Polarized Target Nuclear Magnetic Resonance Measurements with Deep Learning

Devin Seay, Ishara Fernando, Dustin Keller
University of Virginia

11/07/2023
Trento, Italy

Table of Contents

Acknowledgement

Special thanks to UNH, EuroLabs, Jefferson Lab, INFN and ECT*

Spin-1 Target Material I

- Spin-1 target material that are polycrystalline materials with noncubic symmetry, such as deuterium, have a characteristic Pake double NMR lineshape that arises from transitions in quadrupolar nuclei that possess an orientation dependence.
- Spin-1 polarized nuclear targets can be used to investigate partonic degrees of freedom in nucleons/nuclei and explore how these degrees of freedom manifest into partonic dynamics and nuclear properties.
- We can manipulate ascpet of target polarization to achieve spin configurations that optimize a particular observable in scattering experiments. This can be done via highly controlled modulation of RF near the Larmor frequency of the target spins.
  - This requires two sources of irradiation: microwaves for the DNP process, which transfers polarization from free electrons to the nucleons, and an additional RF near the Larmor frequency that is used to manipulate the population of energy levels from equilibrium.

Spin-1 Target Material II

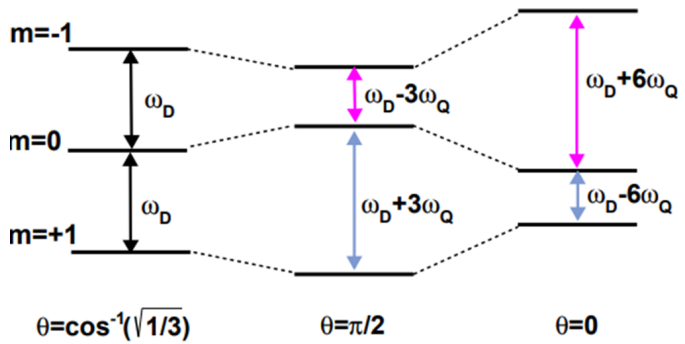


Figure: Energy level diagram for deuteron in a magnetic field for three values of θ where $\hbar\omega_D$ is the deuteron Zeeman energy and $\hbar\omega_Q$ is the quadrupole energy. Colors indicate which transition corresponds to which peak is shown.

Nuclear Magnetic Resonance (NMR) I

- Nuclear Magnetic Resonance, or NMR, is the physical phenomenon that occurs when a constant magnetic field is applied to nuclei at resonance which is perturbed by a weak oscillating magnetic field, which causes the nuclei to respond by producing an electromagnetic signal with a frequency characteristic of the magnetic field of the nuclei.

Nuclear Magnetic Resonance (NMR) II

- For a polarizing environment, let's assume a magnetic field $\vec{B}$ is parallel to the target's central axis. Since $\vec{B}$ sits in the most homogenous region of the field and the polarized material crystals domain is arbitrary, the stastic magnetic susceptibility tensor is isotropic and approximated by the unit tensor.
- In a magnetic field, a spin-1 target will have Zeeman splitting and a quadrupole contribution that depends on the field strength. At 5T, a small correction can be made to the Zeeman energy levels such that the spin-1 target undergoes separation into three energy levels E_m, where $m = \pm 1, 0$.
- For a polarized target setup that includes a magnet producing a cylindrically symmetryic field oriented in the z-direction, the energy levels of deuterium are expressed as

$$E_m = -\hbar\omega_d m + \hbar\omega_q \{3\cos^2(\theta) - 1 + \eta \sin^2(\theta)\cos(2\phi)\}(3m^2 - 2) \quad (1)$$

Where $\hbar\omega_d$ is the deuteron Zeeman energy and $\hbar\omega_d$ is the quadrupole energy. θ is the polar angle between the magnetic field and the deuteron electric field gradient, and ϕ and η are parameters that describe the deuterons' bonds' orientation in the target molecule.

