Electron Spin Resonance

Andrew D. Missert\textsuperscript{1,*} and Peter Thompson\textsuperscript{1,†}

\textsuperscript{1}Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627

We attempt to observe the energy level structure due to spin in several substances. We place the substance in a magnetic field to align the magnetic moments, then we expose it to an electromagnetic wave. At the right frequency, the oscillating magnetic field present in this wave will cause some of the electrons to switch to the other energy level. Initially, there are more electrons in the lower energy state than the upper, so the switch will result in a net absorption of energy. We can use the frequency and magnetic field strength that cause this absorption to figure out the Lande factor of the substance.

An electron in a magnetic field possesses a magnetic dipole moment quantified by its spin quantum number. When an electromagnetic wave of the right frequency is applied, usually in the microwave realm, the dipole moment may change and the electron will emit or absorb energy. This is known as electron spin resonance. This technique is often used to study free radicals.

An electron in an atom with orbital angular momentum \( \vec{L} \) and spin angular momentum \( \vec{S} \) will have corresponding orbital and spin angular momenta

\[
\vec{\mu}_{\text{orbital}} = -\frac{e}{2m} \vec{L}
\]

\[
\vec{\mu}_{\text{spin}} = -\frac{e}{m} \vec{S}
\]

The total magnetic moment is the sum of these:

\[
\vec{\mu}_{\text{total}} = \vec{\mu}_e = -\frac{e}{2m} [\vec{L} + 2\vec{S}]
\]

Consider a magnetic dipole with moment \( \vec{\mu} \) oriented at an angle \( \theta \) to a homogeneous magnetic field \( \vec{B} \). There will be a torque \( \vec{\tau} = \vec{\mu} \times \vec{B} \) on the dipole. We can express the potential energy of the dipole as

\[
V(\theta) = -\int_0^\theta \vec{\tau} \cdot d\vec{\theta} = -\vec{\mu} \cdot \vec{B}
\]

Thus, the potential energy of the electron in a homogeneous magnetic field is

\[
V = \frac{e}{2m} [\vec{L} + 2\vec{S}] \cdot \vec{B}
\]

This product is the same as the product of the projection of each multiplicant in the direction of the total angular momentum, \( \vec{J} = \vec{L} + \vec{S} \):

\[
V = \frac{e}{2m} \frac{(\vec{L} + 2\vec{S}) \cdot \vec{J}}{\vec{J}} \vec{B} \cdot \vec{J}
\]

which simplifies to

\[
V = g\mu_BB m_j B
\]

where \( \mu_B = \frac{e\hbar}{2m_e} \), \( m_j = \frac{j}{2} \), and \( g = 1 + \frac{\Delta j(j+1)+s(s+1)+l(l+1)}{2j(j+1)} \). \( g \) is called the Lande g-factor.

Consider a very large number of electrons in a homogeneous magnetic field. We can use Boltzmann factors to determine the proportional populations of the lower and upper energy states. That of the upper energy state is

\[
\frac{N_{+\frac{1}{2}}}{N_{\text{total}}} = \frac{\exp(-g\mu_BB)}{\exp(-g\mu_BB) + \exp\left(\frac{2\Delta E}{kT}\right)}
\]

and that of the lower is

\[
\frac{N_{-\frac{1}{2}}}{N_{\text{total}}} = \frac{\exp(\frac{2\Delta E}{kT})}{\exp(-g\mu_BB) + \exp\left(\frac{2\Delta E}{kT}\right)}
\]

Notice that the population of the lower state will always be greater.

Now we apply an electromagnetic wave perpendicular to the magnetic field. If the energy in the wave, \( E = \hnu \), equals the energy difference between the two electron quantum states, \( \Delta E = \mu_BB \), some of the electrons will switch to the other state. This is called resonance. If we know the frequency of the wave and the magnitude of the magnetic field, we can calculate the Lande g-factor:

\[
g = \frac{\hnu}{\mu_BB}
\]

The number of electrons of each state that switch is proportional to the initial number of electrons in that state, so there will be more electrons jumping from the lower state to the upper than vice versa. Thus there will be a net absorption of energy by the group of electrons.

