Physics 457W Section 1

Electron Spin Resonance

Version 3

Joseph Chang

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Partner: Jacob Mclain

TA: Nathan Mckee

Professor: Ying Liu

Abstract

This experiment aims to measure the energy difference of unpair electron cause applying a magnetic field on the DPPH sample molecule and find g-factor for an unpair electron. The mechanism of this experiment uses a concept called electron spin resonance. The magnetic moment of electrons would be either parallel or antiparallel to the magnetic field around them, and each state of magnetic moment corresponds to different energy levels. When electrons are fed with the exact energy to flip between two spin states, electron spin resonance occurs. Using the concept of electron spin resonance and an assumption of the energy difference $\Delta E = g\mu_B B = hv$. A value g-factor of an unpaired electron was experimentally obtained be $g_{exp} = 2.1 \pm 0.2$. The theoretical g-factor of the unpaired electron is $g_{theo} = 2.0023$. The percentage difference between experimental and theoretical results is 4%. The experiment result does overlap with the theoretical prediction.

Introduction

When a magnetic field is applied to the electron, that electron can have two different energy based on its spin direction. If a photon collides with an electron in a magnetic field with the exact energy $\Delta E = g\mu_B B$, this can result in a flip of electron spin, which is when electron spin resonance occurs.

In this experiment, a sample called DPPH is used for an electron container. a Helmholtz coils setup is used to apply a uniform magnetic field to the DPPH sample that split the state energy between two opposite spin directions. An inner RF probe coil is used to apply electromagnetic waves that let photons deliver the same energy to electrons in the DPPH sample. When photons' energy matches the state energy difference of electrons, electron spin resonance occurs, which can be observed with an oscilloscope attached to the neutral cable of RF oscillator and small AC of Helmholtz coils. If there are spikes on the neutral current of the RF oscillator when a small AC current of Helmholtz coils is at zero, it indicates ESR has occurred at the given magnetic field and frequency of an electromagnetic wave.

A significant application of ESR is that the ESR system can act as a probe to solve molecules' structures. In this experiment, the DPPH sample forms a simple energy difference follows equation $\Delta E = g\mu_B B = hv$. However, some molecule samples form much complex energy distribution because of their unique electromagnetic environment, given their unique molecule structure. ESR system can be used to observe the complex energy distribution of the molecule system, which gives a clue about how the molecule is structured.

Theoretical and background

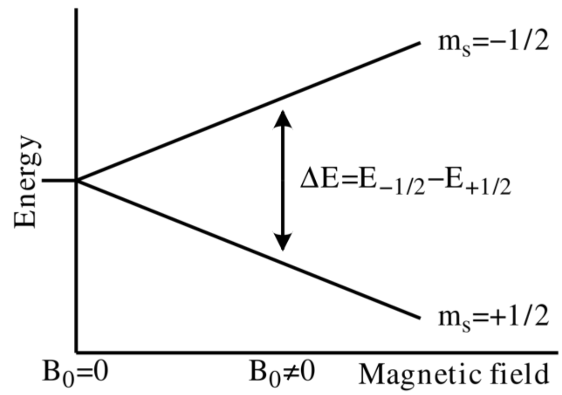

Figure 1 The energy of a spin half electron on a steady orbit branches base on its spin direction if magnetic field is applied due to Zeeman effect. As magnetic field increases, the energy difference between two spin states increases. This relation follows equation 1, $\Delta E = g\mu_B B$.

If a magnetic field is being applied to an electron, the energy of orbit branches by the spin direction of the electron. As the magnetic field increases, the energy varies by spin ΔE increases, as shown in figure 1. The energy of spin is given by $E = E_0 + m_s g \mu_B B$ where the spin of an electron $m_s = \pm\frac{1}{2}$, g-factor for electrons $g_{electron} = 2.0023$, Bohr magneton $\mu_B = \frac{eh}{2m_e} = 5.788 \times 10^{-9}\frac{eV}{G}$, and magnetic field B depends on the system. The energy varies by spin half particles including electrons is $\Delta E = E_{-\frac{1}{2}} - E_{+\frac{1}{2}}$. Equation 1 can be obtained by combining two previous equations.

$$\Delta E = g\mu_B B \quad (1)$$

Electron spin resonance occurs if an energy $E = hv$ carries by photons is fed to electrons, and the energy matches the energy difference used to send a lower energy state into a higher energy state $\Delta E = g\mu_B B$. When the energy of electrons shifts, the permeability of the sample also changes. This change of permeability affects the magnetic field around the sample.

