valence, quasi-free electron in the organic molecule diphenyl-picra-hydrazyl (DPPH). This electron only possesses an induced magnetic moment from its spin (so only $\boldsymbol{\mu_S}$), and so we will limit the rest of the discussion to this.

When an electron is placed in a magnetic field it interacts with the field through its spin magnetic moment. This induces a change in energy of the electron, depending on the direction of the electron's spin in the field. This change is given by:

$$\Delta E = -\boldsymbol{\mu_s}\cdot\mathbf{B} \tag{14}$$

The direction of the spin is defined relative to the external magnetic field. The leading negative sign indicates that a spin-up electron will be in a lower energy state than a spin-down electron.

To switch the electron between the spin and down energy states requires an additional energy of

$$\Delta E' = hf = g_s \mu_B B \tag{15}$$

where g_s is the Landé g factor, B is the strength of the external field and μ_B the Bohr magneton, defined in equation 9. The hf term is included as the additional energy is typically provided by photons.

The Landé g factor is from theory (in particular, Dirac's equation) exactly 2. However, due to various quantum mechanical effects, g_s for the electron has been measured as 2.002319. It is g_s that you will be looking to measure in this experiment.

2.4 Resonance absorption

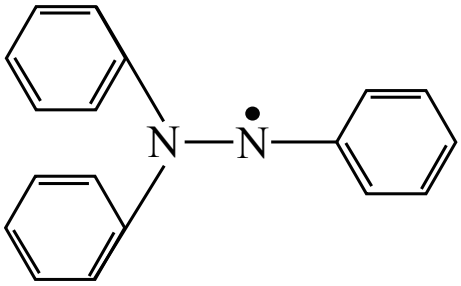


Figure 3: The DPPH molecule showing the isolated unpaired electron in the molecular configuration.

The electrons in this experiment are is the provided by the organic molecule diphenyl-picrahydrazyl, or DPPH (Fig. 3). This molecule is convenient in that it has one valence, unbonded electron on the second N atom. The interaction of that electron with the mean Coulomb field generated by the other electrons in the molecule ascribe an energy E_0 to it.

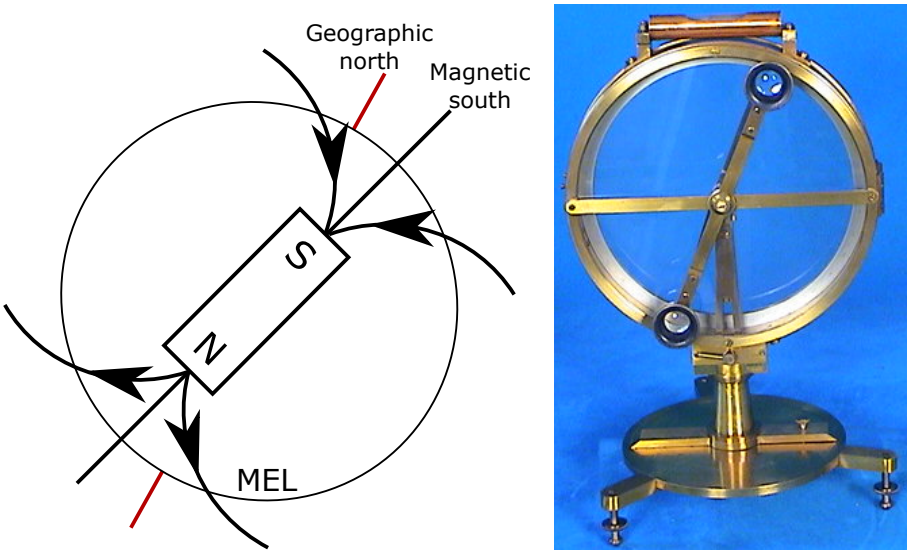
As well as having an unpaired electron, DPPH has a predominantly spin-down molecular configuration. The lifetime of the spin-up state is also short, so we're easily able to flip the electron spin and observe the changes.

