Electron Paramagnetic Resonance

Tianyi Zhou, Fan Zhang

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Abstract

In this experiment we studied the electron paramagnetic resonance in organic compound DPPH. We produce a microwave with constant frequency 9GHz using a microwave generator, measure the interference of one signal that is absorbed and reflected by DPPH sample and another reflected signal which is out of phase and observe the resonance signal on scope using lock-in amplification. The magnetic field is ramped at a low frequency to sweep through resonance region and modulated at a high frequency for detection purpose. We find that the input-output characteristics of the diode detector have a transitional region near 5dBm input power. We observe the absorption signal at $H = 3326.63 \pm 223.32$Gs. And we find the g factor of electron to be $g = 1.9338 \pm 0.1356$ and spin-spin relaxation time to be $T_2 = 19.7 \pm 2.1$ns.

1 Introduction and Theory

1.1 Electron Spin Resonance

1.1.1 Spin Precession

For an free electron, the magnetic moment is given by

$$\vec{\mu} = -\mu_B(\vec{L} + g\vec{S}) \tag{1}$$

where μ_B is the Bohr magneton and g_e is the electronic g-factor. The energy of the free electron is simply given by

$$E = -\vec{\mu} \cdot \vec{H} \tag{2}$$

We now consider the simplest case where the orbital angular momentum is zero $\vec{L} = 0$, in the presence of a magnetic field, the two fold degeneracy of spin energy will be broken. The energy level is given by

$$E = \pm\frac{1}{2}g\mu_B H \tag{3}$$

and the energy difference between spin up and spin down state is

$$\Delta E = g\mu_B H \tag{4}$$

If the electron absorbs energy from a weak RF(radio frequency) electromagnetic field(microwave field in our experiment) where

$$\Delta E = h\nu_R = g\mu_B H \tag{5}$$

then the electron will transit from lower energy state to higher energy state. And the frequency ν_R is the resonant frequency where the absorption occurs.

1.1.2 Resonant Absorption and Relaxation

In the frequency domain, the absorption is not infinitely narrow due to several origins. In this experiment, we are going to examine the Lorentzian line-shape function $f(\nu)$

$$f(\nu) = \frac{1}{1 + (2\pi T_2(\nu - \nu_R))^2} \tag{6}$$

which describes the shape of the absorption line. In this equation, T_2 is known as spin-spin relaxation time, ν_R is the resonant frequency. Thus, the FWHM is given by $\Gamma = 2/2\pi T_2$.

1.2 Sample Information

Sample used in this experiment is chemical compound diphenyl-picryl-hydrazil(DPPH). As shown in figure 1, it has one unpaired valence electron in one of the nitrogen atom. In this free nitrogen atom, 6 electrons pair off and contribute no orbital angular momentum. The field produced by the surrounding lattice make this nitrogen atom to be 'quenched', where the orbital angular momentum is almost zero. In this case, the electron behaves almost like a free electron with no orbital angular momentum.

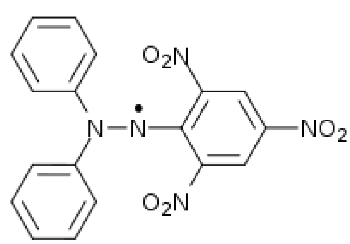

Figure 1: Molecular structure of DPPH, black dot above nitrogen atom denotes the one unpaired electron

2 Setup and Procedures

In order to observe the resonance, a good tuning of the apparatus is the key point. This is the most important and the most time-consuming part in this experiment. Therefore, we will spend a great deal of time in this report talking about setups and apparatus tuning. Setup is shown in figure 2.

