

Welcome to the NMR lab. Let's enjoy this physics experiment utilizing nuclei of protons in water to observe the motion of nuclear spin through an oscilloscope. Do not worry about nuclear radiation; there are no α , β or γ -rays in NMR. This is why the magnetic resonance imaging (MRI) in hospital is known to be safe to the human body.

1 Introduction

Every elementary particle is characterized by its mass and charge. For example the proton or hydrogen nucleus has positive charge e and approximate mass of $mc^2 \approx 1$ GeV. There is another quantity which characterizes each particle: that is a "spin" or the angular momentum. Many elementary particles possess a spin and rotate on its axis. Its rotation is persistent and shall never be decelerated. When a charged particle rotates, the magnetic moment arises along the rotating axis. This is quite analogous to the solenoid of electromagnet, in which electron moves around the solenoid axis to produce magnetic flux along the solenoid axis. Thus, we know that proton has a tiny magnetic moment. Although its size is very small, we can utilize them by the nuclear magnetic resonance (NMR) technique to explore within materials. The principle of NMR is applied to vast fields such as development of new drugs or functional materials such as superconductor, and also analyses of genome or protein.

One of the goal of this lab. is to understand the principle of NMR technique, which is a microscopic method to measure the magnetic field within the material utilizing the magnetic moment μ possessed by nuclei. Its principle (Fig. 1) is quite simple, that is, only the photons with energy $\hbar\omega$ can be absorbed by nuclear spins with energy $2\mu H$ under the magnetic field. The magnetic field inside the material varies widely depending on the character of the material, whether it is metal, semiconductor, magnet or superconductor *etc.* This is because the electrons in the material produce additional field within it. Through the investigation of magnetic field inside the material, we can understand the properties of electrons which play an important role in many phenomena that materials exhibit.

Before starting lab, let's note another subject. That is, to enjoy watching beautifully-oscillating NMR signal, called as a free induction decay (FID), which kaleidoscopically transforms as one change field. This also gives you better understanding of Fourier transformation, which might have been a difficult jargon in a class of mathematics.

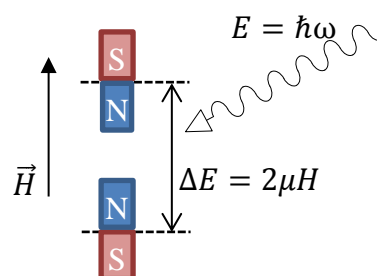


Fig. 1 Basic concept of NMR

2 The nuclear magnetic moment μ

The nucleus of hydrogen, which consists of a proton has a magnetic moment $\vec{\mu}$, for it has both finite charge and spin \vec{I} . The direction of $\vec{\mu}$ is parallel with \vec{I} , and it can be described as $\vec{\mu} = \gamma\hbar\vec{I}$ or with their absolute values $\mu = \gamma\hbar I$, where \hbar is the plank constant divided by 2π and γ is the constant called as the nuclear gyromagnetic ratio¹. Table 1 shows values of μ for various common nuclei.

nucleus	¹ H	² D	¹⁹ F	²⁷ Al	⁶³ Cu	⁶⁵ Cu	⁵⁷ Fe	e^-
spin	$I = 1/2$	$I = 1$	$I = 1/2$	$I = 5/2$	$I = 3/2$	$I = 3/2$	$I = 1/2$	$I = 1/2$
$\gamma/2\pi$ (MH/T)	42.5774	6.53566	40.055	11.094	11.285	12.090	1.38	-28024.6

Table 1. Nuclear gyromagnetic ratio γ and spin quantum number I for various nuclei.

Under finite magnetic field, the potential energy of nuclear spin depends on its direction with respect to the field \vec{H} as,

$$E = -\vec{\mu} \cdot \vec{H} = -\gamma\hbar\vec{I} \cdot \vec{H}$$

If one takes the direction of the field along z axis such that $\vec{H} = (0,0,H_0)$, the energy is rewritten as,

$$E = -\gamma\hbar I_z H_0.$$

According to the quantum mechanics, the z -component of spin I_z takes discrete values $-I, -I + 1, \dots, I - 1$ and I . The spin state is stable against time evolution only for these allowed values, which are called *eigen values*. The spin state corresponding to each eigen value is called *eigen state*. The energy difference ΔE between two neighboring eigen states I_z and $I_z + 1$, called Zeeman energy (Fig. 2), is given as,

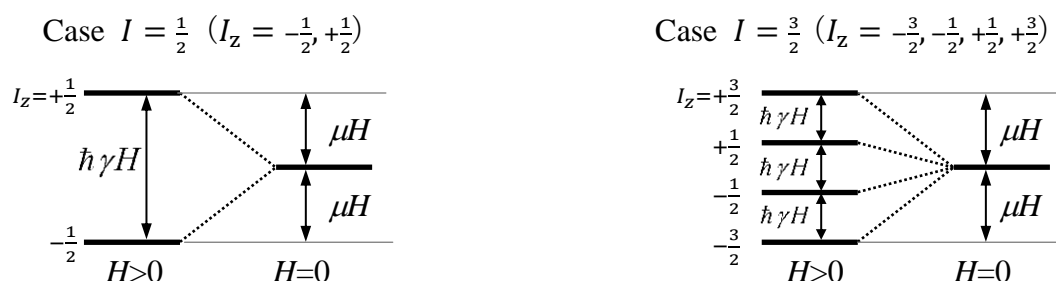


Fig. 2 Zeeman splitting and Zeeman energy for spin with $I = \frac{1}{2}$ and $\frac{3}{2}$.

¹ Although, Fig. 1 suggests that only μ is important, both μ and \vec{I} are in fact indispensable for NMR, which is analogous to a rotating top in the gravitational field.

$$\Delta E = \gamma \hbar H_0.$$

When photons with energy $\hbar\omega$ are irradiated to the system, the quantum mechanics again tells us that the photons are absorbed by nuclear spins only when its energy coincides with ΔE . This gives the famous NMR condition,

$$\omega = \gamma H_0$$

The frequency at the left side is called Larmor frequency. Note that in convenience, the unit of γ is usually given as MHz/T, and the equation is described as $\nu = \gamma H_0$.

- ✚ Q 1². Calculate the resonance frequency of ^1H and ^{19}F under the magnetic field of 0.5 Tesla. Also, obtain H_0 of the two nuclei for $\omega/2\pi = 25$ MHz.
- ✚ Q 2. Convert the photon energy of above 25 MHz to the temperature Kelvin. (Hint) use the Boltzman constant $k_B = 1.381 \times 10^{-12}$ (J/K) and the Plank constant $h = 6.626 \times 10^{-34}$ (J/Hz).
- ✚ Q 3. Refer quantum mechanics text books and find how the *Fermi's golden rule* explains the NMR resonance condition.