Nuclear Magnetic Resonance (NMR) III

- Transition between these energy levels occur at frequencies $\omega_{\pm}$ can be expressed as

$$\hbar\omega_{\pm} = \hbar\omega_d \pm 3\hbar\omega_q(3\cos^2(\theta) - 1) \tag{2}$$

- The total vector (nuclear) and tensor (quadrupole) polarizations of a deuterium NMR system can be written in terms of the total populations of each energy level as

$$P_n = \frac{n_{+1} - n_{-1}}{n} \tag{3}$$

$$Q_n = \frac{n - 3n_0}{n} \tag{4}$$

Where n_i is the population of the m_i magnetic substrate and n is the total population $n = n_{+1} + n_0 + n_{-1}$, normalized to be $n = 1$.

Nuclear Magnetic Resonance (NMR) IV

- In practice, we can define the population densities in terms of the observables P_n and Q_n as

$$n_{+1} = \frac{1}{3}1 + \frac{1}{2}P_n + \frac{1}{6}Q_n \tag{5}$$

$$n_0 = \frac{1 - Q_n}{3} \tag{6}$$

$$n_{-1} = \frac{1}{3}1 - \frac{1}{2}P_n + \frac{1}{6}Q_n \tag{7}$$

  Where n_m are the population densitites integrated over the polar angle θ.

- vector polarization in range $(-1 \leq P_n \leq +1)$ and the tensor polarization is in the range $(-2 \leq Q_n \leq +1)$. When the system is in Boltzmann equilibrium, the tensor polarization is limited to $(0 \leq Q_n \leq +1)$.

Nuclear Magnetic Resonance (NMR) V

- Under normal DNP conditions, the system will be in Boltzmann equilibrium and we can calculate Q_n as

$$Q_n = 2 - \sqrt{4 - 3P_n^2} \tag{8}$$

However, as soon as RF manipulation is applied to enhance polarization, equilibrium is lost.

Deuteron lineshape and simulations I

- The Deuteron lineshape has two corresponding absorption lines, I_+ and I_-, which are associated with the analytical function for $\epsilon = \pm 1$
  - These absorption lines arise due to the interaction of the Deuteron's quadrupole moment with the electric field gradient (EFG), which creates non-degenerate eigenstates in the energy levels.
- Because ND3 lacks cubic symmetry, the previously mentioned interaction breaks degeneracy of energy transitions $\rightarrow$ quadrupole splitting leading to two overlapping absorption lines in the NMR spectra (Pake Doublet).
- This Pake doublet is particular to spin-1 material without cubic symmetry (Deuteron, Butanol). With it, such as in LiD, we obtain a Guassian-like lineshape.

Deuteron lineshape and simulations II

$$\mathcal{F} = \frac{1}{2\pi\mathcal{X}}\left[2\cos(\alpha/2)\left(\arctan\left(\frac{\mathcal{Y}^2-\mathcal{X}^2}{2\mathcal{Y}\,\mathcal{X}\sin(\alpha/2)}\right)+\frac{\pi}{2}\right)\right.$$
$$\left.+\ \sin(\alpha/2)\ln\left(\frac{\mathcal{Y}^2+\mathcal{X}^2+2\mathcal{Y}\,\mathcal{X}\cos(\alpha/2)}{\mathcal{Y}^2+\mathcal{X}^2-2\mathcal{Y}\,\mathcal{X}\cos(\alpha/2)}\right)\right],$$