The layout of the experimental setup used in the ESR experiment is elucidated in Fig. 1. The microwave radiation is generated by the klystron apparatus and transmitted via waveguides. The microwaves have a constant pure frequency \( \nu_0 \) which is set by the klystron which is stabilized by the reference cavity. The first step in our experimental procedure was to find a clean klystron mode. With the attenuators leading to the sample cavity and magic tee fully closed, the reference cavity was tuned to give a sharp dip in the center of the klystron mode. The value of the frequency of this klystron mode was found.
FIG. 1: Schematic diagram of the experimental apparatus used to measure the ESR phenomenon. 1. attenuator 2. detector 3. magic tee 4. phase shifter

using the wavemeter. The signal at detector above the wavemeter was maximized using the tunable short. The wavemeter was then turned so as to minimize the signal, thereby finding the frequency $\nu_0$. The value was calculated to be $\nu_0 = 8.887 \text{GHz}$

this is consistent with the results of Sliwa and Richard (2008) and Farwell and Predergast (2004) [1] [2]

With the frequency found, the Lande g-factors for various paramagnetic materials can be calculated by finding the magnitude of the static field, $H_0$, at resonance. Ideally, $H_0$ is found by sweeping the magnetic field in the sample cavity via the voltage supply while simultaneously monitoring the power at the magic tee via the oscilloscope. The oscilloscope was set to add the signal from one arm of the magic tee to an inverted signal from the other arm. When the magnetic field is at resonance, it will absorb microwaves to make the state transitions and there will be a decrease in power at the magic tee, and a corresponding drop in the observed power on the oscilloscope.

The sample adiphenyl – β – picrylhydrazyl (DPPH) is a particularly good substance to measure ESR since it has almost free spin electrons and is a strong absorber of microwaves. Since it is a spin 1/2 system, the Lande g-factor should have a theoretical value of 2. With the sample in the cavity and the alternating coils set at an appropriate frequency of 40Hz at 10 Volts, we attempted to find resonance. The primary sweeps had a large range of magnitudes, from about 0-7 kG and showed no signs of resonance. Since our value for $\nu_0$ was comparable the that of Farwell and Predergast (2004) [2], who used the same apparatus, we honed our range to be centered around their value of 3.14 kG. Using the Gaussmeter we found the range of current which produced a fields between 2.5 and 4.5 kGauss to be about 5.1-10.5 Amps. We swept carefully and slowly along this range, searching for the power drop characteristic of resonance. No such power drop was found however, even when the oscilloscope was at its most sensitive setting of 10mV. The observed result was a steady voltage on the oscilloscope that was remained unchanged as the magnetic field was varied.

Since the expected results where not found, much time was spent adjusting and fine-tuning the equipment. The reflected signal was minimized using the tunable short in the sample cavity and the phase shifter. The tunable shorts of each arm of the magic tee were adjusted to ensure maximum power at the detectors, and the attenuator was adjusted to balance the power. The function generator was tested on the oscilloscope to verify that it was outputting the correct shape, frequency, and voltage. The sweep frequency and sensitivity of the oscilloscope was adjusted to all possible settings. When no resonance was observed, we changed the oscilloscope to AC setting and tried to detect any decreases in amplitude or other such abnormalities. The frequency of the oscillating magnetic field was adjusted via the function generator from the recommended value of 40Hz to values between 20Hz and 60Hz. After each adjustment of the apparatus, we performed a field sweep in the the range where resonance was expected, however no resonance was detected. The procedure was repeated with a sample of $\text{Cu}_2\text{S}_0\text{S}_4$. No resonance was observed in this sample as well.

The observation of no resonance power dips is contrary to the theory of electron spin resonance, but consistent with the results of K. Sliwa and B. Richard (2008) who observed no resonance using the exact same experimental setup. [1] The failure of this experiment to detect the spin resonance likely is a result of a subtle but crucial equipment error. The klystron was the only piece of equipment not tuned or tampered with in either our experiment or that of Sliwa (2008) and could be source of error. We did not have enough time to adjust the klystron since a blown fuse in the magnet power supply proved difficult to replace and set the experiment back by nearly a week.

The only significant fluctuation observed during a field sweep was a brief period of instability occurring at a current value of 9A. This corresponds to $H_0 = 3.3kG$ Which would give a g-factor of 1.797, significantly different from the expected value of 2. Since this result could not be reproduced, it was most likely a random fluctuation. Further experimentation is necessary to achieve experimental confirmation of the electron spin resonance effect in DDPH.

* Electronic address: amissert@gmail.com
† Electronic address: pthompso@mail.rochester.edu