3 The magnetic field inside the material

The magnetic field that felt by the nuclei is different from the applied field H_{ext} , but includes the additional one H_{int} , which is produced by electrons in material. NMR deals with this H_{int} .

As the quantum statistical physics tells us, H_{int} strongly depends on the electron state, that is, if they are moving or staying localized (note that electrons also have spins and hence magnetic moments). For example, as the quantum statistical physics tells us, the unpaired inner-shell electron, which are localized, shows $1/T$ -temperature dependent magnetization called as the Curie-magnetization, while the conduction electrons in metals, shows temperature independent magnetization, called as Pauli magnetization.

These mean that through the measurement of H_{int} , we can obtain the microscopic character of electrons, which cause many interesting phenomena in solids such as magnetism or superconductivity. The ratio of H_{int} to H_0 is often called as Knight

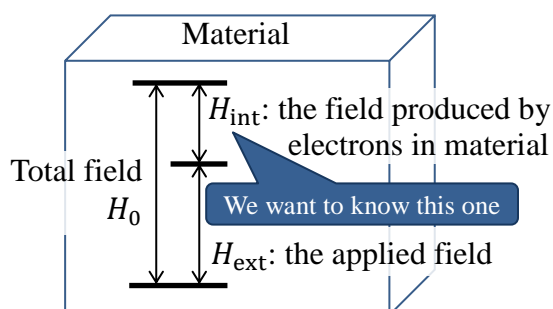


Fig. 3 The field measured by NMR

² Several quizzes are provided in the text for better understanding of NMR. Students are encouraged to answer some of them in his report. Do not fear making mistakes, challenging will be appreciated.

shift (named after the discoverer, W. D. Knight). In chemistry fields, Knight shift is called as chemical shift. NMR can also measure the fluctuation amplitude of H_{int} , which will be demonstrated in Physics lab course III.

4 NMR spectrometer

Before starting experiments, you have to be aware of two important rules for the magnet and pulse controller.

(CAUTION 1) Set the current setting potentiometer knob to zero, before turning ON/OFF the magnet. Otherwise the surge EMF due to $-Ldi/dt$ may appear at terminals of the magnet and give damage to magnet and the power supply.

Next, when you set the pulse condition, that is, pulse width (μsec) and its interval (msec) on PC-2 using the pulse-controlling software,

(CAUTION 2) DO NOT set the pulse interval shorter than 10msec, and DO NOT set the pulse width longer than 100 μsec . If done, the RF power amplifier will be seriously damaged.

Figure 4 shows the schematic diagram of NMR detection. Before proceeding to the next section, the theory of spin motion, let's be familiar with the machine in a nuts-and-bolts way. The NMR machine, usually called as *spectrometer* consists of eight parts:

- 1) DC-pulse generator controlled by PC-2, which determines the pulse interval (10-10000 msec) and the pulse length (1-10 μsec).
- 2) RF-Signal generator, which determines the RF frequency (5-40 MHz).
- 3) RF-switch, which convert the continuous wave to RF pulses.
- 4) Low-noise pre amplifier, which amplifies the extraordinarily small FID signal to visible size (No adjustable knobs).
- 5) Phase sensitive detector, which determines the signal-receiving gain.
- 6) RF-Power amplifier, which determines the applying power (0-100 W)
- 7) Magnet with power supply and field-monitoring digital volt meter (DVM), which applies and measures the DC magnetic field (0-1.0 T).
- 8) Probe with built-in LC circuit, which applies RF pulse and receives FID signal. Adjust two variable capacitors so that the FID signal becomes large.

5 Theory of spin motion

Under zero-field, nuclear spins fluctuate randomly, so that their net moment is zero. One can get a finite net moment by applying a magnetic field H_0 . This moment μ directed along the applied field can be manipulated by weak RF pulses³ oscillating with a frequency ω , which is close to be γH_0 . That is, when electromagnetic wave with frequency ω is irradiated by a small solenoid around the sample, μ starts to tilt from the direction of H_0 as it absorbs the photon energy $\hbar\omega$.

Then, if one stops irradiation just when μ rotates 90° and lies within the xy plane, which in usual takes only a few micro seconds, the nuclear moment starts to rotate in the plane, the motion of which is called as Larmor precession. If you put solenoid