To generate a uniform magnetic field around the sample, Helmholtz coils, shown in figure 2, are attached to a DC generator. The magnetic field at the center of Helmholtz coils is close to uniform given by equation 2.

$$B = \mu_0 \left(\frac{4}{5}\right)^{\frac{2}{3}} N \frac{I}{r} \quad (2)$$

In practice, an ammeter is connected to a DC generator and Helmholtz coils to provide a reading of current on the Helmholtz coils, which can be used to find the sample's magnetic field.

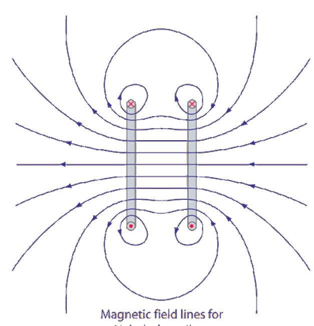

Figure 2 Nave, R. (n.d.). Helmholtz coils and the magnetic field around it. Helmholtz coils system use two coils to produce uniform magnetic field between them.

To feed the energy ΔE to the sample, another RF probe coil is placed around the sample perpendicular to Helmholtz coils. The magnetic field generated by the RF probe coil will not affect Helmholtz coils' magnetic field. The RF probe coil is connected to an AC generator (RF Oscillator), which produces electromagnetic waves known as photons to the sample. The energy is fed to an electron in the sample when a photon creates energy given by equation 3.

$$E = hv \quad (3)$$

Previously, permeability changes while the spin of electrons shift was mentioned. This change of permeability affects the magnetic field around the sample, which ultimately disrupts the probe coils' current. Therefore, the disruption of current on Helmholtz coils indicates the exact energy ΔE is fed to the sample.

For a photon to be absorbed by a spinning electron, the energy of the photon needs to be precisely the same as $\Delta E,$ as mentioned before. As a result, equation 4 can be obtained by combining equations 1 and 3.

$$hv = g\mu_B B \; (4)$$

It is practically difficult to match the exact magnetic field to the RF probe coil's energy to create resonance, so a small AC is fed into Helmholtz coils to sweep through a range of magnetic fields.

Methods

The experiment setup starts connecting Helmholtz coils to a DC and AC generator, where the DC is used to control the base magnetic field and the AC sweep through a small range of magnetic field on the top of the AC. By doing so, it's easier to find the right magnetic field corresponding to resonance energy ΔE. The DC/AC generator in this experiment would be the Control Unit. In other words, both AC and DC output of the Control Unit is attached to Helmholtz coils. Between Helmholtz coils and Control Unit, an ammeter is connected to read the current on Helmholtz coils. The magnetic field at the center of Helmholtz coils is decided by the current with equation 2, $B = \mu_0 \left(\frac{4}{5}\right)^{\frac{2}{3}} N \frac{I}{r}$. For proof of concept, a gaussmeter is used to measure the approximate magnetic field at the center of Helmholtz coils to check if the magnetic field value matches the value given by current using equation 2.

Once the Helmholtz coils, ammeter, and control unit are in place, a DPPH sample shown in figure 3 is attached to an RF probe coil. There are three different coils; each size can generate a diverse range of frequency of an electromagnetic wave. Then, the RF probe coil with the DPPH sample is inserted into the RF probe unit connected to the Control Unit's Y channel. The setup so far is shown in figure 4.

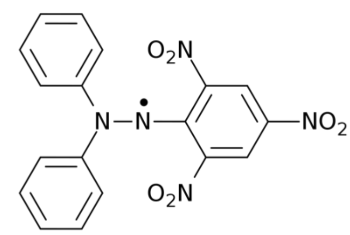

Figure 3 DPPH (organic chemical compound 2,2-diphenyl-1-picrylhydrazyl) sample molecule.