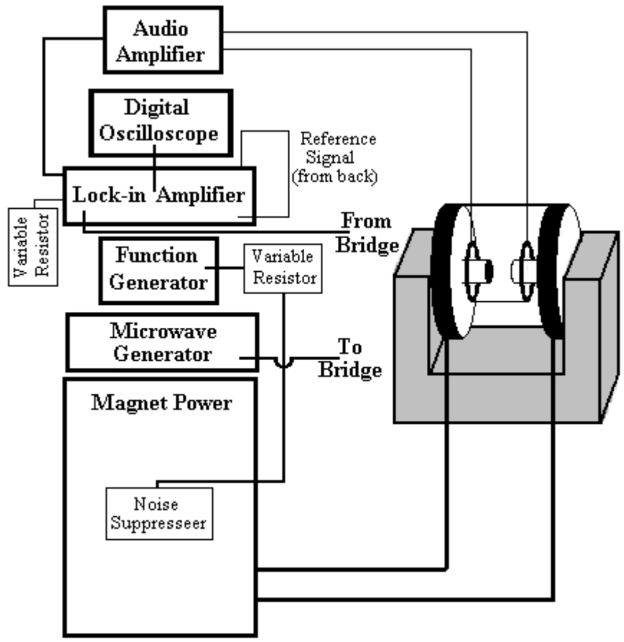

Figure 2: Setup of the resonance detection

2.1 Microwave Generator and Magnet

Microwave generator consists of a sweep oscillator and an RF plug-in. It produces the electronic oscillations at certain frequency or at a range of sweeping frequency. In this experiment, we keep the frequency of the microwave and change the magnitude of the magnetic field to detect the resonant signal. We set the central frequency to be 9GHz and the input power to be 10dBm.

The constant magnetic field is provided by the big magnet. We can change the magnitude of the magnetic field by changing the current directly, or through the external input of the magnet power supply. As shown in figure 2, the external input is connected to a function generator in series with a variable resistor. Due to the equipment internal constraint, we first adjust the current to get a magnetic field near the resonant value, then apply the triangle wave with low frequency (0.05Hz) and amplitude of 0.5V to the power supply to slowly sweep through the resonance region.

2.2 Waveguide Spectrometer and Magic T

The generated microwaves will be directed and controlled using rectangular waveguides. Here X-band(8 to 12 GHz) waveguides are used and it electromagnetic waves propagate in TE_{10} mode. After passing through an isolator, which allows for the passing of the power in one direction but not in the reverse, the microwave enters the magic T. Magic T has four ports, connected to the isolator, sample arm, reference arm and detector arm respectively. The relative orientation of the arms let the incident microwave undergo a 180 degree phase shift between waves in sample and reference arm. And the returning signal from these two arms undergo destructive interference and and enters the detector arm without phase shift.

Thus what we observe will directly be the difference of two signals.

Mathematically, let the incident wave into two arms to be $E_{s,0}cos(\omega t)$. Wave returning from sample arm $E_s(t)$ is the sum of reflected incident wave and wave due to resonant absorption. Wave returning from reference arm passes through an attenuator and a phase shifter. Waveforms are given as follows:

$$E_s(t) = E_{s,0}cos\omega t + E_{s,0}(a\ cos\omega t + b\ sin\omega t) \tag{7}$$
$$E_r(t) = E_{r,0}cos(\omega t + \varphi) \tag{8}$$

where a and b are some function of magnetic field H due to absorption and dispersion, respectively. We first adjust the phase shifter on the detector arm so that the the diode detector picks up the maximum signal of the standing wave. Next we adjust the attenuator on the reference arm(i.e. adjusting $E_{r,0}$) to ensure there is no reflection of signal on this device. Then the phase shifter is adjusted so that phase difference in Eq. 7 and Eq. 8 is sure to be 180 degrees.(i.e.$\varphi = 180°$). In this well balanced case, the combination of the two signal is

$$|E_s(t) + E_r(t)|^2 = |(\Delta E + E_{s,0}a)cos\omega t + E_{s,0}bsin\omega t|^2 \tag{9}$$
$$= [\,(\Delta E)^2 + 2a\Delta E E_{s,0}]\,cos^2\omega t + ... \tag{10}$$

where higher order of a and b terms are dropped because a and b are small quantities so that $a, b \ll \frac{\Delta E}{E_{s,0}}$. And the output voltage we detected is proportional to time average of combined signal

$$V_D \sim \langle |E_s(t) + E_r(t)|^2 \rangle_t = (\Delta E)^2(\frac{1}{2} + \frac{aE_{s,0}}{\Delta E}) \tag{11}$$

2.3 Phase Sensitive Detection

The output picked up by the diode detector is quite small so that lock-in amplifier is used to pick out the resonance signal from the background noise. The key point of the lock-in amplification process is that, the output signal is the product of reference and return signals, which is a DC signal after a low pass filter, with amplitude proportional to the cosine of phase difference between reference and return signals.

