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THEORY AND APPLICATIONS OF MAPS ON $SO(3)$ IN NUCLEAR MAGNETIC RESONANCE

H.M. Cho
(Ph.D. Thesis)

February 1987

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Theory and Applications of Maps on $SO(3)$
in Nuclear Magnetic Resonance

by

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February 1987

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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THEORY AND APPLICATIONS OF MAPS ON $SO(3)$
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Herman M. Cho

ABSTRACT

Theoretical approaches and experimental work in the design of multiple pulse sequences in Nuclear Magnetic Resonance (NMR) are the subjects of this dissertation. Sequences of discrete pulses which reproduce the nominal effect of single pulses, but over substantially broader, narrower, or more selective ranges of transition frequencies, radiofrequency field amplitudes, and spin-spin couplings than the single pulses they replace, are developed and demonstrated.

The derivation of multiple pulse sequences is considered as, and separated into, two distinct problems. The first is the determination of sequences which result in the desired response. Several rules are proposed for guiding the selection of field parameters which help resolve this difficulty. The second problem arises from the fact that not only are such rules often difficult to determine, but they must also be compatible with obtaining the desired bandwidth properties.

Two approaches for deriving sequences with desirable bandwidth properties are employed. Coherent averaging theory is the first. Short sequences effective over wide ranges of chemical shifts, radiofrequency amplitudes, and quadrupolar and dipolar couplings are explicitly developed by this formalism. Some of these sequences

provide for a deadtime period after their completion to compensate for probe and receiver ringing for solid state NMR.

The second theoretical approach draws on the formalism of iterative map: and their fixed points. The generation of pulse sequences by an iterative procedure is introduced, and the relationship of these procedures to nonlinear maps on the three dimensional space $SO(3)$ pointed out. The consequences of fixed points and their stability for the bandwidth properties of sequences generated by these procedures are examined. Methods for specifying maps with certain stable and unstable sets are treated. Broadband, narrowband, and bandpass sequences for isolated two level systems are some of the results obtained from this analysis.

Experiments verifying the efficacy of these sequences in solid and liquid state NMR are included along with a short discussion on the modifications of an NMR spectrometer necessary for the practical implementation of these sequences.

ACKNOWLEDGEMENTS

Professor Alexander Pines has generously shared the ideas, inventiveness, and time which have enabled me to carry out the research presented in this dissertation. I am deeply grateful to him for the many ways he has encouraged and contributed to my education and intellectual maturation while a graduate student in his group.

Much of this dissertation follows upon work initiated by Robert Tycko. I owe him thanks for his advice, legacy, and efforts at getting me started in this research. I have learned much while endeavoring to uphold the high standards of scholarship he established in this area.

I have benefitted from and enjoyed the collaboration of several outstanding colleagues at Berkeley. Emil Scoffone participated in the work of Chapter Four, and Jean Baum in the work of Chapter Six; they have been both incisive and tolerant coworkers. John Guckenheimer has given freely his time and expert counsel, and has assisted me in understanding many of the ideas related in Chapters Five and Six.

The able technical aid of David Shykind and Malaine Trecoske and many educational moments with Dan Weitekamp are appreciatively remembered. Dione Carmichael did much to ease the trials of being a student. The rest of the Pines group I wish to thank collectively (and inadequately) for the memories of the way it was.

I am thankful, finally, for the support of my family through all of the long years I have spent in school.

TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION.....	1
I. OVERVIEW.....	1
II. PREVIEW OF FUTURE CHAPTERS.....	5
CHAPTER TWO: FUNDAMENTALS.....	9
I. INTRODUCTION.....	9
II. LABORATORY FRAME NMR HAMILTONIAN.....	9
A. Linear terms.....	10
B. Bilinear terms.....	13
III. MOTION IN QUANTUM MECHANICS.....	15
A. Solution of Schrödinger's equation.....	15
B. Rotations and time development operators in NMR.....	19
C. Representations of the rotation group.....	23
IV. QUANTUM STATISTICAL DESCRIPTION OF AN NMR EXPERIMENT.....	25
A. Definition and properties of the density operator.....	25
B. Relation to an NMR measurement.....	32
C. Final comments on the density operator.....	34
CHAPTER THREE: INTERACTION PICTURES IN NMR.....	36
I. PURPOSE OF THE CHAPTER.....	36
II. INTERACTION PICTURE.....	37
A. Motivation.....	37
B. Transformations to different frames of reference:	
Formalism.....	39
C. Rotating frame transformation.....	42

D. Rotating frame detection.....	47
III. INTERACTION PICTURE DEFINED BY A TIME DEPENDENT	
HAMILTONIAN.....	49
A. Introduction to coherent averaging theory.....	49
B. Final remarks.....	58
CHAPTER FOUR: COHERENT AVERAGING THEORY ANALYSIS OF COMPOSITE	
PULSES.....	59
I. INTRODUCTION.....	59
A. The propagator $\mathcal{R}_\phi(\pi)$	59
B. The propagator $\mathcal{R}_\phi(\pi/2)$	62
II. STATEMENT OF THE PROBLEM.....	64
A. Specification of $U_{rf}(\vec{\phi}, \vec{\alpha}) = \bar{\mathcal{R}}$	66
B. Specification of $U_V(\vec{\phi}, \vec{\alpha}, \vec{\tau}, \vec{\lambda}) = 1$	72
III. APPLICATIONS AND RESULTS	79
A. Radiofrequency inhomogeneity.....	79
B. Strong couplings in solids.....	81
IV. CONCLUSION.....	115
CHAPTER FIVE: ITERATIVE MAPS ON $SO(3)$	
I. INTRODUCTION.....	118
A. One dimensional iterated functions.....	121
B. Iterated functions in NMR.....	124
II. NMR ITERATIVE SCHEMES.....	127
A. NMR propagators and $SO(3)$	127
B. Specification of invariance.....	130
C. Specification of stability.....	133

D. Digression on numerical methods.....	135
III. RESULTS AND DISCUSSION.....	140
A. Bandwidth properties.....	140
B. Previous work.....	144
C. Fixed point analysis of iterative schemes.....	146
IV. CONCLUSION.....	158
CHAPTER SIX: BISTABLE ITERATIVE MAPS ON $SO(3)$	160
I. INTRODUCTION.....	160
II. GENERAL THEORY.....	165
A. Bistable iterative maps in one dimension.....	165
B. Flow diagrams.....	169
III. DERIVATION OF ITERATIVE SCHEMES.....	174
A. Iterative schemes and maps on $SO(3)$	174
B. One dimensional maps on $SO(3)$	176
C. Specification of stability.....	180
D. Bistability in phase symmetric schemes.....	183
IV. PROPERTIES OF BISTABLE ITERATIVE SCHEMES.....	184
A. Convergence properties of the 7 and 9 shift sequences: Basin images.....	184
B. Bandwidth properties of bistable schemes.....	192
C. Role of the initial condition and some specific sequences.....	198
V. OTHER ROUTES TO BISTABLE MAPS.....	213
VI. RESONANCE FREQUENCY SELECTIVE INVERSION.....	217

CHAPTER SEVEN: BASIN IMAGES.....	225
I. INTRODUCTION.....	225
A. Phase shift schemes.....	227
B. Iterative schemes containing inverses.....	242
C. Waugh decoupling iterative schemes.....	245
D. MLEV schemes.....	253
CHAPTER EIGHT: EXPERIMENTAL DETAILS.....	270
I. INTRODUCTION.....	270
II. INSTRUMENTAL MODIFICATIONS.....	270
A. Radiofrequency phase modulation.....	270
B. Simulating resonance offset.....	273
C. Simulating amplitude offset.....	275
D. Inversion measurements.....	276
E. Measurements of composite $\pi/2$ pulse performance.....	278
F. Samples.....	280
APPENDIX A: LINESHAPE TRANSFER FUNCTIONS.....	282
REFERENCES.....	290

CHAPTER ONE:INTRODUCTION

I. OVERVIEW

The excitation and detection of specific, well-defined responses are fundamental and widespread objectives of nuclear magnetic resonance (NMR) and other branches of spectroscopy. The selective modulation of pulsed radiofrequency (rf) fields tuned to nuclear spin transition frequencies is the standard method in high field NMR by which this is accomplished. In a typical NMR experiment, applied rf fields are used to prepare nonequilibrium final states from nuclear spin systems initially in a state of thermal equilibrium. For some nonequilibrium states, the nuclear spins respond by emitting detectable, coherent dipole radiation at their transition frequencies. Others of these nonequilibrium states must be observed by less direct means. Often, the preparation and detection of these responses must be achieved over a range of experimentally variable parameters and in the presence of a variety of practical constraints, such as limitations on irradiation power. This dissertation concerns recent experimental and theoretical advances which address these fundamental problems in NMR spectroscopy.

Since the demonstration by Hahn¹ of the two pulse spin echo experiment, time, amplitude and phase modulation of the applied rf field has become a common and well established technique for the excitation of special responses in NMR.²⁻⁶ The necessity for pulse modulation of the incident field can arise for two reasons. Many experiments in NMR call for a response which can nominally be

accomplished with a single pulse. The most commonly encountered single pulse experiments in NMR are the familiar $\pi/2$ and π pulses. The effect of a single π pulse is to invert the populations of the high field nuclear Zeeman energy levels, while the best known effect of a $\pi/2$ pulse is to rotate the familiar magnetization vector from its equilibrium position, aligned with the static magnetic field, to a nonequilibrium position in the plane perpendicular to the static field. Despite their relative ease of implementation and nominal sufficiency, single pulse excitation may be undesirable or inadequate nonetheless. In an NMR spectrum with several widely spaced lines, for example, most transitions will not be resonant with the applied rf field, precluding the uniform excitation of all lines simultaneously with a single pulse. The bandwidth response of single pulses has been investigated for a variety of experimental parameters, and is known to be deficient in many common applications.⁶ Another reason why single pulse excitation may nominally suffice, but nevertheless still be undesirable, was pointed out by Hahn in his original work on spin echoes. There is usually a time after the rf pulse has been turned off when the NMR detection apparatus is blocked and cannot be used to observe the transient NMR signal. This, plus the harmful line broadening caused by the inhomogeneity of the static magnetic field, are two of the problems resolved by replacing a single $\pi/2$ pulse with a two pulse, two delay spin echo. Hence, even though a single pulse might actually suffice to excite the desired response in the spin system, instrumental limitations may still make necessary a more sophisticated excitation and detection scheme. Considerations such as these constitute the first motive for employing phase, time and amplitude modulation in NMR.

The second motive for performing modulated pulse excitation in NMR is that some nonequilibrium states and responses may be intrinsically inaccessible from the initial, high field equilibrium condition by a single pulse. Multiple quantum coherences,^{7,8} dipolar and quadrupolar ordered states,^{9,10} and cross polarization enhancement^{11,12} are some conspicuous examples of nonequilibrium states in NMR which cannot be prepared with a single rf pulse. Moreover, since many of these multiple pulse experiments rely on single pulse units, they too can suffer from the same bandwidth constraints and instrumental limitations which interfere with single pulse experiments.

The preceding paragraphs hopefully make plain both the practical and intellectual relevance of multiple pulse techniques in coherent spectroscopy. In spite of the great activity in this area since the inception of the spin echo, however, attention has only recently been drawn to the basic units which comprise almost all of these multiple pulse experiments, namely, $\pi/2$ and π pulses. There are several conceivable reasons, discussed previously, why single pulses might perform inadequately in conventional or multiple pulse applications, but the most prominent and important ones have to do with their limited bandwidth response. To overcome this fundamental bandwidth constraint, Levitt and Freeman have proposed replacing these single pulses with composite pulses,¹³ i.e., closely spaced trains of pulses with their amplitudes, durations, phases, and frequencies selectively modulated so as to produce some desired effect and be insensitive to the deficiencies of individual pulses in the sequence. In the earliest applications of a composite pulse, Levitt and Freeman and others¹³⁻²⁵ demonstrated that simple sequences consisting of three or more discrete

pulses could uniformly invert the equilibrium populations of isolated two level systems (i.e., spin-1/2 nuclei) over ranges of transition frequencies and rf amplitudes considerably broader than those of a single π pulse. The great majority of the work on composite pulses since then has been devoted to other modifications of the effective bandwidth of response of nuclear spins with respect to these and other experimental parameters.²⁶⁻³⁵

The communication and discussion of some original work in composite pulse excitation are the main objects of this dissertation. Composite pulses which reproduce the effect of $\pi/2$ and π pulses, but over broader, narrower, or shaped bandwidths, are the specific subjects of this investigation. These sequences are customarily referred to as composite $\pi/2$ pulses and composite π pulses, respectively. Although specifically derived for, and verified by, solid and liquid state NMR experiments, the sequences proposed here have wide potential applicability in other spectroscopies as well. As a test case for these multiple pulse techniques, however, NMR possesses several decisive advantages over other spectroscopies. The fact that the number of spin angular momentum eigenstates of a nucleus is bounded means that the number of energy levels of weakly coupled spin systems can be considered finite. To a good approximation, no continuum of energy levels exists for such systems, as they do, e.g., in vibrational spectroscopy. The NMR of small, weakly coupled spin systems, such as exist in simple liquids, can therefore serve as prototypical, textbook cases of quantum mechanical systems coupled to a coherent, resonant field.

The comparatively long relaxation times in NMR is another

advantage of NMR over other types of spectroscopy. While coherently excited vibrational states typically relax in less than picoseconds, coherent states for commonplace samples in NMR can sometimes persist for seconds. The factors responsible for this difference are clearly beneficial and important for research in NMR, but will not be explored here.

The longer time scales and lower energies of NMR point to a third advantage of NMR, which is that established, relatively well developed technologies can be employed in NMR experiments. Although the smaller frequencies imply lower sensitivity, less stringent timing requirements and the advanced state of radiofrequency instrumentation make possible many coherence experiments in NMR which cannot currently be tried in any other spectroscopy.

The combination of these factors makes NMR an appropriate choice for the development of these multiple pulse methods. The relevance of the methods presented here to other branches of spectroscopy is assumed to be self-evident. The practical and purely intellectual pertinence of these topics to NMR, however, provide the immediate motivation for the work in this dissertation.

II. PREVIEW OF FUTURE CHAPTERS

Irradiation of a nuclear spin system with a sequence of resonant pulses transforms the system from some starting state, usually a state of thermal equilibrium, to some desired final state. Due to the inherently statistical nature of a NMR experiment, the state of the system must be specified by a density operator³⁶ rather than a single wave function. The motion of operators in quantum mechanics is

governed by the unitary operator known as the time development operator.³⁷ The time development operator depends, obviously, on time, but can also depend on experimental parameters as well, which, in NMR, might include the rf amplitude, the spin transition frequencies, spin-spin coupling constants, position in space, or the value of the local electric field gradient.

Pulse sequences represent one way to bring about a time development operator which transforms the initial density matrix to the desired final density matrix. Theoretical analyses of composite pulses thus tend to focus on the form and parameter dependence of the time development operator rather than on the actual state of the spin system itself. If, for some pulse sequence, the final time development operator assumes a single, specific mathematical form $\bar{U}$ over a wide range of values of a parameter λ , then the sequence is said to be broadband with respect to λ . If, for a sequence, the final time development operator assumes a specific form $\bar{U}$ only over a small range of λ , then the sequence is called narrowband over λ . Finally, if the time development operator assumes one form $\bar{U}_1$ for some values of λ , and another form $\bar{U}_2$ for all other values of λ , then the sequence is termed a bandpass or bistable sequence.

The problem of choosing optimum combinations of pulse phases, frequencies, durations, amplitudes, and spacings for composite pulses has been the subject of a variety of theoretical treatments in NMR. Two conceptually distinct, but complementary, methods are employed in the present work. The first formalism, called coherent averaging theory,^{2,4,38} is covered in the third and fourth chapters of this thesis. Originally introduced by Haeberlen and Waugh to derive

homonuclear decoupling sequences for solid state NMR, coherent averaging theory has since been used principally as a way of calculating the long time evolution of strongly coupled spin systems subjected to irradiation by cyclic pulse sequences.^{2,4,7,8} An account of this formalism and its adaptation by Tycko, et al.,^{18,22,33,35,39} to the analysis and derivation of composite pulses for solid and liquid state NMR experiments are provided later. Experimental and theoretical results based on this analysis are included in these chapters.

Chapters Five through Seven are devoted to a second form of composite pulse analysis based on the theory of iterative maps on $SO(3)$ and their fixed points. The use of an iterative procedure to derive a pulsed excitation sequence in NMR was first suggested by Warren, et al.,⁴⁰ as a means for obtaining sequences which selectively pumped high order multiple-quantum transitions. The close formal resemblance of these procedures to iterative maps of the type studied in nonlinear dynamics was recognized by Tycko, et al., and a comprehensive, unified reformulation of iterative procedures in terms of a nonlinear iterative map formalism has subsequently been given by them.^{24,39} The utility of iterative maps and their fixed points for modeling nonlinear dynamical processes has been well established, and is widely appreciated in many fields outside of NMR.⁴¹⁻⁴⁶ The chapters on this formalism provide a short synopsis of some general and useful topics in the theory of iterative maps. The applicability of these ideas to iterative schemes in NMR is demonstrated, with an emphasis on how concepts such as the stability of an iterative map's fixed points relate to the bandwidth properties of the composite pulses they generate.

The thesis concludes with a chapter containing a short discussion

of the experimental implementation and verification of these composite pulses. The test samples and the nonstandard alterations of NMR hardware necessary for producing these composite pulses in an experiment are also mentioned. Most of the sequences introduced here can be realized experimentally with only slight modifications of a conventional NMR spectrometer. Indeed, considerations of experimental practicality figured in the design of many of these sequences.

CHAPTER TWO: FUNDAMENTALS

I. INTRODUCTION

Three subjects of an introductory nature are covered in this chapter. First, a brief compilation of the important laboratory frame interactions in NMR is presented. The purpose of this listing is to identify in one place the terms in the NMR Hamiltonian referred to in later chapters.

The quantum mechanical equations of motion and their solutions are the main topic of the second part of this chapter. It will be shown that for some NMR interactions, the motion of the nuclear spin system can be depicted as a simple rotation in spin angular momentum Hilbert space. A concise review of some pertinent issues in the quantum theory of angular momentum and rotations accompanies this section.

The final subject discussed is the density operator and its applications in NMR.

II. LABORATORY FRAME NMR HAMILTONIAN⁴⁷

Terms in the NMR Hamiltonian can be separated into two groups, one group containing terms linear in the spin angular momentum operator I_x , I_y , and I_z , and the other group containing terms which are bilinear in these operators. This classification scheme is equivalent to dividing the NMR Hamiltonian into single spin interactions and interactions involving the couplings of spins to one another. The lone

exception to this equivalence is the quadrupolar interaction of nuclei with spin $I \geq 1$. The Hamiltonians below are segregated in accordance with this linearity criterion.

A. Linear terms

i. Zeeman interaction

The magnetic dipole moment of nuclear spins with nonzero spin angular momentum interacts with externally applied magnetic fields according to the classical Hamiltonian:

$$\mathcal{H}_Z(\vec{r}, t) = -\gamma_I \vec{I} \cdot \vec{H}_{\text{ext}}(\vec{r}, t) \quad (2.1)$$

The constant γ_I is called the gyromagnetic ratio and is a property of the nuclear isotope under consideration; equation (2.1) assumes the presence of only one magnetically active isotope in the spin system and thus shows only one gyromagnetic ratio. $\vec{H}_{\text{ext}}(\vec{r}, t)$ represents the time dependent magnetic field and $\vec{I}$ the spin angular momentum vector operator in this equation. Spatial inhomogeneities of the applied field, both intentional and unintentional, are accounted for by making $\vec{H}_{\text{ext}}$ a function of $\vec{r}$.

The magnetic field in a conventional high field NMR experiment is the vector sum of two fields, one a large static field $\vec{H}_0(\vec{r})$, and the other a much smaller, linearly polarized, oscillating field $\vec{H}_1(\vec{r}, t)$ oriented perpendicular to the static field. Choosing the direction of the static field as the z axis, this summed field can be written:

$$\vec{H}_{\text{ext}}(\vec{r}, t) = 2H_1(\vec{r}, t)\cos[\omega t + \phi(\vec{r}, t)]\hat{i} + H_0(\vec{r})\hat{k} \quad (2.2)$$

$$\begin{aligned}
& - H_1(\vec{r}, t) \left[\cos[\omega t + \phi(\vec{r}, t)] \hat{i} + \sin[\omega t + \phi(\vec{r}, t)] \hat{j} \right] \\
& + H_1(\vec{r}, t) \left[\cos[\omega t + \phi(\vec{r}, t)] \hat{i} - \sin[\omega t + \phi(\vec{r}, t)] \hat{j} \right] \\
& + H_0(\vec{r}) \hat{k}
\end{aligned} \tag{2.3}$$

The second equation follows from the first by decomposing the linearly polarized field into two counter-rotating circularly polarized fields. Choosing an appropriate unit for γ_I , and substituting (2.3) into (2.1), the Zeeman Hamiltonian becomes:

$$\begin{aligned}
H_Z(\vec{r}, t) &= \omega_1(\vec{r}, t) \left[I_x \cos[\omega t + \phi(\vec{r}, t)] + I_y \sin[\omega t + \phi(\vec{r}, t)] \right] \\
&+ \omega_1(\vec{r}, t) \left[I_x \cos[\omega t + \phi(\vec{r}, t)] - I_y \sin[\omega t + \phi(\vec{r}, t)] \right] \\
&+ \omega_0(\vec{r}) I_z
\end{aligned} \tag{2.4}$$

where $\omega_0(\vec{r})$ and $\omega_1(\vec{r}, t)$ are in units of angular frequency. The parameter $\omega_1(\vec{r}, t)$ corresponds to the amplitude of the applied rf field, and the parameter $\phi(\vec{r}, t)$ to the phase of the rf field.

The relative energies of the Zeeman interactions depend on the experimental apparatus. In practice, the size of the fields are such that $\omega_0(\vec{r})$ exceeds the eigenvalues of all other terms in the Hamiltonian by orders of magnitude. In the absence of resonant rf fields, therefore, the eigenvalues of I_z are good quantum numbers of the laboratory frame Hamiltonian.

The quantities $\omega_0(\vec{r})$, $\omega_1(\vec{r}, t)$ and $\phi(\vec{r}, t)$ are experimentally adjustable parameters. The functional forms they can assume are limited primarily by the sophistication of the experimental apparatus.

Most modern NMR spectrometers are capable of generating rf radiation in discrete, fixed amplitude, fixed frequency pulses. The phase and duration of the pulses can usually be varied from pulse to pulse, but within each pulse, the phase remains constant. Due to these practical constraints, $\vec{H}_1(\vec{r}, t)$ will be considered a piecewise constant function of time. Moreover, throughout this work, it is assumed that $\omega_1(\vec{r}, t)$ for fixed $\vec{r}$ can take on only one of two values, $\omega_1(\vec{r}, t) = 0$ or $\omega_1(\vec{r}, t) = \omega_1(\vec{r})$, depending on whether the rf is off or on, respectively. Clearly, $\phi(\vec{r}, t)$ will also be a piecewise constant function of time.

Despite the capability to vary these parameters, $\omega_1(\vec{r}, t)$, $\phi(\vec{r}, t)$, and $\omega_0(\vec{r})$ can deviate from their putative values nevertheless, due to a variety of causes. Two common sources of field imperfections are spatial inhomogeneities in the rf and static field. The parameters $\omega_1(\vec{r}, t)$ and $\omega_0(\vec{r})$ can therefore take on a distribution of values throughout a macroscopic sample. Losses of signal intensity and coherence are the consequence. These imperfections necessitate a redefinition of $\omega_1(\vec{r}, t)$ and $\omega_0(\vec{r})$:

$$\omega_1(\vec{r}, t) = \omega_1^0(\vec{r}, t) + \Delta\omega_1(\vec{r}, t) \quad (2.5)$$

$$\omega_0(\vec{r}) = \omega_0^0(\vec{r}) + \Delta\omega_0(\vec{r}) \quad (2.6)$$

The putative values of the static and oscillating field are denoted ω_0^0 and ω_1^0 , respectively, and their imperfections as $\Delta\omega_0$ and $\Delta\omega_1$. For simplicity, $\omega_1^0(\vec{r}, t)$ and $\Delta\omega_1(\vec{r}, t)$ are presumed to differ only by a proportionality constant.

Other field imperfections are possible, but will not be considered.

ii. Chemical shift

The presence of a large magnetic field can induce microscopic currents in the vicinity of nuclei arising from delocalized electronic charges. These currents generate magnetic fields, which, interact with nearby nuclei according to the Hamiltonian:

$$\mathcal{H}_{cs} = \sum_i \vec{I}_i \cdot \vec{S}_i \cdot \vec{B}_0 \quad (2.7)$$

The summation takes place over all distinct nuclei. The quantity $\vec{S}_i$ is called the chemical shift interaction tensor, and is manifested in high fields by a shift in the resonance frequency by an amount proportional to the magnitude of the static field ω_0 .

B. Bilinear terms

i. Dipolar interaction

A magnetic dipole can couple to neighbouring magnetic dipoles with an energy of interaction calculable from the Hamiltonian:

$$\mathcal{H}_D = \sum_i \sum_{i>j} \omega_{D,ij} \left[\vec{I}_i \cdot \vec{I}_j - \frac{3(\vec{I}_i \cdot \vec{r}_{ij})(\vec{I}_j \cdot \vec{r}_{ij})}{r_{ij}^2} \right] \quad (2.8)$$

with:

$$\omega_{D,ij} = \frac{\gamma_i \gamma_j \hbar}{r_{ij}^3} \quad (2.9)$$

The summation over i again includes all distinct, coupled nuclei. The

quantity $\vec{r}_{ij}$ is the vector drawn from nucleus i to nucleus j . Like the chemical shift, $\mathcal{H}_D$ is a product of the local nuclear environment.

ii. Quadrupolar interaction

Nuclei with spin angular momentum quantum number greater than or equal to one possess a quadrupole moment which interacts with local electric field gradients. The energy of this interaction is:

$$\mathcal{H}_Q = - \sum_i A_i \vec{I}_i \cdot \vec{\nabla}_i \cdot \vec{I}_i \quad (2.10)$$

with:

$$A_i = \frac{eQ_i}{2I(2I-1)\hbar} \quad (2.11)$$

The constant e is the fundamental electron charge, Q_i the quadrupolar moment, and $\vec{\nabla}_i$ the electric field gradient tensor at the nucleus.

Quadrupolar and dipolar couplings are the dominant interactions in solids, with dipolar energies for ^1H nuclei ranging from 1 to 10^2 kHz. The quadrupolar and dipolar interaction tensors are traceless and symmetric. Consequently, these interaction tensors have a time average of zero in the presence of rapid, isotropic molecular reorientations, as occur in most liquids.

iii. Scalar couplings

Perturbation of electron orbitals by the positive charge of the nucleus gives rise to an indirect interaction between nuclei called the scalar or J coupling. A Hamiltonian of the form in equation (2.12)

describes this interaction:

$$\mathcal{H}_J = \sum_{i \neq j} \vec{I}_i \cdot \vec{J}_{ij} \cdot \vec{I}_j \quad (2.12)$$

$\vec{J}_{ij}$ is the J coupling tensor. The magnitude of this coupling is small, usually less than 100 Hz for protons.

III. MOTION IN QUANTUM MECHANICS

A. Solution of Schrödinger's equation

The time dependence of wave functions in quantum mechanics is determined by Schrödinger's equation:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \mathcal{H}(t) |\psi(t)\rangle \quad (2.13)$$

When the Hamiltonian $\mathcal{H}(t)$ is time independent, this first order differential equation is readily integrated:

$$|\psi(\tau)\rangle = U(\tau) |\psi(t=0)\rangle \quad (2.14)$$

where:

$$U(\tau) = 1 + \sum_{j=1}^{\infty} \left(\frac{-i\hbar\tau}{\hbar} \right)^j \quad (2.15)$$

$$= e^{-i\hbar\tau/\hbar} \quad (2.16)$$

Equation (2.16) defines the operator known as the time development operator or propagator. An important property of this

operator which immediately derives from this definition and the Hermiticity of $\mathcal{H}$ is that $U(r)$ is unitary. Its inverse is therefore the transpose of its complex conjugate, and is denoted by the expression:

$$U^\dagger(r) = e^{i\mathcal{H}r/\hbar} \quad (2.17)$$

If the Hamiltonian is time dependent but piecewise constant, Schrödinger's equation must be repeatedly integrated for each interval to solve for $|\psi(t)\rangle$. This procedure modifies the propagator in the following way. Let $\mathcal{H}_1$ be the Hamiltonian during the first interval t_1 , $\mathcal{H}_2$ the Hamiltonian during the second interval, and $\mathcal{H}_i$ the Hamiltonian during the i th interval t_i . By equation (2.14) above, $|\psi(0)\rangle$ after the first interval has evolved to the state:

$$|\psi(t)\rangle = e^{-i\mathcal{H}_1 t_1/\hbar} |\psi(0)\rangle \quad (2.18)$$

After the second interval, the state becomes:

$$|\psi(t_1+t_2)\rangle = e^{-i\mathcal{H}_2 t_2/\hbar} |\psi(t_1)\rangle \quad (2.19)$$

$$= e^{-i\mathcal{H}_2 t_2/\hbar} e^{-i\mathcal{H}_1 t_1/\hbar} |\psi(0)\rangle \quad (2.20)$$

and after the M th interval:

$$\begin{aligned} |\psi(t_1+t_2+\dots+t_{M-1}+t_M)\rangle &= e^{-i\mathcal{H}_M t_M/\hbar} e^{-i\mathcal{H}_{M-1} t_{M-1}/\hbar} \times \dots \\ &\dots \times e^{-i\mathcal{H}_2 t_2/\hbar} e^{-i\mathcal{H}_1 t_1/\hbar} |\psi(0)\rangle \end{aligned} \quad (2.21)$$

The propagator and its inverse for this time dependent Hamiltonian are:

$$U(t) = e^{-i\mathcal{H}_M t_M/\hbar} e^{-i\mathcal{H}_{M-1} t_{M-1}/\hbar} \times \dots \times e^{-i\mathcal{H}_2 t_2/\hbar} e^{-i\mathcal{H}_1 t_1/\hbar} \quad (2.22)$$

$$U^\dagger(t) = e^{i\mathcal{H}_1 t_1/\hbar} e^{i\mathcal{H}_2 t_2/\hbar} \times \dots \times e^{i\mathcal{H}_{M-1} t_{M-1}/\hbar} e^{i\mathcal{H}_M t_M/\hbar} \quad (2.23)$$

$$t = \sum_{j=1}^M t_j \quad (2.24)$$

It is perhaps obvious, but important enough to mention anyway, that the product of exponentials on the right side of equations (2.22) and (2.23) cannot, in general, be reduced to single exponentials by simply summing the arguments of each of the terms on the right and exponentiating. This is evident from considering the definition of $U(t)$ in equation (2.16). Since $\mathcal{H}(t)$ may not commute with itself at all times, the usual product rules for combining exponentials cannot be assumed when the arguments contain linear operators instead of c-numbers. To perform the reduction to a single exponential, the multiplication of propagators in equations (2.22) and (2.23) must either be carried out explicitly, which is rarely possible, or some sort of clever approximation must be attempted. The latter route is discussed in the next chapter.

The extension to Hamiltonians which vary continuously in time can be made by considering the limit in which the intervals t_j in equation (2.24) above go to zero. The propagator for this case can be written symbolically as a single exponential:

$$U(t) = \mathcal{T}_+ \exp \left\{ -\frac{i}{\hbar} \int_0^t \mathcal{H}(t') dt' \right\} \quad (2.25)$$

$\mathcal{T}_+$ here denotes the Dyson time ordering operator,⁴⁸ and is included as a reminder that, because $\mathcal{H}(t)$ may not commute with itself at all times, $U(t)$ actually represents a product of time development operators for infinitesimal time intervals ordered from right to left in the direction of increasing time. The corresponding inverse operator will be denoted:

$$U^\dagger(t) = \mathcal{T}_- \exp \left\{ \frac{i}{\hbar} \int_0^t \mathcal{H}(t') dt' \right\} \quad (2.26)$$

$\mathcal{T}_-$ is a Dyson reversed time ordering operator, ordering operators in the opposite sense as $\mathcal{T}_+$, i.e., from left to right in the order of increasing time.

In this treatment the dynamical behaviour has been explicitly assigned to the wave function. This way of viewing time dependence in quantum mechanics is referred to as a Schrödinger picture. The choice of regarding motion as a property of the state vector of the system is not unique, however, and it is equally valid to assign the time dependence to the operators instead. This alternative view of motion is referred to as a Heisenberg picture. The usual convention in NMR is to adopt the Schrödinger picture. The work in this thesis will at all times conform to this convention.

B. Rotations and time development operators in NMR

The motion of nuclear spin systems can sometimes be interpreted as a series of rotations performed on a nuclear spin coordinate space. The reasoning behind this assertion, the conditions under which it is true, and some of the consequences which follow are the primary topics of this section.

An ordinary, counterclockwise rotation of a real, three dimensional vector $\vec{r}$ through an angle α about the normalized axis $\hat{n} = (\cos\phi\sin\theta, \sin\phi\sin\theta, \cos\theta)$ (where θ and ϕ are the usual polar and azimuthal angle of a spherical polar coordinate system), results in a linear transformation of $\vec{r}$ which can be symbolically written:

$$\vec{r}' = R(\alpha)\vec{r} \quad (2.27)$$

An explicit expression for $R(\alpha)$ in the Cartesian basis (x,y,z) appears on the next page as equation (2.28). From this matrix, the following results can be deduced:

$$\cos\alpha = \frac{1}{2} \left[\text{Tr}\{R(\alpha)\} - 1 \right] \quad (2.29)$$

$$n_x = \frac{R_{zy} - R_{yz}}{2\sin\alpha} \quad (2.30)$$

$$n_y = \frac{R_{xz} - R_{zx}}{2\sin\alpha} \quad (2.31)$$

$$n_z = \frac{R_{yx} - R_{xy}}{2\sin\alpha} \quad (2.32)$$

The resemblance of rotations in a Cartesian space to certain mathematical transformations occurring in the quantum theory of angular

$$R(a) =$$

$$\begin{pmatrix} \sin^2\theta\cos^2\phi + \cos a \left\{ \cos^2\theta\cos^2\phi + \sin^2\phi \right\} & -\sin a\cos\theta + \sin^2\theta\cos\phi\sin\phi(1-\cos a) & \cos\theta\sin\theta\cos\phi(1-\cos a) + \sin a\sin\theta\sin\phi \\ \sin a\cos\theta + \sin^2\theta\cos\phi\sin\phi(1-\cos a) & \sin^2\theta\sin^2\phi + \cos a \left\{ \cos^2\theta\sin^2\phi + \cos^2\phi \right\} & \cos\theta\sin\theta\sin\phi(1-\cos a) - \sin a\sin\theta\cos\phi \\ -\sin a\sin\theta\sin\phi + \cos\theta\sin\theta\cos\phi(1-\cos a) & \sin a\sin\theta\cos\phi + \cos\theta\sin\theta\sin\phi(1-\cos a) & \cos^2\theta + \cos a\sin^2\theta \end{pmatrix}$$

$$= \begin{pmatrix} R_{xx} & R_{xy} & R_{xz} \\ R_{yx} & R_{yy} & R_{yz} \\ R_{zx} & R_{zy} & R_{zz} \end{pmatrix} \quad (2.28)$$

momentum can be discerned in the following way. As a consequence of the spin angular momentum operator commutation relations:⁴⁹⁻⁵²

$$[I_x, I_y] = iI_z \quad (2.33)$$

$$[I_y, I_z] = iI_x \quad (2.34)$$

$$[I_z, I_x] = iI_y \quad (2.35)$$

it follows that the unitary operator defined by the equation:

$$\mathcal{R}(\alpha) = e^{-i\alpha \cdot \vec{I}} \quad (2.36)$$

if applied to the vector operator:

$$\mathbf{A} = \vec{a} \cdot \vec{I} \quad (2.37)$$

$$= a_x I_x + a_y I_y + a_z I_z \quad (2.38)$$

results in a linear transformation of $\mathbf{A}$ equivalent to the rotation of $\vec{a}$ above, namely:

$$\mathcal{R}(\alpha) \mathbf{A} \mathcal{R}^\dagger(\alpha) = [\mathcal{R}(\alpha) \vec{a}] \cdot \vec{I} \quad (2.39)$$

$$\begin{aligned} &= \left(R_{xx} a_x + R_{xy} a_y + R_{xz} a_z \right) I_x \\ &+ \left(R_{yx} a_x + R_{yy} a_y + R_{yz} a_z \right) I_y \\ &+ \left(R_{zx} a_x + R_{zy} a_y + R_{zz} a_z \right) I_z \end{aligned} \quad (2.40)$$

Due to the fundamental similarity of this expression to equation (2.27), the unitary transformation specified by $\mathcal{R}(\alpha)$ is referred to as a rotation on spin space. Rotation operators acting on spin degrees of

freedom will be represented as $\mathcal{R}$, while rotation operators acting on Cartesian coordinates will be written R .

The NMR propagator for a nuclear spin system assumes the form of a rotation operator $\mathcal{R}(\alpha)$ if the Hamiltonian of the spin system is linear in the spin operators I_x , I_y , and I_z . This fact is revealed by writing the Hamiltonian as below, substituting into equation (2.16), and comparing with equation (2.36):

$$\mathcal{H} = \omega \hat{n} \cdot \vec{I} \quad (2.41)$$

The propagator defined by this Hamiltonian specifies a rotation in spin angular momentum Hilbert space about the axis $\hat{n}$ through the angle ωt . The group property of rotations⁴⁹ ensures the truth of this assertion even if $\mathcal{H}$ in equation (2.41) is time dependent.

Hamiltonians linear in the operators I_x , I_y , and I_z occur naturally in NMR if bilinear couplings to other spins and local electric field gradients are absent. Spin systems lacking such couplings are rare and, for the most part, uninteresting. It is frequently not a bad approximation in the NMR of liquids, however, to assume that the Hamiltonian during intense rf pulses is linear if spin-field interactions are large compared to spin-spin and spin-lattice couplings. This assumption is obviously less well justified in solids, where internal couplings are larger than in liquids, but is often made nevertheless.^{2,4}

The equivalence of a nuclear spin propagator $U(t)$ to a real, three dimensional rotation $R(\alpha)$ holds only if the Hamiltonian defining $U(t)$ is linear in I_x , I_y , and I_z . The propagator for a Hamiltonian which contains bilinear terms represents a more complex unitary

transformation of nuclear spin coordinates. Except in special cases where arguments based on symmetry can be made, calculations of the dynamical behaviour of a coupled spin network can only be performed numerically, and only after assuming a specific configuration of spins and coupling constants. Some examples of numerical simulations done on a computer are presented in Chapter Four.

