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Design and Construction of Low-Cost EPR Spectrometers for Education

Zeehoon JANG*
Department of Physics, Kookmin University, Seoul 02707, Korea

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Electron paramagnetic resonance (EPR) spectroscopy, which is currently used in various research fields, will be a very important research technique for future researchers. However, because not many experimental apparatuses are suitable for education, experimental education of EPR spectroscopy is not proceeding well in undergraduate courses. The EPR spectrometers applied in research are not used by inexperienced undergraduate student education because of potential problems such as equipment damage. Nonetheless, education on the EPR technique for future researchers is very important and necessary. We have designed and constructed a low-cost EPR spectrometer for educational purposes. The EPR spectrometer described in this paper does not use a radiofrequency (RF) cavity or a waveguide, both of which are hard to use, but is constructed using easy-to-use LC resonators, coaxial cables, and commercially-available RF devices. The EPR spectrometer designed in this way is simple in construction, so undergraduates can easily assemble it and perform experiments. In this way, students will be able to acquire practical experience with equipment production and operation.

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I. INTRODUCTION

After the first observation of the Electron Paramagnetic Resonance (EPR) by Yevgeny K. Zavoisky [1], the EPR technique has been adopted in various fields like physics, chemistry, biology, geochemistry, food industry, material science, medicine, and many other fields [2]. The EPR technique played key role in understanding electromagnetic properties and in obtaining direct structural information of the subjects under investigation. For that reason, the education of the EPR technique is very important to the next generation researchers.

EPR instruments sold as research equipments are typically equipped with radiofrequency (RF) cavities and waveguides, and are very sensitive. However, it is very delicate and difficult to use and maintain due to the use of cavities and waveguides. Thus these research-grade EPR instruments are inadequate for undergraduate courses. Also, commercially available education-purpose EPR instruments usually have sealed structure thus they cannot offer a detailed hands-on experience of the technique. Therefore, the design of a low-cost EPR instrument that is easy to operate, maintainable and can be assembled during class is significant from an educational point of view.

Over the past several decades, the development of the RF devices is splendid and the newly developed devices enable the construction of the low-cost educational-purpose EPR instruments. Recently, many commercial RF devices are sold with a SMA (SubMiniature version A) or BNC (Bayonet Neill-Concelman) connector that can be connected with coaxial cables. At the same time, the characteristics of the coaxial cable has been improved, the loss of the signal is reduced and can be used in a wider frequency range.

In this paper, the design and the construction of the low-cost education-purpose EPR spectrometers is described. In the EPR instruments, LC resonators and

*E-mail: zeehoonj@kookmin.ac.kr

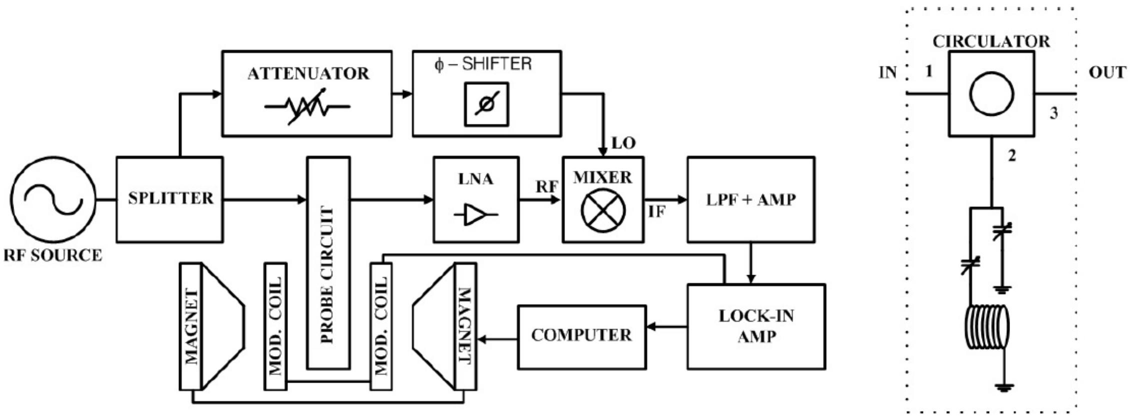

Fig. 1. Schematic diagram of the EPR spectrometer constructed with a circulator. This design is very similar to that of the research-grade EPR spectrometer in terms of circuit architecture.