Additionally, the output signal is the derivative of the resonance signal due to field modulation. We modulate the magnetic field using modulation coils driven by an audio amplifier shown in figure 2. As the magnetic field is modulated with constant amplitude at the reference frequency, the response of the output signal at the same frequency has the amplitude proportional to the slope of the absorption signal.

2.4 Data Taking Highlight

Before operating the main magnet, we need to calibrate the dependence of the magnetic field on input current and voltage using gauss meter. In order to reduce error, we first do the probe zeroing by inserting the probe in zero gauss chamber. Besides, since in most of the time we are using 10k scale range on the gauss meter, reading by eyes might bring errors. So we make use of the output jacks on the gauss meter to provide the electrical output with better stability and accuracy. It outputs voltages with 1 volt for full scale and proportional to the magnetic field at the probe.

3 Data Analysis

3.1 Diode Detector Characteristics

We first set up the initial apparatus to do the calibration of the output voltage and input microwave power. We set the microwave frequency to be 9GHz, and varying the input power from -5dBm to 20dBm. Since the measurement of power is in units of dBm, [2]

$$\mathrm{dBm} = \log_{10}(\mathrm{P}/1\mathrm{mW}) \tag{12}$$

where P is in untis of mW. We plot the log of output voltage of diode detector vs microwave input power in figure 3. We can see that the the output voltage dependence of input power does not always follow square-law. For small signals when input power ranges from -5dBm to 5dBm, output voltage is proportional to RF input voltage squared(i.e. power). For input above 5dBm, the output voltage is proportional to the input voltage. We assume this transitional curve is due to some characteristics of the rectifying process of the diode detector.

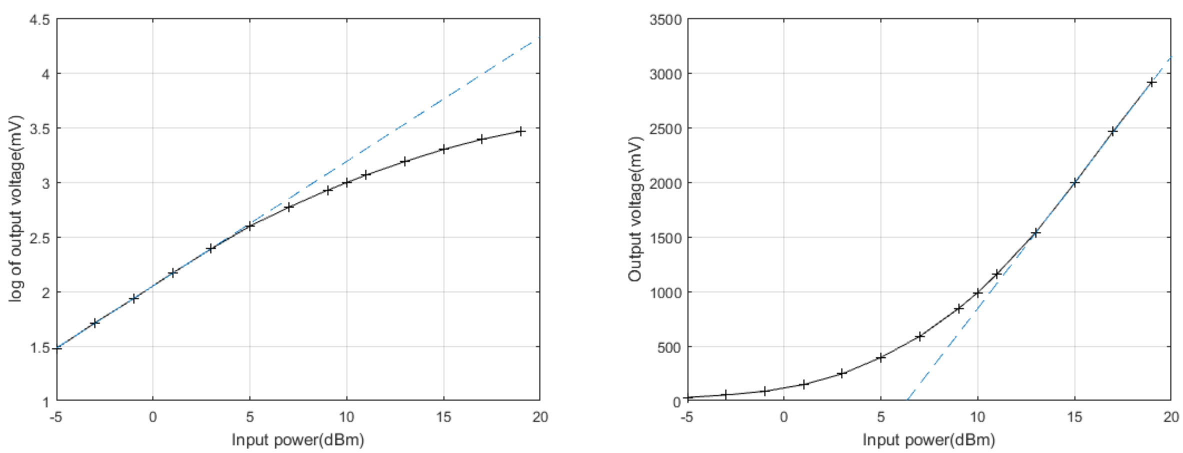

Figure 3: The diode detector output voltage characteristics plot in log of V vs P(left) and V vs P(right), same data points in both figures. Blue dashed line is a straight line fitted with first 5 data points(left) and last 4 data points(right)