C. Representations of the rotation group

The set of basis operators (I_x, I_y, I_z) and the unitary transformation defined by equation (2.36) together comprise an irreducible representation of the full rotation group.^{49,51} The adjective "irreducible" indicates that this representation cannot be decomposed into representations of lower dimensionality by a similarity transformation.

Irreducible representations of the rotation group of dimension both less than and greater than three exist. The $(2\ell+1)$ operators, where $\ell = 0, 1/2, 1, 3/2, \dots$, satisfying the commutation relations:

$$[I_{\pm}, T_{\ell m}] = [\ell(\ell+1) - m(m+1)]^{1/2} T_{\ell m \pm 1} \quad (2.42)$$

$$[I_z, T_{\ell m}] = m T_{\ell m} \quad (2.43)$$

comprise, for instance, a complete, orthonormal basis set for a $(2\ell+1)$ -dimensional irreducible representation of the full rotation group.⁵¹ The raising and lowering operators $I_{\pm}$ in (2.42) are defined by the equation:

$$I_{\pm} = I_x \pm iI_y \quad (2.44)$$

The basis operators, written as $T_{\ell m}$ above, are referred to as irreducible spherical tensor operators of rank ℓ . The subscript m is a label identifying the operator within the basis, and by convention lies within the range $-\ell \leq m \leq \ell$.

Irreducible spherical tensor operators of rank ℓ transform among themselves under the rotation operator $R(\beta)$ according to the relation:

$$R(\beta) T_{\ell m} R^\dagger(\beta) = \sum_{p=-\ell}^{\ell} T_{\ell p} D_{pm}^{(\ell)}(\beta) \quad (2.45)$$

$D_{pm}^{(\ell)}(\beta)$ is the (p,m) element of the $(2\ell+1)$ dimensional Wigner rotation matrix. Usually, a rotation about an arbitrary axis is represented by a product of three Wigner rotation matrices, each corresponding to a rotation about one of the three Euler angles. For brevity, this arbitrary rotation has been condensed in equation (2.45) into a single generalized Wigner matrix $D^{(\ell)}(\beta)$. The difference is merely one of notation.

All of the NMR Hamiltonians introduced earlier can be decomposed into linear combinations of $T_{\ell m}$ operators with $\ell \leq 2$. Tensor operators with $\ell = 0$ transform under rotations as scalars, and therefore constitute a rather trivial and uninformative representation of the rotation group.

The three dimensional operator basis with $\ell = 1$, $\{T_{1+1}, T_{1-1}, T_{10}\}$, is related to the basis set discussed earlier, viz., $\{I_x, I_y, I_z\}$, by a unitary transformation. Although useful for simplifying computations in many physical problems, especially if there is an axis of energy quantization, the $\{T_{1+1}, T_{1-1}, T_{10}\}$ basis does not provide the same

appealing, accessible geometric picture of the rotation group that the $\{I_x, I_y, I_z\}$ basis affords. Calculations in this dissertation involving rotations in a three dimensional spin operator space will therefore always be performed in the basis of $\{I_x, I_y, I_z\}$.

Terms in the NMR Hamiltonian which transform under rotations as T_{2m} operators appear in the dipolar and quadrupolar Hamiltonians. The T_{2m} operators span a five dimensional representation of the rotation group for which there is no convenient geometric picture. In future calculations, rotations will frequently be performed on these operators about axes lying in the xy plane. Writing such an axis as:

$$\hat{n} = (\cos\phi, \sin\phi, 0) \quad (2.46)$$

and the angle of rotation as β , an explicit form for the Wigner rotation matrix $D^{(2)}(\beta)$, where $\beta = \beta\hat{n}$, can be derived. This matrix, written in the $(T_{22}, T_{21}, T_{20}, T_{2-1}, T_{2-2})$ basis, appears on the next page as equation (2.47). The phase convention of reference 52 is assumed for this matrix.

IV. QUANTUM STATISTICAL DESCRIPTION OF AN NMR EXPERIMENT

A. Definition and properties of the density operator³⁶

After sufficient time in a large magnetic field, bulk matter samples can develop a measurable magnetic dipole moment aligned with the field and proportional to the size of the field in accordance with Curie's Law. This macroscopic moment is commonly called magnetic polarization, or simply magnetization. At the microscopic level, this polarizing effect of the field can be explained quantum mechanically as a manifestation of the splitting in energy of the nuclear spin Zeeman

$$D^{(2)}(\beta) =$$

$$\begin{array}{c}
 \begin{array}{ccccc}
 |2\rangle & |1\rangle & |0\rangle & |-1\rangle & |-2\rangle
 \end{array} \\
 \begin{array}{l}
 \langle 2| \\
 \langle 1| \\
 \langle 0| \\
 \langle -1| \\
 \langle -2|
 \end{array}
 \left[\begin{array}{ccccc}
 \frac{1}{4}(1+\cos\beta)^2 & -\frac{1}{2}e^{-1\phi}\sin\beta(1+\cos\beta) & -\sqrt{\frac{3}{8}}e^{-2\phi}\sin^2\beta & \frac{1}{2}e^{-3\phi}\sin\beta(1-\cos\beta) & \frac{1}{4}e^{-4\phi}(1-\cos\beta)^2 \\
 -\frac{1}{2}e^{1\phi}\sin\beta(1+\cos\beta) & \cos^2\beta - \frac{1}{2}(1-\cos\beta) & -1\sqrt{\frac{3}{8}}e^{-1\phi}\sin 2\beta & e^{2\phi}\left[\cos^2\beta - \frac{1}{2}(1+\cos\beta)\right] & \frac{1}{2}e^{3\phi}\sin\beta(1-\cos\beta) \\
 -\sqrt{\frac{3}{8}}e^{2\phi}\sin^2\beta & -1\sqrt{\frac{3}{8}}e^{1\phi}\sin 2\beta & \frac{1}{2}(3\cos^2\beta-1) & 1\sqrt{\frac{3}{8}}e^{-1\phi}\sin 2\beta & -\sqrt{\frac{3}{8}}e^{-2\phi}\sin^2\beta \\
 \frac{1}{2}e^{3\phi}\sin\beta(1-\cos\beta) & e^{2\phi}\left[\cos^2\beta - \frac{1}{2}(1+\cos\beta)\right] & -1\sqrt{\frac{3}{8}}e^{1\phi}\sin 2\beta & \cos^2\beta - \frac{1}{2}(1-\cos\beta) & -\frac{1}{2}e^{-1\phi}\sin\beta(1+\cos\beta) \\
 \frac{1}{4}e^{4\phi}(1-\cos\beta)^2 & \frac{1}{2}e^{3\phi}\sin\beta(1-\cos\beta) & -\sqrt{\frac{3}{8}}e^{2\phi}\sin^2\beta & -\frac{1}{2}e^{1\phi}\sin\beta(1+\cos\beta) & \frac{1}{4}(1+\cos\beta)^2
 \end{array} \right]
 \end{array}$$

(2.47)

states of magnetically active nuclei. For N coupled spin I nuclei, the nuclear spin Hilbert space is of dimension $(2I+1)^N$. The splitting of the energy levels makes certain of the Zeeman nuclear spin eigenstates energetically preferred, consistent with constraints imposed by Boltzmann statistics and the maximization of entropy. The occupation probability of a state when the spin system is at equilibrium in the field is determined by the lattice temperature through the Boltzmann law; equilibration of the temperature of the spin system with the temperature of the lattice (which normally has a much greater heat capacity than the spin system) is achieved through various spin lattice relaxation mechanisms.⁴⁷ The time constant of this process is usually designated T_1 .

The signal detected in a magnetic resonance experiment arises when the magnetization is disturbed from its static equilibrium condition. The connection between this macroscopically observable quantity and processes occurring at the nuclear level is provided by quantum statistical methods based on the density operator or density matrix. According to the postulates of quantum mechanics, the state of a single, isolated system, e.g., N coupled spin I nuclei, is completely determined by its wave function $|\psi\rangle$. Because of the wave particle duality of matter, the result of a measurement of some observable $\hat{A}$ performed on this system can only be predicted probabilistically, with a mean or expectation value given by the relation:

$$\langle \hat{H} \rangle = \int \psi^*(\vec{r}) \hat{H} \psi(\vec{r}) d\vec{r} \quad (2.48)$$

$$= \langle \psi | \hat{H} | \psi \rangle \quad (2.49)$$

where the integration is carried out over the relevant phase space.

Most spectroscopic experiments are performed on macroscopic samples rather than single, isolated systems. Detection of a magnetic resonance signal thus corresponds to a measurement performed simultaneously on an ensemble of isolated nuclear spin states $|\psi\rangle$, populated according to some statistical distribution function. It follows, therefore, that to compute the expectation value of the observable $\hat{H}$, it is necessary to average $\langle \hat{H} \rangle$ over all states in the ensemble, weighted according to the probability of the occurrence of $|\psi\rangle$ in the ensemble. This is summarized by the equation:

$$\overline{\langle \hat{H} \rangle} = \sum_{i=1}^M p_i \langle \psi_i | \hat{H} | \psi_i \rangle \quad (2.50)$$

where

$$1 = \sum_i^M p_i \quad (2.51)$$

The summation is carried out over all distinct states $|\psi_i\rangle$ present in the ensemble. If each state $|\psi_i\rangle$ is expanded as a linear superposition in some arbitrary set of basis states $|j\rangle$ as below

$$|\psi_1\rangle = \sum_j^P \langle j|\psi_1\rangle |j\rangle \quad (2.52)$$

$$= \sum_j^P c_j^{(i)} |j\rangle \quad (2.53)$$

and this expansion substituted into equation (2.50) above, the result

$$\overline{\langle \mathcal{H} \rangle} = \sum_i^M \sum_j^P \sum_k^P p_i c_k^{*(i)} c_j^{(i)} \langle k|\mathcal{H}|j\rangle \quad (2.54)$$

is obtained. In the chosen basis, the (j,k) element of the density operator is defined by the relation:

$$\rho_{jk} = \sum_i^M p_i c_j^{(i)} c_k^{*(i)} \quad (2.55)$$

The equivalent operator definition is:

$$\rho = \sum_i^M \sum_j^P \sum_k^P p_i c_j^{(i)} c_k^{*(i)} |k\rangle\langle j| \quad (2.56)$$

The Hermiticity of ρ is apparent from this expression. With this definition, the ensemble averaged expectation value of $\langle \mathcal{H} \rangle$ becomes:

$$\overline{\langle \mathcal{H} \rangle} = \sum_j^P \sum_k^P \rho_{jk} \langle k|\mathcal{H}|j\rangle \quad (2.57)$$

Using the orthonormality of the basis states, this expression can be rewritten:

$$\overline{\langle \hat{H} \rangle} = \sum_j^P \langle j | \rho \hat{H} | j \rangle \quad (2.58)$$

$$= \text{Tr}(\rho \hat{H}) \quad (2.59)$$

which is a quantity independent of the basis. This equation provides the fundamental quantum statistical foundation for relating macroscopic observations to processes occurring at a microscopic level. The relations below are readily obtained from these definitions:

$$\text{Tr}(\rho) = 1 \quad (2.60)$$

$$0 \leq \rho_{jj} \leq 1 \quad (2.61)$$

$$\text{Tr}(\rho^2) \quad (2.62)$$

The first two relations are simple assertions about conservation of probability, while the last inequality is a natural consequence of the two previous statements.

From the Schrödinger equation and the definition of ρ in equation (2.57) above, the equation of motion the density operator is straightforwardly derived:

$$i\hbar \frac{\partial \rho}{\partial t} = [\hat{H}, \rho] \quad (2.63)$$

This equation is known as the Liouville-von Neumann equation, and has as its solution:

$$\rho(t) = U(t)\rho(0)U^\dagger(t) \quad (2.64)$$

where $U(t)$ is the time development operator introduced in section IIIA

of this chapter. A notable difference between the density operator and other quantum mechanical operators revealed by the two prior equations is that the density operator is time dependent in the Schrödinger picture and time independent in the Heisenberg picture, which is the exact opposite of the case for all other quantum mechanical operators.

For a system at thermal equilibrium with a large heat bath at temperature T , the laws of statistical mechanics dictate that the eigenstates of the Hamiltonian will be populated by members of the ensemble according to a Boltzmann distribution. At thermal equilibrium, the density operator can have no off-diagonal elements in the eigenbasis of the Hamiltonian, and so must be of the form:

$$\rho_E = e^{-\mathcal{H}/kT} / \text{Tr}\{e^{-\mathcal{H}/kT}\} \quad (2.65)$$

$$= \frac{e^{-\mathcal{H}/kT}}{Z(t)} \quad (2.66)$$

where the trace in the denominator normalizes the trace of ρ_E . This equation can also be easily arrived at by calculating $\overline{\langle \mathcal{H} \rangle}$ using equation (2.57) in the eigenbasis of the Hamiltonian.

The ratio E/kT for NMR transitions in most magnetic fields and for temperatures above 1 K is normally orders of magnitude smaller than unity. This fact permits the expansion, and truncation after the first order term, of the exponential in (2.66) above, yielding a result known as the high temperature approximation:⁴⁷

$$\rho_E \approx \frac{1}{Z(t)} \left[1 - \frac{\mathcal{H}_{\text{NMR}}}{kT} \right] \quad (2.67)$$

Since the term proportional to the identity in the truncated expansion

commutes with all operators, it cannot evolve in time, and hence provides no useful information in a spectroscopic experiment. For this reason, it is usual to work with the traceless operator known as the reduced density matrix, or:

$$\rho_{E,R} = - \frac{1}{Z(\tau)} \frac{\mathcal{H}_{NMR}}{kT} \quad (2.68)$$

The adjective "reduced" will from now on be assumed in all references to the density matrix.

If large quadrupolar couplings and low fields are ignored, the dominant term in $\mathcal{H}_{NMR}$ is the static Zeeman term corresponding to the interaction of the spins with the magnetic field. Because this term is proportional to I_z , the reduced density matrix is well approximated by:

$$\rho_{E,R} \approx I_z / \text{Tr}(I_z^2) \quad (2.69)$$

An important consequence of the proportionality of $\rho_{E,R}$ to I_z is that $\rho_{E,R}$ is unaltered by transformation into the rotating frame. That is, $\rho_{E,R}$ is the same in both the fixed laboratory frame and in the rotating frame. This point is examined in the next chapter on the interaction representation.

B. Relation to an NMR measurement⁴⁷

If properly excited, nuclear spin magnetization disturbed from equilibrium will begin to oscillate coherently in time at frequencies characteristic of the effective Hamiltonian. These oscillations are detected by a conventional NMR probe as the emf induced in a tuned coil

operating according to Faraday's Law. Despite the wide variety of coil geometries employed in NMR, virtually all are assumed to transmit and detect oscillating magnetic dipole radiation exclusively. In the usual configuration, the probe coil is oriented with the long axis of the coil lying in the plane perpendicular to the direction of the static field. By Faraday's Law, and because of the uniaxial geometry of most NMR pickup coils, only linearly polarized magnetic dipole radiation oscillating in this plane can thus be detected. The induced emf measured in this way will be proportional to the instantaneous size of the dipole moment.

The bulk dipole moment in this plane arising from nuclear spin polarization is calculable as the ensemble-averaged expectation value of the spin angular momentum operator I_x . Using the density matrix, this quantity is proportional to the expression:

$$\overline{\langle I_x(t) \rangle} = \text{Tr}(I_x \rho(t)) \propto U(t) \quad (2.70)$$

where $U(t)$ is the induced emf.

A characteristic of NMR spectroscopy which makes this calculation possible, and, indeed, makes the whole density matrix formalism so well suited to NMR, is the disparate relationship between the size of the sample and the coil compared to the wavelength of radiofrequency radiation. Radiation with the relatively large NMR frequency of 360 MHz has a wavelength of approximately 83 cm, greatly exceeding the dimensions of a typical NMR sample. To a good approximation, then, the rf has the same phase at all points in the sample. This, in turn, permits the assumption that the rf Hamiltonian is identical for all

spins (ignoring for the moment magnetic susceptibilities and rf field inhomogeneities). While couplings to other spins, for example, may vary from one location in the sample to the next, all spins nevertheless have the rf term in common. Although it is rarely acknowledged, the work presented throughout this thesis and elsewhere implicitly rely on this crucial assumption about the phase uniformity of the rf interaction.

C. Final comments on the density operator

The matrix elements of ρ have a convenient physical interpretation important in the understanding of many phenomena observed in coherent spectroscopic experiments. The diagonal elements of ρ can be determined from equation (2.55) by letting $j = k$:

$$\rho_{jj} = \sum_{i=1}^M P_i |c_j^{(i)}|^2 \quad (2.71)$$

Assuming the basis states $|j\rangle$ are the eigenvectors of the observable $\mathcal{H}$, ρ_{jj} is simply the probability that a measurement of $\mathcal{H}$ performed on a member of the ensemble yields the eigenvalue $\mathcal{H}_{jj}$. That is, ρ_{jj} is an occupation probability of the eigenstate $|j\rangle$. For this reason, the diagonal elements ρ_{jj} can be considered as populations of the eigenstates $|j\rangle$.

The off-diagonal elements of ρ have a slightly more complicated interpretation. These elements reveal statistical correlations between eigenstates of $\mathcal{H}$, meaning, for example, that if ρ_{ij} , $i \neq j$, is nonzero, then the probability of finding a particle in one eigenstate $|j\rangle$ is dependent on the probability of finding the particle in the other

eigenstate $|i\rangle$, and vice versa. Cross-correlations between eigenstates such as this are given the name coherences.

As defined, both coherence and populations are wholly statistical properties of the ensemble. It is meaningful to ascribe such properties, therefore, only to the bulk, macroscopic sample, and only given a specified set of basis states.

CHAPTER THREE: INTERACTION PICTURES IN NMR

I. PURPOSE OF THE CHAPTER

A short account of the semiclassical theory of the interaction of light with matter, with a particular emphasis on its applications to pulsed NMR, is the main topic of the current chapter. The adjective "semiclassical" is used to describe this theory to signify that, in the following development, matter will be regarded as behaving quantum mechanically, while the radiation field will be regarded as behaving classically, i.e., as obeying Maxwell's equations. For intense fields, as typically encountered in NMR experiments, this approximation is well justified, and enables the complications arising from second quantization of the field to be conveniently avoided.⁵³

As with the previous chapter, authoritative treatments of the formalisms presented in this chapter exist in other texts.^{47,54} The rationale for summarizing these other sources is twofold. The first reason is to concisely identify and introduce problems arising in the semiclassical theory of light-matter interactions. In so doing, mathematical notation and conventions will be established for later chapters. Much of the notation, terminology, and early applications for the work in this area originated in research in NMR. However, these problems and their solutions are not unique to NMR, and it should be realized that many of the methods discussed here are of greater generality.

A second reason for including this chapter is to direct attention

to some of the approximation methods developed to handle time-dependent problems in quantum mechanics, particularly for cases where the source of the time dependence is an interaction with coherent, resonant radiation. A detailed discussion is given of variations specifically conceived to address bandwidth excitation problems in coherent spectroscopy. It has been known since Bloch's original work⁵⁵ that the exact dynamics of systems coupled to an intense, coherent, resonant field is relatively simple to picture physically, and model mathematically. The real complications appear when imperfections and nonidealities in the field, and couplings to other degrees of freedom are considered in the motion of the system. One of the principal objectives of the following discussion is to describe some of the ways of including these effects in calculations of the dynamical behaviour of a spin system coupled to a coherent rf field, with the ultimate aim of developing pulsed NMR experiments capable of producing unusual bandwidth responses.

II. INTERACTION PICTURE

A. Motivation

The integration of quantum mechanical equations of motions for cases where the Hamiltonian varies with time is the focal point of this chapter. As in classical mechanics, the difficulty of performing this task depends considerably upon the choice of the reference frame. The significance of this choice lies in the fact that transformation to different frames of references, perhaps one moving with the particles or the field, can modify the equations of motion, sometimes in ways which make them simpler to solve. If the mathematical transformation

from the original frame to the simpler frame is known, then integration of the equations of motion in the simpler frame, optionally followed by transformation back into the original frame, frequently provides the most direct and physically intuitive method for handling time dependent problems in quantum mechanics. Selecting frames of reference with tractable equations of motion forms the crux of the approach adopted throughout this dissertation.

The size and exact form of the time dependent terms play a critical role in deciding the necessity for a change of reference frame. When a time dependent term oscillates at a frequency resonant with a transition between energy levels, for example, it is clear that it cannot be ignored regardless of its size. On the other hand, it is often possible to discard large terms provided they oscillate at frequencies much greater than any transition frequencies. Both of these factors enter into the NMR picture known as the rotating frame and will be examined presently.

Through Schrödinger's equation, equation (2.13), and its generalization to ensembles of states, the Liouville-von Neumann equation, equation (2.63), the Hamiltonian operator plays a central role in determining time dependence in quantum mechanics. If the Hamiltonian is stationary, energy is conserved at all times, and integration of the quantum mechanical equations of motion becomes, in principle, a fairly straightforward procedure (cf. equation (2.16)). When the Hamiltonian does depend on time, however, the solution of these equations is usually not so easy.

An immediately obvious and common approach to this problem is to find a reference frame in which energy is conserved, or approximately

conserved, i.e., one in which the Hamiltonian appears stationary. A reference frame of great usefulness and generality known as the interaction picture often fulfills this criterion. Even though a static frame may not be readily apparent, it sometimes suffices in a dynamics calculation to substitute an appropriate stationary Hamiltonian for the original time dependent Hamiltonian. This method can be justified in certain special cases where a stationary Hamiltonian can be shown to produce approximately the same net effect as a time dependent Hamiltonian after a specified time, or set of times, τ , even if in the intervening time the motion of the system may have followed widely different trajectories under the two Hamiltonians. This kind of "stroboscopic" approximation of a time dependent Hamiltonian forms the basis for the perturbation approach known as coherent averaging theory. This topic will be discussed at length further on.

B. Transformations to different frames of reference: Formalism

A change of reference frames for a system with the wave function $|\psi(t)\rangle$ is accomplished mathematically by transforming $|\psi(t)\rangle$ as below:³⁷

$$|\lambda(t)\rangle = U_T^\dagger(t) |\psi(t)\rangle \quad (3.1)$$

The wave function in the new frame is designated here as $|\lambda(t)\rangle$. The transformation operator $U_T^\dagger(t)$ is unitary, insuring, first, the existence of an inverse for $U_T^\dagger(t)$, namely $U_T(t)$, and, second, that the norm of $|\psi(t)\rangle$ is conserved by the transformation. The corresponding

transformation in bra notation is:

$$\langle \lambda(t) | = \langle \psi(t) | U_T(t) \quad (3.2)$$

The Hamiltonian in this new frame will be designated $\mathcal{H}_R(t)$.

Schrödinger's equation can be used to determine this Hamiltonian by differentiating $|\lambda(t)\rangle$ with respect to time:

$$\mathcal{H}_R(t) |\lambda(t)\rangle = i\hbar \frac{\partial}{\partial t} |\lambda(t)\rangle \quad (3.3)$$

$$= i\hbar \left[\frac{\partial U_T^\dagger(t)}{\partial t} |\psi(t)\rangle + U_T^\dagger(t) \frac{\partial}{\partial t} |\psi(t)\rangle \right] \quad (3.4)$$

Writing the Hamiltonian in the original frame as $\mathcal{H}(t)$ and substituting into the second term in the lower expression above, the equality

$$\mathcal{H}_R(t) |\lambda(t)\rangle = i\hbar \frac{\partial U_T^\dagger(t)}{\partial t} |\psi(t)\rangle + U_T^\dagger(t) \mathcal{H}(t) |\psi(t)\rangle \quad (3.5)$$

follows. Replacing $|\psi(t)\rangle$ in equation (3.5) with the expression:

$$|\psi(t)\rangle = U_T(t) |\lambda(t)\rangle \quad (3.6)$$

the result below derives:

$$\mathcal{H}_R(t) |\lambda(t)\rangle = \left[i\hbar \frac{\partial U_T^\dagger(t)}{\partial t} U_T(t) + U_T^\dagger(t) \mathcal{H}(t) U_T(t) \right] |\lambda(t)\rangle \quad (3.7)$$

Getting rid of $|\lambda(t)\rangle$ on both sides of (3.7), the Hamiltonian $\mathcal{H}_R(t)$ in the new reference frame is related to the Hamiltonian $\mathcal{H}(t)$ of the old reference frame by the equality:

$$\mathcal{H}_R(t) = i\hbar \frac{\partial U_T^\dagger(t)}{\partial t} U_T(t) + U_T^\dagger(t) \mathcal{H}(t) U_T(t) \quad (3.8)$$

Since $|\lambda(t)\rangle$ and $|\psi(t)\rangle$ coincide at $t = 0$, then by equation (3.1), the time development operators of the two frames are related by:

$$U(t) = U_T(t) U_R(t) \quad (3.9)$$

where $U(t)$ represents the time development operator in the original frame, and $U_R(t)$ is the corresponding operator in the new frame. A symbolic expression for $U_R(t)$ may be obtained by integrating equation (3.3) as prescribed in section 2.III.A.

A result of great importance and utility can be deduced from equation (3.8) by dividing $\mathcal{H}(t)$ into two parts:

$$\mathcal{H}(t) = \mathcal{H}_0(t) + \mathcal{H}_1(t) \quad (3.10)$$

If $U_T(t)$ is defined as the time development operator for the Hamiltonian $\mathcal{H}_0(t)$ only, as below:

$$U_T(t) = \mathcal{I}_+ \exp \left\{ -\frac{i}{\hbar} \int_0^t \mathcal{H}_0(t') dt' \right\} \quad (3.11)$$

and this operator used in equation (3.8), the following expression derives:

$$\mathcal{H}_R(t) = U_T^\dagger(t) \mathcal{H}_1(t) U_T(t) \quad (3.12)$$

By equations (2.25) and (3.12), $U_R(t)$ can be evaluated:

$$U_R(t) = \mathcal{T}_+ \exp \left\{ -\frac{i}{\hbar} \int_0^t \mathcal{H}_R(t') dt' \right\} \quad (3.13)$$

Equation reveals that in the reference frame defined by the operator $U_T(t)$ in equation (3.11), $\mathcal{H}_0(t)$ appears to have vanished from the total Hamiltonian. Its only effect in the new interaction picture is to modulate $\mathcal{H}_1(t)$ in accordance with equation (3.12). If $\mathcal{H}_0(t)$ represents some large, uninformative interaction, a transformation of the form in equation (3.11) serves to selectively excise this term from the Hamiltonian in the new reference frame. Although this transformation imparts an additional time dependence on the remaining, presumptively small, term $\mathcal{H}_1(t)$, this difficulty can often be circumvented with an appropriate approximation. A well known example, viz., the interaction picture known in NMR as the rotating frame, will help clarify this point.

C. Rotating frame transformation

If slow motions of the nuclei are ignored, the time dependence of the normal NMR Hamiltonian in the fixed laboratory frame arises entirely from the Zeeman coupling of the nuclei to the oscillating magnetic field of the rf radiation. This is explicitly indicated by writing the NMR Hamiltonian from Chapter Two as:

$$\begin{aligned} \mathcal{H}_{\text{NMR},L}(t) = & \omega_0 I_z + \omega_1(t) \left[I_x \cos[\omega t + \phi(t)] \right. \\ & \left. + I_y \sin[\omega t + \phi(t)] \right] + \mathcal{V}_L \end{aligned} \quad (3.14)$$

The subscript "L" stands for laboratory frame. As is usual, the counter-rotating, non-resonant component of the linearly polarized rf field has been neglected.^{3,47} The static Zeeman term $\omega_0 I_z$ has been written separately to emphasize that it is by far the dominant term in this Hamiltonian. Although the amplitude ω_1 and the phase ϕ of the rf are expressed as functions of time, in most cases, and in all the cases discussed in this thesis, these functions are either piecewise constant or otherwise slowly varying functions of time. All other terms are grouped in V_L .

Because of how the spin angular momentum operators transform under rotations, the time dependence of these terms is largely removed in the frame defined by the change of reference operator:

$$U_T(t) = e^{-i\omega I_z t} \quad (3.15)$$

where it is assumed $\omega \approx \omega_0$. Substituting this operator and $\mathcal{H}_{\text{NMR},L}(t)$ for $\mathcal{H}(t)$ in equation (3.8), and converting energies to angular frequencies, the Hamiltonian in the new frame is:

$$\begin{aligned} \mathcal{H}_{\text{NMR},R}(t) = & (\omega_0 - \omega) I_z \\ & + \omega_1(t) \left[I_x \cos\phi(t) + I_y \sin\phi(t) \right] \\ & + U_T^\dagger(t) V_L U_T(t) \end{aligned} \quad (3.16)$$

The subscript "R" distinguishes operators in the rotating frame from operators in the laboratory frame. Besides the slowly varying functions $\phi(t)$ and $\omega_1(t)$, only one set of terms remains time dependent

in this frame. These are due to components of V_I , which do not commute with $U_T(t)$, or, more accurately, I_z . The non-commuting terms oscillate at harmonics of the frequency ω , and are called non-secular, while the commuting terms are static, and are called secular. In this new frame, these frequencies are far from resonance, hence any terms in V_L which do not commute with I_z can be neglected. The secular counterparts of laboratory frame NMR interaction Hamiltonians are shown in table 3.1. The defining property of these terms, namely, that they commute with I_z , implies, by equation (2.43), that they can all be written as linear combinations of irreducible spherical tensor operators of the form T_{l0} . The remaining oscillatory terms transform under rotations as linear combinations of T_{lm} tensor operators, with $m \neq 0$. Retention of only terms which commute with I_z can be rationalized using a standard first order perturbation theory argument as well.

If the rf frequency is nearly resonant with spin transitions, transformation into this new frame simplifies the NMR Hamiltonian in three significant ways. First, as has been mentioned, the oscillatory time dependence of the rf Zeeman interaction disappears, to a very good approximation, leaving the desired static Hamiltonian. Terms oscillating in the laboratory frame at frequencies close to ω_0 cannot be ignored no matter how small, because in this frame this frequency is close to the nuclear spin transition frequencies. It is permissible to neglect terms oscillating at this frequency in the rotating frame, however, since transition frequencies of the Hamiltonian $\mathcal{H}_{\text{NMR},R}(t)$ in this new frame are no longer centered around ω_0 . This approximation is an excellent one so long as ω is much greater than the magnitude of the eigenvalues of V_L . With few exceptions, ω is in fact greater by two

Table 3.1: Rotating frame Hamiltonians

Radiofrequency Zeeman Hamiltonian:

$$\mathcal{H}_{\text{rf}}(t) = \omega_1^0(t) \left[I_x \cos\phi(t) + I_y \sin\phi(t) \right]$$

Radiofrequency inhomogeneity Hamiltonian:

$$\begin{aligned} \mathcal{H}_{\text{in}}(t) &= \epsilon \mathcal{H}_{\text{rf}}(t) & \epsilon \omega_1^0(t) &= \Delta\omega_1(t) \\ & & &= \Delta\omega_1(t) \left[I_x \cos\phi(t) + I_y \sin\phi(t) \right] \end{aligned}$$

Chemical shift Hamiltonian:

$$\mathcal{H}_{\text{cs}} = \sum_i \delta_i I_{zi}$$

Resonance offset Hamiltonian:

$$\mathcal{H}_{\text{off}} = (\omega - \omega_0) I_z + \mathcal{H}_{\text{cs}}$$

Homonuclear dipolar interaction Hamiltonian:

$$\begin{aligned} \mathcal{H}_{\text{D}} &= \sum_i \sum_{i>j} \omega_{\text{D},ij} \left[3I_{zi} I_{zj} - \vec{I}_i \cdot \vec{I}_j \right] \\ \omega_{\text{D},ij} &= \frac{\gamma^2 \hbar}{2r_{ij}^3} \left(1 - 3\cos^2\theta_{ij} \right) \end{aligned}$$

Heteronuclear dipolar interaction Hamiltonian:

$$\begin{aligned} \mathcal{H}_{\text{D}}^{\text{het}} &= \sum_i \sum_j \omega_{\text{D},ij} I_{zi} S_{zj} \\ \omega_{\text{D},ij} &= \frac{\gamma_I \gamma_S \hbar}{r_{ij}^3} \left(1 - 3\cos^2\theta_{ij} \right) \end{aligned}$$

Quadrupolar coupling Hamiltonian:

$$\mathcal{H}_Q = - \sum_i \omega_{Q,i} \left(3I_{zi}^2 - \vec{I}_i \cdot \vec{I}_i \right)$$

$$\omega_{Q,i} = \frac{e^2 q_i Q_i}{8I(2I-1)\hbar} \left(1 - 3\cos^2\theta \right)$$

Strong J coupling Hamiltonian:

$$\mathcal{H}_J = \sum_{i \neq j} J \vec{I}_i \cdot \vec{I}_j$$

Weak J coupling Hamiltonian:

$$\mathcal{H}_J = \sum_{i \neq j} J I_{zi} I_{zj}$$

orders of magnitude or more.

A second simplification resulting from the near equivalence of ω with ω_0 is that in this new frame the large static Zeeman term disappears. That this term vanishes, remarkably, is independent of the size of $\omega_1(t)$, demonstrating the dramatic effects possible by switching frames of reference.

The final point to note is that besides the Zeeman rf term, all terms in the rotating frame Hamiltonian commute with I_z . Many important consequences derive from this result, which, for brevity, will not be explored here.

D. Rotating frame detection

In the laboratory frame, the NMR Hamiltonian is dominated by the Zeeman interaction of the spins with the large static field. All other interactions appear as small modulations on top of the large Zeeman energy. Most terms of greatest interest, the chemical shift interaction being a typical example, are a factor of 10^{-6} smaller than the Zeeman term, consequently requiring sub parts per million resolution for their measurement.

A result revealed by equation (3.16) for $\omega = \omega_0$ is that in the frame rotating about the static field at the spin Larmor frequency, the Zeeman interaction is absent. Observations of magnetic dipole radiation in this frame, therefore, are not obscured by this common, uninformative interaction. The removal of the Zeeman frequency is reflected in the convention in NMR to center all spectra about zero frequency. It should be remembered, however, that because of the truncation of non-secular terms in V_L , the transformation to the

rotating frame does not merely result in a subtraction of ω from the eigenvalues of the NMR Hamiltonian; the effect is somewhat more complex.

Phase sensitive measurements of NMR signals in the rotating frame are conducted in the following way. The actual signal detected is a voltage proportional to the magnetic dipole as shown in equation (2.70). It is clear that the signal from this source can oscillate only with the characteristic frequencies of the spin Hamiltonian, i.e., near the Larmor frequency. By using equations (2.56), (3.1), and (3.15), an expression for the density operator in the rotating frame can be arrived at:

$$\rho_L(t) = e^{-i\omega I_z t} \rho_R(t) e^{i\omega I_z t} \quad (3.17)$$

Re-expressed in terms of the rotating frame density operator, the signal becomes:

$$S_L(t) = \cos\omega t \operatorname{Tr}(I_x \rho_R(t)) - \sin\omega t \operatorname{Tr}(I_y \rho_R(t)) \quad (3.18)$$

After passing this time domain signal through a superheterodyne detector and filtering, two demodulated signals 90° out of phase with each other are recorded. These are related to the original high frequency signal $S_L(t)$ by the proportionalities:

$$S_{R,x}(t) \propto S_L(t) \cos\omega t \quad (3.19)$$

$$S_{R,y}(t) \propto S_L(t) \sin\omega t \quad (3.20)$$

Since the two components above are orthogonal, the detection actually

discriminates between signals with different phases.

Substituting equation (3.18) into $S_{R,x}(t)$ and $S_{R,y}(t)$ and discarding harmonics oscillating at frequency 2ω (which are attenuated by the filters anyway), the demodulated time domain signals are obtained:

$$S_{R,x}(t) \propto \text{Tr}\{I_x \rho_R(t)\} \quad (3.21)$$

$$S_{R,y}(t) \propto \text{Tr}\{I_y \rho_R(t)\} \quad (3.22)$$

Equations (3.21) and (3.22) represent the sought after result: a prescription for phase sensitive detection of magnetic dipole radiation in the rotating frame. The critical experimental detail in reaching this stage is the heterodyne step, where the so-called carrier frequency is mixed away. Heterodyne detection, a technique common in radiofrequency electronics, turns out to be a useful and sensitive means of detecting low power, high frequency signals from a practical standpoint as well.⁵⁶ Figure 8.2 illustrates the demodulation process in greater detail.

III. INTERACTION PICTURE DEFINED BY A TIME DEPENDENT HAMILTONIAN

A. Introduction to coherent averaging theory

As presented above, transformation to the rotating frame succeeds only partially in removing the time dependence of the NMR Hamiltonian. Two sources contribute to the time dependence of the laboratory frame rf-spin Hamiltonian, but only one disappears by switching reference frames. The first and most important source of the time dependence is the simple, sinusoidal oscillation of the linearly polarized rf field

at the photon frequency ω . This is the frequency which must be matched to the spin resonance frequencies in order to effectively induce transitions between spin energy levels. This frequency will henceforth be regarded as being fixed. The second source of the time dependence of the rf-spin Hamiltonian is the phase and amplitude modulation of the applied rf field. Within fairly broad experimental limits, a wide range of phase and amplitude functions can conveniently be implemented by most modern NMR hardware. Unlike the oscillatory time dependence, therefore, the time dependence due to these terms is unspecified and potentially more complex. Transformation to the rotating frame eliminates the first, but not the second, of these sources of time dependence. To integrate Schrödinger's equation, then, it is necessary to search again for an interaction picture where the Hamiltonian is more closely stationary. Interaction picture transformations and approximations which accomplish this purpose are the main subject of this section.

The interaction picture approach adopted here is fundamentally the same as the approach introduced by the rotating frame example. Again, the objective will be to seek out a reference frame where large, uninformative interactions (such as, in this case, the rf-spin coupling) are absent, and where the total Hamiltonian appears static. Determining a unitary transformation which achieves this objective, however, is somewhat more complicated than in the rotating frame example for several important reasons. The first reason concerns the functional form of the time dependent terms. In the laboratory frame, the oscillation of the field at a single large frequency ω was the primary source of the time dependence. A straightforward rotation

around the z axis suffices to remove this sinusoidal time dependence. The rf-spin interaction in the rotating frame does not, in general, have this simple oscillating time dependence, and is correspondingly more difficult to analyze.

Another reason why time dependent terms in the rotating frame present greater difficulties is because of their relative magnitudes. The dominant term in the laboratory frame Hamiltonian -- the one removed by transformation to the rotating frame -- is due to the static Zeeman interaction. This term exceeds all other terms in the laboratory frame Hamiltonian by several orders of magnitude, and thereby legitimizes the truncation of non-secular terms in the rotating frame Hamiltonian. The dominant term in the rotating frame Hamiltonian, however, is a time dependent coupling, namely, the rf-spin interaction. Moreover, in most practical situations, this coupling is not greatly larger than other terms in the rotating frame Hamiltonian, and therefore cannot be counted on to have the same truncating effect as the static Zeeman interaction in the laboratory frame. These factors together necessitate rather more clever approximations than were used in the rotating frame case.

