A portable EPR system for the absolute polarimetry of noble gases

Takashi Ino

KEK, High Energy Accelerator Research Organization, Tsukuba 305-0801, Japan
takashi.ino@kek.jp

Abstract. A simple and portable electron paramagnetic resonance (EPR) system has been developed for the absolute polarimetry of noble gases polarized by spin-exchange optical pumping. By using modern digital technology together with software implementation of phase-sensitive detection and feedback control, the new system has become much more compact than the conventional EPR apparatus and can be easily transported anywhere. The main components of the new EPR system are a computer and a PC-based oscilloscope with a built-in function generator. The raw signal data is processed in real time by a computer, which offers great flexibility to the new system. By modifying the data-processing algorithm, it can be customized and applied to other scientific and engineering measurements that utilize phase-sensitive detection.

1. Introduction

Spin-polarized noble gases take active roles in scientific research as well as in medical applications [1]. Polarized $^3$He gas is regularly used as a neutron spin filter in neutron scattering, as a scattering target with charged particle and photon beams for studying nuclear and nucleon structures, as a marker gas in magnetic resonance imaging (MRI), etc. Polarized $^{129}$Xe gas is also used in MRI as well as in fundamental physics research such as electric dipole moment searches and symmetry breaking.

The nuclear spins of noble gases can be aligned by spin-exchange optical pumping (SEOP) or by metastability exchange optical pumping (MEOP). In SEOP, the atomic polarization of an alkali-metal is achieved by optical pumping, and then the spin exchange between alkali-metal atoms and noble gas nuclei accomplishes the nuclear polarization of a noble gas. MEOP is another method for polarizing $^3$He gas. Instead of the alkali-metal atoms in SEOP, optically polarized metastable helium atoms act as the spin carrier for the $^3$He nuclear polarization in MEOP.

The absolute polarization of noble gases is a key parameter since the quality of the measurement strongly depends on the degree of gas polarization; higher polarization provides better quality in almost all applications. Nuclear magnetic resonance (NMR) is a common method to evaluate nuclear spin polarizations. Although NMR usually has a high sensitivity, the absolute polarization cannot be determined without a proper calibration.

Electron paramagnetic resonance (EPR) of alkali-metal atoms is an alternative method that can be used in SEOP to measure the nuclear spin polarization of noble gases. Unlike NMR, calibrations for the absolute polarimetry are essentially unnecessary. In the presence of a polarized noble gas, the EPR frequency of an alkali-metal is shifted in proportion to the noble gas magnetization. The EPR frequency shift of an alkali-metal with the nuclear spin $I$ becomes [2, 3]
\[ \Delta |v_A| = \frac{1}{\hbar} \mu_B |g_S| \frac{8\pi}{3} (1 + \epsilon) \frac{\mu_K}{K} \kappa_{AX} [X] \langle K_z \rangle, \tag{1} \]

where \( \hbar \) is the Planck constant, \( \mu_B \) is the Bohr magneton, \( g_S \) is the Landé g-factor, \( [X] \) is the noble gas number density, and \( \langle K_z \rangle \) is the longitudinal spin of the noble gas nuclei. The magnetic moment and spin of the noble gas nuclei are denoted by \( \mu_K \) and \( K \), respectively. The dimensionless constant \( \kappa_{AX} \) accounts for an enhancement to the classical magnetic shift due to the overlap of the alkali-metal electrons and the noble gas nuclei. The nonlinear Zeeman effect on the alkali-metal magnetic moment by the external magnetic field cannot be neglected, and results in a correction \( \epsilon \).

2. Principle of EPR frequency measurement

We focus on the absolute polarimetry of \(^3\)He gas polarized by SEOP with Rb. Figure 1 shows the atomic energy levels of \(^{85}\)Rb and \(^{87}\)Rb. During the optical pumping of Rb, either the \( m_F = +3 \) or \(-3 \) sublevel of the ground state is populated for \(^{85}\)Rb and \( m_F = +2 \) or \(-2 \) for \(^{87}\)Rb depending on the circularity of the pumping light. When a radio frequency (RF) field with a frequency matched to the \( m_F = +3 \rightarrow +2 \) or \( m_F = -3 \rightarrow -2 \) transition is applied, the \(^{85}\)Rb atoms absorb more pumping photons, resulting in more emission of the D\(_2\) fluorescent light at 780 nm. The same is true for the \( F = +2 \rightarrow +1 \) or \( F = -2 \rightarrow -1 \) transition of \(^{87}\)Rb.