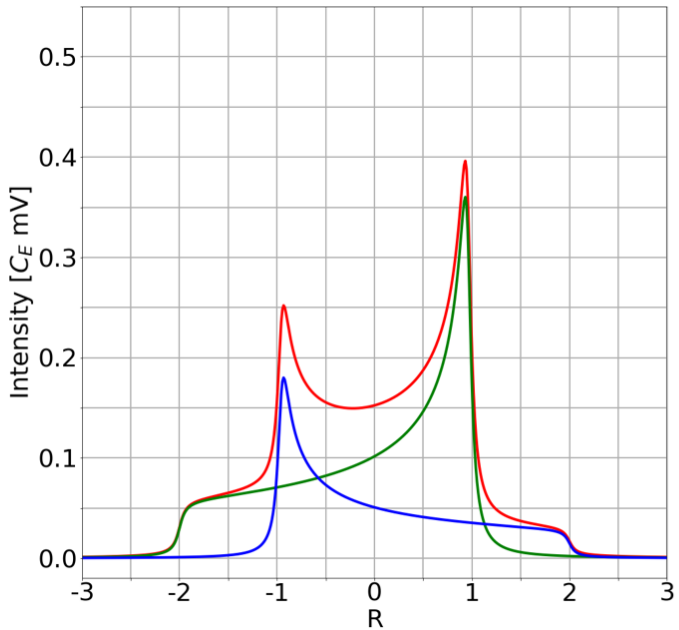
$$\mathcal{Y} = \sqrt{3-\eta\cos 2\phi}$$

$$\mathcal{X}^2 = \sqrt{\Gamma^2+(1-\varepsilon R-\eta\cos 2\phi)^2}$$

$$\eta\cos 2\phi \sim 0.04$$

$$\Gamma \sim 0.05$$

$$\cos\alpha = (1-\varepsilon R-\eta\cos 2\phi)/\mathcal{X}^2$$



Deuteron lineshape and simulations III

- The absorption line intensities can be used to describe the polarizations at any frequency position in R, which represents the polarizations of the target sample at a particular frequency. After integrating over R, we obtain the total vector and tensor polarizations respectively as

$$P = C(I_+ + I_-) \tag{9}$$

$$Q = C(I_+ - I_-) \tag{10}$$

  Where C is the calibration constant and $I_\pm$ is the total area of $I_\pm(R)$ over the two absorption lines in Boltzmann equilibrium.

- In Boltzmann equilibrium, the two absorption lines result from the distribution over the polar angle between the direction of the electric field gradient and the local magnetic field vector, preserving the general shape of the NMR line. In this way, only the scale of the intensities changes with respect to one another as polarization changes.

Q-Meter System I

- Q-meter couples to the magnetic susceptibility of target material (e.g. Solid Ammonia)
- Signal passes through $\lambda/2$ length cable (358.0 cm for 5T), so the continuous wave NMR signal has a tuning range of $\lambda/2$ to $7\lambda/2$
- With a frequency range of 3-300 MHz
- Within these limits, we expect a linear relationship between Polarization and scale (ideal settings of 2% relative error)

Q-Meter System II

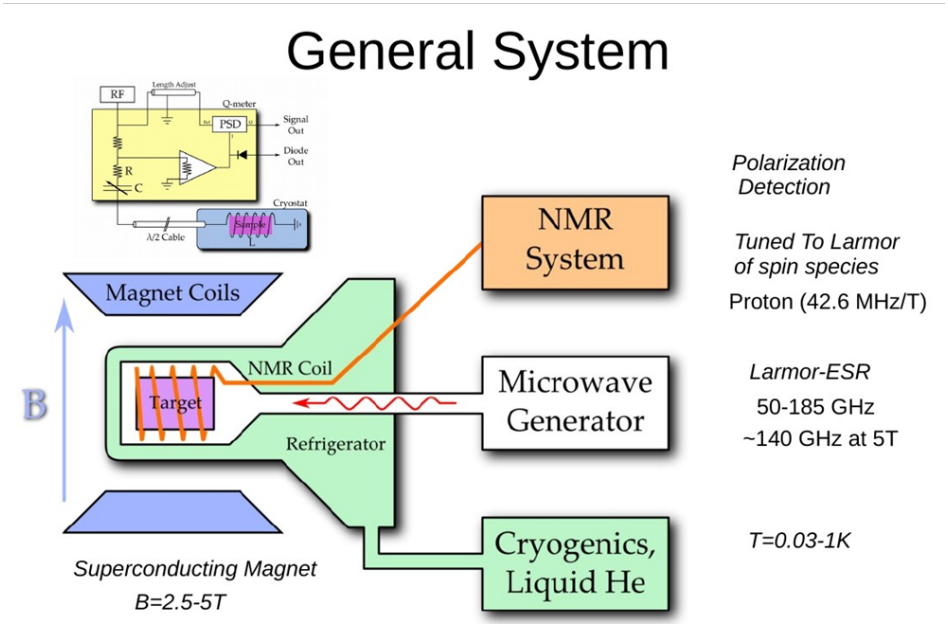


Figure: Q-Meter based NMR system.