coaxial cables are used instead of cavity resonator and waveguide. The EPR spectrometer described in this paper is easy to construct, operate and maintain at the undergraduate/low graduate level, and is considered to have a lot of potential as educational instruments for EPR technique. Also, it is very easy to change the frequency in contrast to the research-grade spectrometers. By taking advantage of this point, one can easily perform EPR experiments but also can observe the quantum mechanical phenomena such as the Zeeman effect. One other advantage of the spectrometer described in this paper is that students can acquire hands-on experience of RF devices when they construct the spectrometers with those individual RF devices.

II. DESIGN OF THE SPECTROMETER

Basically, EPR spectrometer is composed of a device which can apply RF to a sample, a device which can detect the RF generated from the sample, and a magnet which can apply variable magnetic field to the sample, *etc*. A typical modern EPR spectrometer uses an RF cavity for both applying and detecting RF signal. And, all RF signal paths are constructed with waveguides. The RF cavity is an extremely low loss resonator with a high quality factor, which is a major reason for its use for EPR spectroscopy. However, RF circuits based on cavities and waveguides are very sensitive and even simple maintenance tasks require professional services. In addition, changing the operating frequency is virtually impossible.

Compared to a cavity, LC tank resonator is easy to handle and inexpensive even though the LC resonator is worse in sensitivity due to the smaller quality factor. It is also noted that coaxial cables are much easier to handle and cost less than waveguides. Thus, the construction of an EPR spectrometer using an LC resonator and coaxial cables is advantageous in terms of handling and cost, and has the additional advantage that the resonant frequency of the LC resonator can easily be changed by changing the capacitance of the trimmer capacitors of the tank circuit.

In this study, two types of spectrometers were designed, constructed and tested. The schematic diagram of the first setup is shown in Fig. 1. As shown in Fig. 1, an RF signal is generated from the source and the RF is fed to the power splitter. The power splitter divides the input RF signal into two RF signals, which have about 3 dB smaller signal strength than that of the input signal.

One of the outputs of the splitter is connected to a reference arm circuit consisting of an attenuator and a phase shifter. As the RF signal passes through the reference arm circuit, the signal is adjusted in terms of phase and amplitude to provide the appropriately adjusted reference RF signal to the LO (Local Oscillator) port of the mixer.

The other output of the splitter is connected to the probe circuit. The function of the probe circuit is to apply RF power to the sample and detect the RF signal coming out of the sample, and both signals must be well separated from each other to prevent interference.

For this purpose, the probe circuit consists of an LC resonator and a circulator. The RF from the splitter enters the circulator and is then applied to the sample via the LC resonator. The RF signal from the sample is transferred to the circulator through the LC resonator and then to the LNA (Low Noise Amplifier).

It is noted that the trimmer capacitors from Voltronics, Co. are used in the resonator but any other trimmer capacitors from other vendors can be used if the capacitance range is appropriate. The resonance characteristics of the resonator can be checked with a vector network analyzer but a setup with an RF source and an oscilloscope can also be used.

Separation of input and output signals is performed using a circulator. Circulator is a passive non-reciprocal device with three or four ports numbered sequentially. Signal transmission in the circulator is cyclic. Signals are forwarded from port 1 to port 2, from port 2 to port 3, and from port 3 to port 1. However, the signal cannot pass from port 2 to port 1, from port 3 to port 2, and from port 1 to port 3. Many circulators are constructed using ferrite materials, which may cause malfunction in a space with a strong magnetic field. The operating frequency range of the circulator is narrow because the operating principle is based on magnetic resonance. Typical circulators with operating frequency lower than a few hundred MHz tend to be bulky and are rarely commercially available. It is noted that, recently, solid state circulator designs using Operational Amplifier (OP AMP) that operates in the low frequency region have been reported [3].