![Figure 1. Atomic energy levels of (a) \(^{85}\)Rb and (b) \(^{87}\)Rb. During the optical pumping, the energy sublevel \( m_F = +3 \) or \(-3 \) of the S\(_{1/2}\) state is populated for \(^{85}\)Rb and \( m_F = +2 \) or \(-2 \) for \(^{87}\)Rb.](image)

The EPR frequency can be determined from the dependence of the Rb fluorescence on the applied RF field frequency. If the applied RF field is periodically modulated in frequency, the fluorescent intensity increases at the moment the RF field frequency \( \nu(t) \) coincides with the transition energy (Fig. 2). The modulated RF field frequency can be written as

\[ \nu(t) = \nu_0 + \nu_{\text{mod}}(t) \]
for the center frequency $\nu_0$ and the modulation $\nu_{\text{mod}}(t)$. When the frequency is modulated by a sinusoidal function with a frequency deviation $\nu_1$ and a modulation frequency $\omega$,

$$\nu_{\text{mod}}(t) = \nu_1 \sin(\omega t).$$  \hspace{1cm} (3)

The time average of the product of the fluorescent intensity $I(t)$ and the modulation $\nu_{\text{mod}}(t)$ will be

$$X = \frac{\int I(t) \cdot \nu_{\text{mod}}(t) \, dt}{\int dt}. \hspace{1cm} (4)$$

This time-averaging is called phase-sensitive detection (PSD), a powerful technique commonly used in lock-in amplifiers for precision measurements [4]. The modulation $\nu_{\text{mod}}(t)$ or $\sin(\omega t)$ is a reference waveform for the PSD of $I(t)$ in Eq. (4). Assuming the EPR frequency $\nu_{\text{EPR}}$ is situated within the modulated frequencies, $X < 0$ if $\nu_{\text{EPR}} < \nu_0$ and $X > 0$ if $\nu_{\text{EPR}} > \nu_0$ as schematically shown in Fig. 2 (a) and (c), respectively. The PSD output $X$ can be applied as feedback to $\nu_0$ to attain $X = 0$ and hence $\nu_0 = \nu_{\text{EPR}}$.

![Figure 2](image.png)

**Figure 2.** Schematic showing the frequency modulation of the applied RF field and the Rb fluorescent emission. The applied RF field is frequency modulated (sinusoidal curves) and the fluorescence intensity increases when the RF field frequency coincides with the EPR frequency $\nu_{\text{EPR}}$ (shown with circles).

A block diagram of an EPR system for the absolute polarimetry of noble gases is presented in Fig. 3. The modulation source generates a sine waveform with a typical modulating frequency of 100 Hz ($\omega \sim 600 \text{ rad/s}$) and a typical frequency deviation $\nu_1$ of 10 kHz. The output voltage of the feedback & mixer circuit is the sum of $V_{\text{mod}}(t)$ and $\Delta V_0$, which correspond to $\nu_{\text{mod}}(t)$ and $\Delta \nu_0$, respectively. Here, $\Delta \nu_0$ is a correction to $\nu_0$ to bring $\nu_0 + \Delta \nu_0 \rightarrow \nu_{\text{EPR}}$ in the feedback loop; and a PI (proportional-integral) controller is usually used as a transfer function to convert $X$ into $\Delta V_0$. The voltage-controlled oscillator (VCO) generates a frequency modulated RF waveform depending on the output voltage of the feedback & mixer circuit, where $\nu_0$ is set internally. The RF is provided to an EPR coil to apply an RF field to the optically pumped Rb. The Rb fluorescent intensity is converted into a voltage signal by a photodetector and fed to the lock-in amplifier for PSD; the output of the PSD is $X$. See [2, 5, 6, 7] for details of the EPR system.
Figure 3. Block diagram of an analog EPR system. The feedback loop locks $\nu_0 + \Delta\nu_0 = \nu_{EPR}$.