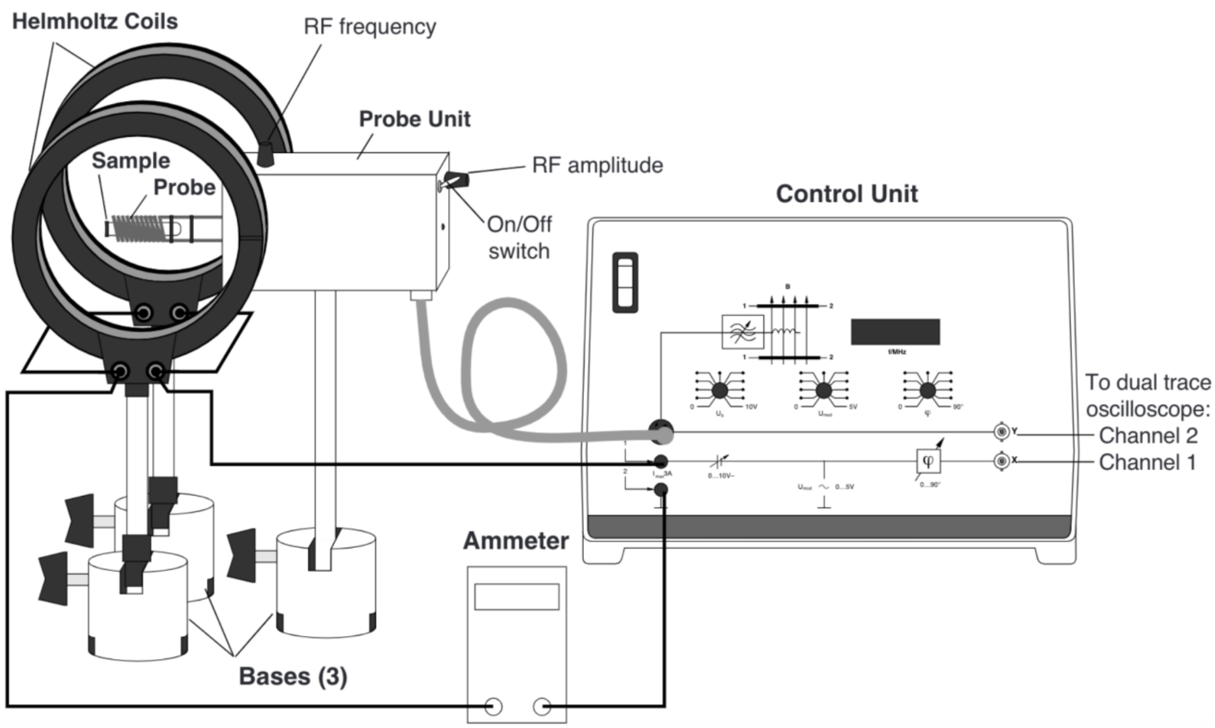

Figure 4 Instrument setup without an oscilloscope

When electron spin resonance occurs on the DPPH sample, the permeability of the DPPH sample shifts affects the magnetic field around it. This distortion of the magnetic field can be observed on the current RF probe coil. In this experiment, the neutral current of the probe unit changes when ESR occurs. So, the neutral current of probe unit (Y output on Control Unit) and the alternating current of Helmholtz coils (X output on Control Unit) are connected to oscilloscope Channel 2 and Channel 1 as indicated in figure 4.

The purpose of this experiment is to find the g-factor in equation 4 by measuring v and B and assume frequency and magnetic field have a relationship. A frequency is set to see the data points, and a magnetic field is found to match the given frequency. To confirm resonance has occurred, the screen of the oscilloscope should look similar to figure 5. Figure 5 shows that the neutral current of the RF probe coil (channel 2 blue curve) drops precisely when the AC of Helmholtz coils (channel 1 yellow curve) is at zero. AC of Helmholtz coils is used for sweeping through a range of magnetic fields to match the energy of resonance ΔE. The spikes occur at AC at zero means DC of Helmholtz coils produces the exact magnetic field for the energy of resonance ΔE. The technique to create this graph is to tuned DC until the drops of the blue curve is evenly distributes across the x-axis and spread apart by half wavelength of the yellow curve, then adjusted phase shift of Control Unit to horizontal change the blue curve that the spike occurs when the yellow curve is at zero.