3.2 Calibration of Magnetic Field Dependence on Input

We employ the data taking method described in section 2.4 and do the calibration of magnetic field dependence on input current and voltage. The calibration result of input current and voltage is shown in figure 4. Error in measuring magnetic field is ±2.25% of full scale and ±1.3% of reading according to the manual of F.W. Bell Gaussmeter Model 620. [3] We can see that the H field linear dependence on current not valid in high current input region. We attribute this nonlinear behavior to be the effect of hysteresis of field caused by interaction between the main magnet and the sweep coil. We can clearly see from the right plot in figure 4 that the error bar is obviously too big for the fit. And also, the scale change affects the value greatly as we can see a obvious rise of all data points using 10k scale range on the gauss meter. This inconsistence of data may arise from the internal structure of gauss meter. Now if we exclude the first 4 data points, and scale the error bar down to±0.65%, we will get a more reasonable H-V dependence as shown in figure 5. All data fitting used here are least-squares fit, fitting result is given in section 3.3.2.

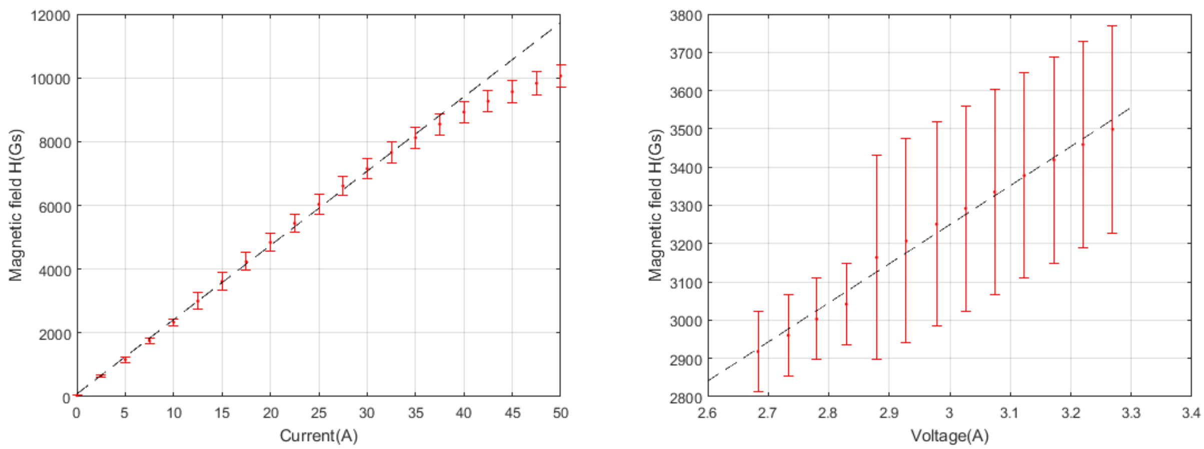

Figure 4: The dependence of magnetic field H on input current I(left) and input voltage(right). Fit of the H-I line is based on first 21 data points, nonlinear region data points are excluded. Fit of the H-V line is based on all 13 data points.

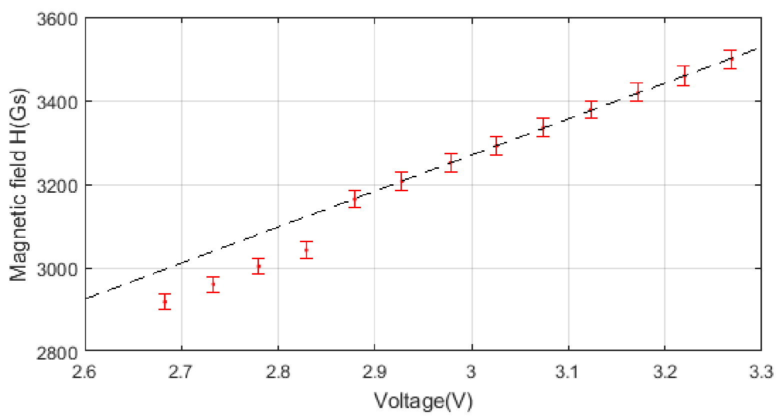

Figure 5: Dependence of magnetic field H on input voltage with scaled smaller error bar, first 4 data points excluded