3. Digital EPR system

The conventional analog EPR system in Fig. 3 includes several electronic modules: a lock-in amplifier, a feedback & mixer circuit, a VCO, a modulation source, and a frequency counter. Some of their functions are simple and can be implemented with software. The PSD in the lock-in amplifier and the following feedback & mixer functions will be replaced by numerical computation, and the modulation source and VCO will be substituted by a modern function generator (FG). Simplified by the use of modern technology, the EPR system has evolved in a digital way. The block diagram of a new digital EPR system is presented in Fig. 4. It is much simpler than that of the conventional analog EPR system. In order to attain $\nu_0 = \nu_{EPR}$ by means of the feedback loop, an initial frequency expected for the isotope being measured is determined and designated as $\nu_0$; then, the following procedure is carried out:

1. A frequency modulated RF signal is generated by the FG integrated in the oscilloscope. Using the sweep mode, the frequency is periodically swept up and down, which is equivalent to triangular frequency modulation.

2. The intensity of the Rb fluorescence is converted into a voltage signal by a photodetector, and it is stored in the oscilloscope while the modulated RF is applied to the optically pumped Rb.

3. The storage data is transferred to a computer for real-time data processing. Using Eq. (4), $X$ is computed with a virtual reference waveform, which is a software-generated triangular function synchronized with $v_{mod}(t)$. A correction $\Delta\nu_0$ that brings $\nu_0 + \Delta\nu_0 \rightarrow \nu_{EPR}$ is calculated from $X$ using the PI (proportional-integral) control algorithm.

4. A new frequency $\nu_0 (= \nu_0 + \Delta\nu_0)$ is set, and the above procedure is repeated continuously from (1).

This process is essentially the same as the feedback loop mechanism in the analog EPR system.

The digital EPR system consists only of a computer and a PC-based oscilloscope with a photodetector and an EPR coil as presented in Fig. 5. The oscilloscope (Pico Technology PicoScope 5000 series) has a built-in FG and is controlled by a computer. The photodetector (Thorlabs PDA36A-EC) output is directly connected to the oscilloscope input. A few-turn coil with a diameter of 80 mm (EPR coil) generates an RF magnetic field. The relevant specifications of the oscilloscope and built-in FG are listed in Table 1. The output voltage swing of the FG is limited to $\pm 2$ V, and an RF amplifier or an impedance-matching circuit can optionally be placed between the FG and the EPR coil to boost the RF field strength. The circuit diagrams are shown in Fig. 6 for the RF amplifier [8] and the impedance-matching network.
4. EPR frequency measurement

The EPR frequencies were measured for optically pumped Rb using a SEOP $^{3}$He cell fabricated as a neutron spin filter (Fig. 7). The cylindrical cell is 60 mm in diameter and 70 mm in length. It was filled with a $^{3}$He gas density of 3.3 amagat (An amagat is the density of the gas at 1 atm at 273 K.) and a N$_2$ gas density of ~0.1 amagat together with a small amount of Rb and K for hybrid-SEOP [9]. The $^{3}$He cell was placed inside an oven. The fluorescent light from Rb was guided to the photodetector with an aluminum tube that collimated the view to the $^{3}$He cell only and did not allow any light from the pumping laser to enter the photodetector. Additionally, a 780 nm optical bandpass filter (Thorlabs FBH780-10) was placed in front of the photodetector. An EPR coil was located inside the oven near the $^{3}$He cell, and an impedance-matching network was used in this apparatus as shown in Fig. 7.
Table 1. Specifications of the oscilloscope with a built-in function generator relevant to the digital EPR system.

| Oscilloscope                  | Built-in function generator |
|-------------------------------|-----------------------------|
| Input ADC resolution          | Output signal               |
| 16 bit                        | Sine wave                   |
| Sampling rate                 | Signal frequency            |
| Up to 62.5 MS/s (16 bit mode) | Up to 20 MHz                |
| Buffer memory                 | Frequency sweep mode        |
| 64 to 256 MS (model dependent)| Up and down (linear)        |
| Input range                   | Output voltage range        |
| ±10 mV to ±20 V               | ±2 V                        |
| Bandwidth                     |                             |
| 60 to 200 MHz (model dependent)|                             |

Figure 6. Circuit diagrams of (a) the RF amplifier and (b) the impedance-matching network. Either can be optionally used for boosting the RF field strength.

