## Preface

Until recently, the teaching and understanding of modern (pulse) Nuclear Magnetic Resonance has made successful use of vector descriptions, including handwaving, since the pulse sequences were relatively simple. The advent of two-dimensional NMR made it practically impossible to explain the intricate effects of combined pulses and evolutions exclusively on the basis of vector representation. It thus became necessary to use an appropriate tool, the density matrix (DM) formalism. The DM treatment is generally found in specialized books which emphasize its quantum mechanical foundation. The quantum mechanical approach, however, constitutes a significant barrier for a growing number of students and scientists in the fields of chemistry, biology, medicine and materials research who want to gain a better understanding of 2D NMR.

This book constitutes a guide for the use of density matrix calculations in the description of multipulse NMR experiments. In keeping with its didactic nature, the text follows a step-by-step procedure which contains more detail than usual. This will give readers with modest mathematical background the possibility to work out or to create sequences of various degrees of complexity. Our treatment begins with an intuitive representation of the density matrix and continues with matrix calculations without trying to explain the quantum mechanical origin of pulse effects (*rotations*) and *evolution* of the matrix elements. The quantum mechanical approach is deferred to Appendix B. Those who do not want to take anything for granted may actually begin with Appendix B (it is assumed, of course, that the reader is familiar with the principles and experimental aspects of Fourier transform NMR).

The first part of the book contains a detailed DM description of the popular two-dimensional sequence, 2DHETCOR (2D heteronuclear correlation). It starts with the characterization of the system of nuclei at equilibrium in a magnetic field and concludes with the calculated signal which results from application of pulses and evolutions. This section is written in such a way as to be accessible to students with only an undergraduate mathematical background (there is even a Math Reminder in Appendix A). In order to ensure the continous flow of the minimal information needed to understand the sequence without too many sidetracks a number of detailed calculations of secondary importance are given in Appendix I.

Once familiar with 2DHETCOR, the student is led, step-by-step, through the calculations of a double-quantum coherence sequence and those of the widely used COSY (correlation spectroscopy). Throughout this book we did not use the $t_1$ and $t_2$ notations for the two time variables in a 2D experiment.in order to avoid confusion with the relaxation times $T_1$ and $T_2$. Also, there is still no consensus as to what notation should be given to the detection period (some call it $t_1$, some $t_2$).

The second part is entirely dedicated to the product operator (PO) formalism. The student will appreciate the significant economy of time provided by this elegant condensation of the density matrix procedure. He or she will be able to handle in reasonable time and space systems of more than two nuclei which would require much more elaborate calculations *via* the unabridged DM treatment.

Appendix B offers an accessible quantum mechanical presentation of the density matrix. Appendix C contains a selection of angular momenta and rotation operators written in matrix form, while Appendix D summarizes the properties of product operators. Appendices E through M are for students interested in a demonstration of the relations and procedures used in the text.

Throughout the book, relaxation processes have been neglected; this does not affect the essential features of the calculated 2D spectra and contributes to the clarity of the presentation.

The teaching method presented in this book has been successfully used in an Instrumental Analytical Chemistry graduate course for the past few years at Case Western Reserve and in several short courses. Being essentially a self-sufficient teaching tool (lecture notes), this book does not contain literature references. Numerous citations can be found in the books indicated in the Suggested Readings section. One of us being a passionate skier, we may say our *class* is for *beginners,* Farrar and Harriman's, for *intermediates,* and Ernst-Bodenhausen-Wokaun's, for *advanced*. In fact, our work is a synergic complement to Martin and Zektzer's *Two-Dimensional NMR Methods for Establishing Molecular Connectivity: A Chemist's Guide to Experiment Selection, Performance, and Interpretation*.