3.3 Resonance Signal and Calculations

3.3.1 Resonance Detection

After we tune the apparatus described in section 2, the absorption signal is observed as shown in figure 6. This signal is inverted vertically, we assume this implies that the reference signal in lock-in amplification is off phase. Luckily, it makes no influence on the determination of resonance frequency. We set the magnet power to be 28.1% of full scale, which is 14.05A when full scale is 50A. When the absorption signal(channel 1) hits minimum and maximum, the input voltage(channel 2) is -20mV and -24mV, respectively.

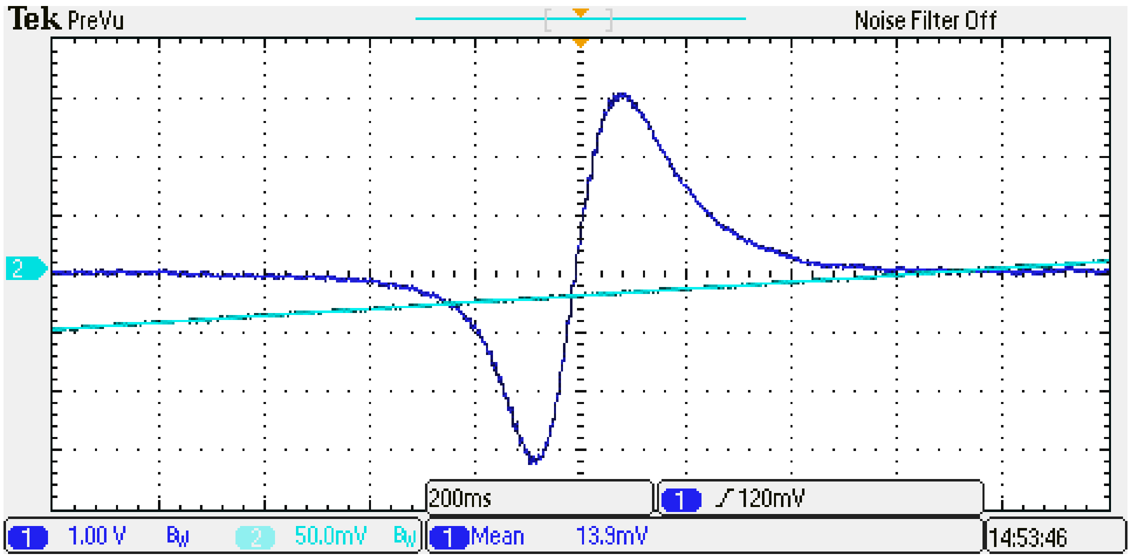

Figure 6: Resonance signal observed on the oscilloscope

3.3.2 Determination of g Factor and T2 Time

Bohr magneton is $\mu_B = e\hbar/2m_e = 9.27\times10^{-24}$J/T and with Eq. 5 we get the Lande g-factor is given by

$$g = \frac{h\nu}{\mu_B H_R} \tag{13}$$

where H_R is the magnetic field at resonance. The absorption signal is in the shape of Lorentzian function described in Eq. 6, and we observe the first derivative of this signal due to field modulation in the lock-in amplification. So we take the first derivative of Eq. 6 to get

$$\frac{df(\nu)}{d\nu} = -\frac{8\pi^2 T_2^2(\nu-\nu_R)}{[\,1+(2\pi T_2(\nu-\nu_R))^2]^{\,2}} \tag{14}$$

Let $\frac{df(\nu)}{d\nu} = 0$, we will get $\nu = \nu_R$, which is exactly we see in figure 6. Then we take second derivative to examine T_2.

$$\frac{d^2 f(\nu)}{d\nu^2} = -\frac{8\pi^2 T_2^2[\,12\pi^2 T_2^2(\nu-\nu_R)^2-1]}{[\,1+(2\pi T_2(\nu-\nu_R))^2]^{\,3}} \tag{15}$$

