Graphical Programming for Pulse Automated NMR Experiments

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Abstract

We describe a software program designed to control a broadband pulse Nuclear Magnetic Resonance (NMR) spectrometer used in zero-field NMR studies of magnetic metals. The software is written in the graphical language LabVIEW. This type of programming allows modifications and the inclusion of new routines to be easily made by the non-specialist, without changing the basic structure of the program. The program corrects for differences in the gain of the two acquisition channels [U (phase) and V (quadrature)], and automatic baseline subtraction. We present examples of measurements of NMR spectra, spin-echo decay (T_2), and quadrupolar oscillations, performed in magnetic intermetallic compounds.

1   Introduction

Pulse Nuclear Magnetic Resonance (NMR) has been successfully applied to the study of a variety of materials in Physics and Chemistry, and other areas of knowledge. The technique consists in the application of a sequence of radiofrequency pulses, which modulate a carrier signal tuned to the Larmor frequency of the precessing nuclear moments, and the observation of the system response, which in the case of a pair of pulses is the so-called *spin-echo*. The physical principles of nuclear magnetism and NMR can be found in the classical texts by Slichter [1] and Abragam [2].

Particularly fruitful has been the investigation of the magnetic properties of magnetically ordered materials using NMR, including alloys and intermetallic compounds. Spectroscopy and relaxation measurements yield detailed information about the crystallographic and magnetic structure, as well as the lattice dynamics involving conduction electrons, magnons, phonons, etc. Important reviews about these applications can be found in the literature [3, 4, 5].

The basic construction of a pulse Nuclear Magnetic Resonance spectrometer is described in [6]. It requires a frequency synthesizer, a pulse generator, a radiofrequency (rf) power amplifier and the means for the detection and amplification of the spin-echo signal. This is usually done by acquiring the signal in phase and quadrature, the components of the echo being called U and V.

The application of NMR to the study of the hyperfine interactions in magnetic metals through the spectroscopy and relaxation times has to deal with the short duration of signals, arising from the broadening of the lines of the spectra. Echo widths in these systems are typically between 0.5 μs to 1 μs, whereas relaxation times are about 50 μs to 100 μs for T_2 and 300 μs to 500 μs for T_1 [3, 5]. Considering the broadening due to electric quadrupolar interaction and hyperfine field inhomogeneities, linewidths can reach several tens of MHz.

Fast signals and broad spectra impose some conditions upon the spectrometer design, as discussed in references [3, 5]. Particular attention must be given to the variations of the baseline and gain which must be corrected at each measuring cycle. Usually, a cycle starts with the setting of the rf frequency (and possibly the rf power). The $U(t)$ and $V(t)$ signals are digitized within a "time window" for a pre-fixed number of times, and after some sort of averaging, the signals are integrated and the echo amplitude ϵ is calculated:

$$\epsilon = \sqrt{[\int U(t)dt]^2 + [\int V(t)dt]^2} \tag{1}$$

The magnitude of ϵ will depend on the NMR frequency ν. A plot of $\epsilon(\nu)$ against the frequency ν is the NMR spectrum. In the case of relaxation measurements, the amplitude ϵ is measured for different pulse separations, keeping the frequency constant.

In an actual experiment, the voltage amplitudes $U(t)$ and $V(t)$ must have the baseline subtracted. This problem becomes particularly critical for small signal-to-noise ratio and short pulses separation, due to "ringing" tails of pulses. In order to perform the subtraction operation, one has to know, at least in principle, the actual form of the baseline, which can depend on the NMR frequency, the radiofrequency power, and so

on; this subtraction in the present work was made by least square fitting a straight line to the baseline. Moreover, if two amplification channels are used, possible variations in their gain have to be compensated, otherwise instrumental effects can appear in the NMR spectra. Nadolski et al. have recently described an interesting measuring sequence [7] to avoid this problem.

In the present report we describe a software to perform automatic measurements of NMR spectra and relaxation times in magnetically ordered metals (zero-field NMR), with the possibility of controlling the rf output power, using the graphical language LabVIEW. In this type of programming, mathematical and logical operations are represented by icons which are linked together to assemble the program. Subroutines can be built and assigned new icons, and may be incorporated into the main program without changing its structure. The extreme versatility of graphical programming allows non-expert programmers to modify easily, or to improve the acquisition software.

2 The Spectrometer

Our spectrometer is home-made and similar to others reported in the literature [8, 9, 10]. It operates between 20 to 200 MHz, and can be very easily extended to higher frequencies. The transmitter is composed of a Fluke 6061A synthesizer, a Tecmag Mini Pulse Kit pulse programmer, a ENI 100-Watt, 400-MHz broadband rf power amplifier, and double balanced mixers (DBM) used for pulse modulation. The output power is controlled through a Wavetek P556 programmable attenuator. The receiver is built from a Doty Scientific (LN-2L) 500-MHz 31 dB pre-amplifier, a module for signal detection in quadrature (phase shifter, DBM's, power splitter) and a home-made 40 dB audio amplifier. The demodulated signals (U and V) are digitized in a Tektronix TDS 520A digital oscilloscope. A reference signal is sent to the demodulator and its phase is controlled through a relay. This, combined with the polarity of the pulses, allows full rotation of the signal through 0, 90, 180 and 270 degrees.

The synthesizer and oscilloscope are connected to a PC through standard GPIB interfaces, whereas the pulse programmer, attenuator and relay are connected via a parallel port. Figure 1 shows a simplified scheme of the spectrometer. The pulse programmer, originally developed to run under Macintosh environment, had to be adapted for an IBM compatible PC. For that an interface was built, whose diagram is shown in Figure 2.