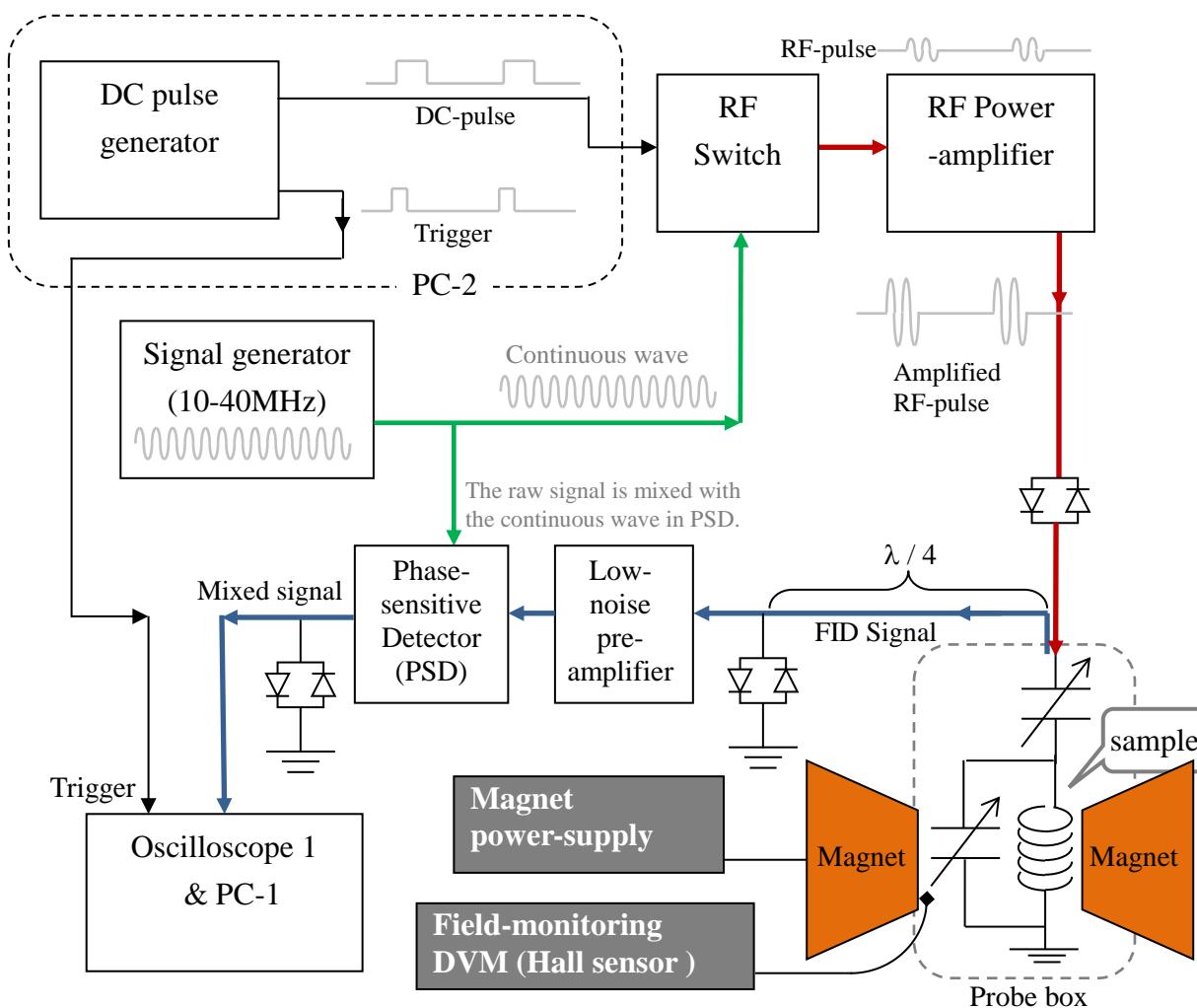


Fig. 4 Schematic diagram of NMR spectrometer

³ Why the nuclear spins polarized along the strong magnetic field can be manipulated by a weak oscillating field? This can be explained by *Larmor's theorem*, which demonstrates that on a rotating frame, the nuclear spins feels a fake field, the size of which is $-\omega/\gamma$.

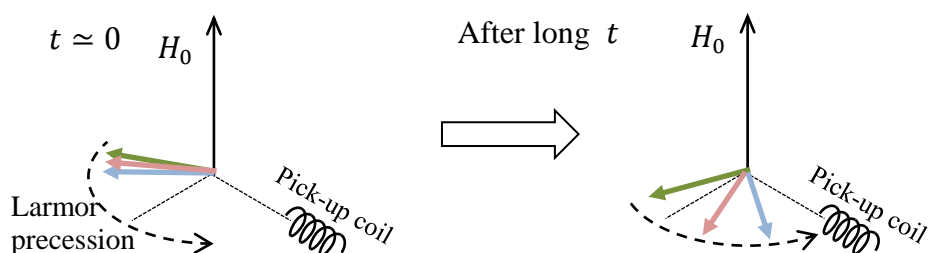


Fig. 5 Time evolution of spin motion after RF-pulse irradiation. Note that as the spins precess within xy -plane, the direction of each spins becomes random, reflecting the field inhomogeneity. Thus, the amplitude of FID at the terminals of pick-up coil gradually decreases with time.

parallel with the plane, you will see an oscillating voltage appears at its terminals due to Faraday's law. This is called as a free induction delay (FID) signal. In fact, the solenoid is the same one that was used to irradiate electromagnetic wave.

The frequency of Larmor precession, which is just the rotating frequency of nuclear moment, corresponds to γH , where H is the internal field applied onto nuclei. For the induced voltage at the coil due to the Larmor precession is usually as small as a few micron volts, it must be amplified also processed by the phase sensitive detector (PSD) to make it visible by oscilloscope. In the PSD, the induced voltage with the frequency γH is *mixed* with the continuous wave from the signal generator with the frequency ω , often referred as the reference. Here, the process *mixing* actually corresponds to multiplication of the two oscillating signals. The output frequency of PDS the same as the difference of the two as $|\gamma H - \omega|$ (See Q 4).

Next, the decaying rate of FID signal with time also gives the important information in the material. See Fig. 4, and note that there are tremendously many nuclear spins in a test tube, that is, the order of Avogadro number N_A . Each spin feels slightly different H , depending on its environment or position. This means that the rotating frequency is also slightly different for each spin⁴. Therefore, above FID does not last eternally but decreases in a finite time $T_2^* \approx 2\pi/(\gamma\delta H)$, where δH is the *inhomogeneity* in H . The size of T_2^* varies from a few micro seconds to a few seconds and depends on the sample homogeneity, magnetization and whether or not it is liquid or solid.

⁴ There is an another mechanism that reduces the FID amplitude, that is, the spin-spin interaction. The effect of these two can be measured as separated by utilizing the spin-echo technique. You can find the interesting song on this topic, *Twinkle, Twinkle (song by Science Groove) – YouTube*.

- ✚ Q 4. Show how PSD works. The principle is quite simple: by multiplying the two oscillating signals one can get another oscillating signal with the frequency of difference between the two. Explain why the difference frequency appears when multiplied.
- ✚ Q 5. In previous section, the quantization of spin angular momentum has been described. In microscopic physics, many quantities are quantized. Show other examples of *quantization*; consult any text books of quantum mechanics if necessary.

6 How to get FID signal

By following the procedures below you can easily observe a beautiful signal in the oscilloscope. Although students in many lab-courses are generally encouraged to learn each experiment in rather a cut-and-try manner, they are expected to be prudent and to handle the spectrometer carefully in NMR lab, for some of the apparatus are quite fragile. Do not hesitate ask TA or prof whenever you are not sure of operation.

- 1) (TA must do this.) Switch all the apparatuses except for RF power amp on.
- 2) (TA must do this.) Set the hall-probe current on by executing the batch script on No. 2 spectrometer.
- 3) (TA must do this.) Set the signal generator's output amplitude $2.00V_{pp}$.
- 4) Set the PSD gain +32 dB, that is, push down two green buttons.
- 5) Set the sample glass tube containing aqueous solution of copper sulfate into the hole of NMR probe. **CAUTION: glass tube is fragile. Handle it carefully.**
- 6) Move the probe to the center position between of the pole pieces of the magnet.
- 7) Set the signal generator's frequency 23.4 MHz.
- 8) Set the pulse width and pulse interval 4 μ sec and 40 msec, respectively. Confirm that the green lamp on the pulse-generator is lighted, and that the horizontal axis of oscilloscope is properly swept.
- 9) Increase the magnet current slowly and confirm that the hall probe DVM show an increase. If it does not call TA or prof.
- 10) Adjust the magnet current so that the magnetic field is about 0.55 Tesla. Use the V-H relation or the graph to convert the observed voltage (V) to the field (T).
- 11) Increase the output level of power amp slowly, watching the oscilloscope to find a FID signal.

If you do not see any FID signal on oscilloscope at this stage, consult TA's.

Otherwise, you can proceed and make the signal stronger and more beautiful, that is, with less noise. You can also adjust frequency and field strength slowly and slightly to enjoy how the signal transforms.