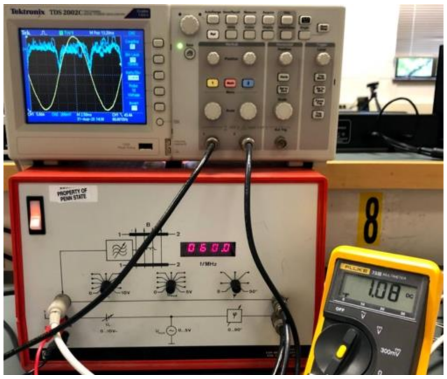

Figure 5 ESR occurs when spikes on the neutral current of RF (blue curve) peak at zeros of AC current on Helmholtz coils (yellow curve). This picture is corresponding to one data points in appendix. The resonant frequency is 60MHz, and the current on Helmholtz coils is 1.08A.

Results

1. The radius of Helmholtz coils is $r = 7.3 \pm 0.1cm$

   The rounds of Helmholtz coils are $N = 320$

   These are the essential information to calculate the magnetic field at the center of Helmholtz coils based on current.

2. To show the current of Helmholtz coils can be used to calculate the magnetic field at the center of Helmholtz with equation $B = \mu_0 \left(\frac{4}{5}\right)^{\frac{2}{3}} N \frac{I}{r}$.

   Table 1. A current across Helmholtz coils was measured using an ammeter, and a magnetic field at the center of Helmholtz coils was measure using a gaussmeter.

2I (A) $\pm 0.01A$	B (mT) $\pm 0.05mT$
1.19	0.29

   The magnetic field calculated using a measured current does not match with the magnetic field measured using gaussmeter. The speculation is that the probe of the gaussmeter did not function as expected. So, the magnetic field for resonance in result 3 is calculated using current measured by the ammeter.

3. Magnetic fields with the corresponding frequencies at resonance

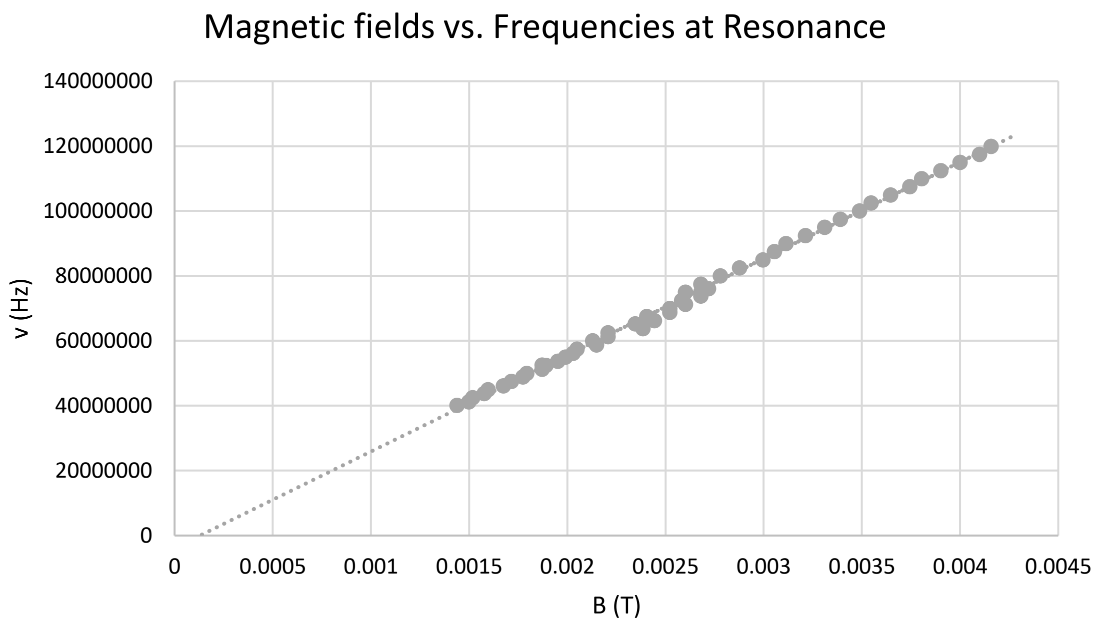

Figure 6 Linear fit on Magnetic field vs. frequency obtained experimentally at ESR. The data points match the theoretical prediction given by equation 4 that the resonant frequency increases linearly as the magnetic field increase $hv = g\mu_B B$. The linear fit function is $v(\frac{1}{s}) = 2.97 \times 10^{10}(\frac{1}{sT})B(T) + 3.85 \times 10^{6}(\frac{1}{s}), R^2 = 0.998$. The 0.998 R-square value indicates that the data fit the linear function quite well. Raw data points are shown in appendix 1.

