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# Advances in Pulsed Zero-Field NMR Spectroscopy 

by

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University of California, Berkeley

Committee in charge:

Professor Alexander Pines, Chair
Professor Dmitry Budker
Professor David Wemmer

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# Advances in Pulsed Zero-Field NMR Spectroscopy 

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Tobias Fredrik Sjölander

Abstract<br>Advances in Pulsed Zero-Field NMR Spectroscopy<br>by<br>Tobias Fredrik Sjölander<br>Doctor of Philosophy in Chemistry<br>University of California, Berkeley<br>Professor Alexander Pines, Chair

Nuclear Magnetic Resonance (NMR) is ubiquitous as a tool for investigating the structure of both molecules and materials. In most cases the best results are obtained by placing the sample under study in the largest possible magnetic field, since this maximizes both the sensitivity and the resolution of the experiment. This fact underlies the momentous engineering effort that has gone into developing ever larger super-conducting magnets for use in NMR experiments. However, there are many applications of NMR where the sheer size, not to mention the cost, of a high-field instrument can not be accommodated. Therefore there has been a sustained research effort aimed at developing small, mobile, NMR systems that are not based on super-conducting magnets.

NMR performed in zero-field, using magnetic shielding to screen out the ambient field of the earth, and detected using vapor-cell magnetometers, is one such approach. In zerofield NMR the signal originates entirely in the spin-spin coupling part of the Hamiltonian, and chemically informative spectra are obtained even in the absence of chemical shifts. The very large absolute field homogeneity obtainable at zero-field ensures that the spectral resolution is even better than in high-field spectrometers. Perhaps even more interestingly the different geometry that results from not having a preferred axis imposed on the system enables experiments that are not possible in the presence of magnetic fields. Examples include the ability to distinguish enantiomers based on the phase of an NMR signal.

This work extends directly detected zero-field NMR beyond pulse-acquire type experiments. New methods for spin control and excitation, as well as two-dimensional spectroscopy and various decoupling techniques are introduced and demonstrated experimentally. For completeness this dissertation also contains a review of zero-field $J$-spectroscopy, as well as a detailed guide to the relevant instrumentation. It is my hope that the techniques presented herein will find use in future NMR experiments performed in the regime of zero and ultralow field, whether the application is portable chemical analysis, fundamental physics, or anything in between.

To my family.
Who have always been the constant in my life.
De säger att hem är där hjärtat är.

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It is done! After more than five years in grad school the end is finally in sight. It has been a great, though oftentimes deeply confusing, journey and as the fog slowly clears I thought I should take a few moments to reflect. I have learned a lot of science, I would like to say that I have learned to think science. And while my personal contribution to the vastness that is the sum of human knowledge is undeniably very small, part of me still harbors hope that it will be of some use to someone.

A great many people have been instrumental in me getting this far, and while I would want to I could not possibly list, or even remember, all the names. First and foremost then, I would like to thank everyone who has ever made me think, wonder or reflect, who has ever explained something, or challenged me. Without curiosity, humility, and resilience forged in response I could not have finished this. I am humbly and eternally grateful to all of you.

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## Chapter 1

## Introduction

This chapter contains material previously published under the following titles:

- Transition-Selective Pulses in Zero-Field Nuclear Magnetic Resonance by Sjolander, Tayler, King, Budker, and Pines [1]
- ${ }^{13}$ C-Decoupled J-Coupling Spectroscopy Using Two-Dimensional Nuclear Magnetic Resonance at Zero-Field by Sjolander, Tayler, Kentner, Budker, and Pines [2]
as well as material being prepared for publication under the title
- Two-Dimensional Single and Multiple-Quantum Correlation Spectroscopy in Zero-Field Nuclear Magnetic Resonance by Sjolander, Blanchard, Budker, and Pines [3].

When Rabi first discovered the Nuclear Magnetic Resonance (NMR) phenomenon in 1938 the delighted physics community remarked that this new technique would offer an opportunity to establish once and for all the gyromagnetic ratios of all the nuclides in the periodic table [4]. However, when people set out to apply NMR methods to the study of various metallic and molecular compounds they found something curious, the observed magnetic moment for a given nucleus varied depending on the physical and chemical characteristics of the material the measurement was performed on [5-7]. It was quickly realized that this effect was because of electrons in the compound of interest either augmenting or screening out the external magnetic field used to perform the resonance experiment. The consequences were remarkable; careful measurements of nuclear magnetic moments could be used to report on local electronic structure. Of course the electronic structure of a compound is intimately related to its chemical nature and within a few decades NMR had become one of the workhorses of analytical and synthetic chemistry.

Modern NMR techniques provide an abundance of information on the chemical and structural composition of matter. High-field chemical-shifts probe the electronic environment, the magnitudes of spin-spin coupling constants correlate strongly with both bond distances and bond angles, and geometric constraints may be obtained from the rates of inter-nuclear cross-relaxation [8-11]. NMR is employed as a tool in cutting edge biological research, affording structures of both proteins in their native water environment [12] as well as extended bio-aggregates [13]. Further, NMR is used as a tool in large throughput screening of pharmaceuticals, and it is a mainstay of synthetic research laboratories. NMR is also employed as an imaging technique under the safer sounding name Magnetic Resonance Imaging (MRI). Both the coherence and energy relaxation times of the nuclear magnetic states of the water in our bodies depend on its immediate biological environment, and this remarkable fact is used as a source of image contrast. Beyond chemical analysis and imaging, NMR has been used as a testbed for coherent control algorithms and quantum simulation [14]. In fact the first ever demonstration of Shor's algorithm was performed using a liquid-state NMR system [15].

A modern conventional NMR spectrometer is based around large, superconducting magnet operating at liquid helium temperatures. There are two primary reasons why so much effort has gone into engineering instruments capable of generating ever larger magnetic fields. First: performing NMR experiments in a large magnetic field ensures easily separable and interpretable spectra. This is partly because the energy of nuclear spin transitions depends on the magnitude of the external field. A larger field therefore amplifies differences in transition frequencies between spins in different chemical environments, thus increasing the effective spectral resolution. In addition, by magnifying these chemical-shift terms it is ensured that they are the dominant interaction terms in the Hamiltonian, allowing spectra to be interpreted based on simple rules derived from first-order perturbation theory. Second: nuclear spins interact only very weakly with their surroundings. Even at 20 Tesla, which is close to the largest magnetic field attainable in a modern spectrometer the energy difference between a proton spin being 'aligned' and 'anti-aligned' with the magnetic field is only 850 MHz , or $3.4 \cdot 10^{-4} \mathrm{~kJ} / \mathrm{mol}$. This corresponds to a net thermal spin-polarization at

300 K of only 68 ppm , according to the Boltzmann distribution. Further, higher transition frequencies also improve the efficiency of conventional detection, thereby increasing sensitivity. These facts taken together mean that large magnetic fields make NMR spectra easier to interpret both by simplifying the structure of spectra and by improving the attainable Signal-to-Noise-Ratio (SNR).

However, while large magnetic fields bring important and undeniable benefits to NMR the bulk and cost of spectrometers based on super-conducting magnets precludes their use in many situations where NMR spectrometers or MRI systems would otherwise be beneficial. Examples include monitoring food safety [16] and compliance with environmental regulations 'on-site', as well as medical diagnosis outside of hospital environments. Due to the many potential applications there has been a large push towards developing portable, cheap NMR and MRI systems [17-19] based on either permanent magnet designs [20] or electromagnets, with several companies manufacturing commercial benchtop-sized NMR spectrometers for 'in-the-hood' reaction monitoring [21] as well as teaching applications. However, there are a number of challenges that must be overcome in order to design a successful portable spectrometer. Firstly the magnetic-field homogeneity must be good enough to permit spectroscopy. Chemical shifts are of the order of ppm, so field homogeneities need to be sub ppb. This is challenging to accomplish with permanent magnets, and even more so with nonsuperconducting electromagnets. In addition, as chemical-shift differences decrease at small magnetic fields they become comparable to the spin-spin coupling terms, thereby giving rise to 'strong-coupling', or 'non first-order' effects, which make spectra significantly harder to interpret [22]. Smaller chemical shifts also lower spectral resolving power and make it harder to distinguish chemically distinct sites.

This dissertation concerns recent advances in, and the current state-of-the-art of, liquidstate zero-field magnetic resonance. Performing NMR experiments in the regime of zero or near-zero external magnetic field is a convenient way of side-stepping the field homogeneity challenge associated with low-field portable spectrometers; when the interaction of the spins with the residual field is on the order of 1 mHz to 1 Hz even a gradient as large as one part-per-thousand is irrelevant. The result is ultra-narrow linewidths, down to 20 mHz full-width-half-max has been demonstrated [23]. Even more importantly, by letting the Zeeman interaction approach zero, one emerges on the other side of the 'strong-coupling' regime, and it once again becomes possible to describe spectra with simple first-order perturbation theory arguments, but now with spin-spin couplings as the zeroth-order term [22, 24]. As we shall see it turns out that the instrumentation required for detection of NMR signals at near DC frequencies presents both challenges and possibilities. Optical magnetometers based on alkali vapor-cells can easily be made sensitive to magnetic fields in the $0-1000 \mathrm{~Hz}$ range. They also operate without cryogenics, which is an important point of developing lowfield NMR instrumentation. The result is an ultra-high resolution spectroscopy that yields sharp, relatively easy to interpret magnetic resonance spectra, but without the cost and bulk otherwise associated with high-field NMR. The instrumentation is cheap and miniatureazible [25-27] and one can therefore envision the technology as a candidate for a chip-scale point-of-care device.

In addition to having the potential to provide the same or higher quality spectral information as a modern high-field spectrometer at a fraction of the size and cost, there are particular cases and specialized applications for which performing NMR experiments in low or zero magnetic fields confers advantages over doing so in high fields. For example when the sample under study is heterogeneous and contains phase or grain boundaries the presence of magnetic fields tend to result in very broad and featureless spectra on account of inhomogeneity in the magnetic susceptibility of the material. The increased skin-depth penetration associated with low frequencies also enables imaging and through metal containers [28, 29]. Beyond increasing the scope of available samples, the absence of magnetic fields equalizes the Larmor frequencies of distinct spin-species, thereby allowing the study of physics not accessible at high fields. Examples include nuclear spin-singlet states formed by different nuclides [30], and the observation of terms in the nuclear spin-coupling Hamiltonian that are quenched by large chemical shift differences between nuclei. Such 'non-secular' terms may be interesting for characterization of ordered materials [31], and have been proposed as a means to detect both chirality [32] and molecular parity non-conservation [33] using NMR. This also implies a potential use in quantum simulation experiments - in liquids the nuclear spin Hamiltonian in zero magnetic field is made up of pure exchange interactions, which is something that has been challenging to realize in other experimental systems. Indeed, a complete set of one and two qubit gates were recently realized with high fidelity in a zero-field NMR model [34]. Relaxation is another NMR phenomenon that is strongly field dependent, and the methods described herein would allow convenient access to relaxation dispersion curves in the range of 1 to $100 \mathrm{~Hz}[35,36]$.

In this dissertation particular focus will be spent on new methods developed over the course of this work for manipulating spin states in the zero-field regime. Previous work in liquid state zero-field NMR has focused on the task of how to acquire and interpret pure $J$-coupling spectra, as well as the equally important problem of how to generate and store spin-polarization in zero-field. With this work we move our attention to the sort of multiplepulse and multi-dimensional experiments that have made traditional high-field NMR so flexible and powerful. The goal is to start building an expanded toolbox of techniques for use in future zero-field spectroscopy work, whether that is chemical analysis, searching for novel spin interactions, or quantum simulation.

The material is organized as follows: in Chapter 2 we will start by summarizing some of the necessary theoretical background and we give a more complete introduction to the concept of zero-field $J$-spectroscopy, which is at the heart of this dissertation. The experiments in this work were performed on a home-built spectrometer based on a ${ }^{87} \mathrm{Rb}$ vapor-cell magnetometer and in Chapter 3 we summarize the physics of vapor-cell magnetometry and describe in detail the operation and the various configurations of the spectrometer. The new methods for spin-control in zero-field presented in this thesis required the design of new magnetic field pulsing hardware and this is also described in this chapter. Chapter 4 concerns a new way of obtaining $J$-spectra based on low-amplitude resonant excitation fields that drive transitions directly between the zero-field eigenstates, rather than hereto used broadband DC excitation. This method affords the possibility to selectively excite only
those transitions that are of interest as well as the ability to perform spectral editing in zero-field. Chapter 5 meanwhile, introduces the possibility of manipulating individual spins based on their chemical identities as part of a zero-field experiment. This is achieved by switching a static holding field inside the zero-field spectrometer in conjunction with resonant magnetic field pulses. In Chapter 6 we move beyond one-dimensional spectroscopy and introduce the concept of two-dimensional correlation spectroscopy in zero-field NMR. We describe how single-quantum correlation spectra may be obtained and interpreted. We also introduce the concept of multiple-quantum spectroscopy in zero-field and show a number of proof-of-concept experiments. It is a feature of zero-field NMR that only spin-systems comprising at least two different kinds of spins may generate observable signals. In Chapter 7 we describe a spin-decoupling technique that for the first time, in spite of this, enables the acquisition of homonuclear zero-field $J$-spectra. With the large and growing interest in quantum information science, more approaches for how to 'dynamically decouple' spinsystems from environmental and other noise are always of interest. In Chapter 8 we present coherent control methods that enable rank selective decoupling of zero-field heteronuclear spin-systems. We show how these techniques enable high-resolution zero-field spectroscopy in poorly shielded, or inadequately shimmed environments. Finally Chapter 9 contains a summary of the current status of the field, reflections and thoughts about the future, as well as potential new avenues for research.

## Chapter 2

## Theoretical Background

This chapter provides a review of the basics of liquid-state zero-field NMR. It is meant to serve as a reference for the following chapters.

### 2.1 Notes on Notation

Before beginning in earnest I would like to make a few notes regarding the notation used throughout this work. I have tried to be consistent but mistakes will invariably have been made, and I apologize in advance for any confusion thus caused.

- We will use italic bold face to denote vector (operators), and italic with subscripts to denote the components thereof. For example a spin angular momentum operator $\boldsymbol{I}$ has the components $\left\{I_{x}, I_{y}, I_{z}\right\}$.
- Quantum numbers for the magnitude of angular momentum are denoted with capital italics with no subscripts, e.g. the eigenvalues of the operator $\boldsymbol{I}^{2}$ are denoted $I$. Quantum numbers for the projection of angular momentum on the chosen quantization axis are denoted $m$ with a subscript indicating the 'parent' operator. For example, the eigenvalue of $I_{z}$ is $m_{I}$.
- We will use $\boldsymbol{I}_{i}$ to denote the $i^{\text {th }}$ spin of a general spin system. In the case of a two-spin ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ system we will generally use $\boldsymbol{I}$ and $\boldsymbol{S}$ to denote the proton and carbon- 13 spins respectively.
- The dot product '.' is defined for vector operators the same way as it is for normal vectors meaning

$$
\begin{equation*}
\boldsymbol{I} \cdot \boldsymbol{S}=I_{x} S_{x}+I_{y} S_{y}+I_{z} S_{z} \tag{2.1}
\end{equation*}
$$

where $I_{x} S_{x}$ corresponds to matrix multiplication of the relevant representations of the two operators.

- We will write energies in angular frequency units, meaning we will let $\hbar=1$ throughout. We will also use the notation $|\alpha\rangle$ and $|\beta\rangle$ to denote 'spin-up' and 'spin-down' states. For example the action of the z-component of angular momentum on the ket corresponding to a spin- $1 / 2$ parallel to a magnetic field would be written

$$
\begin{equation*}
I_{z}|\alpha\rangle=\frac{1}{2}|\alpha\rangle \tag{2.2}
\end{equation*}
$$

- We will use $C_{j_{1} m_{1} j_{2} m_{2}}^{j m}$ to denote the Clebsch-Gordan coefficient $\langle j m|\left|j_{1} m_{1}, j_{2} m_{2}\right\rangle$
- We will denote a general spherical tensor operator [37] $T_{l m}$, where $l$ is the rank, and we will refer to $m$ as the ' $m$-value'. If we wish to refer to the full tensor, without specifying a component, we will use bold-face.


### 2.2 Semi-Classical Description of NMR

This section contains a (very) brief overview of the standard quantum mechanical framework for understanding magnetic resonance experiments. More complete treatments can be found elsewhere [8, 38].

Many NMR experiments can be conveniently interpreted in terms of entirely classical equations of motion for the torque experienced by a magnetic moment $\boldsymbol{M}$ in a magnetic field $\boldsymbol{B}$

$$
\begin{equation*}
\frac{d \boldsymbol{M}(t)}{d t}=\boldsymbol{M}(t) \times \boldsymbol{B} \tag{2.3}
\end{equation*}
$$

In this view the effect of chemical shifts and spin-spin couplings is to modify the magnetic field experienced by each individual spin.

Sometimes it is often more convenient to think of the magnetic resonance phenomenon not in terms of precessing vectors, but in terms of transitions between eigenstates of the system Hamiltonian induced by the (magnetic) dipole moment operator. This is especially the case when dealing with 'strong-coupling', i.e. spin-spin couplings that include terms of the form $\boldsymbol{I} \cdot \boldsymbol{S}$.

The Hamiltonian for a system of $N$ spins in a magnetic field along the z-axis is

$$
\begin{equation*}
H=B_{z} \sum_{i}^{N} \gamma_{i} I_{z, i}+H_{J} \tag{2.4}
\end{equation*}
$$

where we have used $H_{J}$ to denote any potential spin-spin couplings in the system. In high magnetic fields, where $B_{z} \gamma$ is much larger than any spin-spin couplings the energy of such a system is determined by the total projection of angular momentum on the z axis. The physical observable in a high-field NMR experiment is transverse magnetization, $\left\langle M_{x}\right\rangle$. Within the rotating wave approximation [39] the corresponding operator becomes $O=\sum_{i}^{N} \gamma_{i} I_{+, i}$, where $I_{+}|\beta\rangle=|\alpha\rangle$. Allowed transitions are those for which $\langle i| O|j\rangle \neq 0$, which corresponds to 'flipping' the direction of a single spin with respect to the magnetic field. The energy of such a transition is given by $\Delta E=\omega_{i j}=\langle i| H|i\rangle-\langle j| H|j\rangle$, and in the spectrum we would see peaks at the frequencies $\left\{\omega_{i j}\right\}$.

The concepts of a 'spin system' and a corresponding 'density operator' are ubiquitous in NMR and we will make repeated use of them throughout this work. A spin system is group of spins that do not interact coherently with other spins in sample. The most common example would be the spins in a given molecule in a liquid. The combination of rapid motion and a spherical distribution of molecules ensures that there are no net interactions between the spins on different molecules. In such cases [40] it is valid to consider the dynamics of only single molecule and average the result over the entire sample. This is extremely convenient since it allows us to work with a $2^{N_{\text {sys }}}$ dimensional Hilbert space where $N_{\text {sys }}$ is the number of spins in a single molecule, instead of the number of spins in an NMR tube. However, even if we can write down a state vector for the spins of a given molecule, it is in general not true that all molecules in the sample will share that same state vector. In fact in almost all NMR
experiments the spin-states of different molecules are quite uncorrelated. The upshot is that NMR systems are highly mixed states [41]. The solution is to define a density operator

$$
\begin{equation*}
\rho=\sum_{i=1}^{N_{\text {tot }}} c_{i}\left|\Psi_{i}\right\rangle\left\langle\Psi_{i}\right|, \tag{2.5}
\end{equation*}
$$

where $|\Psi\rangle$ is the $2^{N_{\text {sys }} \text {-dimensional state vector for the spins on a given molecule and the sum }}$ runs over all molecules in the sample. We now have a single $2^{N_{\text {sys }}} \times 2^{N_{\text {sys }}}$ matrix defining the spin state of an entire macroscopic sample.

There is no time dependence in the transition based picture of NMR presented above. The 'spectrum' is a static property of a given spin system. However, actual experiments are generally preformed in pulsed Fourier transform mode meaning that the evolving magnetization of the system is monitored as a function of time (often while simultaneously performing additional manipulations or changes to the state of the system) and the resulting time trace is subject to a Fourier transform, revealing peaks at the frequencies of the oscillations. To describe such experiments we use the Liouville-Neumann equation of motion for the density matrix

$$
\begin{equation*}
\frac{d \rho(t)}{d t}=-\mathrm{i}[H, \rho(t)] \tag{2.6}
\end{equation*}
$$

which in the case of a time-independent Hamiltonian can be integrated to give

$$
\begin{equation*}
\rho(t)=\mathrm{e}^{-H t} \rho(0) \mathrm{e}^{H t} . \tag{2.7}
\end{equation*}
$$

The expectation value of the transverse magnetization as a function of time can be calculated as

$$
\begin{equation*}
\langle O\rangle(t)=\operatorname{Tr}\left\{O^{\dagger} \rho(t)\right\} \tag{2.8}
\end{equation*}
$$

The Fourier transform of the result gives the NMR spectrum.
In order to make this concrete we need to determine what $\rho$ actually is. It can be shown that the density operator at thermal equilibrium is

$$
\begin{equation*}
\rho_{T H}=\frac{\mathrm{e}^{-H / k_{\mathrm{B}} T}}{\mathbb{Z}} \tag{2.9}
\end{equation*}
$$

where $\mathbb{Z}=\operatorname{Tr}\left\{\exp \left(-H / k_{\mathrm{B}} T\right)\right\}$ is the partition function for the system. For spins in a magnetic field of strength $B_{0} H=-B_{0} \sum_{i}^{N} \gamma_{i} I_{z, i}$. Note that we have ignored any spin-spin couplings when writing $H$, this is valid at high-fields since $\gamma B_{0}$ is usually many orders of magnitude larger than any coupling constants. This is equivalent to saying that at thermal equilibrium all 'spin-order' in the system comes from the Zeeman term. Since $\gamma B_{0} / k_{\mathrm{B}} T \ll 1$ for all currently attainable field strengths Equation (2.9) is commonly evaluated in a Taylor series truncated to first order

$$
\begin{equation*}
\rho_{T H}=\frac{\mathbb{1}}{2^{N}}+\frac{\hbar B_{p o l}}{2^{N} k_{B} T} \sum_{i}^{N} \gamma_{i} I_{z, i}, \tag{2.10}
\end{equation*}
$$

where $\mathbb{1}$ denotes the identity matrix and $N$ is the number of spins in the spin system. There are instances where truncating the Taylor series like this is not valid [40], however no such experiments are treated in this work. As $\mathbb{Z}$ occurs only in the denominator and $\gamma B / k_{\mathrm{B}} T \ll 1$, we have kept only the zeroth order term in the Taylor expansion for $\mathbb{Z}$. A spin system of $N$ spin- $1 / 2$ particles has $2^{N}$ energy levels and thus we obtain $\mathbb{Z} \approx 2^{N}$. Equation (2.10) is the starting point for most NMR experiments.

We refer to the second term in Eq. (2.10) as the "deviation density matrix", and the prefactor is known as the "spin-polarization". The deviation density matrix is extremely important since it is the only part of $\rho$ that can actually evolve in time or correspond to magnetization. Consider the infinite temperature case, where the deviation density matrix goes to zero. Then we have

$$
\begin{align*}
\rho(t) & =\frac{1}{2^{N}} U(t) \mathbb{1} U^{\dagger}(t) \\
& =\frac{\mathbb{1}}{2^{N}} \tag{2.11}
\end{align*}
$$

where $U(t)$ denotes the unitary transformation associated with some arbitrary combination of pulses and delays, i.e. if the spin-polarization is zero there is no coherent process whatsoever that can change $\rho$. It follows that if the deviation density matrix is zero, the expectation value for the magnetization along some arbitrary direction, $M_{\alpha}$, will be zero for all time

$$
\begin{align*}
\left\langle M_{z}\right\rangle(t) & =\operatorname{Tr}\left\{M_{\alpha}^{\dagger} \mathbb{1}\right\} \\
& =0, \tag{2.12}
\end{align*}
$$

since magnetization is a vector operator, and therefore the corresponding matrix representation must be traceless, see Appendix 2.4. Since NMR relies on detecting magnetization this means that no NMR can be observed in the infinite spin-temperature limit. Conversely, the observed NMR signal will be proportional to the spin-polarization. The part of $\rho$ proportional to the identity matrix never contributes to the dynamics (observable or not) of the spin system and we will often find it convenient to ignore it and work only with the deviation density matrix. In this work this has been done whenever a given density matrix is traceless.

### 2.3 J-Spectroscopy

As explained above NMR spectroscopy is the study of nuclear spin transitions, that is to say transitions between eigenstates of the nuclear spin Hamiltonian. However, there is no reason in principle why the Zeeman term (i.e. the energy of the spins due to their orientation with respect to some externally imposed magnetic field) must take a privileged position. This Dissertation concerns zero-field $J$-spectroscopy [42-44], which is magnetic resonance experiments performed in the regime where the dominant term in the Hamiltonian is the indirect spin-spin coupling (often termed $J$-coupling), and the Zeeman term is either
absent (zero-field) [45] or a perturbation (ultralow field) [24]. The absence of an external quantizing field along which the spins can be either 'up' or 'down' does not change the fact that the $J$-coupling Hamiltonian for a given spin system has a spectrum of eigenvalues, and that coherent evolution of superpositions of the corresponding eigenstates may generate a time dependent magnetization. The Fourier transform of such a time trace is known as a $J$-spectrum [46, 47], and it will have peaks at the transition energies of the spin system in question. The usefulness of $J$-spectroscopy is predicated on these transitions providing chemically relevant information, which indeed they do [23, 48].

The following aims to provide a review of $J$-spectroscopy and present relevant theoretical and practical considerations.

### 2.3.1 The Hamiltonian and the Detection Operator

In the liquid state, under complete motional averaging, the Hamiltonian of $N J$-coupled spins is the sum of all pairwise isotropic couplings

$$
\begin{equation*}
H_{J}=2 \pi \sum_{i>j}^{N} J_{i j} \boldsymbol{I}_{i} \cdot \boldsymbol{I}_{j} . \tag{2.13}
\end{equation*}
$$

The $J_{i j}$ are coupling constants in Hz and $\boldsymbol{I}_{i}$ is the spin angular momentum operator for the $i^{\text {th }}$ spin. Note that there is no magnetic field term and the energy is given exclusively by the orientation of the spins with respect to each other and the coupling topology. Let us consider what we can say about the eigenstates of this Hamiltonian based purely on symmetry considerations. All spin operators appear only in scalar products and therefore this Hamiltonian is guaranteed to be invariant under all global rotations in spin-space. This in turn implies that $H_{J}$ commutes with the magnitude of the total spin angular momentum, $\boldsymbol{F}^{2}=\left(\sum_{i}^{N} \boldsymbol{I}_{i}\right)^{2}$, as well as its projection on an arbitrary axis, $F_{\alpha}=\sum_{i}^{N} I_{\alpha, i}$. Since $H_{J}$ commutes with the operators defining total (nuclear-spin) angular momentum there is a common basis that diagonalizes both the angular momentum operators and $H_{J}$. The eigenstates of $H_{J}$ are therefore angular momentum eigenstates [49] and may be labeled $\left|F, m_{F}, \xi\right\rangle$, where $\xi$ denotes any extra quantum numbers needed to completely specify the state. Because the system is spherically symmetric its energy cannot depend on the orientation of the coordinate system, and so states of given $F$ and $\xi$ must be degenerate for all $m_{F}=-F:+1:+F$. Further, there is no favored choice of quantization axis and $m_{F}$ may denote the projection on any arbitrary axis. However, as we will see later, the detection scheme used in this work measures the time-dependent magnetic field along a given direction generated by an ensemble of spins evolving under $H_{J}$, and this direction is fixed in the laboratory frame. The most common choice of coordinate system in zero-field NMR is to take this externally imposed axis to be collinear with the quantization axis along which $m_{F}$ is defined and call this the z-axis, and with one exception to be explained in detail later, we will follow that convention throughout this work.

It follows from the above discussion that we may define a detection operator as the total sample magnetization in the z direction

$$
\begin{equation*}
M_{z}=\sum_{i}^{N} \gamma_{i} I_{z, i} \tag{2.14}
\end{equation*}
$$

where $\gamma_{i}$ is the gyromagnetic ratio of spin $i$. It is worthwhile to consider the matrix elements of this operator in order to gain insight into the structure of a general zero-field $J$-spectrum. The transition matrix element for two arbitrary zero-field states with angular momentum $F$ and $F^{\prime}$ is

$$
\begin{equation*}
M_{z, F^{\prime} F}=\left\langle F^{\prime}, m_{F}^{\prime}, \xi^{\prime}\right| M_{z}\left|F, m_{F}, \xi\right\rangle \tag{2.15}
\end{equation*}
$$

We can immediately make one observation that is going to become very important as we start to consider $J$-spectroscopy in more detail, and that is that only spin systems containing more than one kind of spin-isotope may give observable $J$-spectra. To see this consider the detection operator for a homonuclear system

$$
\begin{align*}
M_{z} & =\gamma \sum_{i}^{N} I_{z, i} \\
& =\gamma F_{z} \tag{2.16}
\end{align*}
$$

However, as shown above the zero-field states must be eigenstates of $F_{z}$, so the transition matrix element becomes

$$
\begin{equation*}
M_{z, F^{\prime} F}=\gamma\left\langle F^{\prime}, m_{F}^{\prime}, \xi^{\prime}\right| F_{z}\left|F, m_{F}, \xi\right\rangle=\gamma m_{F} \delta_{F^{\prime} F} \delta_{m_{F}^{\prime} m_{F}} \delta_{\xi^{\prime} \xi}, \tag{2.17}
\end{equation*}
$$

since by construction $F, m_{F}$, and $\xi$ specifies a state completely this means that $M_{z}$ does not couple different eigenstates. Thus, we have the result that in the absence of a magnetic field, transitions between different eigenstates in a homonuclear system may not generate observable magnetization.

Having established that only heteronuclear spin systems yield $J$-spectra the next question is what possible changes in $F$ are allowed. From the Wigner-Eckart theorem we know that the matrix elements of a spherical tensor operator are proportional to the appropriate ClebschGordan coefficients. Since magnetization is a first rank spherical tensor operator and $M_{z}$ has $m$-value 0 , the transition matrix element can be written

$$
\begin{equation*}
M_{z, F^{\prime} F}=C_{10, F m_{F}}^{F^{\prime} m_{F}^{\prime}}\left\langle F^{\prime}, \xi^{\prime}\right|\left|M_{z}\right||F, \xi\rangle, \tag{2.18}
\end{equation*}
$$

where the second part of the right hand side is the reduced matrix element [37]. From the properties of Clebsch-Gordan coefficients we can now immediately see that zero-field transitions have $\Delta F=F^{\prime}-F= \pm 1,0$. We can also see that $\Delta m_{F}=0$ [49], however the selection rule on $m_{F}$ is merely a consequence of this particular choice of axis convention. If we had chosen magnetization along the x -axis as our detection operator we would instead
have had $\Delta m_{F}= \pm 1[24]$. Of course experimentally the results must be the same in both cases.

Throughout this Dissertation we will repeatedly return to the case of two coupled spins so it will be worthwhile to consider the eigenstates of such a system in some detail. They are $\{|1,1\rangle,|1,0\rangle,|1,-1\rangle,|0,0\rangle\}$, where the only necessary quantum numbers are $F$ and $m_{F}$. Commonly the three states with $F=1$ are referred to as a 'triplet' and the state with $F=0$ as a 'singlet'. In this notation the eigenstates are $\left\{\left|T_{1}\right\rangle,\left|T_{0}\right\rangle,\left|T_{-1}\right\rangle,\left|S_{0}\right\rangle\right\}$. On the high-field basis these states are

$$
\begin{align*}
\left|T_{1}\right\rangle & =|\alpha \alpha\rangle  \tag{2.19}\\
\left|T_{0}\right\rangle & =\frac{1}{\sqrt{2}}(|\alpha \beta\rangle+|\beta \alpha\rangle)  \tag{2.20}\\
\left|T_{-1}\right\rangle & =|\beta \beta\rangle  \tag{2.21}\\
\left|S_{0}\right\rangle & =\frac{1}{\sqrt{2}}(|\alpha \beta\rangle-|\beta \alpha\rangle) . \tag{2.22}
\end{align*}
$$

### 2.3.2 Polarization in Zero Field

In the presence of a large magnetic field, thermal equilibrium at room temperature corresponds to a state of significant spin-polarization, meaning that thermal equilibrium is an entirely fine starting point for a high-field NMR experiment. In contrast, at zero-field, thermal equilibrium at 300 K corresponds to a state of essentially infinite spin temperature. In fact, for a 2 -spin $J$-coupled system in zero-field to reach the same level of thermal spin-polarization as protons in a standard 300 MHz magnet the system would need to be cooled to 0.1 mK (assuming $J=100 \mathrm{~Hz}$ ). In contrast at room temperature the polarization would be 1 in $8 \cdot 10^{-12}$, or 0.000008 ppm . If this is what we had to make do with, zero-field $J$-spectroscopy would not be possible. (See Eqs. (2.11) and (2.12).) In fact, there are a number of ways to prepare a non-equilibrium spin-state in zero-field. The main difference compared with high-field NMR is that in high-field energy relaxation (T1) will tend to bring the system back to a polarized state, whereas in zero-field thermalization means decay to a trivial, infinite temperature state. The initialization into a non-equilibrium state thus needs to be performed in advance of every experiment, and every transient.