Under these conditions, we then have a source of photons with frequency f. Looking back at equation 15 we can write

$$hf = g_s \mu_B B. \tag{16}$$

As before there is a B dependence, due to the increasing energy level splitting with increasing magnetic field. To determine a value for g_s, we will fix the magnetic field value and scan through frequency to observe the electron spin resonance. The experiment should engineer the apparatus to place the photon frequency outside of the wavelength range of any background light.

2.5 The Earth's magnetic field



(a) (b)

Figure 4: (a) Representation of the Earth's magnetic field. (b) Dip circle currently on display in the physics museum. Photo courtesy Mr. Phil Lyons.

We can see from equation 16 that our value of g_s will depend on accurate measurements of the photon frequency f and the magnetic field B. We are controlling f by placing the photons outside of the range of background light. For the magnetic field though, we should consider the effect of the Earth's magnetic field.

An instrument called a dip circle can be used to determine the inclination (or 'dip') of the Earth's magnetic field at our location. Dip circles take a bit of calibrating, and are easily startled, so instead you can use the website below to look up a calculated value using a model:

`http://www.ngdc.noaa.gov/geomag-web/#igrfwmm`

This will give you nice values for the strength and three-dimensional orientation of the Earth's magnetic field at Melbourne.

This will give you a better value for the magnetic field experienced by the DPPH electron.

3 Equipment

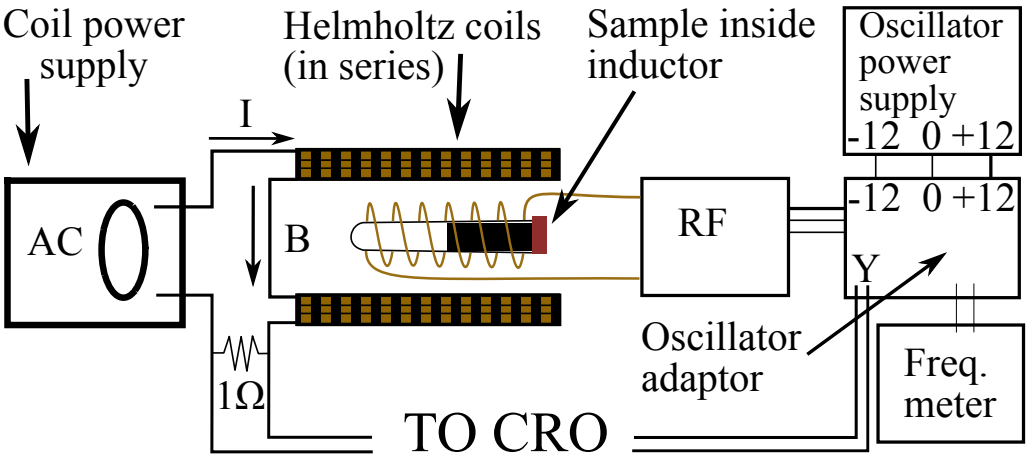


Figure 5: The field generated by the coils is in the direction as indicated. The AC supply is 50 Hz, and the voltages indicated are in V.

Helmholtz coils

The Helmholtz coils are the large rings which carry current on the desk. The coils will be connected to an AC power supply (50 Hz), so the current will vary sinusoidally with time.

Radio frequency (RF) oscillator

The RF oscillator **provides the photons** needed to excite the electrons between states to examine resonance absorption. It converts a signal into a magnetic field and back again. The field produced periodically bathes anything within the coil in a sea of photons of the frequency selected using the knob on the unit.

The oscillator can produce photons with frequencies between 30 and 130 MHz depending on the coil attached. (Smaller coils are higher frequency.) On the rear of the oscillator you can connect a micro-ammeter to the socket marked '$I/\mu A$'. The ammeter then monitors the current flowing through the unit.

The tank circuit

Also included is what is termed a 'tank' circuit. It's a standalone unit with no wires and consists of a variable capacitor connected to a coil of wire similar to the one on the RF unit. The circuit is actually an LC circuit and will resonate at the frequency f, determined by the values of capacitance C, and inductance L, where

$$f^{-1} = 2\pi\sqrt{LC}. \tag{17}$$

With the frequency supplied by the RF emitter. The tank circuit is simply used to demonstrate the idea of resonance. The tank circuit resonance is not later used for in observing the electron spin resonance.