Q-Meter System III

Q-meter setup can be modeled in terms in frequency ω such that the output of the Q-meter can be expressed in terms of voltage as

$$V_{out}(\omega, V, C_{knob}, trim, \eta, \phi, C_{stray}) = -IZ_{Total}(\omega)e^{i\phi(\omega)\frac{\pi}{180}} \tag{11}$$

Where V is the input voltage, C_{knob} is the capacitance of the system, $trim$ is the cable length defined by $n\lambda/2$ where n is an integer number and λ is the Larmor frequency of the material, η is the filling factor of the coil, ϕ_{const} is the azimuthal angle between EFG and magnetic field, and C_{stray} is the parasitic capacitance of the system.
The parameters are involved in other quantities which describe the Q-meter system, such as

- Inductance: $L(\omega) = L_0(1 + 4\pi\eta\chi(\omega))$, where $\chi(\omega)$ is the magnetic susceptibility
- Stray Impedance: $Z_{stray} = \frac{1}{i\omega C_{stray}}$
- Capacitance: $C(\omega) = 20 * (10^{-12}) * C_{knob} + C_{trim}(\omega) * (10^{-12})$
- Current: $I = \frac{U}{R} * 1000$
- Phase: $\phi(\omega) = \phi_{trim}(\omega) + \phi_{const}$
- $l_{const} = trim * \frac{1}{\beta_1 \omega_d}$

Q-Meter System IV

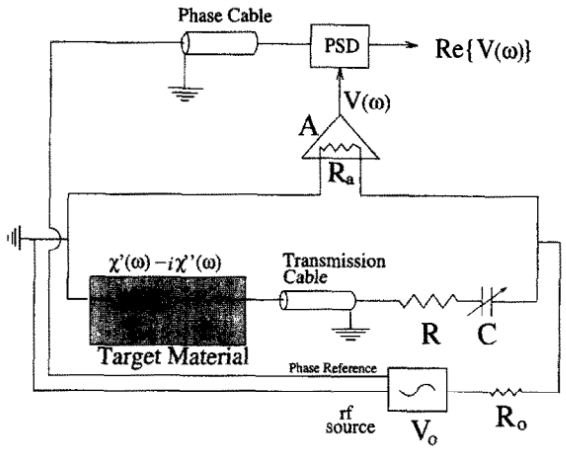


Figure: Circuitry Diagram of Q-meter setup

Extracting Polarization I

- Thermal Equilibrium (Previous Technique)
  - When the lattice (L-Helium) and the target material are at the same temperature, we can obtain the TE polarization by the equation $P_{TE} = \frac{4}{3}\tanh(\hbar\omega_d/2kT)$
  - Then for any polarization not in TE, $P = CP_{TE}$, where C is the calibration constant
  - Dulya et. al.: deuteron polarization can be approximated by $P = C\int \frac{\omega_d S(\omega)}{\omega}$, where $S(\omega)$ is the resulting NMR signal
  - $S(\omega) = \Re\{V(\omega,\chi) - V(\omega,0)\}\chi^{''}(\omega)$, where $\chi^{''}(\omega)$ is the absorption function and $\chi(\omega)$ is the magnetic susceptability.
- TE method comes with considerable error ($\sim 7\%$ relative error) from the change in the area of the TE signal and the fitted signal.