Let $\frac{d^2 f(\nu)}{d\nu^2} = 0$, we will get

$$\nu = \nu_R \pm \frac{1}{2\sqrt{3}\pi T_2} \tag{16}$$

That is to say, the frequency difference between observed signal hits maximum and minimum $\Delta\nu$ is given by

$$\Delta\nu = \frac{1}{\sqrt{3}\pi T_2} \tag{17}$$

Replace frequency difference by magnetic field difference through Eq. 5, we get the spin-spin relaxation time T_2

$$T_2 = \frac{h}{\sqrt{3}\pi\mu_B g\Delta H} \tag{18}$$

where $\Delta H = |H_1 - H_2|$, H_1 and H_2 is the magnitude of magnetic field corresponds to minimum and maximum observed signal. Therefore, we just need the value of H_R and ΔH to determine g and T_2.

The straight line fit in figure 4 and figure 5 gives

$$H_i = a_1 I + b_1 \text{ with } \mathrm{a}_1 = 235.4 \pm 3.3\mathrm{Gs/A}, \quad \mathrm{b}_1 = 38.79 \pm 2.75\mathrm{Gs} \tag{19}$$

$$H_v = a_2 V + b_2 \text{ with } \mathrm{a}_2 = 862.6 \pm 57.4\mathrm{Gs/V}, \ \mathrm{b}_2 = 681.9 \pm 176.1\mathrm{Gs} \tag{20}$$

Therefore, known the initial offset current $I_0 = 14.05A$, $V_R = -22\mathrm{mV}$, $\Delta V = 4\mathrm{mV}$, we can calculate that

$$H_R = 3326.63 \text{ Gs} \tag{21}$$

$$\Delta H = 3.450 \text{ Gs} \tag{22}$$

Substitute these into Eq. 13 and Eq. 18, we get

$$g = \frac{h\nu}{\mu_B H_R} = \frac{6.626 \times 10^{-34} \times 9 \times 10^9}{3326.63 \times 10^{-4} \times 9.27 \times 10^{-20}} = 1.9338 \tag{23}$$

$$T_2 = \frac{h}{\sqrt{3}\pi\mu_B g\Delta H} = \frac{6.626 \times 10^{-34}}{1.73205 \times 3.1416 \times 1.9338 \times 9.27 \times 10^{-24} \times 3.450 \times 10^{-4}} = 19.7\mathrm{ns} \tag{24}$$

3.3.3 Error Analysis

Error analysis in this section mainly focuses on the calculation of error propagation. The error originates from the process of data taking when we calibrate the dependence of magnetic field on input parameter, mainly comes from the uncertainty of the reading on gauss meter. This is already included in the fitting process and shows in the uncertainty of fitting parameters. Besides, the oscilloscope we use in this experiment has 8-bit resolution, giving us an uncertainty in V so that $\sigma_V = 1.95 \times 10^{-4}$V. [4]

$$\sigma^2_{H_R} = H^2_R[\frac{\sigma^2_V}{V^2_R} + \frac{\sigma^2_{a_2}}{a^2_2}] \tag{25}$$

$$\sigma^2_{\Delta H} = \Delta H^2[\frac{\sigma^2_{a_2}}{a^2_2} + \frac{\sigma^2_V}{\Delta^2_V}] \tag{26}$$

$$\sigma^2_g = g^2\frac{\sigma^2_{H_R}}{H^2_R} \tag{27}$$

$$\sigma^2_{T_2} = T^2_2[\frac{\sigma^2_{\Delta H}}{\Delta H^2} + \frac{\sigma^2_g}{g^2}] \tag{28}$$