Haeberlen and Waugh have proposed a formalism they call coherent averaging theory³⁸ as a way to meet the difficulties posed by the phase and amplitude modulation of the rf field. The analysis of these problems by coherent averaging theory commences with the separation of the rotating frame Hamiltonian, equation (3.16), into two parts, one part arising from the Zeeman interaction of the nuclear spin system to external, applied fields, and the second part arising from the interaction of the spins with internal, naturally occurring fields.

This separation is acknowledged by writing the Hamiltonian symbolically as below:

$$\mathcal{H}_{\text{NMR},R}(t) = \mathcal{H}_{\text{rf}}(t) + V_R \quad (3.23)$$

The term due to the interaction of the spins with external fields, $\mathcal{H}_{\text{rf}}(t)$, depends on parameters over which there is nominal experimental control. For the transverse field assumed in equation (3.16), these parameters are the instantaneous phase, amplitude, and direction of the applied field, given by the time dependent quantities $\phi(t)$, $\omega_1(t)$ and $[\cos\phi(t), \sin\phi(t), 0]$ respectively. In an actual experiment, however, these parameters can differ from their presumptive values, as explained in Chapter Two. Because of these pulse imperfections, the $\vec{H}_1(t)$ field defining $\mathcal{H}_{\text{rf}}(t)$ in equation (3.23) should, realistically, be regarded as the vector sum of two fields, one an "ideal" field with some nominal phase, amplitude and direction, and one a "nonideal" field, consisting of commonly encountered rf field imperfections. Dividing $\vec{H}_1(t)$ in this way, and modifying equation (3.23) above, the NMR Hamiltonian in the rotating frame becomes:

$$\mathcal{H}_{\text{NMR},R}(t) = \mathcal{H}_{\text{rf},I}(t) + \mathcal{H}_{\text{rf},N}(t) + V_R \quad (3.24)$$

where the subscript "I" stands for ideal and the subscript "N" stands for nonideal.

The final term in equation (3.19) is customarily referred to as the "internal" Hamiltonian to distinguish the interactions it encompasses from those due to the coupling of the spin system with externally applied magnetic fields. The prominent internal

interactions in NMR were summarized earlier in table 3.1. These particular interactions are considered time independent, even in the rotating frame. Consequently, no dependence on t is indicated for V_R in equation (3.19).

If $\mathcal{H}_{rf,I}(t)$ is set equal to $\mathcal{H}_0(t)$ in equation (3.10), then from equation (3.9), the time development operator of $\mathcal{H}_{NMR,R}(t)$ can be written as a product of two unitary operators:

$$U(t) = U_{rf}(t)U_V(t) \quad (3.25)$$

where, by equations (3.11) and (3.13), $U_{rf}(t)$ and $U_V(t)$ are given by:

$$U_{rf}(t) = \mathcal{T}_+ \exp \left\{ -i \int_0^t \mathcal{H}_{rf,I}(t') dt' \right\} \quad (3.26)$$

$$U_V(t) = \mathcal{T}_+ \exp \left\{ -i \int_0^t \tilde{V}(t') dt' \right\} \quad (3.27)$$

$$\tilde{V}(t') = U_{rf}^\dagger(t') \left[\mathcal{H}_{rf,N}(t') + V_R \right] U_{rf}(t) \quad (3.28)$$

By analogy with the rotating frame example, $U_V(t)$ is the time development operator in the new interaction picture, a picture which has been given the name "togglng frame" by Haeberlen and Waugh. Evidently, $\tilde{V}(t')$ is the Hamiltonian in the togglng frame.

The expressions in (3.26), (3.27), and (3.28) are exact and so far have involved no approximations. Writing the total propagator as in (3.25) enables the conceptual division of the time evolution into a part due only to interactions with large rf fields, and a part due to smaller internal couplings of the spin system and field imperfections,

modulated by the rf irradiation.

If, during an experiment of duration t , there are M time intervals, with $\mathcal{H}_{rf,I}(t')$ and $\mathcal{H}_{rf,N}(t')$ constant within each interval, an exact expression for $U_{rf}(t)$ can be explicitly derived:

$$U_{rf}(t) = \exp\left[-i\mathcal{H}_{rf,M}\tau_M\right] \exp\left[-i\mathcal{H}_{rf,M-1}\tau_{M-1}\right] \times \dots \\ \dots \times \exp\left[-i\mathcal{H}_{rf,2}\tau_2\right] \exp\left[-i\mathcal{H}_{rf,1}\tau_1\right] \quad (3.29)$$

with:

$$t = \tau_M + \tau_{M-1} + \dots + \tau_2 + \tau_1 \quad (3.30)$$

In these equations, τ_i is the duration of the i th interval and $\mathcal{H}_{rf,i}$ the ideal rf Hamiltonian within that interval. By the assumptions mentioned earlier in Chapter Two, $\mathcal{H}_{rf}(t)$ during the i th interval will be of the form:

$$\mathcal{H}_{rf,i} = \omega_1 \left[I_x \cos\phi_i + I_y \sin\phi_i \right] \quad (3.31)$$

with ϕ_i and ω_1 constant, or:

$$\mathcal{H}_{rf,i} = 0 \quad (3.32)$$

depending on whether the rf is on or off respectively.

The central point to observe is that each of the time development operators in the product on the right side of equation (3.29) must either be a rotation operator or an identity operator. For $\mathcal{H}_{rf,i}$ of the form in equation (3.31), the rotation is through the angle $\omega_1\tau_i$ about the axis $(\cos\phi_i, \sin\phi_i, 0)$. The two parameters determining this

rotation, $\omega_1 \tau_1$ and ϕ_1 , are referred to as the flip angle and the phase of the pulse, respectively. It follows from the group property of rotations that $U_{rf}(t)$ on the left side of this equation must also be a rotation, and can therefore be readily reduced to a single exponential:

$$U_{rf}(t) = e^{-i\alpha(t)\hat{n}(t) \cdot \vec{I}} \quad (3.33)$$

even though the Hamiltonian $\mathcal{H}_{rf,I}(t)$ is time dependent.

The remaining problem is the evaluation of $U_V(t)$. Since the time dependence of $\tilde{V}(t)$ is imposed by the piecewise constant time dependence of the rf field $\tilde{H}_1(t)$, $U_V(t)$ assumes a product form similar to equation (3.29), specifically:

$$U_V(t) = U_{V,M}(\tau_M) U_{V,M-1}(\tau_{M-1}) \times \dots \\ \dots \times U_{V,2}(\tau_2) U_{V,1}(\tau_1) \quad (3.34)$$

The propagator $U_{V,i}(\tau_i)$ refers to the i th discrete time interval of the pulse sequence. Although $\mathcal{H}_{rf}(t)$ is piecewise constant, $\tilde{V}(t)$ will not be since it is modulated continuously in time during a pulse.

An exact reduction of the product on the right side of equation (3.34) to a single exponential can be performed by making use of the Magnus expansion.⁵⁷⁻⁵⁹ $U_V(t)$ can be re-expressed in terms of this expansion by the equation:

$$U_V(t) = \exp \left[-i \left(\tilde{V}^{(0)} + \tilde{V}^{(1)} + \tilde{V}^{(2)} + \dots \right) t \right] \quad (3.35)$$

where the first three terms of the series are given by:

$$\bar{V}^{(0)} = \frac{1}{t} \int_0^t \bar{V}(t') dt' \quad (3.36)$$

$$\bar{V}^{(1)} = -\frac{1}{2t} \int_0^t dt_2 \int_0^{t_2} dt_1 [\bar{V}(t_2), \bar{V}(t_1)] \quad (3.37)$$

$$\begin{aligned} \bar{V}^{(2)} = & -\frac{1}{6t} \int_0^t dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \left\{ [\bar{V}(t_3), [\bar{V}(t_2), \bar{V}(t_1)]] \right. \\ & \left. + [[\bar{V}(t_3), \bar{V}(t_2)], \bar{V}(t_1)] \right\} \end{aligned} \quad (3.38)$$

Equations for higher order terms can be found elsewhere, but will not be considered here.^{2,61} As defined, each term $\bar{V}^{(i)}$ in the expansion will necessarily be Hermitian.

A parameter of some kind, such as a dipole coupling constant or a chemical shift, usually characterizes the magnitude of $\bar{V}(t)$ in relation to $\mathcal{H}_{rf,I}(t)$. The Magnus expansion is a power series in this parameter. If the time t over which the integrals above are defined is small compared to the inverse of this parameter, the expansion is well approximated by truncating after the first few terms. The Hermiticity of each term in the expansion guarantees the Hermiticity of the truncated sum and hence its validity as an approximate, stationary Hamiltonian. This truncation permits the approximation of $U_V(t)$ within some suitable range of the parameter.

The ultimate utility of this exercise is made perhaps more apparent by writing out the total propagator explicitly:

$$U(t) = U_{rf}(t)U_V(t) \quad (3.39)$$

$$\approx \exp\left[-i\alpha\hat{n}\cdot\vec{I}\right] \exp\left[-i\hat{H}_N t\right] \quad (3.40)$$

$\hat{H}_N$ is a shorthand expression for the truncated Magnus expansion:

$$\hat{H}_N = \bar{V}^{(0)} + \bar{V}^{(1)} + \dots + \bar{V}^{(N-1)} + \bar{V}^{(N)} \quad (3.41)$$

The first expression in (3.40) is simply a rotation operator, and, as has been pointed out, is readily evaluated for a piecewise constant rf field.

The second expression in the product of equation (3.40) contains the main result of coherent averaging theory, for it shows how, by a change of reference frame and some suitable approximations, time dependent Hamiltonians can justifiably be replaced with static Hamiltonians to explicitly evaluate the time development operator $U(t)$. The approximation can be improved, in principle, by evaluating higher order terms in the Magnus formula and adding to the truncated expansion $\hat{H}_N$. Theorems have indeed been derived to simplify calculation of some of these higher terms.⁶⁰⁻⁶³ The evaluation of terms past the first order terms is generally a difficult task, however, and can rarely be performed analytically without some assumptions about the form of the toggling frame Hamiltonian.^{33,39} A few of the practical and inherent problems associated with this calculation are encountered in the next chapter.

B. Final remarks

Haerberlen and Waugh developed coherent averaging theory to determine decoupling sequences for dipolar coupled heteronuclear spin systems in solid state NMR. Their original proposal involved finding pulse sequences for which, after integral numbers of some cycle time t_c , U_{rf} and U_V assumed the forms:

$$U_{rf}(nt_c) = 1 \quad (3.42)$$

$$U_V(nt_c) = 1 \quad (3.43)$$

where $V_R = \mathcal{H}_D$ from table 3.1.

By equations (3.25) and (3.42), the rotating and toggling frames coincide at the time nt_c . Nuclear magnetization sampled only at these specific times appears to evolve, in both the rotating and toggling frames, as if the dipole couplings were not present, enabling the enhanced resolution of other, smaller interactions such as chemical shifts.

The adaptation of coherent averaging theory to the derivation of composite pulses consists of allowing $U_{rf}(t)$ to equal other kinds of rotations besides the identity. This adaptation is investigated in Chapter Four.

CHAPTER FOUR: COHERENT AVERAGING THEORY

ANALYSIS OF COMPOSITE PULSES

I. INTRODUCTION

The composite pulses sought in this work are those which result in evolution of the spin system specified by rotating frame propagators of the form:

$$\mathcal{R}_{\phi}(\pi) = e^{-i\pi I_{\phi}} \quad (4.1)$$

$$\mathcal{R}_{\phi}(\pi/2) = e^{-i(\pi/2)I_{\phi}} \quad (4.2)$$

The expressions $\mathcal{R}_{\phi}(\alpha)$ and I_{ϕ} denote the operators in equations (4.3) and (4.4) respectively:

$$\mathcal{R}_{\phi}(\alpha) = e^{-i\alpha I_{\phi}} \quad (4.3)$$

$$I_{\phi} = I_x \cos \phi + I_y \sin \phi \quad (4.4)$$

Composite pulses which effect rotation operators of these forms over broad ranges of dipolar couplings, quadrupolar couplings, rf field strengths and resonance offsets are derived by coherent averaging theory in this chapter.

A. The propagator $\mathcal{R}_{\phi}(\pi)$

The response of a nuclear spin system to pulse sequences with propagators of the form $\mathcal{R}_{\phi}(\pi)$ is referred to as population inversion.

This is because the action of such a pulse sequence results in an exchange of populations of the m th Zeeman manifold with the $-m$ th Zeeman manifold of the spin density operator written in the basis of I_z . This assertion can be shown to follow from the fact that:³⁹

$$\mathcal{R}_\phi^\dagger(\pi) I_z \mathcal{R}_\phi(\pi) = \mathcal{R}_\phi(\pi) I_z \mathcal{R}_\phi^\dagger(\pi) = -I_z \quad (4.5)$$

Rotation operators of the form $\mathcal{R}_\phi(\pi)$ are not the only unitary operators which can transform I_z to $-I_z$. Any unitary operator of the general form:

$$I(t) = U_z(t) \mathcal{R}_\phi(\pi) \quad (4.6)$$

where:

$$[U_z(t), I_z] = 0 \quad (4.7)$$

can cause this transformation to take place. $I(t)$ need not even be a rotation operator for this to be true.

A measure of the population inversion achieved by a pulse sequence is the normalized quantity defined by:

$$\langle M_z \rangle = \text{Tr} \left\{ I_z U(t) I_z U^\dagger(t) \right\} / \text{Tr} \left\{ I_z^2 \right\} \quad (4.8)$$

where $U(t)$ is the propagator describing the effect of the pulse sequence. Since $U(t)$ is a unitary operator:

$$-1 \leq \langle M_z \rangle \leq 1 \quad (4.9)$$

with $1 = \langle M_z \rangle$ indicating that no inversion takes place, and $-1 = \langle M_z \rangle$

indicating that complete inversion takes place.

Population inversion can be ascertained experimentally by allowing a spin system to equilibrate in a large magnetic field, whereupon its density operator, by equation (2.69), is proportional to I_z . Application of the pulse sequence followed by detection of the expectation value of I_z then corresponds to a measurement of the quantity $\langle M_z \rangle$. The actual details of this procedure are provided in Chapter Eight. An experiment such as this alone cannot discriminate between propagators of the form $\mathcal{R}_\phi(\pi)$ and a propagator such as $I(t)$ above. The possibility of such propagators arising will be ignored for now.

It is apparent from equations (4.1) and (4.6) that a set of unitary operators, rather than a single unique one, can convert I_z to $-I_z$. If the only objective in an experiment is to transform, at some stage, an initial state to its population inverted counterpart, then any operator of the form $I(t)$ will suffice to perform this function. However, there are many applications in NMR which require that a π rotation be performed on the density operator about a specific axis in the xy plane. Experiments requiring this capability include multiple pulse line narrowing in solids,^{2,4,64} time reversal,⁶⁵ polarization transfer,^{11,12,66} pulsed spin-locking,⁶⁷ and multiple quantum excitation.^{7,8} In these experiments, rotations are performed on a spin system not at equilibrium, i.e., with the magnetization not aligned with the static magnetic field. For these applications, only sequences with propagators of the form $\mathcal{R}_{\bar{\phi}}(\pi)$, where $\bar{\phi}$ has a single, well defined value, are admissible. A coherent averaging theory approach to this problem will be discussed further on.

B. The propagator $\mathcal{R}_\phi(\pi/2)$

Pulse sequences which cause propagators of the form $\mathcal{R}_\phi(\pi/2)$ to come about are known as composite $\pi/2$ pulses. The best known application of such pulses is the rotation of equilibrium, longitudinal magnetization, characterized by the density operator I_z , into the transverse plane, followed by detection of the free induction decay (FID). Such a response can obviously be obtained with a single rf pulse, just as in the population inversion case, but only over small bandwidths limited by the rf amplitude (see, e.g., figure 4.1).

If the sole objective in a particular experiment is the conversion of longitudinal magnetization to transverse magnetization, it is not necessary that the rotation be of angle $\pi/2$ about an axis in the xy plane. Many different rotations about axes both in and out of the transverse plane make this transition of initial state to final state possible. Instances of these will be encountered later.

Composite pulses which simply convert longitudinal magnetization to transverse magnetization are rarely satisfactory for most NMR experiments, however, even for the basic case where only an FID is desired. In coherent spectroscopy, where the phase of the signal and the shapes of the absorption lines contain important information, variations in parameters such as resonance frequencies or spin-spin couplings can cause loss of phase coherence and intensity in the time domain signal. Severe spectral distortions are the result. Thus, it does not suffice that the sequence merely rotate longitudinal magnetization into the transverse plane; it is essential that the phases and the intensities of the signal produced by the sequence be

unaffected by variations in spectral parameters.

Composite pulses have been developed which convert longitudinal magnetization to phased, transverse magnetization, but which do so with an effective time development operator not equal to $\mathcal{R}_\phi(\pi/2)$. A prominent example is the two pulse spin echo. Other examples will be discussed later. There are a variety of experiments, however, which specifically require $\pi/2$ rotations of the magnetization about a certain axis in the xy plane. These include many of the same experiments as were pointed out for the composite π pulse case. A way of arriving at broadband $\pi/2$ pulses which really do perform $\pi/2$ rotations of the density operator is proposed in the next section.

The efficacy of the composite $\pi/2$ pulses developed in this thesis were measured in ways similar to the experiments for the composite π pulses. The nuclear spins were allowed to equilibrate in the magnetic field and then a composite $\pi/2$ pulse sequence delivered to the sample. A rotating frame, phase sensitive measurement of the quantities:

$$\langle M_x \rangle = \text{Tr} \left\{ I_x U(t) I_z U^\dagger(t) \right\} / \text{Tr} \left\{ I_z^2 \right\} \quad (4.10)$$

$$\langle M_y \rangle = \text{Tr} \left\{ I_y U(t) I_z U^\dagger(t) \right\} / \text{Tr} \left\{ I_z^2 \right\} \quad (4.11)$$

was performed as described in section 3.II.D. The amplitude of the signal after the composite pulse is:

$$\langle M_{xy} \rangle = \left[\langle M_x \rangle^2 + \langle M_y \rangle^2 \right]^{1/2} \quad (4.12)$$

and the phase of the signal:

$$\phi_s = \arctan \left(\frac{\langle M_y \rangle}{\langle M_x \rangle} \right) \quad (4.13)$$

This kind of measurement, like the one described for the composite π pulse case, does not distinguish between $\mathcal{R}_\phi(\pi/2)$ and operators of the form $I(t)$:

$$I(t) = U_z(t) \mathcal{R}_\phi(\pi/2) \quad (4.14)$$

where $U_z(t)$ satisfies the commutation relation in (4.7). Some variant experiments are proposed later which constitute a more discriminating test for determining pulse sequences with the propagator $\mathcal{R}_\phi(\pi/2)$.

II. STATEMENT OF THE PROBLEM

The derivation of broadband composite pulse sequences by coherent averaging theory is separable into two distinct problems, one concerned with the form of $U_{rf}(t)$ in equation (3.39), and one concerned with the form of $U_V(t)$. The first operator, $U_{rf}(t)$, is the propagator of the spin system coupled to the applied rf field, in the absence of field imperfections and internal spin interactions. It is a function of $\mathcal{H}_{rf,I}(t)$, and thus depends only on the parameters of the pulse sequence. The parameters which specify a piecewise constant pulse sequence consisting of m pulses and n delays are the m phases and flip angles of the pulses. The dependence of $U_{rf}(t)$ on these parameters is summarized by the equation:

$$U_{rf}(T) = U_{rf}(\phi_1, \phi_2, \dots, \phi_{m-1}, \phi_m, \alpha_1, \alpha_2, \dots, \alpha_{m-1}, \alpha_m) \quad (4.15)$$

$$= U_{rf}(\vec{\phi}, \vec{\alpha}) \quad (4.16)$$

The phases are written as ϕ_i and the flip angles as α_i . The flip angle of a pulse is related to its duration by the proportionality $\alpha_i = \omega_1 t_i$, where the amplitude ω_1 is the same for each pulse. T is the total duration of the experiment, and is equal to the sum of the lengths of all pulses and all delays.

The propagator $U_V(t)$ depends on $\mathcal{H}_{rf,I}(t)$ through equation (3.27), and thus is also a function of the pulse sequence parameters. $U_V(t)$ depends, however, on other parameters as well, such as coupling constants or field imperfections, and the durations of delays. This is readily seen by recalling the definition of $\tilde{V}(t)$ in equation (3.28). Denoting these parameters as the vector $\vec{\lambda}$, the dependence of $U_V(t)$ on these and the pulse sequence parameters is signified by expressing $U_V(T)$ as:

$$U_V(T) = U_V(\vec{\phi}, \vec{\alpha}, \vec{\tau}, \vec{\lambda}) \quad (4.17)$$

The n delay times τ_i are represented by the n dimensional vector $\vec{\tau}$. If the interactions responsible for $U_V(t)$ are absent, that is, if $\vec{\lambda} = 0$, then $U_V(t) = 1$.

The two problems to be overcome in the formulation of broadband composite pulses can now be stated. Let $\bar{K}$ be the desired time development operator, for example, a $\pi/2$ or π rotation operator. The first problem is the determination of phases and flip angles for which:

$$U_{rf}(\vec{\phi}, \vec{\alpha}) = \bar{K} \quad (4.18)$$

The second problem is to find, from the values of $\vec{\phi}$ and $\vec{\alpha}$

satisfying equation (4.18), the phases, flip angles, and delay times for which:

$$U_V(\vec{\phi}, \vec{\alpha}, \vec{\tau}, \vec{\lambda}) \approx 1 \quad (4.19)$$

$$\vec{\lambda} \neq 0 \quad (4.20)$$

The Magnus expansion is instrumental for evaluating $U_V(T)$ for this purpose.

The simultaneous solution of equation (4.18) and (4.19) means that:

$$U(\vec{\phi}, \vec{\alpha}, \vec{\tau}, \vec{\lambda}) = U_{rf}(\vec{\phi}, \vec{\alpha}) U_V(\vec{\phi}, \vec{\alpha}, \vec{\tau}, \vec{\lambda}) \quad (4.21)$$

$$\approx \bar{R} \quad \text{for } \lambda \neq 0 \quad (4.22)$$

A sequence resulting in a propagator $U(T)$ satisfying (4.21) for large ranges of $\vec{\lambda}$ is broadband over the parameters $\vec{\lambda}$.

The ways in which these problems were approached are explained in the next two sections.

A. Specification of $\bar{R} = U_{rf}(\vec{\phi}, \vec{\alpha})$

Phases and flip angles leading to the desired $\bar{R}$ can be conveniently determined by performing a brute force grid search through all possible combinations of the m phases and flip angles from 0 to 2π . Clearly, this method is practical only if a computer is available to conduct the search.

An automated search of this sort is implemented by programming a computer to evaluate $U_{rf}(\vec{\phi}, \vec{\alpha})$, and to store values of $\vec{\phi}$ and $\vec{\alpha}$ which satisfy some predetermined criteria. The criteria used for this

procedure can be of two types. The first, stricter criterion is represented by equation (4.18). The computer explicitly calculates $U_{rf}(\vec{\phi}, \vec{\alpha})$ and then compares it to $\vec{R}$. Only values of $\vec{\phi}$ and $\vec{\alpha}$ for which $U_{rf}(\vec{\phi}, \vec{\alpha}) = \vec{R}$ are then stored.

It is possible to use a second, looser criterion if a transformation from a specified initial state to a specified final state is what is desired, rather than a particular propagator. The computer can then be programmed to perform a search using the criterion:

$$\rho_F = U_{rf}(\vec{\phi}, \vec{\alpha}) \rho_I U_{rf}^\dagger(\vec{\phi}, \vec{\alpha}) \quad (4.23)$$

The initial state is represented by the density operator ρ_I , and the final state by the density operator ρ_F . This criterion is generally less restrictive than the first since the computer is not confined to searching for propagators of a single unique form.

With phases and flip angles filtered and stored in this manner, $\vec{\phi}$ and $\vec{\alpha}$ are searched again for values which approximately satisfy equation (4.19).

Despite the convenience of carrying out such a procedure, a random search is undesirable for several reasons. A random search can be a time consuming and inaccurate procedure even for high speed computers. The time required depends of course on the number of variables and the fineness of the grid used in the search, but becomes rapidly impractical and less accurate for more than four pulses. Moreover, brute force searches do not guarantee that a solution will be found even if one exists; the solution may slip through the grid.

These, and other considerations, necessitate a less random, more directed procedure for discovering phases and flip angles leading to the desired $\bar{R}$.

Most of the sequences shown in this and subsequent chapters were determined by combining phases and flip angles according to certain rules. The rules were formulated so that any combination of phases and flip angles chosen in conformance with the rules would be guaranteed to produce an operator $U_{rf}(\vec{\phi}, \vec{\alpha})$ of the desired form $\bar{R}$. The rules act as constraints on the possible values of $\vec{\alpha}$ and $\vec{\phi}$ which can be used to satisfy equation (4.19).

An example of a rule which can be utilized to select for pulse sequences with propagators of the form $R_{\phi}(\pi)$ is to specify that all α_i be equal to π , and that the number of pulses m be equal to an odd integer. It is intuitively obvious (and relatively easy to prove in a number of ways) that combining an odd number of π rotations, each about an axis in the xy plane, results in a π rotation also about an axis in the same plane. If the m phases of the concatenated π rotations are denoted ϕ_i , then the product π rotation is directly calculable from the equations:

$$R_{\phi_T}(\pi) = R_{\phi_m}(\pi) R_{\phi_{m-1}}(\pi) \times \dots \times R_{\phi_2}(\pi) R_{\phi_1}(\pi) \quad (4.24)$$

and:

$$\phi_T = \phi_1 - \phi_2 + \dots - \phi_{m-1} + \phi_m \quad (4.25)$$

This rule has been exploited by several workers to guide searches for composite π pulses.^{18,20,21,24,26-29} The important feature to note

about this rule is that the phases of the rotations are left unspecified. This permits the phases to be used as free variables to solve equation (4.19).

Several similar, but less obvious, rules are conceivable for combining phases and flip angles to form operators of the form $\mathcal{R}_\phi(\pi/2)$. These rules were adopted with an emphasis on experimental practicality. It is often feasible to calibrate only a few pulse times accurately and conveniently, viz., $\pi/2$ pulse times or multiples thereof, especially in solid state NMR, where high rf power and short pulse times are the rule. Standard methods exist to determine these particular times with a high degree of accuracy.⁶⁸ Less difficult than finding other pulse times, and more precise for most NMR spectrometers, is the capability to generate pulses with variable phases. For this reason, only sequences comprised of $\pi/2$ and π pulses, and variable delays, are considered.

One procedure involves the formation of a cycle, or series of cycles, out of single, phase shifted $\pi/2$ pulses, followed by the insertion of a final $\pi/2$ pulse at the end, beginning, or between cycles. The term cycle is used here to refer to a sequence of pulses and delays leading to an effective rf propagator $U_{rf}(t)$ equal to the identity. Some simple cycles which can be formed from phase shifted $\pi/2$ pulses are:

$$\left(\frac{\pi}{2}\right)_\phi \left(\frac{\pi}{2}\right)_{\phi+\pi} \quad (4.26)$$

$$\left(\frac{\pi}{2}\right)_\phi, \left(\frac{\pi}{2}\right)_\phi, \left(\frac{\pi}{2}\right)_\phi, \left(\frac{\pi}{2}\right)_\phi \quad (4.27)$$

$$\left(\frac{\pi}{2}\right)_\phi, \left(\frac{\pi}{2}\right)_{\phi+(\pi/2)}, \left(\frac{\pi}{2}\right)_{\phi+(3\pi/2)}, \left(\frac{\pi}{2}\right)_\phi \quad (4.28)$$

The standard notation $(\alpha)_\phi$ denotes an rf pulse of duration α/ω_1 and phase ϕ . The last sequence is a cycle of the WAHUHA type.⁶⁴

A trivial example of a cycle which is used later on is a variable length delay with no rf pulse on. During a delay, the rf plays no role in the time evolution of the system, so the system is free to evolve under its own internal couplings; $U_{rf}(t)$ in this interval remains constant. The addition of the single $\pi/2$ pulse before, between (but not within), or after cycles will produce a propagator $U_{rf}(\vec{\alpha}, \vec{\phi})$ of the form in equation (4.2). Furthermore, cycles may be inserted within cycles without destroying the overall cyclicity.

A second special kind of cycle can be constructed out of $\pi/2$ pulses by forming sequences with the net rf propagators:

$$U_{rf}(\vec{\phi}, \vec{\alpha}) = e^{-i\pi I_z} \quad (4.29)$$

$$U_{rf}(\vec{\phi}, \vec{\alpha}) = e^{i\pi I_z} \quad (4.30)$$

$$U_{rf}(\vec{\phi}, \vec{\alpha}) = e^{-i(\pi/2)I_z} \quad (4.31)$$

$$U_{rf}(\vec{\phi}, \vec{\alpha}) = e^{i(\pi/2)I_z} \quad (4.32)$$

A pulse sequence constructed only from $\pi/2$ pulses with the net propagator in equation (4.2) can be obtained, e.g., by concatenating

phase shifted pulses to form sequences such as:

$$\left(\frac{\pi}{2}\right)_{\phi} \left(\frac{\pi}{2}\right)_{\phi+(\pi/2)} \left(\frac{\pi}{2}\right)_{\phi+(\pi/2)} \left(\frac{\pi}{2}\right)_{\phi+\pi} \quad (4.33)$$

The second of the four propagators above can be obtained from this sequence by adding π to the phases of the two middle pulses.

Several rules for combining sequences of this form with a $(\pi/2)_0$ pulse to create a composite $\pi/2$ pulse can be perceived. One is to concatenate a sequence with propagator given by equation (4.29) with another sequence with the same propagator, forming a cycle, and then appending a $(\pi/2)_0$ pulse. Another is to sandwich a $(\pi/2)_0$ pulse between one sequence with the propagator (4.29) and one sequence with the propagator (4.30), resulting in a propagator of the form $\mathcal{R}_{\pi}(\pi/2)$. Other variations are easily imaginable.

The final operation considered here consists of phase shifting $(\pi/2)_0$, and concatenating it with itself, forming:

$$\left(\frac{\pi}{2}\right)_{\phi} \left(\frac{\pi}{2}\right)_{\phi} \text{ or } (\pi)_{\phi} \quad (4.34)$$

$U_{rf}(\vec{\phi}, \vec{\alpha})$ for this two pulse sequence is $\mathcal{R}_{\phi}(\pi)$. Concatenation of N phase shifted versions of these two pulse sequences, N odd, generates a composite π pulse sequence with net rf propagator $\mathcal{R}_{\gamma}(\pi)$, where γ can be computed from the relation in equation (4.25). Inserting the pulse $(\pi/2)_{\gamma+\pi}$ or $(\pi/2)_{\gamma}$ at the beginning or end of this sequence results in a sequence with $U_{rf}(\vec{\phi}, \vec{\alpha})$ equal to $\mathcal{R}_{\gamma}(\pi/2)$ or $\mathcal{R}_{\gamma+\pi}(\pi/2)$, respectively.

These procedures meet the constraint imposed by equation (4.18), but still provide free parameters, namely, the phases, necessary for

the solution of $U_V(\vec{\phi}, \vec{\alpha}, \vec{\tau}, \vec{\lambda}) = 1$.

B. Specification of $U_V(\vec{\phi}, \vec{\alpha}, \vec{\tau}, \vec{\lambda}) = 1$

Deviations from ideality in the performance of multiple pulse sequences are represented in equation (3.25) by the propagator $U_V(t)$. The problem of minimizing the effect on the evolution of the system of the imperfections responsible for this term is treated in this section. The objective is to find values of $\vec{\phi}$, $\vec{\alpha}$, and $\vec{\tau}$ for which $U_V(\vec{\phi}, \vec{\alpha}, \vec{\tau}, \vec{\lambda}) = 1$, and which obey the constraints set forth in the preceding section.

Equations (3.35) through (3.41) suggest that determining values of $\vec{\alpha}$, $\vec{\phi}$, and $\vec{\tau}$ which lead to $U_V(\vec{\phi}, \vec{\alpha}, \vec{\tau}, \vec{\lambda}) = 1$ entails solving the equation:

$$\hat{H}_N = 0 \quad (4.35)$$

Evidently, the larger N is, the wider the bandwidth over $\vec{\lambda}$ of the sequence's effectiveness. Explicit methods for solving this equation for N up to $N = 1$ for resonance offsets, rf inhomogeneity, and dipole and quadrupole couplings are presented in the following subsections.

1. Resonance offset

By equation (3.28) and table 3.1, the toggling frame resonance offset Hamiltonian is:

$$\bar{V}_{\text{off}}(\tau) = \Delta\omega \bar{I}_z(\tau) \quad (4.36)$$

Two different kinds of toggling frame Hamiltonians can appear in a sequence consisting of pulses and delays, one kind arising during

pulses, and the other arising during delays. During the j th pulse,

$\bar{V}_{\text{off}}(t)$ assumes the form:

$$\Delta\omega_{z,j}^{(\text{pulse})}(\tau_j) = \Delta\omega \left\{ \mathcal{R}_{\phi_1}^\dagger(\alpha_1) \mathcal{R}_{\phi_2}^\dagger(\alpha_2) \dots \mathcal{R}_{\phi_{j-1}}^\dagger(\alpha_{j-1}) \mathcal{R}_{\phi_j}^\dagger(\omega_1 \tau_j) \times \right. \\ \left. \times I_z \mathcal{R}_{\phi_j}(\omega_1 \tau_j) \mathcal{R}_{\phi_{j-1}}(\alpha_{j-1}) \dots \mathcal{R}_{\phi_2}(\alpha_2) \mathcal{R}_{\phi_1}(\alpha_1) \right\} \quad (4.37)$$

$$= \Delta\omega \left\{ R^{-1}(\alpha_1) R^{-1}(\alpha_2) \dots R^{-1}(\alpha_{j-1}) R^{-1}(\alpha_j(\tau_j)) \hat{k} \right\} \cdot \bar{I} \quad (4.38)$$

The second equation follows from the first by equation (2.39). The variable τ_j denotes the length of time the j th pulse has been on. The vectors α_j in (4.38) are defined as in equation (2.27), with $\theta = \pi/2$ and $\phi = \phi_j$.

Suppose there are n delays in the sequence and that one of these delays follows the i th pulse. The toggling frame Hamiltonian during this delay is:

$$\Delta\omega_{z,k}^{(\text{delay})} = \Delta\omega \left\{ \mathcal{R}_{\phi_1}^\dagger(\alpha_1) \mathcal{R}_{\phi_2}^\dagger(\alpha_2) \dots \mathcal{R}_{\phi_{i-1}}^\dagger(\alpha_{i-1}) \mathcal{R}_{\phi_i}^\dagger(\alpha_i) I_z \times \right. \\ \left. \times \mathcal{R}_{\phi_i}(\alpha_i) \mathcal{R}_{\phi_{i-1}}(\alpha_{i-1}) \dots \mathcal{R}_{\phi_2}(\alpha_2) \mathcal{R}_{\phi_1}(\alpha_1) \right\} \quad (4.39)$$

$$= \Delta\omega \left\{ R^{-1}(\alpha_1) R^{-1}(\alpha_2) \dots R^{-1}(\alpha_{j-1}) R^{-1}(\alpha_j) \hat{k} \right\} \cdot \bar{I} \quad (4.40)$$

The zeroth order term of the Magnus expansion after all m pulses and n delays is given by the integral:

$$\bar{V}_{\text{off}}^{(0)} = \frac{\Delta\omega}{T} \int_0^T \bar{I}_z(t) dt \quad (4.41)$$

For a piecewise constant $\mathcal{H}_{\text{rf}, I}(t)$ Hamiltonian, this integral becomes a sum:

$$\begin{aligned} \bar{V}_{\text{off}}^{(0)} = \frac{\Delta\omega}{T} \left\{ \sum_{j=1}^m \left[\int_0^{T_j} \bar{I}_{z,j}^{(\text{pulse})}(t) dt \right] + \sum_{k=1}^n \tau_k \bar{I}_{z,k}^{(\text{delay})} \right\} \quad (4.42) \\ = \Delta\omega \left[a_x^{(0)}(\vec{\phi}, \vec{\alpha}, \vec{\tau}) I_x + a_y^{(0)}(\vec{\phi}, \vec{\alpha}, \vec{\tau}) I_y + a_z^{(0)}(\vec{\phi}, \vec{\alpha}, \vec{\tau}) I_z \right] \quad (4.43) \end{aligned}$$

T_j denotes the duration of the j th pulse and τ_k the duration of the k th delay. The duration of the entire sequence is T .

Higher order terms can be evaluated using equations (3.37), (3.38), (4.38), and (4.40). If the number of pulses and delays is small, the first and sometimes second order terms can be written down explicitly. Because all higher order terms involve commutators of I_x , I_y , and I_z with each other, they will all be linear in these operators. The N th order term will thus look like:

$$\bar{V}_{\text{off}}^{(N)} = \Delta\omega^{N+1} \left[a_x^{(N)}(\vec{\phi}, \vec{\alpha}, \vec{\tau}) I_x + a_y^{(N)}(\vec{\phi}, \vec{\alpha}, \vec{\tau}) I_y + a_z^{(N)}(\vec{\phi}, \vec{\alpha}, \vec{\tau}) I_z \right] \quad (4.44)$$

Solving $\hat{H}_N = 0$ thereby reduces to the problem of solving $3(N+1)$ nonlinear equations in $2m + n$ unknowns. A similar numerical problem is encountered and treated more thoroughly in the next chapter.

ii. Radiofrequency inhomogeneity

The effects of rf inhomogeneity in the i th pulse are modeled by the time dependent rotating frame Hamiltonian:

$$\mathcal{H}_{in}(t) = \Delta\omega_1(t) \left[I_x \cos\phi_i + I_y \sin\phi_i \right] \quad (4.45)$$

$$= \Delta\omega_1(t) I_{\phi_i} \quad (4.46)$$

A calculation of terms in the Magnus expansion for this Hamiltonian is similar to the one detailed for the resonance offset Hamiltonian except for two minor differences. The first difference is that this Hamiltonian is time dependent, but constant within each pulse and delay. The second difference is that this term is a linear combination of I_x and I_y , rather than I_z .