The RF signal emitted by the spins in the sample is passed to the LNA via the probe circuit, and amplified by the LNA and delivered to the RF port of the mixer. The signal output from the IF port of the mixer is passed to a low-frequency amplifier with a low-pass filter (LPF), where the high-frequency component of the signal is removed and only the low-frequency portion is amplified. The amplified signal is fed into a lock-in amplifier (SR830) for phase-locked detection. The output signal of the lock-in amplifier is applied to the field modulation coil. Therefore, only phase-locked signals with field modulation are detected at the lock-in amplifier. A master computer is used to collect data from the lock-in amplifier and to control the sweeping of the DC magnetic field strength.

The knowledge of the function of the mixer is very important in understanding the signal detection method. A mixer is a nonlinear device that can perform frequency conversion of a signal [4]. Typical mixers have an RF input port, a local oscillator (LO) input port, and an IF (intermediate frequency) output port. The RF passing through the reference arm (attenuator and phase shifter) is fed into the LO input of the mixer and the signal acts as a reference signal for "signal detection". The RF applied to the probe circuit eventually reaches the sample and interacts with the electron spins in the sample. The RF signal from sample is extracted from the probe circuit, amplified by the LNA, and transmitted to the RF input of the mixer. In this case, the signal at the output (IF port) of the mixer is expressed as [4], $A_{RF}A_{LO}\sin(\omega_{RF}t)\sin(\omega_{LO}t)$. With the triangular identity, it can be rewritten as,

$$(A_{RF}A_{LO}/2)(\cos(\omega_{RF}-\omega_{LO})t+\cos(\omega_{RF}+\omega_{LO})t). \quad (1)$$

In the equation, A_{RF} and A_{LO} are the amplitudes of the RF signals at RF port and LO port respectively. ω_{RF} and ω_{LO} are the angular frequencies of the RF signals at RF port and LO port. It is noted that, because the signal frequencies at the RF port and the LO port are the same, the signal at the IF port has two frequency components, $2\omega_{LO}$ and 0 (DC).

The next-stage low-pass filter blocks the high-frequency component and the signal transmitted to the lock-in amplifier is $A_{RF}A_{LO}$. (factor 2 is omitted for simplicity.) The amplitude of the RF signal applied to the LO port of the mixer is constant over time since it is not affected by the magnetic resonance. In contrast, the amplitude of the RF applied to the RF port of the mixer is modulated at the frequency of the magnetic field modulation. The lock-in amplifier then only detects the modulated signal at the field modulation frequency.

As shown in Fig. 2, the second setup uses a perpendicular loop antenna and the circulator is not used. An important motivation in constructing the second setup was to construct the spectrometer with a minimum number of devices which is good for inexperienced students. In the second setup, the RF from the RF source is applied

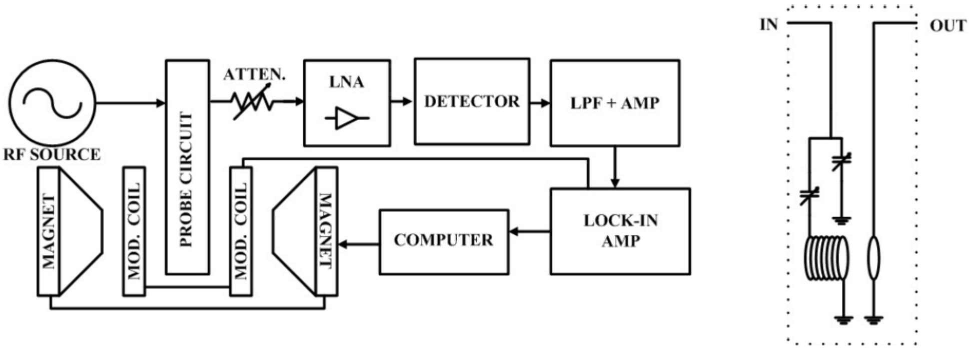

Fig. 2. Schematic diagram of the EPR spectrometer constructed with a perpendicular loop antenna used as a detecting antenna.

to the sample via the LC resonator. The signal from sample is detected with the perpendicular loop antenna and is transmitted to the LNA. In front of the LNA an appropriate attenuator is connected in series because it is quite probable that the LNA can be saturated due to the high power level of the RF from the perpendicular loop antenna. RF signal passing through the LNA (or bypassed the LNA) is transferred to the detector diode and the detector diode outputs a DC signal that is proportional to the logarithm of the RF power at the input of the detector diode. The output of the detector diode is again fed to the preamplifier (SR560) and only the signal at the field modulation frequency is amplified and fed into the lock-in amplifier (SR830).