Thermal Polarization The most general way of preparing a non-equilibrium initial state in zero-field is to let the spin system come to thermal equilibrium in a large magnetic field according to Eq. (2.10), followed by transport to zero-field. We refer to this as pre-polarization and we will continue to use $\rho_{T H}$ to denote a state corresponding to a thermal equilibriumstate at high-field, keeping in mind that while in a zero-field environment during the course of the experiment, the density matrix will tend to the trivial state given by $\rho=\mathbb{1} / \mathbb{Z}$, after which the system has to be repolarized in a magnetic field. The pre-polarization step may be done either in-situ using electromagnetic coils to generate a rapidly switched polarizing field, as has been done in a number of experiments [46, 47, 50, 51], or outside of the magnetically


Figure 2.1: Magnetic field profiles for different polarization schemes. Not to scale. (a) Prepolarization with a small switched field inside the magnetically shielded region. The field is switched rapidly ensuring a sudden transition. (b) Pre-polarization in a large field (e.g. in a permanent magnet) located outside the shielded chamber, followed by adiabatic transport to zero-field. (c) Same as in (b) but once the sample leaves the permanent magnet it is kept in a small holding field generated by a solenoid wound around the shuttling path. The holding field is switched off rapidly once the sample reaches zero field in order to ensure a sudden transition.
shielded region using a permanent magnet [45, 52, 53]. If done outside, the sample needs to be mechanically moved, or 'shuttled', between the pre-polarizing magnet and the shielded region during the course of the experiment [54]. The state of the spin system at the start of the zero-field NMR experiment, termed $\rho(0)$, depends on how quickly the magnetic field changes from being the dominant interaction to 'zero' [44]. The two limiting cases are (i) sudden transport, in which the field changes instantaneously with respect to the internal spin variables, and the system therefore retains its original state. In the this case we have

$$
\begin{align*}
\rho(0) & =\rho_{T H} \\
& =\frac{\mathbb{1}}{\mathbb{Z}}+\frac{1}{\mathbb{Z}} \sum_{i}^{N} \frac{\gamma_{i} B_{0}}{k_{\mathrm{B}} T} I_{z, i} . \tag{2.23}
\end{align*}
$$

Example schematics of a field trajectory that would give this behavior are shown in Fig. 2.1a and Fig. 2.1c. We also have the case of (ii) adiabatic transport shown in Fig. 2.1b, in which the system remains in a stationary state of the Hamiltonian at all points on the field trajectory. In this case calculating $\rho(0)$ is slightly more involved since it involves following the density matrix through the field switching [30]. Let us do this for the instructive case of a $J$-coupled ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ two-spin system. Figure 2.2 shows a numerical simulation of how the


Figure 2.2: Eigenstates of a $J$-coupled two-spin system as a function of the field strength. When the interaction with the field is dominant the system is described by the projection of the individual spin angular momenta onto the field. When the $J$ coupling dominates the eigenstates are the strongly coupled singlet and triplet states.
eigenstates change as a function of field-strength. We know that in the adiabatic limit the density matrix will remain diagonal in the eigenbasis of the Hamiltonian at all points during the transfer and the populations of the states will not change even as the nature of the states do. We first evaluate the populations, i.e. the diagonal elements of the density matrix, in the pre-polarizing field, where $\left(\omega_{I}-\omega_{S}\right) \gg J$. We obtain

$$
\begin{align*}
p_{\alpha \alpha} & =\frac{\langle\alpha \alpha| \mathrm{e}^{\left(\omega_{I} I_{z}+\omega_{S} S_{z}\right) /\left(k_{\mathrm{B}} T\right)}|\alpha \alpha\rangle}{\mathbb{Z}} \\
& =\frac{1}{4}+\frac{\omega_{I}+\omega_{S}}{8 k_{\mathrm{B}} T}, \tag{2.24}
\end{align*}
$$

for the population of the $|\alpha \alpha\rangle\langle\alpha \alpha|$ state, and similarly

$$
\begin{align*}
& p_{\alpha \beta}=\frac{1}{4}+\frac{\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T}  \tag{2.25}\\
& p_{\beta \alpha}=\frac{1}{4}+\frac{-\omega_{I}+\omega_{S}}{8 k_{\mathrm{B}} T}  \tag{2.26}\\
& p_{\beta \beta}=\frac{1}{4}+\frac{-\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T} \tag{2.27}
\end{align*}
$$

for the other three populations and we have used $\gamma_{I} B_{0}=\omega_{I}$. From the simulation in Fig. 2.2 we know how the high-field states transform into the zero-field ones and we can now write

$$
\begin{equation*}
\rho(0)=p_{\alpha \alpha}\left|\mathrm{T}_{-1}\right\rangle\left\langle\mathrm{T}_{-1}\right|+p_{\alpha \beta}\left|\mathrm{S}_{0}\right\rangle\left\langle\mathrm{S}_{0}\right|+p_{\beta \alpha}\left|\mathrm{T}_{0}\right\rangle\left\langle\mathrm{T}_{0}\right|+p_{\beta \beta}\left|\mathrm{T}_{+1}\right\rangle\left\langle\mathrm{T}_{+1}\right| \tag{2.28}
\end{equation*}
$$

for the initial density matrix of a two-spin system in zero-field following adiabatic transport from a high-field pre-polarizing region. Following Ref. [30] we note that

$$
\begin{align*}
\boldsymbol{I} \cdot \boldsymbol{S} & =-\frac{3}{4}\left|\mathrm{~S}_{0}\right\rangle\left\langle\mathrm{S}_{0}\right|+\frac{1}{4}\left(\left|\mathrm{~T}_{-1}\right\rangle\left\langle\mathrm{T}_{-1}\right|+\left|\mathrm{T}_{0}\right\rangle\left\langle\mathrm{T}_{0}\right|+\left|\mathrm{T}_{+1}\right\rangle\left\langle\mathrm{T}_{+1}\right|\right)  \tag{2.29}\\
I_{z} S_{z} & =\frac{1}{4}\left(\left|\mathrm{~T}_{-1}\right\rangle\left\langle\mathrm{T}_{-1}\right|-\left|\mathrm{T}_{0}\right\rangle\left\langle\mathrm{T}_{0}\right|+\left|\mathrm{T}_{+1}\right\rangle\left\langle\mathrm{T}_{+1}\right|-\left|\mathrm{S}_{0}\right\rangle\left\langle\mathrm{S}_{0}\right|\right),  \tag{2.30}\\
I_{z}+S_{z} & =\left|\mathrm{T}_{+1}\right\rangle\left\langle\mathrm{T}_{+1}\right|-\left|\mathrm{T}_{-1}\right\rangle\left\langle\mathrm{T}_{-1}\right|,  \tag{2.31}\\
\mathbb{1} & =\left|\mathrm{T}_{+1}\right\rangle\left\langle\mathrm{T}_{+1}\right|+\left|\mathrm{T}_{-1}\right\rangle\left\langle\mathrm{T}_{-1}\right|+\left|\mathrm{T}_{0}\right\rangle\left\langle\mathrm{T}_{0}\right|+\left|\mathrm{S}_{0}\right\rangle\left\langle\mathrm{S}_{0}\right| . \tag{2.32}
\end{align*}
$$

Now we can use Eqs. (2.29) to (2.32) and Eqs. (2.24) to (2.27) to rewrite Eq. (2.28) as

$$
\begin{equation*}
\rho(0)=\frac{\mathbb{1}}{4}+\frac{\omega_{I}+\omega_{S}}{8 k_{\mathrm{B}} T}\left(I_{z}+S_{z}\right)-2\left(\frac{\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T}\right)\left(\boldsymbol{I} \cdot \boldsymbol{S}-I_{z} S_{z}\right), \tag{2.33}
\end{equation*}
$$

which is the result of adiabatically transporting a $J$-coupled 2 -spin system from the high-field regime to zero-field. The deviation part of Eq. (2.33) contains three different operators that describe different ways in which the spins are polarized. We talk about different types of spin-order. The first term $\left(I_{z}+S_{z}\right)$ transforms under rotations as a vector, and we will refer to it as vector spin-order. The second term $(\boldsymbol{I} \cdot \boldsymbol{S})$ is invariant to spin rotations and we term it scalar spin-order, while the third term contains both rank-2 and rank-0 components. It has been demonstrated that these three forms of polarization all have different energy-relaxation rates [30].

If the rate of transport is neither sudden nor adiabatic it is hard to say anything a priori about the state of the system once it reaches zero-field. It will depend on the exact details of trajectory of the magnetic field, as well as the coupling constants. Therefore, to enable predictable and repeatable experiments, it is important that the transport is either sudden, or adiabatic.

Hyperpolarization Thermal equilibration in a strong magnetic field is not the only way to obtain $\rho(0) \neq \mathbb{1} / \mathbb{Z}$. Several methods for obtaining non-thermal polarization (or 'hyperpolarization') have been developed for use in high-field and can be adapted for use with a zero-field spectrometer.

To date the by far most successful hyperpolarization technique used in zero-field NMR is chemical reaction with parahydrogen [55]. Parahydrogen refers to the nuclear singlet state of hydrogen which has a lifetime of days and can readily be prepared in $\sim 100 \%$ abundance by simply cooling hydrogen to liquid He temperatures in the presence of a suitable catalyst. Under the right conditions hydrogenation reactions using parahydrogen transfers
nuclear spin-order to the target molecule, leading to remarkably high polarization. More recently, reversible versions of this reaction have been developed which are currently subject to great research interest in the wider NMR community [56]. Parahydrogen has been used successfully as a polarization source in zero-field NMR both in hydrogenative [57] and reversible [58] modes. Polarization with para-hydrogen in zero-field generates purely scalar spin-order [59, 60], see Eq. (2.33). The details of exactly which spin-pairs get polarized during the chemical reaction depend on the spin system topology and the relevant $J$-coupling constants. Parahydrogen offers significant advantages over polarization in a magnetic field, most notably greatly increased sensitivity which is key for any future practical application of $J$-spectroscopy. It also obviates engineering issues surrounding sample shuttling and decreases the instrumentation footprint. However, it is currently limited to certain classes of molecules and reaction conditions, and often those systems yield slightly more complicated $J$-spectra than what is convenient for proof-of-principle demonstrations of new pulse sequences. Further, several of the coherent-control techniques developed in this work rely on the spin system being in a well defined initial state before the experiment and it is challenging to accurately start and stop the polarizing reaction with the requisite millisecond timing. For these reasons parahydrogen is not used as a polarization source in this Dissertation, even though it holds great promise for zero-field NMR in general.

Spin Exchange Optical Pumping is a means of obtaining high spin-polarization on noble gases by means of transferring polarization from optically pumped alkali vapor, see Section 3.2.1. It has been used as a polarization source in low-field $(1 \mu \mathrm{~T}) \mathrm{NMR}$ of gaseous xenon [26]. But since the technique is limited to gases it was not an option in this Dissertation.

Dissolution Dynamic-Nuclear-Polarization (DNP) [61], is the gold standard for obtaining hyper-polarized liquid state NMR spectra. The technique is well established and further developments are pursued in many labs around the world. However, dissolution-DNP has not yet been applied to zero-field $J$-spectroscopy even though its versatility and generality would make it a near perfect fit. Overhauser-DNP has been successfully applied to ultralowfield NMR [62]. However, the origin of the spin-order in this case was the $\sim 50 \mathrm{mHz}$ hyperfine interaction in the radical, which is smaller than the proton frequency in a 2 T pre-polarizing permanent magnet (and thus corresponds to lower spin-order).

### 2.3.3 Signal Excitation and Detection in Zero Field

The observed signal in a zero-field NMR experiment is the expectation value of the detection operator $\left\langle M_{z}\right\rangle(t)$, i.e. the time-dependent magnetization along the z-axis. For a macroscopic observable to be time-dependent the spin system must be in a state that does not commute with the nuclear spin Hamiltonian. In making this statement we are ignoring relaxation effects which would oblige us to consider either non-unitary dynamics, or expand our view of the 'system' to encompass something rather more complex than the nuclear spins
of a single molecule. The equation of motion for the expectation value is

$$
\begin{align*}
\left\langle M_{z}\right\rangle(t) & =N_{\text {tot }} \times \operatorname{Tr}\left\{M_{z}^{\dagger} \mathrm{e}^{-\mathrm{i} H_{J} t} \rho(0) \mathrm{e}^{\mathrm{i} H_{J} t}\right\} \\
& =N_{\text {tot }} \times \sum_{i, j} M_{(z, j i)} \rho_{i j} \mathrm{e}^{-\mathrm{i} \omega_{i j} t} \tag{2.34}
\end{align*}
$$

where $N_{\text {tot }}$ is the number of molecules in the sample, and in order to obtain the expression in Eq. (2.34), we have inserted two resolutions of the identity and evaluated the trace. $M_{(z, j i)}$ and $\rho_{i j}$ denote matrix elements of the corresponding operators and $\omega_{i j}$ is the energy difference between states $|i\rangle$ and $|j\rangle$ in angular frequency units. The sum runs over all the eigenkets of the system. We now see explicitly that, as long as we ignore relaxation, the diagonal elements of $\rho$, the populations, are static in time and the signal comes from the off-diagonal elements of $\rho$, the coherences. Equation (2.17) gave selection rules for the matrix elements of $M_{z}$; those selection rules define what coherences are observable. In this section we seek to investigate how to ensure that the corresponding $\rho_{i j}$ are non-zero, that is to say, how to excite the corresponding coherences.

Sudden Transport We saw in Section 2.3.2 that the initial state of the spin system, $\rho(0)$, depends greatly on how the polarization was generated. In the case of a two-spin system and pre-polarization in a magnetic field followed by sudden transport to zero-field, $\rho(0)$ is given by Eq. (2.23). On the coupled basis we can rewrite this as

$$
\begin{align*}
\rho(0) & =\rho_{T H}  \tag{2.35}\\
& =\frac{\mathbb{1}}{4}+\frac{\omega_{I}+\omega_{S}}{8 k_{\mathrm{B}} T}\left(I_{z}+S_{z}\right)+\frac{\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T}\left(I_{z}-S_{z}\right)  \tag{2.36}\\
& =\frac{\mathbb{1}}{4}+\frac{\omega_{I}+\omega_{S}}{8 k_{\mathrm{B}} T}\left(\left|\mathrm{~T}_{+1}\right\rangle\left\langle\mathrm{T}_{+1}\right|-\left|\mathrm{T}_{-1}\right\rangle\left\langle\mathrm{T}_{-1}\right|\right)+\frac{\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T}\left(\left|\mathrm{~S}_{0}\right\rangle\left\langle\mathrm{T}_{0}\right|-\left|\mathrm{T}_{0}\right\rangle\left\langle\mathrm{S}_{0}\right|\right) . \tag{2.37}
\end{align*}
$$

We see that in this case $\rho(0)$ already contains coherences between the $\left|\mathrm{S}_{0}\right\rangle$ and $\left|\mathrm{T}_{0}\right\rangle$ states, $\rho_{S_{0} T_{0}}=\rho_{T_{0} S_{0}}=\left(\omega_{I}-\omega_{S}\right) /\left(8 k_{B} T\right)$. These coherences also obey the selection rules of Eq. (2.17), $\Delta m_{F}=0$ and $\Delta F=0, \pm 1$, and if we evaluate the reduced matrix elements we get $M_{\left(z, S_{0} T_{0}\right)}=M_{\left(z, T_{0} S_{0}\right)}=\left(\gamma_{I}-\gamma_{S}\right) / 2$, and $M_{\left(z, T_{1} T_{1}\right)}=-M_{\left(z, T_{-1} T_{-1}\right)}=\left(\gamma_{I}+\gamma_{S}\right) / 2$. Finally, we insert these results into Eq. (2.34) and obtain (remember that $\omega_{i}=B_{\text {pol }} \gamma_{i}$ )

$$
\begin{align*}
\left\langle M_{z}\right\rangle(t) & =N_{\mathrm{tot}} \frac{B_{\mathrm{pol}}\left(\gamma_{I}+\gamma_{S}\right)\left(\gamma_{I}-\gamma_{S}\right)}{8 k_{\mathrm{B}} T}+N_{\mathrm{tot}} \frac{B_{\mathrm{pol}}\left(\gamma_{I}-\gamma_{S}\right)^{2}}{16 k_{\mathrm{B}} T}\left(\mathrm{e}^{\mathrm{i} 2 \pi J t}+\mathrm{e}^{-\mathrm{i} 2 \pi J t}\right) \\
& =O_{z}+N_{\mathrm{tot}} \frac{B_{\mathrm{pol}}\left(\gamma_{I}-\gamma_{S}\right)^{2}}{8 k_{\mathrm{B}} T} \cos (2 \pi J t) . \tag{2.38}
\end{align*}
$$

i.e. the net magnetization of the system oscillates along the z-axis at the coupling frequency. $O_{z}$ denotes static magnetization along the z-axis. The Fourier transform of $\left\langle M_{z}\right\rangle(t)$ would in this case yield a $J$-spectrum consisting of a single peak centered at $J$. There is also a stationary component of $\rho(t)$ which simply results in static magnetization along the initial


Figure 2.3: Simulated excitation curves for a DC pulse on a ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ two-spin system following sudden transport to zero-field. The signal is normalized to the maximum achievable intensity. (a) An $x$ or a y-pulse changes the relative orientation of the proton and carbon spin polarizations, leading to a maximum increase in the signal intensity by $(5 / 3)$. The curve corresponds to Eq. (2.41). (b) A z-pulse does nothing since the initial state commutes with a field along z .
direction of polarization. Note that the intensity of the peak at $J$ is proportional to the square of the difference of the gyromagnetic ratios. One of the two factors $\left(\gamma_{I}-\gamma_{S}\right)$ comes from the detection operator, and is a manifestation of what we pointed out earlier - only heteronuclear systems yield directly observable $J$-spectra. The second factor of $\left(\gamma_{I}-\gamma_{S}\right)$ comes from the matrix element $\rho_{T_{0} S_{0}}$; we term this the coherence amplitude.

DC Pulses The density matrix in zero-field may be manipulated by rapidly switching on a static magnetic field using an electromagnetic coil, letting the spins precess around this field for some time $t_{p}$ before rapidly switching it off. We refer to this as a DC pulse. The Hamiltonian for such a pulse is given by

$$
\begin{equation*}
H_{p}=\sum_{i} \gamma_{i} \boldsymbol{B} \cdot \boldsymbol{I}_{i}, \tag{2.39}
\end{equation*}
$$

where we assume that $\gamma_{i}|\boldsymbol{B}| \gg J$ for all $J$-couplings in the system, and so $J$-coupling evolution under the pulse may be ignored. The effect of such a pulse is to rotate each individual spin in the sample by an angle $\gamma_{i}|\boldsymbol{B}| t_{p}=\theta_{i}$ around the axis defined by $\boldsymbol{B}$.

We can use a DC pulse to increase the intensity of the signal given by Eq. (2.38). This is most easily seen by considering the operator form of $\rho(0)$ in Eq. (2.36). The term $\left(I_{z}+S_{z}\right)$ is diagonal in the zero-field basis, which can also been seen by noting that it is proportional to $F_{z}$, and so does not evolve and the signal comes entirely from the ( $I_{z}-S_{z}$ ) term, which
has a smaller prefactor. However, by applying a static magnetic field perpendicular to the z-axis the prefactors of the two terms can be exchanged by rotating the polarization of one of the spins by $\pi$ rad. relative to the other. During a DC pulse applied in the xy plane $\rho(0)$ is given by

$$
\begin{equation*}
\rho(0)=\frac{\mathbb{1}}{4}+\frac{\omega_{I}+\omega_{S}}{8 k_{\mathrm{B}} T}\left(\cos \left(\theta_{I}\right) I_{z}+\cos \left(\theta_{S}\right) S_{z}\right)+\frac{\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T}\left(\cos \left(\theta_{I}\right) I_{z}-\cos \left(\theta_{S}\right) S_{z}\right), \tag{2.40}
\end{equation*}
$$

where we have kept only terms that lie along the z -axis (detector axis), this simplification will be justified in Section 2.3.6. If we are interested solely in how the detected signal changes with the duration of the applied pulse we can consider only terms proportional to $I_{z}-S_{z}$ and write the following equation for the coherence amplitude

$$
\begin{equation*}
\rho_{T_{0} S_{0}}=\frac{\omega_{I}+\omega_{S}}{8 k_{\mathrm{B}} T}\left(\cos \left(\theta_{I}\right)-\cos \left(\theta_{S}\right)\right)+\frac{\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T}\left(\cos \left(\theta_{I}\right)+\cos \left(\theta_{S}\right)\right), \tag{2.41}
\end{equation*}
$$

we term such an expression an excitation curve. Note that the excitation curve does not depend on the axis of the pulse (as long as it is perpendicular to the z-axis), and the observed spectrum will be the same whether an $x$ - or a $y$-pulse is used. However, if the pulse is along the z-axis nothing happens since $\rho(0)=\rho_{T H}$ and $\rho_{T H}$ commutes with a z-field by construction. Simulations showing excitation curves for a 2 -spin ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ system are shown in Fig. 2.3. The location of the maximum can be understood by noting that for the specific case of a ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ system we have the property $\gamma_{I} / \gamma_{S} \approx 4$, so if we chose $\theta_{S}=\pi$ we get $\theta_{I}=4 \pi$. In this case we have

$$
\begin{equation*}
\rho(0)=\frac{\mathbb{1}}{4}+\frac{\omega_{I}+\omega_{S}}{8 k_{\mathrm{B}} T}\left(I_{z}-S_{z}\right)+\frac{\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T}\left(I_{z}+S_{z}\right), \tag{2.42}
\end{equation*}
$$

and the oscillating magnetization becomes

$$
\begin{equation*}
\left\langle M_{z}\right\rangle(t)=O_{z}+N_{\mathrm{tot}} \frac{B_{\mathrm{pol}}\left(\gamma_{I}+\gamma_{S}\right)\left(\gamma_{I}-\gamma_{S}\right)}{8 k_{\mathrm{B}} T} \cos (2 \pi J t) \tag{2.43}
\end{equation*}
$$

which corresponds to an increase in the signal magnitude by a factor of $\frac{\gamma_{I}+\gamma_{S}}{\gamma_{I}-\gamma_{S}} \approx 5 / 3$ over the result in Eq. (2.38).

Adiabatic Transport The initial state of a two-spin system following adiabatic transport to zero-field is given by Eq. (2.33). By construction this state commutes with $H_{J}$ and so does not evolve. Writing the operators on the coupled basis we obtain

$$
\begin{equation*}
\rho(0)=\frac{\mathbb{1}}{4}+\frac{\omega_{I}+\omega_{S}}{8 k_{\mathrm{B}} T}\left(\left|\mathrm{~T}_{+1}\right\rangle\left\langle\mathrm{T}_{+1}\right|-\left|\mathrm{T}_{-1}\right\rangle\left\langle\mathrm{T}_{-1}\right|\right)+\frac{\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T}\left(\left|\mathrm{~S}_{0}\right\rangle\left\langle\mathrm{S}_{0}\right|-\left|\mathrm{T}_{0}\right\rangle\left\langle\mathrm{T}_{0}\right|\right) . \tag{2.44}
\end{equation*}
$$

The first term, $\left(I_{z}+S_{z}\right)$, corresponds to a population imbalance between the $\left|T_{ \pm} 1\right\rangle$ states, the same as in the sudden case. Under the application of a DC pulse in the transverse plane
this term will evolve into observable oscillating magnetization as shown above. In this case it is straightforward to show that the excitation curve is simply

$$
\begin{equation*}
\rho_{T_{0} S_{0}}=\frac{\omega_{I}+\omega_{S}}{8 k_{\mathrm{B}} T}\left(\cos \left(\theta_{I}\right)-\cos \left(\theta_{S}\right)\right) \tag{2.45}
\end{equation*}
$$

which is the first part of Eq. (2.42). The second term, which is proportional to singlet-triplet population imbalance, is not converted to magnetization oscillating along the z-axis by an x-pulse. On the other hand, while a field along the z-axis does nothing to the $I_{z}+S_{z}$ term, a z-pulse does in fact access scalar order. The singlet-triplet population difference may also be written as $\boldsymbol{I} \cdot \boldsymbol{S}-I_{z} S_{z}$. The part of this term that evolves under a z-pulse is $I_{x} S_{x}+I_{y} S_{y}$. Rotations about the z-axis may never convert $I_{x / y}$ or $S_{x / y}$ into $I_{z}$ or $S_{z}$ terms, and thus a z-pulse cannot turn scalar order into $I_{z}-S_{z}$. However, all we need to detect signal is a term in the density matrix that transforms as a $T_{10}^{\lambda}$ spherical tensor (see Section 2.3.6), which under $J$-coupling evolution is allowed by symmetry to generate z-magnetization. For a two-spin system there are three $T_{10}^{\lambda}$ tensors. Two of them, $I_{z}$ and $S_{z}$ can obviously not be generated with a z-pulse, however the third first-rank tensor is

$$
\begin{equation*}
T_{10}^{3}=I_{x} S_{y}-I_{y} S_{x} \tag{2.46}
\end{equation*}
$$

which can indeed be accessed with a z-rotation. To see this we write the $T_{10}^{3}$ operator on the coupled basis

$$
\begin{equation*}
\left(I_{x} S_{y}-I_{y} S_{x}\right)=\mathrm{i}\left|T_{0}\right\rangle\left\langle S_{0}\right|-\mathrm{i}\left|S_{0}\right\rangle\left\langle T_{0}\right| . \tag{2.47}
\end{equation*}
$$

We also note that under a z-rotation the initial density matrix is equal to

$$
\begin{align*}
\rho(0)=O_{z}+\frac{\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T}\left\{\left[\cos \left(\theta_{I}\right) I_{x}\right.\right. & \left.\left.-\sin \left(\theta_{I}\right) I y\right)\right]\left[\cos \left(\theta_{S}\right) S_{x}-\sin \left(\theta_{S}\right) S_{y}\right] \\
& \left.+\left[\cos \left(\theta_{I}\right) I_{y}+\sin \left(\theta_{I}\right) I_{x}\right]\left[\cos \left(\theta_{S}\right) S_{y}+\sin \left(\theta_{S}\right) S_{x}\right]\right\}, \tag{2.48}
\end{align*}
$$

where we have collected all the terms that commute with the z-pulse into $O_{z}$. Next, we drop the terms proportional to $I_{x} S_{x}$ and $I_{y} S_{y}$ since they commute with $H_{J}$, and after some algebra we obtain

$$
\begin{equation*}
\rho(0)=O_{z}+\frac{\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T}\left(I_{x} S_{y}-I_{y} S_{x}\right)\left[\sin \left(\theta_{I}\right) \cos \left(\theta_{S}\right)-\sin \left(\theta_{S}\right) \cos \left(\theta_{I}\right)\right] \tag{2.49}
\end{equation*}
$$

Employing the difference angle formula and Eq. (2.47) we obtain the following expression for the excitation curve for a pulse along the z -axis

$$
\begin{equation*}
\rho_{S_{0} T_{0}}=-\rho_{T_{0} S_{0}}=\mathrm{i} \frac{\omega_{I}-\omega_{S}}{8 k_{\mathrm{B}} T} \sin \left(\theta_{I}-\theta_{S}\right) \tag{2.50}
\end{equation*}
$$

Maximum signal is thus achieved when the difference in rotation angles for the two spins is $\pi / 2$. For a proton-carbon system this corresponds to $\theta_{C} \approx \pi / 6$. Further, the largest signal that can be achieved when exciting with a pulse along the detector axis is a factor $\frac{\gamma_{I}+\gamma_{S}}{\gamma_{I}-\gamma_{S}}$


Figure 2.4: Simulated excitation curves for a DC pulse on a ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ two-spin system following adiabatic transport to zero-field. The signal is normalized to the maximum achievable intensity. (a) An x or a y-pulse converts vector spin-order into oscillating magnetization. The curve corresponds to Eq. (2.45) (b) A z-pulse converts singlet-triplet population difference into oscillating magnetization. The curve corresponds to Eq. (2.50)
weaker than what can be achieved with a transverse pulse, at least in the two-spin case. However, it has been shown that the life-time of the corresponding spin-order is significantly longer [30].

Inserting Eq. (2.47) into Eq. (2.34) we obtain

$$
\begin{align*}
\left\langle M_{z}\right\rangle(t) & =O_{z}+N_{\mathrm{tot}} \frac{B_{\mathrm{pol}}\left(\gamma_{I}-\gamma_{S}\right)^{2}}{16 k_{\mathrm{B}} T}\left(\mathrm{e}^{\mathrm{i} 2 \pi J t}-\mathrm{e}^{-\mathrm{i} 2 \pi J t}\right) \\
& =O_{z}+N_{\mathrm{tot}} \frac{B_{\mathrm{pol}}\left(\gamma_{I}-\gamma_{S}\right)^{2}}{8 k_{\mathrm{B}} T} \sin (2 \pi J t) . \tag{2.51}
\end{align*}
$$

Note that the magnetization is zero at time zero, and the signal will appear $90^{\circ}$ out of phase relative to a signal excited with a transverse pulse. This is consistent with the fact the the initial state does not contain any $I_{z}$ or $S_{z}$ operators.

Figure 2.4 shows numerical simulations of excitation curves for a 2 -spin ${ }^{1} \mathrm{H}^{13} \mathrm{C}$ system following adiabatic transport to zero-field.

To summarize the results of the preceding paragraphs: transverse ( $=\mathrm{x}$ or y ) pulses convert vector spin order $I_{z}+S_{z}$, which corresponds to a population imbalance between states of different $m_{F}$ into observable magnetization, and pulses along the z-axis access scalar order, $\boldsymbol{I} \cdot \boldsymbol{S}$, i.e. population imbalance between states of different $F$ and $\xi$.

### 2.3.4 Experimental Examples

Equation (2.34) describes a general zero-field signal, the Fourier transform of which will show peaks at the frequencies $\left\{\omega_{i j}\right\}$. In general such $J$-spectra provide chemically distinct fingerprints of molecules, and their complexity grows both with the number of distinct couplings and the number of spins. As a demonstration, Fig. 2.5 shows $J$-spectra of four different molecules acquired over the course of this work. The spectra were acquired following adiabatic transport from a pre-polarizing region to zero-field, followed by inversion of the ${ }^{13} \mathrm{C}$ spin using a DC pulse. All molecules in Fig. 2.5 are ${ }^{13} \mathrm{C}$-labeled since, as we have seen, only heteronuclear systems yield $J$-spectra. All four also feature chemically exchanging protons, which do not contribute to the coherent spin dynamics, since the exchange rate is significantly faster than the timescale for $J$-coupling evolution. Significant effort has gone into the interpretation of $J$-spectra [48, 49], and we will not repeat the analysis in detail here, but simply present a few useful rules.

Two coupled spins $1 / 2$, can only ever result in a single peak at the coupling frequency $J$, as we saw in Eq. (2.38). Such a system is realized experimentally by ${ }^{13} \mathrm{C}$-formic acid, the spectrum of which is shown in Fig. 2.5a. A spin-1/2 coupled to a spin-1 gives a single peak at $3 / 2 J$ and a spin $1 / 2$ coupled to a spin $3 / 2$ gives a peak at $2 J$. These rules indicate that the $J$-spectrum of a ${ }^{13} \mathrm{C}$-labeled methylene group should be a single peak at $3 / 2 J$, while a ${ }^{13} \mathrm{C}$-labeled methyl group should give one peak at $1 J$ as well as one at $2 J$. This is because the angular momenta of the two equivalent protons in a methyl group may add to give either an effective spin- 0 or a spin 1 particle, and the spin- 0 case yields no spectrum. Meanwhile, three protons may add to give either a spin $1 / 2$ or a spin $3 / 2$ particle. The example of ${ }^{13} \mathrm{C}$ methanol is shown in Fig. 2.5b. In Fig. 2.5c we see the slightly more complicated example of ${ }^{13} \mathrm{C}_{2}$-acetic acid. Here the methyl pattern is still the dominant feature as it corresponds to the largest coupling, but now there are two peaks around $1 J$ and three around $2 J$. There are also additional peaks close to zero. These peaks are caused by the methyl-group energy levels being split by the smaller couplings to the second carbon-13. Often in such causes it is enough to treat the additional couplings with 1st order perturbation theory and simply project them on the primary coupling [48]. But while perturbative approaches suffice for small systems with one dominant coupling there are many molecules that do not correspond to such spin systems. For example consider the spectrum of $1-{ }^{13}$ C-propionic acid shown in Fig. 2.5d. There are only six spins, but all three couplings are of approximately the same magnitude and there is no simple shorthand way of interpreting the spectrum. In this case computer simulations are necessary to correctly assign all the peaks and obtain chemical information. Simulations are also necessary to extract quantitative information even from simpler spectra that can otherwise be treated perturbatively.

The resonances in these spectra are broader than what has been reported for some zerofield systems [23]. We believe that scalar relaxation of the second kind causes the exchanging protons to act as a linewidth limiting relaxation sink for these molecules.


Figure 2.5: Representative zero-field $J$-spectra of increasing complexity. (a) ${ }^{13} \mathrm{C}$-formic acid, a two spin system. (b) ${ }^{13} \mathrm{C}$-methanol, a four spin system with three equivalent protons. The large peak at 180 Hz is the third harmonic of the line noise. (c) ${ }^{13} \mathrm{C}_{2}$-acetic acid, a 5 spin system with 3 equivalent protons. (d) $1-{ }^{13} \mathrm{C}$-propionic acid, a 6 spin system, with 2 groups of 3 and 2 equivalent protons. In all four cases the hydroxyl proton exchanges rapidly compared to the evolution time and does not contribute to the spin-dynamics. However, it does limit the linewidths via chemical exchange broadening.

### 2.3.5 Near-Zero Field NMR

So far we have considered 'true' zero-field NMR, i.e. the case where the Hamiltonian only contains spin-spin couplings, and no Zeeman terms at all. This is a good approximation when the field is low enough that the Larmor frequencies of the spin-species under study is significantly smaller than the life-time limited spectral linewidths. In this section we will briefly outline what happens the magnetic field is large enough to have an effect on the
spectrum, but the Larmor frequencies are still significantly smaller than the $J$-couplings of the system. This is termed 'near-zero' or 'ultralow' field NMR and has been described in detail in the literature by Ledbetter et al. [24] and Appelt et al. [22].

The Hamiltonian for a $J$-coupled spin system in the presence of a small magnetic field is

$$
\begin{equation*}
H=H_{J}-B_{z} \sum_{i} \gamma_{i} I_{z, i}, \tag{2.52}
\end{equation*}
$$

where $B_{z}$ is the magnitude of magnetic field and we have chosen our coordinate system so that the field is applied along the z-axis. Ultralow-field NMR thus constitutes the one exception to the rule that we take the z-axis to be along the detector axis of the magnetometer. When there is a residual magnetic field it is significantly more convenient to quantize the spins along the field, whatever that direction is. To first order in perturbation theory the effect of $B$ is to change the energies of the states while leaving their nature unchanged.

2-spin case For the simple case of a two spin system within this approximation Eq. (2.52) becomes

$$
\begin{equation*}
H=H_{J}-B_{z} \frac{\gamma_{H}+\gamma_{C}}{2} F_{z}, \tag{2.53}
\end{equation*}
$$

which corresponds to an energy shift by $\mp B_{z} \frac{\gamma_{H}+\gamma_{C}}{2}$ for the $|1, \pm 1\rangle$ states, while to first order the $|1,0\rangle$ and $|0,0\rangle$ remain unperturbed. If the field is applied perpendicularly to the detection axis, the detection operator is given by $M_{x}$, and within this coordinate system observable transitions are those for which $\Delta m_{F}= \pm 1$. This means that the $J$-spectrum of a single coupled spin-pair, which in zero-field consists of a single peak at $J$, splits into a doublet in a small field applied perpendicularly to the detection axis. The splitting is given by $\Delta \nu=B_{z}\left(\gamma_{H}+\gamma_{C}\right)$.

More spins The case of a system where more than two spins are present is more complicated to treat generally. See Refs $[24,42,43]$ for detailed matrix element calculations of larger spin systems.

### 2.3.6 Signal Direction and Symmetry Considerations

We saw in Section 2.3.3 how a system of two $J$-coupled spins at zero-field, if initialized appropriately, will yield an oscillating magnetization along the z-axis. In this section we answer the question, "what if we had access a complete vector sensor that was capable of measuring the magnetic field along all 3 axes simultaneously?". This question can in fact be answered quite generally by considering the rotational symmetry properties of the relevant operators. The upshot of this section is that zero-field NMR signals always correspond to magnetization oscillating along a single axis, meaning that as long as the system can be reliably initialized along the detection axis 'quadrature detection' would add nothing to the experiment.

Magnetization is a rank-1 (vector) operator with three Cartesian components, $M_{x}, M_{y}$, and $M_{z}$. We will denote the full tensor $\boldsymbol{M}$. The components of $\boldsymbol{M}$ transform under rotations of the spin system according to Eq. (2.60). The expectation value for the magnetization along some direction is given by

$$
\begin{equation*}
\left\langle M_{z}\right\rangle(t)=\operatorname{Tr}\left\{M_{z}^{\dagger} \rho(t)\right\} . \tag{2.54}
\end{equation*}
$$

In order to evaluate the symmetry constraints on Eq. (2.54) we decompose $\rho(t)$ in terms of spherical tensors as

$$
\begin{equation*}
\rho(t)=\sum_{\lambda, l, m} c_{\lambda l m}(t) T_{l m}^{\lambda} \tag{2.55}
\end{equation*}
$$

where $\lambda$ is an extra index denoting the fact that in general there will be more than one tensor of a given $l$ and $m$ and the $c$ are expansion coefficients. Now we can use the fact that the product of two spherical tensor operators is itself a linear combination of spherical tensors with weights given by the appropriate Clebsch Gordan coefficients and write the expectation value in Eq. (2.54) as

$$
\begin{equation*}
\left\langle M_{z}\right\rangle(t)=\operatorname{Tr}\left\{\sum_{\lambda} \sum_{l=0}^{l_{\max }} \sum_{m=-l}^{l} \sum_{l^{\prime}=0}^{l_{\max }+1} \sum_{m^{\prime}=-l^{\prime}}^{l^{\prime}} C_{10, l m}^{l^{\prime} m^{\prime}} U_{l^{\prime} m^{\prime}}^{\lambda} c_{\lambda l m}(t)\right\}, \tag{2.56}
\end{equation*}
$$

where the $U_{l^{\prime} m^{\prime}}^{\lambda}$ are spherical tensors, and we have used the fact that $z$ is the $m=0$ spherical component of $M$. Equation (2.56) appears fierce but the vast majority of the terms are zero by necessity. First we note that only those $U_{l^{\prime} m^{\prime}}^{\lambda}$ for which $l^{\prime}=m^{\prime}=0$ may have non-zero trace (see Appendix 2.4). Second, the Clebsch-Gordan coefficients with $l^{\prime}=0$ and $m^{\prime}=0$ are zero if $l \neq 1$ or if $m \neq 0$. With these constraints Eq. (2.56) becomes

$$
\begin{equation*}
\left\langle M_{z}\right\rangle(t)=\operatorname{Tr}\left\{\sum_{\lambda} C_{1,0,10}^{00} U_{00}^{\lambda} c_{\lambda 10}(t)\right\} . \tag{2.57}
\end{equation*}
$$

We can now see that only the rank- 1 components of $\rho(t)$ may correspond to magnetization, and only those components with $m=0$ may correspond to magnetization along the z-axis.