4 Procedure

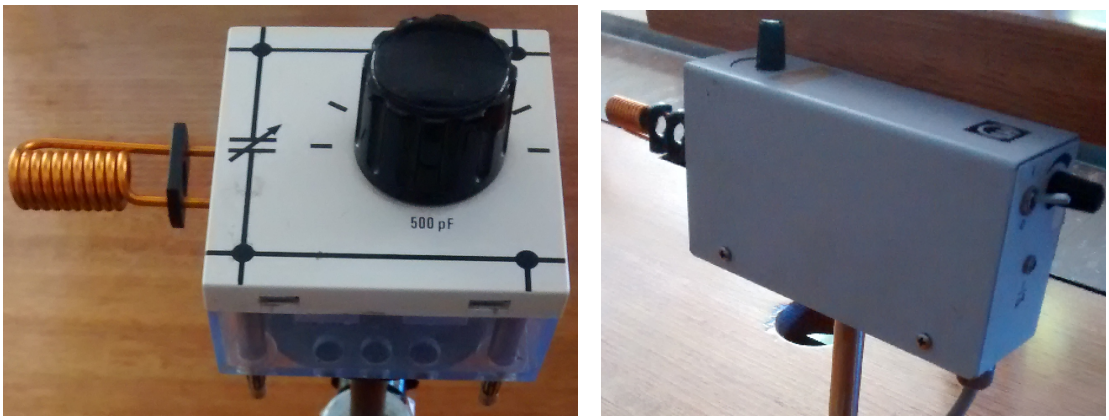


Figure 6: (a) the tank circuit and (b) the RF emitter.

4.1 Setting up the equipment

The equipment has been disassembled for you to assemble. On your bench you will find:

- the tank circuit (Fig. 6a)
- the RF emitter (Fig. 6b)
- two Helmholtz coils on a stand
- a power supply for the coils
- the DPPH sample in a glass vial
- a box of RF coils
- an oscilloscope
- various cables
- a 1 Ω resistor

With the equipment powered OFF and disconnected from the mains, plug in the appropriate cables from the power supply to the RF emitter, as in figure 5. We'll connect the Helmholtz coils later.

4.2 Investigating the resonance

Turn on the RF unit and use the multimeter to measure the oscillation frequency from the '$f/1000$' output of the oscillation adapter. Now, observe resonance between the RF unit and the tank circuit:

1. Bring the tank circuit up to the RF unit such that the coils are ALMOST touching (make sure the RF unit is outside of the Helmholtz coils).

2. Connect the tank circuit up to the CRO to monitor the voltage across the capacitor.
3. Slowly adjust the variable knob on top of the tank circuit until the voltage observed on the CRO reaches a maximum. This indicates resonance.
4. If you don't observe a maximum you may have to change the frequency of the RF unit as tank variable capacitor has a limited range.
5. When you have determined the resonance point, use the ammeter to examine the current through the RF unit.

Question 1 *What is happening in both the tank circuit and RF emitter as you move in and out of the resonance? Explain.*

4.3 Investigating other coils

You'll see a box of RF coils on the desk. These fit in to the RF emitter **ONLY**, and NOT the tank circuit.

Put a different coil in the RF emitter and perform your resonance investigation again.

Question 2 *Do you notice any difference using a different coil? Is the resonance as strong with two different sized coils or is it the same but at a different frequency?*

Put aside the tank circuit. Take a moment to consider what you observed and how this will later apply to the resonance of the electron spins in the DPPH molecule.

4.4 Setting up the coils

Now connect the Helmholtz coils, including the 1 Ω resistor.

Question 3 *Should the Helmholtz coils be connected in parallel or in series? If it helps, draw a diagram to understand.*

You can verify the the coils are working correctly using the Gaussmeter. You can also bring the bar magnet between the coils and you should experience a force.

