Nuclear Magnetic Resonance Laboratory course
Assignment 2

RF Nuclear Spin excitation

Dr. rer. nat. habil. Thomas Meier

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Abstract

Efficient excitation and manipulation of spin systems is fundamental in every Nuclear Magnetic Resonance (NMR) experiment. In particular, when dealing with samples that are subject to significant spin interactions—such as direct dipole-dipole couplings or quadrupole interactions—accurate Radio Frequency (RF) excitation is essential. Failure to achieve proper RF excitation in such cases can lead to distorted spectra, which may result in incorrect or misleading interpretations of experimental data.

In this experiment, we aim to explore the foundational principles of RF excitation. Specifically, we will cover a range of critical topics, including pulse nutation, excitation profiles, and shaped pulses. Pulse nutation refers to the oscillation of spin magnetization caused by RF pulses. Understanding the nutation process is essential for achieving the desired spin rotation and controlling the coherence of the system. Excitation profiles describe the distribution of magnetization excited by the RF pulse across a frequency spectrum, which is particularly important for samples with large inhomogeneities or broad resonance lines. Shaped pulses are a technique used to modify the amplitude and phase of the RF field over time, providing more selective and efficient excitation. Shaped pulses are especially useful in systems where conventional hard pulses would induce unwanted effects or lead to artifacts in the spectrum.

Through this hands-on approach, we will gain insight into how various RF excitation techniques affect the overall quality of NMR spectra, thereby allowing us to optimize experimental conditions for better data acquisition and interpretation.

1 Theoretical background

For these experiments, you will need the following theoretical background. Please prepare necessary mathematical expressions and derivations:

- What is the NMR resonance condition?
- Describe a simple spin excitation after a $\pi/2$-pulse
- How are RF pulses optimised? Describe the principle of such nutation experiments.
- The optimal $\frac{\pi}{2}$-pulse length of a boxcar pulse is given by

$$t_{\pi/2}^{boxcar} = \frac{\pi}{2\gamma_n B_1} \tag{1}$$

  with the RF magnetic field generated by a solenoidal coil given as:

$$B_1 = \sqrt{\frac{\mu_0 Q P}{2 w V_{coil}}} \tag{2}$$

  Please derive both equations. How do the optimal pulse lengths change when only the coils volume is reduced? Calculate the relative amplification in B_1 by going from a standard sized coil (diameter 4 mm and length 10 mm) to a microcoil (diameter 150 μm length 100 μm). What are the differences in $t_{\pi/2}$? How do $t_{\pi/2}$ and B_1 scale at high frequencies?

- Solve the Fourier transform of the boxcar function $\Xi(\tau)$:

$$\mathcal{F}\left(\Xi(\tau)\right) = \int_{\mathbb{R}} \Xi(\tau) \cdot e^{-i\omega t} dt \tag{3}$$

  with:

$$\Xi(\tau) = \begin{cases} 1 & x \in \{-\frac{\tau}{2}; \frac{\tau}{2}\} \\ 0 & \text{else} \end{cases} \tag{4}$$

- The spin excitation profile of an arbitrary pulse shape in time domain is given by its Fourier transform in the frequency domain. What is the excitation profile of a boxcar and a gauss shaped pulse? Plot both excitation profiles for a pulse length of $\tau = 10\mu s$.

- The optimal excitation bandwidth (OEB) of an RF pulse is given by the FWHM of its excitation profile. What is the OEB of a boxcar pulse and of a gaussian pulse in dependence of the respective pulse lengths?

2 Tasks

Please work on the tasks step-by-step and summarize your observations thoroughly and logically when you hand in the assignment. Please provide data plots and calculations to underline your conclusions. We recommend the use of ONMR running in Origin7 or later, for data analysis when using a Tecmag NMR system and SSNake when using a Bruker system.

This experiment will be performed without the use of a polarizing external magnetic field to lift the degeneracy of the nuclear Zeeman energy levels. Rather, we are going to use a substance which, due to a substantial site specific electric field gradient, exhibits greatly enhanced quadrupole frequencies and allows for observable nuclear spin transitions between the $|\pm\frac{1}{2}\rangle$ and $|\pm\frac{3}{2}\rangle$ states of ^{65}Cu $(I = \frac{3}{2})$.

1. connect the NMR probe to the interface of the spectrometer, tune and match the probe to the respective resonance frequencies for protons at the given field.

2. Free induction decay: use a single RF pulse and optimize spectrometer parameters (dwell time, number of points and scans, last delay etc.)

3. Pulse nutation experiment for boxcar pulses: at 10 W and 40 W of pulse power, increment the pulse length in steps of $1\mu s$ (to a maximum of 30 μs). Plot the signal intensities at $t = 0$ μs in time domain against their respective increment times. What do you observe? What are the optimal pulse lengths? How does the optimal pulse length change by increasing the power by a factor of four?

4. Pulse nutation experiment for Gaussian pulses: repeat the same experiments using a Gauss shaped pulse and compare the optimal pulse lengths with those found in 3. Does the ratio of optimal pulse lengths between boxcar and gauss pulse agree with theoretical predictions?

5. Calculate the RF magnetic field B_1 generated by the coil.

6. Pulse excitation profiles: at optimal $\pi/2$-pulse conditions, record several FID signals by changing the spectrometer frequency incrementally off-resonant from the Cu_2O signals. [**Pulse program**: *FID pulse excitation profile.tps* and *Gauss pulse excitation profile.tps*]. Repeat this for pulse lengths twice as long and half as long as the initial values (remember to compensate for power). Also, record similar profiles for a Gaussian pulse.

7. Plot the intensity (integral over the signal in frequency space or t=0 in time domain) against the respective off-resonance frequency.

8. What do you observe? Are the OEBs of boxcar and Gauss pulses following the predictions from an *ab-initio* Fourier transform? Try to rationalize qualitatively which pulse shape is more advantageous for specific applications.

3 Literature

- Eiichi Fukushima, *Experimental pulse NMR - a nuts and bolts approach*
- Dustin Wheeler and Mark Conradi, *Practical Exercises for Learning to Construct NMR/MRI Probe Circuits*
- Noel Mispelter, *NMR probeheads for biophysical and biomedical Experiments*
- Reyes, A. P., Ahrens, E. T., Heffner, R. H., Hammel, P. C., and Thompson, J. D. (1992). Cuprous oxide manometer for high-pressure magnetic resonance experiments. Review of Scientific Instruments, 63(5), 3120–3122. https://doi.org/10.1063/1.1142564