These are useful statements because we also know that $H_{J}$ as given by Eq. (2.13) is invariant with respect to spin-rotations, i.e. it is a scalar operator, and thus evolution under $H_{J}$ conserves both the rank and the $m$-value of $\rho$. To see why this is true, consider the equation of motion of $\rho(t)$ under $J$-coupling evolution

$$
\begin{align*}
\rho(t) & =\mathrm{e}^{-\mathrm{i} H_{J} t} \rho(0) \mathrm{e}^{\mathrm{i} H_{J} t} \\
& =\left(\sum_{k}^{\infty} \frac{\left(-\mathrm{i} H_{J} t\right)^{k}}{k!}\right)\left(\sum_{\lambda, l, m} c_{\lambda l m} T_{l m}^{\lambda}\right)\left(\sum_{k^{\prime}}^{\infty} \frac{\left(\mathrm{i} H_{J} t\right)^{k^{\prime}}}{k^{\prime}!}\right), \tag{2.58}
\end{align*}
$$

where we have used the expansion for $\rho(t)$ introduced in Eq. (2.55) and the definition of the exponential of an operator. Time evolution is thus equivalent to multiplication by successively higher powers of $H_{J}$. According to Eq. (2.61) the product of a spherical tensor
operator, $T_{l m}$ by a rank-0 operator must result in another spherical tensor operator of rank $l$ and $m$-value $m$. Therefore $\left(H_{J}\right)^{k}$ is a scalar operator for all $k$, and multiplication of $\rho$ with $\left(H_{J}\right)^{k}$ can not change either the rank or $m$-value of any of the components of $\rho$. Thus, for all combinations of (lm) in Eq. (2.55) we have the property that

$$
\begin{equation*}
\sum_{\lambda}\left|c_{\lambda l m}(t)\right|^{2}=K_{l m} \tag{2.59}
\end{equation*}
$$

where $K$ is a constant that is independent of time. This means that each set of $T_{l m}^{\lambda}$ for a given ( $l m$ ) forms a closed space under time-evolution, only the $\lambda$ index may vary. From Eq. (2.57) we know that only $T_{10}^{\lambda}$ operators may give rise to magnetization along the z -axis (and they may never generate either x or y magnetization), but Eq. (2.59) ensures $T_{10}^{\lambda}$ components remain in the $T_{10}^{\lambda}$ space for all time. Similarly only the $T_{ \pm 1}^{\lambda}$ components of $\rho$ may generate x or y magnetization, and they are also conserved. This means that the different components of the sample magnetization, $\boldsymbol{M}$ may never turn into each other by evolution under $H_{J}$, and therefore that a zero-field NMR signal must always be linearly polarized. As such it is always possible to define the z -axis to lie along the axis of oscillation of the magnetization. The trick with signal excitation is to set up an initial condition that ensures that this axis is collinear with the detection axis. Also note that Eq. (2.59) does not imply that the components of $\boldsymbol{M}$ are conserved, it only means that they can not turn into each other.

Finally, we point out that the fact that a zero-field signal may only change its axis of oscillation in the presence of a rank-1 (or higher) term in the Hamiltonian is exploited in proposals for detecting chirality [32] and parity non-conservation [33] using zero-field $J$ spectroscopy.

### 2.4 Appendix I: Properties of Spherical Tensors

The following is summary of useful properties of spherical tensors. For a more complete reference see e.g. Varshalovich et al. [37].

- Spherical tensors can be defined by their transformation properties under rotations

$$
\begin{equation*}
U(R) T_{l m} U^{\dagger}(R)=\sum_{m^{\prime}=-l}^{l} D_{m m^{\prime}}^{l} T_{l m^{\prime}} \tag{2.60}
\end{equation*}
$$

where $D^{l}$ is a rank- $l$ Wigner matrix. A Wigner matrix is the representation of the rotation operator (in either Euler-angle, or axis-angle parametrization), on the angular momentum basis.

- The $T_{l m}$ can be both numbers, e.g. the components of a classical vector, and operators, e.g. the components of the angular momentum operator $\boldsymbol{I}$. If they are operators they are represented by $N \times N$ matrices (where $N$ is the dimensionality of the relevant Hilbert space), but they still obey the transformation law in Eq. (2.60).
- The product of two spherical tensors is a linear combination of spherical tensors, with weights given by the appropriate Clebsch-Gordan coefficient.

$$
\begin{equation*}
X_{k q} Y_{k^{\prime} q^{\prime}}=\sum_{l=\left|k-k^{\prime}\right|}^{k+k^{\prime}} \sum_{m=-l}^{l} C_{k q, k^{\prime} q^{\prime}}^{l m} T_{l m} \tag{2.61}
\end{equation*}
$$

- A scalar operator defined on some Hilbert space is unchanged by rotations

$$
\begin{equation*}
U(R) T_{00} U^{\dagger}(R)=T_{00} \tag{2.62}
\end{equation*}
$$

which implies that it commutes with the representations of the angular momentum operators $\boldsymbol{I}$ as defined on the same space on which we defined $T_{00}$. This can be seen by noting that $U(R)$ is constructed by exponentiating the components of $\boldsymbol{I}$.

- It follows from the above statement that all spherical tensor operators of rank greater than 0 are traceless.
To see this consider an $N \times N$ dimensional spherical tensor operator $T_{l m}$. If $T_{l m}$ has a trace then it can be written as

$$
\begin{equation*}
T_{l m}=\operatorname{Tr}\left\{T_{l m}\right\} \times \frac{\mathbb{1}}{N}+T^{\prime} \tag{2.63}
\end{equation*}
$$

where $\mathbb{1}$ is the $N \times N$ identity matrix and $T^{\prime}$ is a traceless operator. However, the identity matrix commutes with all operators, and therefore it commutes with all components of $\boldsymbol{I}$. That means that the first term in Eq. (2.63) is a scalar operator according
to Eq. (2.62). But a spherical tensor may only have a single rank by definition, therefore if the first term is nonzero, $T^{\prime}$ must be either zero or rank- 0 . It follows that if a spherical tensor operator has a trace, it must necessarily be a scalar operator. Note that the converse is not true, the matrix representation of a scalar operator may still be traceless, c.f. the operator for a two-spin $J$-coupling $\boldsymbol{I} \cdot \boldsymbol{S}$, which transforms as a scalar under rotations, but its matrix representation is traceless.

## Chapter 3

## Vapor-Cell Detected NMR: Background and Experimental Methods

In the previous chapter we provided a review of the concept of zero-field $J$-spectroscopy. Here we will discuss the means by which such spectra are obtained.

We will start with a brief overview of the options available for NMR detection at frequencies below 100 Hz . The experiments in this dissertation were performed using a spectrometer based on a ${ }^{87} \mathrm{Rb}$ vapor-cell magnetometer, and the bulk of the chapter is dedicated to a review of how such a device works, as well as how to set one up as an NMR spectrometer. We will also cover calibrations and design choices for our spectrometer. Finally, we will provide a summary of some of the digital processing methods that we have used to assist data analysis and interpretation.

This chapter contains material previously published under the following titles:

- Instrumentation for nuclear magnetic resonance in zero and ultralow magnetic field by Tayler, Theis, Sjolander, Blanchard, Kentner, Pustelny, Pines, and Budker [63]
- Nuclear Magnetic Resonance at Millitesla Fields Using a Zero-Field Spectrometer by Tayler, Sjolander, Pines, and Budker [64]
- Transition Selective Pulses in Zero-Field Nuclear Magnetic Resonance by Sjolander, Tayler, King, Budker, and Pines [1]
- ${ }^{13}$ C-Decoupled J-coupling Spectroscopy Using Two-Dimensional Nuclear Magnetic Resonance at Zero-Field by Sjolander, Tayler, Kentner, Budker, and Pines [2],
as well as material being prepared for publication under the title
- Rank Selective Decoupling of Heteronuclear Systems in Zero-Field Nuclear Magnetic Resonance by Sjolander, Tayler, Ajoy, Budker, and Pines [145].


### 3.1 Detection of Low-Frequency NMR Signals

### 3.1.1 Inductive Detection at Low-Field

Nuclear Magnetic Resonance signals are conventionally detected using an inductive pickup coil, however this is not suitable for zero-field spectroscopy. To see why consider that the emf, $\epsilon$ induced in a coil is given by Faraday's law of induction as the rate of change of the magnetic field, $B$.

$$
\begin{equation*}
\epsilon=-\frac{d B}{d t} \tag{3.1}
\end{equation*}
$$

In NMR spectroscopy the observed signal corresponds to the magnetic field generated by the bulk magnetization of the sample. The signal, $S$, has an oscillating time dependence which is given by the evolution of the ensemble density matrix under the nuclear spin Hamiltonian, as outlined in the previous chapter.

$$
\begin{equation*}
S(t)=\sum_{i>j} A_{i j} \cos \left(\omega_{i j} t\right) \tag{3.2}
\end{equation*}
$$

where the $\left\{A_{i j}\right\}$ are the amplitudes and the $\left\{\omega_{i j}\right\}$ the frequencies of the different signal components. It follows that the observed $\epsilon$, regardless of spin polarization level, should depend on the frequency of the signal of interest.

$$
\begin{equation*}
\epsilon_{\mathrm{NMR}}=\sum_{i>j} \omega_{i j} A_{i j} \cos \left(\omega_{i j} t\right) . \tag{3.3}
\end{equation*}
$$

The amplitudes $A_{i j}$ are proportional to the sample magnetization, which in turn are generally (but not always - c.f. hyperpolarized NMR) proportional to the static magnetic field. This would imply a scaling of the sensitivity for inductive detection by $\epsilon_{\mathrm{NMR}} \propto B_{0}^{2}$, where $B_{0}$ is the ambient field. However, in general what one cares about in an NMR experiment is the Signal to Noise Ratio (SNR), commonly defined as the signal divided by the standard deviation of the noise. The noise includes contributions from thermal fluctuations in the coil and other unwanted pickup, which in general also decrease at lower frequencies. The actual scaling of of the SNR with field strength varies depending on noise characteristics (which in turn is a sensitive function of the exact experimental parameters) but is generally between $B^{1}$ and $B^{2}$ [65-68]. In any case, detecting NMR signals with inductive pickup coils becomes more challenging the lower the frequencies one wishes to operate at. Savukov et al. [69] introduced a model for the fundamental sensitivity of an inductive pickup coil as a function of frequency. They obtain a sensitivity of $\sim 0.01 \mathrm{fT} \sqrt{\mathrm{Hz}}$ at 100 MHz , and $\sim 100 \mathrm{fT} \sqrt{\mathrm{Hz}}$ at 1 kHz , for a 5 cm diameter surface pickup coil. This represents the size of the magnetic field that can be measured with an SNR of $1 \mathrm{in} 1 / 2 \mathrm{~s}$ of averaging time. (The Nyquist sampling theorem gives the bandwidth in Hz as $(1 / 2) \times\left(1 / \mathrm{s}_{\mathrm{r}}\right)$, where $\mathrm{s}_{\mathrm{r}}$ is the sampling rate in samples per second.)

In spite of the punishing scaling of sensitivity with field strength relaxometry can be performed all the way down to earth's field [70] (corresponding to a proton Larmor frequency
of $\sim 2 \mathrm{kHz}$ ) and within the last decade interest in low-cost and portable NMR/MRI in general, coupled with advances in coil design, has pushed the frequencies where it is possible to perform spectroscopy with inductive detection down to $\sim 1 \mathrm{kHz}$ [71, 72]. This has the potential to be transformative in the field of low-field NMR, but is still one to two orders of magnitude away from the frequencies in zero-field $J$-spectroscopy.
$J$-coupling constants in organic molecules, which are the typical objects of study in $J$ spectroscopy, are generally between $1-200 \mathrm{~Hz}$, so in order to perform zero-field $J$-spectroscopy we require a a detector that is sensitive at essentially DC frequencies. SNR generally improves with the square-root of the measurement time. As a consequence, in the case of weak signals whose amplitude are close to or below the sensitivity level of the sensor, 'just average more' quickly turns into something of a fool's game and it is desirable to use a detector that is as sensitive as possible. We will briefly summarize different detection schemes that have been used to observe $<100 \mathrm{~Hz}$ NMR signals.

### 3.1.2 Detection in High-Field

The first detection of NMR signals originating from nuclear spins evolving in the absence of an external field were done using a high-field spectrometer (superconducting magnet and all) see Refs [73-76] and others. In these experiments the sample was shuttled mechanically in and out of the bore of the magnet into a magnetically shielded region, the signal projection on the z-axis during zero-field evolution was determined indirectly, by monitoring the integral of the high-field spectrum following a $\pi / 2$ pulse once the sample had been shuttled back into high-field. The FID was thus acquired point-by-point. The main goal of these experiments was to use the fact that in the absence of a preferred direction an NMR powder spectrum has the same kind of narrow lines usually associated with single-crystal spectra.

Later it was realized that low-field conditions in some cases can be recreated inside a high-field bore using coherent averaging techniques, thus removing the need for shuttling [77]. The technique was termed 'Zero-Field-in-High-Field' (ZFHF). The catch is that while one can use coherent averaging [78] to take a truncated Hamiltonian and make it 'look' like a zero-field Hamiltonian, those terms which are zero can never be brought back. For example, one can use the ZFHF technique to turn the heteronuclear $J$-coupling $J I_{z} S_{z}$ into its zero-field analogue (with a scaling factor) $(J / 3) \boldsymbol{I} \cdot \boldsymbol{S}$. On the other hand, one could never use ZFHF to generate a term proportional to $J^{1}$ (the rank-1 component of the $J$-coupling tensor). Measurements of this coupling tensor have been suggested as a means to detect both chirality [32] and molecular parity non-conservation using NMR [33]. Consequently the difference between genuine zero-field evolution, and 'zero-field like' evolution in an average Hamiltonian sense is critically important for some experiments.

In the end, while high-field detection provides an excellent means by which to explore ultralow-field physics phenomena (and efforts in this vein are currently underway in the Pines' lab), the use of indirect detection puts limits on the resolution that can be attained, and of course superconducting magnets are not very amenable to portability and miniaturization. However, many potential applications of zero-field NMR are not based on either portable
analysis or fundamental physics. For example studies of chemical reactions inside catalysts and heterogeneous media in general do not necessarily require direct detection and since magnetic shielding is cheap it would be straightforward for current research labs to use zero-field NMR with high-field detection to attack such problems.

### 3.1.3 SQUIDs

DC Superconducting Quantum Interference Devices (SQUIDs) do not suffer from decreasing sensitivity at low frequencies and generally obtain sensitivities around $1 \mathrm{fT} \sqrt{\mathrm{Hz}}[79]$. This makes them excellent candidates for ultra-low field NMR detection. Indeed, SQUIDs have a long history as detectors in NMR [80] and the first experiment directly detecting NMR signals at frequencies below 100 Hz was performed with a SQUID in 2002 [50]. A few years later a SQUID based system was used to obtain the first directly detected NMR spectra where $2 \pi J>\gamma B[46,47]$. There has been continued interest in this field since then, see [51, 81,82 ] and many others, and this paragraph does not purport to give anywhere close to a full review of the subject. While SQUIDs allow for frequency-independent detection of NMR signals with good sensitivity they have one big weakness as a low-field detector - they still require liquid Helium in order to operate. So while SQUID based NMR systems do benefit from many of the advantages of low-field, such as lower field homogeneity requirements, increased skin-depth, and the ability to ignore magnetic susceptibility anisotropy, they can not easily be turned into cheap and portable, sensors or imaging devices.

### 3.1.4 Diamonds

Magnetic field sensing using Nitrogen Vacancy (NV-) Centers in diamond is a growing field. The NV- center is an effective atomic spin-1 particle, the magnetic state of which can be initialized and read out optically. Magnetometers based on NV- centers do not require cryogens and have been used for a number of groundbreaking NMR experiments, such as detection of the magnetic field from a single ${ }^{13} \mathrm{C}$ in the diamond lattice [83], and even the detection of individual protons outside the diamond [84]. This was possible because a single NV- center can be brought within nanometers of a target sample [85, 86]. NV-magnetometers are eminently miniatureizible, easy to set-up and handle, and potentially portable. Their main weakness as NMR detectors come from the fact that ensembles of NV- centers are simply not that sensitive compared to SQUIDs. They attain sensitivities in the $n T \sqrt{\mathrm{~Hz}}[87$, 88] range (though the projected shot-noise limit is significantly better [89]) and are therefore not suitable for applications to bulk NMR (as opposed to single molecule detection, where their small size can be leveraged).

### 3.1.5 Atomic Magnetometers

In this dissertation we detect NMR signals using an atomic vapor-cell magnetometer. Atomic magnetometers are magnetic field sensors that work by monitoring the precession of
the bulk magnetization of atomic spins of an alkali vapor in response to the magnetic field of interest. The principle was first demonstrated experimentally by Bell and Bloom [90] in 1957 and in the decades since significant improvements have been made see [91-93] and references therein. At this point atomic magnetometers operating in the Spin Exchange Relaxation Free (SERF) regime are the most sensitive DC magnetic field sensors available, eclipsing even SQUIDs, with sensitivities $<1 \mathrm{fT} / \sqrt{\mathrm{Hz}}$ [94]. These devices can be used for precision measurement experiments e.g. the ongoing search for a neutron electric dipole moment [95]. An atomic magnetometer was first used to detect coherent NMR at sub- 100 Hz frequencies in 2005 [53]. The experiment measured the Larmor precession of bulk water in a field of $\sim 5 \mu \mathrm{~T}(\nu=20 \mathrm{~Hz})$. While the sensitivity of atomic magnetometers for some configurations is better than that of SQUIDs, this is primarily the case when optimized for an extremely small measurement bandwidth. However, in order to measure zero-field NMR spectra we want a sensor that operates over at least a few hundred Hz . In such a configuration an atomic magnetometer does not necessarily outperform a SQUID in terms of sensitivity. Instead the main advantage of vapor-cell magnetometers comes from the fact that they do not require cryogens, and are in general significantly easier to set up and operate. It took years to develop the specialized electronics that enable SQUIDs to function as NMR sensors [80], meanwhile NMR detection with a SERF vapor-cell magnetometer requires a photodiode and a data acquisition card (e.g. National Instruments 6229, an Arduino can do in a pinch). They can also be miniaturized, while still being fully capable of bulk NMR detection [25-27, 96].

### 3.2 Introduction to Vapor-Cell Magnetometry

Since our zero-field spectrometer is based on an alkali vapor-cell magnetometer, we will briefly outline the principles, operation, and setup of such a device with reference to our instrument. For a more complete overview of vapor-cell magnetometry see [91, 92] and references therein.

There are several different configurations of atomic magnetometers, but the one used for the experiments in this dissertation works as follows: Rubidium vapor contained in a heated glass cell is spin-polarized using circularly polarized laser light, by means of a process known as optical pumping. The bulk spin of the polarized rubidium ensemble coherently precesses around the external magnetic field, $B$ we wish to measure. At the low fields considered in this work the precession rate is much lower than the optical pumping rate, so the effect of $B$ is to slightly change the angle, $\theta$, of the net rubidium magnetization away from the axis of the pump laser. A second laser beam, called the probe, passes through the vapor-cell at right angles to the pump beam. The probe beam is linearly polarized and as it passes through the rubidium vapor the plane of polarization rotates by an angle $\phi_{\text {rot }}$. This effect is known as magneto-optical rotation and is closely related to Faraday rotation. The degree of rotation depends on the strength of the magnetic field generated by the Rubidium electrons along the axis of propagation of the probe. The polarization rotation angle $\phi_{\text {rot }}$ is therefore


Figure 3.1: Illustration of the physics behind the magnetometer operation. (a) Optical pumping with circularly polarized light induces a net rubidium spin-polarization along the $y$ axis. (b) The presence of a field $B_{z}$ along the z -axis causes coherent precession of the rubidium ensemble. Assuming that the precession frequency is much smaller than the optical pumping rate the effect of $B_{z}$ is to rotate the direction of the steady-state rubidium polarization by an angle $\theta$ in the xy-plane. (c) A linearly polarized laser beam passes through the spinpolarized vapor at right angles to both the pump and $B_{z}$, i.e. the x-axis. The plane of polarization rotates proportionally to the degree of spin-polarization along the x -axis, which in turn depends of $\theta$. Measurement of the rotation angle therefore provides a measure of $B_{z}$.
a measure of $\theta$, and $\theta$ in turn depends on the strength and direction of the external magnetic field $B$. The steps linking the magnetic field to be sensed and the optical rotation of the probe beam are shown schematically in Fig. 3.1.

Of course in this dissertation the external fields we are interested in measuring originate in the coherent evolution of the collective magnetization of nuclear spin ensembles i.e. pulsed NMR, and we have $B \propto\left\langle M_{z}\right\rangle(t)$. In general the response of the magnetometer is a sensitive function of the frequency of $B$.

### 3.2.1 Optical pumping

The strength of the optical rotation signal does not depend on $\theta$ alone, i.e. the direction of the rubidium magnetization vector, it also depends on the degree on spin-polarization of
the vapor, i.e. how magnetized the vapor is. Alkali spins in the gas phase may be polarized to near unity via a process known as optical pumping [97, 98]. During this process a laser is used to shine polarized light at the vapor, resonant absorption transfers angular momentum from the light to the atoms, which in turn end up in a spin polarized state. Throughout this work we use ${ }^{87} \mathrm{Rb}$ as the gas and pump with circularly polarized light. The process is outlined schematically in figure 3.2.


Figure 3.2: Schematic describing optical pumping on the rubidium D1 transition using $(+)$ circularly polarized light. The red balls represent units of rubidium spin polarization, and the arrows represent the direction of the polarization with respect to the quantization axis. Since angular momentum is conserved only electrons in $m_{j}=-1 / 2$ spin-orbit state may absorb $(+)$ polarized photons, absorption thus selectively depopulates that state and causes buildup of electron spin polarization in the $m_{j}=+1 / 2$ state.

Atomic States For clarity we ignore the the nuclear spin of the rubidium atoms and consider only the electron spin. In its ground state rubidium has a single valance electron in an S-orbital. Since an S-orbital does not have any orbital angular momentum the angular momentum of the electron in the ground state may simply take one of two values when projected on an arbitrary axis, $m_{j}+ \pm 1 / 2$. We denote these states ${ }^{2} \mathrm{~S}_{1 / 2}\left(m_{j}= \pm 1 / 2\right)$. The lowest energy excited state (that can be accessed with a single photon) is the P-orbital, which has an orbital angular momentum of 1, giving two possible excited spin-orbit states with a total angular momentum $1-1 / 2=1 / 2$, and $1+1 / 2=3 / 2$ denoted ${ }^{2} \mathrm{P}_{1 / 2}$ and ${ }^{2} \mathrm{P}_{3 / 2}$ respectively. Rubidium therefore has two optical resonances. ${ }^{2} \mathrm{~S}_{1 / 2} \rightarrow{ }^{2} \mathrm{P}_{1 / 2}$, referred to as

D1 at 795 nm , and the slightly higher energy D2 transition at 780 nm , which corresponds to ${ }^{2} \mathrm{~S}_{1 / 2} \rightarrow{ }^{2} \mathrm{P}_{3 / 2}$. Spin polarization, by definition, corresponds to an excess of population in one of the two magnetic $\left(m_{j}\right)$ sub-levels of the ground state. This is equivalent to net magnetization of the rubidium spins and it is this magnetization that is ultimately used as a sensor in a vapor-cell magnetometer. Optical pumping generates such a population imbalance by transferring angular momentum from the light via absorption at either D1 or D2. In general it is favorable to pump on the D1 transition since it results in larger maximally attainable polarization and that is what we do throughout this dissertation.

Light absorption Circularly polarized light carries angular momentum of either $+\hbar$ or $-\hbar$ along its axis of propagation. Conservation of angular momentum means that, for the case of $(+)$ light, only atoms in the ${ }^{2} \mathrm{~S}_{1 / 2}\left(m_{j}=-1 / 2\right)$ state may absorb a 795 nm photon and, and upon doing so they must necessarily end up in the ${ }^{2} \mathrm{P}_{1 / 2}\left(m_{j}=+1 / 2\right)$ excited state. Meanwhile, the ${ }^{2} \mathrm{~S}_{1 / 2}\left(m_{j}=+1 / 2\right)$ ground state is optically transparent to $(+)$ light. Thus optical absorption of $(+)$ light results in selective depopulation of the $m_{j}=-1 / 2$ state, which corresponds to spin-polarization of the rubidium vapor. The angular momentum of the light is defined with respect to its axis of propagation and so the rubidium electrons are polarized parallel to the pump laser axis (along the direction of propagation if pumping with $(+)$ light and opposite the direction of propagation in the case of $(-)$ light.

Polarization Decay Pathways If the vapor contained only rubidium gas, the excited ${ }^{2} \mathrm{P}_{1 / 2}\left(m_{j}=+1 / 2\right)$ state would eventually decay radiatively by emitting a photon of random polarization. The branching ratios for the radiative decay are such that most atoms decay back down to the original $m_{j}=-1 / 2$ state. This counteracts the depopulation of the $m_{j}=-1 / 2$ state and decreases the rate at which light absorption causes spin-polarization $\equiv$ the optical pumping rate. To make matters worse, the emitted photon will act as to depolarize the vapor - it has random polarization and thus it may be absorbed equally by atoms in the ${ }^{2} \mathrm{~S}_{1 / 2}\left(m_{j}= \pm 1 / 2\right)$ states. In order to sustain a continuous depopulation of the target ${ }^{2} \mathrm{~S}_{1 / 2}\left(m_{j}=-1 / 2\right)$ state the optical pumping rate needs to be fast compared to the rate of depolarization due to radiative decay as well the rate of depolarization due to absorption by randomly polarized emitted photons, something which requires a lot of laser power. The consequence of these two effects is that optical pumping of pure rubidium vapor is quite inefficient. The solution is to add additional molecular gases, usually nitrogen gas, to the vapor cell. Molecular nitrogen has a wide range of vibrational and rotational energy levels which allows it to absorb the excess energy in the ${ }^{2} \mathrm{P}_{1 / 2}$ state whenever an excited rubidium atom collides with a nitrogen molecule. Collisions with nitrogen thus allow the rubidium atom to decay back to the ground state non-radiatively, i.e. without emitting a depolarizing photon, in a phenomenon known as collisional quenching. Furthermore, the process is unaffected by the electron spin state and the electron is therefore equally likely to decay to the ${ }^{2} \mathrm{~S}_{1 / 2}\left(m_{j}= \pm 1 / 2\right)$ states, as opposed to the case of radiative decay, which favors the original $m_{j}=-1 / 2$ state.

The presence of buffer gas also leads to a process called collisional mixing, the population of the two ${ }^{2} \mathrm{P}_{1 / 2}\left(m_{j}= \pm 1 / 2\right)$ excited states are equalized much faster than the collisional quenching rate (the rate with which they decay to the ground-state). This is beneficial since it increases the population difference between the ${ }^{2} \mathrm{~S}_{1 / 2}\left(m_{j}=-1 / 2\right)$ and the ${ }^{2} \mathrm{P}_{1 / 2}\left(m_{j}=+1 / 2\right)$ states. An increase in this population difference means an increase in the number of photons that can be absorbed per unit time, and therefore the rate of transfer of angular momentum from the light to the alkali vapor. Both excited-state levels have an equal probability of nonradiatively (due to collisions with nitrogen gas) decaying to the target ${ }^{2} \mathrm{~S}_{1 / 2}\left(m_{j}=+1 / 2\right)$ state and so collisional mixing increases the optical pumping efficiency by increasing the population imbalance between the ${ }^{2} \mathrm{~S}_{1 / 2}\left(m_{j}=-1 / 2\right)$ and ${ }^{2} \mathrm{P}_{1 / 2}\left(m_{j}=+1 / 2\right)$ states, and therefore the photon absorption rate.

Taking the above facts together we see that adding buffer gas to the cell increases the optical pumping efficiency.

### 3.2.2 Spin Relaxation

The attainable polarization of the alkali spins does not depend only on the optical pumping process, it also depends on the spin-polarization life time. Various mechanisms may cause the electron spin to flip direction and thus cause depolarization. Which mechanism dominates depends on the properties of the vapor-cell. Wall collisions generally correspond to the dominant relaxation pathway at low pressures. Much work has been put into developing specialized cell coatings that cause wall collisions to not be depolarizing [92, 99, 100], thereby enabling cells to operate at lower pressures.

In cells with large number densities of alkali spins, spin exchange collisions are often the dominant relaxation pathway. The electronic spins of two colliding alkali atoms may flip simultaneously while the net electronic spin is conserved. The reason such a collisions are depolarizing is that the atoms may change hyperfine states during the course of the collision, and different hyperfine states precess in different directions, i.e. the sign of the effective gyromagnetic ratio of the net atomic spin may change [92]. The modulation of the sign of the effective gyromagnetic ratio leads to decoherence of the colliding spins with the overall ensemble. There is a surprising exception to this rule. If the number density is very large, and the ambient magnetic field very low, such that the spin-exchange rate is much larger than the Larmor precession frequency, then the relaxation rate starts to decrease with number density instead [101, 102]. This is called the Spin-Exchange-Relaxation-Free (SERF) regime. What happens is that at high spin exchange rates, the rubidium atoms are effectively in a super position of the hyper-fine states, and precess at a single, average, frequency, at which point the spin-exchange decoherence pathway disappears. The magnetometer used in this dissertation operates in this regime.

Spin-destruction collisions do not conserve total electronic spin and may occur both between two alkali atoms and between alkali atoms and buffer gas atoms. Since the spin angular momentum is transfered into rotational angular momentum of either the dimer formed during the collision or the buffer gas diatomic, spin destruction collisions must necessarily be
depolarizing. Such collisions are the dominant relaxation pathway in the cells used in this dissertation.

Additionally, since the probe beam is linearly polarized, absorption of probe beam photons is depolarizing. This is most easily addressed by detuning the probe beam slightly from the D1 resonance.

### 3.2.3 Magneto-Optical Rotation

Once the alkali vapor has been magnetized using optical pumping, monitoring the precession of the resulting magnetization vector allows for a very sensitive measure of external magnetic fields. To accomplish this the instantaneous direction of the alkali spins must be determined. This may done through a phenomenon known as magneto-optical rotation, which causes the plane of polarization of linearly polarized light to rotate as it passes through a magnetized medium [93].

Spin-polarization implies circular dichroism Near the D1 resonance, the indices of refraction $\mathrm{n}_{ \pm}$for the $(+)$and $(-)$circularly polarized components of the light depend on the degree of spin-polarization of the atomic vapor along the propagation path. The physical origin of this effect is the fact that the index of refraction for light in a medium depends on its absorption rate in the medium. Formally, an attenuating medium is conveniently described with a complex refraction index $n^{\prime}=n+\mathrm{i} \kappa$, with the real part describing refraction (dispersion) and the imaginary part describing the attenuation (absorption) of light in the medium. Since the real and the imaginary parts (i.e. the dispersion and the absorption) must always be related by the Kramers-Kronig relations it follows that the absorption rate in the medium determines the refractive index. Of course this also implies that the refraction index depends on the wavelength of the light, but in this work we are focused solely on a single optical resonance, the rubidium D1 line, and the wavelength dependence is not important.

The next point is that the rate of absorption by $(+)$ and $(-)$ light are indeed different for the case of spin-polarized rubidium vapor and that such a vapor therefore does have different refractive indices for $(+)$ and $(-)$ light. Remember that spin-polarization by definition implies an imbalance in the populations of the $m_{j}= \pm 1 / 2$ ground states, and that conservation of angular momentum implies that only the $m_{j}=-1 / 2$ state may absorb $(+)$ light and vice versa. This means that the absorption rate of $(+)$ light must depends on the ratio of the $m_{j}= \pm$ populations. In fact for the D 1 line the matrix elements for the ${ }^{2} \mathrm{~S}_{1 / 2}\left(m_{j}= \pm 1 / 2\right) \rightarrow{ }^{2} \mathrm{P}_{1 / 2}\left(m_{j}=\mp 1 / 2\right)$ transitions are identical and the difference in absorption rate for $(+)$ and $(-)$ light depends entirely on the relative populations of the ${ }^{2} \mathrm{~S}_{1 / 2}\left(m_{j}= \pm 1 / 2\right)$ states. Therefore, spin-polarization of the rubidium vapor implies different refractive indicies for ( $\pm$ ) light.

However, since the optical pumping process spin-polarizes the rubidium spins along the $y$-axis, the degree of polarization along the x -axis (i.e. the probe propagation path) depends on $\theta$. This is the link between the optical rotation signal and the magnetic field to be sensed.

## CHAPTER 3. VAPOR-CELL DETECTED NMR: BACKGROUND AND

 EXPERIMENTAL METHODSRotation of the plane of polarization of the probe laser Finally, we follow Seltzer [92] and show that the plane of polarization of linearly polarized light actually does rotate as the light propagates through a medium for which $n_{+} \neq n_{-}$. Taking the x-axis as the axis of propagation of the probe beam and the y-axis as direction of the pump beam we can write the electric field vector of a probe beam initially linearly polarized along the z -axis as an equal super position of $(+)$ and $(-)$ light

$$
\begin{align*}
& \boldsymbol{E}(t)=\frac{E_{0}}{2}\left[\mathrm{e}^{\mathrm{i} \omega t} \hat{z}+\mathrm{e}^{-\mathrm{i} \omega t} \hat{z}\right] . \\
& \boldsymbol{E}(t)=\frac{E_{0}}{4}\left[\mathrm{e}^{\mathrm{i} \omega t}(\hat{z}-\mathrm{i} \hat{y})+\mathrm{e}^{\mathrm{i} \omega t}(\hat{z}+\mathrm{i} \hat{y})+\mathrm{e}^{-\mathrm{i} \omega t}(\hat{z}-\mathrm{i} \hat{y})+\mathrm{e}^{-\mathrm{i} \omega t}(\hat{z}+\mathrm{i} \hat{y})\right] . \tag{3.4}
\end{align*}
$$

Here $\omega$ is the frequency of the light. We note that at time $t$ the wave will have propagated a distance $l=c t / n$ through the vapor. But we also know that $n$ is different for the $(+)$ and $(-)$ components so we can rewrite the equation for $\boldsymbol{E}$ in terms of $l$ and $n$ as

$$
\begin{equation*}
\boldsymbol{E}(l)=\frac{E_{0}}{4}\left[\mathrm{e}^{\mathrm{i} \omega n_{-} l / c}(\hat{z}-\mathrm{i} \hat{y})+\mathrm{e}^{\mathrm{i} \omega n_{+} l / c}(\hat{z}+\mathrm{i} \hat{y})+\mathrm{e}^{-\mathrm{i} \omega n_{-} l / c}(\hat{z}-\mathrm{i} \hat{y})+\mathrm{e}^{-\mathrm{i} \omega n_{+} l / c}(\hat{z}+\mathrm{i} \hat{y})\right] \tag{3.5}
\end{equation*}
$$

This in turn can be rewritten using an asymmetry parameter for the refraction index. We define

$$
\begin{align*}
\bar{n} & =\frac{n_{+}+n_{-}}{2}  \tag{3.6}\\
\Delta n & =\frac{n_{+}-n_{-}}{2} \tag{3.7}
\end{align*}
$$

and now we can write

$$
\begin{align*}
\boldsymbol{E}(l)=\frac{E_{0}}{4}\left[\mathrm{e}^{\mathrm{i} \omega \bar{n} l / c} \mathrm{e}^{-\mathrm{i} \omega \Delta n l / c}(\hat{z}-\mathrm{i} \hat{y})\right. & +\mathrm{e}^{\mathrm{i} \omega \bar{n} l / c} \mathrm{e}^{\mathrm{i} \omega \Delta n l / c}(\hat{z}+\mathrm{i} \hat{y}) \\
& \left.+\mathrm{e}^{-\mathrm{i} \omega \bar{n} l / c} \mathrm{e}^{\mathrm{i} \omega \Delta n l / c}(\hat{z}-\mathrm{i} \hat{y})+\mathrm{e}^{-\mathrm{i} \omega \bar{n} l / c} \mathrm{e}^{-\mathrm{i} \omega \Delta n l / c}(\hat{z}+\mathrm{i} \hat{y})\right] . \tag{3.8}
\end{align*}
$$

Rearranging gives

$$
\begin{align*}
& \boldsymbol{E}(l)=\frac{E_{0}}{4}\left[\mathrm{e}^{\mathrm{i} \omega \bar{n} l / c}\left(\mathrm{e}^{\mathrm{i} \omega \Delta n l / c}+\mathrm{e}^{-\mathrm{i} \omega \Delta n l / c}\right) \hat{z}+\left(\mathrm{e}^{\mathrm{i} \omega \Delta n l / c}-\mathrm{e}^{-\mathrm{i} \omega \Delta n l / c}\right) \mathrm{i} \hat{y}\right] \\
&+\frac{E_{0}}{4}\left[\mathrm{e}^{-\mathrm{i} \omega \bar{n} l / c}\left(\mathrm{e}^{\mathrm{i} \omega \Delta n l / c}+\mathrm{e}^{-\mathrm{i} \omega \Delta n l / c}\right) \hat{z}+\left(\mathrm{e}^{-\mathrm{i} \omega \Delta n l / c}-\mathrm{e}^{\mathrm{i} \omega \Delta n l / c}\right) \mathrm{i} \hat{y}\right] \tag{3.9}
\end{align*}
$$

at which point recognizing the the trigonometric functions makes it clear that a linearly polarized beam passing through a medium for which $n_{+} \neq n_{-}$sees its plane of polarization rotate by an angle $\phi_{\mathrm{rot}}=\omega \Delta n l / c$ around the axis of propagation of the beam.

$$
\begin{align*}
& \boldsymbol{E}(l)=\frac{E_{0}}{2} \mathrm{e}^{\mathrm{i} \omega \bar{n} l / c}[\cos (\omega \Delta n l / c) \hat{z}-\sin (\omega \Delta n l / c) \hat{y}] \\
&+\frac{E_{0}}{2} \mathrm{e}^{-\mathrm{i} \omega \bar{n} l / c}[\cos (\omega \Delta n l / c) \hat{z}+\sin (\omega \Delta n l / c) \hat{y}] . \tag{3.10}
\end{align*}
$$

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Since $\Delta n$ is proportional to the population difference between the ( $m_{j}= \pm 1$ ) states defined along the x-axis we have $\phi_{\text {rot }} \propto\left\langle S_{x}\right\rangle$, where $S_{x}$ is the rubidium spin polarization along the xaxis. Further, since the rotation angle depends on the path-length we can infer that a bigger cell will yield a larger optical rotation signal and therefore a more sensitive magnetometer (assuming the entire cell can be uniformly pumped).