Position the Helmholtz coils correctly using the dial caliper ensuring that they are connected correctly and in series with the resistor and AC supply. 'A' identifies the beginning of the coils and 'Z' the end. The mean diameter of the coils is 13.6 cm and the number of turns in each is 320. Remember that the equation for the magnetic field produced by the Helmholtz coils is given as:

$$B = \frac{\mu_0 n I R^2}{2\left(x^2 + R^2\right)^{3/2}}. \tag{18}$$

Question 4 *Draw a voltage vs. time graph for the voltage across the resistor for two full periods of the AC signal. Assuming a peak-to-peak voltage of 5 V across the coils, draw the B vs. time graph for the coils. Why do we use a 1 Ω resistor?*

4.5 Introducing the DPPH sample

The sample of DPPH is contained in a vial. Note that the DPPH is the black powder; the white material is a cotton bud[1].

Gently place the sample within the coil of the RF unit, then place the RF unit centrally in between the Helmholtz coils on the mounted holder.

Question 5 *Draw the B vs. time graph through the coils that indicates the strength of the uniform field experienced by the electrons in the DPPH sample. Under this plot draw the current you would expect to measure through the RF oscillator. Discuss with your demonstrator.*

Question 6 *The relaxation time of the electrons back to the ground state should be short, compared to the frequency of the sweeping B field. Why is this?*

4.5.1 Measuring spin resonance

After everything is connected:

1. Examine the voltage across the resistor and the current through the RF unit simultaneously.
2. Vary the current through the Helmholtz coils.
3. What happens to the current through the RF unit as you adjust the Helmholtz coil voltage?
4. What do you observe on the oscilloscope?

Question 7 *Draw a graph of what changes as you adjust the coil current. Explain the changes.*

You should now be able to determine how best to measure B when resonance occurs.

Question 8 *How will you reduce the error in measuring B while observing resonance? Should you limit B to below certain values?*

Question 9 *Why do we observe a width on the resonance peak?*

Now take specific measurements of the voltage at which resonance occurs, as a function of RF frequency. Change the frequency dial on top of the RF emitter, then slowly change the coil voltage. At what values of f and B do you obtain resonance peaks? Relate it back to the necessary equations to find g_s.

Question 10 *How does your value for g_s compare to the nominal $g_s = 2$? How could you improve this result?*

[1] In case you (I) thought the sample might have been 'burnt' by the photons...

4.6 The Earth's magnetic field

We now want to consider what effect, if any, the Earth's magnetic field is having on our experiment. Use the website

`http://www.ngdc.noaa.gov/geomag-web/#igrfwmm`

to look up values for the magnitude and direction of Earth's magnetic field in Melbourne. Draw a diagram relative with values so you have a clear idea of the information.

We also need to know the cardinal directions so we can align the Helmholtz coils with the Earth's magnetic field. Use the compass provided to determine this. Again, draw a diagram.

Question 11 *Why do we only need a compass and not a dip circle to determine the direction of the Helmholtz magnetic field?*

1. Turn the power supply to the Helmholtz coils off, and disconnect them.
2. Carefully re-orient the Helmholtz stand so the magnetic field they produce is in addition (parallel and in the same direction) to the Earth's magnetic field.
3. Take a second measurement where the Helmholtz field is still parallel but in the *opposite* direction.

Question 12 *What qualitative changes do you notice in the resonance peaks after re-orienting the system?*

Question 13 *Is the equipment sensitive enough to determine the relative orientation of the B field from your first measurement, based on your g_s values?*

5 Appendix: Useful data

Quantity	Value
μ_B, Bohr magneton	9.2740×10^{-24} A m^2
μ_0, magnetic constant	1.2566×10^{-6} H m^{-1}
e, elementary charge	1.6022×10^{-19} C
m_e, electron rest mass	9.1096×10^{-31} kg
h, Planck constant	6.6261×10^{-34} J s
$\hbar$, reduced Planck constant	$h/2\pi$