12) Adjust the two capacitors so that the signal becomes larger.

13) Adjust slightly the pulse length so that the signal becomes larger.

(WARNING) Never set the pulse length longer than 100 μsec ; it will seriously damage the power amplifier.

14) Adjust slightly the probe position so that the signal lasts longer in the oscilloscope.

15) Adjust horizontal axis delay of oscilloscope so that the ring-down noise around the RF pulse at beginning of FID signal just hides at the left side of scope (Fig. 6).

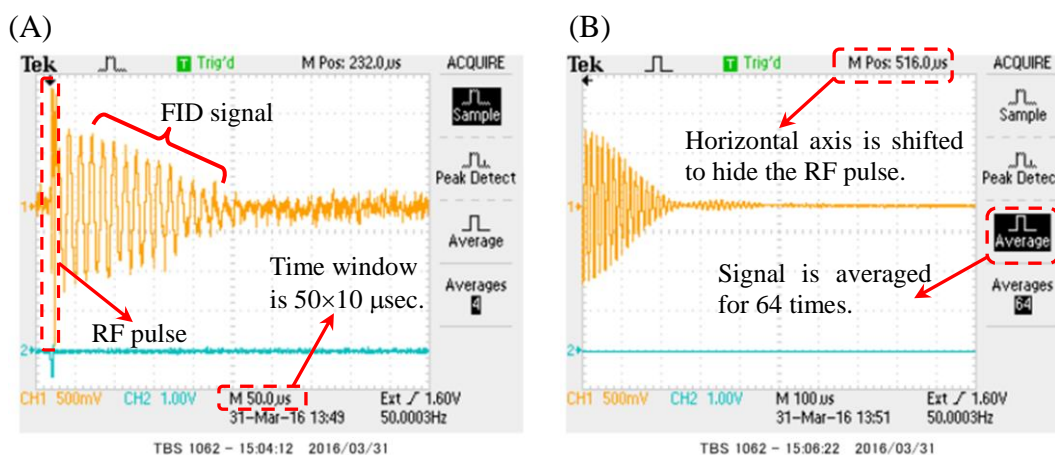


Fig. 6 A typical FID signal taken by oscilloscope, (A) with the horizontal time window 500 (50×10) μsec associated with an RF pulse at the left side, and (B) with the time window 1000 (100×10) μsec , averaged 64 times, and with the horizontal axis shifted slightly to the left so that the RF pulse gets out of the window.

7 Experiments

In this lab, students are expected to perform three experiments in a time. Every experiment is easy, and I hope, will be interesting. As in the other lab's, do not forget to take notes on the measurement condition such as the measurement frequency, the magnetic field (or the applied current to magnet), the pulse length, the pulse interval, and the time window of oscilloscope, which is indispensable to show spectrum

frequency correctly. Description of these on your report will be appreciated.

- 1) Find an FID signal and understand how PSD works

Follow the procedures given below and find an FID signal. Then, carefully observe how the FID changes when you change slowly the magnet current through the resonance condition $\omega = \gamma H$. Sketch or capture the signal in the oscilloscope 1 for the five conditions following, $\omega \gg \gamma H$, $\omega \geq \gamma H$, $\omega \simeq \gamma H$, $\omega \leq \gamma H$ and $\omega \ll \gamma H$.

- 2) Confirm the NMR resonance condition law $\omega = \gamma H$

First, find the FID signal for the appropriate frequency ω . Adjust either H or ω so that the resonance condition is precisely fulfilled. Make a note of (H, ω) set and repeat this with few tens of different ω 's. By using the least-square fitting, find constants a and b for the relation $\omega = a \cdot (H + b)$. Compare the value a with γ in this text. Next, you will probably find that b is finite, then think of its reason (Q6).

- 3) Compare the signal from solid and liquid

Find the drastic change in the FID signal when a sample of butter, chocolate or wax is in liquid state or solid state. Choose one of the samples in a glass tube (ask TA for it) and liquefy it by hot air from a hair dryer. Obtain the FID signal from the sample in liquid state. Transfer the FID data to PC and get the frequency spectrum by the fast Fourier transform (FFT). Next, cool down the sample; use ice if necessary until it completely solidifies again, and measure again the FID signal, after removing water around the test tube completely. Compare signals of solid and liquid, try to explain the reason of difference (Q8).

(CAUTION) HOT air from the hair dryer may insure you.

(CAUTION) Never let water into the sample hole in the probe.

✚ Q 6. Explain why the value b in 3) is finite. (Hint) When b is finite, there may be finite field even if you make the magnet current zero. What does this field come from? Note that the core of the present magnet is made of soft iron.

✚ Q 7. Show that the superposition of cosine waves with different frequencies with a distribution width $\Delta\omega$ makes a decaying oscillation. Also show that it decays faster for larger $\Delta\omega$.

Equivalently, evaluate the integral $\int_{-\infty}^{+\infty} d\omega e^{-\left(\frac{\omega-\omega_0}{\Delta\omega}\right)^2} \cos \omega t$.

✚ Q 8. Read an explanation following on the *motional narrowing* and draw function

curves of FID amplitude for several different τ 's.

First, suppose that the system has a field inhomogeneity of ΔH and that each particle moves to a new position within an average interval τ .

When the FID possesses the frequency inhomogeneity $\Delta\omega = \gamma\Delta H$, its amplitude decreases as $e^{-(t\Delta\omega/2)^2}$ from $t = 0$. At $t = \tau$, the particle position changes, and then the system is reset and FID starts to decrease again obeying the function $e^{-(t\Delta\omega/2)^2}$, which restarts from $t = 0$, although the real time is $t = \tau$. That is, toward the still next interval, the FID amplitude changes from $e^{-(\tau\Delta\omega/2)^2}$ to $e^{-2(\tau\Delta\omega/2)^2}$.

For this sequence will be repeated t/τ times until the longer time t , one obtains the time evolution of FID amplitude as $e^{-(t/\tau)\cdot(\tau\Delta\omega/2)^2} = e^{-(\tau\Delta\omega^2/4)t}$. Note that if τ is very short, that is, if the particles are moving very fast just like in liquids, the amplitude of FID decays only slowly with time, as if the system has little field inhomogeneity.

8 Closing remarks

Do not forget to submit a report within a week; drop it at the post specified.

In your report, you are expected to state, 1. motivation, 2. experimental methods and conditions (such as frequency, pulse length, repetition interval and magnetic field), 3. results and 4. discussion. A challenge to some questions in this text will be appreciated. In results section, do not forget show both the worked data (such as FFT spectra) and also some raw data (such as FID signal).

Do not hesitate to ask questions to Prof. Goto or other TA's.

If you would like to see the NMR apparatus at Goto's lab for low temperature physics research with the superconducting magnet of 16 T and with low temperature cryostat of 0.3 K, just ask TA or Prof. Goto.

