EXPERIMENTAL PULSE NMR

A Nuts and Bolts Approach

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PREFACE

This book is about pulse nuclear magnetic resonance (NMR), with its techniques, the information to be obtained, and practical advice on performing experiments. The emphasis is on the motivation and physical ideas underlying NMR experiments and the actual techniques, including the hardware used. The level is generally suitable for those to whom pulse NMR is a new technique, be they students in chemistry or physics on the one hand and research workers in biology, geology, or agriculture, on the other. The book can be used for a senior or first year graduate course where it could supplement the standard NMR texts.

The contents of this book are not overly scholarly, mathematical, nor complete but, at the same time, includes subjects which are seldom discussed in NMR books. We also attempt to provide some physical insight into subjects whose canonical treatments may be difficult to understand. At the same time, an effort was made to avoid discussions which can easily be found elsewhere. There are two recent books on experimental NMR by Shaw and by Martin, Delpuech, and Martin, both referenced in Appendix A, which are largely complementary to ours.

Unlike many other books, ours does not build the subject systematically from first principles. Rather, it discusses concepts at levels most useful in interfacing to an actual experiment or to the specialized literature. In this way this book is more of a guidebook and a handbook. When someone is in unfamiliar terrain, he consults a guidebook to gain information about the immediate countryside without having to learn the geography of the entire country. Similarly, a handbook is referred to for brief information on individual items. This book is a collection of essays to facilitate its use in these modes. We have cited references to help you look up additional information rather than for giving credit where credit is due and they are grouped at the end of each subsection.

You can see that our book covers a lot of ground. In practical terms, this means that the book is not one to be read in an orderly way from beginning to end, except possibly by reviewers. Instead, different parts of the book should appeal to different groups of people. A unique feature of this book is the discussion of hardware in Chapter V. In it, we cover how the hardware works and how they may be modified as well as what to look for in commercial instruments. We are trying to continue in the tradition of many earlier workers to impart the message that what happens inside the spectrometer "box" is not as mysterious as it might seem.

In addition to the practical necessity for understanding the experimental technique, such an understanding will give added insight into the experimental results. Thus, the knowledge of the experimental methods gives insight into the "why" as well as the "how".

Above all, NMR experiments are great fun, at least to many of us. So many different kinds of information can be gathered by performing the experiments in different ways. We hope that our effort will introduce you to something new and enjoyable and we welcome any feedback.

One of us (EF) has benefited immeasurably from working and talking with Dr. Atholl A. V. Gibson of Texas A&M University. Several of the insights and designs in this book are his, not always so identified. He has also read more than one-half of the manuscript, as has Professor Irving J. Lowe of Pittsburgh. Dr. Robert E. London of Los Alamos has also been very helpful, especially in the area of high resolution solution NMR. There are many other people who contributed ideas to the book as well as tolerated all manner of questions on their ideas, published or otherwise. To all these kind people, we are very grateful for their interest and valuable suggestions. The above contribution notwithstanding, all the errors in the book are the sole responsibility of the authors and we would like to be informed of them at the readers' convenience.

One of us (EF) wrote a part of the manuscript at the University of Florida while on leave from Los Alamos and acknowledge the kind hospitality provided by the university and the solid state physics group of the late Professor Thomas A. Scott.

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CHAPTER I

BASICS OF PULSE AND FOURIER TRANSFORM NMR

I.A. INTRODUCTION

Nuclear magnetic resonance (NMR) can mean different things to different people. To someone interested in studying slow molecular diffusion, it might mean measuring relaxation times of one kind or another as a function of temperature and possibly pressure. To someone interested in magnetism of metals, it might mean sweeping through a large frequency range (like tens of MHz, where MHz = megahertz = million cycles per second) and monitoring the signal height (obtained by spin echoes). To the majority of those coming into contact with NMR, it usually means running some kind of a high resolution spectrum and in the past decade this has come to mean obtaining the spectrum by Fourier transformation of a time varying signal called the free induction decay (FID). All these different kinds of NMR experiments are related and

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we propose to explain some of the considerations necessary in either understanding or in carrying out such experiments.

The Fourier transformation relates representations in two complementary domains. Specifically, the transform as used in NMR relates the spectrum in the frequency domain, as we know it from cw (continuous wave) NMR, to the signal obtained in the time domain called the free induction decay (FID). Such a relation was first demonstrated by Lowe and Norberg (1957). In order to make this correspondence more plausible, consider the following example. If we want to find the frequency response of a high fidelity amplifier, i.e., what notes (frequencies) it amplifies and by how much, one way of doing this is to feed in a pure tone of constant volume (amplitude) and measure the output volume as the tone is changed. In that way, we might learn that the amplifier does not pass very low tones (say, below 100 Hz or cycles per second) nor very high tones (say, above 20 kHz) but it passes everything else in between with quite constant amplification (gain). The plot of the response vs. frequency is called a spectrum and is entirely analogous to the NMR spectrum.

This is a good method for accomplishing our goal and we would be perfectly happy with it as long as we did not have to measure the frequency response of a large number of amplifiers. If we were the impatient sort, however, we could think of several faster methods. One would be to get several tone generators (frequency sources) which put out different tones and use them with tuned detectors which can separately but simultaneously detect those tones. You could perform the required measurement all at once but it is simply not practical to assemble the required number of separate tone generators and detectors if any kind of frequency resolution were required.

This example, with its impracticality, contains the seed for the best solution to the problem. We somehow want to put all the frequencies into the amplifier at once and detect all the frequencies which come out. We state here without proof that a short square pulse contains a continuous distribution of frequencies up to frequencies of the order of the reciprocal of the pulse length in order to shape the sharp corners of the pulse. Thus, for such a pulse, the amplifier sees many frequencies coming into it and will amplify them according to its characteristics. For example, if the amplifier does not respond to the high frequencies needed to shape the sharp corners, the corners will be rounded off in the pulse coming out of the amplifier. If some method were available to decompose the output pulse into its frequency components so they can be plotted out as a spectrum and this is compared with the spectrum of the input pulse, we will have accomplished our goal. The Fourier transform performs the desired decomposition.