### 3.2.4 Magnetometer Response

It is possible to write a Bloch equation for the rubidium spin polarization vector $\boldsymbol{S}$ in the presence of an arbitrary field

$$
\begin{equation*}
\frac{d \boldsymbol{S}}{d t}=\left[\boldsymbol{M} \times \boldsymbol{B}+R_{O P}(\hat{y} / 2-\boldsymbol{S})-R_{r e l} \boldsymbol{S}\right] / q \tag{3.11}
\end{equation*}
$$

where $\boldsymbol{M}$ is the rubidium magnetization and $q$ is the so-called nuclear slowing-down factor. $R_{O P}$ and $R_{r e l}$ are the optical pumping and spin relaxation rates respectively [91]. As shown above $\phi_{\text {rot }} \propto\left\langle S_{x}\right\rangle$ so we solve Eq. (3.11) for $S_{x}$ as a function of $\boldsymbol{B}$

$$
\begin{equation*}
\phi_{\mathrm{rot}} \propto S_{x}=S_{0} \frac{(\Delta B) B_{z}+B_{x} B_{y}}{\Delta B^{2}+B_{x}^{2}+B_{y}^{2}+B_{z}^{2}} \tag{3.12}
\end{equation*}
$$

where $\Delta B=\gamma /\left(R_{O P}+R_{r e l}\right)$ and $\gamma$ is the gyromagnetic ratio of the effective rubidium spin. If $B_{x}=B_{y}=0$ and $\left|B_{z}\right| \ll|\Delta B|$ which are the conditions relevant to the experiments in this dissertation we obtain

$$
\begin{equation*}
\phi_{\mathrm{rot}} \propto B_{z} \tag{3.13}
\end{equation*}
$$

which justifies our choice of detection operator in Chapter 2 as the net nuclear magnetization.
If we solve Eq. (3.11) for the case of an oscillating field of frequency $\omega$ and amplitude $B$ instead we obtain [92]

$$
\begin{equation*}
S_{x}=\frac{1}{2} S_{0} \gamma B\left[\frac{\Delta B \cos (\omega t)+\omega \sin (\omega t)}{\Delta B^{2}+\omega^{2}}+\frac{\Delta B \cos (-\omega t)+\omega \sin (-\omega t)}{\Delta B^{2}+\omega^{2}}\right] . \tag{3.14}
\end{equation*}
$$

Which corresponds to a Lorentzian line centered at zero frequency. This is assuming that the field is applied perpendicularly to the pump and the probe axes. Equation (3.14) implies that the sensitivity of the magnetometer to NMR signals drops rapidly with frequency and is limited by the magnetic linewidth of the rubidium ensemble. For this reason cells with too long transverse relaxation times are not appropriate for zero-field NMR. It also turns out that in practice we are limited by magnetic field noise, not the fundamental sensitivity of the magnetometer, in which case the drop off of the response with frequency does not actually impact the SNR too much across the frequency range we work in in this dissertation.

### 3.2.5 Polarimetry

A sensitive magnetometer requires the ability to accurately measure the change in polarization of the probe beam before and after it passes through the vapor cell. This may be done in a number of ways, we give two examples here.

Perhaps the conceptually most straight forward method is known as balanced polarimetry. In this scheme the laser goes through a linear polarizer right before the cell. After the cell it passes through a polarizing beam splitting cube set at $45^{\circ}$ to the initial axis of polarization. One of the two circularly polarized components of the probe passes through the cube, the other is reflected at a $90^{\circ}$ angle. Two photodiodes are used to measure the intensities of the two beams. If there has been no magneto optical rotation of the probe in the vapor cell the polarization is exactly at $45^{\circ}$ to the cube and the intensities ( $I_{1}$ and $I_{2}$ ) at the two photodiodes are equal. However if the plane of polarization of the probe has rotated by an angle $\phi$ the photo-diodes will record different intensities. For small optical rotation angles $\phi$ is proportional to the difference in intensities recorded at the two photodiodes.

$$
\begin{equation*}
\phi \propto\left(I_{1}-I_{2}\right) \tag{3.15}
\end{equation*}
$$

The magnetometer signal is conveniently measured by feeding the output of the two photodiodes into a low-noise differential amplifier.

The second scheme is based on a lock-in amplifier. A linear polarizer before the vaporcell is followed by a quarter waveplate, a photoelastic modulator (PEM) and a second linear polarizer at $90^{\circ}$ to the first one after the cell. Relative to the axis of polarization set by the first polarizer the optical axis of the quarter-wave plate should be at $0^{\circ}$, and the crystal axis of the PEM should be set at $45^{\circ}$. A PEM is a device that modulates the polarization of light. In this configuration it will symmetrically modulate the probe beam between the $(+)$ and (-) polarization assuming there has been no optical rotation in the cell. If the plane of polarization of the probe has rotated so that it no longer is at $0^{\circ}$ to the quarter waveplate it will be elliptically polarized when it impinges on the PEM, and in this case the modulation will be asymmetric. The output from a single photodiode placed after the second linear polarizer is fed into a lock-in amplifier which is referenced to the PEM modulation frequency at $10-100 \mathrm{kHz}$. For small optical rotation angles the intensity of the light detected at the photodiode at the modulation frequency of the lock-in is proportional to $\phi$.

$$
\begin{equation*}
\phi \propto I \tag{3.16}
\end{equation*}
$$

### 3.2.6 Weaknesses of Atomic Magnetometers as NMR Detectors

Sensitivity The main weakness of atomic magnetometers as NMR detectors is their low sensitivity. This may sound like a weird statement having just made the point that magnetometers are the best DC field sensors known, but the caveat here is 'DC'. While atomic magnetometers perform well relative to other ultra-low field sensors they can not get close to inductive detection with resonant coils at frequencies of 100 s of MHz . This matters because
in routine chemical analysis one often wants to study samples with $\mu \mathrm{M}$ to mM concentration of solute of interest. To make matters worse, zero-field detection of organic molecules rely on the presence of ${ }^{13} \mathrm{C}$, which is only $1 \%$ naturally abundant. In practice throughout this dissertation we have used neat, isotopically enriched liquids, which is obviously not particularly realistic. In the end, if directly detected zero-field NMR is to stop being a subject of 'methods development' and start being used in applications we need either a DC field sensor that is better than the current state-of-the-art by $2-3$ orders of magnitude (or a way of increasing the field generated by the spins at the detector by the same amount, through optimization of sample geometry etc), or a reliable and general hyper-polarization scheme, some suggestions of which were made in Section 2.3.2.

Dead-Time Another issue is the fact that NMR spectrometers based on atomic magnetometers have a large 'dead-time'. Dead-time is a hardware enforced delay between the readout pulse and the start of the data acquisition. In high-field NMR the dead-time is often on the order of $5-10 \mu s$ and arises because the same coil is used for pulsing and receiving, and care most be taken so that the high-power pulse amplifiers do not connect to the sensitive detection electronics. For a spectrometer based on an atomic magnetometer the origin is quite different. The magnetic fields generated by the pulse (or the guiding field used for 'sudden' sample shuttling) are much larger than any other fields inside the magnetic shields. This causes the magnetization of the alkali spins to repolarize along the direction of the pulse field, regardless of whatever small fields are generated by the NMR sample. Consequently the magnetometer does not function as a magnetic field sensor for some time after a magnetic field pulse. This time is dependent on the polarization life time of the alkali ensemble, but is usually $\sim 30 \mathrm{~ms}$ in our setup. There are two main consequences of such long dead-times. (i) It makes stroboscopic sampling impossible. Stroboscopic sampling is a method when only a few points of an FID is acquired in between the pulses in a long pulse sequence. Splicing all the measured points together one can obtain an FID corresponding only to the effective evolution induced by the pulse train. However virtually all pulse sequences require the pulse spacing to be significantly less than 30 ms , meaning that the magnetometer does not have time to recover before it is time for the next pulse. As will be explained in detail later, in this dissertation we solve this problem by using two-dimensional detection. (ii) Additionally, such long dead-times preclude the observation of systems with coherence times much shorter than 30 ms , such as most solid state samples, since the signal will have decayed completely before the magnetometer is ready to begin measurements after the initialization pulse.

However, there is a relatively straightforward (albeit expensive) method for solving the dead-time problem, which has been successfully implemented on the ZULF spectrometer in Mainz, Germany. The solution is to use much (much) higher power pump laser than what is otherwise required. Such high power introduces significant laser noise during the measurement and is thus not desired under normal circumstances. But using an acusto optic modulator, the pump power during the measurement can be decreased to a reasonable number, while it is left as high as possible while the spectrometer is playing out magnetic
field pulses. The large optical pumping rate associated with high laser powers ensures that the rubidium spins are repolarized along the pump direction almost immediately ( $<1 \mathrm{~ms}$ ) after the end of a pulse. While this is a very elegant solution, the associated hardware is quite expensive.

Bandwidth Finally atomic magnetometers have a rather limited bandwidth, meaning they can only detect magnetic fields oscillating over a limited frequency range. In fact the most sensitive SERF magnetometers have bandwidths that are $<1 \mathrm{~Hz}$. The width of the frequency response is determined by the transverse relaxation time of the Rubidium ensemble. This is influenced by pressure, wall-coatings etc. The magnetometer in this work is capable of detecting magnetic fields between $\sim 1$ and $\sim 500 \mathrm{~Hz}$, see Section 3.3. This broad response is achieved by using rather high buffer gas pressures ( 700 Torr $\mathrm{N}_{2}$ ), and it does significantly limit sensitivity. In order to study systems with bigger couplings than we do in this work, such as solid state systems, or certain transition metal compounds (which can have $J$-couplings up to thousands of Hz ) with zero-field NMR one would need a detection scheme with significantly larger bandwidth than what can be obtained with an atomic magnetometer, such as an untuned SQUID or simply indirect detection at high-field.

### 3.3 General Hardware

Having briefly introduced the underlying physics of atomic magnetometers we now turn our attention to how to set up such a magnetometer and operate it as a detector in an NMR experiment. In doing so we will make repeated reference to the particular instrument used to perform the experiments in this work [63].

Data Acquisition We use a National Instruments 6229 Data Acquisition Card to operate the spectrometer. The analogue outputs are used to generate pulses, and the digital outputs are used for triggers for the switches and the shuttling. The optical rotation signal as measured at the output of the lock-in amplifier is read in at one of the analogue inputs. A homebuilt LabVIEW program ensures that the timing between excitation pulses and data acquisition is constant between transients. The flexibility of a commercial data acquisition card is convenient, but the signal frequencies are low enough that e.g. an Arduino could be used instead if cost savings are desired.

Magnetic Shielding This dissertation concerns zero-field NMR, and so it is necessary to create an environment where spin-spin couplings dominate over any residual Zeeman terms in the Hamiltonian. As an added benefit, operation at or near zero magnetic field enables the magnetometer to operate in the SERF regime, thus increasing its sensitivity. The earth's magnetic field corresponds to a ${ }^{1} \mathrm{H}$ Larmor frequency of $\sim 2 \mathrm{kHz}$, which is significantly larger than most $J$-couplings, therefore in order to reach the zero-field regime we need to screen out the ambient field.

Magnetic shielding is conventionally implemented using layers of mu-metal. Mu-metal is a primarily nickel based alloy that has a very high relative magnetic permeability of $\sim$ 80000 , which causes magnetic field lines to preferentially follow a path within the metal, as opposed to cut through it. A spherical or cylindrical geometry of mu-metal therefore prevents external field lines to reach the volume contained inside the shields

In our spectrometer we use four concentric layers of mu-metal to screen out ambient magnetic fields to a level of 1-10 nT. Additionally we use one layer of ferrite to screen the magnetometer from Johnson noise from the mu-metal shields.


Figure 3.3: (a) Photo of the Rubidium cell which fixed with a high temperature cement to a ceramic pillar around which twisted copper wire is wound. (b) Schematic of the heating setup.

Heating and Cell Mounting Rubidium is a solid at room temperature, and thus a ${ }^{87} \mathrm{Rb}$ cell needs to be heated in order to provide adequate vapor pressure. We operate our magnetometer at $\sim 180^{\circ}$. We note that the vapor pressure of rubidium increases rapidly with temperature. A phenomenological expression for the number density of gas phase rubidium atoms is given by Alcock et al. [103]

$$
\begin{equation*}
n=\frac{1}{T} 10^{21.866+4.312-4040 / T} \tag{3.17}
\end{equation*}
$$

where n is in units of $\mathrm{cm}^{-3}$. The rapid increase of $n$ with $T$ manifests in markedly lower magnetometer sensitivity at $160^{\circ}$ than at $180^{\circ}$.

In precision measurement experiments vapor-cells are often heated using hot air flowing through ovens made from glass or fiberglass. This ensures uniform heating of the cell, and since no magnetic materials are used minimal noise is introduced [92]. However, since the experiments in this dissertation rely on shuttling NMR tubes from a pre-polarizing magnet to a measurement region as close to the cell as possible, we cannot easily encase the cell in an oven. Instead we use resistive heating. The cell is fixed with a high temperatures cement to a thermally conductive ceramic pillar (Shapal Hi-M Soft), and around the pillar several layers of copper wire are wound (to a total resistance of $\sim 2 \Omega$ ). When constant current runs trough the wire the heat dissipation heats the ceramic pillar, which in turn heats the vapor-cell. We coat the pillar in a silicone based heat-sink compound before winding the wire in order to ensure good thermal contact and a type $T$ thermocouple is fixed at the top of the pillar, which allows us to monitor the temperature of the cell during operation.

There are a number of important points to note here: (i) The most important is that a flowing current generates a magnetic field, and care must be taken in order not to let the field reach the cell where it would appear as magnetic noise, thus lowering the magnetometer sensitivity. This is accomplished by using twisted pair wire, which ensures that the magnetic field outside the wire cancels to a first approximation. Additionally, we heat the cell using AC current ( 40 kHz ), this ensures that any residual magnetic fields lie well outside the frequency response range of the magnetometer and thus do not impact the NMR measurements. (ii) The copper wire needs to be coated in a high temperature enamel. The standard enamel coatings fail after days or weeks of operation, at which point the heating wire short-circuits. If the resistance of the heater circuit gets too low either the power supply will no longer be capable of supplying the requisite current to heat the cell, or the the wire will just burn off, whichever happens first the magnetometer will cease to function. (iii) The method of fixing the cell to the pillar also matters. We note that some high temperature epoxys contain magnetic material, which is not ideal. Further, several other epoxys which were rated for up to $250^{\circ} \mathrm{C}$ still failed after a few weeks of operation at $180^{\circ} \mathrm{C}$. We went through a number of cycles optimization before settling on a high temperature cement, which has served us well so far.

We use a LVC2016 AE Techron linear amplifier to generate the current. The amplifier is connected to a function generator which is in turn connected to the PID control system of a thermostat controller. There are no particular requirements on the amplifier, beyond it being able to generate sufficient power at the desired frequency. Throughout most of this dissertation the PID control loop was left disabled, it was challenging to prevent the temperature from oscillating rapidly around the set point. Instead we simply change the output voltage on the function generator manually, until the heater reaches equilibrium at the desired temperature.


Figure 3.4: Schematic of possible optical layouts for optical pumping and polarimetry. (a) Optical pumping optics. (b) and (c) Possibilities for optical layouts for the probe laser.

Optics We pump the cell using circularly polarized light sourced from an Eagle Yard Distributed Feedback (DFB) diode laser. The optical path is shown in Fig. 3.4a. The halfwave plate allows for the rotation of the plane of polarization before the linear polarizer, which gives a method of controlling the laser power that reaches the cell. Typically the half-wave plate is adjusted so that 15 mW reaches the cell.

We use a polarimetry scheme based on a lock-in detector and a PEM, as described in Section 3.2.5. The optical path is shown in Fig. 3.4c. Again a half-way plate serves as a power attenuator. Typically the probe power is adjusted to 10 mW .

Shimming and Small Applied Fields The magnetic shields of the spectrometer used in this dissertation do not shield screen ambient fields to a level below the life-time limited linewidths. For that reason it is necessary to apply small fields using electromagnetic coils to cancel out any residual fields. By analogy to high-field NMR we refer to this process as 'shimming'. The shimming is done by means of coils wound around a 10.5 cm diameter cylindrical nylon structure that surrounds both the cell and the pulsing-coil housing. The cylindrical geometry (which is enforced by the shape of the inner most ferrite shield layer) means that the shimming field along the z and the x directions is generated by saddle coils, while along the y direction a solenoid configuration is used. The shimming coils generate fields up to 30-300 nT when fed current between 0.1 and 1 mA . In order to keep the requisite voltages within a convenient range the coils are placed in series with $1 \mathrm{k} \Omega$ resistors. We set the shims using precision DC current sources. Remember from Section 3.2.4 that the magnetometer detection axis in a true zero-field is normal to the plane defined by the pump



Figure 3.5: Calibrations of the transverse shim-coils. The black dots are measured splittings in the $J$-spectrum of ${ }^{13} \mathrm{C}$-formic acid (FA), and the blue solid lines are fits to the expression $\Delta \nu=B\left(\gamma_{H}+\gamma_{C}\right)$, giving $199 \mathrm{nT} / \mathrm{mA}$ for the y -coil, and $47 \mathrm{nT} / \mathrm{mA}$ for the x -coil. Note that the x -axes are given in mA current relative to the settings that give zero splitting.
and the probe lasers, and we call this direction the z-axis. This means that we can shim the magnetic field at the rubidium cell by applying a test-signal (see the following section) along the x -axis using the x -shim, while slowly changing the static field along the y -axis using the y-shim until zero response is recorded by the magnetometer. After that the test-signal is applied along $y$, while the $x$-shim is changed until the magnetometer response is zero. This procedure is best performed iteratively until the magnetometer responds to fields only in the z-direction. However, this procedure ensures zero-field specifically at the location of the rubidium cell, the presence of any gradients in the magnetic field, or a pump laser induced light-shift can lead to a non-zero field at the location of the NMR sample, even while the field at the cell is zero. Since we are concerned with zero-field NMR this is not an acceptable state of affairs.

In order to zero the fields at the NMR sample we rely on the changes in the zero-field NMR spectrum in response to fields in different directions, see Section 2.3.5. To recapitulate: In a small magnetic field perpendicular to the detection operator the $J$-spectrum of ${ }^{13} \mathrm{C}$-formic acid splits into a doublet centered at $J$, with the splitting given by $\Delta \nu=B\left(\gamma_{H}+\gamma_{C}\right)$. If additionally, there is a magnetic field component along the detection axis a third peak, at the unchanged $J$ frequency, will reappear. It follows that we can shim the magnetic field at the NMR sample by changing the voltages applied to the the shim-coils while continuously acquiring NMR spectra of formic acid. The protocol is as follows:

- Obtain a good SNR $J$-spectrum of ${ }^{13} \mathrm{C}$-formic acid.
- Apply a field in the x or y direction until a clear splitting is observed. Record the
natural linewidth.
- Change the field in the z direction until the central peak disappears and only a doublet remains.
- Systematically change the field along x and y , and then extrapolate to zero splitting according to $\Delta \nu=B\left(\gamma_{H}+\gamma_{C}\right)$.
- Carefully adjust the fields until the linewidth matches the natural linewidth recorded in step 2.

As a consequence of this procedure we obtain current-to-field calibrations for the two transverse coils as the slope of a plot of the observed splitting vs applied current, see Fig. 3.5. This is useful since it allows us to calibrate the magnetometer sensitivity - see the following section. Note that the $y$-shim generates a substantially larger field per unit current than the x -shim does, this is a consequence of the fact the y -shim is a solenoid coil, while the x - and z-shims are saddle coils. Since the z-coil has the same geometry as the x-coil we assume that its current to field characteristics are the same.

Magnetometer Sensitivity and Frequency Response The shimming coils fill another very important function beyond canceling out any fields not perfectly screened by the shields. They also enable us to apply oscillating fields to monitor the magnetometer response at different frequencies. We refer to this as applying a 'test-signal', and we do this by feeding the output of a function generate to the shim-coils via a variable resistor ( $1 \mathrm{k} \Omega$ to $1 \mathrm{M} \Omega$ ).

The sensitivity of the magnetometer to fields along a given axis at a given frequency may be calibrated by monitoring the optical rotation signal in response to an oscillating field applied via the shimming coils. To calibrate the magnetometer sensitivity along the detector axis we applied a 4.4 pT magnetic field oscillating at 15 Hz using the z-shim. The magnetometer response to this field was recorded over 20 seconds and the resulting timedomain data was subjected to the same data processing as applied to the experimental data (see Section 3.6), giving the spectrum shown. The Signal-to-Noise-Ratio (SNR) of the magnetometer response was determined by taking the ratio of the peak height to the standard deviation of the baseline. Defining sensitivity as the smallest field that can be observed with an SNR of 1 over a measurement time of 0.5 seconds, and assuming that the SNR increases with the square root of the measurement time, we obtain $30 \mathrm{fT} / \sqrt{\mathrm{Hz}}$ as the sensitivity of our instrument to magnetic fields oscillating at 15 Hz .

We calibrate the amplitude of the magnetometer frequency response over the full bandwidth by applying a 4.4 pT test-signal at a frequency $\nu$ along the z -direction using the z -shim, and record the magnetometer signal as a function of $\nu$. We assume that the current-to-field characteristics of the $z$-shim are the same as of the $x$-shim. The magnetometer signal is subjected to the same data analysis protocol as will be described in Section 3.6 and the amplitude response is taken as the height of the peak at $\nu$. In order to obtain the phase response


Figure 3.6: Magnetometer Response to 4.4 pT field at 15 Hz acquired over 20 s . The signal has been normalized to standard deviation of the baseline between 12 and 14 Hz , thus giving the Y-axis in units of SNR.


Figure 3.7: Amplitude and phase of the magnetometer frequency response when the NMR sample has been calibrated to experience zero-field. The dots are measured values and the solid lines are drawn to guide the eye.
we recorded output of the function generator that serves as the source of the test-signal simultaneously with the magnetometer response, fit both peaks to complex Lorentzians. The phase response is then simply the difference in phase between the two peaks. The results of such a calibration are shown in Fig. 3.7. The amplitude response drops by $\sim 80 \%$ over 400 Hz , suggesting a rather limited bandwidth for NMR spectroscopy. However, we find that the SNR remains basically flat out to $\sim 500 \mathrm{~Hz}$. This is consistent with the sensitivity being


Figure 3.8: Amplitude and phase of the magnetometer frequency response when the NMR sample has been calibrated to experience a 30 nT field along the $\mathrm{x}, \mathrm{y}$, and z directions.
limited by magnetic field noise (e.g. Johnson noise from the shields), the response to which decreases at the same rate as the response to the NMR signal. The phase response varies by $\pi$ over 400 Hz , meaning that a signal at 1 Hz and 400 Hz will appear $\pi$ rad. out of phase. However since the phase response is close to linear it is straightforward to correct for it by a simple first-order phase correction.

We note that the shape of the amplitude is consistent with a non-zero field at the rubidium cell, since maximum amplitude occurs at non-zero frequency. To confirm that this is indeed the case we obtained calibration data at 30 nT , the results are shown in Fig. 3.8, and demonstrate that the magnetometer response changes drastically depending on the field. The fact that zero-field at the NMR sample does not necessarily correspond to zero-field at the rubidium cell has consequences for some experiments, since a finite field at the rubidium cell changes the detection axis away from z . The detection axis being off-axis from z led to the observation of nominally forbidden peaks in Refs [31] and [1].

Polarization and Shuttling In order to obtain spin-polarized NMR sampled in zero-field we use thermal pre-polarization in a permanent magnet (see Section 2.3.2), and transport the samples pneumatically to zero-field for each transient. We use a 2 T magnet and keep the samples in standard 5 mm outer diameter NMR tubes. The tubes are kept in a plexi-glass

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Cell Characteristics Our vapor cell is sourced from Twin-Leaf LLC and contains 2-5 mg of Rubidium metal and 700 Torr nitrogen gas. The cell has interior dimensions of $5 \times 5 \times 8$ $\mathrm{mm}^{3}$ (see Fig. 3.3). The optical resonance of the cell was characterized by transmission spectroscopy, see Fig. 3.9a. Figures 3.9b and 3.9c show how the normalized magnetometer


Figure 3.9: (a) Optical transmission spectrum of the rubidium cell acquired with 10 mW power. The width of the peak is 0.1 nm at half-max. (b) In (a) and (b) we see fringes characteristic of a Fabry Perot effect.


Figure 3.10: Photo of the pulsing coils, and a general schematic of the experiment.
sensitivity (as measured with a test-signal along the z-axis applied at 100 Hz ) depends on the wavelength of the probe and the pump lasers respectively. We see clearly that when the probe is applied on resonance the sensitivity drops to zero. This is because at these high vapor densities very few probe photons actually pass through the cell if the probe is perfectly on resonance with the optical absorption line. Instead we find that the optimal setting for the probe is 794.88 nm . Meanwhile, as expected the sensitivity is maximal when the pump beam is applied perfectly on resonance at 794.97 nm , thus maximizing the optical pumping rate.


Figure 3.11: Experimental excitation curves for ${ }^{13} \mathrm{C}$-formic acid following adiabatic transport to zero-field for DC pulses along x, y, and z, c.f. Fig. 2.4, acquired using the setup in Fig. 3.10. The black dots are measured amplitudes of the formic acid $J$-spectrum and the blue solid lines are fits to the excitation curves derived in Section 2.3.3 (Eqs. (2.45) and (2.50)). The measured data are normalized to the maximum signal amplitude obtained when pulsing along the x -axis.

### 3.4 Magnetic Pulsing Setup

### 3.4.1 Strong Pulses - Amplifiers

The work in Chapters 5 and 7 required the ability to quickly and accurately generate large $(>0.1 \mathrm{mT})$ static magnetic field pulses. For this purpose we used three orthogonal Helmholz pulsing-coils (radius $=2.2 \mathrm{~cm}$ ) wound around a PEEK (Polyetheretherketone) structure with holes to allow for laser and shuttling access. The pulsing coils were powered by AE Techron LVC2016 linear amplifiers. Figure 3.10 shows the pulsing coil and a general schematic of the experimental setup.

The sensitivity of our spectrometer is around $30 \mathrm{fT} / \sqrt{\mathrm{Hz}}$, see Fig. 3.6, and typical ZULF signal magnitudes for a $150 \mu \mathrm{~L}$ sample range from $0.1-1000 \mathrm{fT}$ depending on sample concentration and the number of distinct frequency components. However, the amplifier current noise (at zero input) corresponds to a noise floor of $\sim n T$. This is a large enough field to impact spin-evolution in the time between pulses, while also making the detection of NMR signals impossible. Therefore, a symmetric fast-switching MOSFET relay, shown in the bottom panel of Fig. 3.10, was put in series with each coil. The MOSFETs were controlled using the same DAQ-card used to control the amplifiers. When the amplifiers are not generating pulses the relay is non-conducting, thereby preventing noise from the amplifiers to reach the cell. During the pulses the noise was negligible compared to the $>0.1 \mathrm{mT}$ pulse field. It is important that both the switches and the amplifiers are bipolar, since there is no equivalent to high-field phase shifts in zero-field, and positive and negative pulses require current in physically different directions. Experimental calibrations of the three coils are shown in Fig. 3.11. The pulses were $50 \mu$ s long, giving us a voltage-to-field conversion of $6.169 \mathrm{G} / \mathrm{V}$
for the z-coil, $5.950 \mathrm{G} / \mathrm{V}$ for the x -coil, and $5.372 \mathrm{G} / \mathrm{V}$ for the y -coil when using the Techron amplifiers. (variations may occur both because of slightly different coil characteristics, but also due to differences in gain between the amplifiers).

The DC pulses generate $\sim 0.2-2 \mathrm{mT}$ fields at the sample, which is positioned less than 1 mm away from the rubidium cell, meaning the atoms in the vapor-cell also experience a significant field. The result is that each pulse rotates the rubidium spins away from the direction of the pump laser, effectively imposing a $\sim 30 \mathrm{~ms}$ dead time after each pulse, determined by the pump-light-power dependent rubidium-polarization lifetime. This means that with this experimental setup it is not possible to obtain a 1 D decoupled spectrum by sampling the signal in between pulses at the end of each cycle, termed stroboscopic observation, as is commonly done in high-field NMR. For the decoupling experiments we instead relied on two-dimensional detection as described in Chapter 7.

The advantage of using a pulsing setup based on linear amplifiers is that it allows for shaped pulses. In Chapter 5 we use the amplifiers to generate adiabatic remagnetization pulses and frequency swept inversion pulses.

### 3.4.2 Weak Pulses



Figure 3.12: Schematic of the experimental setup. The current amplifier is used to generate strong DC pulses for broadband manipulations. The DAQ in conjunction with the $1 \mathrm{k} \Omega$ resistor is used to generate the weak selective AC pulses and bias the static field. The sensitive axis of the magnetometer, denoted $\hat{\boldsymbol{s}}$, lies along the axis of the NMR tube, perpendicular to the plane defined by the pump and probe lasers (not shown).

The work in Chapter 4 required very weak $\sim 10 \mathrm{nT}$ AC magnetic field pulses. This is approximately equal to the noise floor of the amplifiers we used for the hard DC pulses and the adiabatic pulses, and therefore they were unsuitable in this case. However, it turns out the the $\pm 10 \mathrm{~V}$ analogue outputs on the National Instruments 6229-DAQ card we use to control the spectrometer can source up to 5 mA current. From Fig. 3.7 we know that 1 mA current in the x - and z -shims is enough to generate $\mathrm{a} \sim 47 \mathrm{nT}$ field at the location of the NMR sample, and it was therefore possible to use the DAQ card directly as a low-


Figure 3.13: Diagram for the DC power supply based pulser. The polarity of the switches is critical. The $100 \Omega$ resistor provides an escape path for the energy in the coil when the switch closes, thereby preventing ringing and shortening the fall time.
power 'amplifer'. The strength of the magnetic field generated by this process was calibrated by measuring the proton Larmor precession frequency in a sample of water, the measured frequencies ranged from 0.5 to 4 Hz . In order to generate and control the DC magnetic field pulses we used the same setup as described in the previous section, though this work required DC pulses only along the detection axis.

### 3.4.3 Strong Pulses - DC Power Supplies

Using the Techron amplifiers and the MOSFET based switch we were able to obtain the first ${ }^{13} \mathrm{C}$ decoupled $J$-spectrum, see Chapter 7 . However, we were unable to reproduce these results on molecules with larger $J$-couplings. To obtain the heteronuclear decoupling results presented in Chapter 8 we designed a new pulsing circuit based on DC power supplies (Agilent 6653A) gated with high voltage switches (Willamette High Voltage), rather than linear amplifiers. The circuit that allows us to generate bipolar pulses using monopolar power supplies is shown in Fig. 3.13. We readily achieve a $\pi$ pulse on carbon in $30 \mu \mathrm{~s}$, with a rise time of $\sim 2 \mu \mathrm{~s}$. Excitation curve calibrations are shown in Fig. 3.14. The one issue is the fact that the resistance for individual switch units varies slightly. This means that the circuit is not perfectly bipolar as written, positive and negative pulses will have slightly different amplitude. To correct for this we installed a SpinCore PulseBlaster ESR PRO-II 400 MHz TTL generator to trigger the pulses as opposed to using the NI card directly. The PulseBlaster card allows us to change the duration of the pulses in steps of 2.5 ns (as opposed to the NI DAQ card which is limited to $2 \mu \mathrm{~s}$ ). This allows us to balance the flip angles for positive and negative pulses by finely tuning the pulse duration for the two channels separately. We applied $80 \pi$ pulses, alternating positive and negative directions, and measured the response as a function of the duration of the negative pulse. The pulse sequence was $(x \bar{x})_{40}$, meaning that no NMR signal should be excited if the pulses are perfectly balanced. We calibrated a single positive $\pi \mathrm{x}$ pulse to be $31.9 \mu \mathrm{~s}$ and stepped


Figure 3.14: Experimental excitation curves for ${ }^{13} \mathrm{C}$-formic acid following adiabatic transport to zero-field for DC pulses along the x , y directions acquired using the pulsing setups based on DC power supplies. The pulse duration was $30 \mu \mathrm{~s}$. The black dots are measured amplitudes of the formic acid $J$-spectrum and the blue solid lines are fits to the excitation curves derived in Section 2.3.3. The measured data are normalized to the maximum signal amplitude obtained when pulsing along the x -axis. The right most panel shows the result of balancing positive and negative pulses by sweeping the length of the $\bar{x}$ pulse in a $(x \bar{x})_{4} 0$ sequence.
the negative pulse from 31 to $33 \mu$ s in steps of 2.5 ns . The result is shown in the right most panel in Fig. 3.14. The minimum is clearly offset from 31.9, indicating a pulse imbalance. Therefore when executing a $-\pi$ pulse along the x axis we chose the duration to be $31.98 \mu \mathrm{~s}$ instead of $31.9 \mu \mathrm{~s}$.

The high voltage switches requires a 5 V trigger to open, but the PulseBlaster card outputs 3.3 V logic. We boost the pulse blaster signal to $\sim 4 \mathrm{~V}$ (which in practice is enough to reliably trigger the switch) by routing the signal through 2 successive NOT gates and using a 5 V power supply to power the integrated circuit component.

### 3.5 Extraction of $J$-Coupling Constants From $J$-Spectra

While simple rules govern the appearance of $J$-spectra of small molecules it is still not easy to determine the actual values of the coupling constants for systems with more than 2 couplings by hand. However, the exact values of $J$-coupling constants carries chemical information and therefore it is useful to be able to determine them quantitatively. For example, one-bond ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ couplings vary from $\sim 110 \mathrm{~Hz}$ to $\sim 220 \mathrm{~Hz}$ depending on the other substituents on the carbon. Smaller changes, on the order of $\sim 1 \mathrm{~Hz}$, arise due to solvent effects, pH , temperature, and more. With quantitative spectral analysis we would be able
to extract such information from $J$-spectra, and we could do so with higher accuracy than in high-field NMR, due the narrower linewidths obtained in zero-field NMR.

In this section we introduce a simple fitting algorithm that can be used to quickly extract accurate $J$-coupling constants from the $J$-spectra of small molecules with known identity. We first introduced this algorithm in Ref. [2]. It provides an easy way of quickly obtaining coupling constants with mHz precision using standard curve fitting tools available in e.g. MATLAB. More sophisticated methods have been published in the literature [104].

Given the standard $J$-coupling Hamiltonian in Eq. (2.13) we start by introducing a simple model for a general experimentally measured $J$-spectrum, denoted $S_{\text {expt }}$. We model the spectrum as a simple sum of absorptive Lorentzian peaks

$$
\begin{equation*}
S_{\text {model }}\left(\left\{J_{i j}\right\}\right)=N \sum_{n} \mathcal{L}\left(A_{n}, \nu_{n}\right), \tag{3.18}
\end{equation*}
$$

where $\mathcal{L}\left(A_{n}, \nu_{n}\right)$ is an absorptive Lorentzian with amplitude $A_{n}$ centered at frequency $\nu_{n}$, and $N$ is a normalization constant. The width parameter should be chosen to best match the data, we find 0.005 Hz (formic acid) to 0.02 Hz (ethanol) works well.

The $\nu_{n}$ are calculated by taking all differences larger than 1 Hz between the eigenvalues of $H_{J}$, which in turn are obtained by numerical diagonalization of the Hamiltonian. The corresponding $A_{n}$ are calculated as the matrix elements of the detection operator given by Eq. (2.14) using the eigenvectors also obtained from the diagonalization. This algorithm thus requires the coupling topology to be known, even if the values of the coupling constants are not. Note that since the $\nu_{n}$ and $A_{n}$ are calculated deterministically given a set of coupling constants, $S_{\text {model }}$ is a function of the set $\left\{J_{i j}\right\}$ alone.

Since the linewidth of a peak depends on the quantum numbers of the corresponding states, better accuracy would be obtained if we allowed the width to be a fit parameter as well. But this would greatly increase the number of parameters that $S_{\text {model }}$ depends on. For example in the case of $1-{ }^{13} \mathrm{C}$-propionic acid there are three distinct coupling constants but $14+$ peaks. Therefore as written the model has three free parameters, but it would explode to $17+$ if we let the line-widths width vary.