References

Principles of magnetic resonance, C. P. Slichter (Springer-Verlag); available at the library.

MIT Junior lab text for NMR; Available on the web site of MIT.

An advanced and detailed NMR text (in Japanese) for the junior course is available at Prof Goto's web site,

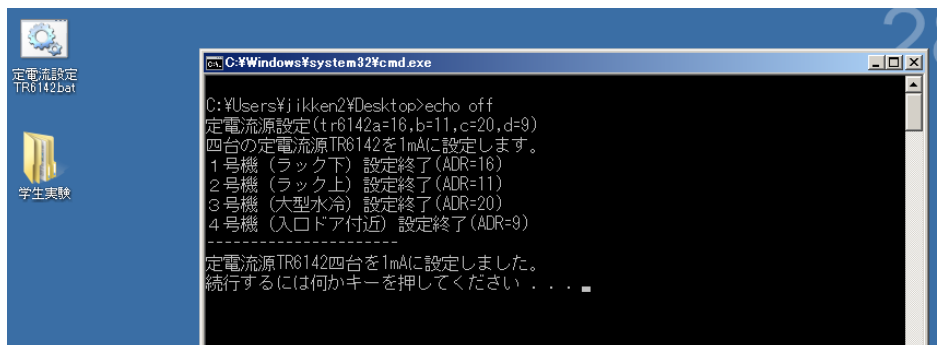
http://nile.ph.sophia.ac.jp/~goto-ken/text/nmr_text2015.pdf

Appendices

1. Some PC techniques

1) Hall probe current setting (Must be done by TA)

Set current of hall probe as 1mA for all the four magnets. This should usually be done by TA before starting class at the No. 4 site, which automatically sets current for all the four spectrometers

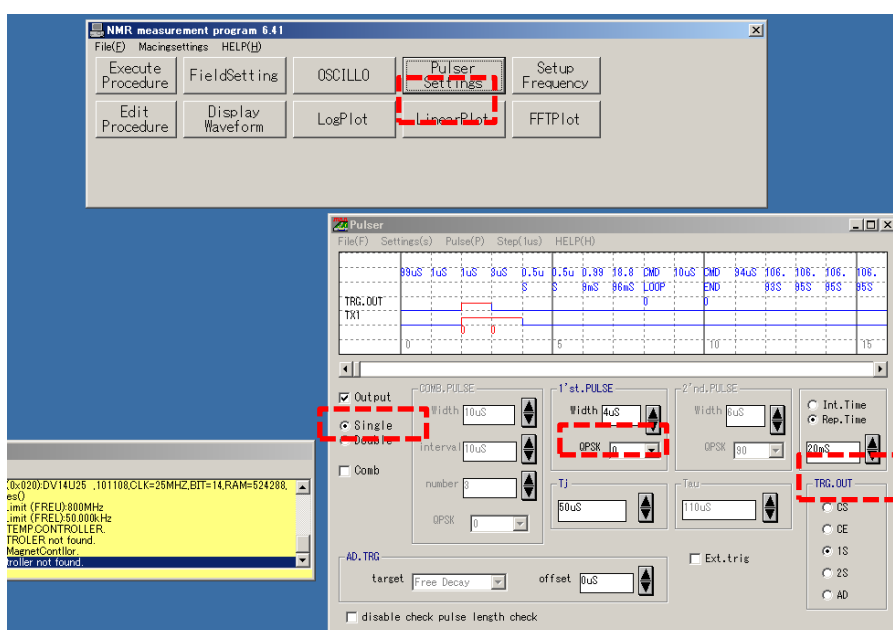


2) NMR pulse setting

First, execute icon “NMR 6.41” on the desktop, then, hit the button of “Pulsar Settings” shown below. Set the 90-pulse length to be 3-6 μ sec, and the interval to be 10-10000 msec, and also make a check in pulse out.

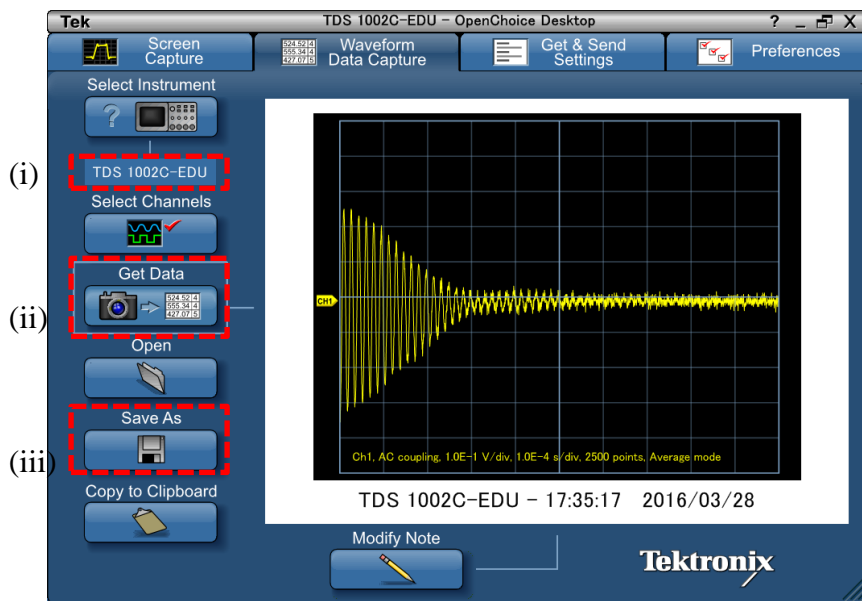


Never set the pulse length larger than 100 μ sec or the interval shorter than 10 msec. It will damage the power amplifier.



3) Data transfer from the oscilloscope-1 to PC-1

Use the tool of *OpenChoice Desktop*. Then, after confirming that it is correctly connected to the oscilloscope (i), get data (ii), and save a file (iii). Be sure to use “text format” on saving.



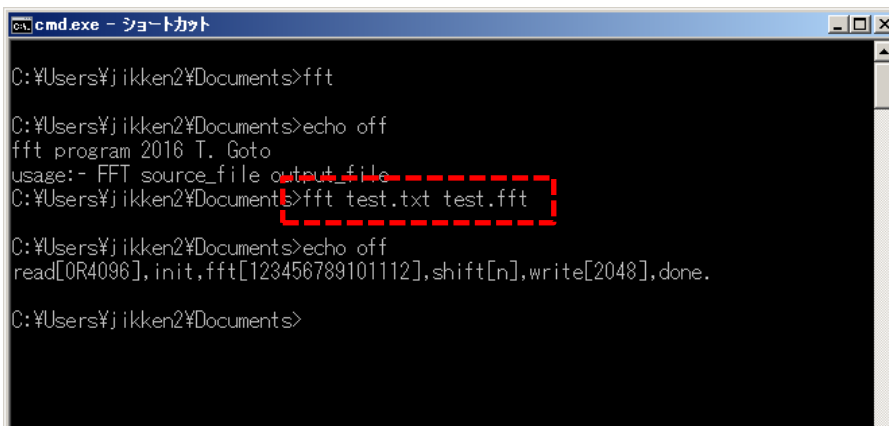
4) FFT

Use FFT.BAT in command shell (CMD).