The reason for placing the loop antenna perpendicular to the coil is to minimize electromagnetic coupling. Nonetheless, capacitive coupling exists between the coil and the loop antenna due to the proximity. In this case, the RF power from the source may be directly transmitted to the loop antenna. Since the RF signal can be relatively large compared to the signal from the sample, the amount of signal measured by the lock-in amplifier is relatively reduced, and the S/N (Signal-to-Noise) is reduced.

In building the entire circuit, we used semi-rigid coaxial cables extensively. Semi-rigid cables are easy to handle. In addition, semi-rigid coaxial cables have superior electrical properties over conventional flexible coaxial cables.

Many parameters must be carefully considered when selecting a particular RF device to be installed in a spectrometer. The two most important parameters are the operating frequency range and the appropriate operating voltage range. Particularly, since the operating frequency range of a general ferrite circulator is very narrow, the selection of the circulator must be done at the initial stage of the design. When selecting circulator, one should also consider the acceptable RF level at the ports. The operating frequency range of the voltage-controlled phase shifter is very limited. Therefore, one should carefully examine the frequency range for the correct operation. It should be noted that, although a mechanical phase shifter having a fairly wide operating frequency range may be used, it is quite expensive and bulky. LNAs also have a limited operating frequency range, but they are not as narrow as circulators. Instead, one should check the input and output power dynamic range for proper operation. In addition, the noise figure is another important parameter that needs to be taken care in selecting the LNA. The output level of the LNA must match the RF port input level specification of the mixer and the RF level at the reference arm must be able to meet the specification of the LO port of the mixer. A preamplifier with a low-pass filter in front of a lock-in amplifier is a typical low-frequency, low-noise amplifier. The filter of the amplifier is set to amplify only the signal at the frequency of the field modulation so that the lock-in amplifier can detect the field-modulated electron paramagnetic resonance signal. The modulation field should be aligned with the main external field. In our setup, small solenoid type coil was used. The coil was wound on the cylinder type bobbin with outer diameter of 10 mm and was made of 100 turns of 0.1 mm Cu wire. The test results of the coil showed that the analog output of the lock-in amplifier (V_{pp} = 3 V, f = 100 kHz) could

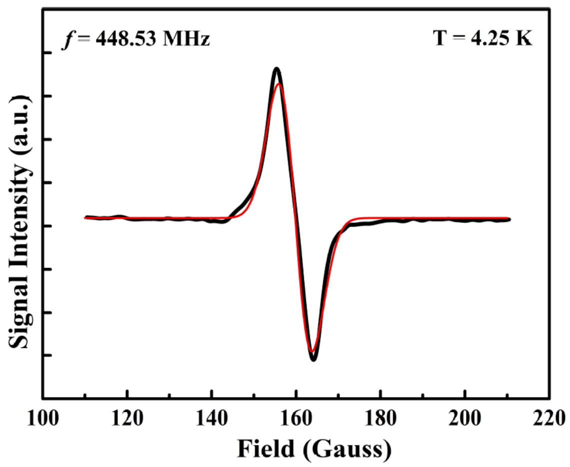

Fig. 3. (Color online) EPR signal detected with the probe circuit using a circulator. The RF frequency is set to be 448.53 MHz and the measurement was done at 4.25 K. The magnetic field sweeping rate was 1 G/s. The red solid line is the best fitting result with the derivative of the Gaussian function.

generate AC magnetic field with amplitude of 1.187 G at the center of the solenoid. At the center of the modulation coil, the coil of the LC resonator is installed and the inductor is directly connected to the semi-rigid coaxial cable which runs from the bottom of the probe to the top of the probe where the cable is connected to tuning-matching capacitor circuit of the LC resonator.