Given $S_{\text {model }}$ as the objective function for the fit and the vector of data $S_{\text {expt }}$, we use the non-linear regression algorithm (nlinfit) in MATLAB to obtain least-squares best-fit values for the $\left\{J_{i j}\right\}$. $95 \%$ confidence intervals for the fit are obtained from the covariance matrix (also returned from nlinfit) using the nlinparci function. The code for the implementation is given in the Appendix.

Figure 3.15 shows the result of the algorithm applied to the $J$-spectrum of $1-{ }^{13} \mathrm{C}$-propionic acid. The spectrum, which is discussed in more detail in Chapter 7, has 3 distinct couplings which were optimized in the least-squares sense to ${ }^{2} J_{\mathrm{CH}}=-7.084 \pm 0.002 \mathrm{~Hz},{ }^{3} J_{\mathrm{CH}}=$ $5.497 \pm 0.003 \mathrm{~Hz}$, and ${ }^{3} J_{\mathrm{HH}}=7.563 \pm 0.006 \mathrm{~Hz}$.


Figure 3.15: Fit of $J$-values for propionic acid. The experimental $J$-spectrum has been overlayed with the fit to $S_{\text {model }}$. The fit gives the coupling constants with $\sim \mathrm{mHz}$ accuracy.

### 3.6 Data Processing

NMR data is usually recorded in the time domain, but presented as a function of frequency. Spectra are obtained from time series data by means of a Fourier transform, but in order to increase the quality of the spectra it is customary in NMR to subject the data to a series of digital processing steps first. This section outlines the additional digital data processing steps taken in order to obtain the $J$-spectra presented throughout this dissertation. The DAQ card records voltages proportional to the optical rotation signal $\phi$ as a function of time. Using nomenclature borrowed from high-field NMR we refer to such a time series as an 'FID', even though of course no induction has actually taken place. The steps we take to convert an FID into a $J$-spectrum are the following:

- Drop initial corrupted data points.
- Correct DC offset drift.
- Replace the corrupted points.
- Multiply by decaying exponential
- Zero-fill.
- Fast Fourier Transform (FFT).
- Phase correct.
- Correct for the magnetometer response.

The spectrometer is set up so that the FID starts right when the last pulse ends. However, the magnetometer dead-time, see Section 3.1.5, means that the first $\sim 30 \mathrm{~ms}$ of data will be corrupted, so the first step of the processing is to remove the corresponding points in the FID. We usually remove 45 points, corresponding to 45 ms worth of data at a sampling rate of 1 kHz , in order ensure that no residual pulse decay shows up in the spectrum.

The next point of action is to correct for DC drift. In practice it turns out that baseline optical rotation response changes continually during the experiment. In part this is due to the decay of static magnetization of the NMR sample (remember from Section 2.3.3 that $\rho(0)$ in general contains non-evolving terms) but this does not account entirely for the observed drift in the optical response. Additional explanations include temperature changes on account of the pneumatic shuttling, small magnetic fields generated by pulse induced eddy currents, or a small degree of magnetization of the inner most ferrite shield. In the end the reasons are not entirely understood. But from the point of view of NMR detection it also does not matter very much, we care only about the modulation of the optical rotation signal at the characteristic frequencies of the nuclear spin system. In order to obtain a nice and clean baseline after the Fourier transform we correct for the DC drift by fitting the FID to a simple polynomial and subtracting the fit. We generally use a 20 th order polynomial, which seems to work well empirically, but care should be taken that actual coherent oscillations are not captured by the fit. Especially when working with samples that give signals purely below $\sim 5 \mathrm{~Hz}$.

The fact that we removed 45 ms worth of data from the FID does not mean that the spins were not evolving during that time. Since different components of the spectrum have different frequencies this means that they will be out of phase relative to the zero time point if this is not corrected for. In some cases in high-field NMR it is sufficient to correct for the dead-time with a simple first order phase correction but often one finds that the required correction introduces an unacceptably large, nonlinear baseline distortion [105]. This is a known problem in high-field NMR, and there are a number of solutions in the literature. We use the procedure suggested by Marion and Bax [106], which consists of using 'linear prediction' to estimate what the corrupted points would have been, had they been measured, and then adding the predicted points back into the FID. Linear prediction is a technique used in the signal processing community and works as follows: The $n^{\text {th }}$ time point is estimated a linear combination of the $k$ preceding time points, where $k$ is known as the order of the model

$$
\begin{equation*}
S\left(t_{n}\right)=\sum_{i=1}^{k} c_{i} S\left(t_{n-i}\right) \tag{3.19}
\end{equation*}
$$

The expansion coefficients $\left\{c_{i}\right\}$ are a set of parameters that define the signal to some order of approximation. There are known algorithms for determining the $\left\{c_{i}\right\}$ for given time series data. We use the "arburg" function in MATLAB, take $k$ to be 100 , and use only the first 1000 points in the FID. This seems to work well empirically. Note that the 'directionality'
of the FID is not important, one can simply reverse the ordering of the points before feeding them to the fitting function.

Once a clean FID has been obtained following the DC offset correction and the backwards prediction we proceed with the conventional steps of zero-filling to increase the number of points defining each peak, and line broadening by multiplication by a decaying exponential. Line-broadening is particularly important when the acquisition time is not well matched to the signal life-time. If the acquisition time is too short, line-broadening prevents truncation artefacts, if it is too long line-broadening improves SNR by effectively down weighting the points at the end of the FID, which contribute only noise. In practice, for high resolution spectroscopy, we generally acquire the FID for longer than what is necessary, and then turn up the line-broadening until the apparent line-width starts to increase. This ensures that the measured line-width is not artificially broadened by the number of points used to acquire the FID.

Following FFT, we then apply a first and zeroth order phase correction (very rarely a second order correction is required) in order to show all the peaks in absorptive mode. We also scale the amplitude of the spectrum according the magnetometer frequency response profile (see Sections 3.2.4 and 3.3. We generally only calibrate the amplitude this way, since the phase is taken care of by the first order phase correction (remember from Section 3.3 that the phase response of our magnetometer is very close to linear over the magnetometer bandwidth).

Figure 3.16 shows the stepwise results of the processing steps outlined here when applied to the $J$-spectrum of ${ }^{15} \mathrm{~N}$-pyridine. The first panel shows the unprocessed FID, and in each subsequent panel the raw FID has been subjected to one of the data processing steps before FFT, yielding the displayed spectra. It is clear that the processing as presented significantly improves clarity and resolution. Note in particular how Fig. 3.16e shows that the phase roll introduced by removing the initial corrupted data points can not be removed by a simple first order phase correction without introducing an unacceptable baseline distortion.

### 3.7 Simulations

Numerical simulations is one of the standard tools used in magnetic resonance research today. The prevalence of simulations is owed at least partly to the fact that well described by finite dimensional Hilbert spaces, which makes it easy to 'digitize' the various operators. Simulations have been used throughout this work to inform new experiments, to investigate new pulse sequences, and to interpret results. All spin systems studied with zero-field NMR to date have fewer than 12 spins, which makes it possible to write down Hilbert space matrix representations for the operators and observables, and brute force the time propagation without any further bells and whistles.


Figure 3.16: Raw FID and $J$-spectra of ${ }^{15} \mathrm{~N}$-pyridine in different stages of the data processing scheme. (a) Unprocessed FID. The spikes around the time origin are due to the magnetometer saturating in the pulse field. (b) Direct FFT of the raw data yields a very non-flat baseline. (c) Removing the corrupted points flattens the baseline, but there is now a large phase roll, and still a big spike at zero. (d) Correcting for the DC drift removes the spike at zero but the phase roll remains. (e) Trying to correct for the removed points by a first order phase correction results in a large non-linear phase distortion. (f) Back predicting the corrupted points results in a nice and clean spectrum without any additional phase correction.

## Chapter 4

## Frequency Selective Pulses

In this chapter we start introducing new techniques for manipulating spin states in zero and ultralow magnetic fields. In particular we use low-amplitude, ultra-low frequency pulses to drive nuclear spin transitions. In analogy to high-field NMR, a range of sophisticated experiments becomes available as these pulses allow narrow-band excitation of $H$-spectra. As a first demonstration, pulses with excitation bandwidths $0.5-5 \mathrm{~Hz}$ are used for population redistribution, selective excitation, and coherence filtration. These methods are helpful when interpreting zero -and ultralow-field NMR spectra that contain a large number of transitions.

The material in this chapter has previously been published under the title

- Transition Selective Pulses in Zero-Field Nuclear Magnetic Resonance by Sjolander, Tayler, King, Budker, and Pines [1].


### 4.1 Background and Motivation

A strength of the NMR technique is the ability to selectively measure the data of interest by choosing out of hundreds of experimental protocols [107]. Many of these protocols require exciting only a select portion of the frequency spectrum, using narrow-band pulses. Basic frequency selectivity is implicitly assumed in the design of all heteronuclear high-field NMR pulse sequences, as the resonance frequencies of different spin species are widely separated. Many techniques also rely on selectivity beyond differentiating spin species, to the extent of addressing individual transitions[107-110]. Selective irradiation is the basis for many polarization-transfer methods (e.g. INAPT, Insensitive Nuclei Assigned by Polarization Transfer[111, 112]), spin-spin correlation experiments (e.g. SELCOSY[113]) and solvent suppression techniques.

Narrow-band pulses have yet to be explored in zero to ultra-low field (ZULF) NMR where the leading fields are $<1 \mu \mathrm{~T}$. Indeed, prior to this work, ZULF NMR experiments have used DC magnetic field pulses for excitation and manipulation of the spin system. Pulsed fields stronger than $100 \mu \mathrm{~T}$ are sufficient to rotate nuclear spins effectively instantaneously with respect to the time scale of free evolution, so that the result is a rotation about the field axis through angles $\theta_{i}=\gamma_{i} B t$ where $\gamma_{i}$ is the gyromagnetic ratio of the $i^{\text {th }}$ spin, $B$ is the field strength, and $t$ is the duration of the pulse. This method of manipulating spins has limitations. It is necessarily broadband with respect to the ZULF spectrum and the range of available operations depends on the ratios of the $\gamma_{i}$ s of the spins involved. For example, using DC pulses one can perform a simultaneous $\theta \approx 4 \pi$ rotation on ${ }^{1} \mathrm{H}$ and $\theta=\pi$ on ${ }^{13} \mathrm{C}$, however a $\theta \approx \pi$ rotation on both nuclei, as required by many decoupling and refocusing sequences, is more challenging; using a single DC pulse it is impossible to simultaneously rotate ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ spins through the same angle, other than near- $2 \pi / 3$ multiples (e.g. $\theta_{\mathrm{H}} \approx 8 \pi / 3$, $\theta_{\mathrm{C}} \approx 2 \pi / 3 ; \gamma_{\mathrm{H}} / \gamma_{\mathrm{C}} \approx 3.97$ ). Composite pulses have been suggested [75] but performing arbitrary rotations is not a solved problem and generally speaking the control of multiple spin species is significantly restricted.

In this chapter we demonstrate frequency selective pulses in the ZULF regime with a typical excitation bandwidth $0.5-5 \mathrm{~Hz}$, and thus we take zero-field $J$-spectroscopy out of the regime of broadband-only excitation. As an application we introduce an experiment that identifies groups of connected transitions between the ZULF energy levels of a spin system. This is conceptually similar to spin-tickling experiments performed in high-field NMR, where connected transitions are used to identify the spin topology and energy-level structure. [114, 115] Simplification of ZULF NMR spectra into such connected groups assists with assignment and helps resolve ambiguity with interpretation, particularly in the case of molecules with large numbers of transitions. We demonstrate further selectivity by taking advantage of the selection rules for circularly polarized pulses [51], thereby allowing us to address narrow splittings caused by small DC magnetic fields.

### 4.2 Theory of Resonant Pulses at Zero-Field

The resonant pulses demonstrated in this work drive spin populations directly between the zero-field eigenstates and therefore allow greater control over which transitions are excited. We write the liquid state zero-field Hamiltonian, in angular frequency units, as

$$
\begin{equation*}
H_{J}=2 \pi \sum_{i, j>i} J_{i j} \boldsymbol{I}_{i} \cdot \boldsymbol{I}_{j}, \tag{4.1}
\end{equation*}
$$

where the $\boldsymbol{I}$ are the total angular momentum operators for groups of equivalent spins and the $J$ are scalar spin-spin coupling constants. The eigenstates of $H_{J}$ are total spin angular momentum states denoted $\left|F, m_{F}\right\rangle$, where $F$ is the total spin angular momentum quantumnumber and $m_{F}$ is the projection on the spin quantization axis (for systems with more than two spins, additional quantum numbers are necessary)[49]. The observable quantity is the total magnetization along the sensitive axis, $\hat{\boldsymbol{s}}$, of the magnetometer, represented by the operator

$$
\begin{equation*}
O_{s}=\sum_{i} \gamma_{i} \boldsymbol{I}_{i} \cdot \hat{\boldsymbol{s}} . \tag{4.2}
\end{equation*}
$$

This operator supports transitions with $\Delta F=0, \pm 1$. The selection rules for $m_{F}$ are $\Delta m_{F}=0$ if $\hat{\boldsymbol{s}}=\hat{\boldsymbol{z}}$ and $\Delta m_{F}= \pm 1$ if $\hat{\boldsymbol{s}}=\hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}$.

The Hamiltonian for a pulse with frequency $\omega$ and amplitude $\boldsymbol{B}$ is written as

$$
\begin{equation*}
H_{P}(t)=\cos (\omega t) \sum_{i} \gamma_{i} \boldsymbol{B} \cdot \boldsymbol{I}_{i} \equiv \cos (\omega t) P \tag{4.3}
\end{equation*}
$$

Evolution of the spin system under the total Hamiltonian $H=H_{J}+H_{P}$ is analyzed in an interaction frame where both $H_{J}$ and $H_{P}$ are approximately time independent. To this end we consider the interaction frame Hamiltonian when irradiating close to a peak of frequency $f$ and define

$$
\begin{equation*}
\tilde{H}=\mathrm{e}^{\mathrm{i} \frac{\omega}{f} H_{J} t} H \mathrm{e}^{-\mathrm{i} \frac{\omega}{f} H_{J} t}-\frac{\omega}{f} H_{J}, \tag{4.4}
\end{equation*}
$$

where ~ denotes the interaction frame. A more detailed treatment of this process is given in Appendix 4.7, where we also treat the case of a small static field perturbing $H_{J}$. The result is that the Hamiltonian above can be block diagonalized to a time-independent Hamiltonian acting on a two-level system with each 2 x 2 block given by

$$
\tilde{H}=\left(\begin{array}{cc}
\Omega & P_{\alpha \beta}  \tag{4.5}\\
P_{\beta \alpha} & -\Omega
\end{array}\right)
$$

where $\Omega$ is the total frequency offset of the transition from $\omega$ and the $P_{\alpha \beta}$ are matrix elements of $P$ in the eigenbasis of $H_{J}$. If the peak at $f$ involves degenerate energy levels, Eq. (4.5) holds for each block and the observed signal is the sum of the solutions obtained for each one. Specific conditions for when this is true are given in Appendix 4.7.


Figure 4.1: Zero-field NMR of $\left[{ }^{13} \mathrm{C}\right]$-methanol. a: When excited by a strong DC pulse the spectrum consists of one peak at $J_{\mathrm{CH}}=140.65 \mathrm{~Hz}$ and one peak at $2 J_{\mathrm{CH}}=281.3 \mathrm{~Hz}$. The amplifier used for pulsing generates strong 60 Hz overtones seen in the spectra. $\mathrm{b} / \mathrm{c}$ : Using weak resonant pulses the transitions can be addressed separately and selectively. The amplifiers used for DC pulsing are turned off, decreasing the 60 Hz noise. d: Signal amplitude versus pulse length, showing the coherent driving between the $|0,0\rangle$ and $|1,0\rangle$ states. Red crosses are experimental data points, the blue line corresponds to $\sin \left(P_{\alpha \beta} t\right)$ and the black dashes to a full numerical simulation. e: Driving the $\left|1, m_{F}\right\rangle$ to $\left|2, m_{F}\right\rangle$ transition. The blue line is now a weighted sum of $\sin \left(P_{\alpha \beta} t\right)$ for each $m_{F}$ as described in the text, giving two frequencies. The two observed transitions are shown in the energy level diagram on the right-hand side. $I$ is the quantum number for total proton angular momentum, which is conserved.

### 4.3 Resonant Excitation of Methanol in Zero-Field

We demonstrate selective pulses in zero field using $\left[{ }^{13} \mathrm{C}\right]$-methanol $\left({ }^{13} \mathrm{CH}_{3} \mathrm{OH}\right)$ as an example. The zero-field energy level diagram for the four non-exchanging spins in the molecule, namely the ${ }^{13} \mathrm{CH}_{3}$ group (an $\mathrm{AX}_{3}$ spin system), is displayed in Fig. 4.1. There are two observable transitions, one where the total angular momentum quantum number, $F$, changes from 0 to 1 , and another where it goes from 1 to 2 . We have taken the spin quantization axis to be parallel to the detector axis, $\hat{\boldsymbol{s}}=\hat{\boldsymbol{z}}$, implying $\Delta m_{F}=0$. The two transitions occur at frequencies $J_{\mathrm{CH}}$ and $2 J_{\mathrm{CH}}$ respectively, where $J_{\mathrm{CH}}=140.65 \mathrm{~Hz}$ is the one-bond carbonproton coupling constant. Simultaneous excitation of the two transitions can be achieved using either a DC pulse or non-adiabatic switching to ZULF, affording the spectrum shown
in Fig. 4.1a. The spectra in Figs. 4.1b/c were recorded after applying selective pulses, at the $J_{\mathrm{CH}}\left(0.167 \mathrm{~s}, B_{z}=0.94 \mathrm{mG}\right)$ or $2 J_{\mathrm{CH}}\left(0.182 \mathrm{~s}, B_{z}=0.94 \mathrm{mG}\right)$ transition frequencies. Since the bandwidth is much less than the peak separation only the resonant transition is excited. The pulses were applied along the $\hat{\boldsymbol{z}}$ axis in order to excite observable $\Delta m_{F}=0$ transitions.

The excitation of the two transitions versus pulse length (Rabi curves) as shown in Fig. 4.1d/e was used to determine the length of the pulses that gives maximum signal. The $J_{\mathrm{CH}}$ signal is expected to be described by $S\left(t_{p}\right) \propto \sin \left(P_{\alpha \beta} t\right)$ [116], and thus we expect to see maximum signal for $P_{\alpha \beta} t=\pi / 2$. The evaluation of $P_{\alpha \beta}$ may be simplified by noting that the operator can be split into two parts, one proportional to the sum of the spin operators, and one proportional to the difference. The sum term commutes with $H_{J}$, and therefore does not induce transitions between states of different $F$. Thus the relevant matrix elements are $P_{\alpha \beta}=\left[\left(\gamma_{a} B_{z}-\gamma_{b} B_{z}\right) / 2\right]\left\langle F^{\prime}, m_{F}\right|\left(I_{a, z}-I_{b, z}\right)\left|F, m_{F}\right\rangle$, which can be expanded in terms of Clebsch-Gordan coefficients (further detail is shown in Appendix 4.8) as $P_{\alpha \beta}=$ $\left[\left(\gamma_{a} B_{z}-\gamma_{b} B_{z}\right) / 2\right] \sum_{m_{a}, m_{b}}\left(m_{a}-m_{b}\right) C_{I_{a}, m_{a}, I_{b}, m_{b}}^{F^{\prime}, m_{m}} \times C_{I_{a}, m_{a}, I_{b}, m_{b}}^{F, m_{F}}$, where $m_{F}$ is conserved and $a$ and $b$ refer to the proton and carbon spins. This expression for the matrix element predicts the $1 J$ transition to be driven at 1.5 Hz . However, the $2 J$ Rabi curve contains two components, using the formula above the frequencies are 1.5 Hz and 1.3 Hz with a relative weighting of 1:2 respectively. The $2 J$ Rabi curve being composed of two different frequencies is understood by noting that the line consists of several overlapping transitions, originating in the $m_{F}=0$ and the $m_{F}= \pm 1$ levels and these transitions have different matrix elements. Thus the pulse length that gives maximum signal does not correspond to a single angle. In general the number of frequency components in the Rabi curve is equal to $F_{\max }$ rounded down to the nearest integer. For example both a $F=0$ to $F=1$ and a $F=1 / 2$ to $F=3 / 2$ transition will have one Rabi frequency but a $F=2$ to $F=3$ transition will have three.

### 4.4 Resonant Excitation of Formic Acid in Ultralow Field

We now consider the possibilities of selective excitation in the presence of a small perturbing DC field on the order of mG applied at right angles to $\hat{s}$; such small field perturbations have been shown to be useful in ZULF spectroscopy, by splitting lines into multiplets that reveal the quantum numbers involved [24]. The experiments are most conveniently analyzed in a coordinate system where the spin quantization axis is along the direction of the perturbing DC field, so we assign the detection axis to $\hat{\boldsymbol{s}}=\hat{\boldsymbol{x}}$. From this view, observable transitions occur between states where $\Delta m_{F}= \pm 1$ and the effect of the DC field is to lift degeneracies between states of different $m_{F}$, leading to splittings in the spectra. The $\Delta m_{F}=+1$ and $\Delta m_{F}=-1$ transitions, in this case correspond to magnetization rotating either clockwise or anticlockwise in the laboratory frame. This is in contrast to the high-field-NMR case where all of the observable transitions correspond to magnetization rotating in the same sense, equal to the direction of Larmor precession around the static field.


Figure 4.2: Ultralow-field NMR ( $B_{0}=0.19 \mathrm{mG}$ ) of $\left[{ }^{13} \mathrm{C}\right]$-formic acid. a: The spectrum after excitation with a DC pulse contains two peaks of equal intensity centered about the $J$ coupling frequency $J_{\mathrm{CH}}=222.15 \mathrm{~Hz}$ with splitting $2 \nu=B_{0}\left(\gamma_{\mathrm{C}}+\gamma_{\mathrm{H}}\right)$. The corresponding transitions are $|0,0\rangle \rightarrow|1,1\rangle$ and $|0,0\rangle \rightarrow|1,-1\rangle$. b: Excitation using a weak near-resonant $\left(=J_{\mathrm{CH}}\right)$ rotating field in opposite senses about the axis of the static field. The dashed blue trace is the expected excitation profile, for the pulse used $(|B|=0.47 \mathrm{mG}$ and 0.25 s$)$, defined by the signal magnitude. The inset shows the corresponding energy level diagram. c: Signal magnitude for the $J+\nu$ transition plotted versus pulse length. The red crosses are experimental data, the black dashes to the result of a full numerical simulation, and the blue line corresponds to the predicted signal magnitude when solving for the evolution under Eq. (4.5), as shown in Appendix 4.7.

The use of two orthogonal pulsing coils to generate a rotating magnetic field allows us to select transitions with $\Delta m_{F}=+1$ or $\Delta m_{F}=-1$. Figure 4.2 shows an example using $\left[{ }^{13} \mathrm{C}\right]-$ formic acid $\left(\mathrm{H}^{13} \mathrm{COOH}\right.$, an AX spin system, ignoring the exchanging acidic proton). A weak DC field $(0.19 \mathrm{mG})$ is applied at $90^{\circ}$ to $\hat{\boldsymbol{s}}$ and the resulting spectrum contains two observable transitions centered about the $J$-coupling frequency, corresponding to $|0,0\rangle \rightarrow|1,-1\rangle$ and $|0,0\rangle \rightarrow|1,+1\rangle$. A strong DC pulse parallel to $\hat{\boldsymbol{s}}$ simultaneously excites both transitions as shown in Fig. 4.2a. Figure 4.2b shows the selective excitation achieved by AC magnetic-field pulses, rotating in the plane defined by $\hat{\boldsymbol{x}}$ and $\hat{\boldsymbol{y}}$ : amplitude 0.47 mG , frequency 222.15 Hz (giving a resonance offset of $\pm 0.52 \mathrm{~Hz}$ ), pulse duration 0.25 s . The coupling matrix element
$P_{\alpha \beta} / 2 \pi$ evaluates to 1.06 Hz using a Clebsch-Gordan expansion similar to the one used above, as shown in Appendix 4.8. Although the excitation bandwidth of this pulse covers both transitions they may be addressed selectively based on their sense of rotation, effectively sidestepping the usual limit on frequency selectivity. The signal magnitude vs. pulse duration for the higher-frequency peak is shown in Fig. 4.2c to be in quantitative agreement with both the theory and numerical simulation based on the parameters used. The decay of the signal at long pulse lengths may be attributed to relaxation or inhomogeneity of the field.


Figure 4.3: Spectral editing at zero-field. The zero-field spectrum of $\left[{ }^{15} \mathrm{~N},{ }^{13} \mathrm{C}_{2}\right]$-acetonitrile is split into three different frequency regions for convenience. Bottom blue trace: experimental spectrum recorded after applying a DC pulse in the $\hat{\boldsymbol{s}}$ direction, bottom green trace: Difference spectrum after selective inversion of the 155 Hz line (AC pulse, $0.47 \mathrm{mG}, 1.08$ s). Stars denote peaks that are still clearly visible in the difference spectrum meaning they belong the $I=1 / 2$ manifold. Top Traces: Simulated spectra for the same conditions. The traces are offset for clarity and the peaks at $120 \mathrm{~Hz}, 240 \mathrm{~Hz}$ and 300 Hz are overtones of the 60 Hz line noise.

### 4.5 Spectral Editing with Selective Pulses

Selective irradiation may also be used for saturation or population inversion between two or more pairs of spin eigenstates. A "coherence filter" based on this principle is demonstrated in Fig. 4.3 to edit the zero-field NMR spectrum of $\left[{ }^{15} \mathrm{~N},{ }^{13} \mathrm{C}_{2}\right]$-acetonitrile $\left({ }^{13} \mathrm{CH}_{3}^{13} \mathrm{C}^{15} \mathrm{~N}\right)$. The spectrum nominally contains a large number of observable transitions ( $>32$ different frequencies), but this number can be greatly reduced, and thus assignment of the spectrum made easier, by exciting transitions that share a common energy level. The coherence filter is no more than a difference experiment requiring an even number of signal acquisitions to be performed. Every odd numbered acquisition the full spectrum is excited using a broadband DC pulse parallel to $\hat{\boldsymbol{s}}=\hat{\boldsymbol{z}}$, taking the spin quantization axis parallel to $\hat{\boldsymbol{s}}$ as in our first example (Fig. 4.1). On even acquisitions, the broadband pulse is preceded by a selective AC pulse, applying the field along the same axis as the DC pulse, which inverts the population difference of a single transition. The difference between the odd and even spectra will contain only peaks corresponding to coherences belonging to the same spin manifold as the inverted transition. Other transitions will remain unchanged by the selective inversion and therefore cancel when the difference spectrum is made. The result of this filtering may be interpreted in the following way: since magnetically equivalent spins will rotate identically about the axis of an applied magnetic field, their total angular momentum cannot change during either the selective inversion pulse or the DC pulse. In the case of $\left[{ }^{15} \mathrm{~N},{ }^{13} \mathrm{C}_{2}\right]$-acetonitrile a conserved quantum number is the total proton angular momentum, $I$, which has two possible values $(I=1 / 2$ and $I=3 / 2)$ leading to two isolated spin manifolds. This is also the case for $\left[{ }^{13} \mathrm{C}\right]$ methanol, shown in Fig. 4.1, but for $\left[{ }^{15} \mathrm{~N},{ }^{13} \mathrm{C}_{2}\right]$-acetonitrile there is additional structure due to presence of more than one $J$-coupling. The zero-field NMR spectrum is partitioned into three distinct parts. The corresponding signal frequencies are around the one-bond ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ $J$-coupling frequency at 136 Hz with $I=1 / 2$, around $2 J=272 \mathrm{~Hz}$ with $I=3 / 2$ and close to 0 Hz arising from the internal splitting of the two manifolds due to the second carbon and the nitrogen. The selective inversion protocol presented here allows us to filter the observed NMR signal and display only peaks belonging to either the $I=1 / 2$ or the $I=3 / 2$ manifolds.

Figure 4.3 shows both a simulation of this protocol and the experimental result for the case when the selective inversion pulse is applied at 155 Hz . It is expected that only peaks originating in the $I=1 / 2$ manifold to be visible in the difference spectrum. The persistence of the peaks in the region around 136 Hz is consistent with population redistribution within the $I=1 / 2$ manifold. There are no observed peaks in the difference spectrum around 272 $\mathrm{Hz}(I=3 / 2)$. The region around zero Hz is the most interesting, four peaks are observed in the difference spectrum so these must belong to the proton spin $I=1 / 2$ manifold.

Figure 4.3 demonstrates another use for selective inversion pulses. Note how in the simulation the peak at $\approx 126 \mathrm{~Hz}$ is not visible in the control spectrum, but is clearly apparent in the difference spectrum. This indicates that before the DC pulse there is no population difference between the two states involved. The selective inversion pulse swaps the initial population of one of the two states with a third state so that the population difference becomes nonzero. This is analogous to the technique of interchanging spin populations for
signal enhancement in NMR studies of quadrupolar nuclei [117]. In the experimental data, the peak at $\approx 126 \mathrm{~Hz}$ also becomes significantly enhanced. However, the peak is also visible in the control spectrum, which we attribute to the sensitive axis of the magnetometer being slightly off-axis from $\hat{\boldsymbol{z}}$ [31].

### 4.6 Conclusions

In conclusion we have demonstrated selective excitation and editing of zero-field $J$-spectra using weak AC fields. Simple analytical theory based on a two-level system reproduces the results from full numerical simulations and experiments. As a chemically relevant application we have shown a method that discriminates between signals belonging to manifolds of different total proton angular momentum in the zero-field spectrum of $\left[{ }^{15} \mathrm{~N},{ }^{13} \mathrm{C}_{2}\right]$-acetonitrile. Further we have shown how the sense of rotation of pulsed fields may select between positive and negative changes in angular-momentum projection. These techniques should facilitate zero-field NMR spectroscopy of larger, more demanding spin systems or mixtures, and open a way to adapting a suite of established high-field experiments to zero-field.

### 4.7 Appendix I: Derivation of Excitation Curves

We derive in this section approximate analytical expressions for the signal amplitude as a function of pulse area and resonance offset for a general zero-field spin system. We explicitly treat the case of a linearly polarized excitation field, however a rotating field may be treated similarly. We write the Hamiltonian as consisting of groups of equivalent spins

$$
\begin{equation*}
\boldsymbol{I}_{i}=\sum_{k=1}^{N_{i}} \boldsymbol{I}_{i}^{k} \tag{4.6}
\end{equation*}
$$

where the $\boldsymbol{I}^{k}$ are angular momentum operators for the individual spins and $N_{i}$ is the number of spins in group $i$. Sometimes in zero-field NMR it is useful to apply a small perturbing static field in order to break the degeneracy of the $m_{F}$ sub-levels and split the spectrum into multiplets depending on the total angular momentum quantum numbers involved in the transition [24]. In the presence of such a field the static Hamiltonian expressed in angular frequency units is

$$
\begin{equation*}
H_{0}=2 \pi \sum_{i, j>i} J_{i j} \boldsymbol{I}_{i} \cdot \boldsymbol{I}_{j}+\sum_{i} \omega_{0}^{i} I_{z, i}, \tag{4.7}
\end{equation*}
$$

where $\omega_{0}^{i}$ is the Larmor frequency of the $i^{\text {th }}$ group of spins in the static field and $J_{i j}$ are the $J$-coupling constants. The Hamiltonian for a linearly polarized AC pulse of amplitude $\boldsymbol{B}$ is

$$
\begin{equation*}
H_{P}(t)=\cos (\omega t) \sum_{i} \gamma_{i} \boldsymbol{B} \cdot \boldsymbol{I}_{i} \equiv \cos (\omega t) P \tag{4.8}
\end{equation*}
$$

where $\omega$ the the pulse frequency. Defining $H_{J}=2 \pi \sum_{i, j>i} J_{i j} \boldsymbol{I}_{i} \cdot \boldsymbol{I}_{j}$ the total Hamiltonian for the system during application of the pulse is

$$
\begin{equation*}
H(t)=H_{J}+\sum_{i} \omega_{0}^{i} I_{z, i}+\cos (\omega t) P \tag{4.9}
\end{equation*}
$$

We want to analyze the evolution in a frame where the Hamiltonian is time independent and since we are concerned with driving transitions between zero-field states, the natural basis to work in is the eigenbasis of $H_{J}$. To this aim we define the following transformation:

$$
\begin{equation*}
\tilde{\rho}=\mathrm{e}^{-\mathrm{i} \frac{\omega}{f} H_{J} t} \rho \mathrm{e}^{\mathrm{i} \frac{\omega}{f} H_{J} t} \tag{4.10}
\end{equation*}
$$

where $\rho$ is the density operator and $f$ is the frequency of the transition being driven in the absence of any perturbing static field. $\tilde{\rho}$ obeys the Liouville-von Neuman equation of motion

$$
\begin{equation*}
\frac{d \tilde{\rho}}{d t}=-\mathrm{i}[\tilde{H}(t), \tilde{\rho}(t)] \tag{4.11}
\end{equation*}
$$

with $\tilde{H}(t)$ given by

$$
\begin{equation*}
\tilde{H}(t)=\left(1-\frac{\omega}{f}\right) H_{J}+\mathrm{e}^{\mathrm{i} \frac{\omega}{f} H_{J} t}\left(\sum_{i} \omega_{0}^{i} I_{z, i}+\cos (\omega t) P\right) \mathrm{e}^{-\mathrm{i} \frac{\omega}{f} H_{J} t} . \tag{4.12}
\end{equation*}
$$

We now begin dropping terms that retain time dependence in this frame. First we note that the part of the static field Hamiltonian proportional to total angular momentum, $F_{z}$, commutes with $H_{J}$, we drop the remaining part (This particular approximation is valid for systems with 2 spins only).

$$
\begin{equation*}
\tilde{H}(t)=\left(1-\frac{\omega}{f}\right) H_{J}+\omega_{0} F_{z}+\cos (\omega t) \mathrm{e}^{\mathrm{i} \frac{\omega}{f} H_{J} t} P \mathrm{e}^{-\mathrm{i} \frac{\omega}{f} H_{J} t}, \tag{4.13}
\end{equation*}
$$

where $\omega_{0}$ is a constant of proportionality that depends on the spin system. Writing the matrix elements of the operators in the eigenbasis of $H_{J}$ results in

$$
\begin{equation*}
\tilde{H}(t)=\sum_{\alpha}\left(\left(1-\frac{\omega}{f}\right) H_{J, \alpha \alpha}+\omega_{0} F_{z, \alpha \alpha}\right)|\alpha\rangle\langle\alpha|+\frac{\left(\mathrm{e}^{\mathrm{i} \omega t}+\mathrm{e}^{-\mathrm{i} \omega t}\right)}{2} \sum_{\alpha, \beta} P_{\alpha \beta} \mathrm{e}^{\mathrm{i} \frac{\omega}{f}\left(E_{\alpha}-E_{\beta}\right) t}|\alpha\rangle\langle\beta| \tag{4.14}
\end{equation*}
$$

where $E_{\alpha}$ is the energy of state $|\alpha\rangle$ in the absence of the static field. States with $E_{\alpha}-E_{\beta}=f$, will give time independent terms, off-resonant terms retain time dependence and are dropped.

$$
\begin{equation*}
\tilde{H}=\sum_{\alpha}\left(\left(1-\frac{\omega}{f}\right) H_{J, \alpha \alpha}+\omega_{0} F_{z, \alpha \alpha}\right)|\alpha\rangle\langle\alpha|+\frac{1}{2} \sum_{\alpha \neq \beta} P_{\alpha \beta}|\alpha\rangle\langle\beta|, \tag{4.15}
\end{equation*}
$$

where the sum over states is now restricted to the $(2 F+1)+\left(2 F^{\prime}+1\right)$ states involved in a single zero-field multiplet centered at $f$. Next we define fictitious spin-half operators for each transition within the multiplet as follows:

$$
\begin{align*}
\sigma_{z}^{\alpha \beta} & =\frac{1}{2}(|\alpha\rangle\langle\alpha|-|\beta\rangle\langle\beta|), \\
\sigma_{x}^{\alpha \beta} & =\frac{1}{2}(|\alpha\rangle\langle\beta|+|\beta\rangle\langle\alpha|), \\
\sigma_{y}^{\alpha \beta} & =\frac{1}{2} \mathrm{i}(|\alpha\rangle\langle\beta|-|\beta\rangle\langle\alpha|), \\
E^{\alpha \beta} & =(|\alpha\rangle\langle\alpha|+|\beta\rangle\langle\beta|) . \tag{4.16}
\end{align*}
$$

Using these operators the Hamiltonian for one two-level system can be written

$$
\begin{equation*}
\tilde{H}^{\alpha \beta}=\Omega \sigma_{z}+P_{\alpha \beta} \sigma_{x}+\Xi E . \tag{4.17}
\end{equation*}
$$

Here we have defined $\Omega=\left(1-\frac{\omega}{f}\right)\left(H_{J, \alpha \alpha}-H_{J, \beta \beta}\right)+\omega_{0}\left(F_{z, \alpha \alpha}-F_{z, \beta \beta}\right)$, the total resonance offset frequency. $\Xi=0.5\left(\left(1-\frac{\omega}{f}\right)\left(H_{J, \alpha \alpha}+H_{J, \beta \beta}\right)+\omega_{0}\left(F_{z, \alpha \alpha}+F_{z, \beta \beta}\right)\right)$ and arises from the fact that the energy levels do not have to be centered around zero. We note that Eq. (4.15) corresponds to several two-level subspaces of the form Eq. (4.17) but since none of the operators involved are shared between subspaces, they must all commute with one another. Thus we can calculate the signal arising from each subspace separately and sum the results. This is true for $\Delta m_{F}=0$ transitions, as well as for $\Delta m_{F}= \pm 1$ transitions when excited by a rotating field.