Note that the output file does not contain *x*-data. You must remember the time window of the oscilloscope to calculate it. (see below).

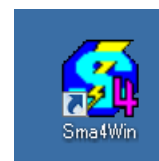


Usage of FFT.BAT: `C>FFT source_file destination_file`



5) Draw graphs

Use Sma4win, which is one of the most famous graph-drawing tool in Japan. You can alternately use Excel if you prefer it.

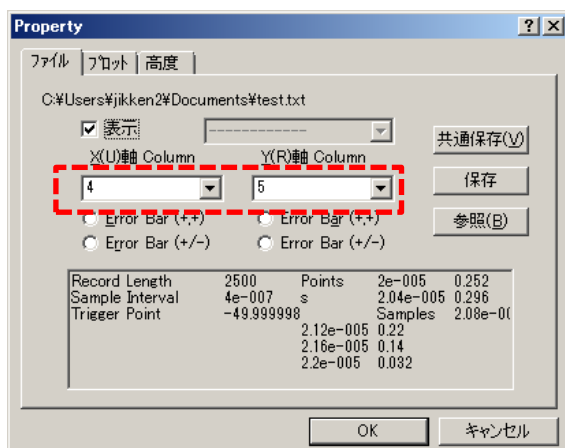


In using Sma4, fist, open a data file first (not a graph file) by hitting Data-Open.

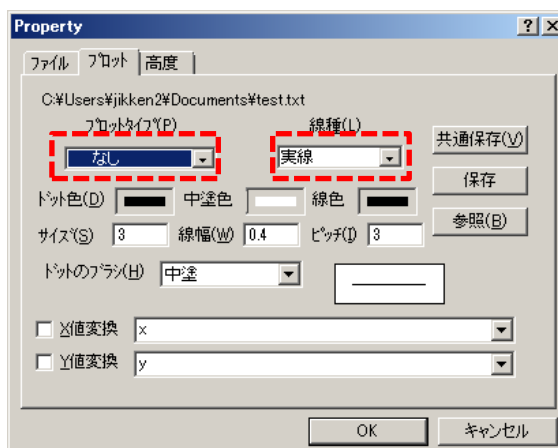
Then, for FID signal data, as shown (i), open the data property menu by Data-Update, and assign 4th and 5th column to x and y-axis, respectively. Next, move to the plot-tab (ii), and set the plot symbol to be none, and choose the line style.

Finally, move to the most right side tab (iii) and set Skip 17 lines at the top, where verbose information of the oscilloscope is contained. This will successfully bring you to a beautiful plot of FID signal (iv).

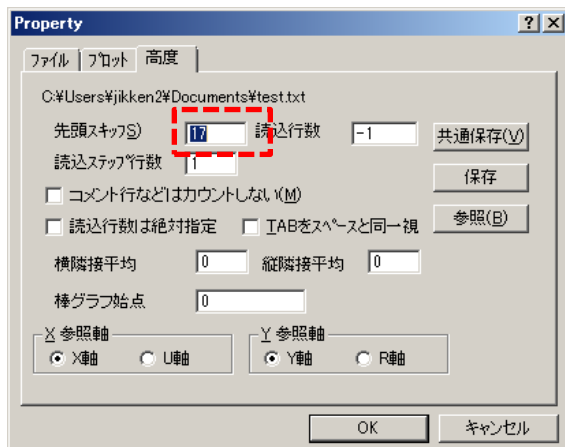
(i) Data column



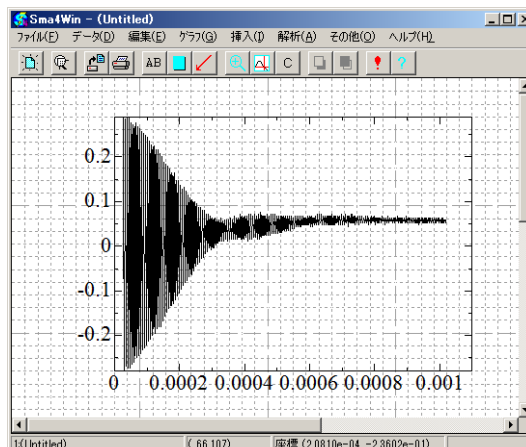
(ii) symbol of plot



(iii) Top line skip



(iv) FID signal



For an FFT data, first as shown in (v), assign “Numbering” to x -axis and leave the y -axis as it is. Then proceed to the next tab (vi) to set y -conversion as,

$$\text{sqrt}((\#0002)^2+(\#0003)^2),$$

which will calculate the power spectrum of 2nd and 3rd columns. And as for x -conversion, set, though not shown in (vi) below,

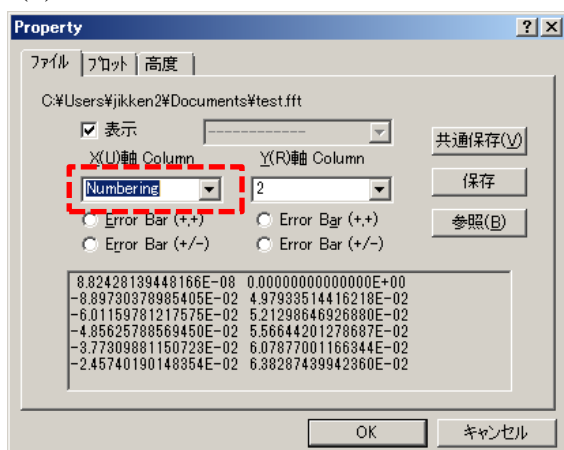
$$x / (\text{time_window} / 2500 * 4096)$$

to show correctly x -axis value in MHz unit; you have to remember for this purpose the time windows of oscilloscope in μsec unit for each data transferred to PC-1. If you leave the x -values as blank, x -axis becomes natural numbers.