For the generation of the main magnetic field, a sweepable superconducting magnet is used because it is the only available magnet at the time of experiment. But a small laboratory electromagnet or, even Helmholtz type coil could also be used without much modification. Only the probe part should be modified in structure and size according to the magnet and cryostat.

III. EXPERIMENT AND EVALUATION

The signal from DPPH (2,2-diphenyl-1-picrylhydrazyl), which is an EPR standard reference sample, was observed to confirm the operation of the spectrometers. In general, DPPH is used to calibrate the sensitivity of a research-grade EPR spectrometer. The amount of DPPH used in this experiment was less than 1 μg. (It is confirmed with a laboratory precision scale with 1 μg resolution.) As a sample container, a quartz tube with an outer diameter of 4 mm was used, in which a laboratory wiping paper (Kimwipes) sheet impregnated with DPPH was placed and tightly sealed.

In the sweepable superconducting magnet used, the sample space is immersed in a low-temperature cryogen liquid. In order to conduct experiments at room temperature, the heater in the cryostat must be continuously supplied with electric power and liquid helium consumption rate is quite high. Therefore, this experiment was carried out at the temperature in the vicinity of 4.2 K without heater.

Due to the magnetic field measurement scheme of the magnet power supply, there was a difference between the magnitude of the external magnetic field measured by the magnet power supply and the actual value of the magnetic field applied to the sample. Magnet power supply measures current and converts it into a magnetic field value. Therefore, discrepancies may occur due to remnant magnetic fields. The correct way to measure the magnetic field is to use a separate magnetic field sensor. Such a magnetic field sensor could not be installed on the magnets due to the structure of the magnet. The error of the measured magnetic field values was corrected through the theoretical calculation of the resonance condition after the experiment. And the value of G factor could not be obtained because of the error in the measured magnetic field.

The first experiment was carried out using the spectrometer with a circulator. (Fig. 1) As shown in Fig. 3, the measurement result is a signal in the form of the derivative of a typical absorption line since a field modulation method is adopted. The line width obtained from the data is 8.8 G, which is somewhat larger than the known value of 1.5 - 4.7 G for the solid state DPPH [5], probably due to the large inhomogeneity of the sweepable superconducting magnet.

The measured S/N ratio is about 280, which is smaller than the results from typical research EPR spectrometer with cavity resonator. It is due to weak RF intensity at the sample of the LC resonator. Weak RF intensity in LC resonator is due to smaller quality factor of LC resonator compared to that of cavity resonator. Also, the bad inhomogeneity of the sweepable superconducting magnet may have the effect of reducing the magnitude of the signal because of the line broadening effect.

Table 1. RF devices used to construct the first setup.

Devices	Model Number	Manufacturer
Circulator	RFLC101M30M50	RF-Lambda
LNA	GNA-117T	RF Bay, Inc.
Power splitter	ZSC-2-4+	Minicircuits, Inc.
Attenuator	ZX76-31R5A-PPS+	Minicircuits, Inc.
Phase shifter	JSPHS-446+	Minicircuits, Inc.
Mixer	ZX05-1+	Minicircuits, Inc.

As a practical guide, we enlisted the RF devices installed in this setup in Table 1. It is noted that the operating frequency range of the phase shifter used in the setup is from 366 to 446 MHz. However, this device is confirmed to operate normally at 448.53 MHz where the experiment was performed.

The experimental result obtained by using the second alternative experimental setup without the circulator is shown in Fig. 4.

Measured S/N ratio was 34 which is even smaller than the result from the first setup. We believe the smaller S/N ratio is due to the structure of the setup. The spurious capacitive coupling between the perpendicular loop antenna and the coil of the LC resonator increases background RF level at the loop antenna. The increase causes the reduction of the S/N ratio. Similar to the results from the first setup, line width obtained from the measured data is 7.2 G which is larger than the known value (1.5 - 4.7 G) [5]. We attribute the large line width is due to the inhomogeneity of the magnet.

In the second setup, the LC resonator coil was fabricated with a gap between the windings. Through this gap, the RF emitted from the sample can pass through to the loop antenna. Considering the operating frequency, the coil was fabricated by winding a 0.5 mm wire in 2 turns and the gap size is 1 mm. The loop antenna used in this apparatus was wound with 0.1 mm wire into a circular ring shape with a diameter of 5 mm.