The consequences of these difference can be appreciated by examining the rf inhomogeneity toggling frame Hamiltonian. During the j th pulse, this Hamiltonian is:

$$\begin{aligned} \Delta\omega_1 \tilde{I}_{\phi_j}^{(\text{pulse})}(t_j) = & \Delta\omega_1 \left\{ \mathcal{R}_{\phi_1}^\dagger(\alpha_1) \mathcal{R}_{\phi_2}^\dagger(\alpha_2) \dots \mathcal{R}_{\phi_{j-1}}^\dagger(\alpha_{j-1}) \mathcal{I}_{\phi_j}^\dagger(\omega_1 t_j) \right. \\ & \left. \times I_{\phi_j} \mathcal{R}_{\phi_j}(\omega_1 t_j) \mathcal{R}_{\phi_{j-1}}(\alpha_{j-1}) \dots \mathcal{R}_{\phi_2}(\alpha_2) \mathcal{R}_{\phi_1}(\alpha_1) \right\} \end{aligned} \quad (4.47)$$

But, from the definition of $\mathcal{R}_\phi(\alpha)$ and I_ϕ , it is evident that:

$$\left[\mathcal{R}_{\phi_j}(\omega_1 t_j), I_{\phi_j} \right] = 0 \quad (4.48)$$

Equation (4.47) therefore simplifies to:

$$\begin{aligned} \Delta\omega_1 \bar{I}_{\phi_j}^{(\text{pulse})} &= \Delta\omega_1 \left\{ \mathcal{R}_{\phi_1}^\dagger(\alpha_1) \mathcal{R}_{\phi_2}^\dagger(\alpha_2) \dots \mathcal{R}_{\phi_{j-1}}^\dagger(\alpha_{j-1}) \right. \\ &\quad \times \left. I_{\phi_j} \mathcal{R}_{\phi_{j-1}}(\alpha_{j-1}) \dots \mathcal{R}_{\phi_2}(\alpha_2) \mathcal{R}_{\phi_1}(\alpha_1) \right\} \quad (4.49) \end{aligned}$$

$$= \Delta\omega_1 \left\{ R^{-1}(\alpha_1) R^{-1}(\alpha_2) \dots R^{-1}(\alpha_{j-1}) \hat{n}_j \right\} \cdot \bar{I} \quad (4.50)$$

The unit vector $\hat{n}_j$ in (4.50) denotes the quantity:

$$\hat{n}_j = \cos\phi_j \hat{i} + \sin\phi_j \hat{j} \quad (4.51)$$

During a delay, $\Delta\omega_1(t)$ is zero. The toggling frame rf inhomogeneity Hamiltonian is therefore also equal to zero. Evidently, evolution during delays makes no contribution to a Magnus expansion of the rf inhomogeneity Hamiltonian.

The zeroth order term of the Magnus expansion, under the piecewise constant time dependence assumption, becomes:

$$\bar{V}_{in}^{(0)} = \frac{\Delta\omega_1}{T} \sum_{j=1}^m T_j \bar{I}_{\phi_j}^{(\text{pulse})} \quad (4.52)$$

$$= \Delta\omega_1 \left[b_x^{(0)}(\vec{\phi}, \vec{\alpha}) I_x + b_y^{(0)}(\vec{\phi}, \vec{\alpha}) I_y + b_z^{(0)}(\vec{\phi}, \vec{\alpha}) I_z \right] \quad (4.53)$$

The notation used here is the same as for equation (4.43) and (4.44).

The dependence of the zeroth order term on delay times has been omitted since $\bar{V}_{in}(t)$ during delays vanishes. Again, because $\mathcal{H}_{in}(t)$ is a linear function of I_x , I_y , and I_z , higher order terms will also be linear functions of these operators. The Nth order term takes the form:

$$\bar{v}_{in}^{(N)} = \Delta\omega_1^{N+1} \left[b_x^{(N)} \langle \vec{\phi}, \vec{\alpha} \rangle I_x + b_y^{(N)} \langle \vec{\phi}, \vec{\alpha} \rangle I_y + b_z^{(N)} \langle \vec{\phi}, \vec{\alpha} \rangle I_z \right] \quad (4.54)$$

The numerical problem of solving for $\hat{H}_N = 0$ is similar to the one for the resonance offset case, namely, the simultaneous solution of $3(N+1)$ equations, but, in this instance, with only $2m$ unknowns.

iii. Dipolar and quadrupolar couplings

The spin operator parts of the dipolar and quadrupolar Hamiltonians both transform under rotations as a T_{20} irreducible spherical tensor operator.⁴⁷ In recognition of this fact, these Hamiltonians will temporarily be written as:

$$V_{20} = \delta T_{20} \quad (4.55)$$

The rotational symmetry of this term is different from I_x , I_y , and I_z , necessitating a few modifications of the calculations presented for the resonance offset and rf inhomogeneity Hamiltonians. The toggling frame Hamiltonian during the j th pulse for a Hamiltonian with T_{20} symmetry becomes:

$$\begin{aligned} \delta \bar{T}_{20,j}^{(\text{pulse})}(\tau_j) = & \delta \left\{ R_{\phi_1}^\dagger(\alpha_1) R_{\phi_2}^\dagger(\alpha_2) \dots R_{\phi_{j-1}}^\dagger(\alpha_{j-1}) R_{\phi_j}^\dagger(\omega_1 \tau_j) T_{20} \times \right. \\ & \left. \times R_{\phi_j}(\omega_1 \tau_j) R_{\phi_{j-1}}(\alpha_{j-1}) \dots R_{\phi_2}(\alpha_2) R_{\phi_1}(\alpha_1) \right\} \end{aligned} \quad (4.56)$$

$$\begin{aligned}
& - \delta \left[\sum_{r_j=-2}^2 D_{r_j 0}^{(2)}(-\omega_1 \tau_j) \sum_{r_{j-1}=-2}^2 D_{r_{j-1} r_j}^{(2)}(-\alpha_{j-1}) \times \dots \right. \\
& \quad \left. \dots \times \sum_{r_2=-2}^2 D_{r_2 r_3}^{(2)}(-\alpha_2) \sum_{r_1=-2}^2 T_{2r_1} D_{r_1 r_2}^{(2)}(-\alpha_1) \right]
\end{aligned}
\tag{4.57}$$

The Wigner rotation matrix elements $D_{ij}^{(2)}(-\alpha)$ can be explicitly determined from the matrix in equation (2.47).

The toggling frame V_{20} Hamiltonian during a delay preceded by k pulses is:

$$\begin{aligned}
\delta \bar{T}_{20,k}^{(\text{delay})} = & \delta \left\{ \bar{R}_{\phi_1}^\dagger(\alpha_1) \bar{R}_{\phi_2}^\dagger(\alpha_2) \dots \bar{R}_{\phi_{k-1}}^\dagger(\alpha_{k-1}) \bar{R}_{\phi_k}^\dagger(\alpha_k) T_{20} \times \right. \\
& \left. \times \bar{R}_{\phi_k}(\alpha_k) \bar{R}_{\phi_{k-1}}(\alpha_{k-1}) \dots \bar{R}_{\phi_2}(\alpha_2) \bar{R}_{\phi_1}(\alpha_1) \right\}
\end{aligned}
\tag{4.58}$$

$$\begin{aligned}
& - \delta \left[\sum_{r_k=-2}^2 D_{r_k 0}^{(2)}(-\alpha_k) \sum_{r_{k-1}=-2}^2 D_{r_{k-1} r_k}^{(2)}(-\alpha_{k-1}) \times \dots \right. \\
& \quad \left. \times \dots \sum_{r_2=-2}^2 D_{r_2 r_3}^{(2)}(-\alpha_2) \sum_{r_1=-2}^2 T_{2r_1} D_{r_1 r_2}^{(2)}(-\alpha_1) \right]
\end{aligned}
\tag{4.59}$$

The zeroth order term in the Magnus expansion for this toggling frame Hamiltonian is a sum of T_{2m} operators with complex coefficients. The coefficients can be computed from the general expression:

$$\bar{V}_{20}^{(0)} = \frac{\delta}{T} \left\{ \sum_{j=1}^m \left[\int_0^{T_j} \bar{T}_{20,j}^{(\text{pulse})}(t) dt \right] + \sum_{k=1}^n \tau_k \bar{T}_{20,k}^{(\text{delay})} \right\} \quad (4.60)$$

$$= \delta \left[c_2^{(0)}(\vec{\phi}, \vec{\alpha}) T_{22} + c_1^{(0)}(\vec{\phi}, \vec{\alpha}) T_{21} + c_0^{(0)}(\vec{\phi}, \vec{\alpha}) T_{20} + \right. \\ \left. + c_{-1}^{(0)}(\vec{\phi}, \vec{\alpha}) T_{2-1} + c_{-2}^{(0)}(\vec{\phi}, \vec{\alpha}) T_{2-2} \right] \quad (4.61)$$

The calculation of the coefficients of the T_{2m} operators is simplified by inferring from the Hermiticity of $\bar{V}_{20}^{(0)}$ the relationship:

$$c_{-m}^{(0)}(\vec{\phi}, \vec{\alpha}) = (-1)^m c_m^{*(0)}(\vec{\phi}, \vec{\alpha}) \quad (4.62)$$

where the star denotes complex conjugation.

General expressions for higher order terms cannot be derived without assuming a size of the spin system. The commutators appearing in higher order terms mixes the spin operators in ways which generate T_{2m} components of higher dimensionality than $l = 2$. The maximum size l can attain is limited by the size of the spin system; for dipolar coupled spin-1/2 nuclei, l cannot exceed the number of interacting spins, while for an isolated quadrupolar nucleus, the maximum value of l is $2I$. A more rigorous discussion of this observation has been given by Tycko.³⁹

III. APPLICATIONS AND RESULTS

A. Radiofrequency field inhomogeneity

A computer search over $\vec{\phi}$ and $\vec{\alpha}$ for values satisfying the test criteria:

$$0 = \text{Tr} \left\{ I_z U_{rf}(\vec{\phi}, \vec{a}) I_z U_{rf}(\vec{\phi}, \vec{a}) \right\} \quad (4.63)$$

and:

$$0 \approx \bar{V}_{in}^{(0)} \quad (4.64)$$

led to the discovery of the three pulse composite $\pi/2$ sequence

$(90)_0(180)_{105}(180)_{315}$. Adding a third criterion:

$$0 \approx \bar{V}_{in}^{(1)} = 0 \quad (4.65)$$

required that a fourth pulse be added in order to simultaneously solve the necessary equations. One such sequence is

$(270)_0(360)_{169}(180)_{33}(180)_{178}$. The zeroth order term of the Magnus expansion for the three pulse sequence is:

$$\bar{V}_{in}^{(0)} = -\Delta\omega_1(0.0071)I_x \quad (4.66)$$

The zeroth and first order term for the four pulse sequence is:

$$\bar{V}_{in}^{(0)} = \Delta\omega_1 \left[(0.0001)I_x - (0.0002)I_z \right] \quad (4.67)$$

$$\bar{V}_{in}^{(1)} = -\frac{(\Delta\omega_1)^2}{\omega_1} (0.0003)I_y \quad (4.68)$$

Neither of these sequences has an rf propagator of the form $\mathcal{R}_\phi(\pi/2)$.

The criterion represented by (4.63) selects for a set of operators

$U_{rf}(\vec{\phi}, \vec{a})$ which contains rotation operators of the form $\mathcal{R}_\phi(\pi/2)$ as a

subset. The axis of the rotation for $(90)_0(180)_{105}(180)_{315}$ is the

vector (0.7746, 0.4472, 0.4472) and the angle of rotation 104.478° . For $(270)_0(360)_{169}(180)_{33}(180)_{170}$, the axis is (0.7106, -0.4975, -0.4975) and the angle 109.208° .

Experimental and theoretical data for the two sequences appear in figures 4.1 and 4.2, with simulated data for a single $\pi/2$ pulse drawn in for comparison. Two observations are apparent from these plots. The first is the obviously larger bandwidth of effective spin excitation of the composite $\pi/2$ pulses. An essentially unattenuated signal is obtained even if the rf amplitude is 50% lower or 50% higher than the presumptive value.

A second feature illustrated by these plots is a lessening of the phase distortion of the signal as N increases for $\hat{H}_N = 0$. Over a range of normalized rf amplitudes between zero and two times the nominal value ω_1^0 , the signal phase for $(90)_0(180)_{105}(180)_{315}$ varies by approximately 45° , while over a similar range of amplitudes for $(270)_0(360)_{169}(180)_{33}(180)_{178}$, the phase variation of the signal is less than 15° . The decrease in phase distortion is attributable to the higher order compensation of the rf inhomogeneity error in going from the three pulse sequence to the four pulse sequence.

B. Strong couplings in solids

In solid materials the coupling of abundant spins to one another or, for quadrupolar nuclei, to the local electric field gradient, is the dominant, internal rotating frame NMR interaction. Relatively few composite pulses have been proposed which explicitly take this kind of interaction into account. The principal cause of this lies in the more complicated form of an NMR Hamiltonian which includes spin-spin

18: 845-1697

Figure 4.1: Signal magnitude (a) and phase (b) following excitation by the composite $\pi/2$ pulse $(90)_0(180)_{105}(180)_{315}$ as a function of normalized rf field amplitude. Experimental data appear in dots and simulations in solid lines. The signal magnitude following a single $\pi/2$ pulse is drawn in a dark line in (a).

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Figure 4.2: Same as figure 4.1, but for the composite $\pi/2$ pulse $(270)_0(360)_{169}(180)_{33}(180)_{178}$. The amount of phase distortion diminishes significantly as the order of rf amplitude error compensation increases.

interactions. The NMR Hamiltonian for isolated spins, in the absence of quadrupolar interactions, is linear in the spin angular momentum operators I_x , I_y , and I_z . The Bloch equations without relaxation describe the motion of such systems, allowing the familiar and elementary interpretation of a pulsed NMR experiment as a series of rotations performed on a three dimensional vector.^{47,55} Composite pulses have been utilized in this context to overcome pulse imperfections related to the chemical shift or radiofrequency (rf) field inhomogeneity, but not internuclear couplings.

Inclusion of dipolar, quadrupolar, or J couplings introduces terms in the Hamiltonian which are bilinear in the spin angular momentum operators. The evolution of the spin system can therefore no longer be described as a rotation of the spin magnetization vector. Consequently, more sophisticated analyses are required to understand the interactions of the spins with the rf and with each other.

The sequences proposed in this section are designed to produce rotations of the form $R_\phi(\pi/2)$ and be insensitive to the kinds of internal spin interactions which exist in solids. The sequences presented here can excite nuclear spins over broader ranges of couplings than a simple solid echo, and without the need for a refocusing pulse. Moreover, these sequences consist only of pulses with easily calibrated lengths, i.e., $\pi/2$, π , or 2π pulses, permitting more convenient and accurate experimental implementation.

A novel feature of these composite pulse sequences is the inclusion of a delay of specified length at the end as an integral component of the sequence. The wide spectral bandwidths of solid state NMR spectra necessitates greater rf power and faster digitization of

the NMR transient than is typical in liquid experiments. These requirements directly conflict since high rf power unavoidably leads to harmful probe and receiver dead time. The usual solution to this situation is to employ a solid echo sequence to excite the NMR signal.⁶⁹⁻⁷² Indeed, versions of this experiment which utilize composite pulses have already been proposed for quadrupolar interactions. The differences between these composite echo sequences and the ones developed here will be enumerated fully further on, but the most important distinction will be made now: the sequences of this section do not use "refocusing" pulses to effectively reverse free evolution during one time period to cancel free evolution during another. The free evolution period for the sequences here instead cancels out part of the dipolar (or quadrupolar) evolution accumulated during the pulses themselves. This dead time period is part of the sequence, and thus makes the refocusing pulse unnecessary. This point and others will be discussed presently.

1. Suppression of dipolar and quadrupolar interactions

The theoretical procedures described in sections 4.II.A and 4.II.B can be employed to analytically derive multiple pulse sequences with an average dipolar Hamiltonian which either vanishes or is proportional to T_{20} . The two sequences detailed in figure 4.3 were discovered in this manner.

The first sequence is comprised of five phase shifted $\pi/2$ pulses and a delay at the end of duration $(5/4)t_p$, where t_p is the duration of a single $\pi/2$ pulse. The average dipolar and quadrupolar Hamiltonians are not zero, but are proportional to T_{20} . This sequence, to lowest

Figure 4.3: Composite $\pi/2$ pulses for solid state NMR with dead time compensation. The phase ϕ above is equal to $\cos^{-1}(-1/4) = 104.48^\circ$. The standard notation $\bar{\phi} = \phi + 180^\circ$ is used. The duration of a single $\pi/2$ pulse is denoted τ_p . For sequence I, $t_1 = (5/4)\tau_p$; for sequence II, $t_1 = (1/3)\tau_p$ and $t_2 = (11/6)\tau_p$. The composite pulses are not considered completed until after the last prescribed delays.

order, therefore satisfies the condition $[U_V(t), \rho_0] = 0$, where $\rho_0 \propto I_z$. The second sequence consists of the same five phase shifted $\pi/2$ pulses, but has three windows of well-defined length instead of one. The average dipolar Hamiltonian identically vanishes for this sequence. Although both sequences contain delays, free evolution periods are not necessary to obtain a vanishing average dipolar Hamiltonian. The windowless thirteen pulse sequence (with phases and flip angles given in degrees) $(90)_\alpha(180)_{\alpha+90}(90)_{\bar{\alpha}}(90)_{-\alpha}(180)_{(90-\alpha)}(90)_{-\bar{\alpha}}(90)_\beta(90)_{\bar{\beta}}(90)_{-\beta}(90)_{-\bar{\beta}}(90)_0(360)_\gamma(360)_{-\gamma}$, where $\alpha = 64.34^\circ$, $\beta = 104.48^\circ$, and $\gamma = 37.76^\circ$, for example, contains no delays, but has an average dipolar Hamiltonian equal to zero. The sequences are designated I, II, and III, respectively. The tabulated results appear in table 4.1.

Windowless, phase alternated schemes employing pulses with unusual flip angles have been proposed in unpublished work by Tycko.³⁹

These average Hamiltonian results were calculated with finite pulse lengths; that is, $\bar{V}(t)$ was integrated during both delays and pulses. As a result, the length of the delays in sequences I and II bear a fixed relationship to the $\pi/2$ pulse time t_p . This fact has been noted by Mehring in a similar calculation on the choice of optimal pulse spacings in solid state NMR line narrowing sequences.⁷³ A notable feature of the last two sequences is that the delay at the end is an integral part of both sequences. Free evolution of the spin system during this delay is essential for the vanishing of the average perturbation Hamiltonian.

This point is graphically verified by figure 4.4, which shows the powder average time domain signal from dipolar coupled pairs of nuclei peaking some time after the last rf pulse in the sequence (in this

Table 4.1: Average Hamiltonians for the three sequences shown in figure 4.3. The average quadrupolar Hamiltonians will be identical to the average dipolar Hamiltonians. The average shift Hamiltonian has been abbreviated, with the chemical shift $\Delta\omega_I$ and the summation over the spins omitted for clarity.

<u>Sequence</u>	<u>Average dipolar Hamiltonian</u>	<u>Average shift Hamiltonian</u>
I	$\frac{1}{10} \kappa_D$	$-\frac{1}{5} I_y + \frac{8}{5\pi} I_z$
II	0	$-\frac{2}{9} I_y + \frac{4}{3\pi} I_z$
III	0	$(0.1093)I_y + (0.2728)I_z$

Figure 4.4: Computer simulations of the powder averaged free induction decay immediately following (A) a single $\pi/2$ pulse and (B) the composite pulse labeled as I in figure 4.1. The Fourier transform of these time domain signals is the familiar Pake doublet, with a maximum splitting of 72 kHz. The rf amplitude for both simulated experiments is 72 kHz. After a single $\pi/2$ pulse, the signal is at a maximum, and damps quickly and monotonically. The signal for the composite $\pi/2$ pulse, however, reaches its maximum some time after the last pulse, reflecting the fact that the sequence is not over until some delay after the pulse. The amplitudes of both signals are scaled by the same amount to show that there is no loss of intensity for the composite pulse compared to the strong if single pulse.

case, the sequence I). By comparison, the FID for a single $\pi/2$ pulse attains its maximum amplitude immediately after the pulse. The signal originating from the composite pulse has not been "refocused" in the usual sense. During the last delay, free evolution reverses the preceding dipolar evolution occurring during both the delays and the pulses.

ii. Simulations

The efficacy of these sequences at extending the excitation bandwidth of dipolar broadened lines for a given level of rf power may be ascertained in several ways. The first consists of conventional computer simulations of the NMR spectra of two dipole-dipole coupled spin-1/2 nuclei for varying rf strengths. The ensemble of spin pairs is assumed to have an isotropic distribution of orientations. This so-called powder averaging results in a lineshape corresponding to the well-known Pake doublet. The ease of computing this spectrum exactly, its resolved structure, its familiarity, and its applicability to quadrupolar systems make this an ideal test case for judging composite pulse performance in solids.

Simulated Pake patterns are displayed in figure 4.5. An exact calculation of the dynamical evolution of the density operator for two coupled spin-1/2 nuclei was performed for the evaluation of these Pake patterns. The effects of dipolar evolution during the pulses were included explicitly in this computation. The splitting of the two singularities is 16 kHz, and the homogeneous line broadening 400 Hz. The line remains relatively undistorted with an rf amplitude of only 75% of the line splitting, and appears superior to a two pulse solid

Figure 4.5: Computer simulations of powder averaged NMR spectra for pairs of dipole-dipole coupled spin-1/2 nuclei assuming detection by (A) a conventional solid echo sequence $(\pi/2)_x - t_1 - (\pi/2)_y - (t_1 + t_p)$, and (B) the composite $\pi/2$ pulse II. The splitting is 18 kHz. The rf strengths ω_1 for each pair of spectra are as indicated in the middle.

echo sequence at low power levels at preserving the overall symmetry of the lineshape.

A second, perhaps more sensitive, way of viewing lineshape distortions due to incomplete excitation is with a transfer function. The transfer function and some of its properties are considered in detail in the Appendix A and in reference 74. The "ideal", undistorted lineshape $F_I(\omega_D)$ used in the calculation of the transfer function is defined as the lineshape for two coupled spin-1/2 nuclei with a continuum of dipole coupling constants, each of equal probability. The function $F_I(\omega_D)$ may be represented mathematically as:

$$F_I(\omega_D) = 1 \quad -1.0 \leq \omega_D/\omega_1 \leq 1.0 \quad (4.69)$$

$$F_I(\omega_D) = 0 \quad \omega_D/\omega_1 \geq 1.0 \text{ or } \omega_D/\omega_1 \leq -1.0 \quad (4.70)$$

Individual spin packet transitions within the region where $F_I(\omega) = 1$ are broadened by 1/100 of the entire spectral bandwidth. These assumptions have significant implications for the form and generality of the transfer function, and are discussed fully in Appendix A.

The enlargement of the excitation bandwidth for the compensated sequences compared to an uncompensated single pulse is made plain by the transfer functions in figure 4.6. The composite $\pi/2$ pulse does well compared to a regular solid echo as well, and is actually superior in the regions near the center of the spectrum.

Further theoretical tests of the performance of composite $\pi/2$ pulse II appear in figure 4.7, 4.8, and 4.9. Figure 4.7 shows simulations of population inversion as a function of dipole coupling strength achieved by the composite $\pi/2$ pulse II applied two times in

Figure 4.6: Calculated transfer functions for two dipolar coupled spin-1/2 nuclei with a continuum of equally probable dipole coupling constants, as given by equations (4.69) and (4.70). The lineshapes used for the calculation of these functions were in (a) the perfect, undistorted lineshape; in (b) the lineshape following excitation by the solid echo sequence $(\pi/2)_0 - t_1 - (\pi/2)_{90} - t_2$; in (c) the lineshape resulting from excitation by a single $\pi/2$ pulse; and in (d) the lineshape obtained by the composite $\pi/2$ pulse numbered II.

Figure 4.7: Simulation of population inversion as a function of the dipole coupling normalized to the rf field amplitude ω_1 for two coupled spin-1/2 nuclei. The spin density operator has an initial value $-\langle I_z \rangle$. In the solid line is the result for a single π pulse, in the dashed line is the result for the composite $\pi/2$ pulse labeled II in figure 4.3 given twice in a row.

Figure 4.8: Same as figure 4.7 for a system consisting of four dipole coupled spin-1/2 nuclei arranged in a square. The solid line corresponds to the inversion following a single π pulse, and the dashed line to the inversion of the composite $\pi/2$ pulse II given twice in a row.

Figure 4.9: Simulation of the projection onto I_y of the spin density operator as a function of the dipole coupling constant normalized to the rf amplitude ω_1 for four spin-1/2 nuclei arranged in a square. The solid line is the result for a single $\pi/2$ pulse, and the dashed line for the composite $\pi/2$ pulse labeled II.

succession. The inversion produced by a single π pulse is drawn in a solid line for comparison. A dipole-dipole coupled spin pair with a continuum of equally probable dipole coupling constants was assumed in these simulations. Figure 4.8 shows the same for four spins arranged in a square, with dipole couplings equal between spins in adjacent corners. For the two spin case, and, to a lesser extent, the four spin case, the inversion produced by the composite $\pi/2$ pulse has a noticeably broader effective bandwidth of inversion than a single pulse. A plot of the $\langle I_y \rangle$ component of the transverse signal for a composite $\pi/2$ pulse and a single $\pi/2$ pulse as a function of normalized dipole coupling strength is depicted in figure 4.9. Again, the spin system is a set of four spins arranged in a square. The composite pulse's performance is slightly better for a range of dipole coupling strengths, but degenerates quickly outside this range.

iii. Experimental results

The simulations of the previous subsection are verified by experiments performed on protonated and perdeuterated hexamethylbenzene (HMB), displayed in figures 4.10 and 4.11. All spectra are averages of 256 scans, with a recycle delay between scans of 3 s. The first delay for the proton solid echo data was 15 μ s; for the deuterium echo data, this delay was 30 μ s. The second delay for the echo data was set using a standard finite pulse width correction,^{72,74} and thus varied for each level of rf amplitude. The effective deuterium dipole-dipole coupling constants are sufficiently weak and the methyl group rotation sufficiently fast so that the deuterons on the methyl groups in perdeuterated HMB can be considered equivalent, isolated spin-1 nuclei

Figure 4.10: Proton spectra of hexamethylbenzene, obtained with a $(\pi/2)_0 - t_1 - (\pi/2)_{90} - t_2$ sequence and the composite $\pi/2$ pulse labeled II. The rf amplitudes used in these experiments, shown in the middle, are approximately 3/2, 1, and 3/4 times the full linewidth of the inhomogeneously broadened resonance.

Figure 4.11: Deuterium spectra of perdeuterated hexamethylbenzene obtained with a $(\pi/2)_0 - \tau_1 - (\pi/2)_{90} - \tau_2$ solid echo sequence and the composite $\pi/2$ pulse II. The rf amplitudes are indicated by the numbers in the middle, and are approximately 3/2, 1, and 3/4 times the main splitting of the Pake pattern.

with a relatively small quadrupolar splitting of 16 kHz. These same factors result in a narrow but structureless proton resonance line. Although the proton dipole coupling is attenuated by fast motion in HMB, it is nevertheless a many spin network.⁷⁵

The experiments corroborate the conclusion indicated in the simulations that the composite $\pi/2$ pulse with deadtime compensation is at least as effective as the quadrupolar echo at low power levels. The theoretical calculations, indeed, reproduce many of the subtle features and asymmetries appearing in the experimental data.

The proton data in figure 4.10 reveal a fact not accounted for in a simulation, which is that there is frequently a loss in signal intensity in solid echo experiments due to imperfect refocusing and irreversible relaxation of the FID. The composite pulse spectra, plotted on the same intensity scale, show significantly more signal than the spectra obtained by a solid echo experiment, even though the duration of both experiments was approximately equivalent.

iv. Chemical shift scaling

The average Hamiltonian treatment given so far applies generally to perturbation terms with the rotational symmetry properties of the irreducible tensor operator T_{20} . An important interaction found in solids which does not transform under rotations as T_{20} is the chemical shift. Though typically not as large in solids as the dipolar or quadrupolar coupling, the effect of this term on the performance of composite pulses is nevertheless a significant concern. An average Hamiltonian analysis of this term is the topic of this section.

The chemical shift transforms under rotations as the operator I_z ,

hence, the average chemical shift Hamiltonian will be a sum of I_x , I_y , and I_z with real coefficients. Following the general procedure outlined in section 4.II.B, average shift Hamiltonians were calculated for each of the sequences presented here, with the results appearing in table 4.1.

These results show that in lowest order, the effect of the chemical shift appears as a rotation of the spin density operator about an axis in the plane perpendicular to the x-axis. The x-axis, incidentally, is the axis of the rotation described by $U_{rf}(\vec{\phi}, \vec{a})$. The angle of rotation depends linearly on the chemical shift $\Delta\omega$.

The worst effects of the chemical shift interaction can be reduced by making simple modifications to sequences I and II. One solution is to include a $(\pi)_0$ "refocusing" pulse at the end of both sequences. The resultant sequence for II appears in figure 4.12. It is important to observe that this modification does not fundamentally alter $U_{rf}(\vec{\phi}, \vec{a})$; it remains a rotation operator of the same general form as in equation (4.2). With the pulse and delay times as indicated on the figure, the average dipolar Hamiltonian for sequence I becomes $(13/58)\hbar_D$, while the average shift Hamiltonian becomes $(24/29\pi)\hbar_{CS}$. Inclusion of this refocusing pulse is thus seen to result in an average shift Hamiltonian which commutes with I_z . To lowest order, then, the condition $[U_V(t), I_z] = 0$ is fulfilled, for both dipolar and shift Hamiltonians. Similarly, for sequence II, the average dipolar Hamiltonian remains zero, while the average shift Hamiltonian reduces to $(4/7\pi)\hbar_{CS}$. These results are summarized in table 4.2.

Further modifications can probably be found to totally eliminate the average shift Hamiltonian, but these may be undesirable for several

Figure 4.12: Composite $\pi/2$ pulse with compensation for deadtime, dipole couplings, and chemical shifts. All pulses except the last are $\pi/2$ pulses, with the same phases as for II in figure 4.3; the last is a π pulse with zero phase. The following delay times are indicated: $t_1 = (13/15)t_p$; $t_2 = (11/10)t_p$; and $t_3 = (2/3)t_p$, where $t_p = \pi/2\omega_1$.

Table 4.2: Average Hamiltonians of modified versions of sequence I and II. The modifications embodied by sequences IA and IIA were made to suppress chemical shift effects.

<u>Sequence</u>	<u>Average dipolar Hamiltonian</u>	<u>Average shift Hamiltonian</u>
IA	$\frac{13}{58} \hbar_D$	$\frac{24}{29\pi} \hbar_{cs}$
IIA	0	$\frac{4}{7\pi} \hbar_{cs}$

reasons. Foremost of these is the fact that any modification will inevitably make the sequence longer and more complicated, leading to larger higher order terms in the Magnus expansion and greater difficulty with experimental implementation. The larger higher order terms may, indeed, offset any benefit gained by a vanishing average shift Hamiltonian. A second reason for leaving the average shift Hamiltonian unchanged stems from the idea of second averaging.^{4,76} Large terms proportional to I_z in $\bar{V}^{(0)}$ have been shown to truncate higher order terms in the Magnus expansion, leading to, e.g., measurably superior performance of line narrowing sequences when the rf carrier frequency is moved off resonance. A nonzero average shift Hamiltonian proportional to I_z can thus actually serve a beneficial purpose in further suppressing evolution due to dipolar interactions.

To conclude this section, it has been established that suppression of dipolar and quadrupolar interactions by these sequences is not necessarily gained at the expense of increasing spectral distortions due to the chemical shift. In fact, the effect of this interaction can be explicitly minimized by simple modifications of these sequences. These modifications, importantly, do not fundamentally change the form of the net rf propagator, leaving it an effective $\pi/2$ rotation.

v. Other refinements

The rf pulse times chosen for these sequences were restricted to integer multiples of the $\pi/2$ pulse time largely as a matter of experimental convenience. If the pulse times are short and the pulse programmer bandwidth too small, this goal is partially defeated by the

unusual delay times appearing within some of the composite pulses. A simple average Hamiltonian calculation indicates, however, that minor alterations can be made to the delay times to enable more convenient experimental usage without appreciably impairing the desirable bandwidth properties of the sequences.

The effects of some of these changes on the average dipolar and shift Hamiltonians can be seen in table 4.3. Transfer function calculations of these modified sequences support the conclusion that the effects of the modifications are minor.

vi. Calculation of higher order terms in the Magnus expansion

In the calculation of the zeroth order term of the Magnus expansion, the size of the spin system was not specified. This is because the only information needed to evaluate this term is the transformation behaviour of V_R under rotations, which is independent of the size of the spin system. The same is generally not true for higher order terms. These terms all involve commutators of $\bar{V}$ with itself but at different times. If V_R includes terms bilinear in spin angular momentum operators, the number of uncoupled spins must be stipulated in order to calculate higher order terms in the Magnus expansion.

An additional complication arises because of the type of pulse sequences considered in this chapter. Frequently, theorems based on the symmetry of the toggling frame Hamiltonian $\bar{V}(t)$ can be exploited to simplify calculation of higher order terms.^{2,40,62,63} For example, if $\bar{V}(t)$ is symmetric in time, all odd order terms in the Magnus expansion identically vanish. However, the toggling frame Hamiltonian of an anisotropic term such as the dipolar coupling cannot be made symmetric

Table 4.3: Effect on the average Hamiltonians of rounding the delay times in sequences I, II, and IIA. The adjusted delay times in the fourth column are given relative to the $\pi/2$ pulse time, designated as t_p . The modified version of I is IB, the modified version of II is IIB, and the modified version of IIA is IIAB. The average Hamiltonians below have been abbreviated, with coupling constants, chemical shifts, and the summation over spins all omitted for clarity. Thus, the average dipolar Hamiltonian column shows the average value of the toggled T_{20} operator, while the average shift Hamiltonian column contains the average value of the toggled I_z operator.

<u>Sequence</u>	<u>Average dipolar Hamiltonian</u>	<u>Average shift Hamiltonian</u>	<u>Adjusted delay times</u>
IB	$\frac{1}{8} T_{20} + \frac{1}{48} \left[\frac{3}{2} \right]^{1/2} [T_{22} + T_{2-2}]$	$-\frac{1}{6} I_y + \frac{5}{3\pi} I_z$	$t_1 = t_p$
IIB	$-\frac{1}{32} T_{20} + \frac{1}{128} \left[\frac{3}{2} \right]^{1/2} [T_{22} + T_{2-2}]$	$-\frac{7}{32} I_y + \frac{5}{4\pi} I_z$	$t_1 = \frac{1}{2} t_p; t_2 = 2t_p$
IIAB	$\frac{1}{44} T_{20}$	$\frac{1}{22} I_y + \frac{6}{11\pi} I_z$	$t_1 = t_2 = t_3 = t_p$

if the net rf propagator is of the form in equation (4.2). For such sequences, the initial and final state of the toggled Hamiltonian must be different, precluding symmetrization (an exception arises for the case where $U_{rf}(t)$ commutes with V_R ; this possibility is neglected here). Although the toggling frame Hamiltonian for the overall sequence is not symmetric, $\bar{V}(t)$ may be symmetric for certain time intervals. The first order term for sequence II, for example, can be divided as follows:

$$\bar{V}^{(1)} = -\frac{i}{2\tau} \left\{ \int_0^{2\tau_P + \tau_1} dt' \int_0^{t'} [\bar{V}(t'), \bar{V}(t'')] dt'' + \int_{2\tau_P + \tau_1}^{\tau} dt' \int_0^{t'} [\bar{V}(t'), \bar{V}(t'')] dt'' \right\} \quad (4.71)$$

The first term is an integral over a symmetric subsequence and thus vanishes. Other occurrences of symmetry within the sequence can be similarly searched for and exploited.

In general, though, calculation of even a first order correction is tedious, and must involve at some stage an assumption about the size of the spin system.³⁹ The smallness of this term for some of these sequences can be approximately verified by assuming that the dipolar couplings are predominantly arranged in pairs. Note that this is not equivalent to assuming that the spin pairs have the same coupling constant but different orientations with respect to the field. It should be emphasized, however, that such a calculation can only be regarded as an estimate of the true first order term.

vii. Coherent averaging analysis of the quadrupolar echo

Composite $\pi/2$ pulses for strongly coupled spin systems have appeared previously in work by Levitt, et al.,³² and Siminovitch, et al.³⁴ The sequences they presented were designed for use in a specific experiment, i.e., the quadrupolar echo. A sketch of this experiment appears in figure (4.13). The variation on this basic experiment they proposed was to substitute a composite $\pi/2$ pulse for the first, excitation pulse and second, refocusing pulse. These composite pulses were calculated using a fictitious spin-1/2 formalism,⁷⁷⁻⁷⁹ which, as Levitt, et al., have shown, leads to the conclusion that a broadband composite π pulse can be adapted for broadband quadrupolar echo excitation of spin-1 nuclei simply by halving the durations of all the pulses. The sequences that result are quite effective at obtaining undistorted quadrupolar broadened spectra with rf amplitudes as small as 85% of the main quadrupolar splitting.

In spite of their similarities, these composite pulses differ from the ones presented here in several fundamental respects. The first is that the composite echo pulses are compensated for quadrupolar evolution during the pulses only when used in tandem in an echo experiment. If an FID is recorded after just one of these composite $\pi/2$ pulses, without a 90° phase shifted partner to refocus free evolution, a profoundly distorted lineshape is obtained, even for relatively small quadrupolar splittings.⁸⁰ Hence, such sequences cannot be used effectively by themselves as composite $\pi/2$ pulses. This limits them to a single purpose, i.e., the quadrupolar echo experiment. It is conceivable that such composite pulses can be used in an

Figure 4.13: The solid echo experiment. The first pulse group is a composite $\pi/2$ pulse with an overall phase of 0° . The second pulse group is also a composite $\pi/2$ pulse group with an overall phase of 90° . The second delay is not necessarily the same as the first, nor do the two pulse groups have to be phase shifted versions of one another (see text).

experiment requiring pairs of $\pi/2$ pulses phase shifted by 90° to one another as in a WAHUA cycle. If kept together in pairs, these sequences might extend the effective range of coupling constants at a given rf amplitude for some of these experiments. However, this application has not been demonstrated.

The necessity of combining these composite $\pi/2$ pulses in paired units points to a second major distinction between these sequences and the sequences developed in this paper. The pairing of these sequences means that the overall rf propagator of the compensated echo sequence will be:

$$U_{\text{rf}}(\vec{\phi}, \vec{\alpha}) = \exp \left\{ - \frac{2\pi i}{3\sqrt{3}} \left[-I_x \pm (I_y + I_z) \right] \right\} \quad (4.72)$$

depending on whether the refocusing pulse group is -90° or $+90^\circ$ out of phase with the first pulse group. The difference between this rf propagator and the one in equation (4.2) corresponding to a true $\pi/2$ rotation is apparent. The rotation described by (4.72), when performed on magnetization at equilibrium, aligned with the static magnetic field, has the same ultimate effect as a sequence with the rf propagator in (4.2). The two propagators are not generally interchangeable, however. The fact that the paired sequences have this net rf propagator makes them unsuitable for multiple pulse experiments which require true $\pi/2$ rotations of the density operator or where the spin system is not at equilibrium.