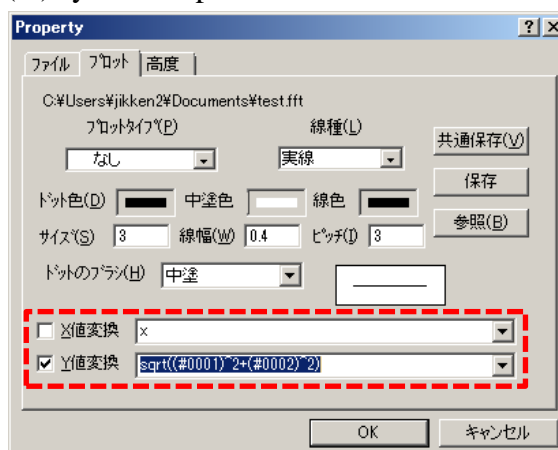
Do not forget to reset the skip lines value 0, if you once set it some finite values in the previous jobs (vii). Then finally, hope you will see the beautiful frequency spectrum (iix).

Note that the sharp peak as in example appears only when the FID oscillates much as in the example shown in (iv).

(v) Data column



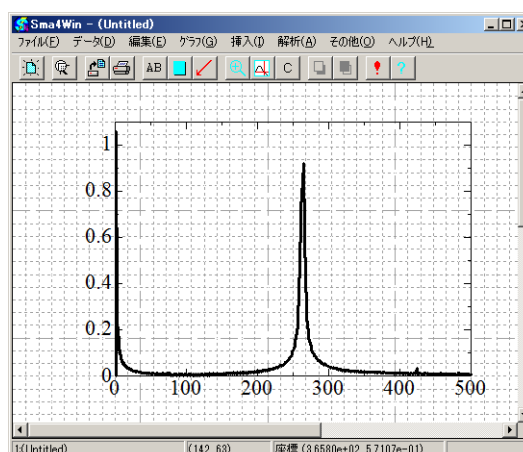
(vi) symbol of plot and data conversion