Figure 6 shows the photon's frequency corresponding to the magnetic field at electron spin resonance. This result matches the theoretical prediction of equation 4, in which the resonant frequency should be proportional to the magnetic field in a linear way. The linear fit function is $v(\frac{1}{s}) = 2.97 \times 10^{10}(\frac{1}{sT})B(T) + 3.85 \times 10^{6}(\frac{1}{s}), R^2 = 0.998$. The value of g-factor can be solved by using the linear fit function and equation 4 $hv = g\mu_B B$.

$$v = \frac{\mu_B}{h} gB = 1.399 \times 10^{10}(\frac{1}{sT})gB$$

$$g = 2.97 \times 10^{10}\left(\frac{1}{sT}\right) \div \left(1.399 \times 10^{10}\left(\frac{1}{sT}\right)\right) = 2.12$$

4. Average Magnetic field half-width is $dB_{\frac{1}{2}} = 2.6 \pm 0.4\ mT$

This half width is much larger than the predicted half-width measured in $dB_{\frac{1}{2}} = 0.15 - 0.81mT$. The speculation is that the Helmholtz coils setup used in this experiment was small compared to the test tube used for containing the DPPH sample. As a result, the magnetic field across the DPPH sample generated by Helmholtz coils was not uniform.

Error Analysis

$$B = \mu_0 \left(\frac{4}{5}\right)^{\frac{2}{3}} N \frac{I}{r}$$

A partial differential equation gives the uncertainty of the magnetic field:

$$\Delta B = \sqrt{\left(\frac{\partial B}{\partial I}\Delta I\right)^2 + \left(\frac{\partial B}{\partial r}\Delta r\right)^2} = \sqrt{\left(\mu_0 \left(\frac{4}{5}\right)^{\frac{2}{3}} \frac{N}{r}\Delta I\right)^2 + \left(-\mu_0 \left(\frac{4}{5}\right)^{\frac{2}{3}} N \frac{I_{max}}{r^2}\Delta r\right)^2}$$

$$= \sqrt{\left(\mu_0 \left(\frac{4}{5}\right)^{\frac{2}{3}} \frac{320}{0.073} 0.01\right)^2 + \left(-\mu_0 \left(\frac{4}{5}\right)^{\frac{2}{3}} 320 \frac{2.11}{0.073^2} 0.001\right)^2} = 0.00006T = 0.06mT$$

$$g = 1.399 \times 10^{10} (\frac{1}{sT}) \frac{B}{v}$$

The partial differential equation gives the uncertainty of g-factor:

$$\Delta g = \sqrt{\left(\frac{\partial g}{\partial B}\Delta B\right)^2 + \left(\frac{\partial g}{\partial v}\Delta v\right)^2}$$

$$= \sqrt{\left(1.399 \times 10^{10} \frac{1}{v_{min}}\Delta B\right)^2 + \left(-1.399 \times 10^{10} \frac{B_{max}}{v^2}\Delta v\right)^2}$$

$$= \sqrt{\left(1.399 \times 10^{10} \frac{1}{40.1\times10^6} 0.0002\right)^2 + \left(-1.399 \times 10^{10} \frac{0.0004}{(40.1\times10^6)^2} 0.01 \times 10^6\right)^2}$$

$$= 0.2$$

$$g = 2.1 \pm 0.2$$

$$g_{theoretical} = 2.0023$$

The percent difference compare to theoretical value is the following:

$$Percent\ difference = |\frac{g_{exp} - g_{theo}}{g_{theo}}| = 4\%$$

Discussion and Conclusion

In this experiment, electron spin resonance was studied. ESR occurs when a magnetic field is given to electrons that vary the energy of the state of an electron and a photon with the exact energy to push energy to go between spin up and spin down state $\Delta E = g\mu_B B = h\nu$. Helmholtz coils were used to generate a uniform but slightly oscillating magnetic with a dominant direct current and a small alternating current. RF probe unit with another AC was used to create an electromagnetic wave, also known as photons, to deliver energy that lets electrons to jump between spin states. The RF probe unit frequency was set, and DC on Helmholtz coils was tuned to match the frequency at ESR. The ESR occurrence was confirmed by checking if the spikes of RF probe unit uniformly distributed at zero of small AC on Helmholtz coils. Ultimately, the value of g-factor for electron was found to be $g_{exp} = 2.1 \pm 0.2$ which agrees with the theoretical g-factor for electron $g_{theo} = 2.0023$ with a 4% difference.