Extracting Polarization II

- Fitting the lineshape
  - Using the analytical function for the Deuteron lineshape, one can fit Deuteron NMR signals by first averaging the dependence on the azimuthal angle ϕ with the integral

$$F_\epsilon(R, A, \eta) = \frac{2}{\pi}\int_0^{\pi/2} \frac{\sqrt{3} f_\epsilon(R, A, \eta, \phi)}{\sqrt{3 - \eta\cos(2\phi)}} d\phi \approx \frac{1}{J+1}\sum_{j=0}^{J} \frac{\sqrt{3} f_\epsilon(R, A, \eta, \phi)}{\sqrt{3 - \eta\cos(2\phi)}} \tag{12}$$

  Where $J = 64$ with ϕ_j evenly distributed over $0 \leq \phi \leq \pi/2$ range.
  - We can then approximate the polarization as

$$P = \frac{r^2 - 1}{r^2 + 1 + r} \tag{13}$$

  Where $r = \frac{I_+}{I_-}$, the ratio of the intensity curves.

  - Alongside that, the method of **differential binning** allows us to understand the signal and the overlapping absorption lines by the area in a set of bins for any equilibrium or non-equilibrium condition. This provides direct means of understanding the signal numerically without a model of the target material spin dynamics.

Limitation for Deuteron Polarization Determination

- Liverpool Q-meter system allows for relative accuracy of a deuteron signal's polarization (error: $\sim 1\%$). In an experimental setting, however, the expected relative uncertainty of $4 - 6\%$.
- Sources of error
  - $\frac{n\lambda}{2}$ cable length (Deuteron's small magnetic moment can lead to large Q-curves)
  - Q-meter configurations (calibration constant)
  - Changes in radiofrequency (RF) environment
  - Statistical errors dependant on DAQ
  - Previous NMR lineshape fitting method does not apply for tensor polarization, area under curve changes over time from radiation damage.

Experimental Parameter Extraction I

- Using data acquired from Hall B at Jefferson laboratory, we used a χ^2 minimization algorithm to fit the input parameters of functions used to simulate the signal to real-life data.

Migrad

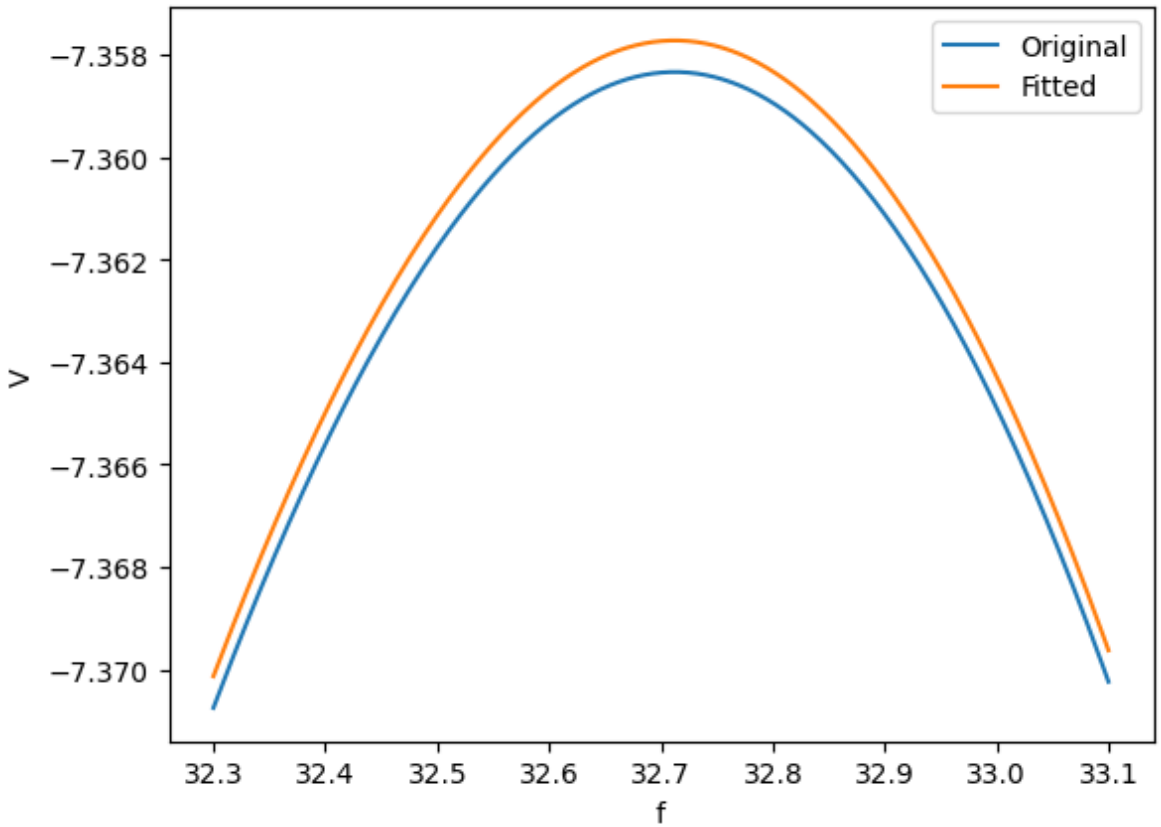
FCN = 0.01316		Nfcn = 309	
EDM = 0.000175 (Goal: 0.0002)			
Valid Minimum		SOME Parameters at limit	
Below EDM threshold (goal x 10)		Below call limit	
Covariance	Hesse ok	Accurate	Pos. def. Not forced