A third difference of these sequences lies in their derivation. The method used to derive these sequences was directed to a particular spin system, that is, an anharmonic three level system, typified in NMR

by an isolated spin-1 nucleus. The analysis holds for two dipolar coupled spin-1/2 nuclei as well, but evidently not for larger coupled spin networks. To first order, this is not a limitation of the coherent averaging approach, which makes no reference to the size of the spin system.

Numerical computations of the average quadrupolar and chemical shift Hamiltonians for compensated echo sequences appear in table 4.4. Echo delays of $t_1 = t_2 = 0$ were selected for these calculations. A surprising fact revealed by this table is that none of the echo sequences results in a vanishing average quadrupolar Hamiltonian. The residual chemical shift is quite significant for each sequence as well. Although the choice of refocusing times used here is clearly not optimal, it can readily be demonstrated from the results in table 4.4 that no set of refocusing times can be found for any of these sequences which completely eliminates the average quadrupolar or shift Hamiltonian.

Within the context of coherent averaging theory, two criteria can be imagined for deciding optimal refocusing times for these experiments. One way to estimate the proper refocusing time is to consider the five T_{2m} operators as basis vectors in a five dimensional space, and to regard as the "best" echo times the choice of t_1 and t_2 which minimizes the norm of the average quadrupolar Hamiltonian vector. A second, related, way is to ignore the T_{20} component and concentrate on minimizing the norm of the other four basis vectors. A nonzero T_{20} component in the average quadrupolar Hamiltonian can be tolerated, since terms with this symmetry commute with the presumed initial density operator I_z .

Table 4.4: Average quadrupolar and chemical shift Hamiltonians for composite quadrupolar echo experiments. The following composite $\pi/2$ pulses were used in the echo: for sequence IV, $(3\pi/4)_0(\pi/2)_\pi(\pi/4)_0$; for sequence V, $(\pi/2)_0(\pi)_\pi(\pi/2)_0(3\pi/4)_\pi(\pi/4)_0$; for sequence VI, $(3\pi/4)_0(\pi)_\pi(\pi/2)_0(3\pi/4)_\pi(\pi/4)_0(\pi/2)_\pi(\pi)_0(\pi/2)_\pi(3\pi/4)_0$; and for sequence VII, $(3\pi/4)_0(\pi)_\pi(\pi/2)_0(3\pi/4)_\pi$. The echo times chosen for these calculations were $t_1 = t_2 = 0$. Again, coupling constants, chemical shifts, and the summation over spins have been suppressed for clarity. The coefficients of T_{2-1} and T_{2-2} are not included, but can easily be determined from equation (4.62).

<u>Sequence</u>	<u>Average quadrupolar Hamiltonian</u>			<u>Average shift Hamiltonian</u>		
	<u>operator coefficients</u>			<u>operator coefficients</u>		
	T_{20}	T_{21}	T_{22}	I_x	I_y	I_z
IV	-0.2842	-0.0650	-0.0881 + 0.0650i	0.4062	-0.5123	0.1061
V	-0.1648	0	-0.1368	-0.1281	0.3622	0.2342
VI	-0.1051	0	-0.1612	-0.0110	-0.2562	0.2671
VII	-0.0852	0	-0.1693	0.1281	0.1501	0.2781

It is possible with the proper choice of echo times to eliminate all T_{2m} components in the average quadrupolar Hamiltonian except the T_{20} component for sequences V, VI, and VII. This satisfies the second criterion above. However, it is not possible to make vanish the $T_{2\pm1}$ components for sequence IV. These components are partly responsible for the serious spectral distortions arising from antiphase magnetization, as noted by Siminovitch, et al., in their analysis of this sequence. Consequently, this sequence has been found, experimentally and theoretically, to be least satisfactory of the four in table IV.

As an example of how coherent averaging theory can be used to choose optimal refocusing times, consider the case of a quadrupolar echo experiment employing single $\pi/2$ pulses. The average quadrupolar Hamiltonian for the sequence in figure (4.13) with S equal to a single $\pi/2$ pulse is proportional to:

$$\begin{aligned} \bar{V}_Q^{(0)} \propto & \frac{\omega_Q}{2\tau_p + \tau_1 + \tau_2} \left\{ \left[-\frac{1}{2} (\tau_1 + \tau_2) - \frac{1}{4} \tau_p \right] T_{20} \right. \\ & - \frac{1\tau_p}{\pi} \left[\frac{3}{2} \right]^{1/2} (T_{2-1} + T_{21}) \\ & - \left[\left[\frac{3}{8} \right]^{1/2} \tau_p \left[\frac{1}{2} - \frac{2i}{\pi} \right] + \left[\frac{3}{8} \right]^{1/2} (\tau_1 - \tau_2) \right] T_{22} \\ & \left. - \left[\left[\frac{3}{8} \right]^{1/2} \tau_p \left[\frac{1}{2} + \frac{2i}{\pi} \right] + \left[\frac{3}{8} \right]^{1/2} (\tau_1 - \tau_2) \right] T_{2-2} \right\} \end{aligned} \quad (4.73)$$

The magnitudes of the T_{22} and T_{2-2} coefficients are minimized

when

$$t_2 = t_1 + (1/2)t_p \quad (4.74)$$

The magnitude of the T_{20} coefficient is additionally minimized if $t_1 = 0$. The correct result in the δ pulse limit is obtained by letting t_p go to zero, but even in this ideal limit, $\bar{V}_Q^{(0)}$ does not vanish, but is proportional to T_{20} .

These observations are corroborated by the findings of Bloom, et al.,^{71,72} and Murdoch,⁷⁴ who were able to show by other means that the correct choice of echo times can be determined from the relation (4.74) above. Although the average Hamiltonian calculation predicts an optimal t_1 delay of zero, this choice, in practice, is not feasible since the dead time recovery period this allows of one half the $\pi/2$ pulse time is too short for most high power NMR probes.⁸¹

A similar calculation can be easily performed for the composite echo sequences of Levitt, et al. and Siminovitch, et al., using the average Hamiltonian results in table 4.4. These computations agree well with the theoretical expression derived by Levitt, et al., for phase alternated composite $\pi/2$ pulses. However, such calculations are usually not meaningful for a variety of reasons. One reason is that the echo time t_2 is typically a sensitive function of the rf amplitude ω_1 . Although ω_1 can, in principle, be inferred from the $\pi/2$ pulse time, pulse imperfections frequently make it difficult to determine ω_1 from this pulse length with enough accuracy to be used as a basis for selecting the t_2 echo time. Furthermore, the optimal refocusing times, defined as the times which lead to the least distorted spectrum and maximum signal intensity, will depend on experimental conditions such

as the ratio of ω_1 to the quadrupolar splitting, the lineshapes and intensities in the spectrum, the Q of the probe, signal propagation delays in the rf receiver, or the composite sequences used. The dependence on these factors largely arises from the asynchronous refocusing of spin packets with different quadrupolar frequencies, and cannot easily be accounted for in most calculations of the type presented here and elsewhere. Though these calculations can provide good initial guesses for refocusing times, the most accurate and practical method for determining these times remains experimental trial and error.

Alternatively, elaborate phase cycling schemes may be employed to reduce spectral distortions occurring in quadrupolar broadened lineshapes with low rf power.⁸² However, a significant loss of signal to noise accompanies the use of such schemes owing to the cross addition of signals not in phase with another. A hybrid of composite pulse excitation and phase cycling of echo transients offers perhaps the best solution for minimizing spectral distortions due to incomplete excitation of an inhomogeneously broadened line.

IV. CONCLUSION

The work presented in this Chapter establishes that efficient excitation of transverse coherence in NMR over broad ranges of radiofrequency amplitudes, and dipolar and quadrupolar couplings can be accomplished with relatively simple sequences consisting only of $\pi/2$ pulses and delays. The effective rf propagator of most of these sequences is a $\pi/2$ rotation operator about the x axis, allowing these sequences to be substituted for a single $\pi/2$ pulse in any multiple

pulse experiment requiring a $\pi/2$ rotation of the spin density operator. They can thus be used in both simple experiments, such as excitation of an FID, and in more complicated multiple pulse applications, such as line narrowing sequences.

The incorporation of a delay at the end of some of these sequences is a unique and useful property of these composite pulses, particularly for solid state NMR. The delays for the sequences derived here are perhaps short compared to the blocking times for most high power NMR probes, but can sometimes be increased by lengthening other delay times within the composite pulse. Short delay times do have the advantage, however, of minimizing attenuation of the NMR signal due to irreversible spin relaxation, and cannot be increased arbitrarily.

Although the delay makes echo detection largely unnecessary, these sequences can obviously be used for that purpose. Because dipolar evolution of the spins during the irradiation period is effectively nulled, the echo times t_1 and t_2 will be approximately equal. This is confirmed by solid echo simulations substituting the sequences here for the two $\pi/2$ pulses.

Compensation for chemical shift effects has also been demonstrated for some of these sequences, thereby reducing the spectral distortions associated with being off resonance. This problem can be especially acute in composite pulse excitation of a spectrum with many lines, since the increased irradiation period of a sequence of pulses can occasionally exacerbate the observed effects of uncompensated perturbations.

Improvement of these sequences by the coherent averaging approach will depend mainly on minimizing higher order terms in the Magnus

expansion of $\bar{V}(t)$. The complications arising from higher order terms were briefly described; it is expected that any calculation of these terms will rely heavily on a combination of more sophisticated computational techniques (such as iterative maps),²⁴ simplifying approximations, theorems based on the properties of the Magnus expansion, and perhaps artificial intelligence software. A small zeroth order term is a necessary prerequisite, however, and consideration of this term by itself can lead to sequences with considerably improved excitation characteristics.

CHAPTER FIVE: ITERATIVE MAPS ON $SO(3)$

I. INTRODUCTION

Composite pulses can be derived by stipulating that a sequence of pulses fulfill certain criteria, and selecting only those phases, flip angles, delay durations, and other pulse parameters which meet the stated criteria. In the coherent averaging theory procedure of the previous chapter, the criterion for the selection of these parameters consisted of a system of nonlinear equations to be solved. Other methods have been developed which take a similar approach, but which employ slightly different criteria for deciding the suitability of a pulse sequence.

Broadband composite pulses devised by such techniques are effective over substantially wider ranges of transition frequencies, rf amplitudes, and spin coupling constants than single pulses at a given level of rf power. Despite this success, formalisms based on this general approach are deficient in several crucial respects. One drawback is that a sequence of discrete pulses and delays rapidly becomes impractical to analyze and derive as the number of pulses increases. This point can be appreciated by re-examining the equations in section 4.II which must be evaluated and solved in order to determine an approximate expression for $U_V(\vec{\phi}, \vec{\alpha}, \vec{\tau}, \vec{\lambda})$. For some applications, this is not a serious limitation since a small number of pulses might suffice to bring about the desired response anyway. For other, more demanding, applications, however, a large number of pulses

is essential. Many pulses may be required, for instance, in an experiment where the effects of some perturbation must be suppressed to a very high order. A notable example of this is heteronuclear decoupling in liquid state NMR.⁸³⁻⁹¹ The high resolution attainable in such experiments necessitates a decoupling scheme capable of eliminating the observed effects of carbon-proton J couplings to a very high degree. It is difficult to envision how an approach requiring an explicit integration of Schrödinger's equation, as is effectively done in coherent averaging theory, could be applied to determine such a sequence. The number of equations to be solved and the complexity of higher order terms in the Magnus expansion make this an intractable problem for coherent averaging theory.

A second shortcoming of coherent averaging theory and related approaches is that few provide any guidance on how to derive sequences with something besides a broadband response. A more useful sequence in some experiments in NMR, for example, would be one which was effective over a specific, tailored bandwidth rather than a merely broad bandwidth.⁹²⁻⁹⁵ Moreover, some of these experiments, like heteronuclear decoupling in liquids, and narrowband and bandpass excitation, may inherently require large numbers of pulses, necessitating a correspondingly more complicated analysis. This subject is examined more closely in the next chapter.

Iterative schemes^{24,40} represent a fundamentally different way of addressing the derivation of composite pulses. Long, highly refined sequences can both be constructed and studied by an iterative scheme analysis. An iterative scheme is a set of operations which can be applied to an arbitrary pulse sequence S_i to generate a new sequence

S_{i+1} :

$$f(S_i) = S_{i+1} \quad (5.1)$$

The propagator $U(\vec{\phi}_i, \vec{\alpha}_i, \vec{\lambda})$ for S_i is accordingly transformed:

$$F(U(\vec{\phi}_i, \vec{\alpha}_i, \vec{\lambda})) = U(\vec{\phi}_{i+1}, \vec{\alpha}_{i+1}, \vec{\lambda}) \quad (5.2)$$

The propagator determining the time evolution of the sequence has been written $U(\vec{\phi}_i, \vec{\alpha}_i, \vec{\lambda})$ to signify the dependence of the time evolution of the system on the parameters of both the spin system and the incident radiation. Since $\vec{\lambda}$ may vary for different spins in the sample, it is possible for $U(\vec{\phi}_i, \vec{\alpha}_i, \vec{\lambda})$ to assume a distribution of values at the end of the pulse sequence. One of the basic objectives of broadband composite sequence design is to derive sequences for which $U(\vec{\phi}_i, \vec{\alpha}_i, \vec{\lambda})$ assumes a specific form after the pulse sequence, and is insensitive to the value of $\vec{\lambda}$.

From these basic definitions, iterative schemes may be viewed as algorithms which can be applied repetitively to generate a sequence of iterates S_0, S_1, S_2 , etc. These algorithms are comprised of transformations selected to improve arbitrary pulse sequences with respect to some stated criterion, such as the broadband inversion of spin populations. One possible transformation, for example, would be to add some constant amount to the phases of all the pulses. Other transformations which have been suggested in the past include the concatenation of pulses, the cyclic permutation of pulses, and the formation of inverse sequences.^{21,24,30,40,87,90}

The transformation of a pulse sequence to another pulse sequence

has been represented mathematically by equation (5.2) as a transformation of the time development operator corresponding to the first pulse sequence to the time development operator corresponding to the second pulse sequence. The operation represented by the function F can thus be regarded as a function which maps points on a propagator space L to other points on the same space. A special feature of such functions, as summarized by equation (5.2), is that they can be applied iteratively. Well established formalisms and ideas exist to study and unify the theory of iterative schemes in NMR. In the next section, a short synopsis of some general and useful topics in the mathematics of iterated functions is provided. More complete and rigorous definitions introduced there can be found in several texts and articles,⁴¹⁻⁴⁶ but for the ensuing discussion it will be helpful to briefly review some of the more important concepts. A description of how these ideas may be adapted to iterative schemes in NMR follows, and a specific example, namely, iterative schemes for generating propagators of the form $\mathcal{R}_\phi(\pi/2)$, treated in depth in the latter part of the Chapter.

A. One dimensional iterated functions

The properties and behaviour of the iterates of a function constitute the dynamics of the function. The dynamics of iterated functions can be rich and complex, even for elementary nonlinear functions on one dimensional, bounded intervals.^{41,45} Despite the global complexities exhibited by an iterated function, certain points of equilibrium known as fixed points can exist. If such points exist, the identification and characterization of these points greatly simplifies the description of a function's dynamics in their vicinity.

Fixed points of a function are defined by the equality:

$$\bar{U} = F(\bar{U}) \quad (5.3)$$

These points may be classified according to their stability.⁴¹⁻⁴⁶ The stability of a fixed point refers to the effect the function has on points in the neighborhood of the fixed point. Operationally, a fixed point is considered stable if points in the neighborhood of the fixed point remain in the neighborhood of the fixed point for all time, i.e., as the map is iterated to infinity. If, as the number of iterations goes to infinity:

$$\lim_{i \rightarrow \infty} U_i = \bar{U} \quad (5.4)$$

then $\bar{U}$ is said to be an asymptotically stable fixed point of F .^{44,46} For brevity, the term stability will be used henceforth to refer to asymptotic stability. For the special case of a function on the one dimensional space $\mathbb{R}^1$, the derivative of the function at stable fixed points obeys the inequality:

$$\left| \frac{dF}{dU} \right|_{U=\bar{U}} < 1 \quad (5.5)$$

The fixed point is superstable when this derivative equals zero. By performing a Taylor series expansion of F around $\bar{U}$ and truncating after the linear term, it becomes apparent why points in the neighborhood of a function satisfying the inequality in (5.5) converge to $\bar{U}$ as F is iterated. Stable fixed points are also referred to as sinks, attractors, stable zeroes, equilibria, or invariants.

If points in the neighborhood of a fixed point do not remain

within the neighborhood of the fixed point as the function is iterated, then the fixed point is unstable. This occurs in the case of a one dimensional function when the derivative of the function evaluated at the unstable fixed point satisfies the inequality:

$$\left| \frac{dF}{dU} \right|_{U=\bar{U}} > 1 \quad (5.6)$$

These definitions can be generalized to a function F on a higher dimensional space by replacing the derivative of the one dimensional function with the eigenvalues of the Jacobian matrix of F evaluated at the fixed points. Since the magnitude of some eigenvalues may be less than one and others greater than one, it is possible for fixed points in a multidimensional space to be stable along some directions but unstable along others. Examples of this kind of behaviour are observed in pulse iteration schemes, and will be pointed out later.

The set of points which converge to a stable fixed point as a function is iterated is termed the basin of the fixed point. Although the stability of a fixed point is determined by a linear approximation of F , the basin of a fixed point may extend beyond the linear regime. Moreover, the basin may be discontinuous and can be composed of many disconnected regions. In such cases, the fixed point can have a pronounced influence on a large neighborhood of points around it. The trajectories of individual points in a basin may be complicated, but the overall movement of points within the entire basin, called the flow, is relatively simple to picture as a local migration towards the fixed point.

The basins, stability, and fixed points are determined by certain parameters which define F . If F is an n th degree polynomial, for example, then the parameters which determine F are the $n + 1$ coefficients of the polynomial. The applicability and utility of an iterated function for modeling chaotic phenomena or producing some desired flow depends on the selection of these parameters.

The parameters of an iterated function on a nuclear spin propagator space can be partially specified by the experimental parameters defining the iterative scheme $S_i \rightarrow S_{i+1}$. Since there is nominal experimental control over these parameters, they provide a way for specifying the propagator space function, its fixed points, and the stability of the fixed points, corresponding to the iterative scheme as in equations (5.1) and (5.2). This point is considered in the next section.

B. Iterated functions in NMR

A fixed point analysis of iterative schemes can be used to address bandwidth excitation problems in the following way. Pulse iteration schemes are rules which transform one pulse sequence S_i into another pulse sequence S_{i+1} with improved, more desirable properties. They may therefore be regarded as iterated functions on a propagator space insofar as they transform the propagator $U(\vec{\phi}_i, \vec{a}_i, \vec{\lambda})$, corresponding to the pulse sequence S_i , to the propagator $U(\vec{\phi}_{i+1}, \vec{a}_{i+1}, \vec{\lambda})$, corresponding to the pulse sequence S_{i+1} , in the manner of equation (5.2). The initial propagator $U(\vec{\phi}_0, \vec{a}_0, \vec{\lambda})$ may have a range of possible values due to the fact that the parameter $\vec{\lambda}$, on which $U(\vec{\phi}_0, \vec{a}_0, \vec{\lambda})$ depends, may itself range over a spectrum of values. The object, then,

is to obtain $\bar{U}$ from an iterated function given the dependence of propagators on the parameter $\bar{\lambda}$.

In order to create a broadband sequence by using an iterative scheme, the associated function must generate a series of iterates $U(\vec{\phi}_1, \vec{\alpha}_1, \bar{\lambda})$ which converge to the desired propagator for a wide range of $\bar{\lambda}$ values. To achieve this, the limit of convergence of the function must be insensitive to the choice of the initial condition $U(\vec{\phi}_1, \vec{\alpha}_1, \bar{\lambda})$. In the language of nonlinear dynamics, $\bar{U}$ is a stable fixed point of the function on the propagator space; nearby points converge to $\bar{U}$ as the function is iterated, and $\bar{U}$ is itself invariant upon iteration of the function.

Narrowband sequences on the other hand are generated by functions which are unstable at their fixed points. Because of this instability, the only point which is mapped to the fixed point $\bar{U}$ is the fixed point itself. The implication then, is that only a very narrow range of parameters result in pulse sequence propagators which get mapped to the unstable fixed point.

A slightly different way of viewing iterated functions on a propagator space can be arrived at by writing the i th iterate time development operator as:

$$U(\vec{\phi}_1, \vec{\alpha}_1, \bar{\lambda}) = e^{-iH_i} \quad (5.7)$$

where H_i is a Hermitian operator. This expression is entirely general, even if the Hamiltonian is time dependent, since U must always be unitary.

A function on a propagator space transforms this time development

operator to another time development operator:

$$U(\vec{\phi}_{i+1}, \vec{a}_{i+1}, \lambda) = e^{-iH_{i+1}} \quad (5.8)$$

Two functions are in evidence here, one a function defined on a unitary propagator space, mapping U_i to U_{i+1} , and one a function on a Hermitian operator space, mapping H_i to H_{i+1} . For a spin system consisting of N coupled spin- I nuclei, both the operator space and the propagator space are $(2I+1)^{2N}$ -dimensional.

If $N = 1$ and $I = 1/2$, four operators are necessary to specify H_1 or U_1 . As was shown in section 2.III.B, however, U_1 for isolated spins is a rotation operator regardless of I , and H_1 is a linear sum of only three operators, I_x , I_y , and I_z . The fourth operator needed to complete the basis is an operator proportional to the identity. This operator, if included in H_1 , gives rise to an inconsequential phase factor in a macroscopic measurement and can be ignored.

An iterative scheme of the form in equation (5.1) does not always stipulate a well-defined transformation from U_i to U_{i+1} or from H_i to H_{i+1} . This situation might be encountered if the iterative scheme were incompletely specified^{24,85,90} or if the scheme involved an operation necessitating that some assumption be made about the parameters of the nuclear spin system or rf field.²⁴ A fixed point analysis of such schemes would then have to proceed with some appropriate assumptions. Some of these are discussed in Chapter Seven. Informative and unique insights about these schemes can still be gained, however, by such an analysis.

II. NMR ITERATIVE SCHEMES

A. NMR propagators and $SO(3)$

The propagator space for isolated spins, by the above, consists only of rotation operators. The space of propagators appropriate to the analysis of an ensemble of isolated nuclei is the space of real rotations $SO(3)$.^{96,97} This space can be graphically portrayed as a solid sphere of radius π , as shown in figure 5.1. A rotation is uniquely defined in this representation by a unit vector drawn from the origin, denoting the axis of the rotation, and a distance from the origin, denoting the angle of the rotation. Elements of this space will be written $R(\alpha)$ to emphasize the fact that they represent rotations about an axis α , through an angle $|\alpha|$.

The analysis of an iterative scheme as an iterative propagator map will be performed on the locus of points comprising the set of rotations which take I_z into the xy plane, appearing within the sphere of figure 5.2 as a cylinder-like surface. This set represents the apparent $\pi/2$ rotations of I_z . True $\pi/2$ rotations of I_z into the transverse plane comprise the subset of this surface which intersects the xy plane of $SO(3)$. These rotations are represented in $SO(3)$ by vectors of the form:

$$\alpha = \frac{\pi}{2}[\cos\psi, \sin\psi, 0] \quad (5.9)$$

This set of rotations in $SO(3)$ will be written $R_\psi(\pi/2)$, where ψ is an arbitrary phase shift measured from the x axis. While the rest of the surface will rotate a longitudinal vector into a transverse vector, the actual angle of the rotation will be greater than $\pi/2$ and will be about

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Figure 5.1: Example of a general mapping of $SO(3)$ onto itself.

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Figure 5.2: Surface in $SO(3)$ representing the set of rotations which rotate the z -component of an arbitrary vector into the transverse plane. The three dimensional rotation operators corresponding to such points are those which have the R_{zz} element identically equal to zero.

an axis not in the xy plane of $SO(3)$.

Two problems similar in nature to the ones appearing in the previous Chapter arise when considering iterative schemes of any sort. The first is the determination of an iterative scheme resulting in a map on the propagator space with the desired time development operators as fixed points. These are iterative schemes which, if applied to a sequence S_i which already brings about the desired propagator $\bar{U}$, generate a sequence S_{i+1} with the same propagator $\bar{U}$. After a general class of operations has been identified, a way of specifying the stability properties at the desired fixed points is investigated.

B. Specification of Invariance

The iterative schemes developed in this Chapter consist of two operations, namely, the addition of a constant phase shift to all the pulses of a sequence, followed by concatenation of N phase shifted versions of the sequence. Adhering to past convention,²¹ a sequence S_i with all of its pulses phase shifted by some constant amount ϕ will be denoted $S_i(\phi)$. Concatenation of N phase shifted versions of S_i constitutes the iterative scheme:

$$S_{i+1} = S_i(\phi_1)S_i(\phi_2) \dots S_i(\phi_{N-1})S_i(\phi_N) \quad (5.10)$$

with the corresponding transformation of rotation operators:

$$R(\alpha_{i+1}) = R(\alpha_{i,N})R(\alpha_{i,N-1}) \dots R(\alpha_{i,2})R(\alpha_{i,1}) \quad (5.11)$$

where $R(\alpha_{i,j}) = R_z(\phi_j)R(\alpha_i)R_z^{-1}(\phi_j)$. The operator $R_z(\phi_j)$ denotes a positive rotation around the z axis by the angle ϕ_j . Equation (5.11)

generally holds true for high field NMR Hamiltonians regardless of whether spins are isolated or not. This combination of operations will be summarized by the notation $[\phi_1, \phi_2, \dots, \phi_{N-1}, \phi_N]$.

The transformation of rotation operators specified by the operation in (5.11) is a well defined function on $SO(3)$. There are several regions in $SO(3)$ which are fixed in common for all functions of this general form. The first is the origin, specified by the operator $R(\alpha)$, $\alpha = 0$. This operator corresponds to the identity operator in $SO(3)$. Transforming the identity operator in accordance with equation (5.11) obviously gives the identity.

A second fixed set is the z axis, consisting of operators of the form $R(\alpha)$, with $\alpha = (0, 0, \alpha)$. The function in (5.11) maps $R(\alpha)$ to $R(N\alpha)$. Points satisfying the equality $2\pi = N\alpha$ are individually invariant.

If N is odd, a third fixed set is the equator of $SO(3)$. This is seen to derive from the fact that the product of an odd number of rotations, all of which take z to $-z$, equals a single net rotation which also transforms z to $-z$.

Because of the intrinsic invariance of these sets, elaborate phase shift schemes need not be contrived to specify functions with these three regions as fixed sets. The same is generally not true for the rest of $SO(3)$. Other points in $SO(3)$ require somewhat more sophisticated schemes in order to have their invariance specified.

The problem addressed in this section is the determination of possible iterative transformations of pulse sequences which result in maps on $SO(3)$ with $R_\psi(\pi/2)$ as a fixed set. These are iterative operations which, when performed on a composite $\pi/2$ pulse S_i , guarantee

that S_{i+1} will also be a composite $\pi/2$ pulse.

Several operations are conceivable. One possibility is to form a cycle, or several cycles, with S_i , concatenate the cycles, and then insert S_i at the end, beginning, or between cycles. The strict definition of cycle is adopted here to denote sequences which have the unit operator as a net propagator. If applied to a sequence producing a $R_\psi(\pi/2)$ rotation, the following phase shift-concatenation operations constitute cyclic sequences:

- i. $[\phi, \phi+180]$
- ii. $[\phi, \phi, \phi, \phi]$
- iii. $[\phi, \phi+90, \phi+270, \phi+180]$

Insertion of a cycle anywhere within a composite $\pi/2$ pulse will leave the sequence a composite $\pi/2$ pulse.

A second operation is to phase shift S_i and concatenate it with itself, forming $S_i(\phi_j)S_i(\phi_j)$. If S_i is a true $\pi/2$ pulse sequence, with a corresponding rotation operator which can be written $R_\psi(\pi/2)$, $S_i(\phi_j)S_i(\phi_j)$ will be an inverting, or π sequence, with net rotation operator $R_{\psi+\phi_j}(\pi)$. Concatenation of N phase shifted versions of $S_i(\phi_j)S_i(\phi_j)$ produces a nominal inverting sequence with a net π rotation operator $R_\gamma(\pi)$, where γ can be computed from the relation:²⁴

$$\gamma = \psi + \phi_1 - \phi_2 + \dots - \phi_{N-1} + \phi_N \quad (5.12)$$

Inserting $S_i(\gamma-\psi)$ or $S_i(\gamma-\psi+\pi)$ at the beginning or end of this sequence will then result in a true $\pi/2$ pulse sequence.

The final operation to be considered are rotations of the

operator $R_\psi(\pi/2)$ around the z axis. This operation can be understood as follows. If S_1 is a sequence with net rotation operator $R_\psi(\pi/2)$, then the sequence formed by the phase shift concatenation scheme $[\phi, \phi+\pi/2, \phi+\pi]$ has as its net rotation operator $R_z(\pi/2)$. A variation of this scheme is given by $[\phi, \phi+\pi/2, \phi+\pi/2, \phi+\pi]$ which results in the net rotation $R_z(\pi)$. Sandwiching S_1 between two such z rotation sequences, e.g., the schemes $[\phi, \phi+\pi/2, \phi+\pi]$ and $[\theta, \theta+3\pi/2, \theta+\pi]$, results in the overall scheme:

$$[\phi, \phi+\pi/2, \phi+\pi, 0, \theta, \theta+3\pi/2, \theta+\pi]$$

with a net rotation operator which can be written $R_{\psi+\pi/2}(\pi/2)$.

The above mentioned schemes clearly do not exhaust the potential operations which lead to the desired invariance of $R_\psi(\pi/2)$. Nor are such schemes confined solely to the case of composite $\pi/2$ pulses; by straightforward extensions, they can be applied to conceive operations with other rotations or propagators as invariants as well. In addition, the various schemes can be combined with one another to produce more exotic sequences with the desired invariant propagators. The criteria governing the choice, ordering, phase, and number of these schemes is the topic of the next section.

C. Specification of Stability

Denoting a fixed point of some mapping F in $SO(3)$ as $R(\bar{\alpha})$, points in the neighborhood of $R(\bar{\alpha})$ can be written:

$$R(\beta_1) = R(\bar{\alpha})R(\delta_1) \quad (5.13)$$

where $|\delta_i|$ is small. This separation of an operator into a product of two operators, one an "ideal" operator, and the other arising from some perturbation, is formally identical to the separation of operators performed when transforming into an interaction representation in time-dependent quantum mechanical problems.

Applying the mapping F with fixed point $R(\bar{\alpha})$ to some point $R(\beta_i)$ results in a new point $R(\beta_{i+1})$ which can be expressed as:

$$R(\beta_{i+1}) = R(\bar{\alpha})R(\delta_{i+1}) \quad (5.14)$$

For a generalized phase shift-concatenation scheme $[\phi_1, \phi_2, \dots, \phi_{N-1}, \phi_N]$, δ_{i+1} , in the linear approximation, is transformed to:

$$\begin{aligned} \delta_{i+1} \approx & \delta_i(\phi_1) + R^{-1}(\bar{\alpha}_1)\delta_i(\phi_2) + R^{-1}(\bar{\alpha}_1)R^{-1}(\bar{\alpha}_2)\delta_i(\phi_3) \\ & + R^{-1}(\bar{\alpha}_1)R^{-1}(\bar{\alpha}_2)R^{-1}(\bar{\alpha}_3)\delta_i(\phi_4) + \dots \end{aligned} \quad (5.15)$$

$$= T_{\bar{\alpha}}\delta_i \quad (5.16)$$

The notation $\delta_i(\phi_j) = R_z(\phi_j)\delta_i$ and $R(\bar{\alpha}_j) = R_z(\phi_j)R(\bar{\alpha})R_z^{-1}(\phi_j)$ has been used here. The last equality in equation (5.14) reveals the fact that the expression above it is a well defined linear transformation in three dimensions of δ_i .

The fixed point $R(\bar{\alpha})$ will be stable in all directions if the three complex eigenvalues λ_1 , λ_2 , and λ_3 of $T_{\bar{\alpha}}$ satisfy the inequality:

$$|\lambda_j| < 1 \quad (5.17)$$

and will be superstable in all directions if $|\lambda_j| = 0$ for all j . These conditions ensure that $|\delta_{i+1}| < |\delta_i|$ for $|\delta_i|$ small, and hence imply

that $R(\theta_1)$ converges to $R(\bar{\alpha})$.

The set for which invariance and stability are sought consists of all rotations which can be written $R_\psi(\pi/2)$. Employing the principles outlined in the previous section, the iterative scheme $[0,135,135,0]$, which has a map on $SO(3)$ with $R_\psi(\pi/2)$ as an invariant set, was modified by inserting two cycles within the phase shift scheme to form the new eight shift scheme:

$$[0, \phi_1, \phi_1+180, 135, 135, \phi_2, \phi_2+180, 0]$$

The phase shifts have been specified in degrees. The scheme $[0,135,135,0]$ was chosen as a starting point since the $SO(3)$ map of this scheme is already stable at $R_\psi(\pi/2)$ for displacements in the xy plane of $SO(3)$. Insertion of the two additional cycles was necessary to obtain stability in all directions at $R_\psi(\pi/2)$. A general analytical expression for the eigenvalues of the linear operator $T_{\bar{\alpha}}$ can be derived for schemes of this form using equation (5.13), with ϕ_1 and ϕ_2 as independent variables. The variables ϕ_1 and ϕ_2 were then searched on a computer for values which satisfied the eigenvalue inequalities (5.12). Iterative schemes identified in this way appear in table 5.1. Based on the magnitude of the eigenvalues, and the number of phases in the scheme coincident with the four quadrature phases, the sequence $[0,0,180,135,135,150,330,0]$ was selected from this table for closer examination.

D. Digression on numerical methods

The transformation $T_{\bar{\alpha}}$ in equation (5.16) defined by phase shift

Table 5.1: Phase iteration schemes which generate broadband rotations of the form $R_{\psi}(\pi/2)$, as determined by the numerical procedure described in section II. The phases are given in degrees. Symmetric schemes have been starred.

[0, 0, 180, 135, 135, 150, 330, 0]
[0, 0, 180, 135, 135, 160, 340, 0]
[0, 280, 100, 135, 135, 100, 280, 0]*
[0, 280, 100, 135, 135, 110, 290, 0]
[0, 280, 100, 135, 135, 120, 300, 0]
[0, 280, 100, 135, 135, 130, 310, 0]
[0, 280, 100, 135, 135, 140, 320, 0]
[0, 290, 110, 135, 135, 90, 270, 0]
[0, 290, 110, 135, 135, 100, 280, 0]
[0, 290, 110, 135, 135, 110, 290, 0]*
[0, 290, 110, 135, 135, 120, 300, 0]
[0, 290, 110, 135, 135, 150, 330, 0]
[0, 300, 120, 135, 135, 90, 270, 0]
[0, 300, 120, 135, 135, 100, 280, 0]
[0, 300, 120, 135, 135, 110, 290, 0]
[0, 300, 120, 135, 135, 160, 340, 0]
[0, 310, 130, 135, 135, 100, 280, 0]
[0, 310, 130, 135, 135, 170, 350, 0]
[0, 320, 140, 135, 135, 100, 280, 0]
[0, 320, 140, 135, 135, 170, 350, 0]
[0, 330, 150, 135, 135, 110, 290, 0]
[0, 330, 150, 135, 135, 160, 340, 0]
[0, 330, 150, 135, 135, 170, 350, 0]
[0, 340, 160, 135, 135, 120, 300, 0]
[0, 340, 160, 135, 135, 150, 330, 0]
[0, 340, 160, 135, 135, 160, 340, 0]*
[0, 340, 160, 135, 135, 170, 350, 0]
[0, 350, 170, 135, 135, 130, 310, 0]
[0, 350, 170, 135, 135, 140, 320, 0]
[0, 350, 170, 135, 135, 150, 330, 0]
[0, 350, 170, 135, 135, 160, 340, 0]
[0, 350, 170, 135, 135, 170, 350, 0]*

concatenation schemes generally have three independent eigenvalues, each a function of the N phase shifts comprising the scheme. The determination of a phase shift scheme giving rise to superstability at some fixed point entails the solution of three nonlinear equations in N unknowns:

$$0 = |\lambda_1(\vec{\phi})| \quad (5.18)$$

$$0 = |\lambda_2(\vec{\phi})| \quad (5.19)$$

$$0 = |\lambda_3(\vec{\phi})| \quad (5.20)$$

A similar problem was encountered in the coherent averaging analysis of the previous chapter. Nonlinear functions of $\vec{\phi}$, $\vec{\alpha}$, and $\vec{\tau}$ arose there as coefficients of spin operators in the Magnus expansion. These nonlinear functions comprise a system of equations which must be simultaneously solved to obtain the desired result $U_V(\vec{\phi}, \vec{\alpha}, \vec{\tau}) = 1$.

There is no generally applicable numerical method for determining the solution of a set of m nonlinear equations in n unknowns. In many cases, it is difficult if not impossible to ascertain a priori if the number of variables is sufficient to solve the m equations. The solution of systems of nonlinear equations encountered in the course of this work was attempted by two, improvised methods. The first method consists of a brute force search through the n free parameters for values which simultaneously satisfy the system of m nonlinear equations. A search such as this can be conveniently and effectively executed by computer provided the number of parameters being searched is relatively small. This method has several drawbacks, however, some of which were mentioned in section 4.II.A.

A second more efficient numerical method can be arrived at by writing the m functions to be solved as:

$$f_i(x_1, x_2, \dots, x_{n-1}, x_n) - f_i(\vec{x}) \quad (5.21)$$

squaring each one, and defining a single nonlinear equation by the sum:

$$f_T(\vec{x}) = \sum_{i=1}^m w_i f_i^2(\vec{x}) \quad (5.22)$$

Since all terms in the sum on the right must be greater than or equal to zero, it follows that:

$$f_T(\vec{x}) \geq 0 \quad (5.23)$$

for all $\vec{x}$. Furthermore, any root of $f_T(\vec{x})$ must also be a solution to the system of m equations $f_i(\vec{x})$. That is, any value of $\vec{x}$ which solves the equation $f_T(\vec{x}) = 0$ must also solve the m equations $f_i(\vec{x}) = 0$.

A constant, positive coefficient w_i has been included in the sum of $f_i(\vec{x})$ in the event it is deemed important to give greater weight to the solution of some of the equations more than others. In all cases discussed in this dissertation, w_i was set equal to one for all i .