Figure 7. Apparatus for the EPR frequency measurement. The optical pumping laser illuminated the $^3$He cell from the other side.
The EPR frequency shift is extracted with minimal systematic uncertainty by taking the difference of the EPR frequencies measured for the $^3$He nuclear spins in parallel and in anti-parallel with the electron spins of the Rb atoms. The spin reversal of $^3$He nuclei can be accomplished by using an NMR technique called adiabatic fast passage (AFP) [10]. Upon applying an oscillating magnetic field perpendicular to the static field that defines the quantization axis of the spins, the $^3$He nuclear spins are instantaneously reversed by sweeping the oscillating frequency or the static field strength so that it passes through the Larmor resonance. The oven shown in Fig. 7 is equipped with frequency-sweep AFP NMR that is capable of a $^3$He spin reversal and a simultaneous polarization measurement [11]. To further reduce the systematic uncertainty arose from the instability of the static magnetic field strength, a current stabilizing circuit [12] was used for the solenoid power supply.

The $^3$He cell was optically pumped at $250^\circ\mathrm{C}$ for more than 24 hours until the $^3$He polarization reached saturation. The Rb electron spins were aligned in the low energy state; that is, the $m_F = -3$ state was populated for $^{85}\text{Rb}$ and $m_F = -2$ for $^{87}\text{Rb}$. While applying the frequency modulated RF field to the $^3$He cell with a modulating frequency of $120$ Hz and a frequency deviation $\nu_s = 25$ kHz, the center frequency of the modulated RF $\nu_0$ was continuously recorded. During the measurement, the $^3$He spins were reversed several times by AFP. The results are plotted in Fig. 8 for $^{85}\text{Rb}$ and $^{87}\text{Rb}$. The static field strength $B = 2.36$ mT corresponded to $\nu_{\text{EPR}} \approx 11.23$ MHz for $^{85}\text{Rb}$ and $\nu_{\text{EPR}} \approx 16.61$ MHz for $^{87}\text{Rb}$. In each isotope measurement, $\nu_0$ jumped between two frequencies depending on the $^3$He spin state. The EPR frequency shifts $\Delta|\nu_A|$ were 21.3 kHz and 31.8 kHz for $^{85}\text{Rb}$ and $^{87}\text{Rb}$, respectively.

The absolute $^3$He polarization $P_{\text{He}}$ was estimated by Eq. 1 using the temperature dependent enhancement factor for the Rb-$^3$He pair

$$\kappa_{AX} = 6.39 + 0.00914[T - 200]$$

and the magnetic moment correction to the external magnetic field $B$

$$\epsilon = \frac{4I\Omega}{(2I + 1)\delta\nu_{\text{hfs}}} + \frac{6I(2I - 1)\Omega^2}{(2I + 1)^2\delta\nu_{\text{hfs}}^2}$$

taken from Ref. 3, where $\Omega = g_S\mu_B B/\hbar$ and $\delta\nu_{\text{hfs}}$ is the alkali-metal hyperfine splitting (3036 MHz for $^{85}\text{Rb}$, 6835 MHz for $^{87}\text{Rb}$). In equation (5), $T$ is the temperature in °C. Note that $\kappa_{AX}$ is valid only for spherical cells, and geometrical corrections are necessary for cells in different shapes [3, 13]. We calculated a geometrical correction for our cylindrical cell following [13], and it was found to be much less than 1% and omitted. The other errors are listed in Table 2. The number density of $^3$He atoms in the cell was measured by the neutron transmission; the uncertainty mainly comes from the neutron path length in the gas and cell window thickness as well as the statistical error. The temperature was measured using a non-magnetic thermocouple attached to the cell; considering the laser heating and thermal conductivity of the cell, the uncertainty of the gas temperature is assumed to be 10 K, and the corresponding uncertainty on the enhancement factor becomes 1%. The error of $\kappa_{AX}$ is taken from [3, 7].