	Name	Value	Hesse Error	Minos Error-	Minos Error+	Limit-	Limit+	Fixed
0	U	0.030	0.016			0	1	
1	knob	0.20	0.13			0.1	0.3	
2	trim	1.500	0.015					yes
3	eta	0.005	0.013			0.005	0.03	
4	phi_const	0.1	3.2			0.05	6.28	
5	Cstray	1.00e-15	0.01e-15					yes

	U	knob	trim	eta	phi_const	Cstray
U	0.000243	0.0057 **(0.998)**	0	-2.73e-06 **(-0.110)**	-0.00122 **(-0.013)**	0
knob	0.0057 **(0.998)**	0.134	0	-6.76e-05 **(-0.116)**	0.0793 **(0.035)**	0
trim	0	0	0	0	0	0
eta	-2.73e-06 **(-0.110)**	-6.76e-05 **(-0.116)**	0	2.52e-06	9.6e-06	0
phi_const	-0.00122 **(-0.013)**	0.0793 **(0.035)**	0	9.6e-06	38.7	0
Cstray	0	0	0	0	0	0

Figure: Hessian Fit with Covariant Matrix results performed using the Iminuit python library.

Experimental Parameter Extraction II



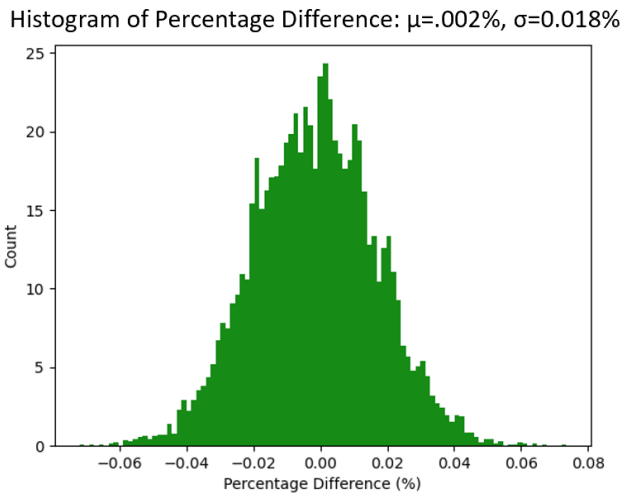
Artificial Neural Networks

- Neural networks learn (or are trained) by processing examples, each of which contains a known "input" and "result," forming probability-weighted associations between the two, which are stored within the data structure of the net itself.
- The training of a neural network from a given example is usually conducted by determining the difference between the processed output of the network (often a prediction) and the target output. This difference is the error.
- The network then adjusts its weighted associations according to a learning rule and uses this error value. Successive adjustments will cause the neural network to produce output that is increasingly like the target output.