The solution of m equations in n unknowns is reduced by this trick to the solution of a single equation in n unknowns. One way a solution to this equation, if one exists, can be determined is by forming the n -dimensional gradient of $f_T(\vec{x})$:

$$\nabla f_T(\vec{x}) = \left(\frac{\partial f_T}{\partial x_1}, \frac{\partial f_T}{\partial x_2}, \dots, \frac{\partial f_T}{\partial x_n} \right) \quad (5.24)$$

A well known theorem of multivariable calculus asserts that the vector defined by $\nabla f_T(\vec{x})$ points in the direction along which $f_T(\vec{x})$ increases the fastest.⁹⁸ The vector in the opposing direction, $-\nabla f_T(\vec{x})$, can therefore be interpreted as the direction of steepest descent of $f_T(\vec{x})$. Presumably, this vector points in a direction, which if followed in sufficiently small steps, leads to a value of $\vec{x}$ where $f_T(\vec{x})$ is at a minimum. Since $f_T(\vec{x}) \geq 0$, a solution of $f_T(\vec{x})$, if one exists, will lie in one of these minima.

These observations suggest that the sequence of iterates generated by the equation:

$$\vec{x}_{i+1} = \vec{x}_i - p_i \frac{\nabla f_T(\vec{x}_i)}{|\nabla f_T(\vec{x}_i)|} \quad (5.25)$$

converges to a value of $\vec{x}$ where the function $f_T(\vec{x})$ is at a minimum. A solution of $f_T(\vec{x})$ will be one of these minima. The parameter p_i is some small positive real number determining the size of the step from one iterate to the next.

A procedure such as this is readily implemented on a computer. For each iterate generated by the above expression, the computer checks if $f_T(\vec{x})$ falls within some specified range of zero. If not, then the computer calculates the next iterate and checks $f_T(\vec{x})$ again. At a minimum, the gradient is zero, and so the iterates cease to change by much. By experimenting with different starting points x_1 , solutions of $f_T(\vec{x})$ can usually be found quickly and without great difficulty. This method was used successfully to determine the phase shift schemes of Chapter Six.

III. RESULTS AND DISCUSSION

A. Bandwidth Properties

The simplest composite pulse sequence which can be generated from the scheme [0,0,180,135,135,150,330,0] is an eight pulse sequence, each a nominal $\pi/2$ pulse ordered consecutively with the eight prescribed phases. The efficacy of this eight pulse sequence at creating transverse magnetization from the initial state I_z as a function of rf field strength is presented in figure 5.3 for zero, one and two iterations of the scheme. The y axis in this plot represents the projection of the density operator onto the transverse plane, and is defined by equation (4.12). The increase in the effective bandwidth of the sequence is plain.

A similar plot is shown in figure 5.4 for the excitation of transverse coherence, this time as a function of resonance offset. A single pulse is more effective at creating transverse magnetization from the initial condition I_z than a composite pulse. This phenomenon is well understood as arising from the fact that the net rotation produced by a single, off-resonance pulse $\pi/2$ pulse, while neither about an axis in the xy plane nor about an angle $\pi/2$, nevertheless does rotate I_z into the transverse plane quite effectively.^{22,99}

This point can be made clearer by comparing the off-resonance population inversion produced by a pulse sequence consisting of two concatenated $\pi/2$ pulses versus that of two concatenated composite $\pi/2$ pulse sequences. Theoretical simulations of the population inversion produced by these concatenated sequences as a function of resonance offset are shown in figure 5.5. It is apparent from these simulations that the concatenated composite pulses produce a better π rotation than

Figure 5.3: Transverse magnetization created from the initial state I_z as a function of normalized rf field strength. Theoretical values appear as lines, experimental points as dots. Shown are the results for a single nominal $\pi/2$ pulse, a nominal $\pi/2$ pulse iterated once according to the scheme [0,0,180,135,135,150,330,0] (8 pulses), and the single pulse iterated twice (64 pulses).

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Figure 5.4: Transverse magnetization created from the initial state I_z as a function of normalized resonance offset. The progression of pulse sequences for the three boxes follows that of figure 5.3. Experimental points appear as dots, and theoretical predictions as lines.

Figure 5.5: Simulations of the normalized population inversion ($-I_z$) as a function of resonance offset for a single nominal π pulse (0), the sixteen pulse sequence generated by concatenating $[90_0, 90_0, 90_{180}, 90_{135}, 90_{135}, 90_{150}, 90_{330}, 90_0]$ with itself (1), and the 128 pulse sequence formed by concatenating the second iterate of the eight shift scheme with itself (2). The greater bandwidth range of the concatenated composite $\pi/2$ pulse sequences is a sensitive demonstration of the quality of the rotations which they produce.

do the concatenated single pulses, even though the composite pulse sequence appears less effective at converting longitudinal polarization to transverse polarization than the single pulse. Moreover, the phase of the signal from a single $\pi/2$ pulse varies linearly as a function of the rf offset; this phase distortion is diminished in the composite pulse sequence over a small range of offsets. Following Levitt's classification scheme,²⁵ the eight pulse sequence can be considered an A type of sequence within this range. Outside this range, the sequence becomes of the B1 type.

B. Previous Work

Levitt and Ernst have proposed designing composite pulse sequences for converting longitudinal magnetization to transverse magnetization by use of an iterative procedure.²² One version of their procedure, which they called a recursive expansion, consists of concatenating a starting sequence S_i with its inverse sequence S_i^{-1} phase shifted by $\pi/2$ radians. These two operations are summarized by the notation $S_{i+1} = S_i(S_i^{-1})_{90}$. Denoting the propagator describing the time evolution of the spin system during the sequence S_i as $U_i(\lambda, t)$, the inverse sequence S_i^{-1} can be defined as the sequence which has as its propagator the unitary operator $U_i^\dagger(\lambda, t)$.

Two features distinguish the recursive expansion approach from the phase shift-concatenation schemes developed in this paper. The first is that the fixed set of the map on $SO(3)$ of the recursive expansion does not include rotations of the form $R_\psi(\pi/2)$. The procedure instead generates rotations which take place about unit vectors of the form $\{(2/3)^{1/2} \cos\psi, (2/3)^{1/2} \sin\psi, -3^{-1/2}\}$ through an

angle of $2\pi/3$, leading to the effective propagator:

$$\bar{U} = \exp\left\{-\frac{2\pi i}{3\sqrt{3}} \left[\sqrt{2}\cos\psi I_x + \sqrt{2}\sin\psi I_y - I_z \right]\right\} \quad (5.26)$$

One consequence of this fact is that concatenating two identical such sequences will not result in an inverting (π) pulse sequence.

The second difference of the recursive expansion is that it requires, as one step of the procedure, the formation of the inverse sequence S_1^{-1} . If such an inverse sequence could be constructed, the recursive expansion would generate sequences effective at virtually all resonance offsets and ω_1 values. However, when the resonance offset is not zero, there is no known method for creating the inverse sequence S_1^{-1} . To minimize this problem, methods for constructing approximate inverses have been suggested, and starting with an initial sequence which is itself compensated for resonance offset errors has been proposed. Even with these measures, it is difficult to accurately implement the recursive expansion procedure off-resonance. A large phase distortion in the spectrum as a function of offset results.²²

A second iterative procedure for generating $\pi/2$ rotations is the phase shift-concatenation scheme $[0,135,135,0]$.²⁴ Iteration of this scheme transforms rotation operators of the form $R_\psi(\pi/2)$ to operators of the form $R_{\psi+\pi/2}(\pi/2)$. Sequences generated by this scheme have been shown to be compensated for rf inhomogeneity effects, and hence are broadband over ω_1 . However, such sequences are not compensated for resonance offset errors, and the performance of these sequences is accordingly degraded when the rf is moved away from the spin resonance frequency.

C. Fixed Point Analysis of Iterative Schemes

The direction of the flow for the function of the scheme $[0,0,180,135,135,150,330,0]$ is schematically shown in figure 5.6 by the arrows pointing in towards the $R_{\psi}(\pi/2)$ circle, indicative of the stability of the this fixed point of the function. The origin is an incidental, unstable fixed point of the function, which is reflected in the outward directed arrows emanating from this point. A two dimensional version of this image appears in figure 5.7. This two dimensional image can be contrasted with the two dimensional flow for the function of the scheme $[0,135,135,0]$ shown in figure 5.8. Points displaced from the fixed set $R_{\psi}(\pi/2)$ in the xy plane converge towards the fixed set for this function, but move away from this fixed set if there is a displacement in the z direction. The fixed set is therefore stable only in certain preferred directions.

The recursive expansion procedure has a function on $SO(3)$ producing flow of the type diagrammed in figures 5.9 and 5.10. This flow assumes formation of a perfect inverse rotation in the scheme $S_i(S_i^{-1})_{90}$. The whole of $SO(3)$ excluding the z-axis and the equator converges smoothly to rotation operators of the type specified by equation 5.26. It has been shown previously that this fixed set is superstable.²⁴ The superstability of this fixed set was demonstrated for small displacements from the fixed set; however, the assumption of small displacements is not necessary, and it can be shown that for the idealized recursive expansion, the whole of $SO(3)$ excluding the z-axis and the equator must converge to the stable fixed set indicated. The first step of the proof, the demonstration of:

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Figure 5.6: The movement of points in $SO(3)$ resulting from the iteration of a map with the set $R_\psi(\pi/2)$ as a stable fixed set and the origin as an unstable fixed set. $R_\psi(\pi/2)$ is shown here as being stable in all directions. The map of the scheme $[0,0,180,135,135,150,330,0]$ possesses this type of stability.

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Figure 5.7: Two dimensional projection of figure 5.6. For simple phase shift-concatenation schemes, cylindrical symmetry permits such two dimensional representations. The distance between points 1 and 2 is $\pi/2$.

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Figure 5.8: Flow for a map which has $R_p(\pi/2)$ as a fixed set unstable in the z direction but stable otherwise. The map of the scheme $\{0,135,135,0\}$ exhibits flow of this type. The instability off the transverse plane means that sequences generated by this scheme will not be compensated for imperfections caused by off-resonance effects. The origin is an incidental, unstable fixed point of this map.

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Figure 5.9: The fixed sets and flow for a map on $SO(3)$ of the recursive expansion scheme $S_1(S_1^{-1})_{90}$. The stable fixed set is a circle on the set of "apparent $\pi/2$ rotations" shown in figure 5.2. This flow assumes the formation of a perfect inverse rotation in the recursive expansion, and hence represents an idealization of its stability properties.

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Figure 5.10: Two dimensional version of figure 5.9 for the recursive expansion procedure. The idealized recursive expansion procedure produces a mapping on $SO(3)$ with cylindrical symmetry. The distance in $SO(3)$ between points 1 and 2 is $2\pi/3$, and the angle θ is $\cos^{-1}(3^{-1/2})$.

$$(R_{i+1})_{zz} - (R_i)_{zz}^2 \quad (5.27)$$

does not require a linear approximation as was assumed. This is straightforwardly shown by forming the product of the rotation matrix in equation (2.28) with a second matrix having the same form, but with α replaced by $-\alpha$ and ϕ replaced by $\phi + 90^\circ$.

The remainder of the space for this function converges to the origin, which is superstable only in the z direction.

The flow of these mappings can be further studied by following the individual trajectories of an initial distribution of points in $SO(3)$. One possible configuration appears in figure 5.11. The movement of points from this initial state for the three iterative schemes $\{0,135,135,0\}$, $\{0,0,180,135,135,150,330,0\}$, and $S_i(S_i^{-1})_{90}$ to their respective fixed points is clearly evidenced in figures 5.12, 5.13, and 5.14 by the congregation of points around the fixed points. Again, the difference in the fixed sets of the recursive expansion scheme and the phase shift-concatenation schemes is obvious.

A second notable feature to observe in these figures is the orderly flow resulting from the recursive expansion, as contrasted with the two phase iteration schemes. This orderly flow is a consequence of the use of an exact inverse operation as part of the iterative scheme. Any practically realizable operation for forming an inverse sequence, however, results in chaotic flow similar to that exhibited by the two other schemes.

A final point to note about these diagrams is the reflection symmetry present in the diagram for the scheme $\{0,135,135,0\}$. This

Initial Condition

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Figure 5.11: An initial distribution of points in $SO(3)$. The general movement of points in $SO(3)$ when transformed by some map can be inferred by following how points progress away from this initial condition as the map is iterated. Stable fixed points can be identified by the clustering of points around certain areas. The trajectory of points for various maps with this configuration of points as the initial condition are displayed in the next three figures.

$[0, 135, 135, 0]$

(a) One iteration

(b) Two iterations

(c) Four iterations

(d) Eight iterations

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Figure 5.12: The distribution of points in $SO(3)$ following iteration of the scheme $[0,135,135,0]$, assuming the initial configuration in figure 5.11. The results of one, two, four, and eight iterations are shown.

$[0, 0, 180, 135, 135, 150, 330, 0]$

(a) One iteration

(b) Two iterations

(c) Four iterations

(d) Eight iterations

Figure 5.13: Configuration of points following iteration of the scheme $[0, 0, 180, 135, 135, 150, 330, 0]$, assuming the initial condition in figure 5.11. Again, one, two, four, and eight iterations are shown.

Recursive Expansion

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Figure 5.14: Distribution of points following iteration of the idealized recursive expansion scheme $S_i(S_i^{-1})_{90}$, assuming the initial condition in figure 5.11. The results of one, two, four, and eight iterations are shown.

symmetry is a natural result of the symmetry of the scheme itself.²⁴ Since $[0,0,180,135,135,150,330,0]$ is not a symmetric scheme, the reflection symmetry is absent in the diagram of the map for this scheme.

Computer generated basin images showing the regions of $SO(3)$ which converge to the fixed set $R_\psi(\pi/2)$, and the number of iterations required for convergence, for maps of the schemes $\{0,135,135,0\}$ and $\{0,0,180,135,135,150,330,0\}$ are shown in figures 7.1 and 7.2. The program written to generate these images employed two criteria for determining convergence to the fixed set: the first is that the net angle α_1 of the rotation operator must meet the inequality $|90^\circ - \alpha_1| \leq 5^\circ$; the second is that the square of the R_{zz} element of the three dimensional rotation matrix $R(\alpha_1)$ must be less than 0.0076. These two criteria in combination test for convergence to only those rotations of the general form $R_\psi(\pi/2)$. As expected, the basin image for $\{0,135,135,0\}$ is mostly dark, indicating the instability of the fixed set for displacements in the z direction. This is to be contrasted with the lighter basin image for the scheme $\{0,0,180,135,135,150,330,0\}$, which is stable in all directions around the fixed set. Again, the xy reflection symmetry in the image for $\{0,135,135,0\}$ is absent in the basin image for $\{0,0,180,135,135,150,330,0\}$. The additional symmetry of basin images for symmetric schemes is more readily apprehended for broadband schemes, which have bigger basins.

A z and xy slice basin image for the recursive expansion procedure is shown in figure 7.12. The basin images appearing there were generated by testing only for the second of the two criteria enumerated above. The contours of the top basin are smooth and well

defined, and suggest in shape the object shown in figure 5.2 containing the set of apparent $\pi/2$ rotations. Adding the first criterion from above results in an image which is completely dark, while adding the criterion $|120^\circ - \alpha_1| \leq 5^\circ$ results in a basin image indistinguishable from the one in figure 7.12.

IV. CONCLUSION

An eight pulse iterative scheme, consisting only of conveniently calibrated $\pi/2$ pulses, has been demonstrated which provides substantial compensation of off-resonance and timing miset pulse errors. This sequence produces a net rotation of the spin density operator about an axis in the xy plane of angle $\pi/2$. Although the sequence requires pulses with phases other than the four standard quadrature phases, the eight pulse sequence should still be relatively easy to generate by placing a programmable, variable phase shifter in series with the quadrature circuit. This phase shifter need only be able to produce three distinct phase shifts of 0° , 135° , and 150° for the sequences examined here. This capability is becoming increasingly standard in most modern commercial NMR spectrometers. Furthermore, simulations indicate that systematic phase errors of at least $\pm 5^\circ$ can be tolerated without significant degradation in performance.

Improvement and analytical development of these sequences might proceed along several lines. The first is to develop similar phase shift-concatenation schemes which are either symmetric or antisymmetric. Several of the sequences appearing in table 5.1 are, indeed, symmetric, though none are antisymmetric. Antisymmetric schemes are, in principle, more desirable, since they offer the

possibility of generating sequences which excite phase coherent NMR signals. The role and utility of the symmetry of a composite pulse sequence has been thoroughly considered elsewhere.²⁴

A second improvement would be to determine schemes with functions on $SO(3)$ which are superstable at the fixed set. It is a remarkable feature of the schemes in this paper that none of them results in a vanishing first order error term, i.e., none of them are superstable, and yet the sequences they generate are still well compensated for pulse errors. Nevertheless, improved sequences might be discovered with the use of functions with superstable fixed sets.

Another route to an improved sequence would be to investigate other initial sequences on which to begin iterating. Initial sequences represented by rotations in $SO(3)$ preferentially concentrated within the basin of the fixed set might provide a better starting point than a single $\pi/2$ pulse.

Deriving schemes with other fixed sets in addition to $R_y(\pi/2)$ is a fourth possible area of development. Functions with more than one stable fixed set provide the means for a shaped or tailored bandwidth response, as has been demonstrated elsewhere.^{27,28} The methods proposed in this paper can serve as the guidelines for specifying one or more other arbitrary fixed sets.

The formalism presented here has distinct advantages in the design and analysis of highly compensated NMR pulse sequences. Though the focus of this paper has been on the special case of $\pi/2$ pulse sequences, the general principles used here can be applied to find iterative schemes for other types of responses as well.

CHAPTER SIX: BISTABLE ITERATIVE MAPS ON $SO(3)$

I. INTRODUCTION

An iterative scheme which generates broadband sequences specifies a map on the propagator space with the desired propagator as a stable fixed point. If the point is stable in all directions, the basin can occupy a substantial fraction of the entire propagator space, as was seen in the previous chapter. Outside the basin of the fixed points, the dynamics of an iterated function can become extremely complicated. This is evidenced in the erratic boundaries of basins in the images discussed in Chapter Five.

Because of the complicated dynamics outside basins, the measure of a broadband sequence's performance often undergoes a transition from smooth, uniform behaviour if the original propagator started out in the basin of the fixed point, to chaotic, unpredictable behaviour if the original propagator lay outside the basin of the stable fixed set. The plots of M_{xy} vs. $\Delta\omega$ in Chapter Five and previous studies of schemes generating broadband inverting sequences all manifest the complicated dynamics occurring away from a fixed point's basin.

The maximization of the effective excitation bandwidth of resonant radiation of a given power level is clearly an important gain in a spectroscopic experiment. What occurs outside the effective bandwidth is of little concern so long as the effective bandwidth is broad. For many experiments in NMR, however, a more useful sequence is one which can excite a specific, tailored response. The tailoring of a

response refers to the selective and uniform excitation of nuclear spins depending on the value of certain specified parameters, e.g., the Larmor frequency ω_0 or the rf amplitude ω_1 . In contrast to broadband or narrowband behaviour, a tailored response exhibits bandpass behaviour.

Bandpass behaviour is obtained in NMR when nuclear spins are selectively excited, meaning that some spins in the sample evolve to one final state, and all other spins to a second and distinct final state. Ideally, the final state to which a given spin, or group of spins, evolves is determined solely by the value of some experimental parameter λ or set of parameters $\vec{\lambda}$. Assuming the two final states are experimentally distinguishable, variations in λ may then be used to discriminate between nuclear spins.

A finite time must elapse in order to allow nuclear spins differing in the value of the parameter λ to evolve to measurably distinct final states. Often, this parameter can be expressed as an energy, or, equivalently, as a frequency. If so, a lower bound for the time required to differentiate between spins based on the value of λ can be estimated by a simple calculation. Consider a nuclear spin system consisting of two sets of spins. The two sets are distinguished by different values of the parameter λ , the first set consisting of spins characterized by a value of the parameter equal to λ_1 , and the second set comprised of spins characterized by a value of λ equal to λ_2 . A situation such as this might arise, for example, if the two groups of spins occupy different positions within an inhomogeneous rf field. The rf field amplitude at the spins' coordinates would then play the role of the variable parameter λ . If λ can be written as a

frequency, then the length of time necessary to perform a measurement which discriminates between the two sets of spins will be on the order of the inverse of their frequency difference, or $|\lambda_1 - \lambda_2|^{-1}$.

The reasoning behind this assertion is made perhaps more apparent by examining a specific example. In an inhomogeneous rf field, the value of $\tilde{\omega}_1(t)$ for one part of a sample is:

$$\tilde{\omega}_1(t) = \omega_1^0 [\cos\phi(t)\hat{i} + \sin\phi(t)\hat{j}] \quad (6.1)$$

and for the spins in another part of the sample:

$$\tilde{\omega}'_1(t) = \omega_1^0 (1 + \epsilon) [\cos\phi(t)\hat{i} + \sin\phi(t)\hat{j}] \quad (6.2)$$

$$\epsilon = \frac{\Delta\omega_1}{\omega_1^0} \quad (6.3)$$

Suppose that the initial density operator for both sets of spins is the same, e.g., is proportional to the operator I_z , and that relaxation effects, chemical shifts, and couplings between spins can be neglected. With these assumptions, the evolution operator describing the effect of the pulse sequence on the spins will be a pure rotation operator. The exact form of the rotation operator depends on the value of $\tilde{\omega}_1(t)$ and will therefore vary throughout the sample. The final state reached by the first set of spins will be of the form:

$$\rho_1 = a_x I_x + a_y I_y + a_z I_z \quad (6.4)$$

while for the second group of spins the final state will be:

$$\rho_2 = b_x I_x + b_y I_y + b_z I_z \quad (6.5)$$

The coefficients (a_x, a_y, a_z) and (b_x, b_y, b_z) are assumed to be normalized. The angle separating the two magnetization vectors specified by these density operators can be computed by forming the inner product:

$$\cos \beta = a_x b_x + a_y b_y + a_z b_z \quad (6.6)$$

$$\beta = \cos^{-1}(a_x b_x + a_y b_y + a_z b_z) \quad (6.7)$$

The angle β can differ from zero only if ϵ in equation (6.3) is nonzero. If ϵ is zero, then the propagators for the two groups of spins will be identical, and their density operators evolve identically in time to the same final state.

The final states of the two groups of spins are distinguishable by an NMR measurement if β is not zero or an integer multiple of 2π . The maximum size β can attain is π , corresponding to the case where the magnetization vectors of the two sets are antiparallel. This condition would come about, for instance, if one group of spins were returned to its original equilibrium state I_z by the pulse sequence, while the other was transformed to its population inverted counterpart $-I_z$. By equations (6.1), (6.2) and (6.3), the minimum time required for this difference in nutation angle to develop is:

$$t_{\min} = \frac{\pi}{\epsilon \omega_1} \quad (6.8)$$

Alternatively, the smallest normalized frequency difference which can theoretically be resolved in a selective inversion experiment by a pulse sequence of fixed duration τ is:

$$\epsilon = \frac{\pi}{\omega_1 \tau} \quad (6.9)$$

Equation (6.8) confirms the earlier assertion that the duration of the pulse sequence will be of the order of the inverse of the frequency difference of the rf amplitudes for the two groups of spins. Although demonstrated for the case where it is the rf amplitude which differs for different spins in the sample, an analogous statement clearly holds if the spins differ in their transition frequencies, coupling constants, or other parameters as well.

The preceding examples establish that a bandpass response with sharp cutoff frequencies can be achieved by a pulse sequence alone only if the pulse sequence exceeds a certain minimum duration. The minimum length of the pulse sequence will depend on how finely differences in the parameter λ are to be resolved, by equations (6.8) and (6.9).

It is clear from these considerations that the excitation of a bandpass response by a pulse sequence inherently calls for a large number of pulses. The difficulty of deriving and analyzing composite pulses by a Magnus expansion approach or related formalisms have been pointed out in the previous Chapter. An iterative map analysis does not suffer from this limitation.

In this Chapter, it is demonstrated how iterative maps with more than one stable fixed set can be utilized to generate NMR pulse sequences with bandpass specificity. The sequences derived here

selectively and completely invert isolated spin-1/2 nuclei for designated ranges of ω_1 and ω_0 , and leave undisturbed from equilibrium all spins which lie outside the selected frequency passbands. These kinds of sequences permit the precise discrimination of nuclear spins which differ in some parameter of interest and thus act as spin filters. Experiments in topical NMR, for example, rely on spatially inhomogeneous rf fields to distinguish between spins in different locations in the sample.⁹² In zero field NMR,^{93,94} where the Zeeman energy of nuclear spins is absent, amplitude selective pulse sequences can also be utilized to discriminate between different types of nuclei based on their different gyromagnetic ratios. Other applications of bandwidth specific excitation methods include nk-quantum selective multiple quantum NMR,^{7,8,95} solvent signal suppression in liquids, and optical information storage.¹⁰³

II. GENERAL THEORY

A. Bistable iterative maps in one dimension

An iterative procedure for transforming a pulse sequence S_i to a different pulse sequence S_{i+1} defines a function F on the nuclear spin propagator space. The dimensionality of the propagator space is determined by the size of the spin system. For an ensemble of isolated spins, any evolution operator can be represented as a rotation operator. Three orthogonal coordinates are needed to specify a point in the space of rotations $SO(3)$. An iterative function on this space is therefore a multi dimensional mapping.

Iterative functions on multidimensional spaces are considerably more difficult to analyze than iterative functions on a one dimensional

interval.⁴⁵ Occasionally, however, a multidimensional function can be reduced to a simpler, underlying one dimensional function. An obvious advantage of reducing a multidimensional function to a one dimensional function is the mathematical simplicity of one dimensional spaces as compared to spaces with several dimensions. Perhaps more importantly, a reduction in the number of dimensions can assist in the analysis of an iterative scheme by making available theorems and results applicable to one dimensional functions but not higher dimensional functions. An important result which can be demonstrated in one dimension, but evidently not in higher dimensions, is depicted in figure 6.1. This figure provides a simple proof that a function with two stable fixed points must have at least one unstable fixed point between these two points.⁴⁵ The fixed points of a map on $\mathbb{R}^1$ appear as the points where the iterative map F intersects the linear function $y = x$. As mentioned earlier, the derivative of F evaluated at stable fixed points is less than unity. The figure shows that between two such points, there must be at least one point where F crosses the $y = x$ line and has derivative greater than unity. From this, it follows that at least one unstable fixed point exists between the two stable fixed points. Note that this does not exclude the possibility of additional fixed points, both stable and unstable, between the two postulated stable fixed points.

A more rigorous proof for this theorem can be deduced by recalling the definition of a stable fixed point from section 5.I.A. Let $\bar{x}_0$ and $\bar{x}_1$ be stable fixed points of the continuous, one dimensional function f . Furthermore, suppose that $\bar{x}_0 < \bar{x}_1$, and that no other stable fixed point lies in the range $\bar{x}_0 \leq x \leq \bar{x}_1$. Defining the function g by the relation:

XBL 854-11076

Figure 6.1: An example of a one dimensional map with two stable fixed points, appearing as the intersection points of the map with the line $y = x$ with first derivative less than unity. The stability of these two fixed points necessitates the presence of an unstable fixed point intermediate between the two stable points. This point is the intersection point of the map with the $y = x$ line where the first derivative is greater than one.

$$g(x) = f(x) - x \quad (6.10)$$

with the first derivative:

$$\frac{dg}{dx} = \frac{df}{dx} - 1 \quad (6.11)$$

it follows from the stability of f at $\bar{x}_0$ and $\bar{x}_1$ that:

$$\left. \frac{dg}{dx} \right|_{x=\bar{x}_0} < 0 \quad (6.12)$$

$$\left. \frac{dg}{dx} \right|_{x=\bar{x}_1} < 0 \quad (6.13)$$

From the definition of the first derivative, for some sufficiently small ϵ satisfying $(x_1 - x_0) > \epsilon > 0$, the inequalities:

$$g(\bar{x}_0 + \epsilon) < 0 \quad (6.14)$$

and:

$$g(\bar{x}_1 - \epsilon) > 0 \quad (6.15)$$

hold. By the intermediate value theorem of calculus,⁹⁸ there must be at least one point $\bar{x}_2$ between $\bar{x}_0 + \epsilon$ and $\bar{x}_1 - \epsilon$ where:

$$g(\bar{x}_2) = 0 \quad (6.16)$$

At this point:

$$f(\bar{x}_2) = \bar{x}_2 \quad (6.17)$$

The point $\bar{x}_2$ is a fixed point between $\bar{x}_0$ and $\bar{x}_1$. By hypothesis, no stable fixed points lie between $\bar{x}_0$ and $\bar{x}_1$, therefore $\bar{x}_2$ must be an unstable fixed point. This completes the proof.

It is a relatively straightforward procedure to extend this proof to show that if no stable fixed points lie between $\bar{x}_0$ and $\bar{x}_1$, then only one fixed point can exist in the range $\bar{x}_0 \leq x \leq \bar{x}_1$, and that this fixed point must be unstable. Since no analog of the intermediate value theorem exists in higher dimensional spaces, a similar bistability evidently cannot be demonstrated for such spaces.

The consequences of these results for iterative schemes in bandpass sequences will be discussed in the next section.

B. Flow Diagrams

The set of rotations commonly referred to as π or inversion pulses appears in figure 6.2 as the circumference of the sphere in the xy plane, known as the equator. This set contains all rotations which take $+z$ to $-z$. The identity operator is represented on this picture by the origin.

Broadband inversion sequences for uncoupled spins are generated from iterative schemes specifying functions in $SO(3)$ with the equator as a stable fixed set. For an initial point $R(\alpha_0)$ in the neighborhood of the equator, such maps generate a series of iterates $R(\alpha_1)$ which converge to the equator, that is, to a π rotation. The convergence to the equator of points in the neighborhood of the equator is depicted in figure 6.3a. This figure shows an xy cross section of $SO(3)$. A second fixed point of this hypothetical map is the origin, shown here as an unstable fixed point. The arrows indicate the direction in which

Figure 6.2: Graphic representation of the real three dimensional space of rotations $SO(3)$ as a sphere of radius π . Rotations are represented as vectors in this space, with the direction of the vector defining the axis of the rotation and the norm of the vector defining the angle of the rotation.

XBL 855-8871

Figure 6.3: Cross section of the xy plane of $SO(3)$ illustrating the flow of maps for (a) broadband, (b) narrowband, and (c) bandpass iterative schemes. The arrows indicate symbolically the direction in which points on this plane move when operated on by the various maps, towards stable fixed points and away from unstable fixed points.

points in this plane move, away from the origin and towards the equator, when the map is iterated. This motion is the flow of the map. It should be noted here that this map is atypical in the sense that it shows points in the xy plane being mapped only to other points in the same plane. In general, a map on $SO(3)$ will not behave in this way. Special cases of maps which do have this property play an important role in the future discussion, however, and will be examined presently.

Figure 6.3b illustrates the flow of points in the xy plane of $SO(3)$ for maps which produce narrowband π pulse sequences. Here, the equator and origin are fixed points as for the broadband case. The direction of the flow, though, has been reversed; it is now the equator which is unstable and the origin which is stable. The equator is fixed so that if $R(\bar{\alpha})$ is a point on the equator, i.e., is a π rotation, then $F(R(\bar{\alpha}))$ will remain a π rotation. All other points on this plane, however, converge to the origin, becoming identity operations. The result is a sequence which inverts spins over a narrow range of some parameter λ , and does not affect spins which lie outside this narrow range.

The flow of points for a map that produces a square, or bistable, inversion sequence is shown in figure 6.3c. This map has the origin and the equator as fixed sets, but in contrast to the two previous cases, both, instead of one, of the fixed sets are stable. A significant consequence of this bistability is the presence of an unstable fixed circle in the xy plane between the origin and the equator. In the previous section, the necessity of an unstable fixed point between two stable fixed points for a one-dimensional function was demonstrated. This result does not generally apply to maps on

$SO(3)$, since $SO(3)$ is not a one-dimensional space. The particular map shown here is exceptional, however, because it maps points on the xy plane only to points also on the xy plane. It will be shown in the next section that if the rotation around the z axis produced by the map is ignored, then a map on $SO(3)$ with this property can be considered fundamentally one-dimensional. Given this, the bistability theorem introduced in the previous section becomes applicable to the present case.

The bistability of the map in figure 6.3c is evidenced by the opposing arrows showing convergence to two fixed sets, *viz.*, the equator and the origin. The existence of the third unstable fixed set is required by the continuity of the map, and will be examined more thoroughly later on. This figure suggests that on this plane, three distinct classes of points exist. First are the points within the unstable fixed circle; these points move towards the origin as the map is iterated. Second is the unstable fixed circle itself, which, by definition, remains invariant, and to which no other points converge. The third class is the set of points which lie outside the unstable fixed circle and converge to the equator as the map is iterated.

The effect of iterating the map is to move points closer to the origin or the equator depending on whether the initial point $R(a_0)$ is inside or outside the unstable fixed circle. This movement to one of two stable fixed sets of propagators is the origin of the bistable bandpass response.

The preceding sections have established the following ideas. Pulse iteration schemes transform a pulse sequence S_i to S_{i+1} . Associated with this transformation of pulse sequences is a

transformation of the propagator U_i to the propagator U_{i+1} . This transformation is a map on the propagator space. To obtain a desired propagator $\bar{U}$ from a pulse sequence with an iterative scheme, the iterative scheme must have a corresponding map on the space which has $\bar{U}$ as a fixed point. The stability of the map in various directions determines the bandwidth properties of the sequence. Sequences which excite a bandpass response may be obtained from iterative maps with two stable fixed points. A bistable map causes most points to converge to either one of the two desired propagators $\bar{U}_1$ or $\bar{U}_2$ depending on the value of some parameter λ , and thereby produces the bandpass response. This idea is demonstrated here for maps which have the equator and the origin of $SO(3)$ as the two stable fixed sets. Iteration of the map results in the convergence of propagators to the two stable fixed points associated with the two possible responses of the spin system to the rf radiation. Experimentally, these propagators represent sequences which selectively invert nuclear spins depending on the rf amplitude at the spin's position.

III. DERIVATION OF ITERATIVE SCHEMES

A. Iterative Schemes and Maps on $SO(3)$

The pulse iteration schemes developed in this section are comprised of two basic operations. These will be demonstrated schematically on an arbitrary pulse sequence designated S_i . The schemes sought are those defining maps on $SO(3)$ with the equator and the origin as stable fixed sets and the xy plane as an invariant set of the map.

The first operation consists of forming phase shifted versions of

S_i . This transformation is performed by adding some constant amount ϕ_k to the phase of each pulse in S_i . The pulse sequence thus transformed will be denoted $S_i(\phi_k)$. The phase index k ranges from 1 to N , where N is the number of different phase shifts to be performed.

The second operation is to concatenate the N phase shifted versions of S_i . The result will be a sequence N times longer than S_i . The new sequence, S_{i+1} , will be:

$$S_{i+1} = S_i(\phi_1)S_i(\phi_2)\dots S_i(\phi_{N-1})S_i(\phi_N) \quad (6.18)$$

Clearly, both operations can be applied repetitively on any starting sequence. The uniquely defined rotation operator corresponding to S_i can be expressed similarly in the form:

$$R(\alpha_{i+1}) = R(\alpha_{i,N})R(\alpha_{i,N-1})\dots R(\alpha_{i,2})R(\alpha_{i,1}) \quad (6.19)$$

where $\alpha_{i,j}$ equals the vector $\alpha_i[\sin\theta_i\cos(\phi_i+\phi_j), \sin\theta_i\sin(\phi_i+\phi_j), \cos\theta_i]$ and $R(\alpha_{i,j}) = R_z(\phi_j)R(\alpha_i)R_z^{-1}(\phi_j)$. Here, θ_i and ϕ_i are the usual polar and azimuthal angles of a spherical polar coordinate system. Because of the group property of rotations, the product of rotation operators on the right always equals a rotation operator.

By limiting the analysis to these two operations, the problem of designing a pulse iteration scheme is reduced to a matter of selecting the N phases $\phi_1, \phi_2, \phi_3, \dots, \phi_N$. In choosing these phases, two constraints will be observed. The first is that N will be limited to an odd number. This constraint insures that the equator of $SO(3)$ will be a fixed set of the map specified by this pulse iteration scheme. This assertion follows from the fact that concatenating an odd number

of inversion sequences results in an inversion sequence. The necessity of making the equator a fixed set was discussed previously. No such restriction is required in this case to make the origin a fixed point since the origin is always a fixed point for any mapping derived from a simple phase shift scheme.

The second constraint imposed will be to demand that the phase shift scheme be symmetric. A symmetric phase shift scheme is one for which $\phi_i = \phi_{N-i+1}$, e.g., $\phi_1 = \phi_N$, $\phi_2 = \phi_{N-1}$, etc. This last constraint deserves special comment. In the preceding section, it was noted that maps on $SO(3)$ usually do not transform points on the xy plane only to other points on the xy plane. Symmetric phase shift schemes provide a convenient way to obtain maps with this property. Schemes for which the rf amplitude $\omega_1(t)$ and phase $\phi(t)$ are symmetric functions of time have corresponding maps which transform points on the xy plane only to other points in this same plane, hence making this plane an invariant set. A formal proof of this assertion and associated symmetry related properties has been reported in reference 24.

B. One dimensional maps on $SO(3)$

A single pulse produces a rotation around an axis in the xy plane provided the radiofrequency irradiation is exactly resonant with the transition frequency. This is evident from considering the rotating frame Hamiltonian during irradiation:

$$\mathcal{H}' = \omega_1(I_x \cos\phi + I_y \sin\phi) + \Delta\omega I_z \quad (6.20)$$

which results in the propagator:

$$U(t) = \exp\left\{-i[\omega_1(I_x \cos\phi + I_y \sin\phi) + \Delta\omega I_z]t\right\} \quad (6.21)$$

The unnormalized axis of rotation is given by the vector $(\omega_1 \cos\phi, \omega_1 \sin\phi, \Delta\omega)$, and lies in the xy plane if and only if $\Delta\omega$ is zero.

Consider now a general pulse sequence S_i which produces as its net effect on the density operator a rotation around an axis in the xy plane. The rotation operator corresponding to S_i can be written as $R(\alpha_i)$, where α_i is the vector:

$$\alpha_i = \alpha_i(\cos\phi_i, \sin\phi_i, 0) \quad (6.22)$$

Again, α_i is the angle and $(\cos\phi_i, \sin\phi_i, 0)$ the normalized axis of the rotation. The phase symmetry theorem states that if S_i is transformed according to a phase shift algorithm which is symmetric, the new rotation operator corresponding to the transformed sequence S_{i+1} must be of the form $R(\alpha_{i+1})$, where:

$$\alpha_{i+1} = \alpha_{i+1}(\cos\phi_{i+1}, \sin\phi_{i+1}, 0) \quad (6.23)$$

The map $F(R(\alpha_i)) = R(\alpha_{i+1})$ corresponding to a phase shift-concatenation operation is a well defined function on $SO(3)$. This point is made clear by equation (5.11). For a function which maps points on the xy plane only to other points on the xy plane, this implies that α_{i+1} and ϕ_{i+1} are determined uniquely by α_i and ϕ_i . In fact, for such maps, α_{i+1} is specified solely by α_i , as can be seen from the following considerations.