With $V_R = 0.022$V, this gives

$$\sigma_{H_R} = 223.32 \text{ Gs} \tag{29}$$

$$\sigma_{\Delta H} = 0.285 \text{ Gs} \tag{30}$$

$$\sigma_g = 0.1356 \tag{31}$$

$$\sigma_{T_2} = 2.1 \text{ ns} \tag{32}$$

Finally, we calculate that the resonance magnetic field H_R, ΔH, g factor and T_2 are given by

$$H_R = 3326.63 \pm 223.32 \text{ Gs} \tag{33}$$

$$\Delta H = 3.450 \pm 0.285 \text{ Gs} \tag{34}$$

$$g = 1.9338 \pm 0.1356 \tag{35}$$

$$T_2 = 19.7 \pm 2.1 \text{ ns} \tag{36}$$

4 Conclusion

In this experiment we investigate the electron paramagnetic resonance and find that the EPR signal of DPPH occurs at $H = 3326.63 \pm 223.32$ Gs, the g factor of electron is $g = 1.9338 \pm 0.1356$ and spin-spin relaxation time is $T_2 = 19.7 \pm 2.1$ ns. Compared to the established value $g = 2.0023$, our result is quite reasonable for a 3.48% relative error and the 'true' value lies within 1σ region.

The key point of this experiment lies in good tuning of the apparatus. We have to familiarize ourselves with the waveguide spectrometer phase-sensitive detection before we try to sweep the magnetic field to find the resonance signal. Due to the extension of last experiment, there is no enough time left for us to play with the lock-in amplifier and the scope.

The error produced in this experiment mainly comes from the calibration of magnetic field. The gauss meter we use is F.W. Bell Gaussmeter Model 620. The manual of this gauss meter gives detailed accuracy description and we follow this to determine our error in measuring the magnetic field. But the plot in section 3.2 shows the error bar is far too big. If we simply take this tolerance value as our error of measurement, the fitting parameter will get a huge uncertainty. Therefore, in our fitting process, we scale down the error bar. A gauss meter with higher accuracy might be needed to get a more precise g factor.

Furthermore, as shown in the lab manual [2], greater sensitivity of transition between energy levels is achieved at low temperatures. If we can work in low temperature, a better measurement of g factor can be made.

References

[1] A. C. Melissinos and J. Napolitano, *Experiments in Modern Physics*, (Academic Press, New York, 2003).

[2] *EPR lab manual*, available at
`https://wiki.brown.edu/confluence/display/PhysicsLabs/PHYS+2010+Lab+Files`.

[3] *Manual of Gaussmeter*, available at
`https://wiki.brown.edu/confluence/pages/viewpage.action?pageId=1164129&preview=/1164129/1164132/620-Manual.pdf`.

[4] P.R.Bevington, D.K.Robinson *Data Reduction and Error Analysis for the Physical Sciences*, (McGraw-Hill, New York, 2003).