To recapitulate, the frequency response of the amplifier can be obtained by measuring the gain at each frequency or alternatively by measuring the response of the output of the amplifier to a rectangular input pulse and a subsequent Fourier transform. (Clearly, there are other pulse shapes which contain many different frequency components, too, but the square pulse is easy to form and its frequency distribution is well known.) The efficiency of the latter method is due to the multiplexing effect, i.e., the fact that we are not taking the data at one frequency at a time and not due to the Fourier transform itself, and this fact was first demonstrated in NMR by Ernst and Anderson (1966). All the spectral information desired is already contained in the transient response to a pulse and the transform merely allows us to decompose the signal into its spectral components.

The above considerations are common to many phenomena and it turns out that an NMR spectrum of a sample is analogous to the frequency response of the amplifier. The difference is that in NMR, we are dealing with the nuclei responding to radio frequencies (rf) in the MHz range. The inefficient solution in the above example corresponds to a cw NMR experiment where each part of the spectrum is measured sequentially whereas the final solution corresponds to Fourier transform NMR.

Having said that the Fourier transform process enables us to transform information in the time domain into equivalent information in the frequency domain and vice versa, we will now consider the NMR experiment in the time domain. NMR is possible because nuclei of many atoms possess magnetic moments and angular momenta. (Electrons possess moments about 1000 times larger than the largest nuclear moment.) Now a magnetic moment interacts with a static magnetic field in such a way that the field tries to force the moment to line up along it just like a compass needle lines up with the earth's field. The significance of the angular momentum, which is proportional to the moment, is that it makes the nuclei precess around the magnetic field when it experiences the torque due to the field acting on the moment. The result is that the nuclei precess about the field rather than oscillating in a plane like a compass needle. This precession is exactly analogous to a top, with its angular momentum along its spinning axis, precessing about the earth's gravitational field. The precession frequency of the moment is proportional to and uniquely determined by the gyromagnetic ratio γ and the strength of the magnetic field H_0. It is given by the Larmor relation $\omega_0=\gamma H_0$ where ω_0 is called the Larmor speed which is 2π times the Larmor frequency ν_0. γ is the proportionality constant between the moment μ and the angular momentum $I\hbar$, so that $\mu=\gamma I\hbar$. Therefore, in a given magnetic field, the precession frequency is different for every distinct nucleus because each has a uniquely defined γ. For typical nuclei used in NMR, the Larmor frequency falls in the range of a few to a few hundred MHz in magnetic fields of commonly available magnets.

Now consider the nuclear moment precessing about a static magnetic field. Because there is no friction, it will precess forever while maintaining a fixed angle with respect to the magnetic field if left alone. Quantum mechanics requires that the orientation of a magnetic moment with respect to the field be quantized. The number of allowed orientation is 2I+1 where I is the nuclear spin quantum number. For example, protons, carbon-13, and fluorine-19, being spin-½ nuclei, are restricted to two orientations. The two allowed orientations for these nuclei are not collinear with the magnetic field but rather at some angle so that the nuclear moment can be thought of as precessing about the field on the surface of a cone with its axis either parallel or anti-parallel to the field. This quantum mechanical representation is not essential to our presentation and we will assume for the sake of these discussions that the permitted orientations are parallel and anti-parallel to the field.

Classically, the energy of a magnetic moment $\bar{\mu}$ in a magnetic field $\bar{H}_0$ is $-\bar{\mu}\cdot\bar{H}_0$ so that a positive moment will always want to line up parallel with the field. Such a moment already parallel to the field, i.e., in a lower energy state, can undergo a transition to the higher energy state by receiving an appropriate amount of energy. By Planck's law, the quantum of work required to reverse the orientation of a moment is $\hbar\omega$

where $\hbar = h/2\pi$ is Planck's constant divided by 2π and ω is the angular velocity of the applied rf field. We will develop a formalism in the next section whereby the frequency of the rf irradiation needed to cause such a transition is equal to the Larmor velocity ω_0. If the frequency of the radiation applied to induce transitions is too high or too low, the nucleus will not undergo the transition; it is this fact of requiring exactly the right frequency to do something which makes NMR very useful and provides the word "resonance" in its name. The fact that the frequency required for causing transitions is precisely the Larmor frequency of precession is no coincidence. We will see that the applied rf radiation provides a rotating magnetic field component and when it is rotating at the same angular velocity and in the same sense as the nuclei, it applies torque to the nucleus causing its angle with the static field to change.

$N_{\uparrow}/N_{\downarrow} = 1 - e^{-\mu H/kT}$

Let us now consider a macroscopic NMR sample, such as 1 gm of water containing roughly 10^{23} protons in a static magnetic field. All protons have identical positive moments and they would all line up with the field, i.e., be in the lower energy state, if it were not for the thermal motion of the molecules and atoms counteracting the effect of the field. The population ratio of the two states depends on the sample's absolute temperature T and the strength of the magnetic field H by the Boltzmann factor $\exp(-\mu H/kT)$ with k being the Boltzmann constant. For NMR experiments at room temperature, this factor differs from unity by only 10^{-5} or 10^{-6} so that most of the protons are randomly distributed (parallel and antiparallel to the field) and their effects cancel. Even so, 10^{17} to 10^{18} protons do line up and provide a macroscopic magnetization $\overline{M}$ whose precession can be detected under certain conditions. In this book, we will mainly deal with the behavior of