3 Control Program

Figure 3 shows the NMR spectra acquisition program diagram. Commands and subroutines are represented by icons which are wired to each other according to the type of variable. These are codified in the colors and in the thickness of the wires: orange for floating numbers, blue for integers, green for logical variables and pink for strings. Thin wires carry single numbers, and the thick ones, arrays. The program is divided into three nested loops. Input parameters are: the initial and final frequencies, the frequency step, the pulse widths and separation, the number of acquisitions to be made in the scope, and the range of attenuations. The program starts initializing the oscilloscope and pulse

programmer. The outermost loop sets some graphical features and the attenuation values. The middle one controls the synthesizer and the timing of the experiment. The innermost loop controls the whole acquisition process. It starts the oscilloscope, accumulates and acquires the signals, and rotates the reference phase. Each NMR spectral point corresponds to 4 cycles in this loop, that is, to 4 pairs of phase and quadrature signals. At the end of the fourth cycle, baseline and channel gain corrections are performed, the signals integrated, and the spin-echo amplitude calculated and plotted in the graph. This appears as in figure 4, the program panel. Then the acquired data point is saved, the frequency is changed, and the whole cycle starts again. After measurement of the last point, a backup file is created, the attenuation is changed, and a new spectrum is started.

The number of subroutines used in this program is over one hundred. Each new subroutine can be very easily incorporated into the main program (for instance, signal smoothing, filtering, or FFT) without changing its structure. The graphical display enhances the logical structure of the program, and facilitates the task of including new routines or modifications by non-specialists. As an example, consider the subroutine to perform baseline subtraction. This appears in the diagram of Fig. 3 as the little box labeled '$\int(uv)$'. Just before entering this routine, the program performs a channel-by-channel subtraction in the echo components obtained after rotating the reference signal phase. The routine then splits each echo component into four segments, takes the first and fourth ones and performs a linear least square fit. With the fitted parameters a full straight line is generated, and subtracted channel-by-channel from the original signal. After this operation, the components are integrated and the spin echo magnitude calculated.

The gain compensation for the two channels is made by combining the rotation of the phase of the reference signal with the polarity of the first pulse. This procedure also compensates for deviations in the actual phase angles of U and V [6].

Figure 5 shows the panel of a program used to measure relaxation times. One can choose a sequence of either two or three pulses, the pulse widths, separations, etc. The actual acquisition of the signal uses the same subroutine (the innermost loop) of figure 4. The example shown is a measurement of spin-echo decay (T_2) in the intermetallic compound $GdAl_2$ at 49 MHz, 4.2 K. The decay exhibits very large electric quadrupolar oscillations, in accordance with [11].

4   Conclusions

Graphical language is an easy and suitable way to implement control programs for NMR experiments, for it does not require expertise in computer programming. We described a software program, using the graphical package LabVIEW, designed to make automated measurements of NMR spectra and relaxation times in magnetically ordered metals. Our program includes automatic compensation for channel gain and phase differences, and baseline subtraction at each measured point. The first correction is accomplished by rotating the reference signal phase and inverting the pulses polarity, whereas the second one uses channel-by-channel subtraction and linear least square fitting. The inclusion of new subroutines for either control or data treatment can be easily implemented by the

non-specialist without changing the structure of the main program.

References

[1] C.P. Slichter, *Principles of Magnetic Resonance* 3rd ed. (Springer-Verlag, Berlin, 1990)

[2] A. Abragam, *Principles of Nuclear Magnetism* (Clarendon, Oxford 1985)

[3] M.A.H. McCausland and I.S. Mackenzie, *Adv. Phys.* **28** (1979) 305

[4] E. Dormann, *Handbook on the Physics and Chemistry of Rare Earths* Eds. K.A. Gschneider Jr. and L. Eyring (Elsevier, 1991), **14** (1991) 63

[5] A.P. Guimarães, *Magnetism and Magnetic Resonance in Solids* (Wiley, New York, 1998)

[6] E. Fukushima and S.B.W. Roeder, *Experimental Pulse NMR: a Nuts and Bolts Approach* (Addison-Wesley, Reading, 1981)

[7] S. Nadolski, M. Wójcik, E. Jędryka and K. Nesteruk, *J.Mag.Mag.Mat.* **140-144** (1995) 2187

[8] G.D. Webber and P.C. Riedi, *J. Phys. E: Sci. Instrum.* **14** (1981) 1159

[9] T. Dumelow and P.C. Riedi, *Hyp. Int.* **35** (1987) 1061

[10] H. Figiel, *Mag. Res. Rev.* **16** (1991) 101

[11] T. Dumelow, P.C. Riedi, J.S. Abell and O. Prakash, *J.Phys.F: Met. Phys.* **18** (1988) 77

Figure Captions

Figure 1 - Simplified scheme of the spectrometer. Green lines show the parts controlled by the program.

Figure 2 - Pulse programmer interface.

Figure 3 - NMR spectra acquisition program. Subroutines are represented by icons, and type of variables in the color of wires. There are over one hundred subroutines in this program.

Figure 4 - The front panel generated by the NMR acquisition program (figure 3). After baseline and gain corrections, each spectrum point is plotted on the screen, and saved in a backup file. Echo components are also shown.

Figure 5 - Relaxation times measuring program. The figure shows a measurement of spin-spin decay (T_2) at the aluminum site (49 MHz) in the intermetallic compound $GdAl_2$ at 4.2 K.