Artificial Neural Networks

- By training a neural network (NN) on sample data that replicate experimentally accurate noise levels that evolve through time, we can go beyond the capability of the Q-meter and make up for where it lacks.
- Using to optimize precision and accuracy, regardless of Signal-to-Noise Ratio (SNR)
  - SNR: ratio of the maximum of the amplitude of the signal to the maximum of the amplitude of noise, represents how overwhelming the noise is
  - $SNR = \frac{|Signal_{Max}|}{|Noise_{Max}|}$

Offline Analysis I



$$P_{Diff} = P_{True} - P_{Predicted}$$

- Prediction by NN model for 10K sample events between $0\% - 100\%$.
- SNR ~ 2.5
- Accuracy: 99.8%
- Precision 98.2%

GUI Simulation (Online Analysis) I

- Simulation can be done with DearPyGui (DPG) for real-time results
- By utilizing a powerful GPU (NVIDIA GeForce 4090 RTX), Neural Network predictions performed by the Tensorflow package can be performed significantly faster.

GUI Simulation (Online Analysis) II

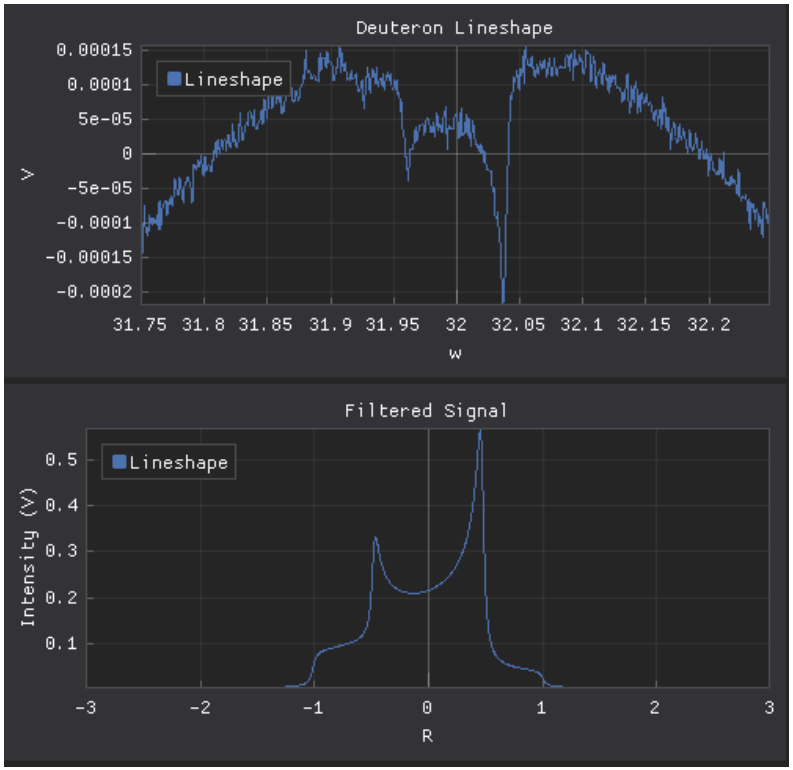


Figure: Simulation and Real-Time Prediction done within a GUI made by the DearPyGui python library.

