Preface

In this second edition I have tried to address some of the deficiencies of the first edition, but without disturbing the structure of the text too much. I have now included an overview of the NMR of quadrupolar nuclei, given the important subject of pulsed field gradients more prominence, and addressed the subject of spin-1/2 pairs in solids more thoroughly. It is a complex task to revise a large book, and I am not sure whether I have been successful. Let's see what you think.

I am very grateful to all the people who pointed out errors in the first edition, which I hope to have corrected in this new version. These include Juan Alberdi, Bernard Ancian, Stefan Berger, Tom Bloemberg, Geoffrey Bodenhausen, Dave Bryce, Shidong Chu, André Dorsch, Nick Higham, Vladimir Hnizdo, Eric Johnson, Alan Kenwright, Karel Klika, Olivier Lafon, Linda Lai, Young Lee, Phil Lucht, Slobodan Macura, P. K. Madhu, Ian Malcolm, Arnold Maliniak, Emi Miyoshi, Gareth Morris, Norbert Müller, Juan Paniagua, Tanja Pietrass, Tatyana Polynova, E. J. Pone, Jan Rainey, Michael Roehrl, David Siminovitch, Chunpen Thomas, Bill Wallace, John Waugh, and Steven Wimperis. I also thank Zosia Beckles for help with the initial computer spadework.

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Special thanks to Geoffrey Bodenhausen and Angelika Sebald for giving detailed criticism on the text. Thanks to P. K. Madhu for the photograph from India.

Fiona Woods and Andy Slade at Wiley have been patient, encouraging and helpful during the preparation of this edition.

As usual, I take sole responsibility for any errors and omissions.

Finally, I thank my wife and daughter Latha and Leela again, for their renewed patience and support.

Technical Details

The book was written on Apple Macintosh© computers. The text was written in LaTeX©, using a large number of self-programmed macros. Most of the diagrams were drawn by the author using a combination of Mathematica© and Adobe Illustrator©. Errata and supplementary notes are available through the website www.mhl.soton.ac.uk

Preface to the First Edition

This book has a long prehistory. It began approximately 12 years ago, when I was persuaded by my friend (and squash court enemy) Jim Sudmeier, to give a short series of lectures on the basics of NMR at Tufts University in Boston, MA. The lectures were probably not a tremendous success, but I was inspired to write up the material as some sort of short book. I was naive enough to feel that I could probably cover the basics in perhaps 100 pages using a minimum of equations. I worked on this 'proto-book' for over a year in Cambridge, England, before I realised that I was only scratching the surface of the subject and that I was not yet prepared for the task.

The situation changed in Stockholm where I became involved in teaching an intensive course each year on NMR to third-year undergraduates. Over a period of around seven years I built up a large set of handwritten lecture notes. The experience of teaching made me realise how difficult it is to keep the subject accessible while still imparting something useful to those students wishing to continue into NMR research. Over many years I experimented with various permutations of the material until I ended up with a set of notes which form the basis of this book.

The bulk of the final writing was done in India where I enjoyed the hospitality of Professor Anil Kumar at the Indian Institute of Science in Bangalore for three months.

The book which emerged is still not precisely the one I wanted to write: I wanted to communicate the beauty and usefulness of NMR in a rather simple and non-mathematical way. In the end, I did not succeed at all in keeping down the number of equations. Teaching showed me that equations are simply the only way to present the subject clearly. Nevertheless, although some of the mathematics may look a little frightening to the uninitiated, I think none of it is truly difficult. Most workers in NMR, including myself, have somehow learnt to muddle through the mathematics without any formal training, and the mathematics given here is just a distillation of my own muddling.

The one thing more discouraging to students than anything else is bad terminology and notation, especially when its defects are not pointed out plainly. Faced with a confusing but accepted term, many students draw the conclusion that the problem lies in their own stupidity, rather in the true cause, which is often simple carelessness by its originators, amplified by uncritical perpetuation. This problem falls into a general pattern of teaching science as if everything is already understood and 'engraved in stone'. I care too much about NMR to accept such a static view of the subject and I have tried to combat the most offending eyesores in this book. Some of these suggestions may be controversial with established workers in the field. Nevertheless, I stand by these suggestions and hope that they will catch on in time. I point out the following items here: (i) I consistently distinguish between 'rate' (the change in something over a small time interval, divided by the duration of that interval) and 'rate constant' (a factor appearing in a rate equation); (ii) I consistently distinguish between 'time' (needs no explanation) and 'time constant' (inverse of a rate constant); (iii) I consistently distinguish between a 'time point' and an 'interval' (which is the separation between two time points); (iv) I use the notation t for a time point, and τ for an interval (with the single exception of the evolution interval in a two-dimensional experiment, for which I use the widespread notation t_1); (v) I consistently use the correct physical sign for the nuclear Larmor frequency,

the correct physical sign for the spectral frequency axes, and the correct sign for all spin interactions; (vi) I change the sign of the cross-relaxation rate constant in the Solomon equations (Chapter 20), so as to bring it into line with a kinetic description; (vii) I avoid terminology such as 'emission peak', 'rotating-frame experiment', 'phase-sensitive 2D experiment', and 'time-reversal experiment' which are widely used in the field but which have no physical basis. I also avoid terminological fossils such as 'low field' and 'high field', whose original physical basis has been undermined by the development of NMR methodology, leaving them sadly marooned in a world in which they no longer make sense.