First, the current on Helmholtz coils was measured using an ammeter. The magnetic field at the center of Helmholtz coils was measured using a gaussmeter; unfortunately, the results did not agree with each other. The expected magnetic field given by the current was $2.35 \pm 0.06mT$, but the magnetic field provided by the gaussmeter was $0.29 \pm 0.05mT$. The speculation for this result was that the probe of the gaussmeter did not function as expected. Second, when swept through a range of magnetic fields to create ESR, the desired magnetic field half-width given by LD Didactic GmbH in their article regarding electron spin resonance at DPPH was $0.15 - 0.81mT$. Still, the average magnetic field half-width obtained in this experiment was $2.6 \pm 0.4mT$. The speculation is that the experiment setup caused the larger magnetic half-width. The Helmholtz coils setup was small compared to the test tube used for containing the DPPH sample in this experimental setup. Therefore, the magnetic field across the DPPH sample was not uniform, so the average magnetic field half-width in this experiment was much larger than the expected value on the paper.

Reference

LD Didactic GmbH. Electron spin resonance at DPPH. *Atomic and Nuclear Physics*, 6.2.6.2 https://psu.box.com/s/9vypuazf8yi3ymk1h6g3azr952ycrnzd

Nave, R. (n.d.). Helmholtz Coils. *Hyperphysics.Phy-Astr.Gsu.Edu.* Retrieved September 13, 2020, from http://hyperphysics.phy-astr.gsu.edu/hbase/magnetic/helmholtz.htm

Appendix

1. Table 2. The corresponding current across Helmholtz coils, magnetic field at the center of Helmholtz, the AC frequency of the RF probe unit, current width, and half magnetic field width of Electron Spin Resonance. The analysis of these raw data points are shown in results.

2I (A) $\pm 0.01A$	B (mT) $\pm 0.06mT$	v (MHz) $\pm 0.01MHz$	Width I (A) $\pm 0.2A$	Half width B (mT) $\pm 0.4mT$
0.73	1.44	40.1		
0.76	1.50	41.2		
0.77	1.52	42.5		
0.8	1.58	43.8		
0.81	1.60	45	1.3	2.6
0.85	1.68	46.2	1.45	2.9
0.87	1.71	47.5	1.2	2.4
0.9	1.77	48.9	1.45	2.9
0.91	1.79	50	1.2	2.4
0.95	1.87	51.3	1.45	2.9
0.96	1.89	52.5	1.2	2.4
0.95	1.87	52.6	1.2	2.4
0.99	1.95	53.7	1.25	2.5
1.01	1.99	55	1.3	2.6
1.03	2.03	56.2	1.3	2.6
1.04	2.05	57.5	1.3	2.6
1.09	2.15	58.8	1.45	2.9
1.08	2.13	60	1.4	2.8
1.12	2.21	61.3	1.3	2.6
1.12	2.21	62.5	1.2	2.4
1.21	2.38	63.8	1.35	2.7
1.19	2.35	65.3	1.3	2.6
1.24	2.44	66.3	1.5	3.0
1.22	2.40	67.5	1.2	2.4
1.28	2.52	68.8		
1.28	2.52	70	1.2	2.4
1.32	2.60	71.3		

1.31	2.58	72.5	1.2	2.4
1.36	2.68	73.8		
1.36	2.68	75	1.2	2.4
1.32	2.60	75		
1.38	2.72	76.1	1.2	2.4
1.36	2.68	77.5		
1.41	2.78	80		
1.46	2.88	82.5		
1.52	3.00	85	1.3	2.6
1.55	3.05	87.5		
1.58	3.11	90		
1.63	3.21	92.5		
1.68	3.31	95		
1.72	3.39	97.5		
1.77	3.49	100		
1.8	3.55	102.5		
1.85	3.65	105	1.35	2.7
1.9	3.74	107.5		
1.93	3.80	110		
1.98	3.90	112.5		
2.03	4.00	115		
2.08	4.10	117.5		
2.11	4.16	120		