Observations and Next Steps I

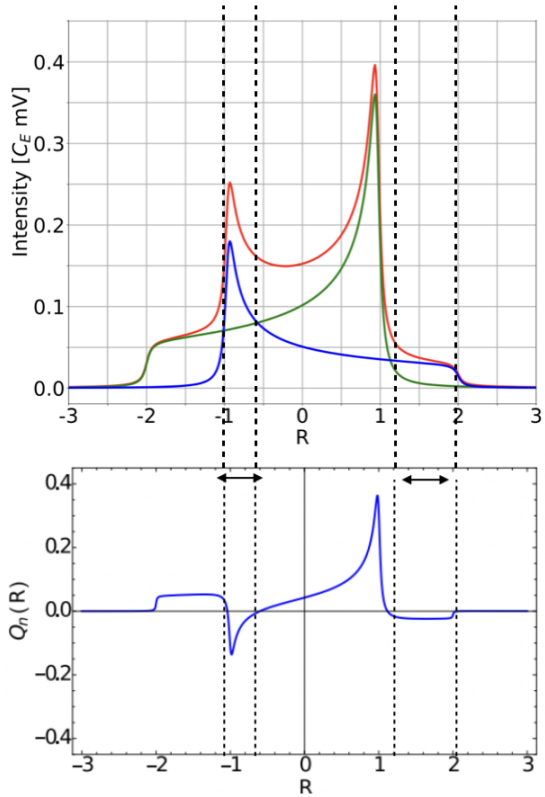
- ANN can allow for the efficient filtering of background noise from deuteron signal (could also be applied to any NMR signal)
- The adaptability of the ANN allows for changes in baseline and scanning range of an NMR to quickly and easily be considered
- For the future: optimize the ANN for smaller polarizations to increase precision and accuracy
- Plans to use ML to improve extraction of tensor polarization in Spin-1 material in real-time settings.

Observations and Next Steps II

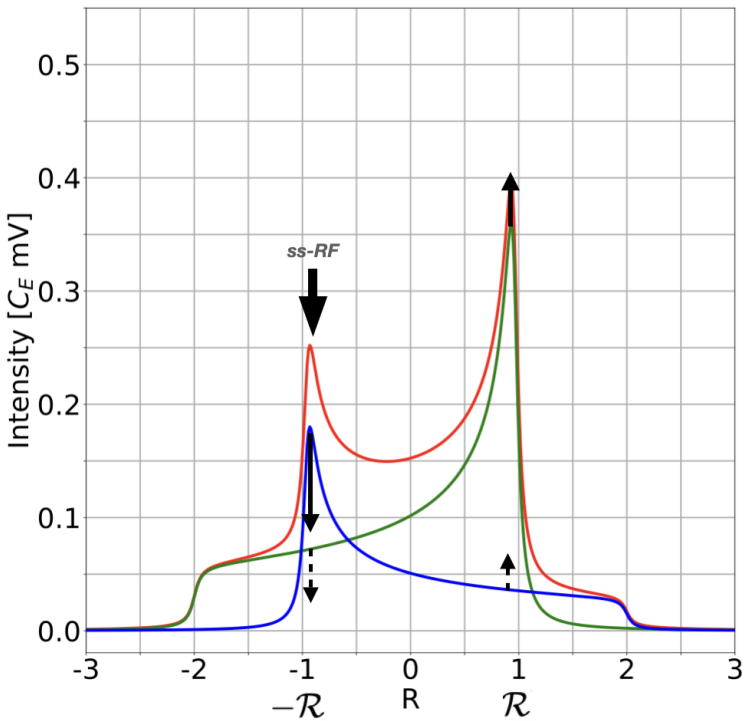
Three main principles to improve using machine learning:

- Differential Binning: Binning data points of NMR signal as sum of intensities allows for polarization extraction without care for equilibrium condition
- Rates Response: When burning any set of bins, that will give you an absorption line that is half of what you burned.
- Spin Temperature Consistence: At any vector polarization, the relationship between vector polarization and temperature is consistent.

Observations and Next Steps III



Observations and Next Steps IV



Observations and Next Steps V

Steps:

- Measure signal (with ANN) and write code for applying ss-RF to signal.
- Apply ss-RF and measure again.
- Continue applying ss-RF, measuring, and modifying the lineshape.

Thank you!

This work was supported by DOE contract DE-FG02-96ER40950