Figure 4.4: Bloch-sphere representation of Eq. (4.17) showing how $\tilde{\rho}$ rotates around the Hamiltonian in the interaction frame during the application of the AC pulse. In this representation the magnitude of the detected signal is proportional to the projection of the final state onto the $\mathrm{x}-\mathrm{y}$ plane.

Given an initial density operator with some population difference between the two connected states $|\alpha\rangle$ and $|\beta\rangle$ we write $\rho(0)=\tilde{\rho}(0) \propto \sigma_{z}$. We see then that the effect of $\tilde{H}$ is to rotate $\tilde{\rho}$ in this fictitious spin half subspace by an angle $\left(\sqrt{\Omega^{2}+P_{\alpha \beta}^{2}}\right) t=\xi t$, about the axis $\boldsymbol{n}=\left(P_{\alpha \beta}, 0, \Omega\right)$. We are interested in the signal magnitude, which is proportional to the coherence amplitude, as a function of pulse time: $\left.A\left(t_{p}\right) \propto\left|\langle\alpha| \tilde{\rho}\left(t_{p}\right)\right| \beta\right\rangle \mid$. We note that $\tilde{\rho}$ transforms as a vector under this rotation so it is convenient to solve for the time evolution as follows

$$
\begin{equation*}
\tilde{\rho}\left(t_{p}\right)=D^{1}\left(\xi t_{p}, \theta, 0\right) \tilde{\rho}(0) \tag{4.18}
\end{equation*}
$$

where $D^{1}$ is a first rank Wigner matrix [37] in axis-angle parametrization and $\theta=\arctan \left(\frac{P_{\alpha \beta}}{\Omega}\right)$ Using the standard transformation properties of spherical tensors this becomes

$$
\begin{equation*}
\tilde{\rho}\left(t_{p}\right)=\sqrt{2}|\alpha\rangle\langle\beta| D_{-1,0}^{1}\left(\xi t_{p}, \theta, 0\right)+\sigma_{z} D_{0,0}^{1}\left(\xi t_{p}, \theta, 0\right)+\sqrt{2}|\beta\rangle\langle\alpha| D_{1,0}^{1}\left(\xi t_{p}, \theta, 0\right) . \tag{4.19}
\end{equation*}
$$

It follows that the signal amplitude as a function of pulse length is given by

$$
\begin{equation*}
A\left(t_{p}\right) \propto\left|D_{1,0}^{1}\left(\xi t_{p}, \theta, 0\right)\right| \tag{4.20}
\end{equation*}
$$

The elements of a Wigner matrix in axis-angle form are well known [37], giving the following expression for the signal amplitude as a function of pulse length and resonance offset

$$
\begin{equation*}
A\left(t_{p}\right) \propto\left\{2 \sin ^{2}\left(\frac{\xi t}{2}\right) \sin ^{2}(\theta) \times\left(\cos ^{2}\left(\frac{\xi t}{2}\right)+\sin ^{2}\left(\frac{\xi t}{2}\right) \cos ^{2}(\theta)\right)\right\}^{\frac{1}{2}} \tag{4.21}
\end{equation*}
$$

In order to predict the signal magnitude for given pulse parameters, one would need to calculate the matrix elements of $H_{J}, F_{z}$ and $P$, which depend on the specific spin system
under study. This expression is plotted in Fig. 2c in the main body of the paper, for $\Omega / 2 \pi$ $=0.52 \mathrm{~Hz}$ and $P_{\alpha \beta} / 2 \pi=1.06 \mathrm{~Hz}$.

When the AC field is being applied perfectly on resonance, $\Omega=0$, making $\theta=\frac{\pi}{2}$ and $\xi t=P_{\alpha \beta} t$. In this case Eq. (4.21) reduces to

$$
\begin{equation*}
A\left(t_{p}\right)=\left|\sin \left(P_{\alpha \beta} t\right)\right| . \tag{4.22}
\end{equation*}
$$

### 4.8 Appendix II: Evaluation of Matrix Elements

We show here in detail how to evaluate the coupling matrix elements $P_{\alpha \beta}$ for a system of two groups, $a$ and $b$, of spins both in the case of a linear and a rotating excitation field.

For a linear pulse along z we have

$$
\begin{equation*}
P_{z}=\gamma_{a} B_{z} I_{a, z}+\gamma_{b} B_{z} I_{b, z} . \tag{4.23}
\end{equation*}
$$

This is conveniently rewritten as

$$
\begin{equation*}
P_{z}=\left(\frac{\gamma_{a} B_{z}+\gamma_{b} B_{z}}{2}\right)\left(I_{a, z}+I_{b, z}\right)-\left(\frac{\gamma_{a} B_{z}-\gamma_{b} B_{z}}{2}\right)\left(I_{a, z}-I_{b, z}\right) . \tag{4.24}
\end{equation*}
$$

The first term commutes with $H_{J}$ and is thus not going to induce transitions between states of different energy at zero-field. Thus the matrix elements that give time independent terms in the interaction frame defined by Eq. (4.10) are

$$
\begin{equation*}
P_{\alpha \beta}=\left\langle F^{\prime}, m_{F}\right| P_{z}\left|F, m_{F}\right\rangle=\left(\frac{\gamma_{a} B_{z}-\gamma_{b} B_{z}}{2}\right)\left\langle F^{\prime}, m_{F}\right|\left(I_{a, z}-I_{b, z}\right)\left|F, m_{F}\right\rangle \tag{4.25}
\end{equation*}
$$

where $m_{F}$ is conserved. Inserting two resolutions of the identity and rearranging gives

$$
\begin{align*}
& P_{\alpha \beta}=\left(\frac{\gamma_{a} B_{z}-\gamma_{b} B_{z}}{2}\right) \sum_{\substack{m_{a}^{\prime}, m_{b}^{\prime} \\
m_{a}, m_{b}}}\left\langle F^{\prime}, m_{F}\right|\left|I_{a}^{\prime}, m_{a}^{\prime}, I_{b}^{\prime}, m_{b}^{\prime}\right\rangle\left\langle I_{a}, m_{a}, I_{b}, m_{b}\right|\left|F, m_{F}\right\rangle \times \\
&\left\langle I_{a}^{\prime}, m_{a}^{\prime}, I_{b}^{\prime}, m_{b}^{\prime}\right|\left(I_{a, z}-I_{b, z}\right)\left|I_{a}, m_{a}, I_{b}, m_{b}\right\rangle \tag{4.26}
\end{align*}
$$

Identifying the Clebsch-Gordan coefficients and noting that
$\left\langle I_{a}^{\prime}, m_{a}^{\prime}, I_{b}^{\prime}, m_{b}^{\prime}\right|\left(I_{a, z}-I_{b, z}\right)\left|I_{a}, m_{a}, I_{b}, m_{b}\right\rangle=\left(m_{a}-m_{b}\right) \delta_{m_{a}, m_{a}^{\prime}} \delta_{m_{b}, m_{b}^{\prime}}$ gives, for a linear pulse

$$
\begin{equation*}
P_{\alpha \beta}=\left(\frac{\gamma_{a} B_{z}-\gamma_{b} B_{z}}{2}\right) \sum_{m_{a}, m_{b}}\left(m_{a}-m_{b}\right) C_{I_{a}, m_{a}, I_{b}, m_{b}}^{F^{\prime}, m_{F}} \times C_{I_{a}, m_{a}, I_{b}, m_{b}}^{F, m_{F}} \tag{4.27}
\end{equation*}
$$

as given in the main body of the paper. Evaluating this expression for $B_{z}=0.94 \mathrm{mG}, \gamma_{a}=$ $42.576 \mathrm{MHz} / \mathrm{T}, \gamma_{b}=10.705 \mathrm{MHz} / \mathrm{T}, I_{a}=1 / 2$, and $I_{b}=1 / 2$ results in $P_{\alpha \beta} / 2 \pi=1.5 \mathrm{~Hz}$ for a $F=0, F^{\prime}=1, m_{F}=0$ transition. If $I_{b}=3 / 2$, as for the $2 J$ peak in methanol, it is also
possible to get $F=1, F^{\prime}=2$ transitions. In this case $P_{\alpha \beta} / 2 \pi=1.5 \mathrm{~Hz}$ if $m_{F}=0$ and 1.3 Hz if $m_{F}= \pm 1$

In the main body of the paper we also consider the case of an excitation field rotating in the plane normal to the quantization axis. In this case for a given sense of rotation

$$
\begin{equation*}
H_{P}(t)=|\boldsymbol{B}|\left[\cos (\omega t)\left(\gamma_{a} I_{a, x}+\gamma_{b} I_{b, x}\right)+\sin (\omega t)\left(\gamma_{a} I_{a, y}+\gamma_{b} I_{b, y}\right)\right] \tag{4.28}
\end{equation*}
$$

In the interaction frame defined by Eq. (4.10) we now have

$$
\begin{equation*}
P_{\alpha \beta}=\left(\frac{\gamma_{a}|\boldsymbol{B}|+\gamma_{b}|\boldsymbol{B}|}{2}\right)\left\langle F^{\prime}, m_{F}+1\right|\left(I_{a,+}-I_{b,+}\right)\left|F, m_{F}\right\rangle, \tag{4.29}
\end{equation*}
$$

again only considering terms that have different energy at zero field. $I_{ \pm}$are the usual raising and lowering operators and only terms where the higher energy state also has higher $m_{F}$ give time independent terms for this sense of rotation of the excitation field. This expression can be expanded in terms of Clebsch-Gordan coefficients the same way as above in order to give
$P_{\alpha \beta}=\left(\frac{\gamma_{a}|\boldsymbol{B}|+\gamma_{b}|\boldsymbol{B}|}{2}\right) \sum_{\substack{m_{a}^{\prime}, m_{b}^{\prime} \\ m_{a}, m_{b}}} C_{I_{a}, m_{a}, I_{b}, m_{b}}^{F^{\prime}, m_{F}+1} \times C_{I_{a}, m_{a}, I_{b}, m_{b}}^{F, m_{F}}\left(C_{+, a} \delta_{m_{a}^{\prime}, m_{a}+1} \delta_{m_{b}^{\prime}, m_{b}}-C_{+, b} \delta_{m_{a}^{\prime}, m_{a}} \delta_{m_{b}^{\prime}, m_{b}+1}\right)$,
where we have used $I_{a,+}\left|I_{a}, m_{a}, I_{b}, m_{b}\right\rangle=C_{+, a}\left|I_{a}, m_{a}+1, I_{b}, m_{b}\right\rangle$. Evaluating this expression for $|\boldsymbol{B}|=0.47 \mathrm{mG}, \gamma_{a}=42.576 \mathrm{MHz} / \mathrm{T}, \gamma_{b}=10.705 \mathrm{MHz} / \mathrm{T}, I_{a}=1 / 2$, and $I_{b}=1 / 2, F=$ $0, F^{\prime}=1$, and $m_{F}=0$ gives $P_{\alpha \beta} / 2 \pi=1.06 \mathrm{~Hz}$.

## Chapter 5

## Spin-Species Selective Pulses

In the previous chapter we presented a method for achieving spectral selectivity in zerofield, in spite of all spins having zero Larmor frequency, by relying on the characteristic frequencies of the overall system in the strongly-coupled zero-field regime. In this chapter we introduce a method for obtaining selectivity based on the chemical identity of individual spins rather the zero-field resonance frequencies.

The material in this chapter has previously been published under the title

- Nuclear Magnetic Resonance at Millitesla Fields Using a Zero-Field Spectrometer by Tayler, Sjolander, Pines, and Budker [64].


### 5.1 Background and Motivation

While performing NMR experiments in the zero-field regime has advantages, there are features of high-field NMR that are virtually indispensable. Chief among them is the ability to selectively control individual spins based on their chemical identity. Usually such selectivity is approximated in zero-field by relying on algebraic ratios of the gyromagnetic ratios of the spins of interest, and as we have seen this method has limitations.

In this chapter we describe a method for achieving true high-field selectivity in the zerofield experiment. A magnetic field is temporarily imposed on the sample using electromagnetic coils, allowing one to apply resonant AC pulses that discriminate between different spin-species based on their resonances frequency in the applied field. We perform experiments on ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ in formic acid, as well as ${ }^{1} \mathrm{H}$ and ${ }^{19} \mathrm{~F}$ in diflouroacetic acid, and demonstrate spin-species selective pulses which flexibly vary the initial condition in the zero-field experiment.

A key point here is that while an electromagnet may not produce a homogeneous enough field to do high-resolution spectroscopy, it does allow us to selectively address and manipulate spins based on their resonance frequency in the applied field. This is especially so when B1compensated adiabatic pulses are used, as they are in this work. Thus by temporarily switching on and off millitesla fields inside our zero-field spectrometer we can marshal the machinery of pulsed high-field NMR to manipulate the initial state before performing the detection in an extremely homogeneous zero-field environment. The ability to perform highfield pulsed experiments should add significantly to the low footprint instrumentation and ultra-high resolution of zero-field NMR.

The particular experiments demonstrated here are spin-species selective inversion pulses. Remember from Section 2.3.3 that it is often necessary to invert one of the spin-species in zero-field in order to obtain $J$-spectra, and that for a ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ system this is easily achieved by exploiting the fact that $\gamma_{H} / \gamma_{C} \approx 4$. It is an unfortunate fact however, that most other spin pairs do not have such convenient ratios, complicating the excitation step. However, by the employing the field switching technique demonstrated here this problem can be overcome using high-field chemical-shift selectivity. We show facile selective inversion of the ${ }^{19} \mathrm{~F}$ spins in diflouroacetic acid, even though $\gamma_{H} / \gamma_{F} \approx 1.06$.

### 5.2 Adiabatic-Remagnetization Pulses

We saw in Section 2.3.2 that following pre-polarization in a permanent magnet the density operator describing the spin system at the beginning of the zero-field experiment depends on how the magnetic field experienced by the sample varies from the polarization field to the zero field region. According to Eq. (2.10) we can write the initial density operator in the pre-polarizing field as $\rho_{T H}=\sum_{i}^{N} I_{z, i}$, where for convenience we have ignored both the constants of proportionality describing the degree of polarization and the identity matrix, which commutes with all Hamiltonians and so does not contribute to the spin evolution.

Two limiting cases of switching of the magnetic field are of relevance, sudden and adiabatic switching. In the sudden approximation the field changes rapidly with respect to all Bornfrequencies of the system and one assumes that the density operator remains stationary throughout the process. In adiabatic switching the instantaneous rate of change of the field is small compared to the Born-frequencies of the system at all points of the trajectory. In this case the system continuously remains in an eigenstate of the changing Hamiltonian as the system moves from weak-coupling in the high-field regime to strong-coupling in the zero-field regime [22, 30].

To see the consequences of adiabatic transfer for zero-field spectroscopy consider [ $\left.{ }^{13} \mathrm{C}\right]$ formic acid as an example. Remember that rapidly exchanging acidic protons do not contribute to coherent spin-dynamics in zero-field and thus formic acid constitutes a two-spin system. The density operator in the prepolarizing field is $\rho_{T H}=\gamma_{H} I_{z}+\gamma_{C} S_{z}$, where $I_{z}$ and $S_{z}$ are angular momentum operators for the ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ spins. The Hamiltonian in angular frequency units is $H_{J}=2 \pi J \boldsymbol{I} \cdot \boldsymbol{S}$, where $J$ is 222.15 Hz . The zero-field spectrum of this molecule is shown in Fig. 2.5a. Remember from Section 2.3.3 that the high-field equilibrium density operator $\rho_{T H}$ does not commute with $H_{J}$, a general result for spin systems containing more than one spin-species. Consequently, following sudden switching from high to zero field the initial density operator, $\rho(0)$, contains off-diagonal terms, or coherences, in the zero-field basis and there is an evolving NMR signal without the need for an excitation pulse. However, remember that care must be taken when trying to obtain a zero-field spectrum this way the signal will oscillate along the direction of the prepolarizing field, see Section 2.3.3, and if the orientation of the high-field state before the quenching does not match the detection axis of the magnetometer no signal will be measured, even though the system would generate a time dependent magnetization.

During adiabatic switching the density operator must by definition commute with the Hamiltonian throughout the trajectory and therefore it will be in a stationary state of $H_{J}$ upon reaching zero-field. We saw in Section 2.3.3 that in this case a magnetic field pulse is required to produce an NMR signal. The case of a square pulse applied along the z-axis with a strength $B$ and duration $t_{\text {pulse }}=1 \mathrm{~ms}$ is illustrated in Fig. 5.1a. The plotted data represent the integrated amplitude of the zero-field spectrum obtained with the given excitation conditions. The data all correspond to 10 s acquisitions. As was shown in Section 2.3.3 the excitation curve for a hard pulse along the z-axis will follow the form $\sin \left(\gamma_{H}-\gamma_{C}\right) B t_{\text {pulse }}$, which is what we see in the data.

One could also use the pulse coils to reverse the adiabatic transformation induced by sample shuttling and bring the spins back to the high-field state ( $\rho_{T H}$ ) even though the spins physically remain in the zero-field region. This applied field can be switched off rapidly in order to effect a sudden instead of adiabatic transfer to zero-field. Figure 5.1b shows the integrated amplitude of the formic acid $J$-spectrum obtained after applying a smoothrising pulse (the amplitude profile is a hyperbolic secant: $B(t)=B \operatorname{sech}\left[15\left(t / t_{\text {pulse }}\right)\right]$, with $t_{\text {pulse }}=100 \mathrm{~ms}$ and $0 \geq t \leq t_{\text {pulse }}$ ) followed by sudden quenching of the applied field to excite evolution. We term this an adiabatic-remagnetization pulse. As pointed out in the preceding paragraph it is important that the direction of the spin-polarization before the


Figure 5.1: Excitation with a hard pulse vs an adiabatic-remagnetization pulse. (a) The excitation curve for formic acid for a single pulse along the detection axis is a sine wave when plotted against the pulse-amplitude. (b) For an adiabatic-remagnetization pulse the measured amplitude of the $J$-spectrum is independent of pulse power, as long as the pulse is appreciably stronger than the $J$-coupling.
quench is collinear with the magnetometer detection axis. With the axis convention used throughout this work the remagnetization pulse thus has to applied along the z-axis. The pulse field strength does not have to be comparable to the prepolarization field, it is enough that the spins are returned to the weak-coupling regime, i.e. $\left|\left(\gamma_{H}-\gamma_{C}\right) B\right| \gg|J|$. In the data in Fig. 5.1 b we see that in the case of formic acid this condition is reached for fieldstrengths $\sim 50 \mu \mathrm{~T}$. A significant advantage of the remagnetization pulse is that once the high-field regime is reached the excitation curve is independent of the amplitude of the pulse field. This type of pulse therefore does not require the sometimes arduous coil calibrations described in Section 3.4.

### 5.3 Adiabatic Inversion Pulses

Pulses based on adiabatic-remagnetization extend naturally to the incorporation of conventional high-field NMR pulse sequences. We demonstrate this using the example of spinspecies selective inversion. Such selectivity is taken for granted in almost all high-field NMR, where the bandwidth of the pules is narrow in comparison to the Larmor frequencies, thereby allowing for arbitrary manipulation of a spin-species of choice while leaving the rest unperturbed. As shown in Chapter 4 zero-field spin transitions do not correspond to individual


Figure 5.2: (a) General pulse-sequence schematic for spin-species selective inversion. (b) Simulations of the evolution of the spin system for the case of the B1 field being (i) offresonant, (ii) resonant with the carbon spin, and (iii) resonant with the proton spin.
spins, and this option is not available in zero-field NMR. A schematic of a selective inversion pulse based on adiabatic-remagnetization is shown in Fig. 5.2a. After shuttling to zero-field the sample is adiabatically remagnetized along the z-axis in an applied field of strength $B$. The field is left on, (so the spin system remains in the weakly-coupled regime), and a frequency swept adiabatic inversion pulse, denoted $B 1$ is applied along the x-axis. The amplitude of $B 1$ is typically $10-100$ times weaker than $B$ and follows a half-sine profile. The effect of $B 1$ is to invert only those spins whose resonance frequency in the $B$ field lies within the sweep range $\nu-\Delta \nu / 2$ to $\nu+\Delta \nu / 2$, where $\nu$ is the center frequency. After the $B 1$ pulse the $B$ field is suddenly quenched and the signal is detected in the zero-field regime. In principle a hard resonant pulse could be used as $B 1$ but an adiabatic inversion pulse has the major advantage that the exact resonance frequency of the spins does not matter a great deal. This has two convenient consequences: (i) the stability of the $B$ field is not critical, and (ii) neither the z-coil nor the x-coil have to be perfectly calibrated.

Simulated trajectories of the expectation values for the spin-polarization operators $\left\langle\gamma_{H} I_{z}\right\rangle$, $\left\langle\gamma_{C} S_{z}\right\rangle$, and $\left\langle M_{z}\right\rangle=\left\langle\left(\gamma_{H} I_{z}+\gamma_{C} S_{z}\right)\right\rangle$ for a ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ system during the selective inversion pulse sequence are plotted in Fig. 5.2b. At a $B$ of 1 mT the difference between the ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$

Larmor frequencies is $\sim 3 \mathrm{kHz}$ and so we chose a sweep range $\Delta \nu$ for $B 1$ of 400 Hz to be spin-species selective. Adiabatic shuttling from the prepolarizing magnet equalizes the polarization on ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$, which implies to a non-evolving state in zero-field. In Fig. 5.2b(i) the $B 1$ sweep is not resonant with either the ${ }^{1} \mathrm{H}$ spin or the ${ }^{13} \mathrm{C}$ spin. This case is identical to the adiabatic-remagnetization pulse described earlier, after the field quench the bulk magnetization starts to oscillate as polarization is exchanged between ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ under the action of $H_{J}$ as described in Chapter 2. In Fig. 5.2 b (ii) the $B 1$ pulse inverts the ${ }^{13} \mathrm{C}$ spin before the quench. The result is larger oscillations in the net magnetization of the system, and therefore a larger zero-field NMR signal. In Fig. 5.2 b (iii) the ${ }^{1} \mathrm{H}$ spin is inverted instead of the ${ }^{13} \mathrm{C}$ spin - in this case the resulting oscillations are $180^{\circ}$ out of phase relative to when the ${ }^{13} \mathrm{C}$ spin is inverted.

We demonstrate this pulse sequence experimentally by acquiring zero-field spectra of ${ }^{13} \mathrm{C}$ formic acid as a function of the remagnetization field $B$ for a number of $B 1$ center frequencies $(\nu=2,4,8,16,32,64 \mathrm{kHz})$. The results are shown in Fig. 5.3. Each data point corresponds to the (signed) integrated amplitude of the $J$-spectrum of formic acid. When the value of $B$ is such that the Larmor frequency of neither spin is within the $\nu \pm \Delta \nu$ window the result is identical to Fig. 5.1b. As $B$ increases the ${ }^{1} \mathrm{H}$ spin first comes in resonance with the $B 1$ pulse with the result that the peak changes sign and grows in amplitude. Perfectly on resonance the amplitude has increased by a factor of $\left(\gamma_{H}+\gamma_{C}\right) /\left(\gamma_{H}-\gamma_{C}\right) \approx 1.67$ consistent with inversion of the ${ }^{1} \mathrm{H}$ spin. As $B$ increases further the resonance frequency of the ${ }^{13} \mathrm{C}$ spins starts to enter the inversion window of the pulse. Consequently the signal starts to increase until it is $\sim 1.67$ times larger when $\nu$ corresponds to the Larmor frequency of ${ }^{13} \mathrm{C}$ in a field of strength $B$. These results are consistent with the simulations in Fig. 5.2, as well as the theory which states that there should be no perturbation of the spin system outside the pulse bandwidth, i.e. outside the limits given by $(B \pm \Delta B / 2) \gamma=\nu \pm \Delta \nu / 2$ for each spin-species. These field limits are indicated as shaded bands for each value of $\nu$ in Fig. 5.3. $\Delta \nu$ was 400 Hz in all cases. We note that the width of the ${ }^{13} \mathrm{C}$ resonance in this representation is significantly wider than the ${ }^{1} \mathrm{H}$ resonance. The reason is that since the gyromagnetic ratio of ${ }^{13} \mathrm{C}$ is a factor of four lower than for ${ }^{1} \mathrm{H}$ there is a 4 times larger range of $B$ fields that keeps the ${ }^{13} \mathrm{C}$ Larmor frequency within the 400 Hz sweep width of the inversion pulse. Finally we note that there are spurious resonances (marked by asterisks) in the data. They occur at 3 x and 5 x the $B$ field corresponding to the ${ }^{1} \mathrm{H}$ resonance, and we assign them to the ${ }^{1} \mathrm{H}$ spin coming into resonance with odd-integer harmonics of the inversion pulse. Consider the case of $\nu=4 \mathrm{kHz}$. At this frequency the ${ }^{1} \mathrm{H}$ spin is inverted at $B \sim 0.1 \mathrm{mT}$. However, if $B 1$ also has harmonics at 12 , and 20 kHz we would expect to see ${ }^{1} \mathrm{H}$ inversion at $\sim 0.3$ and $\sim 0.5$ mT as well, which is what we see in the data. Note that the spurious resonances correspond to a decrease in the amplitude of the $J$-spectrum, consistent with partial inversion of the ${ }^{1} \mathrm{H}$ spin. They are broader than the primary resonance because the effective sweep widths of the third and fifth harmonics are increased by a factor of x 3 and x 5 to $\Delta \nu=1200$, and 2000 Hz respectively.

Next we consider the case of diflouroacetic acid. In this case the evolution of $\rho_{T H}$ without further modification corresponds to a very small zero-field signal, since the gyromagnetic


Figure 5.3: Experimental demonstration of the spin-species selective inversion sequence. Each panel corresponds to a given $B 1$ frequency and the amplitude of the formic acid $J$ spectrum is plotted as a function of the strength of the remagnetization field, $B$. The peaks are due to $B$ bringing the spins into resonance with $B 1$, thus modifying $\rho(0)$ in advance of the readout. The asterisks denote spurious peaks due to harmonics of B1.
ratios of ${ }^{1} \mathrm{H}$ and ${ }^{19} \mathrm{~F}$ differ by only a factor of $\sim 1.06$, see Eq. (2.38). The gain in signal upon selective inversion of one of the spins before detection should therefore be very large, $\left(\gamma_{H}+\gamma_{F}\right) /\left(\gamma_{H}-\gamma_{F}\right) \approx 33$. However, performing such an inversion using a simple hard pulse in zero-field would require a flip-angle of $\theta=16 \pi$ on ${ }^{19} \mathrm{~F}$, which is approximately equal to $17 \pi$ on ${ }^{1} \mathrm{H}$. Such a long pulse would be extremely sensitive to mis-calibrations of the pulse field strength as well as to inhomogeneities in the pulse field. We note that in Fig. 5.1a the


Figure 5.4: Selective inversion of proton and fluorine in diflouroacetic acid. The gyromagnetic ratios are so similar that without inverting one of the spins the $J$-spectrum is not observable, even if $\rho(0)$ was prepared by sudden transport to zero-field.
amplitude of the oscillations are damped as the total flip-angle increases (at constant pulse duration) due to dephasing of the spin ensemble during the pulse.

The success of our adiabatic inversion sequence when applied to diflouroacetic acid is demonstrated in Fig. 5.4. The molecule is well described as an $\mathrm{SI}_{2}$ spin system and its $J$-spectrum consists of a single peak at $3 / 2$ times the $J$-coupling frequency $=79.1 \mathrm{~Hz}$, see Section 2.3.4. Each data point is the integrated (signed) signal amplitude of the peak as a function of remagnetization field $B$ at $\nu=64 \mathrm{kHz}$ and $\Delta \nu=800 \mathrm{~Hz}$. Due to the similarity of the gyromagnetic ratios of ${ }^{1} \mathrm{H}$ and ${ }^{19} \mathrm{~F}$ the signal after a plain adiabatic-remagnetization pulse is so low as not to be visible, but when the $B$ field brings the ${ }^{1} \mathrm{H}$ and ${ }^{19} \mathrm{~F}$ spins into resonance with the adiabatic inversion pulse we see corresponding large negative and positive amplitude peaks in the $J$-spectrum. However, even on resonance, the SNR of the diflouro acetic acid spectrum is significantly lower than what was obtained for formic acid. Remember from Section 2.3.3 that the matrix element of the detection operator also depends on the difference in gyromagnetic ratios between the nuclei, and this fact can not be changed by any sort of clever manipulations of the initial state. There is thus a reduction by a factor of $\left(\gamma_{H}-\gamma_{C}\right) /\left(\gamma_{H}-\gamma_{F}\right) \approx 13$ in signal intensity between Fig. 5.3 and Fig. 5.4.

### 5.4 Conclusions

To summarize: the work presented in this chapter demonstrates high-field NMR pulse sequences executed on a zero-field spectrometer, thereby increasing capability for spin-control at zero-field, including selectivity based on spin-species. This complements the ability to selectively address individual zero-field resonances demonstrated in the preceding chapter. At present the electromagnetic coils inside our zero-field spectrometer supply DC magnetic fields up to several millitesla, providing a means to study spin phenomena around the "crossover zone" between the strongly and weakly coupled regimes of spin-dynamics [22], including relaxation dispersion and also parahydrogen induced hyperpolarization, which is strongly influenced by field-dependent level anticrossings and is currently the subject of intense research interest. In the future we expect many opportunities for multidimensional experiments that correlate spin phenomena between the two regimes and make use of the large catalog of existing high-field pulsed NMR methods. With the use of stronger fields (in the region greater than 0.1 T ) chemical-shift selectivity may also be exploited.

## Chapter 6

## Zero-Field Correlation Spectroscopy

In this chapter we present Total Correlation $J$-Spectroscopy and Multiple Quantum Correlation $J$-Spectroscopy detected in zero magnetic field using a ${ }^{87} \mathrm{Rb}$ vapor-cell magnetometer and perform two experimental demonstrations. At zero-field the spectrum of ethanol appears solely as a mixture of ${ }^{13} \mathrm{C}$ isotopomers, and correlation spectroscopy is useful in separating the two composite spectra. We also identify and observe the zero-field equivalent of a double quantum transition in acetic acid, and show that such transitions are of use in spectral assignment. Two-Dimensional spectroscopy further improves the high resolution attained in zero-field NMR since selection rules on the coherence transfer pathways allows for the separation of otherwise overlapping resonances into distinct cross-peaks.

The work is this chapter is currently being prepared for publication under the title

- Single and Multiple Quantum Correlation Spectroscopy in Zero-Field Nuclear Magnetic Resonance by Sjolander, Blanchard, Budker, and Pines [3].


### 6.1 Background and Motivation

While zero-field $J$-spectroscopy provides a route to accurate chemical finger-printing on account of the high achievable resolution, there are limits to what can be obtained from simple 1D spectra. As we have seen it is a feature of $J$-spectroscopy that only heteronuclear spin systems yield directly observable spectra [2]. This means that several common ${ }^{1} \mathrm{H}$ containing solvents give no signal background, obviating the need for deuterated solvents. However, it also means that, since ${ }^{13} \mathrm{C}$ is only $1 \%$ naturally abundant, the observed spectra of ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ systems at natural abundance are superpositions of contributions from the different possible isotopomers. Further complicating matters is the fact that the one-bond $J$-couplings of many organic molecules are order $\sim 100 \mathrm{~Hz}$, which means that the peaks are spread out over only a few 100 s of Hz in frequency space. While some molecules give $J$-spectra with peaks as narrow as 20 mHz [23], many other molecules do not. Additionally, spectral complexity increases rapidly with spin system size. Taken together, these factors often lead to partially resolved or overlapping peaks, which complicates assignment.

Meanwhile, the development of two-dimensional spectroscopy $[118,119]$ is a major reason behind the analytical power of NMR. At a minimum 2D experiments increase signal dispersion, thereby allowing the resolution of more crowded spectra. Additionally, many pulse sequences exist that enable the mapping of coupling networks, the simplification of spectral assignment, and structure elucidation [8].

Multiple-quantum (MQ) spectroscopy [120-122], which in high-field concerns transitions for which $|\Delta m|>1$, where $m$ is the quantum number for the projection of the spin angular momentum on the field axis, has also found extensive use in NMR spectroscopy. In liquidstate analytical chemistry, multiple quantum coherence filters married to two-dimensional detection techniques provide one of the standard ways to map coupling networks [8]. MQspectroscopy also provides a means of simplifying the spectra of partially ordered systems, the smaller number of MQ peaks enables otherwise intractable spectra to be readily interpreted $[123,124]$. In the solid state, MQ coherences may be used to monitor the growth of correlated spin clusters with applications to the investigation of the structure of amorphous solids [125, 126], and more recently in studies of many-body physics [127, 128].

In this chapter we introduce just such two-dimensional correlation and MQ experiments in the context of liquid-state zero-field $J$-spectroscopy. Correlation spectroscopy is an attractive way to approach the problem of natural abundance $J$-spectra containing contributions from different isotopomers, since coherence transfer between distinct molecules in liquids is under normal circumstances not possible. We report two proof of principle experiments on ethanol and acetic acid, and show that the different ${ }^{13} \mathrm{C}$ isotopomers in ethanol may be separated from each other by observing the cross-peak pattern. The cross-peak pattern also simplifies spectral assignment and enables the distinction between otherwise overlapping resonances. We also show that $\left[{ }^{13} \mathrm{C}_{2}\right]$-acetic acid supports the zero-field equivalent of a multiple quantum transition, demonstrating for the first time the concept of Zero-Field-MultipleQuantum (ZF-MQ) NMR. Just as in high-field NMR the number of ZF-MQ transitions is significantly reduced compared to the number of single quantum transitions, potentially
leading to simpler, easier to interpret spectra. The selection rules governing the correlation pattern between single and multiple quantum coherences can be used to further simplify assignment. Finally we note that the ability to perform 2D-experiments with only one indirect dimension is a significant advantage offered by directly detected zero-field experiments employing DC field sensors as done here, as opposed to using indirect detection in high-field [129], which requires two indirect dimensions.

### 6.2 Theory

### 6.2.1 Zero-Field Energy-Level Manifolds

Commonly, the most interesting features of two-dimensional spectroscopy are cross-peaks due to coherence-transfer from one transition to another. Therefore, selection rules that constrain the allowed pathways are important for the interpretation of 2D spectra. Here we show the origin of one such important constraint in zero-field $J$-spectroscopy.

As we have seen, in an isotropic liquid-state system at zero magnetic field, the nuclear spin eigenstates are also eigenstates of the total spin angular momentum operator $\boldsymbol{F}^{2}$ and may conveniently be labeled with the quantum numbers $F$ and $m_{F}$ [49]. This is most easily justified by noting that the nuclear spin Hamiltonian given by Eq. (2.13) is invariant with respect to rotations of the spin system and therefore must commute with $\boldsymbol{F}^{2}$ [49]. However, for systems comprising more than two spins- $1 / 2$ nuclei additional quantum numbers are necessary to fully define the zero-field eigenstates. It is particularly useful to consider the angular momentum of sets of magnetically equivalent spins [38]. 'Equivalent' here denotes a set of indistinguishable spins that also share the exact same couplings to all other spins in the spin system, meaning that they possess permutation symmetry. If a set of spins with total angular momentum $K$ is magnetically equivalent then there is no combination of pulses or evolution intervals that can break the permutation symmetry and $\boldsymbol{K}^{2}$ commutes with all realizable effective Hamiltonians. Therefore, the presence of equivalent spins leads to selection rules in the zero-field spectra - the quantum numbers associated with the total angular momentum of sets of equivalent spins must be conserved throughout any pulsesequence.