(vii) Skip lines at the top



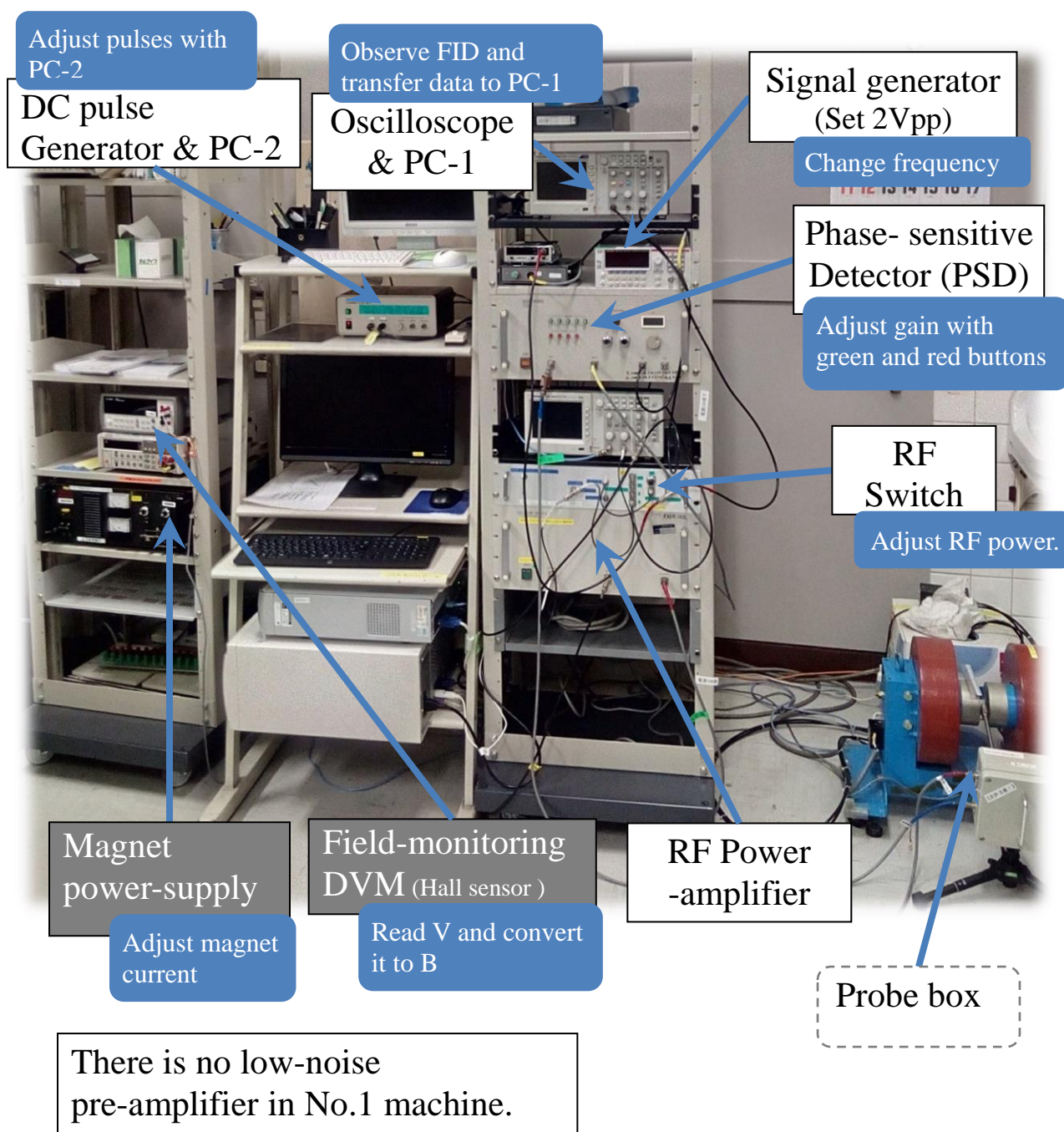
(iix) FFT power spectrum



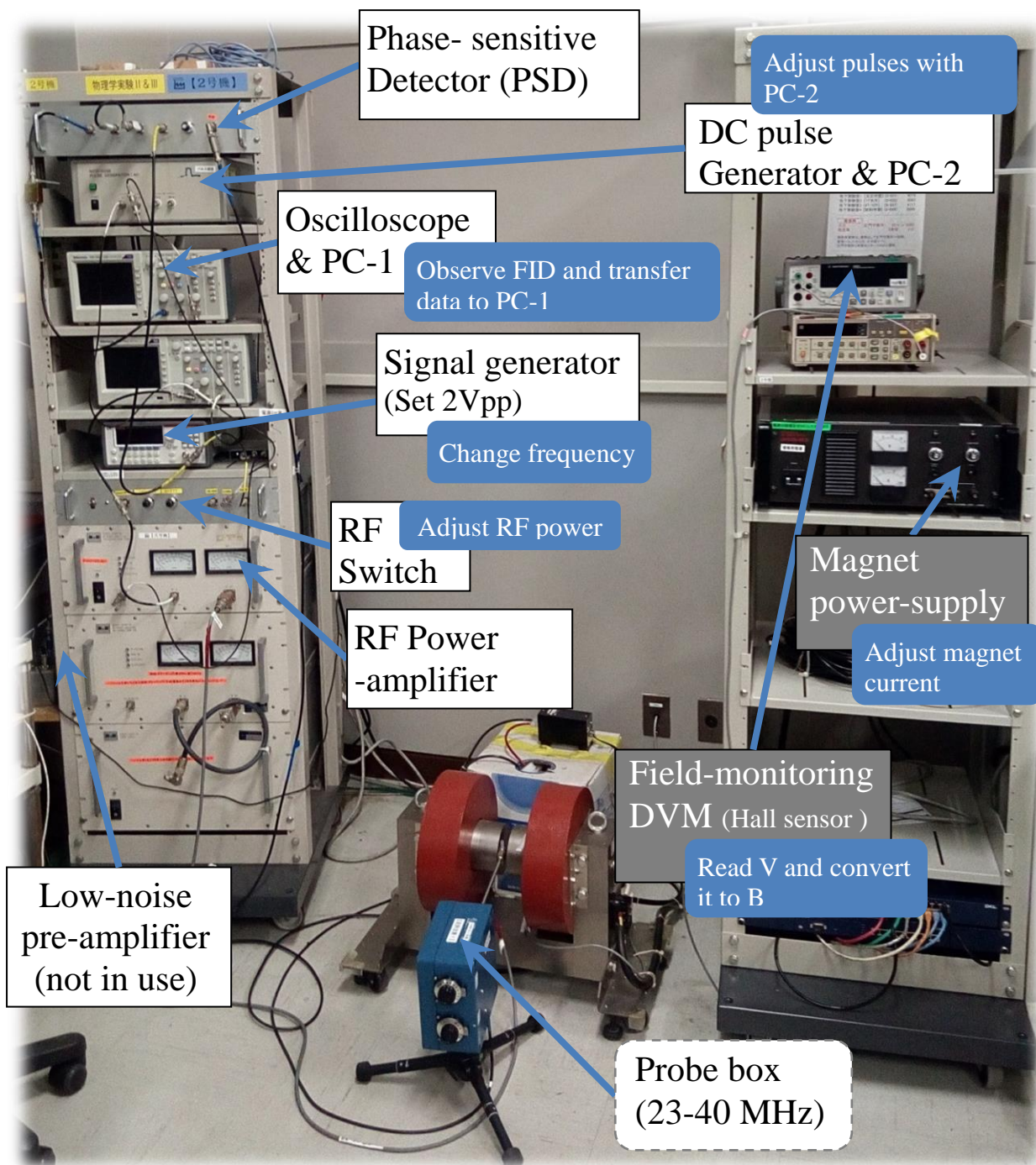
2. NMR spectrometers for this lab course

If you would like to see the NMR apparatus at Goto's lab for low temperature physics research (16 T, 0.3 K), just ask TA or Prof. Goto.

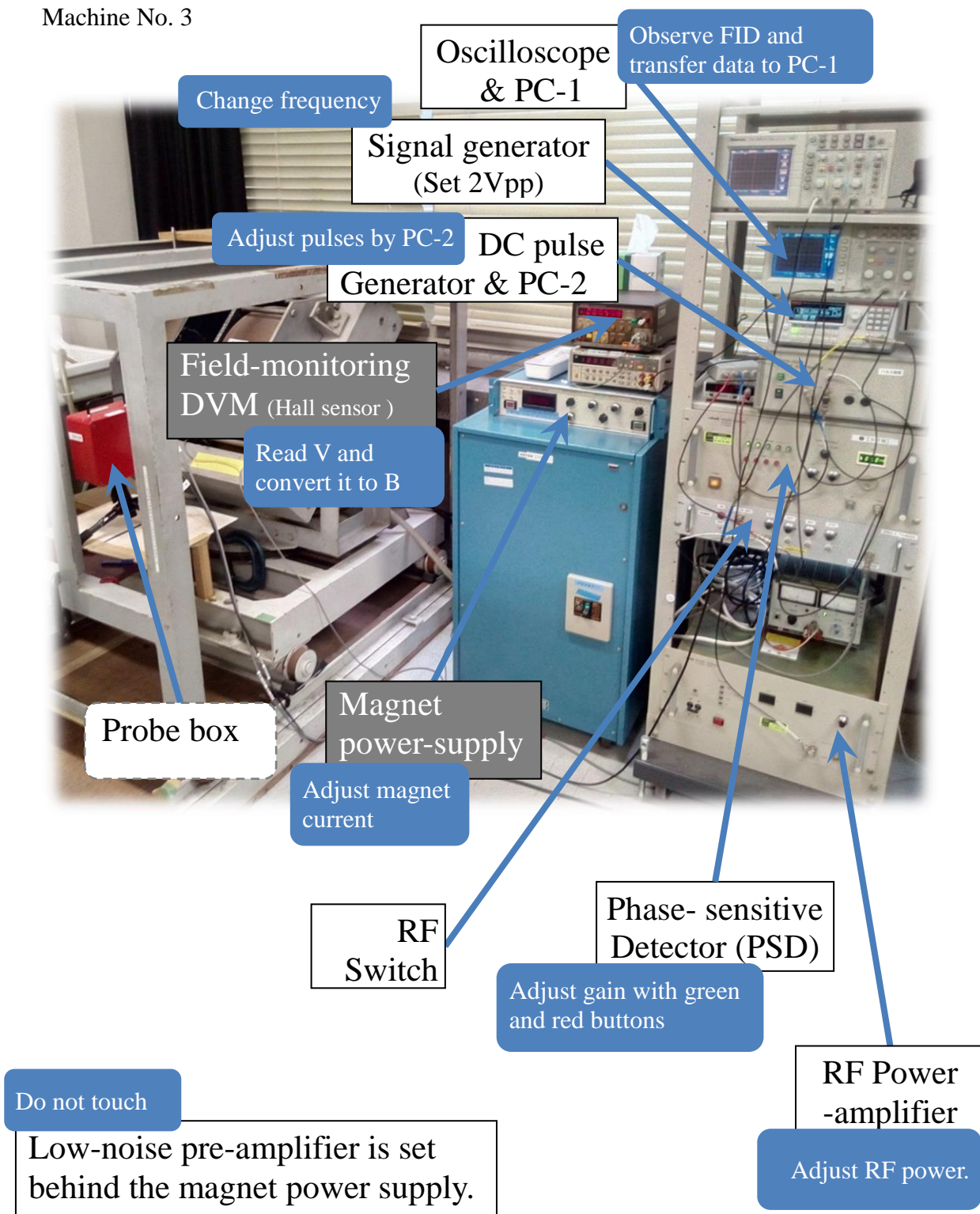
Machine No. 1



Machine No. 2



Machine No. 3



Machine No. 4