The only RF device used in this setup, LNA, is ZX60-P33ULN+ from Minicircuits, inc. It is noted that the noise figure of the LNA is 0.38 dB which is one of the smallest value that can be obtained with commercially available devices. The detector diode used in the setup is ZX47-60LN-S+ (Minicircuits, Inc.).

It is well known that the working principles of the field sweeping Nuclear Magnetic Resonance (NMR) and of the field sweeping Electron Paramagnetic Resonance (EPR) are the same. With this motivation and by utilizing high field generation capability (up to 12 Tesla) of the magnet used in the experiment, we have performed ^{1}H sweeping NMR experiment with the first setup and the result is shown in Fig. 5.

The measured S/N ratio is 2780 which is very large compared to the EPR results. This is because the amount of protons in the sample (mainly on the paper in the sample tube) is much larger than that of the free electron spins in DPPH sample. The line width ob-

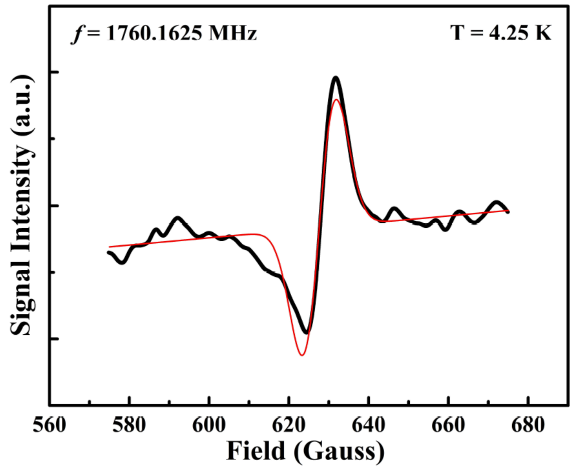

Fig. 4. (Color online) EPR signal detected with the probe circuit using a perpendicular loop antenna. The RF frequency is set to be 1760.1625 MHz and the measurement was done at 4.25 K. The magnetic field sweeping rate was 1 G/s. The red solid line is the best fitting result with the derivative of the Gaussian function.

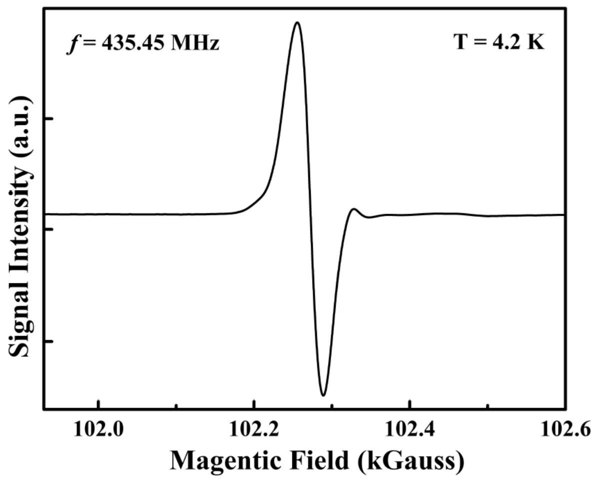

Fig. 5. ^{1}H sweeping NMR result obtained with the first setup. The RF frequency is set to be 435.45 MHz and the measurement was done at 4.25 K. The magnetic field sweeping rate was 1 G/s.

tained from the data is 33.6 G, which is much larger than the value of a few gauss from the liquid phase proton NMR experiments. Considering that the sample is in solid state and the bad inhomogeneity of the sweeping magnet, the large line width is understandable.

IV. CONCLUSION

We have designed and built two different versions of EPR spectrometers with LC resonators and coaxial cables which is different from conventional research grade EPR spectrometer in which cavity and waveguide are extensively used. The operation of the two spectrometers was confirmed through typical EPR experiments on DPPH and ^{1}H sweeping NMR experiment. Obtained sensitivity of the spectrometers are found to be lower than that of research-grade EPR spectrometers but it can be overcome by increasing the amount of the sample.

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