This selection rule reflects the existence of separate spin-manifolds in zero-field. We define such manifolds to be sets of energy-levels which share the same combination of equivalentspin quantum numbers. It follows from the above discussion that there can be no transitions of any kind between states belonging to different manifolds. As an example consider the zero-field energy level structure of ${ }^{13} \mathrm{C}_{2}$-acetic acid, which can be considered an $\mathrm{S}_{\mathrm{A}} \mathrm{S}_{\mathrm{B}} \mathrm{I}_{3}$ spin system with the methyl $\left(\mathrm{CH}_{3}\right)$ protons being to a very good approximation equivalent. The Hamiltonian for this spin system is $H=2 \pi\left({ }^{1} J_{\mathrm{CH}} \boldsymbol{S}_{\mathrm{A}} \cdot \boldsymbol{K}+{ }^{2} J_{\mathrm{CH}} \boldsymbol{S}_{\mathrm{B}} \cdot \boldsymbol{K}+{ }^{1} J_{\mathrm{CC}} \boldsymbol{S}_{\mathrm{A}} \cdot \boldsymbol{S}_{\mathrm{B}}\right)$, where $\boldsymbol{K}$ and $\boldsymbol{S}_{\mathrm{A} / \mathrm{B}}$ are angular momentum operators for the proton group and carbons respectively. The three protons make up the only set of equivalent spins in the molecule and $K$ may take two values, $1 / 2$ and $3 / 2$. The allowed transitions may thus be assigned to two


Figure 6.1: The energy levels of acetic acid may be grouped in two manifolds of different proton angular momentum. Transitions and coherence transfer may only occur within each manifold. Magnetic dipole allowed transitions have $\Delta F= \pm 1,0$ and have been marked with solid lines. The dash/dot line marks a $\Delta F= \pm 2$ transition and the color coding and lines styles match Fig. 6.5
separate manifolds, as shown in the energy-level diagram in Fig. 6.1. In actuality there are two manifolds for which $K=1 / 2$, but they are degenerate, and we are ignoring this point for clarity. There are no transitions between states of different $K$ and the two $K$ manifolds form entirely isolated spin systems. The principle extends readily to systems with more than one set of equivalent spins. For example the Hamiltonian for the spin system of $1-{ }^{13} \mathrm{C}$-ethanol in zero-field is $H_{J}=2 \pi\left({ }^{2} J_{\mathrm{CH}} \boldsymbol{K} \cdot \boldsymbol{S}+{ }^{3} J_{\mathrm{CH}} \boldsymbol{L} \cdot \boldsymbol{S}+{ }^{3} J_{\mathrm{HH}} \boldsymbol{K} \cdot \boldsymbol{L}\right)$, where $\boldsymbol{S}$ and $\boldsymbol{K}$ are defined as above and $\boldsymbol{L}$ is the operator for the angular momentum of the protons in the methylene $\left(\mathrm{CH}_{2}\right)$ group. The energy level diagram for this molecule, as well as the $2{ }^{-13} \mathrm{C}$-isotopomer is shown in Fig. 6.2. In both cases there are four spin-manifolds, corresponding to the four distinct combinations of $K$ and $L$.

Since a spin-state labeled with a certain combination of conserved quantum numbers may not evolve or transform into a spin-state labeled with a different combination, it follows that in 2D zero-field spectroscopy we will never see cross-peaks between transitions belonging to different spin-manifolds.

This phenomenon is of course not unique to zero-field NMR, spin states belonging to different irreducible representations of a given permutation group may never mix or evolve into each other no matter the magnitude of the external field. For example, in high-field NMR a ${ }^{13} \mathrm{CH}_{2}$ group (where the protons are magnetically equivalent) gives only two peaks at the proton frequency, since transitions between the proton singlet and triplet states are forbidden on account of conservation of the angular momentum of the protons.


Figure 6.2: The energy level diagrams of the two (singly labeled) ${ }^{13} \mathrm{C}$ isotopomers of ethanol support four distinct manifolds corresponding to different combinations of total proton angular momentum. For clarity only one transition per manifold is plotted and the quantum number $S=\frac{1}{2}$ for the ${ }^{13} \mathrm{C}$ spin has been omitted. Solid lines correspond to the $1-{ }^{13} \mathrm{C}$ isotopomer and the dotted lines to the $2-{ }^{13} \mathrm{C}$ isotopomer. The color coding and line styles match Fig. 6.5

### 6.2.2 Zero-Field Total Correlation Spectroscopy

A general schematic of a 2D NMR experiment is shown in Fig. 6.3. First the desired coherences are prepared in an excitation step, this is followed by free evolution during which those coherences are allowed to acquire phase, and finally a reconversion step before the readout. Here the excitation and reconversion sequences are generated by a series of strong DC magnetic field pulses around different axes in the laboratory frame. The pulses are much stronger than any $J$-couplings, $\gamma B \gg J$, for these systems and to a good approximation each spin is independently rotated by an angle $\theta_{i}=\gamma_{i} B t$ around the pulse axis, where $\gamma_{i}$ is the gyromagnetic ratio of the $i^{\text {th }}$ spin, $B$ is the amplitude of the pulse, and $t$ its duration. In this work we use proton/carbon systems and all pulses have been calibrated to effect a $\pi$ rotation of the ${ }^{13} \mathrm{C}$ spins, which means that proton spins are rotated by $\pi \times\left(\gamma_{1 \mathrm{H}} / \gamma_{13} \mathrm{C}\right) \approx 4 \pi$.

We take the z -axis to be the detection axis and assume that the initial state in all experiments is given by magnetization along the z-axis generated by adiabatic transport


Figure 6.3: General scheme for 2D NMR spectroscopy. An excitation sequence prepares the desired coherences, this is followed by a period of free evolution and finally a reconversion sequence and detection.
from a pre-polarizing field, giving the initial deviation density matrix $\rho(0) \propto \sum_{i} I_{z, i}$. This state commutes with $H_{J}$ and so does not evolve. We saw in Section 2.3.3 that evolution may be initiated by changing the relative orientation of the proton and carbon spins, for example by a $\pi$ pulse on carbon in the $\mathrm{x} / \mathrm{y}$ plane.

In Chapter 4 we introduced a zero-field 'spin-tickling' method whereby assignment of resonances was simplified by monitoring the response of the spectrum to low-amplitude irradiation of selected transitions. Here we present a two-dimensional variant, where the complete spectral connectivity is established in one experiment. In this experiment $t_{1}$ evolution is initiated with a $\pi$ pulse on carbon along the x-axis followed by a second $\pi$ pulse and $t_{2}$ evolution (detection). The Fourier transform with respect to $t_{1}$ and $t_{2}$ gives a $\mathrm{J} / \mathrm{J}$ correlation spectrum. The sequence is summarized schematically in Fig. 6.4a. The experiment relies on similar physics to high-field Total Correlation Spectroscopy (TOCSY) [130], but does not require a mixing time. This follows from the fact that the unmodified zero-field free evolution Hamiltonian already is strongly coupled for all spin pairs (both homo- and heteronuclear) and thus allows complete coherence transfer throughout the molecule by default. Of course the same fact also means that $\mathrm{F}_{1}$ and $\mathrm{F}_{2}$ do not correspond to individual spin transitions but rather zero-field $J$-spectra. We refer to this type of experiment as ZF-TOCSY.

Previously directly detected 2D experiments have either been performed with different effective Hamiltonians during the two evolution intervals [2], or in the presence of a magnetic field such that the Larmor frequencies and $J$-coupling frequencies are approximately equal [81]. Both cases lead to significantly different cross-peak patterns than what is seen here.

### 6.2.3 Zero-Field Multiple Quantum Correlation Spectroscopy

In high-field NMR spins are quantized along the external magnetic field and states may be labeled with their projection, $m$, along that field. Directly observable single quantum coherences have $\Delta m= \pm 1$, and indirectly observable multiple quantum coherences are those for which $|\Delta m|>1$. Conversely in zero-field the eigenstates are eigenstates of total angular momentum, labeled $F$. The observable in both high and zero-field NMR experiments is total magnetization along some direction, conventionally taken to be the x-axis in high-field and the z-axis in zero-field. Since the sample magnetization is represented by a vector operator it follows from the Wigner-Eckart theorem [37] that it supports transitions with $\Delta F=0, \pm 1$.


Figure 6.4: Schematics showing the pulse sequences used in this work. (a) The zf-TOCSY sequence. (b) ZF-MQ sequence.

This suggests that the indirect observation of transitions for with $|\Delta F|>1$ may serve as a zero-field analogue to high-field MQ experiments. Figure 6.3 outlines the general scheme by which such spectra may be obtained. An excitation sequence prepares the system in a state that contains coherences for which $|\Delta F|>1$. This is followed by free evolution for a time $t_{1}$ during which the system builds up phase, and finally a reconversion sequence to convert the multiple quantum coherences into observable $\Delta F=0, \pm 1$ coherences. There are many potential excitation and reconversion Hamiltonians that could be used to implement this scheme.

The simplest example is $U_{e x c}=P_{x}-U_{t_{m}}-P_{x}$, and $U_{r e}=P_{x}$, modeled on the original high-field MQ excitation sequence. Here $U_{\text {exc }} / r e$ denotes the unitary operator for the excitation/reconversion sequence, $P_{x}$ is the propagator for a $\pi$ pulse along $x$ on ${ }^{13} \mathrm{C}$ and $U_{t_{m}}$ the propagator for free evolution under $H_{J}$ for a time $t_{m}$. The first pulse initiates evolution under the $J$-coupling Hamiltonian which subsequently generates many-spin terms. The second pulse converts some of those terms into zero-field MQ-coherences. After $t_{1}$ evolution the reconversion is done with a single read-out pulse. With the exception of the first pulse and the waiting interval this pulse sequence is identical to the ZF-TOCSY sequence and can therefore be expected to produce a similar looking spectrum. The difference being that the $t_{1}$ period contains both observable and $n>1$ coherences and we expect the resulting spectrum to look like a ZF-TOCSY spectrum, but with additional cross-peaks in F1 corresponding due to coherences evolving at $n>1$ transition frequencies in $t_{1}$.

Here we show that ZF-MQ experiments may assist with spectral assignment since the possible values of $n$ that can occur during $t_{1}$ depend on the spin topology in a simple way: Given a spin system containing $k$ sets of equivalent spins we can write an expression for the highest order of quantum coherence supported by each energy level manifold. Each manifold is labeled by $k$ quantum numbers and $n_{\text {max }}$ is given by

$$
\begin{equation*}
n_{\max }=2 \times \operatorname{Min}\left\{\sum_{i=1}^{k-1} f_{i}, f_{k}\right\} \tag{6.1}
\end{equation*}
$$

where $f_{i}$ are the total angular momentum quantum numbers for each set of equivalent spins and the sum runs over the $k-1$ smallest $f_{i}$ in a given manifold. $f_{k}$ is the largest quantum number in the manifold. Equation (6.1) can be justified as follows: Each $F$ value in a given spin-manifold is the result of successively coupling all angular momenta $f_{i}$ in that manifold. We have $n_{\max }=F_{\text {max }}-F_{\min }$, where $F_{\max }=\sum_{i=1}^{k} f_{i}$, and $F_{\min }=\left|f_{k}-\sum_{i=1}^{k-1} f_{i}\right|$. Depending on which of $f_{k}$ or $\sum_{i=1}^{k-1} f_{i}$ is bigger we obtain the two cases for Eq. (6.1). As an example consider the energy level diagram of ${ }^{13} \mathrm{C}_{2}$-acetic acid given in Fig. 6.1. The $(1 / 2,1 / 2,1 / 2)$ manifold supports only $n=0,1$ transitions consistent with the fact that the largest quantum number, $f_{k}$, in the manifold is $1 / 2$, whereas the $(1 / 2,1 / 2,3 / 2)$ manifold supports a $n=2$ transition, since the sum of the two smallest quantum numbers in the manifold is 1 . The ZFMQ experiment thus provides direct information regarding the possible quantum numbers associated with a given resonance.

### 6.3 Methods

We performed experimental demonstrations of the ZF-TOCSY and ZF-MQ experiments using ${ }^{13} \mathrm{C}$ labeled isotopomers of acetic acid and ethanol. In the case of ethanol we simulated a natural abundance spectrum by preparing a sample consisting of a mixture of the two singly labeled ${ }^{13} \mathrm{C}$ isotopomers. The acetic acid sample was doubly ${ }^{13} \mathrm{C}$ labeled in order to ensure the presence of a $K$-conserving double quantum transition. The experiments were performed using a ${ }^{87} \mathrm{Rb}$ vapor-cell magnetometer operating in the Spin-Exchange-RelaxationFree (SERF) regime[94], configured for use as an NMR spectrometer as described in Chapter 3. SERF magnetometers are DC magnetic field sensors, which allows us to directly monitor the low-frequency spin evolution in zero-field. All experiments were done using $\sim 80$ $\mu \mathrm{L}$ samples in 5 mm outer diameter standard NMR tubes. The acetic acid sample contained only ${ }^{13} \mathrm{C}_{2}$-acetic acid while the ethanol sample was made from $\sim 40 \mu \mathrm{~L} 1-{ }^{13} \mathrm{C}$-ethanol and $\sim 40 \mu \mathrm{~L} 2{ }^{13} \mathrm{C}$-ethanol. The samples were prepolarized in a 2 T permanent magnet and shuttled pneumatically to a magnetically shielded region for experiment and detection. For the 2 D experiments the samples had to be re-polarized between every point in the indirect dimension.

### 6.4 Results and Discussion

### 6.4.1 One-Dimensional Spectra

As a point of reference we first obtained 1D $J$-spectra of these molecules, the results are presented in Fig. 6.5. The spectra are the result of summing 2 k and 3 k transients respectively for the acetic acid and ethanol data. In both cases each transient corresponds to 20 s of data acquisition. The $J$-coupling constants were obtained from the spectra by a numerical fitting procedure, where the data is matched to the spectra predicted by numerical diagonalization of the spin Hamiltonians given above. The results are given in Table 6.1. Numerical analysis


Figure 6.5: One dimensional zero-field $J$-spectra of ethanol and ${ }^{13} \mathrm{C}_{2}$-acetic acid. The stick spectra correspond to the transition energies predicted by numerical diagonalization of the spin Hamiltonian. The transitions have been labeled and color-coded according to their energy-level manifold. For the ethanol spectrum solid lines correspond to the $1-{ }^{13} \mathrm{C}$ isotopomer and dotted lines to the $2-{ }^{13} \mathrm{C}$ isotopomer. In the acetic acid spectrum the location of a $K$-conserving zero-field double quantum transition is shown for reference.
also gives the eigenvalues of $\boldsymbol{K}^{2}$ and $\boldsymbol{L}^{2}$ for each transition. Simulated spectra based on the best-fit $J$ values, together with the $K$ and $L$ assignments are also shown in Fig. 6.5.

In the case of ethanol we find that the measured 3 -bond ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{Hcoupling}$ constant is different between the two ${ }^{13} \mathrm{C}$-isotopomers within the statistical accuracy of the fit. Since both isotopomers were present in the same NMR tube at the same time during the experiment most potential sources of systematic error may be discarded and we assign the measured difference in the ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ couplings to a secondary isotope shift to the $J$-coupling constant $[104,131,132]$. Such effects have been of interest since they allow for a check on quantum chemical calculations and our understanding of bonding.

We also note that the measured linewidths are significantly larger for ethanol than for acetic acid, and both spectra are in turn significantly broader than what has previously been recorded for $J$-spectra of systems without labile protons [23]. We note that in strongly coupled systems chemical exchange will lead to decreased coherence times via scalar relaxation of the second kind []. Polarization is exchanged throughout the molecule under coherent

| $J(\mathrm{~Hz})$ | $1-{ }^{13} \mathrm{C}-\mathrm{EtOH}$ | $2-{ }^{13} \mathrm{C}-\mathrm{EtOH}$ | ${ }^{13} \mathrm{C}_{2}-\mathrm{AcOH}$ |
| :--- | ---: | ---: | ---: |
| ${ }^{1} J_{\mathrm{CH}}$ | $140.852(1)$ | $125.2572(9)$ | $129.5041(3)$ |
| ${ }^{1} J_{\mathrm{CC}}$ | - | - | $56.7928(8)$ |
| ${ }^{2} J_{\mathrm{CH}}$ | $-4.700(3)$ | $-2.317(3)$ | $-6.7335(3)$ |
| ${ }^{3} J_{\mathrm{HH}}$ | $7.049(3)$ | $7.032(2)$ | - |

Table 6.1: Measured $J$-coupling constants for the two single labeled ${ }^{13} \mathrm{C}$ isotopomers of ethanol (EtOH) and the doubly ${ }^{13} \mathrm{C}$ labeled isotopomer of acetic acid $(\mathrm{AcOH})$. The number in parenthesis denotes the $95 \%$ confidence interval of the fit.
$J$-coupling evolution but coherence with the labile proton is constantly lost due to exchange, decreasing the overall signal lifetime. We assign the broad (relative to non-exchanging systems) $J$-spectra in Fig. 6.5 to this effect, and the difference in linewidths between ethanol and acetic acid to different kinetics for the hydrogen exchange reaction.

The 1D $J$-spectra may be interpreted a follows: $\operatorname{In}{ }^{13} \mathrm{C}_{2}$-acetic acid the dominant coupling is between a single spin $1 / 2$ carbon coupled to a group of three equivalent protons with angular momentum $K$. An $\mathrm{AX}_{3}$ spin system has two transition frequencies depending on the value of $K$, at $J$ and $2 J$, for $K=1 / 2$, and $3 / 2$ respectively. Couplings to the second carbon result in the spectrum being made up of groups of transitions centered at those two frequencies plus additional peaks close to zero [48]. In the experimental data we see two peaks in the $120-150 \mathrm{~Hz}$ range, three peaks between 225 Hz and 280 Hz , and 3 peaks between 20 and 40 Hz , while the best-fit value for ${ }^{1} J_{\mathrm{CH}}$ was 129.504 Hz . Careful inspection of the spectrum also reveals extremely weak signals at $6.75,13.5,129.5$ and 259 Hz . These peaks can be assigned to residual $1-{ }^{13} \mathrm{C}$ and $2-{ }^{13} \mathrm{C}$ acetic acid in the sample. Both isotopomers would yield peaks at 1 J and 2 J on account of being $\mathrm{AX}_{3}$ spin systems, and the corresponding coupling constants according to Table 6.1 are -6.7335 , and 129.5041 Hz respectively, which is consistent with the positions of the weak signals. Finally, the stick-spectrum also shows the expected position of the $K$-conserving $\Delta F= \pm 2$ transition, however since this transition does not correspond to oscillating magnetization it is not observed in the directly detected 1 D data.

For both isotopomers of ethanol the spectrum is to first order [48] determined by a strong ${ }^{1} J_{\mathrm{CH}}$ coupling, which sets up an initial splitting pattern, which is further split by the weaker ${ }^{2} J_{\mathrm{CH}}$ and ${ }^{3} J_{\mathrm{HH}}$ couplings. An $\mathrm{AX}_{2}$ spin system in zero-field gives a single peak at $3 / 2 J$ while an $\mathrm{AX}_{3}$ system gives one peak at $J$ and one peak at $2 J$. We can therefore immediately identify the cluster of peaks at 210 Hz with the $1-{ }^{13} \mathrm{C}$ isotopomer and the peaks around 125 Hz and 250 Hz with the $2-^{13} \mathrm{C}$ isotopomer. This corresponds to a one-bond ${ }^{13} \mathrm{C}-{ }^{1} \mathrm{H} J$-coupling constant of $\sim 140 \mathrm{~Hz}$ when the ${ }^{13} \mathrm{C}$ label is on the methylene group, and $\sim 125 \mathrm{~Hz}$ when the ${ }^{13} \mathrm{C}$ is on the methyl group. This is consistent with the results obtained by numerical fitting of the spectra. While this back of the envelope interpretation gives approximate values for the 1-bond coupling constants, we note that without the aid of numerical simulations it would for example be difficult to say with any certainty where spectrum of the $1-{ }^{13} \mathrm{C}$


Figure 6.6: Zero-Field Total Correlation Spectra acquired using the protocol in Fig. 6.4a. The 1D spectra on the axes correspond to the data in Fig. 6.5.
isotopomer ends and that of the $2-{ }^{13} \mathrm{C}$ isotopomer begins. Without computer assistance it would also not be possible to distinguish the $K=1 / 2$ peaks from the $K=3 / 2$ peaks in the $3 / 2 \mathrm{~J}$ multiplet associated with the $1-{ }^{13} \mathrm{C}$ isotopomer. However, not all spin systems are small enough that their Hamiltonians are readily diagonalizable, and in chemical analysis the exact coupling topology is not always known in advance.

### 6.4.2 ZF-TOCSY of Ethanol and Acetic Acid

Figures 6.6 a and 6.6 b show the ZF-TOCSY spectra of the ethanol mixture and the acetic acid sample acquired using the protocol in Fig. 6.4a. Both positive and negative frequencies are displayed in F1, whereas only the positive part of the F2 axis is shown. This is a consequence of the fact that the recorded signal is purely real, meaning that its Fourier Transform is conjugate symmetric. The spectra are displayed in magnitude mode, so to display all the spectral information it is therefore only necessary to plot two of the four


Figure 6.7: Detailed structure of the high-frequency multiplet in the ZF-TOCSY spectrum of $1-{ }^{13} \mathrm{C}$ ethanol. All peaks in this multiplet have $L=1$. The dashed and dotted lines are drawn to guide the eye to particular cross-peaks (which are marked by boxes) which confirm that the high intensity peak at 211 Hz actually consists of two overlapping resonances which belong to different $K$-manifolds.
quadrants of the Fourier transformed data. Overtones of the line noise lead to vertical streaks in the data at multiples of 60 Hz and a climate control fan causes building vibrations at $\sim$ 10.7 Hz . We do not know the origin of the feature at $\sim 8.7 \mathrm{~Hz}$. The 1D spectra in Fig. 6.5 have been plotted on the axes for reference. As expected there is no coherence transfer, and therefore no cross-peaks, between either the two isotopomers or peaks corresponding to the same isotopomer but different combinations of $K$ and $L$. This allows us to confirm the numerical assignment of the peaks made in Fig. 6.5. For example the peak at $\sim 238$ Hz in the ethanol spectrum in Fig. 6.6a clearly correlates to the 2J multiplet at around 250 Hz and therefore belongs to the $2{ }^{13} \mathrm{C}$ isotopomer. Similarly the peak at $\sim 125 \mathrm{~Hz}$ does not give cross peaks with any of the three other peaks in the 1 J multiplet, and it therefore must belong to a separate spin-manifold, consistent with the numerical assignment of the 125 Hz peak to $L=0$ and the three surrounding peaks to $L=1$. With the same reasoning the ZF-TOCSY spectrum of acetic acid in Fig. 6.6b can be used to distinguish between the three lower frequency peaks of the acetic acid $J$-spectrum, and confirm the numerical assignment of the peak at 31 Hz to the same spin-manifold as the peaks at 119 and 149 Hz .

As an example of transitions close in frequency and corresponding to the same pair of coupled spins behaving as if they are 'uncoupled' on account of belonging to different spinmanifolds, consider the high frequency multiplet of the $1-{ }^{13} \mathrm{C}$ isotopomer (at around $3 / 2 \mathrm{~J}$ in both F1 and F2) shown in more detail in Fig. 6.7. Fitting of the 1D data reveals that the high intensity peak at $\sim 211 \mathrm{~Hz}$ actually consists of two overlapping resonances with different $K$ quantum numbers. This is confirmed by the cross-peak pattern, as Fig. 6.7 shows that the 211 Hz peak correlates to both $K=1 / 2$ and $K=3 / 2$ resonances in F1. In this case 2D spectroscopy allows us to distinguish overlapping resonances by correlating them to distinct, well separated, peaks.

### 6.4.3 ZF-MQ Spectroscopy of Acetic Acid

As mentioned above, inspection of the energy-level diagram of acetic acid shown in Fig. 6.1 reveals a $K$ conserving, and therefore potentially observable, $\Delta F= \pm 2$ transition at $\sim 245 \mathrm{~Hz}$. The results of a ZF-MQ experiment designed to observe this transition in spite of it not corresponding to oscillating magnetization is shown in Fig. 6.8a. The data was acquired using the pulse sequence in Fig. 6.4b and the 1D data from Fig. 6.5, including the expected position of the MQ transition, has been plotted on both axes for convenience. The cross-peak pattern is mostly the same as in the zf-TOCSY spectrum in Fig. 6.6b, however there is one additional cross-peak in F 1 at 245 Hz corresponding to oscillations during $t_{1}$ at the frequency of the $\Delta F= \pm 2$ transition.

According to Eq. (6.1) only the $K=3 / 2$ manifold supports a $n=2$ transition. The MQ transition shows up only as a cross-peak to the transitions at $19 \mathrm{~Hz}, 38 \mathrm{~Hz}, 225 \mathrm{~Hz}, 265 \mathrm{~Hz}$, and 283 Hz , thus confirming the numerical assignment made in Fig. 6.5b of those peaks to the $K=3 / 2$ manifold. This is perhaps seen more clearly in Fig. 6.8 b which shows slices through the indirect dimension taken at the positions of the peaks in 1D spectrum. The MQ-resonance (the expected position is indicated with a pale band) clearly shows up in the indirectly detected data, but only in those spectra that are read out at the frequencies of the $K=3 / 2$ transitions.

We note that it is possible to start a zero-field NMR experiment with scalar order [30, 58], which already contains two-spin terms at time zero. Therefore, this could be turned into a two-pulse experiment if $\pi / 6$ pulses along z are used instead - since such pulses access scalar spin-order instead of vector spin-order [30].

### 6.4.4 Suggested Coherence Filter

It would be desirable to selectively excite or at least detect only those coherences for which $\Delta F=n$, where $n$ is a chosen coherence order. This would assist with assigning quantum-numbers, as the largest available $\Delta F$ value depends on spin-manifold, and it would also simplify the resulting spectra, since the number of transitions decrease rapidly with $n$. Existing schemes for selective excitation [123, 124] and filtration [133] based on $\Delta m$ rely on the fact that coherence operators in high-field have well defined symmetry with respect to


Figure 6.8: ZF-MQ spectra of ${ }^{13} \mathrm{C}_{2}$ acetic acid. (a) 2D ZF-MQ spectrum. F1 corresponds to the indirectly detected dimension, and the 1D spectrum in Fig. 6.5b has been plotted on both axes for reference. (b) Cuts through the 2D-spectrum in panel a. The x-axis corresponds to F1, and each spectrum is the projection of the data around a $\pm 0.5 \mathrm{~Hz}$ slice at the designated frequencies in the directly detected dimension (F2). The red bands indicate $\pm 245 \mathrm{~Hz}$, the expected frequency of the double-quantum transition. Note that for convenience the spectra are simply evenly spaced in the vertical dimension. The top panel shows the directly detected 1D $J$-spectrum.
rotations about the z-axis - a high-field $n^{\text {th }}$ order coherence is invariant with respect to a rotation of $2 \pi / n$ about the z-axis. Meanwhile, at zero-field, transitions in general involve changes in the total angular momentum of the state, not the projection on some axis. The total angular momentum of a spin-state is indicated by the tensor rank of the state. But while operator rank is conserved under free evolution at zero-field, since $H_{J}$ is scalar, the rank of a transition operator does not report on its zero-field coherence order in a unique way. Indeed, a zero-field $n^{\text {th }}$ order transition operator, $\left|F, m_{F}\right\rangle\left\langle F-n, m_{F}\right|$ may be decomposed into many spherical tensors [37] with ranks $|F+n-F|:+1|F+F-n|$. The lowest rank
a given transition operator may contain is thus equal to $\Delta F$ and the highest is $2 F-\Delta F$. In order to obtain simplified spectra one could imagine a using phase-cycling scheme similar to Spherical Tensor Analysis (STA)[134] to filter out components of rank lower than $n$ and higher than $2 F-n$, which would increase the relative intensity of $n$-quantum transitions. However, dipole allowed transitions with $\Delta F=0, \pm 1$ may also contain components with ranks equal to or higher than $n$, so such a filtering process would therefore not suppress allowed transitions entirely.

The same fact that prevents selective filtering of ZF-MQ coherences also prevents selective excitation [123, 124]. Assuming that one can implement an ideal average Hamiltonian of rank $n$, the propagator to second order in time would still contain all ranks from 0 to $2 n$, so beyond the short time limit such a Hamiltonian would still excite the entire spectrum.

Indeed, from the point of view of spectral simplification it might be more fruitful to use an isotropic filtration phase-cycle as described by Pileio and Levitt [135], which retains only those signal components that are rank-0 during $t_{1}$ evolution. If applied to a zero-field experiment the resulting spectrum would consist only of those transitions for which $\Delta F=0$, since only such coherence operators may contain rotationally invariant rank-0 components. There are only two such transitions in the case of ${ }^{13} \mathrm{C}_{2}$-acetic acid (at $\sim 118 \mathrm{~Hz}$, and $\sim 264$ Hz ), so such a phase-cycle would provide an alternative route to spectral simplification. However, in order to implement either isotropic filtering or STA one needs to be able to effect global rotations of the entire spin system with arbitrary angles, and for a zero-field system this remains an unsolved problem. Additionally, the application of a multi-step phase cycle to an indirectly detected spectrum would be a practical challenge.

The result of attempted rank-selective excitation is demonstrated in Fig. 6.9a which is a ZF-MQ spectrum of ${ }^{13} \mathrm{C}_{2}$ acetic acid, but acquired using the effective excitation Hamiltonian

$$
\begin{equation*}
\bar{H}_{D Q}^{1}=\left({ }^{1} J_{\mathrm{CH}} / 2\right)\left(K_{+} S_{A,+}+K_{-} S_{A,-}\right)+\left({ }^{3} J_{\mathrm{CH}} / 2\right)\left(K_{+} S_{B,+}+K_{-} S_{B,-}\right), \tag{6.2}
\end{equation*}
$$

which is implemented using a series of DC pulses $(x y \bar{y} \bar{x})_{n}$, where $x$ and $y$ denote $\pi$ pulses on carbon and the overbars denote reversals of the direction of the pulse. See Appendix 7.6 for a description of how to calculate the effect of this pulse sequence. Such a 'doublequantum' Hamiltonian would excite only even orders of coherence in a high-field system. The spectrum in Fig. 6.9a is the same kind of data as in Fig. 6.8b, but all the individual spectra have been added together. While the $n=2$ transition is successfully excited, it is clear that no selectivity has been gained over excitation with two-pulses and a delay as in Fig. 6.8, consistent with the argument made above.

In contrast, to demonstrate the theoretical benefits of isotropic coherence filtration Figures 6.9b-d show simulated ZF-MQ spectra resulting from the application of an isotropic-filter phase-cycle, which averages to zero components of the coherence operators that during $t_{1}$ have ranks up to 2 (b), 3 (c), and 4 (d) [135]. The largest rank supported by any coherence operator in this spin system is 4 , and consequently there is no reason to average higher rank terms. The peak at $\sim 149 \mathrm{~Hz}$ corresponds to an $F=1 / 2 \rightarrow F=3 / 2$ transition and the corresponding coherence operator may only contain ranks 1 and 2 . This peak disappears


Figure 6.9: (a) Experimental ZF-MQ spectrum acquired using a rank-2 excitation Hamiltonian. (b) Simulated spectra showing the effect of a tetrahedral isotropic-filtering phase cycle. (c) Simulated octahedral phase cycle. (d) Simulated icosahedral phase cycle.
completely when operators up to rank-2 are filtered out using a 12 step cycle. The $n=2$ coherence may only contain ranks 2 and 3 , and disappears when operators up to rank- 3 are averaged out using a 24 step cycle, and when operators up to rank- 4 are filtered out with a 60 step cycle only the two peaks remain which correspond to $\Delta F=0$ transitions. While we are not yet able to selectively filter transitions based on $n$ for $n>0$, it seems isotropic filtering would allow spectral simplification by retaining only those transitions for which $n=0$. Note that the filtering has to be performed on the indirectly detected dimension, since only rank-1 components of the coherence operators correspond to observable magnetization.

We note in passing that, just as in high-field, the rank of a coherence operator reports on the minimum number of correlated spins in the corresponding state. In high field this has been used to investigate spin cluster size and perform many-body physics experiments. The number of phase-cycle steps required to suppress a zero-field transition (plotted vs preparation time) could similarly be used to monitor information transport in spin clusters connected with a Heisenberg-like isotropic Hamiltonian, which is something that has proven challenging to realize experimentally in other systems.

### 6.5 Conclusions

We have shown that direct detection using DC field sensors facilitates 2D zero-field NMR correlation spectroscopy, and how such techniques simplify assignment of crowded $J$-spectra.

The complete coherence transfer enabled by the isotropic zero-field Hamiltonian ensures that cross peaks in the ZF-TOCSY spectrum are seen between all peaks belonging to the same spin-manifold. Consequently, ZF-TOCSY may be used not only to distinguish between different molecules, or different ${ }^{13} \mathrm{C}$ isotopomers of the same molecule, but also to facilitate zero-field spectral assignment of a given isotopomer by providing an easy way to determine if two transitions are labeled with the same quantum numbers. Additionally, 2D-spectroscopy always increases the maximum attainable spectral resolution by introducing a second spreading parameter in the spectrum. In particular, the ability to resolve otherwise overlapping peaks significantly increases the power of zero-field NMR for chemical fingerprinting, beyond what can be obtained with the narrow linewidths associated with high homogeneity zero-field environments.

We have also introduced the concept of multiple-quantum transitions in zero-field NMR (ZF-MQ) and shown that such transitions may only belong to particular spin-manifolds. Therefore, by observing which peaks correlate to a multiple-quantum transition, one can assign quantum numbers to those peaks. Finally, we have suggested a possible means to filter zero-field coherences based on $\Delta F$, but this remains an outstanding experimental challenge.

## Chapter 7

## Homonuclear J-Coupling Spectroscopy Via ${ }^{13}$ C-Decoupling

We present in this chapter a two-dimensional method for obtaining ${ }^{13} \mathrm{C}$-decoupled, ${ }^{1} \mathrm{H}$ coupled, Nuclear Magnetic Resonance (NMR) spectra in zero magnetic field using coherent spin-decoupling. The result is a spectrum determined only by the proton-proton $J$-coupling network. Detection of NMR signals in zero magnetic field requires at least two different nuclear spin species but the pure proton $J$-spectrum is independent of isotopomer. Thus, the ability to acquire such spectra may simplify spectra and thereby improve the analytical capabilities of zero-field NMR. The protocol does not rely on a difference in Larmor frequency between the coupled nuclei, allowing for the direct determination of $J$-coupling constants between chemically equivalent spins. We obtain the ${ }^{13} \mathrm{C}$-decoupled zero-field spectrum of $\left[1-{ }^{13} \mathrm{C}\right]$-propionic acid and identify conserved quantum numbers governing the appearance of cross peaks in the two-dimensional spectrum.

The material in this chapter has previously been published under the title

- ${ }^{13}$ C-Decoupled J-coupling Spectroscopy Using Two-Dimensional Nuclear Magnetic Resonance at Zero-Field by Sjolander, Tayler, Kentner, Budker, and Pines [2].


### 7.1 Background and Motivation

As we saw in Section 2.3 one of the key requirements for obtaining $J$-spectra is the existence of couplings between more than one spin species in the molecule of interest, for example ${ }^{13} \mathrm{C}$ and ${ }^{1} \mathrm{H}$. If a coupled spin system comprises only one type of nucleus (e.g. all ${ }^{1} \mathrm{H}$ spins) the Hamiltonian commutes with the operator for the total magnetization of the system, which therefore must be time-independent. Consequently, homonuclear $J$-spectra at zero-field have until now been unavailable.

In this chapter, we introduce an indirect two-dimensional approach for obtaining ${ }^{13} \mathrm{C}$ decoupled ${ }^{1} \mathrm{H}$-coupled $J$-spectra in ZULF NMR. The presence of a secondary spin species in the molecule, e.g. ${ }^{13} \mathrm{C}$, is still required, but it is made "invisible" by averaging out its couplings to the other nuclei while the pure proton $J$-spectrum is encoded. This is termed homonuclear $J$-spectroscopy. Such spectra are of interest in ZULF NMR, since the $J$ spectrum corresponding to isotopomers of the same molecule are entirely different [48]. While a ${ }^{13} \mathrm{C}$, or some other heteronucleus, is necessary in order to detect $J$-spectra, the proton $J$ spectrum is independent of the location of the label. Homonuclear $J$-spectroscopy therefore offers significant practical advantages for the study of molecules that are not isotopically enriched and thus are made up of mixtures of isotopomers. Decoupling of heteronuclear interactions also simplifies crowded ZULF-NMR spectra, and allows accurate determination of homonuclear $J$-couplings in the presence of heteronuclear couplings even if they are of similar magnitude. With 2D detection we retain information on the location of the ${ }^{13} \mathrm{C}$ label. We also note that in zero-field all spins have zero Larmor frequency, thus our method allows direct determination of $J$-coupling constants between chemically equivalent protons, which is a problem that has attracted interest over the past years [136, 137]. Indeed our protocol should work for strongly coupled systems in high-field as well, though without the advantage in resolution offered by ZULF.