Assume S'_i is a pulse sequence related to the pulse sequence S_i by a constant phase shift of all the pulses $\Delta\phi$. The rotation operator for

$S_i', R(\alpha_i')$, is related to the operator $R(\alpha_i)$ by the similarity transformation:

$$R(\alpha_i) = R_Z(\Delta\phi)R(\alpha_i')R_Z^{-1}(\Delta\phi) \quad (6.24)$$

Now if a phase shift scheme $[\phi_1, \phi_2, \phi_3, \dots, \phi_N]$ is applied to S_i and S_i' to form S_{i+1} and S_{i+1}' , it follows after some algebra (cf. equation (5.11)) that $R(\alpha_{i+1})$ and $R(\alpha_{i+1}')$ are related by:

$$R(\alpha_{i+1}) = R_Z(\Delta\phi)R(\alpha_{i+1}')R_Z^{-1}(\Delta\phi) \quad (6.25)$$

Since $\Delta\phi$ is arbitrary, it can be concluded from this equality that for any map on $SO(3)$ derived from a phase shift scheme, α_{i+1} is independent of ϕ_i .

If the initial iterate, $R(\alpha_0)$, is a point in the xy plane of $SO(3)$ and the map a function derived from a symmetric phase shift scheme, this result, combined with equation (6.22), imply that the only variable determining α_{i+1} will be α_i , i.e.:

$$\alpha_{i+1} = f_s(\alpha_i) \quad (6.26)$$

Comparison of this expression with equation (5.3) reveals that equation (6.9) defines a one-dimensional map in α . This map can have fixed points $\bar{\alpha}$, although the fixed points of f_s correspond to, in actuality, fixed circles of radius $\bar{\alpha}$ in the xy plane of $SO(3)$. The two fixed circles of particular concern here are the equator and the origin, defined by the set $\{\bar{R}\}$:

$$\bar{R} = R_{\phi}(\bar{\alpha}) \quad (6.27)$$

where $0 \leq \phi \leq 2\pi$, and $\bar{\alpha} = 0$ for the origin and $\bar{\alpha} = \pi$ for the equator.

Because points in $SO(3)$ are specified by three coordinates, maps on this space are generally three dimensional functions. Consequently, such maps must normally be analyzed for stability at their fixed points along three orthogonal directions. Equation (6.26) suggests, however, that under a special set of conditions, discussed earlier, this three dimensional problem can be reduced to one dimension.

The simplification of this problem to one dimension now permits the application of the one dimensional bistability theorem stated in section 6.II.A. The values of α sought as fixed and stable points of the map in equation (6.26) are $\bar{\alpha}_1 = 0$ and $\bar{\alpha}_2 = \pi$. Stability at these fixed points, by the bistability theorem, necessitates the existence of a third fixed point $\bar{\alpha}_{\text{unstable}}$ lying in the range $\bar{\alpha}_1 < \bar{\alpha}_{\text{unstable}} < \bar{\alpha}_2$, which is unstable. As for $\bar{\alpha}_1$ and $\bar{\alpha}_2$, $\bar{\alpha}_{\text{unstable}}$ defines a circle in the xy plane of $SO(3)$. Points within the range $\bar{\alpha}_1 \leq \alpha < \bar{\alpha}_{\text{unstable}}$ move away from $\bar{\alpha}_{\text{unstable}}$ and towards $\bar{\alpha}_1$ as the mapping is repeated, becoming identity operators. Points in the range $\bar{\alpha}_{\text{unstable}} < \alpha \leq \bar{\alpha}_2$ also move away from $\bar{\alpha}_{\text{unstable}}$ but towards $\bar{\alpha}_2$ as the mapping is iterated becoming, instead, π rotations. This flow of points was described in section IIE, and is depicted in figure 6.3. In such a way, all points in the xy plane not on the unstable circle eventually get mapped, in some well defined fashion, to one of two possible sets of points, the identity operator or a π rotation.

C. Specification of Stability

The invariance of the equator and the origin of $SO(3)$ is guaranteed for a map corresponding to a phase iteration scheme, provided the scheme obeys the constraints set forth in the previous sections. The present discussion will be devoted to maps which, in addition to this invariance, are stable at these two points.

To begin, methods for specifying the stability of a map at each of these points individually are examined. These methods have already been considered in detail elsewhere,²⁴ and so will be presented only in outline form here.

Points in the neighborhood of the origin are those operators $R(\alpha_i)$ for which $|\alpha_i|$ is small. If an iterative map derived from a phase shift scheme acts on a rotation operator satisfying this condition, the next iterate, given analytically by equation (5.11), is well approximated by the linearized expression:

$$R(\alpha_{i+1}) \approx R \left(\sum_{j=1}^N \alpha_{i,j} \right) \quad (6.28)$$

The expression $\alpha_{i,j}$ is defined as in equation (5.11). The argument of the term on the right is related to α_i by a simple linear transformation, which is denoted $T^{(\text{origin})}$. This linear transformation can be calculated explicitly using equation (5.15), and has eigenvalues N and $\lambda_0^\pm$, where:

$$\lambda_0^\pm = \sum_{j=1}^N \exp(\pm i\phi_j) \quad (6.29)$$

Convergence to the fixed origin is indicated when $|\alpha_i| > |\alpha_{i+1}|$. For displacements in the xy plane, this occurs when two of the eigenvalues of $T(\text{origin})$, $\lambda_0^\pm$, are less than one. The possibility of course exists that only one of these eigenvalue is less than one. In such a case, convergence would occur only in certain directions, specifically, those directions parallel to the eigenvector of the stable eigenvalue. The flow of points in the xy plane produced by a map with a stable origin has been shown in figure 6.3b.

The analysis of convergence to the equator requires a more involved approach. It proceeds first with the completely general decomposition of a rotation $R(\alpha_i)$ into the product rotation:

$$R(\alpha_i) = R_{\phi_i}(\pi) R(\epsilon_i) \quad (6.30)$$

where $\epsilon = (\epsilon_x, \epsilon_y, 0)$. Points close to the equator have small $|\epsilon_i|$. Applying an iterative function to this product rotation in the manner of equation (5.11), the next iterate $R(\alpha_{i+1})$ can be shown in the linear approximation to equal:

$$R(\alpha_{i+1}) = R_{\phi_i + \gamma}(\pi) R(\epsilon_{i+1}) \quad (6.31)$$

To compare the rotation $R(\alpha_{i+1})$ with $R(\alpha_i)$ for convergence to the equator, it is necessary to rotate $R(\alpha_{i+1})$ so that the main part of $R(\alpha_{i+1})$, $R_{\phi_i + \gamma}(\pi)$, is coincident with the main part of $R(\alpha_i)$, $R_{\phi_i}(\pi)$. This reflects the fact that the overall z rotation produced by the mapping, corresponding to a phase shift by γ of the rotation axis, is irrelevant when determining convergence to a fixed circle in the xy plane, e.g., the equator.

Performing this transformation on $R(\alpha_{i+1})$ yields the rotation $R_{\phi_1}(\pi)R(\epsilon'_{i+1})$. The argument ϵ'_{i+1} can be expressed as a linear transformation of ϵ_i with eigenvalues:

$$\begin{aligned} \lambda_e^{\pm} = & (\cos\Gamma'_1 + \cos\Gamma'_3 + \dots + \cos\Gamma'_N) \\ & \pm \left[(\cos\Gamma'_2 + \cos\Gamma'_4 + \dots + \cos\Gamma'_{N-1})^2 \right. \\ & + (\sin\Gamma'_2 + \sin\Gamma'_4 + \dots + \sin\Gamma'_{N-1})^2 \\ & \left. - (\sin\Gamma'_1 + \sin\Gamma'_3 + \dots + \sin\Gamma'_N)^2 \right]^{1/2} \end{aligned} \quad (6.32)$$

where:

$$\Gamma'_n = \Gamma'_N + (-1)^n \phi_T \quad (6.33)$$

$$\phi_T = \phi_1 - \phi_2 + \dots - \phi_{N-1} + \phi_N \quad (6.34)$$

$$\Gamma'_n = \begin{cases} \phi_n + \sum_{m=1}^{n-1} (-1)^{m+1} 2\phi_m & n \text{ odd} \\ \phi_n - 2\gamma + \sum_{m=1}^{n-1} (-1)^m 2\phi_m & n \text{ even} \end{cases} \quad (6.35)$$

As in the case of the origin, these eigenvalues indicate stability for the map along directions coincident with the corresponding eigenvectors when their magnitudes are less than one. The flow in the xy plane expected from a map stable at the equator appears in figure 6.3a.

D. Bistability in Phase Symmetric Schemes

The four eigenvalue equations in (6.12) and 6.(15) suggest that obtaining stability at the equator and the origin requires that four inequalities be simultaneously satisfied, namely:

$$|\lambda_o^{\pm}| < 1 \quad (6.36)$$

$$|\lambda_e^{\pm}| < 1 \quad (6.37)$$

The analysis of section 6.III.B has proven, however, that the function underlying the map on $SO(3)$ is single dimensional. For the one dimensional case, specifying stability at two fixed points entails satisfying only two inequalities. From this, it appears that requiring all four inequalities above overdetermines the desired stability, and that it suffices to meet only two of these inequalities, one at the origin and one at the equator.

Although satisfying these two inequalities assures the stability of the fixed points, the maps investigated in this section actually fulfill a more rigorous condition at the two fixed points, that of superstability. Superstability in this space is obtained when the eigenvalues equal zero, and hence involves solving the two nonlinear equations:

$$|\lambda_e^+| = 0 \quad (6.38)$$

$$|\lambda_o^+| = 0 \quad (6.39)$$

The independent variables in these equations are the phase shifts

ϕ_i of the scheme. The choice of phase shifts is constrained by the criteria enumerated in section 6 III. With these constraints, the number of free parameters available to solve these equations is $(N-1)/2$, where N , the number of phases in the sequence, is odd for reasons explained previously.

Solutions to these two equations were determined numerically on a computer using the steepest descent root-finding procedure described in the previous chapter. One such solution to a good approximation leads to the phase shift scheme:

$$[0, 270, 120, 165, 120, 270, 0] \quad (A)$$

A second phase shift scheme was calculated similarly, but which additionally satisfies the superstability condition for both eigenvalue equations at the equator (see equation (6.32)). Solving this extra equation required one additional parameter, with the result that a nine shift scheme was obtained:

$$[0, 15, 180, 165, 270, 165, 180, 15, 0] \quad (B)$$

IV. PROPERTIES OF BISTABLE ITERATIVE SCHEMES

A. Convergence Properties of the 7 and 9 Shift Sequences:

Basin Images

Both phase shift algorithms proposed above fulfill the criteria stated earlier for invariance and stability at the equator and the origin of $SO(3)$, and hence both produce the flow of points in the xy plane described in figure 6.3. This fact is confirmed by the xy basin

images of the two maps displayed in figures 7.3 and 7.4. The bottom images in figures 7.3 and 7.4 show the basins in the xy plane of $SO(3)$ for the two bistable maps. Convergence for the i th iterate was decided when $|180 - \alpha_i| \leq 5^\circ$ at the equator, and $|\alpha_i| \leq 5^\circ$ at the origin.

Several features are immediately apparent in these images. In their gross features, both images are extremely similar. Both basins possess an axial symmetry about the z axis, corroborating a conclusion drawn in section 6.III.B, i.e., that maps derived from phase shift schemes are independent of the azimuthal angle coordinate ϕ of a point in $SO(3)$. In the xy plane, the only relevant quantity in determining the convergence of a point to one of the fixed sets is α , the distance of the point from the origin.

The lightest areas in these images appear near the equator and in the circular region centered at the origin. These correspond to the loci of points which are mapped after only a few iterations to the nearby stable fixed point, i.e., the equator or the origin. For both images, the basin of the equator is separated from the basin of the origin by a thin, distinct dark circle. This intermediate circle is the unstable fixed set whose existence, as seen earlier, is necessitated by the bistability of the one-dimensional map. Within this circle, all points converge to the origin, most after a relatively small number of iterations. Outside this unstable fixed circle, no points converge to the origin.

Similar behaviour is observed within the basin of the equator. The equator's basin consists of a hollow ring, bounded on the interior by the unstable fixed circle. Outside this circle, all points converge to the equator, becoming π rotations. The bidirectional flow observed

in these figures verifies the flow hypothesized in figure 6.3c.

A different perspective on the flow of points is offered by figures 6.4 and 6.5. These figures show the actual movement in the xy plane of an initial set of points from one iteration to the next. The bidirectional flow of points to the equator and origin depending on their distance from the origin is evident in these pictures, with points in between becoming sparser for increasing iterations.

The analysis of these two schemes thus far has not revealed any substantive differences between them. Qualitatively, both have similar flow properties in the xy plane leading to the desired bistable response. Indeed, the distinction between them is not apparent unless the behaviour of the map is investigated for points off the xy plane. This distinction is illustrated by figures 6.6 and 6.7. The arrows in figure 6.6 indicate the stability of the origin and the equator for the seven shift scheme along directions lying in the xy plane, and the instability of points along directions not in this plane. This instability is symbolized by the arrows pointing outward, away from the origin and the equator in the z direction.

Figure 6.7 is a schematic flow diagram for the map corresponding to the nine shift scheme. In the xy plane, the bidirectional flow properties are similar to the seven shift scheme. In contrast to figure 6.6, however, all arrows at the equator point in towards the equator, including those out of the xy plane. The implication here is that the mapping for the nine pulse scheme is stable in all directions at the equator.

These observations are substantiated by the top basin images in figure 7.3 and 7.4 showing cross sections of $S^0(3)$ containing the z

$$[0, 270, 120, 165, 120, 270, 0]$$

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Figure 6.4: Displacement of points in the xy plane as a result of being transformed by the map of the scheme $[0, 270, 120, 165, 120, 270, 0]$. In (a) is the initial set of points $R(\alpha_0)$. Applying the map once to these points results in a displacement to the set of points in (b), twice, in the set of points in (c), and three times in the points in (d). This figure reveals the expected movement of points both towards the equator and towards the origin.

[0, 15, 180, 165, 270, 165, 180, 15, 0]

(a) Initial Condition

(b) One Iteration

(c) Two Iterations

(d) Three Iterations

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Figure 6.5: A version of figure 6.4 for the scheme
[0,15,180,165,270,165,180,15,0].

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Figure 6.6: Flow in a plane of $SO(3)$ containing the z -axis for a map which is stable at the origin and the equator only for displacements in the xy plane. Points lying out of this plane move away from these two fixed sets when transformed by the map. The stable directions are given by the eigenvectors of the Jacobian of the map with eigenvalues less than one. The flow expected for such a map is depicted here.

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Figure 6.7: Same as figure 6.6, but for a map which is stable in all directions at the equator. All arrows are now shown pointing in towards the equator denoting this flow.

axis. Again, because of axial symmetry, all such z cross sections are identical. As in the xy basin images displayed earlier, these images depict the superposition of the basins of both the equator and the origin. The basin image for the seven shift scheme, while showing some regions out of the xy plane which are convergent to one of the fixed points, nevertheless is mostly black, indicating that most points in $SO(3)$ do not converge to either fixed point. The nine shift scheme on the other hand generates an image which shows a large portion of the space converging to the equator because of the additional direction of stability of this point. Like basin images reported earlier of broadband sequences, this image has a self-similar fractal structure.¹⁰⁴

The reason for the differences between the basin images can be understood by recalling the derivation of these algorithms in section 6.III.B. Four inequalities were derived in this section as necessary criteria for determining the stability of the equator and origin, two at both points. For specifying stability at the equator and origin with respect to displacements in the xy plane, it was found sufficient to satisfy only two of these inequalities. The map of the seven shift scheme does, in fact, satisfy these two inequalities, and therefore is stable only for displacements in the xy plane. The map of the nine shift scheme, however, satisfies the inequalities for both, rather than one, eigenvalues at the equator. Consequently, the map of the nine shift scheme has an additional direction of stability at the equator that the map of the seven shift scheme does not possess. This added direction is given by the eigenvector of the second stable eigenvalue, and is the origin of the extra stability at the equator in the z

direction of the mapping for the nine shift scheme. This means the equator is a stable fixed set of the nine shift map with respect to displacements caused by frequency offset.

B. Bandwidth Properties of Bistable Schemes

Producing specific pulse sequences with schemes (A) and (B) requires that an initial sequence be specified. The simplest initial sequence to consider is the case of a single resonant pulse. Applying the seven shift scheme (A) to this initial condition generates sequences consisting of 7^n pulses, where n is the number of times the scheme is iterated. According to the analysis given earlier, the propagators for these higher iterate sequences will converge either to the identity operator or an inversion operator. The parameter determining this limit of convergence for some initial iterate $R(\alpha_0)$ is α_0 , the initial angle of rotation.

For a single, resonant pulse of fixed duration t_p , α_0 is equal to $\omega_1 t_p$. From this relationship, the conclusion can be drawn that the limit to which the higher iterate propagators converges depends solely on the value of ω_1 . If ω_1 is small enough so that $\omega_1 t_p < \bar{\alpha}_{\text{unstable}}$, then the higher iterate propagators converge to the identity operator. If $\omega_1 t_p > \bar{\alpha}_{\text{unstable}}$, then the iterates converge to an inverting rotation as the scheme is iterated. More generally, the propagator U_0 for a single pulse converges to an inversion operation for rf amplitudes lying in the range:

$$\bar{\alpha}_{\text{unstable}} < \omega_1 t_p \bmod 2\pi < 2\pi - \bar{\alpha}_{\text{unstable}} \quad (6.40)$$

Outside these ranges, the limit of convergence is the identity

operator. Similar results hold for the nine shift scheme.

Exact theoretical simulations of the inversion performance of these sequences as a function of ω_1 are presented in figures 6.8 and 6.9. Formally, the inversion is defined as the projection of the spin density operator after the pulse sequence onto the operator I_z , which can be found from the equation (4.12):

In both figures are three curves, showing the inversion for a single pulse, one iteration of the scheme on a single pulse, and two iterations of the scheme. Two significant features of these plots stand out. First, it is clear that as the schemes are iterated, the bandwidth of the inversion response becomes increasingly more square. Within a sharply defined ω_1 range, the inversion achieved by the second iterate sequences is essentially complete. Outside this range, the rf has virtually no observable effect on the spins, leaving the bulk magnetization in its equilibrium state aligned with the static magnetic field.

The second notable characteristic of these plots are the two points in both where all three inversion curves intersect. The presence of these intersection points signifies an invariance in the inversion performance of these sequences for certain critical values of ω_1 . These critical values are given by:

$$\bar{\alpha}_{\text{unstable}} = \omega_1 t_p \bmod 2\pi \quad (6.41)$$

$$2\pi - \bar{\alpha}_{\text{unstable}} = \omega_1 t_p \bmod 2\pi \quad (6.42)$$

providing indirect evidence of the unstable fixed point between the two stable points predicted earlier.

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Figure 6.8: Theoretical plots of population inversion as a function of normalized rf amplitude for the (1) zeroth, (2) first, and (3) second iterations of the scheme [0,270,120,165,120,270,0]. The initial sequence S_0 is a single pulse with variable ω_1 . The equilibrium polarization (magnetization aligned with the field) is denoted by -1, a complete inversion of the polarization by +1 (magnetization antiparallel to the field).

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Figure 6.9: Same as figure 6.8 but for the scheme [0,15,180,165,270,165,180,15,0].

Figure 6.10: Plot of population inversion as a function of rf amplitude for the zeroth, first, and second iterations of the scheme [0,270,120,165,120,270,0]. The theoretical dependence appears as the black line, the experimental points as the dots.

Figure 6.11: Same as figure 6.10, but for the scheme $[0, 15, 180, 165, 270, 165, 180, 15, 0]$.

C. Role of the Initial Condition and Some Specific Sequences

i. Single pulse initial condition

Experimental verification of the theoretical simulations for the first two iterates of both schemes appears in figures 6.10 and 6.11. The pulse sequence S_0 used to initiate the iterative procedure was a single pulse with variable ω_1 . These results confirm the extreme specificity of these sequences for discriminating between spins based on the local rf field amplitude at the spin's coordinates in space.

The performance of these sequences off resonance is shown in figures 6.12 and 6.13. For single pulses, moving off resonance introduces a z component into the axis of rotation of the operator R . Due to the instability of the map at the origin along the z direction, the introduction of this z component in the initial iterate causes the bistability of the map to break down. As a result, the square response is irrevocably lost, even for the higher iterate sequences.

Although the useful bandpass specificity of these sequences is not retained off resonance, these plots nevertheless reveal an interesting fact. The nine shift sequence it may be recalled was derived to be stable in all directions at the equator. This additional stability, to some degree, compensates for off resonance effects near the equator. This compensation is indeed observed in these figures. Within the effective inversion range of the nine shift scheme, moving off resonance impairs inversion performance very little. For the seven shift sequence, however, the inversion performance is affected much more dramatically by going off resonance. This scheme, unlike the former scheme, does not produce stability at the equator, and hence is

Figure 6.12: Inversion performance of the scheme [0,270,120,165,120,270,0] at various resonance offsets. The sequence shown was generated by iterating once with this scheme on a single pulse of variable ω_1 . Experimental points appear as the black dots.

Offset behavior for $[0, 15, 180, 165, 270, 165, 180, 15, 0]$

$$\Delta = \Delta\omega/\omega_1^0$$

Figure 6.13: Same as figure 6.12, but for the scheme $[0, 15, 180, 165, 270, 165, 180, 15, 0]$.

not compensated for resonance offset related imperfections.

ii. Tailored Inversion

The discussion of the previous sections has emphasized the fact that by varying experimental parameters, such as ω_1 , of a starting sequence S_0 , the coordinates in $SO(3)$ of the corresponding propagator $R(\alpha_0)$ can be varied in a well defined fashion as well. This can lead to interesting bandwidth behaviour if, for example, for some values of ω_1 , $R(\alpha_0)$ lies in the basin of one fixed set, and for other values of ω_1 , $R(\alpha_0)$ lies in the basin of a second fixed set. Figure 6.14 illustrates this principle. Continuous variation of an experimental parameter λ causes $U(\vec{\phi}_0, \vec{\alpha}_0, \lambda)$ to trace out a trajectory in Liouville space, taking it from the basin of one fixed set to the basin of another fixed point. This point was examined specifically for the case of an initial sequence S_0 consisting of a single resonant pulse and is manifested in the inversion vs. ω_1 plots shown in figures 6.8 and 6.9, particularly for the higher iterate sequences. For values of ω_1 for which $R(\alpha_0)$ lies within the basin of the origin, the density operator remains unchanged from its initial state $-I_z$. Where ω_1 assumes values placing $R(\alpha_0)$ in the basin of the equator, however, nearly complete inversion of the density operator takes place.

The choice of a single pulse as the initial sequence resulted in a specific distribution of first iterates $R(\alpha_0)$ as a function of ω_1 . If the phase of this pulse is 0° , this distribution of $R(\alpha_0)$ appears in $SO(3)$ as a continuous line from the origin to the equator along the x-axis, as shown in figure 6.4. This distribution, along with the values of ω_1 for which $R(\alpha_0)$ crosses the unstable fixed circle, fully

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Figure 6.14: Schematic illustration in (a) of a propagator U resulting from some excitation sequence plotted in propagator space as a function of some experimental parameter λ . The parametric dependence causes U to lie in the basin of one fixed point for some values of λ and in the basin of another fixed point for other values of λ , leading to the type of bandwidth behaviour appearing in (b).

determines the bandwidth properties of the higher order iterates.

The variation of ω_1 can result in other, different distributions of $R(\alpha_0)$ simply if a different S_0 is chosen as the starting sequence, for it is the specific form of S_0 which determines how $R(\alpha_0)$ varies as a function of ω_1 . For values of ω_1 for which $R(\alpha_0)$ lies outside the unstable fixed circle, $R(\alpha_1)$ will converge to an inverting rotation as the map is iterated. Accordingly, over these ranges of ω_1 , the density operator will be effectively inverted, particularly for the higher iterate sequences. For the remaining values of ω_1 , $R(\alpha_0)$ will lie within the unstable fixed circle. Over these ranges of ω_1 , $R(\alpha_0)$ converges to the identity operator as the map is iterated, resulting in sequences which do not alter the initial state of the spin system.

Generalizing this technique offers the possibility of a true tailoring of spin excitation. To achieve such tailoring, an initial sequence S_0 is chosen with the property that in the ranges of ω_1 for which population inversion is desired, $R(\alpha_0)$ lies within the basin of the equator. Iterating upon such an initial condition will then result in a pulse sequence which selectively and precisely inverts populations only over those regions of ω_1 for which $R(\alpha_0)$ lies within the proper basin. Although it is possible to obtain such starting sequences by analytical means, a more practical and equally effective approach would be to simply program a computer to search for sequences which fulfill the desired basin criteria.

iii. Broadband and Narrowband Initial Sequences

The rotation operators corresponding to inverting sequences broadband in ω_1 lie close to the equator of $SO(3)$ for a wide range of

ω_1 values. Such sequences result in a distribution of initial rotations $R_\phi(\alpha_0)$ which lie predominantly within the basin of the equator for a bistable iterative scheme. Employing a broadband sequence as the initial iterate S_0 in a bistable iterative scheme therefore results in an inversion profile which becomes both square and broadband as the scheme is repeatedly applied.

The simulated inversion profiles appearing in figure 6.15 confirm this prediction. The sequence used in these plots to initiate the iterative procedure was the three pulse sequence $[0,120,0]$, which has previously been shown to be effective in inverting spin populations over broad ranges of amplitudes.¹⁸ Utilized as the initial iterate of the bistable iterative scheme, in this case the scheme $[0,270,120,165,120,270,0]$, it produces the square, broadband inversion profile displayed in the higher iterates of figure 6.15.

A similar analysis is applicable to narrowband initial sequences as well. Within the theoretical picture presented here, narrowband sequences lead to distributions of rotation operators which, for most values of ω_1 , lie close to the origin of $SO(3)$. For a very narrow range of ω_1 values, the rotation operators corresponding to the pulse sequence lie on the equator. Iterating on points distributed in such a way on $SO(3)$ results in a square, narrowband response.

Again, this can be confirmed by simulations of inversion performance, as shown in figure 6.16 for the initial narrowband sequence $[0,151,255.5,151,0]$. The inversion passband for higher iterates of this five pulse sequence is extremely narrow, reflecting the narrowband properties of the initial sequence.

Both the narrowband and the broadband initial sequences display

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Figure 6.15: Consequence of using a broadband sequence as the initial iterate for the bistable scheme [0,270,120,165,120,270,0] for the (1) zeroth, (2) first, and (3) second iteration of the scheme. The broadband sequence chosen here is the symmetric three pulse sequence [0,120,0].

40 860 0998

Figure 6.16: Consequence of using a narrowband sequence as the initial iterate for the bistable scheme [0,270,120,165,120,270,0] for the (1) zeroth, (2) first, and (3) second iteration of the scheme. The narrowband sequence shown is the symmetric five pulse sequence [0,151,255.5,151,0].

evidence of the unstable fixed point in the two crossing points delineating the effective passband of the two sequences, just as in the case of the single pulse initial condition.

iv. Amplitude Selective $\pi/2$ Pulse Sequences

The inversion vs. ω_1 plots for the higher iterate pulse sequences obtained by the bistable maps reveals that the ω_1 ranges for which inversion of the density operator is complete and the ranges for which there is little inversion are separated by an extremely narrow range of ω_1 values where only partial inversion of the density operator takes place. As noted earlier, these narrow ranges indicate that at, or near these values of ω_1 the function $R(\alpha_0)$ crosses the unstable fixed circle.

Within this narrow range of ω_1 values lies an even narrower range where the projection of the density operator onto I_z is approximately zero after irradiation by the pulse sequence. This situation arises when the density operator has been rotated into the xy plane, and occurs when the overall propagator is of the form in equation (4.2).

The narrowness of the range of ω_1 values which result in such a propagator suggests a method for obtaining a highly amplitude selective $\pi/2$ pulse sequence. The ω_1 selectivity of such a sequence is limited only by the sharpness of the inversion bandpass cutoff, which, as has been demonstrated, can be made arbitrarily sharp by performing more operations of the iterative scheme. The creation of transverse magnetization only over narrow, specific ranges of ω_1 is an essential technique in applications such as slice-selective, in-vivo NMR experiments,⁹² which rely on rf amplitude gradients in order to

preferentially excite selected regions of a macroscopic sample. The success of such an experiment depends on the ability to excite detectable NMR signal only in the regions of interest, and to suppress, or avoid excitation, of signal from other regions. In addition, it is desirable that the excitation sequence be short and consist only of pulses with the four quadrature phases.

The sequence $[(37.5)_{90}, (37.5)_0, (37.5)_{90}]$ was selected with these considerations in mind. The pulse sequence defined by this notation consists of three equal length pulses, each producing a flip angle of 37.5° , with phases $90^\circ, 0^\circ, 90^\circ$. In order to avoid exciting transverse signal at other values of ω_1 besides the intended range, the sequence picked is a broadband near-inverting sequence over ω_1 frequencies. Choosing such a sequence ensures that $R(\alpha_0)$ crosses the unstable fixed circle in the xy plane of $SU(3)$ only once over a large range of ω_1 values, in this case, the normalized range $0 \leq (\omega_1/\omega_1^0) \leq 8$. In this way, the creation of transverse magnetization in the higher iterate sequences at values of ω_1 other than the desired ones is suppressed. A more thorough examination of the problems associated with the inadvertent excitation of transverse coherence has been presented elsewhere.¹⁰⁵

The ω_1 specificity obtainable from this method can be observed in figures 6.17 and 6.18 for this choice of an initial sequence. The top figures show the inversion plotted as a function of ω_1 , while the lower figures show the projection of the density operator onto the xy plane after application of the pulse sequence. This last quantity is formally defined by the quantity $\langle M_{xy} \rangle$. Using this three pulse sequence as the starting point of the iterative procedure generates,

Figure 6.17: Longitudinal ((a), (b), and (c)) and transverse ((d), (e), and (f)) magnetization plotted as functions of normalized radiation amplitude for the scheme $[0, 270, 120, 165, 120, 270, 0]$ using the sequence $(37.5)_{90}(37.5)_0(37.5)_{90}$ as the zeroth iterate. The zeroth, through second iterates are shown.

Initial Pulse $(37.5)_{90} (37.5)_0 (37.5)_{90}$
 Iterative Scheme $[0, 270, 120, 165, 120, 270, 0]$

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Figure 6.18: Same as figure 6.17: but for the iterative scheme
[0,15,180,165,270,165,180,15,0]. Where shown, experimental data appear
as dots.

Initial Pulse $(37.5)_{90} (37.5)_0 (37.5)_{90}$

Iterative Scheme $[0, 15, 180, 165, 270, 165, 180, 15, 0]$

0 Iteration

1 Iteration

2 Iterations

XBL 859 12321

after the n th iteration, sequences of length 3×7^n pulses for the seven shift scheme, and of length 3×9^n pulses for the nine shift scheme. These data verify the extreme specificity that can be obtained from using the cutoff frequency of a sharply defined ω_1 passband.

V. OTHER ROUTES TO BISTABLE MAPS

In section 6.III, it was demonstrated that maps which were stable at the equator and the origin could be obtained by satisfying the stability conditions represented by equations (6.38) and (6.39). Bistable maps can also be devised by forming composite maps out of two singularly stable maps, a topic which will be examined in the present section.

Consider two one dimensional maps F_1 and F_2 on the space L satisfying the relationships below:

$$F_1(\bar{x}_1) = \bar{x}_1 \quad (6.43)$$

$$F_1(\bar{x}_2) = \bar{x}_2 \quad (6.44)$$

$$\left| \frac{dF_1}{dx} \right|_{x=\bar{x}_1} < 1 \quad (6.45)$$

$$\left| \frac{dF_1}{dx} \right|_{x=\bar{x}_2} > 1 \quad (6.46)$$

$$F_2(\bar{x}_1) = \bar{x}_1 \quad (6.47)$$

$$F_2(\bar{x}_2) = \bar{x}_2 \quad (6.48)$$

$$\left| \frac{dF_2}{dx} \right|_{x=\bar{x}_1} > 1 \quad (6.49)$$

$$\left| \frac{dF_2}{dx} \right|_{x=\bar{x}_2} < 1 \quad (6.50)$$

Equations (6.43), (6.44), (6.47) and (6.48) indicate that F_1 and F_2 have the same two fixed points $\bar{x}_1$ and $\bar{x}_2$. By equations (6.45) and (6.46) F_1 is stable at $\bar{x}_1$, but unstable at $\bar{x}_2$, while by equation (6.49) and (6.50), F_2 is unstable at $\bar{x}_1$ but stable at $\bar{x}_2$.

The composition of these two maps is defined by the following relation:

$$F_1 * F_2 = F_1(F_2(x)) \quad (6.51)$$

It is clear that $F_1 * F_2$ will also be a map on L , with $\bar{x}_1$ and $\bar{x}_2$ both as fixed points.

The stability of $F_1 * F_2$ at $\bar{x}_1$ and $\bar{x}_2$ can be determined by evaluating the first derivative of $F_1 * F_2$ at the fixed points. By the chain rule, this derivative can be written:

$$\frac{d}{dx}(F_1 * F_2) = \frac{dF_1}{dF_2} \frac{dF_2}{dx} \quad (6.52)$$

Using the general one dimensional stability criterion appearing in equation (5.5), the conditions for the stability of F_1 and F_2 at $\bar{x}_1$ and $\bar{x}_2$ can be stated as:

$$\left| \frac{dF_2}{dx} \right|_{x=\bar{x}_1} < \left| \left[\frac{dF_1}{dF_2} \right] \right|_{x=\bar{x}_1}^{-1} \quad (6.53)$$

$$\left| \frac{dF_2}{dx} \right|_{x=\bar{x}_2} < \left| \left[\frac{dF_1}{dF_2} \right] \right|_{x=\bar{x}_2}^{-1} \quad (6.54)$$

These inequalities are trivially satisfied if $\bar{x}_1$ is a superstable fixed point of F_1 and $\bar{x}_2$ a superstable fixed point of F_2 (provided the expression on the left hand side of (6.53) is finite). Under these conditions, $\bar{x}_1$ and $\bar{x}_2$ will be stable fixed points of $F_1 * F_2$.

This result was used to devise a composite iteration scheme formed by alternating the broadband iterative scheme $[0,120,0]$ with the narrowband iterative scheme $[0,151,255.5,151,0]$. These sequences were discussed in section 6.IV.C. One iteration of the composite scheme on some sequence results in a sequence fifteen times longer than the previous iterate. The symmetry of these schemes indicates that their corresponding maps will be single dimensional for initial iterates lying in the xy plane of $S0(3)$.

The composite scheme leads to a composite, one dimensional map on the xy plane of $S0(3)$ which is bistable, with all the attendant properties observed earlier for the two schemes (A) and (B). The inversion profiles bear this out, as can be seen in figure 6.19. Although the width of the passband is dependent upon the order of the composition, both still display the distinctive bandpass features seen before indicative of the underlying bistable map.

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Figure 6.19: Population inversion as a function of ω_1 for composite (broadband)*(narrowband) and (narrowband)*(broadband) schemes. The distinctive features of a bistable response are clearly evident in these profiles.

VI. RESONANCE FREQUENCY SELECTIVE INVERSION

The reduction of an iterative function on the three dimensional space $SO(3)$ to an underlying one dimensional function was made possible in the previous sections by the unique symmetry properties of symmetric phase shift concatenation schemes. First, there is the simplification which results from using a symmetric scheme. A point lying in the xy plane of $SO(3)$ is mapped to another point also in the xy plane if the phase shift scheme defining the function on $SO(3)$ is symmetric. The function for the subset of points lying in the xy plane of $SO(3)$ can thereby be reduced to a two dimensional function.

A second simplification arises from the z rotational symmetry common to all phase shift concatenation schemes. For points in $SO(3)$ contained in the xy plane, this cylindrical symmetry reduces the two dimensional function of a symmetric phase shift concatenation scheme still further into a one dimensional function.

The simplifications summarized above apply for rotation operators $R(\alpha_0)$ lying in the transverse plane of $SO(3)$. If the rotation operator does not lie in this plane, as is the case, e.g., for a single spin propagator during an off resonance pulse, then no such reduction is readily apparent using phase shifts and concatenations as the only iterative operations.

Because of this, true passband excitation is attainable as a function of the resonant rf amplitude ω_1 , but evidently not as a function of the resonance frequency ω_0 . The one dimensional bistability theorem of section 6.II.A, which guaranteed the convergence of all points in the xy plane of $SO(3)$ to one of two stable fixed points, cannot be adapted to the ω_0 domain. Additional insight and

$[0, 180, 90, 270, 270, 90, 180, 0]$ premapping

Figure 6.20: Flow of selected points for the map of the iterative scheme $[0, 180, 90, 270, 270, 90, 180, 0]$. All points on the transverse plane are mapped to the origin. All points in the neighborhood of the coordinates $(2\pi/3)(3)^{-1/2}[\cos\phi, \sin\phi, 1]$, designated by the points labeled 1, are mapped to the equator.

iterative operations are required.

The objective, as before, is to devise a scheme defining a function on $SO(3)$ with more than one stable fixed set, so that for some resonance frequencies, the propagator iterates U_i converge to one fixed point, and for other resonance frequencies, U_i converges to the other fixed point. One possible approach to this problem, illustrated by figure 6.20, is to precede the iterative function with a "premapping". The premapping shown in figure 6.20 is a function on $SO(3)$ defined by the phase shift concatenation scheme $[0, 180, 90, 270, 270, 90, 180, 0]$. Globally, the form of this function in $SO(3)$ is, like most such schemes, rather complicated and difficult to evaluate explicitly. Within certain regions of $SO(3)$, however, the trajectories of points generated by this function, can be deduced a priori. All points in the xy plane of $SO(3)$, for instance, are mapped after a single iteration of this function to the origin. This conclusion can be inferred from the observation that the sequence of phase shifts defining the function is composed of 180° alternated phase pairs. For rotations about axes in the xy plane of $SO(3)$, these pairs define cyclic sequences.

A second region in $SO(3)$ of interest are the points in the neighborhood of rotations of the form $R(\tilde{\alpha}_0)$, where:

$$\tilde{\alpha}_0 = \frac{2\pi}{3\sqrt{3}} \left[\sqrt{2}\cos\phi, \sqrt{2}\sin\phi, \pm 1 \right] \quad (6.55)$$

These points define 120° rotations about axes separated from the z axis by the magic angle. Points in $SO(3)$ of this form are mapped after one iteration to $R(\tilde{\alpha}_1)$, where:

$$\tilde{\alpha}_1 = \pi (\cos\phi, \sin\phi, 0) \quad (6.56)$$

Rotations of this type lie on the equator of $SO(3)$.