Appendix
A.1 MATLAB codes of fitting

```
%Plot log of output voltage vs input power
p = xlsread('power.xlsx','A2:A15');
V = xlsread('power.xlsx','G2:G15');
logV = log10(V);

p5 = p(1:5);
V5 = logV(1:5);

load census;
f = fit(p5,V5,'poly1');
ff = fit(p(11:14),V(11:14),'poly1');

figure
plot(p,logV,'k')
hold on
plot(p,logV,'k+')
hold on
plot(f,'--')

xlabel('Input power(dBm)')
ylabel('log of output voltage(mV)')
grid on

figure
plot(p,V,'k')
hold on
plot(p,V,'k+')
hold on
plot(ff,'--')

xlabel('Input power(dBm)')
ylabel('Output voltage(mV)')
grid on
axis([-5 20 0 3500])

%Plot magnetic field vs input current
%Import data
I = 0.5*xlsread('IBdata.xlsx','B3:B23');
H = xlsread('IBdata.xlsx','F3:F23');
err = xlsread('IBdata.xlsx','G3:G23');

If = I(1:15);
Hf = H(1:15);
sd = err(1:15);

f = fit(I(1:15),H(1:15),'poly1');

figure
%plot(I,H,'k')
%hold on
errorbar(I,H,err,'r.')
hold on
plot(f,'k--')

xlabel('Current(A)')
ylabel('Magnetic field H(Gs)')
grid on

%least-squares fit to a straight line
```

```
x = If;
y = Hf;

N = length(y);
m = sum(y)/N;
variance = sum((y(1,:)-m).^2)/(N-1);

xx = x.^2./sd.^2;
xy = x.*y./sd.^2;
ee = 1./sd.^2;
xe = x./sd.^2;
ye = y./sd.^2;

delta = sum(ee)*sum(xx)-(sum(xe))^2;
a = (sum(xx)*sum(ye)-sum(xe)*sum(xy))/delta;
b = (sum(ee)*sum(xy)-sum(xe)*sum(ye))/delta;

sd_a = sqrt(sum(xx)/delta);
sd_b = sqrt(sum(ee)/delta);

fprintf('a = %4.3f +/- %.3f\n',a, sd_a); %a = intercept
fprintf('b = %4.4f +/- %.4f\n',b, sd_b); %b = slope


%Plot magnetic field vs input voltage
%Import data
V = xlsread('VBdata.xlsx','C5:C17');
H = xlsread('VBdata.xlsx','G5:G17');
err = 0.1*xlsread('VBdata.xlsx','H5:H17');

Vf = V(5:13);
HHf = H(5:13);
sd = err(5:13);

f = fit(Vf,HHf,'poly1');
figure
%plot(I,H,'k')
%hold on
errorbar(V,H,err,'r.')
hold on
plot(f,'k--')

xlabel('Voltage(V)')
ylabel('Magnetic field H(Gs)')
grid on
axis([2.6 3.3 2800 3600])


%least-squares fit to a straight line
x = Vf;
y = HHf;

N = length(y);
m = sum(y)/N;
variance = sum((y(1,:)-m).^2)/(N-1);

xx = x.^2./sd.^2;
xy = x.*y./sd.^2;
ee = 1./sd.^2;
xe = x./sd.^2;
ye = y./sd.^2;

delta = sum(ee)*sum(xx)-(sum(xe))^2;
a = (sum(xx)*sum(ye)-sum(xe)*sum(xy))/delta;
b = (sum(ee)*sum(xy)-sum(xe)*sum(ye))/delta;
```

```
sd_a = sqrt(sum(xx)/delta);
sd_b = sqrt(sum(ee)/delta);

fprintf('a = %4.3f +/- %.3f\n',a, sd_a); %a = intercept
fprintf('b = %4.4f +/- %.4f\n',b, sd_b); %b = slope
```

A.2 Inventory Sheet

Electron Paramagnetic Resonance, B&H room 203

Inventory Sheet

06/22/17 AK

Start Up	#	Inventory	Close Out
✓	1	Electromagnet & Power supply	✓
✓	1	Gaussmeter & Probe w/ manual	✓
✓	1	Audio Amplifier	✓
✓	1	Function Generator w/ manual	✓
✓	1	Variable Resistor – Func-Gen	✓
✓	1	Digital Multimeter	✓
✓	1	Microwave Generator	✓
✓	1	Lock-in Amplifier w/ manual	✓
✓	1	Variable Resistor – Lock-In	✓
✓	1	Digital Oscilloscope	✓
✓	1	DPPH Sample with SDS sheet	✓
✓	1	Wave Guide System	✓
✓	1	Noise Suppressor	✓
✓	1	**Safety Manual in Room 203**	✓

Comments: ______________________________

NOTE: Always turn the "magnet power supply" current to "0" (zero) before turning the supply off! Leave the cooling water on for 15 minutes after turning the power supply off.

At start up this area was neat and orderly and the following items were discussed:
✓ Magnet Power & Cooling, ✓ Lab Door, ✓ No Food or Drink in Lab, ✓ Location of Cables & Connectors, ✓ Use & Disposal of Chemicals & ✓ Lab Safety.

Fran Zhy 10/13/2017 Tianyi Zhou 10/13/2017 Xu Zhang 10/13/17

(Student signature) (Date) (Student signature) (Date) (TA/Staff signature) (Date)

At time of close out, this area was neat & orderly & all inventory items were present.

Xu Zhang 10/20/17

(TA/Staff signature) (Date)