I have also not shied away from minor modifications of conventions for the sake of clarity. For example, I consistently use a deshielding convention for all elements of the chemical shift tensor, instead of using the deshielding convention for the isotropic chemical shift and the shielding convention for the chemical shift anisotropy, which seems to be the standard practice.

I have also introduced some novel notation, for example the 'box notation' for coherences in a weakly coupled system. I have personally used this notation for many years, and know that it is useful and that it works. However, I have only rarely used it in a scientific paper. Here, I am taking the opportunity of exposing it to a wider audience.

In one exceptional case I have allowed the convenience of the final equations, and consistency with most of the existing literature, to overrule the transparency of the physics: I have imposed mathematically positive rotations for r.f. pulses (the 'Ernst convention') by manipulating the definition of the rotating frame in a messy way.

Although I have tried to take care, I am sure that this book contains many remaining inconsistencies, and will be very grateful to be informed about them.

Another point of contention may be my presentation of quantum mechanics. In order to make NMR comprehensible I attack vigorously the widespread view that spin-1/2 particles only have two 'allowed orientations' (up and down). Quantum mechanics says no such thing but it is surprising how emotionally this view can be defended. Emotions may also be inflamed over my very 'physical' discussion of the dynamics of single spins. I have been told in all seriousness that quantum mechanics 'forbids' any such discussions. My view is that quantum mechanics is not understood in its completeness by anyone and that the field is wide open to any physical interpretation, as long as that interpretation is demonstrably useful in a particular situation. The interpretation presented in Chapter 9 and the following chapters is neither radical nor original, but is nevertheless very useful for understanding NMR. I am fully aware that this physical picture runs into trouble in certain situations (such as the observation of non-local entangled spin states, as in the Einstein–Rosen–Podolosky paradox). Nevertheless, the 'arrow' picture of a single spin is demonstrably useful over the limited domain of NMR, and I regularly use it myself in thinking about old experiments and developing new ones.

Since NMR is an enormous subject, I have had to select only a very few experiments for detailed discussion. Both my selection of topics and the very basic level at which many of these are treated will probably annoy the specialists. For this I can only apologize. I could simply manage no more material at this stage.

One point on which I am personally dissatisfied is how little I manage to say about solid-state NMR, which is my own main research interest. I had considered having a brief review of the field in a single chapter. However, I decided against that, since it became rapidly clear that I could not maintain a comparable depth of discussion without greatly increasing the size of the book. So I will have to defer the treatment of solid-state NMR to another time, maybe another book.

One remark on my literature referencing: I have been very sparse, and have generally tried to restrict myself to sources that I think will be useful to the reader. The references do not indicate the priority of some group in a particular area.

There are many people other than myself who have contributed to this book. As I mentioned above, the whole thing grew out of a series of lecture notes. Those notes would never have condensed into a useful form without the participation and probing questions of the students I have taught in Stockholm, including Kai Ulfstedt-Jäkel, Tomas Hirsch, Baltzar Stevensson and Clas Landersjö. There are many others: unfortunately I don't remember all of your names, but I do thank you if you read this. I did learn a lot from you all.

I do remember those students who went on to be my graduate students and co-workers, and I have relied over the years on your enthusiasm, support, and amazing hard work. Many of you have also made very specific and useful suggestions about this material. So thanks again to Zhiyan Song, Xiaolong Feng, Dick Sandström, Oleg Antzutkin, Mattias Edén, Torgny Karlsson, Andreas Brinkmann, Marina Carravetta, Xin Zhao, Lorens van Dam and Natala Ivchenko. I have also enjoyed the visits of many wonderful scientists, all of whom have contributed to this book in one way or another, at least in spirit. These include Young K. Lee, S. C. Shekar, K. D. Narayanan, Michael Helmle, Clemens Glaubitz, Angelika Sebald, Stefan Dusold, Peter Verdegem, Sapna Ravindranathan, Pratima Ramasubrahmanyan, Colan Hughes, Henrik Luthman, Jörn Schmedt auf der Günne and P. K. Madhu. I am extremely grateful to the critical reading and detailed suggestions of Gottfried Otting, Gareth Morris, Ole Johannessen, Arnold Maliniak, Dick Sandström, Maurice Goldman, Colan Hughes and Ad Bax. Thanks also to Melinda Duer for ploughing through the first (aborted) version of the book. I am also very grateful to Sapna Ravindranathan, Gottfried Otting, Warren Warren, Jianyun Lu and Ad Bax for supplying some of the figures. Special thanks to Anil Kumar for your hospitality in Bangalore and many delightful discussions. Very special thanks to Jozef Kowalewski for many years of invaluable support in Stockholm and for your constructive comments on the text.

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In addition, I would like to thank Ray Freeman and Richard Ernst, from whom I learnt to think about NMR in two very different ways.

Although many people have commented on the text of this book, I take sole responsibility for any errors and omissions.

Finally, I thank my wonderful wife Latha and daughter Leela for your patience, understanding, advice, encouragement and help, as I climbed this personal mountain.