Points in the neighborhood of the operators defined by $R(\tilde{\alpha}_0)$ lie approximately above and below the set of rotation operators $R_\phi(\pi/2)$ in the spherical representation of $SO(3)$ of figure 6.2. The set of rotation operators corresponding to single, off resonance pulses lie within this neighborhood of $R(\tilde{\alpha}_0)$ for some range of $\Delta\omega$ values. These points will therefore be mapped close to the equator by the function corresponding to the scheme $[0, 180, 90, 270, 270, 90, 180, 0]$. In other words, single, off resonance $\pi/2$ pulses are approximately converted to π pulses by this map; single, on resonance pulses are converted by this phase shift scheme into cycles.

The outcome of following the premapping with a phase shift scheme which generates broadband π pulses appears in figures 6.21 and 6.22. These figures are simulations of the population inversion as a function of resonance frequency of the 8 pulse sequence generated by iterating once with the scheme $[0, 180, 90, 270, 270, 90, 180, 0]$ on a single pulse and of the 40 pulse sequence generated by operating upon the 8 pulse sequence with the scheme $\{0, 330, 60, 330, 0\}$. The scheme $\{0, 330, 60, 330, 0\}$ has been shown by Tycko²⁴ to define a function on $SO(3)$ which has the equator as a superstable fixed set.

These simulations confirm that for some values of ω_0 higher and lower than the actual spin resonance frequency, the premapping transforms the off resonance propagator to an operator approximately of the form $R_\psi(\pi)$. Following the premapping with the broadband π scheme $[0, 330, 60, 330, 0]$ maps these rotation operators even closer to the

Figure 6.21: Plot of inversion vs. resonance offset for (0) the eight pulse scheme generated by the scheme $[0,180,90,270,270,90,180,0]$ applied to a nominal $\pi/2$ pulse; and (1) the five pulse sequence of (0) iterated once with the broadband π iterative scheme $[0,330,60,330,0]$ (40 pulses). The combination of the two symmetric schemes results in distinctive bandpass behaviour over resonance frequencies.

Figure 6.22: Inversion as a function of resonance offset for (a) the 5 pulse sequence of (0) in figure 6.21; (b) the 40 pulse sequence of (1) in figure 6.21; and (c) the 200 pulse sequence generated from the sequence of (b) by iterating with the scheme $[0, 330, 60, 330, 0]$. The discontinuities of the basin image near the xy plane are manifested by the chaotic variations in the inversion between the regions where there is no inversion and the regions where there is complete inversion.

equator of $SO(3)$. On resonance $\pi/2$ pulses become cyclic sequences by this iteration scheme. Near resonance for these sequences, therefore, the spins remain in their equilibrium states and no inversion takes place.

The basin image for this scheme appears in figure 7.5. The premapping step is counted as the first iteration. This image was computed by checking for convergence of points in $SO(3)$ to the equator. Convergence was decided when a point was mapped to within $\pm 5^\circ$ of the equator. As anticipated, large regions above and below the transverse plane converge to the equator. A narrow region encompassing the xy plane where the basin is discontinuous and chaotic lies between the two main basins of the equator. Although it can be deduced that points in the xy plane are mapped to the origin, the trajectories of points slightly above and below this point are not as easy to predict. The discontinuities of this transition region are revealed in the third inversion plot of figure 6.22 by the sharp oscillations between the ranges of ω_0 where there is complete inversion, and the ranges where there is no inversion. The inversion profile in this figure is for the 200 pulse sequence obtained by iterating on the prior 40 pulse sequence by $[0, 330, 60, 330, 0]$.

Two features of this basin image deserve mention. First is the twofold reflection symmetry. The reflection symmetry about the plane containing the z axis is a consequence of the z rotational symmetry of phase shift schemes. The reflection symmetry through the xy plane comes about because of the phase symmetry of the iterative schemes defining the mapping.

Secondly, it should be noted that unlike the schemes presented

earlier, the stable fixed set of this premapped function, viz., the equator, is not situated in the middle of its basin. The premapping function specified by the scheme [0,180,90,270,270,90,180,0] does not have the equator as a fixed set. The points in $SO(3)$ mapped to the equator are indicated by the large, light regions, above and below the xy plane of $SO(3)$.

CHAPTER SEVEN: BASIN IMAGES

I. INTRODUCTION

The propagator functions considered so far map rotation operators into other rotation operators. The rotation group can be conveniently represented by matrices of the form in equation (2.28). An operation which transforms rotations can therefore be represented mathematically by a function which maps real, orthogonal 3×3 matrices with determinant equal to one, such as in equation (2.28), to other, similar 3×3 matrices.

If the number of operations comprising an iterative scheme is small, an analytical expression for the map on $SO(3)$ specified by the scheme can sometimes be explicitly evaluated. In general, the form of such functions are somewhat complex. The evaluation of the function on $SO(3)$ defined by a phase shift scheme comprised of only five phase shifts, for instance, entails the multiplication of five 3×3 matrices. Although this multiplication can clearly be done, it is unlikely in most cases that having an explicit form for a function on $SO(3)$ will provide much insight into the global dynamics of the function.

The complexity of the dynamics of these functions, and indeed of the functions themselves, compels the use of computers in order to investigate the behaviour of the iterates of the functions. The exploration of a function's dynamics by computer is necessarily an approximate and empirical procedure. Numerical methods nevertheless often reveal insights about a function's global dynamics which cannot

easily be predicted from the form of the function itself.

The generation of a basin image is one way in which a computer can be employed to provide a clear and simple picture of a complicated map's dynamics. All of the basin images displayed in this Chapter are two dimensional slices through $SO(3)$. A point in this slice represents a specific rotation $R(\alpha_0)$. To generate the basin image, $R(\alpha_0)$ is numerically mapped to $R(\alpha_1)$. Equation (5.11) illustrates how the mapping would be performed if the iterative scheme defining the mapping were a phase shift concatenation scheme. Convergence to a predetermined point, or set of points, $\bar{R}$ is then checked. If the iterate lies within some specified neighborhood of $\bar{R}$, then the iteration process is terminated and a color is assigned to the coordinates of the initial point $R(\alpha_0)$; if not, then the iteration procedure is repeated until the convergence criterion is satisfied or until some maximum number of iterations have been performed. The shade at a point on this plane is a measure of the number of iterations required to map the indicated point to $\bar{R}$ -- the lighter the shade, the fewer the number of iterations required. A black point signifies that the maximum number of iterations was reached before convergence was found. Such images identify the basin of $\bar{R}$, that is, the set of points in $SO(3)$ which converge to $\bar{R}$ as a result of the repeated iteration of the function.

Although only a simple convergence test was used to generate the images of this Chapter, a more sensitive and accurate check for convergence would include a calculation of the next iterate after the point had been mapped to the neighborhood of $\bar{R}$. If and only if the next iterate were closer to $\bar{R}$ than the previous iterate would

convergence to $\bar{R}$ then be decided. The inclusion of this second test ensures that points which move slowly out of the neighborhood of a fixed point along an unstable direction are not erroneously considered part of the fixed point's basin.

A basin image view of a function's dynamics is limited in a number of respects. Basin images are specific to the point for which convergence is checked. As described here, they do not locate stable fixed points other than the ones specifically identified in the computer program, nor can they be used to locate unstable fixed points. Their appearance to some extent depends on the convergence criterion used, and therefore is largely arbitrary. Round off errors by the computer may cause a distortion of the image, particularly if large regions of $SO(3)$ are not part of the fixed point's basin. Fortunately, none of these factors have been found in practice to be a serious problem of the images presented here, as determined by empirical testing with a computer.

A. Phase shift schemes

The basin images for functions defined by NMR iterative schemes can be grouped according to several different classification schemes. The first eleven images are presented together because they are all images of simple phase shift concatenation schemes. Where shown, the top image is a slice of $SO(3)$ containing the z axis while the lower image is a slice through the transverse plane of $SO(3)$. The first two were discussed in Chapter Five and the next three in Chapter Six. The salient characteristics to observe in all of these are the rotational symmetry about the z axis, a property common to all phase shift

schemes, and the symmetry, or lack thereof, about the xy plane. The latter symmetry arises from the symmetry of the phase shift scheme itself.²⁴

All of the basin images, including those following the first eleven, were computed by checking iterates for convergence to within approximately $\pm 5^\circ$ of the predetermined fixed point.

Figures 7.1 and 7.2:³¹ Two dimensional basin images for the schemes $[0,135,135,0]$ and $[0,0,180,135,135,150,330,0]$ respectively. The basins in these images are for rotation operators of the form $R_\phi(\pi/2)$. The larger size of the basin in 7.2 signifies the stability in all directions of the fixed point $R_\phi(\pi/2)$. This point is stable for the map corresponding to the image in 7.1 only with respect to displacements in the xy plane of $SO(3)$.

Figures 7.3 and 7.4:^{27,28} Two dimensional basin images for the maps defined by the schemes $[0,270,120,165,120,270,0]$ and $[0,15,180,165,270,165,180,15,0]$ respectively. The basins of the equator and the origin are simultaneously displayed in these figures. The presence of a stable origin and equator is manifested in both by the presence of large basins around these sets. The size of the top basin in 7.4 indicates the stability in all directions of the fixed equator. The top basin image in 7.3 shows a smaller basin, indicating the instability of the equator in directions with a z component.

Figure 7.5:²⁹ Two dimensional basin image through a slice of $SO(3)$ containing the z axis of the map specified by the scheme $[0,330,60,330,0]$ preceded by the premapping step $[0,180,90,270,270,90,180,0]$. The basin shown is of the equator. A discussion of this iterative scheme is given at the end of Chapter Six.

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Figure 7.6, 7.7, and 7.8:²⁴ Basin images of the schemes $[0, 330, 60, 330, 0]$, $[0, 0, 120, 60, 120]$, and $[0, 256, 52, 0, 128, 0, -128, 0, -52, -256]$, respectively. All three schemes define maps with the equator as a stable fixed set. The basin of these images is of the equator. The reflection symmetry of 7.6 is result of the symmetry of the scheme itself.²⁴ The dark rings in the lower xy images suggest the functions' complex dynamics even in this plane.

Figure 7.8 is a scheme with an antisymmetric sequence of phases. Antisymmetric phase shift schemes have important properties, discussed in reference 24.

Figures 7.9, 7.10, and 7.11: Basin images for the maps of the schemes $[105, 256, 0, 256, 105]$, $[0, 200, 230, 30, 95]$, and $[0, 120, 240]$ respectively (please note: the top image for 7.10 is upside down). The basins are of the origin for 7.9 and 7.11, and of the origin and the equator for 7.10. The origin is stable only with respect to displacements in the xy plane for these maps. The equator is unstable in all directions for the first and third maps, and stable only with respect to vertical displacements for the second map.

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B. Iterative schemes containing inverses

The maps in this and the following sections have already been given a detailed and comprehensive fixed point analysis.^{24,39} Only the basin images and a brief description of the schemes are given here.

Figure 7.12: Basin images of the idealized recursive expansion procedure.³⁰ This scheme and the details of how the basin image was calculated have been discussed in Chapter Five. The top image is a slice containing the z axis, and the bottom image the slice containing the xy plane. As for phase shift schemes, this scheme possesses a rotational symmetry about the z axis.

Figure 7.13: Basin images of the idealized retrograde compensation procedure.²⁶ The version of the scheme presented here is symbolized by the notation $S_i(S_i^{-1})_{60}(S_i)_{120}$. This notation is explained in Chapter Five. The light region is the basin of the z axis. An exact inverse operator was computed when performing the step of the procedure requiring the formation of S_i^{-1} . The assumption that an inverse sequence can be formed is an idealization of the way this scheme might actually be implemented.

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C. Waugh decoupling iterative scheme

The next six pages contain twelve basin images for the map specified by a Waugh heteronuclear decoupling scheme.⁸⁵ The basins are of the origin of $SO(3)$. The version of Waugh's scheme used to compute these images consisted first of the permutation of a $\pi/2$ pulse from the end of the initial sequence to its beginning, forming the sequence S_p . S_p was then phase shifted by π and the phase shifted version concatenated with S_p .

The special problems associated with schemes involving the permutation of pulses have been thoroughly considered.²⁴ Two of these problems are (1) that a form of the permuted $\pi/2$ pulse must be assumed and (2) that because the permuted pulse has a definite phase, the z rotational symmetry of all the previous schemes will be absent for this scheme. The slice angle of an image containing the z axis must therefore be specified. The figure captions below specify the slice in $SO(3)$ displayed by the image, and $\Delta\omega/\omega_1^0$ for the single $\pi/2$ pulse permuted as part of the scheme.

Figure 7.14: (upper) Basin image containing the z axis of $SO(3)$, with a slice angle of 0° . The normalized offset of the permuted pulse is 0. (lower) Same as the upper image, but for a normalized offset of 0.5.

Figure 7.15: (upper) Same as the upper image of 7.14, but for a normalized offset of 1.0; (lower) same as the upper image of 7.14, but for a normalized offset of 2.0.

Figure 7.16: (upper) Basin image containing the z axis of $SO(3)$, with a slice angle of 90° . The normalized offset of the permuted pulse is 0. (lower) Same as the upper image, but for a normalized offset of 0.5.

Figure 7.17: (upper) Same as the upper image of 7.16, but for a normalized offset of 1.0; (lower) same as the upper image of 7.16, but for a normalized offset of 2.0.

Figure 7.18: (upper) Basin image containing the xy plane of $SO(3)$. The normalized offset of the permuted $\pi/2$ pulse is 0. (lower) Same as the upper image, but for a normalized offset of 0.5.

Figure 7.19: (upper) Same as upper image of 7.18, but for a normalized offset of 1.0; (lower) same as upper image of 7.18, but for a normalized offset of 2.0.

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C. MLEV schemes

The final thirteen pages of basin images are of the MLEV iterative scheme for generating heteronuclear decoupling sequences for liquid state NMR.⁹⁰ Several variants of this scheme are possible, all involving, like the Waugh decoupling scheme, the permutation of a pulse or composite pulse. The simplest variation of this scheme, wherein four versions of an initial sequence containing an even number of π pulses are assembled according to specified rules and then concatenated, has been used in the computation of these images. The fixed point of the basin is the origin.

In the first six pages, containing figures 7.20 to 7.25, a WALTZ $1\bar{2}3$ composite π pulse,^{88,89,91} computed at the stated offset, is the permuted pulse group. In the next six pages, containing figures 7.26 to 7.31, a single π pulse computed at the stated offset is the pulse permuted as part of the scheme. Predictably, the basins of the WALTZ sequences at a given offset are considerably larger than the basins of the maps in which a single uncompensated π pulse is the permuted unit.

The final figure is a generalized interpretation of the MLEV procedure. A point $R(\alpha)$ on a slice containing the z axis was selected, and the product operator $R(\alpha)R(\alpha)R(\bar{\alpha})R(\bar{\alpha})$ formed. This was counted as the first iterate, and convergence to the origin tested. The MLEV scheme was then carried out on this product operator, until convergence was found, using $R(\alpha)$ as the permuted unit for each iteration. Since the permuted operator is not a π or composite π pulse with some specified phase, this basin image will be symmetric about the z axis.

i. MLEV with a WALTZ $1\bar{2}3$ permutation

Figure 7.20: (upper) Basin image containing the z axis of $S_0(3)$, with a slice angle of 0° . The normalized offset of the permuted pulse is 0. (lower) Same as the upper image, but for a normalized offset of 0.5.

Figure 7.21: (upper) Same as the upper image of 7.20, but for a normalized offset of 1.0; (lower) same as the upper image of 7.20, but for a normalized offset of 2.0.

Figure 7.22: (upper) Basin image containing the z axis of $S_0(3)$, with a slice angle of 90° . The normalized offset of the permuted pulse is 0. (lower) Same as the upper image, but for a normalized offset of 0.5.

Figure 7.23: (upper) Same as the upper image of 7.22, but for a normalized offset of 1.0; (lower) same as the upper image of 7.22, but for a normalized offset of 2.0.

Figure 7.24: (upper) Basin image containing the xy plane of $S_0(3)$. The normalized offset of the permuted $\pi/2$ pulse is 0. (lower) Same as the upper image, but for a normalized offset of 0.5.

Figure 7.25: (upper) Same as upper image of 7.24, but for a normalized offset of 1.0; (lower) same as upper image of 7.24, but for a normalized offset of 2.0.

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ii. MLEV with a single π pulse permutation

Figure 7.26: (upper) Basin image containing the z axis of $SO(3)$, with a slice angle of 0° . The normalized offset of the permuted pulse is 0. (lower) Same as the upper image, but for a normalized offset of 0.5.

Figure 7.27: (upper) Same as the upper image of 7.26, but for a normalized offset of 1.0; (lower) same as the upper image of 7.26, but for a normalized offset of 2.0.

Figure 7.28: (upper) Basin image containing the z axis of $SO(3)$, with a slice angle of 90° . The normalized offset of the permuted pulse is 0. (lower) Same as the upper image, but for a normalized offset of 0.5.

Figure 7.29: (upper) Same as the upper image of 7.28, but for a normalized offset of 1.0; (lower) same as the upper image of 7.28, but for a normalized offset of 2.0.

Figure 7.30: (upper) Basin image containing the xy plane of $SO(3)$. The normalized offset of the permuted $\pi/2$ pulse is 0. (lower) Same as the upper image, but for a normalized offset of 0.5.

Figure 7.31: (upper) Same as upper image of 7.30, but for a normalized offset of 1.0; (lower) same as upper image of 7.30, but for a normalized offset of 2.0.

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Figure 7.32: Generalized basin image of the MLEV iterative scheme, carried out as described above. The top image is a cross section of $SO(3)$ containing the z axis and the bottom image a cross section containing the xy plane of $SO(3)$. The origin is evidently a superstable fixed point of the associated function.

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CHAPTER EIGHT: EXPERIMENTAL DETAILS

I. INTRODUCTION

The experiments reported in this dissertation differ from routine NMR experiments in relatively minor ways. Only experimental procedures conceived specifically for the work presented here are discussed. More detailed expositions of the homebuilt NMR instruments employed in these experiments are available elsewhere.^{106,107}

II. INSTRUMENTAL MODIFICATIONS

A. Radiofrequency phase modulation

The pulse sequences derived in earlier chapters require the capability to generate square, phase modulated radiofrequency pulses. The NMR spectrometers used to perform the experiments here generate rf by mixing a fixed intermediate frequency (IF) -- 30 MHz in this case -- with a variable local oscillator (LO) frequency. Before the mixing stage, the IF is split into four channels, each phase shifted relative to the other three. Although the phases are tunable within a certain range, they are normally set to 0° , 90° , 180° , and 270° . The output of each channel is controlled by its own independent, TTL activated, rf switch. The four channels are combined after the switching stage and then mixed with the LO, producing sum and difference frequencies. The non-resonant frequency is filtered, and the output rf sent to a high power transmitter and then the probe. A schematic of this apparatus appears in figure 8.1. The mixing of two frequencies to produce the

Figure 8.1: Diagram of a dual channel rf generation circuit. The intermediate frequency enters from the left, the rf exits from the right. The box labeled S corresponds to an 8 bit digitally controlled phase shifter interfaced to a random access memory (labeled M). The IF passes through a quadrature network where it is split and phase shifts introduced into the four channels by hybrids. The phases and amplitudes are individually adjustable for each channel. After a switching stage, the four channels are combined. Normally, point O_H is connected to point A, but for multiple phase generation, point O_H can be connected to the I_X input providing the capability of generating rf of sixteen, individually selectable phases.

desired rf is a standard method for generating phase shifted rf in NMR spectrometers.

A pulse sequence requiring pulses of only four distinct phases can readily be generated by such a circuit, even if they differ from the four conventional quadrature phases, either by recalibrating the phases with in-line phase adjusters, or by placing different length cables in the four channels. A more complicated sequence consisting of pulses with sixteen or fewer phases can be produced by taking the combined output of the quadrature circuit -- point U_H in figure 9.1 -- and using this as the input to a second four-phase quadrature circuit. Since many NMR spectrometers are designed to perform experiments at two different resonance frequencies simultaneously, a second quadrature network is almost always available for this purpose. Adjusting the four phases of the second quadrature circuit as well as the first provides the capability of generating pulses with 16 different phases. Whenever possible, this technique was used to generate the desired phase modulated pulse sequence.

Pulses sequences requiring even more phases than this were obtained by placing a Daico Industries 100D0898-30 8 bit digital phase shifter at the input to the quadrature network. This unit is indicated as a box labelled S in figure 8.1. A finite settling delay of approximately $4.0 \mu s$ accompanies a shifting of IF phase by this device. The phase resolution attainable is $360/256$ degrees, or about 1.4° . Connected to this unit is an 8 bit $\times$ 1024 programmable RAM which can be used to store a sequence of up to 1024 distinct phase shifts.

The amplitudes and relative phases of the pulses were checked for all experiments with a vector voltmeter to ensure their accuracy and

uniformity.

B. Simulating resonance offset

The Zeeman frequency for most nuclei in commonly encountered NMR magnetic fields lies in the radiofrequency band, around 1 to 10^3 MHz. Rotating frame detection of the precessing magnetization requires a frequency demodulation procedure which removes this large frequency, as described in Chapter Two. The way this is accomplished is illustrated in Figure 8.2. The signal is first amplified then mixed with a LO waveform. The sum frequency produced by this mixing is then filtered, leaving only the difference frequency. The mixer which performs this demodulation usually receives the LO frequency from the same source as the rf generation circuit.

The signal, now oscillating at close to the intermediate frequency (30 MHz), is then split and separately mixed with two IF reference sources 90° out of phase with one another. Filtering and digitization of the transient envelope after the final mixing. As with the LO, the IF used for the final demodulation step originates from the same source as for the rf generation circuit.

The spectrum obtained in such a manner has a bandwidth equal to the digitization frequency and is centered at zero frequency. Zero frequency in this case is defined by the sum of the LO and IF.

In some of the experiments presented here, the rf was intentionally moved away from the known resonance frequency of the spins to determine the efficacy of the sequence off resonance. A problem arises if the rf generation and signal demodulation are performed with IF and LO from the same sources, for by moving the pulse

Figure 8.2: Frequency demodulation and detection of an NMR transient. The box X represents a power splitter, the box F a filter, and D an analog to digital converter. The conversion of the high frequency rf signal to an audio signal is a two stage mixing process.

sequence rf away from resonance, the zero frequency of the spectrum is correspondingly shifted. The fixed frequency NMR signal then appears to move around in the spectrum from experiment to experiment.

To avoid this, the receiver and the rf generation circuit were fed IF from separate, but locked, sources, permitting off resonance excitation with on resonance detection. In this configuration, a blind averaging of successive scans cannot be done, since excitation and detection are conducted in different rotating frames. The phase of the signal for one scan therefore bears no relation to the phase of the signal for other scans.

The inversion and transverse coherence data of previous chapters are reported as functions of resonance offset normalized to the rf field strength. Low rf fields, typically $< 20\text{kHz}$, were used in these experiments. Relatively small shifts of resonance frequency were therefore required to generate these data. The low fields, and hence low resonance offsets, were chosen intentionally to minimize losses of sensitivity and power output as the rf carrier frequency was moved away from the resonance frequency of the tuned probe circuit. Lowering the Q of the probe achieves the same effect.

C. Simulating amplitude offset

Measurements of pulse sequence performance for different values of ω_1 were achieved by fixing the pulse times and varying the power input to a linear rf transmitter with a variable attenuator. Amplitudes of the rf were calculated for these and all other experiments from the measured $\pi/2$, π , and $3\pi/2$ pulse times for each level of attenuation. Pulse times were found using a standard

calibration technique on $\text{H}_2\text{O}(\ell)$ or $^2\text{H}_2\text{O}(\ell)$ samples. To better account for finite pulse rise and fall times and similar sources of systematic error, a linear regression analysis was performed on a plot of flip angle vs. pulse time. The slope of this line yields a best estimate of ω_1 .

The effects of probe ringing and pulse imperfections were minimized by using rf fields as small as was practical. The inverse of the resonance linewidth was regarded as the upper bound for the duration of the sequence. Since the duration of a pulse is inversely related to the amplitude of the pulse for a given flip angle α , ω_1 was set so that the duration of the sequence was less than the linewidth induced limit, but small enough so that pulse shapes were square and uniform.

D. Inversion measurements

The detection of a population inverted state was accomplished by the sequence shown in figure 8.3. First, the pulse sequence, denoted S in the figure, was given, followed by a dephasing delay, a $\pi/2$ read pulse, and then acquisition of the FID. The dephasing delay was chosen to be long with respect to the inverse resonance linewidth, but short compared to spin-lattice relaxation times. The linewidth of the resonance was artificially broadened with the magnet shims, if necessary, to permit this. The purpose of this delay is to allow transverse magnetization created by the composite pulse to decay so as not to interfere with the measurement of the longitudinal magnetization. In order to avoid observations of magnetization refocused by the $\pi/2$ read pulse, the dephasing delay must be longer

figure 8.3: Pulse sequence for measuring the performance of a composite π pulse. The putative inverting sequence, denoted S, is given, followed by a dephasing delay, a strong, on resonance $\pi/2$ read pulse, and detection of the free induction decay.

than the detection period of the FID as well.

The spin system was allowed to equilibrate in the magnetic field before the experiment. The density operator of a system in this state is proportional to the operator I_z . An inverting sequence converts this initial condition to the unobservable operator $-I_z$. To measure the degree of inversion achieved by the sequence, a $\pi/2$ read pulse was required to transform longitudinal magnetization to observable transverse magnetization. The ability to perform phase sensitive detection permits the discrimination of the state I_z from the state $-I_z$ in these experiments. The degree of inversion was obtained as a function of the peak height of the Fourier-transformed absorption signal normalized to the peak height of the absorption signal produced by a single, strong $\pi/2$ read pulse.

To determine inversion performance of a pulse sequence off resonance and at variable rf amplitudes, the radiofrequencies for the pulse sequence and the read pulse were generated in separate rf channels and combined at the input to the rf transmitter, enabling the independent variation of the amplitudes and frequencies of the two channels. This is shown in figure 8.4. In this way, the excitation could be performed off resonance and with weak fields, and the detection performed on resonance and with strong fields.

E. Measurements of composite $\pi/2$ pulse performance

An equilibrium density operator is converted by a composite $\pi/2$ pulse to a form which is a linear combination of the operators I_x and I_y . The measurement of its performance can therefore be done as for the inversion case, but without the dephasing delay and the $\pi/2$ read

Figure 8.4: NMR probe circuit and associated high power and detection components. The box P is a power combiner, and T a high power rf transmitter. A power combiner at this position allows rf of two different amplitudes to be transmitted to the amplifier.

pulse. Such an experiment alone does not definitively establish that the propagator for the sequence is of the form $R_\phi(\pi/2)$, since many propagators can effect this transition of initial state to final state. A more conclusive experiment is to concatenate the pulse sequence with itself and to test its inversion performance, as described in the previous section. This experiment does discriminate between propagators of the form $R_\phi(\pi/2)$ and others which merely rotate longitudinal magnetization into the transverse plane.

F. Samples

All experimental data except those reported in section 4.III.B were collected from the proton resonance of a distilled water sample sealed in a 1.5 mm diameter capillary tube. The length of the sample was approximately 5 mm. Inversion recovery measurements indicate a spin lattice relaxation time of about 3 s for most of the water samples used. The long relaxation times, lack of couplings (due to the rapid isotropic motion of the water molecules in the liquid state), high concentration of protons (or deuterons), and large gyromagnetic ratio make liquid water an ideal isolated spin-1/2 prototype sample.

The experiments of Chapter Six were performed in a 4.2 T superconducting magnet. The remaining experiments took place in an 8.4 T field at a proton Larmor frequency of 362 MHz and a deuterium Larmor frequency of 56 MHz.

Solid hexamethylbenzene, both protonated and perdeuterated, were used in the experiments of section 4.III.B. Spin lattice relaxation times for the proton resonance at 362 MHz is around 1 - 3 s depending on the presence of paramagnetic impurities in the sample. The T_1 for

deuterium is somewhat shorter.

The rapid spinning of the methyl groups and the high frequency jumps around the twofold and sixfold axes of symmetries attenuate the dipole couplings within and between hexamethylbenzene molecules. The consequence, for the deuterium spectrum, is that each methyl group behaves as an isolated spin-1 particle with the relatively small quadrupolar splitting of 16 kHz. Similarly, a single, relatively narrow dipolar broadened linewidth of 24 kHz is observed in the proton spectrum of this compound. The motion is not completely isotropic or fast enough to average all couplings completely to zero, and so hexamethylbenzene can be considered a true many spin solid but with weak dipolar couplings. The strongest couplings are intramolecular, with weaker couplings between methyl groups of different molecules.

APPENDIX A: LINESHAPE TRANSFER FUNCTIONS

Transfer functions were first described and utilized by Murdoch⁷⁴ as a means for quantitatively assessing spectral distortions occurring in complicated NMR lineshapes. In this Appendix, a short review of the transfer function and some of its properties are presented.

Murdoch defines the transfer function $T(\omega)$ by the relation:

$$T(\omega) = \frac{\operatorname{Re}[F_A(\omega)]}{\operatorname{Re}[F_I(\omega)]} \quad (\text{A.1})$$

where $F_A(\omega)$ is the actual, possibly distorted, lineshape, and $F_I(\omega)$ is the ideal, undistorted lineshape. From this definition, it is apparent that spectral distortions in the actual lineshape $F_A(\omega)$ are revealed by deviations of the transfer function from unity.

Assuming phase sensitive detection is employed, both $F_A(\omega)$ and $F_I(\omega)$ will be complex quantities, with the real part containing the absorption spectrum, and the imaginary part the dispersion spectrum. With these assumptions, the inequality:

$$\operatorname{Re}[F_I(\omega)] \geq 0 \quad (\text{A.2})$$

for all ω follows. If lines due to individual transitions are homogeneously broadened, it is possible for $\operatorname{Re}[F_A(\omega)] > \operatorname{Re}[F_I(\omega)]$ to be true for some values of ω . However, since the total integrated intensity of $F_A(\omega)$ cannot be greater than that of $F_I(\omega)$, it must follow

that:

$$\int_{\omega_{\min}}^{\omega_{\max}} \operatorname{Re}[F_I(\omega)] d\omega \geq \int_{\omega_{\min}}^{\omega_{\max}} \operatorname{Re}[F_A(\omega)] d\omega \quad (\text{A.3})$$

where $F_A(\omega)$ and $F_I(\omega)$ are zero outside the range $\omega_{\min} \leq \omega \leq \omega_{\max}$. This relation and the inequality (A.2) above imply that:

$$\int_{\omega_{\min}}^{\omega_{\max}} \frac{\operatorname{Re}[F_I(\omega) - F_A(\omega)]}{\operatorname{Re}[F_I(\omega)]} d\omega \geq 0 \quad (\text{A.4})$$

which gives the result:

$$1 \geq \frac{1}{\omega_{\max} - \omega_{\min}} \int_{\omega_{\min}}^{\omega_{\max}} T(\omega) d\omega \quad (\text{A.5})$$

If two half integer spins coupled by a dipolar interaction are considered, the lineshape function for a particular value of ω_D can be generally written:

$$G(\omega, \omega_D) = \int_{-\infty}^{+\infty} A(\omega', \omega_D) f(\omega - \omega') d\omega' \quad (\text{A.6})$$

where $f(\omega - \omega')$ is some complex line broadening function, e.g., a Lorentzian or Gaussian, and $A(\omega', \omega_D)$ is the complex amplitude of the signal at frequency ω' . $G(\omega, \omega_D)$ thus represents the contribution to

the total spectrum of "spin packets" characterized by a particular value of the dipole coupling constant ω_D .

The total, heterogeneously broadened, spectrum is simply the sum of the contribution of each packet, weighted by the probability of finding ω_D of the packet. Writing the weighting function of ω_D as $P(\omega_D)$, this sum can be re-expressed by the integral:

$$F(\omega) = \int_{\omega_{D,\min}}^{\omega_{D,\max}} P(\omega_D) G(\omega, \omega_D) d\omega_D \quad (A.7)$$

$$= \int_{\omega_{D,\min}}^{\omega_{D,\max}} \int_{-\infty}^{+\infty} P(\omega_D) A(\omega', \omega_D) f(\omega - \omega') d\omega' d\omega_D \quad (A.8)$$

It has been assumed here that the line broadening function $f(\omega - \omega')$ is independent of the value of the dipole coupling constant of the packet. This amounts to saying that the homogeneous broadening is the same for all packets and all frequencies.

A formal expression for the transfer function of the absorption spectrum can now be given:

$$T(\omega) = \frac{\int_{\omega_{D,\min}}^{\omega_{D,\max}} \int_{-\infty}^{+\infty} \text{Re}[P(\omega_D) A_A(\omega', \omega_D) f_A(\omega - \omega')] d\omega' d\omega_D}{\int_{\omega_{D,\min}}^{\omega_{D,\max}} \int_{-\infty}^{+\infty} \text{Re}[P(\omega_D) A_I(\omega', \omega_D) f_I(\omega - \omega')] d\omega' d\omega_D} \quad (A.9)$$

Since the probability of finding a certain value of ω_D is independent of the experiment, $P(\omega_D)$ is the same in both integrals above. The contribution of each packet to the total signal, however, does depend on the experiment, hence the distinction between $A_I(\omega', \omega_D)$ and $f_I(\omega - \omega')$ for the "ideal" lineshape, and $A_A(\omega', \omega_D)$ and $f_A(\omega - \omega')$ for the actual lineshape.

In the limit of infinitely sharp lines from each packet, this transfer function is independent of the weighting function $P(\omega_D)$. This statement can be verified as follows. The assumption that the lines from each packet are not broadened means that the lineshape functions $f_A(\omega - \omega')$ and $f_I(\omega - \omega')$ can be replaced by Dirac delta functions.³⁷ Making this substitution, the transfer function becomes:

$$T(\omega) = \frac{\int_{\omega_{D,\min}}^{\omega_{D,\max}} \operatorname{Re}[P(\omega_D) A_A(\omega, \omega_D)] d\omega_D}{\int_{\omega_{D,\min}}^{\omega_{D,\max}} \operatorname{Re}[P(\omega_D) A_I(\omega, \omega_D)] d\omega_D} \quad (\text{A.10})$$

For two dipolar coupled spins in high field with infinitely sharp transition frequencies, $|A(\omega, \omega_D)|$ will be significantly larger than zero only for the frequencies $\omega \approx \pm(3/2)\omega_D$. $A_A(\omega, \omega_D)$ and $A_I(\omega, \omega_D)$ can thus be approximated by expressions proportional to delta functions:

$$A_A(\omega, \omega_D) = a_A(\omega, \omega_D) \exp[i\phi_A(\omega, \omega_D)] \delta[\omega - (3/2)\omega_D] \quad (\text{A.11})$$

$$A_I(\omega, \omega_D) = a_I(\omega, \omega_D) \exp[i\phi_I(\omega, \omega_D)] \delta[\omega - (3/2)\omega_D] \quad (\text{A.12})$$

where a_A , a_I , ϕ_A , and ϕ_I are purely real functions. These substitutions into the transfer function in (A.10) yield the result:

$$T(\omega) = \frac{a_A(\omega, 2\omega/3) \cos \phi_A(\omega, 2\omega/3)}{a_I(\omega, 2\omega/3) \cos \phi_I(\omega, 2\omega/3)} \quad (\text{A.13})$$

which is independent of $P(\omega_D)$, as asserted.

Numerical simulations of averaged powder lineshapes are typically performed by calculating spectra for particular, incremented values of ω_D over the bandwidth and then summing over all such spectra, weighted according to the ω_D probability distribution $P(\omega_D)$. If the lines due to each packet are infinitely sharp, the result above shows that the weighting step need not be performed in order to evaluate the transfer function. The limit of infinitely sharp lines is well approximated in a numerical simulation by choosing an ω_D increment which is much larger than the packet broadening due to $f(\omega - \omega')$. Hence, in this limit, simplified forms of $P(\omega_D)$ can be chosen to calculate transfer functions, as has been proposed. For this special, but artificial, case, distortions revealed by the transfer function at a frequency ω result only from those packets resonating at this frequency.

It is clear from equation (A.9) that if homogeneous line broadening is included for each packet, however, then the transfer function cannot be accurately calculated without regard to $P(\omega_D)$ or the broadening functions $f_I(\omega - \omega')$ and $f_A(\omega - \omega')$. This is true even if the linewidth $\Delta\omega$ due to each packet is considerably smaller than the width of the spectrum $\omega_{D,\max} - \omega_{D,\min}$. The broadening of packet lines results in constructive and destructive interference between lines of different

packets. The total signal amplitude at a given frequency is thus affected by packets centered at other frequencies. In this way, $P(\omega_D)$, the broadening functions, and the ratio of the rf strength to the spectral bandwidth all play an important role in influencing the form of the transfer function.

The two transfer functions in figure A.1 demonstrate this claim. The dashed line represents the transfer function for an uncompensated quadrupolar echo, with each packet broadened by an amount $1/100$ of the entire spectral bandwidth. The solid line is the transfer function for the same experiment, this time with no line broadening of the spin packet resonances. The ideal lineshape is as defined in section 4.III.B. Apparently, the line broadening, even though very slight, masks the very complicated structure of the transfer function of this simple example.

By this argument, it is evident that a transfer function calculated for a particular choice of $P(\omega_D)$ and $f(\omega - \omega')$ cannot be compared with experimental spectra with different probability functions and line broadenings, as has sometimes been done. This is especially the case for lineshapes such as the Pake doublet, for which the intensities at different frequencies vary widely and discontinuously. The amplitude of the spectrum at the discontinuities $\pm\omega_{D1}$ is so much greater than the rest of the spectrum, lineshape distortions at these frequencies can have a pronounced effect over the whole of the spectrum even for narrow packet line broadening. This disproportionate weighting effect makes the transfer function for a Pake doublet unsuited for comparison with those of most other lineshapes. To perform accurate comparisons, the transfer function must be calculated

Figure A.1: Transfer functions for isolated quadrupolar nuclei assuming a continuum of equally probable quadrupolar coupling constants. The excitation sequence was a quadrupolar echo. The ideal lineshape is as defined in the text. The solid line corresponds to the case where the resonances of the individual spin packets are not broadened (the delta function limit). The dashed line is the resultant lineshape when the resonances are broadened by 1/100 the entire spectral bandwidth.

with lineshapes which resemble the actual and ideal experimental situation as closely as possible.

The forgoing discussion has centered on a particular example of transfer functions, namely, the two half integer spin dipole-dipole coupling case. Such arguments clearly apply to the quadrupolar broadened lineshape of an isolated spin-1 nucleus, and by a straightforward extension, to the many coupled spin case. This extension can be performed by replacing $G(\omega, \omega_D)$ in equation (A.7) by a sum of $G(\omega, \omega_D)$'s over all pairwise couplings, and modifying $F(\omega)$ accordingly. A few complications arise if lines overlap, but the general features of the transfer function can still be discerned by such a calculation.

In summary, it is clear that transfer functions provide an accurate and more quantitative picture of lineshape distortions than simple visual inspection of complex lineshapes. As the preceding discussion has emphasized, however, caution must be observed in the proper use and interpretation of such functions.

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