Finally, we have obtained $P_{\text{He}} = 0.80 \pm 0.03$ and $0.82 \pm 0.03$ for $^{85}\text{Rb}$ and $^{87}\text{Rb}$, respectively. The $^3$He polarizations estimated from the $^{85}\text{Rb}$ and $^{87}\text{Rb}$ EPR frequency shifts are consistent with each other.

As a cross check, the $^{85}\text{Rb}$ EPR frequency shifts are compared with AFP NMR measurements of the polarized $^3$He [11]. The EPR frequencies and AFP NMR signals were measured at the same times during the optical pumping of a $^3$He cell. The results are shown in Fig. 9. A linear correlation between the frequency shifts and AFP NMR signals is clearly seen. A linear fit to the data has resulted in $Y = (0.452 \pm 0.001)X + (0.03 \pm 0.05)$, where $Y$ and $X$ are the $^{85}\text{Rb}$ EPR frequency shift in kHz and the AFP NMR signal height in mV, respectively.
Figure 8. EPR frequencies measured by the digital EPR system for (a) $^{85}$Rb and (b) $^{87}$Rb.

Table 2. List of systematic uncertainties on the absolute $^3$He polarimetry by the Rb EPR frequency shift measurement.

| Source                          | Uncertainty |
|---------------------------------|-------------|
| $^3$He number density [$X$]     | 0.02        |
| Temperature                     | 0.01        |
| Enhancement factor $\kappa_{AX}$| 0.02        |
| $\nu_0$ determination           | < 0.003     |
| Total                           | 0.03        |

Figure 9. $^{85}$Rb EPR frequency shifts and AFP NMR signals. The measurements are plotted as open circles. The measurement errors are smaller than the symbols and omitted. The line shows the linear fit result.
5. Summary
A portable digital EPR system has been developed for the absolute polarimetry of noble gases polarized by SEOP. The system is composed of only a few pieces of electronic equipment: a computer, a PC-based oscilloscope with a built-in function generator, a photodetector, and optional electronics. This approach has significantly reduced the size and cost compared to a conventional analog EPR system, which has made the new system handy and transportable. The key to the development is software implementation of the phase-sensitive detector and feedback control for the EPR frequency measurement. The advantages are not only the size and cost of the system, but also its flexibility. The raw signal is recorded by an oscilloscope and processed in real time by software, which can be easily modified for other applications. In this report, we have demonstrated the EPR frequency measurement for Rb, but this idea can be applied to other scientific and engineering measurements that use phase-sensitive detection to extract weak signals embedded in strong noise or background.

Acknowledgements
This work was partially supported by JSPS KAKENHI Grant Number 16H02125. I would like to thank Prof. K. Sekiguchi and her group of Tohoku University for inspiring me to pursue this new development.

References
[1] Gentile T R, Nacher P J, Saam B and Walker T G 2017 Rev. Mod. Phys. 89 045004
[2] Schaefer S R, Cates G D, Chien T R, Gonatas D, Happer W and Walker T G 1989 Phys. Rev. A 39 5613
[3] Babcock E, Nelson I A, Kadlecek S and Walker T G 2005 Phys. Rev. A 71 013414
[4] Blair D P and Sydenham P H 1975 J. Phys. E: Sci. Instrum. 8 621
[5] Newbury N R, Barton A S, Bogorad P, Cates G D, Gatzke M, Mabuchi H and Saam B 1993 Phys. Rev. A 48 558
[6] Barton A S, Newbury N R, Cates G D, Driehuys B, Middleton H and Saam B 1994 Phys. Rev. A 49 2766
[7] Romalis M and Cates G 1998 Phys. Rev. A 58 3004
[8] The RF amplifier circuit is based on the “NB6M Miniboots” by Wayne McFee, NB6M; http://www.norcalqrp.org/nb6mm miniboots.htm.
[9] Babcock E, Nelson I, Kadlecek S, Driehuys B, Anderson L W, Hersman F W and Walker T G 2003 Phys. Rev. Lett. 91 123003
[10] Abragam A 1961 Principles of Nuclear Magnetism (Clarendon Press)
[11] Ino T 2018 JPS Conf. Proc. 22 011016
[12] Ino T 2012 Rev. Sci. Instrum. 83 045101
[13] Chann B, Babcock E, Anderson L W and Walker T G 2002 Phys. Rev. A 66 032703