### 7.2 Pulses and Decoupling

While the methods for spin-control control introduced in Chapters 4 and 5 allow for added selectivity and flexibility DC pulses remain the fastest way to manipulate spins at zero field. In this dissertation we achieve $30 \mu$ s pulse times for a $\pi$ rotation on carbon-13 using DC pulses, while both the resonant pulses in Chapter 4 and the adiabatic remagnetization pulses in Chapter 5 have durations of 0.1 to 1 s . This matters when trying to implement coherent averaging protocols like the ones introduced here. As shown in Chapter 8 the success of average Hamiltonian theory in describing the evolution over a cyclic pulse sequence depends on the internal timescale of the Hamiltonian relative to the cycle time. The cycle time in turn depends on how fast the pulses can rotate the spins. Since DC pulses enable faster spin manipulations, they will also result in more efficient spin-decoupling, as well as the successful decoupling of larger interactions, assuming a suitable pulse sequence can be built from completely non-selective broad-band pulses.

Remember that during a DC pulse the spin system is primarily governed by the Hamiltonian

$$
\begin{equation*}
H_{p}=\sum_{i} \gamma_{i} \boldsymbol{B} \cdot \boldsymbol{I}_{i} \tag{7.1}
\end{equation*}
$$

where $\boldsymbol{B}$ is the pulse field, $\gamma_{i}$ is the gyromagnetic ratio of spin $i$, and the sum runs over all the spins in the sample. The $J$-coupling terms have been ignored, as for the pulse fields used in this work we have $\left|\gamma_{i} \boldsymbol{B}\right| \gg|J|$. A DC pulse rotates all spins in the sample proportionally to their gyromagnetic ratios. For a ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}$ system limited isotope selectivity can be achieved by exploiting the particular gyromagnetic ratios involved, $\gamma_{\mathrm{H}} / \gamma_{\mathrm{C}} \approx 3.98$, meaning a $\pi$ pulse on ${ }^{13} \mathrm{C}$ is close to an identity operation on ${ }^{1} \mathrm{H}$. Selective inversion of ${ }^{13} \mathrm{C}$ spins is a common method for preparing evolving spin states in ZULF NMR [44]. In this work we also use sequences built from such quasi-selective ${ }^{13} \mathrm{C} \pi$ rotations to perform coherent spin-decoupling.

The pulse sequence $(\tau / 2-x-\tau-y-\tau-x-\tau-y-\tau / 2)_{n} \equiv \mathrm{XY} 4$, where $x$ and $y$ denote $\pi$ pulses along the corresponding axes and $\tau$ is the pulse spacing, averages to zero terms in the Hamiltonian linear in the spin-operator for spins properly rotated by the pulses [138]. The $J$-coupling Hamiltonian, $H_{I S}=2 \pi J \boldsymbol{I} \cdot \boldsymbol{S}$, where $\boldsymbol{I}$ and $\boldsymbol{S}$ are angular momentum operators, is linear in each coupled spin. Thus, to first order in average Hamiltonian theory [78] application of $\mathrm{XY}_{4}$ averages ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C} J$-couplings to zero, giving $\bar{H}_{I S}^{1}=0$ [139-141]. This assumes the pulse angles are chosen to be $\pi$ pulses on ${ }^{13} \mathrm{C}$.

However, the fact that the gyromagnetic ratios of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ are not integer multiples of one another introduces a systematic flip angle error to each pulse. To deal with this, as well as other issues of experimental implementation, we use a modified version of XY4, to be presented in a forthcoming publication

$$
\left(\begin{array}{llllllll}
x y \bar{x} \bar{y} & \bar{x} \bar{y} x y & \bar{x} y x \bar{y} & x \bar{y} \bar{x} y & \bar{y} x y \bar{x} & y \bar{x} \bar{y} x & \bar{y} \bar{x} y x & y x \bar{y} \bar{x})_{n} . \tag{7.2}
\end{array}\right.
$$

The overbar indicates reversal of the direction of the pulse and all pulses have the same duration and spacing. The four-pulse sub-cycles in (7.2) are separated for clarity.

### 7.3 Pulse Sequence for Homonuclear $J$-Spectroscopy

Our pulse sequence for detection of homonuclear $J$-spectra in zero-field consists of two preparatory steps: a single DC pulse to initialize zero-field evolution and a mixing period during which the system is allowed to evolve freely in order to build up the desired coherences. The preparation steps are followed by a period of spin-decoupling for a variable time $\left(t_{1}\right)$ and finally free evolution during which time the signal is detected $\left(t_{2}\right)$. Data are collected as a function of $t_{1}$ and $t_{2}$ and subjected to a 2D Fast Fourier Transform. Current ZULF hardware necessitates the use of 2D-detection due to the large ( $\sim 30 \mathrm{~ms}$ ) dead time after each pulse (See Section 3.1.5). The protocol is summarized in Fig. 7.1.

We will now outline the spin dynamics during each stage of the pulse sequence in turn, from the point of view of a general carbon/proton spin system. The liquid-state zero-field

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Figure 7.1: Schematic representation of the acquisition protocol presented in the text with the Hamiltonian governing the spin system evolution at each stage identified.
spin Hamiltonian may be written in terms of heteronuclear and homonuclear parts as

$$
\begin{align*}
H_{J}= & 2 \pi \sum_{i, n} J_{i n} \boldsymbol{I}_{i} \cdot \boldsymbol{S}_{n}+2 \pi \sum_{i>j} J_{i j} \boldsymbol{I}_{i} \cdot \boldsymbol{I}_{j} \\
& +2 \pi \sum_{n>m} J_{n m} \boldsymbol{S}_{n} \cdot \boldsymbol{S}_{m},  \tag{7.3}\\
= & H_{I S}+H_{I I}+H_{S S},
\end{align*}
$$

where the $\boldsymbol{I}_{i}$ and $\boldsymbol{S}_{n}$ are angular momentum operators for the proton and carbon spins respectively. The $J_{i n}$ are heteronuclear coupling constants, while the $J_{i j}$ and $J_{n m}$ describe the homonuclear couplings. The goal of homonuclear $J$-spectroscopy is to observe the spectrum corresponding only to the average Hamiltonian $\bar{H}_{J}^{1}=H_{I I}+H_{S S}$, which can be implemented by means of (7.2). For the important case of a hydrocarbon with a single ${ }^{13} \mathrm{C}$ label, $H_{S S}$ is zero and the homonuclear part is reflective only of the proton-proton $J$-coupling network, $H_{I I}$. The goal of the preparatory steps in the sequence in Fig. 7.1 is to generate a density operator which is non-stationary not just with respect to $H_{J}$, but also the spin decoupled Hamiltonian $\bar{H}_{J}^{1}$.

The experiment must start with a spin-polarized state. In general there may be two kinds of spin order present at the start of a liquid state ZULF experiment, scalar order and vector order [30, 49]. Magnetic field pulses along the detector axis converts scalar order into observable coherences, pulses transverse to the detector axis convert vector order into coherences [30]. We consider the vector order along the z-axis originating in a pre-polarizing permanent magnet and initiate zero-field evolution by inverting the carbon spin polarization via a transverse DC magnetic-field pulse, calibrated to effect a $\pi$ rotation on ${ }^{13} \mathrm{C}$ and a $\sim 4 \pi$ rotation on ${ }^{1} \mathrm{H}$. After the pulse the part of the density operator containing observable coherences is

$$
\begin{equation*}
\rho^{\prime}(0) \propto\left(\sum_{i} I_{i, z}-\sum_{n} S_{n, z}\right) . \tag{7.4}
\end{equation*}
$$

We note that vector spin order may not be converted into a spin state that evolves under $\bar{H}_{J}^{1}$ by means of a magnetic field pulse since the negligibly small chemical shifts make the protons equivalent during the application of the pulse,

$$
\begin{equation*}
\left[\mathrm{e}^{-\mathrm{i} H_{p} t} \rho^{\prime}(0) \mathrm{e}^{\mathrm{i} H_{p} t}, \bar{H}_{J}^{1}\right]=0 . \tag{7.5}
\end{equation*}
$$

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${ }^{13}$ C-DECOUPLING
However, if the protons are magnetically inequivalent, meaning their couplings to the ${ }^{13} \mathrm{C}$ nucleus are different, then evolution under $H_{I S}$ generates the desired coherences. In effect the ${ }^{13} \mathrm{C}$ nucleus is used to perform a selective pulse [142], affecting the two groups of protons differently.

$$
\begin{align*}
& \rho^{\prime \prime}(0)=\mathrm{e}^{-\mathrm{i} H_{J} t_{\mathrm{m}}} \rho^{\prime}(0) \mathrm{e}^{\mathrm{i} H_{J} t_{\mathrm{m}}}  \tag{7.6}\\
& {\left[\rho^{\prime \prime}(0), \bar{H}_{J}^{1}\right] \neq 0 .} \tag{7.7}
\end{align*}
$$

Following the mixing period, $t_{\mathrm{m}}$, spin decoupling is turned on and the system is allowed to build up phase for a time $t_{1}$ while evolving purely under $\bar{H}_{J}^{1}$

$$
\begin{equation*}
\rho^{\prime \prime}\left(t_{1}\right)=\mathrm{e}^{-\mathrm{i} \bar{H}_{J}^{1} t_{1}} \rho^{\prime \prime}(0) \mathrm{e}^{\mathrm{i} \bar{H}_{J}^{1} t_{1}} . \tag{7.8}
\end{equation*}
$$

The signal is acquired by measuring the total z-magnetization $M_{z}$ as a function of free evolution time, $t_{2}$

$$
\begin{equation*}
S\left(t_{1}, t_{2}\right)=\operatorname{Tr}\left\{M_{z}^{\dagger} \mathrm{e}^{-\mathrm{i} H_{J} t_{2}} \rho^{\prime \prime}\left(t_{1}\right) \mathrm{e}^{\mathrm{i} H_{J} t_{2}}\right\} \tag{7.9}
\end{equation*}
$$

and the 2D Fourier transform of the data gives the spectrum corresponding to $\bar{H}_{J}^{1}$, termed the homonuclear $J$-spectrum, along the indirect dimension $\mathrm{F}_{1}$.

### 7.4 Homonuclear J-Spectroscopy

To demonstrate the technique we used a home-built ZULF NMR spectrometer based on $a^{87} \mathrm{Rb}$ vapor-cell magnetometer (see Chapter 3) and a sample of $\left[1-{ }^{13} \mathrm{C}\right]$-propionic acid. Ignoring the hydroxyl proton, which exchanges rapidly on the $J$-coupling timescale, the atoms in this molecule comprise a spin system of two magnetically inequivalent groups of protons coupled to a single carbon-13, see Fig. 7.2. The $J$-coupling Hamiltonian may be written as

$$
\begin{equation*}
H_{J} / 2 \pi={ }^{2} J_{\mathrm{CH}} \boldsymbol{K} \cdot \boldsymbol{S}+{ }^{3} J_{\mathrm{CH}} \boldsymbol{L} \cdot \boldsymbol{S}+{ }^{3} J_{\mathrm{HH}} \boldsymbol{K} \cdot \boldsymbol{L}, \tag{7.10}
\end{equation*}
$$

where $\boldsymbol{K}$ and $\boldsymbol{L}$ are the total angular momentum operators for the two proton groups and $\boldsymbol{S}$ corresponds to the carbon spin. The sequence (7.2) generates the average Hamiltonian $\bar{H}_{J}^{1}=2 \pi{ }^{3} J_{\mathrm{HH}} \boldsymbol{K} \cdot \boldsymbol{L}$ (See Appendix 7.6).

The data are conveniently analyzed in terms of the quantum numbers $K$ and $L$, corresponding to the eigenvalues of the operators $\boldsymbol{K}^{2}$ and $\boldsymbol{L}^{2}$ respectively. These quantum numbers are conserved throughout the entire acquisition protocol, since both operators commute with all of $H_{J}, H_{p}$, and $\bar{H}_{J}^{1}$. This follows from $\boldsymbol{K}$ and $\boldsymbol{L}$ both being the angular momenta of magnetically equivalent groups of protons.

The non-decoupled zero-field $J$-spectrum of $\left[1-{ }^{13} \mathrm{C}\right]$-propionic acid is presented in Fig. 7.3 with the corresponding energy level diagram shown in Fig. 7.2a. The transitions predicted by exact diagonalization of $H_{J}$ were fit in the least-squares sense to the measured spectrum, giving the following $99.9 \%$ confidence levels for the $J$-coupling constants: ${ }^{2} J_{\mathrm{CH}}=-7.084 \pm 0.002$ $\mathrm{Hz},{ }^{3} J_{\mathrm{CH}}=5.497 \pm 0.003 \mathrm{~Hz}$, and ${ }^{3} J_{\mathrm{HH}}=7.563 \pm 0.006 \mathrm{~Hz}$, see Section 3.5


Figure 7.2: (a) Energy level diagram for propionic acid. (b) Effective energy level diagram during the decoupling. In both cases the states have been labeled with the quantum number for total angular momentum of the spin system, $F$. Allowed transitions have $\Delta F= \pm 1,0$ and are marked with arrows. In addition the angular momentum of groups of equivalent spins is conserved, so the transitions are also grouped according to their $K$ and $L$ values. The color coding is used in later figures. Additional degeneracies have been suppressed for clarity.

We recorded the ${ }^{13} \mathrm{C}$-decoupled, ${ }^{1} \mathrm{H}$-coupled $J$-spectrum of propionic acid following the protocol outlined in Fig. 7.1. The numerically optimized mixing time was 350 ms . After the preparation steps the carbon spin was decoupled from the rest of spin system using (7.2) for a time $t_{1}$ ranging from 0 to 1.8 s , in steps of 17.6 ms . Each pulse had a duration of 200 us and the delay between pulses was 2.0 ms . After the decoupling period the signal was detected under free evolution for 10 s .

The Fourier-transformed 2D dataset is shown in Fig. 7.4 with the spectrum corresponding to the proton-proton $J$-couplings along the carbon decoupled dimension, $\mathrm{F}_{1}$, and the full $J$-spectrum along $\mathrm{F}_{2}$. A $1 \mathrm{D}{ }^{13} \mathrm{C}$-decoupled spectrum was reconstructed by projecting all data points in the shaded red region onto $\mathrm{F}_{1}$. The result is plotted in black in Fig. 7.4 and reveals the first example of a purely homonuclear $J$-spectrum. Following the work in Ref. [48] the characteristic frequencies of $\bar{H}_{J}^{1}=2 \pi^{3} J_{\mathrm{HH}} \boldsymbol{K} \cdot \boldsymbol{L}$ can be readily evaluated. We have $K=\{0,1\}$ (two protons) and $L=\{1 / 2,3 / 2\}$ (three protons) and the spectrum should consist of one peak at $3 / 2{ }^{3} J_{\mathrm{HH}}$ and one peak at $5 / 2^{3} J_{\mathrm{HH}}$. Fitting the transitions predicted by $\bar{H}_{j}^{1}$ to the reconstructed $1 \mathrm{D}{ }^{13} \mathrm{C}$-decoupled spectrum gives ${ }^{3} J_{\mathrm{HH}}=7.61 \pm 0.07 \mathrm{~Hz}$, consistent with the value obtained from the full 1D $J$-spectrum at this level of confidence. Small shifts may result from incomplete decoupling. The individual peak positions were determined to be $11.4 \pm 0.7 \mathrm{~Hz}$ and $19.0 \pm 0.6 \mathrm{~Hz}$. The ${ }^{13} \mathrm{C}$-decoupled spectrum consists of two distinct lines, described by a single parameter, as opposed to $14+$ lines described by three parameters for the ${ }^{13} \mathrm{C}$-coupled spectrum in Fig. 7.3. The decoupling thus significantly simplifies fitting and interpretation. In the context of chemical analysis, assuming spins other than ${ }^{13} \mathrm{C}$ and ${ }^{1} \mathrm{H}$

Full $J$-Spectrum


Figure 7.3: Zero-field NMR $J$-spectrum for $\left[1-{ }^{13} \mathrm{C}\right]$-propionic acid. The superposed stick spectrum corresponds to diagonalization of $H_{J}$, using numerically optimized values for the coupling constants. Each transition has been assigned $K$ and $L$ quantum numbers and color coded according to the scheme in the energy level diagram in Fig. 7.2. The spectrum is the sum of 2500 transients and the magnitude of each transient was $\sim 30 \mathrm{fT}$.
can be ruled out, the ${ }^{13} \mathrm{C}$-decoupled spectrum unambiguously corresponds to an ethyl group. In addition, the exact value of the coupling constant is a sensitive reporter on both the intraand inter- molecular chemical environment [143, 144].

The location of the cross peaks may be explained by comparing the quantum numbers for each transition during the decoupling with those in a free molecule. Inspecting the energy level diagrams in Fig. 7.2 we see that only eigenstates with $K=1$ may give cross peaks in the 2D spectrum as there are no transitions with $K=0$ in the energy level diagram for $\bar{H}_{J}^{1}$. We also note that peaks with $L=1 / 2$ may only give cross peaks at $3 / 2{ }^{3} J_{\mathrm{HH}}$, while peaks with $L=3 / 2$ may give cross peaks at both $3 / 2{ }^{3} J_{\mathrm{HH}}$ and $5 / 2{ }^{3} J_{\mathrm{HH}}$.

There are strong peaks at 5.47 Hz and 10.94 Hz in the 1D propionic-acid spectrum assigned to $K=0$. Consistent with the argument made above, these peaks give no discernible cross peaks in the 2 D spectrum. The rest of the spectrum also conforms to the expected behavior. For example the peak at 5.76 Hz is assigned to $K=1, L=3 / 2$, and may therefore give cross peaks at both $3 / 2{ }^{3} J_{\mathrm{HH}}$, and $5 / 2^{3} J_{\mathrm{HH}}$ in the decoupled dimension. These peaks are partially overlapping in the 1D spectrum, but the 5.76 Hz peak gives strong cross peaks, thereby simplifying assignment. Similarly the two peaks at 13.05 Hz and 13.75 Hz are partially overlapping in the 1D spectrum but are clearly distinct in the correlation spectrum, as the cross peaks occur on different sides of 0 in $\mathrm{F}_{1}$.

We also note the presence of vertical streaks, also known as $\mathrm{F}_{1}$ noise, in the data at 8.65 Hz and 10.9 Hz . The appearance of these features means their phase is uncorrelated with the evolution period $t_{1}$, implying they do not correspond to spin dynamics. We note that a climate control fan causes low-amplitude building vibrations at 10.9 Hz , which are picked up by our detector. This feature becomes negligible when enough scans are taken, as in Fig.

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Figure 7.4: Experimental 2D detected zero-field NMR spectrum of $\left[1-{ }^{13} \mathrm{C}\right]$-propionic acid, recorded using the pulse sequence in Fig. 7.1. $\mathrm{F}_{2}$ corresponds to the full zero-field $J$-spectrum and $\mathrm{F}_{1}$ to the ${ }^{1} \mathrm{H}$-only $J$-spectrum. In $\mathrm{F}_{1}$ there are two peaks at $3 / 2{ }^{3} J_{\mathrm{HH}}=11.4 \pm 0.7 \mathrm{~Hz}$ and $5 / 2{ }^{3} J_{\mathrm{HH}}=19.0 \pm 0.6 \mathrm{~Hz}$. The stick spectra are the results of numerical diagonalization of $H_{J}$ $\left(\mathrm{F}_{2}\right)$ and $\bar{H}_{J}^{1}\left(\mathrm{~F}_{1}\right)$
7.3, but this is not feasible in a 2D-detected experiment. We do not know the cause of the feature at 8.65 Hz .

### 7.5 Conclusions

In conclusion, this chapter describes the first demonstration of heteronuclear spin-decoupling in ZULF NMR and we obtained the first isotopically pure $J$-spectrum by introducing the concept of homonuclear $J$-spectroscopy in zero-field. The two-dimensional scheme used for detection helps with spectral assignment and circumvents the dead time imposed by current ZULF detection hardware.

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The proton-only $J$-spectrum of $\left[1-{ }^{13} \mathrm{C}\right]$-propionic acid is significantly simpler to interpret than the full $J$-spectrum, while still providing the same chemical information. This demonstrates the promise of our approach for the analysis of more complicated molecules. Moving forward, we expect ${ }^{13} \mathrm{C}$-decoupling to become an important part of ZULF NMR, as it provides chemically distinct spectra no matter which part of the molecule is ${ }^{13} \mathrm{C}$ labeled. This opens the door for unambiguous ZULF NMR of molecules at natural isotopic abundance, provided the requisite sensitivity could be attained.

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${ }^{13} \mathrm{C}$-DECOUPLING

### 7.6 Appendix I: Calculation of $\bar{H}_{J}^{1}$

In the limit of delta function pulses the first order average Hamiltonian [78] during the application of a cyclic pulse sequence can be calculated as

$$
\begin{equation*}
\bar{H}^{1}=\sum_{i=1}^{n} \frac{t_{i}}{t_{c}} \tilde{H}_{i} \tag{7.11}
\end{equation*}
$$

where $t_{i}$ is the $i^{\text {th }}$ pulse spacing, $t_{c}$ is the cycle time, and $\tilde{H}_{i}$ is the Hamiltonian in the so called toggling frame

$$
\begin{equation*}
\tilde{H}_{i}=P_{1}^{\dagger} P_{2}^{\dagger} \ldots P_{i}^{\dagger} H P_{i} \ldots P_{2} P_{1} \tag{7.12}
\end{equation*}
$$

$P_{i}$ is the propagator for the $i^{\text {th }}$ pulse. In this work we wish to average to zero couplings involving the $S$ spin, this is accomplished by means of a pulse sequence based on the following sub cycle

$$
\begin{equation*}
P_{x}-\tau-P_{y}-\tau-P_{x}-\tau-P_{y}-\tau \tag{7.13}
\end{equation*}
$$

where $\tau$ is the pulse spacing. $P_{x / y}$ are propagators for DC pulses that perform a $\pi$ rotation on ${ }^{13} \mathrm{C}$. They are defined as $P_{x / y}=\mathrm{e}^{-\mathrm{i}\left(\pi S_{x / y}+4 \pi K_{x / y}+4 \pi L_{x / y}\right)}$. Using this definition the toggling frame Hamiltonians in Eq. (7.12) can be evaluated for the case of $H_{J}$

$$
\begin{aligned}
& H_{1} / 2 \pi={ }^{2} J_{\mathrm{CH}}\left(K_{x} S_{x}-K_{y} S_{y}-K_{z} S_{z}\right)+{ }^{3} J_{\mathrm{CH}}\left(L_{x} S_{x}-L_{y} S_{y}-L_{z} S_{z}\right) \\
& +{ }^{3} J_{\mathrm{HH}}\left(K_{x} L_{x}+K_{y} L_{y}+K_{z} L_{z}\right) \\
& H_{2} / 2 \pi={ }^{2} J_{\mathrm{CH}}\left(-K_{x} S_{x}-K_{y} S_{y}+K_{z} S_{z}\right)+{ }^{3} J_{\mathrm{CH}}\left(-L_{x} S_{x}-L_{y} S_{y}+L_{z} S_{z}\right) \\
& +{ }^{3} J_{\mathrm{HH}}\left(K_{x} L_{x}+K_{y} L_{y}+K_{z} L_{z}\right) \\
& H_{3} / 2 \pi={ }^{2} J_{\mathrm{CH}}\left(-K_{x} S_{x}+K_{y} S_{y}-K_{z} S_{z}\right)+{ }^{3} J_{\mathrm{CH}}\left(-L_{x} S_{x}+L_{y} S_{y}-L_{z} S_{z}\right) \\
& +{ }^{3} J_{\mathrm{HH}}\left(K_{x} L_{x}+K_{y} L_{y}+K_{z} L_{z}\right) \\
& H_{4} / 2 \pi={ }^{2} J_{\mathrm{CH}}\left(K_{x} S_{x}+K_{y} S_{y}+K_{z} S_{z}\right)+{ }^{3} J_{\mathrm{CH}}\left(L_{x} S_{x}+L_{y} S_{y}+L_{z} S_{z}\right) \\
& +{ }^{3} J_{\mathrm{HH}}\left(K_{x} L_{x}+K_{y} L_{y}+K_{z} L_{z}\right) .
\end{aligned}
$$

Given $t_{c}=4 \tau$, Eq. (7.11) evaluates to $\bar{H}_{J}^{1}=2 \pi^{3} J_{\mathrm{HH}} \boldsymbol{K} \cdot \boldsymbol{L}$.
The same procedure can be used to show that the pulse sequence

$$
\begin{equation*}
P_{x}-\tau-P_{y}-\tau-P_{y}^{\dagger}-\tau-P_{x}^{\dagger}-\tau \tag{7.14}
\end{equation*}
$$

which is used in Chapter 6, turns $J \boldsymbol{I} \cdot \boldsymbol{S}$ into $(J / 2)\left(I_{+} S_{+}+I_{-} S_{-}\right)$.

## Chapter 8

## Rank Selective Decoupling

Here we expand the decoupling capabilities introduced in the previous chapter. We demonstrate a method enabling the acquisition of zero-field $J$-spectra even in the presence of magnetic fields. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ spins may simultaneously be decoupled from an external magnetic field while persevering their mutual $J$-coupling by using pulse sequences that target the interaction rank rather than individual spin species. We also demonstrate an improved version of the spin-decoupling experiment introduced in Chapter 7 and use improved pulsing hardware to obtain homonuclear $J$-spectra of molecules with 10 x larger $J$-couplings than achieved in Chapter 7.

The material in this chapter is being prepared for publication under the title

- Rank Selective Decoupling of Heteronuclear Systems in Zero-Field Nuclear Magnetic Resonance by Sjolander, Tayler, Ajoy, Budker, and Pines [145].


### 8.1 Background and Motivation

Selective decoupling of spin interactions has been one of the premier tools of Nuclear Magnetic Resonance (NMR) spectroscopy for decades. For example almost all high-field heteronuclear spectra are taken with broadband proton decoupling, magic angle spinning to decouple magnetic dipole-dipole interactions forms the basis of most solid state techniques, while Carr-Purcell trains are relied on to deal with field inhomogeneities. Additionally, over the past decade dynamical decoupling has attracted interest in the quantum information community, where decoupling of system-environment interactions is used to extend coherence times.

In this chapter we demonstrate coherent control of NMR systems in the zero to ultra-low field regime, where interactions with external fields are weaker than the spin-spin couplings. Under such conditions simplifications often used in high-field NMR no longer apply: interactions are not truncated with respect to the applied field axis (the so called secular approximation does not hold), meaning all components of the interaction tensors must be considered. In addition, as the field approaches zero, the spectral width becomes small with respect to the bandwidth of fast control pulses - resulting in the loss of spin-species selectivity.

To take full advantage of the resolution afforded by zero-field $J$-spectroscopy one requires residual magnetic fields smaller than the lifetime limited resonance linewidths. This is generally achieved using several layers of mu-metal shielding plus a ferrite layer as well as additional shimming of the residual field. This puts limitations on the size (the inner most shield need to be a certain distance removed from the cell in order to to limit Johnson noise, as well as from the coils, to prevent the shield from becoming permanently magnetized), and cost (mu-metal is expensive) of the instrumentation. Recently ultralow and intermediate field $(2 \pi J \approx \gamma B)$ NMR has been performed using unshielded magnetometers for detection [146]. The ability to decouple the residual fields using electromagnetic coils while retaining isotropic heteronuclear $J$-couplings would enable such instrumentation to be used for high resolution zero-field $J$-spectroscopy, thereby further reducing the instrumentation foot-print of zero-field NMR. In this chapter we present such a method for decoupling a heteronuclear nonsecular NMR system from residual fields, while simultaneously detecting true zero-field $J$-spectra. The inability to independently manipulate protons and carbons using pulses at zero-field puts stringent conditions on the allowed flip-angles.

We already demonstrated coherent decoupling of spin-spin interaction in Chapter 7. However technical limitations (in particular fairly long pulse-times) ensured that the technique could only be applied to molecules with $J$-couplings smaller than 10 Hz . In this chapter we demonstrate how improved pulsing hardware (described in Section 3.4.3) enables homonuclear $J$-spectroscopy of molecules with $130 \mathrm{~Hz} J$-couplings. We will also briefly discuss some features of the pulse sequence which makes it useful specifically for $J$-coupling.

### 8.2 Methods and Theory

Average Hamiltonian Theory The work in this paper is based on Average Hamiltonian Theory (AHT) [78]. In AHT the effect of a pulse sequences is analyzed by calculating an effective, or 'average' Hamiltonian, denoted $\bar{H}$, which describes evolution of the system across a full sequence of $n$ pulses with the property $P_{1} P_{2} \ldots P_{n}=I$, where $P_{i}$ is the propagator for the $i^{\text {th }}$ pulse. Such a sequence is termed a 'cycle' and it is repeated for as long as evolution under $\bar{H}$ is desired. To calculate the average Hamiltonian associated with a given pulse sequence the Hamiltonian is written in the so-called toggling frame

$$
\begin{equation*}
\tilde{H}_{i}=P_{1}^{\dagger} P_{2}^{\dagger} \ldots P_{i}^{\dagger} H P_{i} \ldots P_{2} P_{1}, \tag{8.1}
\end{equation*}
$$

where the dagger denotes the complex conjugate transpose. Using the Magnus expansion, in the limit of delta function pulses, the time independent first order average Hamiltonian is then simply the time average of the toggling frame Hamiltonians across the cycle period.

$$
\begin{equation*}
\bar{H}^{1}=\sum_{i=1}^{n} \frac{t_{i}}{t_{c}} \tilde{H}_{i} \tag{8.2}
\end{equation*}
$$

where $t_{c}=\sum_{i} t_{i}$ is the total cycle time and $t_{i}$ is the time between pulse $P_{i}$ and $P_{i+1}$. The $\mathrm{n}^{\text {th }}$ order correction to this expression depends on $t_{c}$ to the $\mathrm{n}^{\text {th }}$ power, making it essential that $t_{c}$ is short compared to the time scale of the interaction being averaged. In practice $t_{i}$ is limited by the duration of the pulses, $t_{p}$, which in turn depends on the hardware used, since for delta function pulses we require $t_{i} \gg t_{p}$. Since this implies that we need $t_{p}$ to be as short as possible it precludes using the relatively slow selective pulse methods introduced in Chapters 4 and 5. Instead we will be working with DC pulses, see Section 2.3.3. The Hamiltonian during such a pulse is well approximated by

$$
\begin{equation*}
H_{P}=B_{\alpha} \sum_{i}^{N} \gamma_{i} I_{\alpha, i} \tag{8.3}
\end{equation*}
$$

where $\alpha$ is the direction of the pulse and we have assumed that $\gamma B_{p} \gg J$ for all $J$ in the spin-system. If the $i^{\text {th }}$ pulse is along the $\alpha$ axis we denote this

$$
\begin{equation*}
P_{i}=\mathrm{e}^{-2 \pi \mathrm{i} H_{P i} t_{p}}=\mathrm{e}^{-2 \pi \mathrm{i} B_{\alpha} \sum_{i}^{N} \gamma_{i} I_{\alpha, i} t_{p}} . \tag{8.4}
\end{equation*}
$$

Isotropic Scaling In this section we aim to introduce the unacquainted reader to the theory of isotropic scaling as developed by Llor et al. [140] in Refs [140, 141]. The theory allows simplified design of pulse sequences that generate average Hamiltonians which simply multiply the original Hamiltonian with a constant, without introducing any mixing between $\mathrm{x}, \mathrm{y}$, and z terms. This is very useful when designing pulse sequences for zero-field NMR since the spherical symmetry means that there is no truncation with respect to an external axis and all components of the interaction tensors must be considered.

In the following analysis an arbitrary pulse sequence is defined by the axis and angle of the set of rotation superoperators $\hat{R}_{i}\left(\boldsymbol{n}_{i}, \omega_{i}\right)$ acting on $H$ throughout the sequence. In Hilbert space the action of $\hat{R}_{i}$ is calculated as $\hat{R}_{i}\left(\boldsymbol{n}_{i}, \omega_{i}\right) H=P_{1}^{\dagger} P_{2}^{\dagger} \ldots P_{i}^{\dagger} H P_{i} \ldots P_{2} P_{1}$. We denote the set $\left\{\left(\boldsymbol{n}_{i}, \omega_{i}\right)\right\}$ a configuration trajectory. Such a trajectory may be visualized by considering a sphere of radius $\pi$. Each point $\left(\boldsymbol{n}_{i}, \omega_{i}\right)$ on the trajectory corresponds to a point somewhere in this sphere. We will term the space of points in this sphere configuration space. The polar angles of a given point are given by the vector $\boldsymbol{n}_{i}$ and the distance from the origin is given by the rotation angle $\omega_{i}$. For example the poles of the sphere correspond to $\hat{R}_{i}(z, \pm p i)$. This representation provides a useful way of analyzing the effect of pulse sequences in terms of the rotational symmetry properties of different terms in the Hamiltonian, as we shall see.

Since we are dealing with the action of the pulses correspond to rotations in spin space it is convenient to decompose the Hamiltonian in terms of irreducible tensors where the rotational dependence of different interactions is made explicit in the rank of the corresponding tensor.

$$
\begin{equation*}
H=\sum_{l=0}^{2} \sum_{m=-l}^{l}(-1)^{m} A_{l-m} T_{l m}, \tag{8.5}
\end{equation*}
$$

Equation (8.5) is a sum over tensor scalar products corresponding to the different ranks of spin interactions considered, and $A_{l, m}$ and $T_{l, m}$ are irreducible tensors representing the spatial and spin dependencies of the Hamiltonian respectively. We note that in the zero-field regime, there is no truncation of 'nonsecular' $(\mathrm{m} \neq 0)$ terms in these interaction tensors and they must all be considered equally. The goal of the coherent averaging schemes presented here is to establish sufficient (but not necessary) conditions for which the first order average Hamiltonian $\bar{H}^{1}$ is a scaled version of $H$, without mixing terms of different $l$ or $m$. Thus we want the following to hold:

$$
\begin{align*}
\bar{H}^{1} & =\sum_{l=0}^{2} \sum_{m=-l}^{l}(-1)^{m} A_{l-m} k_{l} T_{l m} \\
& =\sum_{l=0}^{2} k_{l} H^{l} \tag{8.6}
\end{align*}
$$

where we have made clear that the scaling factor, $k_{l}$ may depend on rank but nothing else. Then sequences can be designed for which $k_{l}<0$ for some interaction of interest (time reversal sequences), allowing spin echoes or $k_{l}=0$ (dynamical decoupling sequences). Further, since the scaling is rank selective one may for example scale to zero first rank tensors, in order to observe the spectrum of only the zeroth or second rank interactions. Scalar interactions (such as zero-field $J$-couplings) correspond to rank-0 Hamiltonians, and are thus always invariant under an isotropic pulse sequence.

We now want to establish general conditions on the $\left\{\hat{R}_{i}\left(\boldsymbol{n}_{i}, \omega_{i}\right)\right\}$ for which Eq. (8.6) is guaranteed to hold. The rotation of a spherical tensor operator $T_{l m}$ by $\hat{R}(\boldsymbol{n}, \omega)$ is given by the appropriate rank- $l$ Wigner matrix, $D^{l}\left(\boldsymbol{n}_{i}, \omega_{i}\right)$. Using Equations (8.2) and (8.5) we can
write

$$
\begin{equation*}
\bar{H}^{1}=\sum_{i=0}^{n} \sum_{l=0}^{2} \sum_{m=-l}^{l} \frac{t_{i}}{t_{c}}(-1)^{m} A_{l-m} D^{l}\left(\boldsymbol{n}_{i}, \omega_{i}\right) T_{l m}, \tag{8.7}
\end{equation*}
$$

where $D^{l}\left(\boldsymbol{n}_{i}, \omega_{i}\right)$ is the representation of the rotation operator on the total angular momentum basis and we have made explicit the fact that rotations do not mix irreducible tensors of different rank. The result of multiplying $T_{l m}$ by $D^{l}$ is given by Eq. (2.60) so Eq. (8.7) becomes

$$
\begin{equation*}
\bar{H}^{1}=\sum_{i=0}^{n} \sum_{l=0}^{2} \sum_{m=-l}^{l} \sum_{m^{\prime}=-l}^{l} \frac{t_{i}}{t_{c}}(-1)^{m} A_{l-m} D_{m^{\prime} m}^{l}\left(\boldsymbol{n}_{i}, \omega_{i}\right) T_{l m^{\prime}} . \tag{8.8}
\end{equation*}
$$

We see that in general a sequence of spin rotations will mix the $\mathrm{x} y$ and z components of the spin operators. In order to satisfy Eq. (8.6) for all possible spatial coefficients $A_{l m}$ we then need the following relation to hold for the matrix elements of $D^{l}\left(\boldsymbol{n}_{\boldsymbol{i}}, \omega_{i}\right)$

$$
\begin{equation*}
\sum_{i=0}^{n} \frac{t_{i}}{t_{c}} D_{m m^{\prime}}^{l}\left(\boldsymbol{n}_{i}, \omega_{i}\right)=k_{l} \delta_{m m^{\prime}} \tag{8.9}
\end{equation*}
$$

which must hold independently for all ranks of interest. It turns out that solutions to this equation can be found by considering the symmetry of the points on the configuration trajectory $\left\{\left(\boldsymbol{n}_{i}, \omega_{i}\right)\right\}$. To see this we expand the matrix elements of $D^{l}$ in terms of functions with known symmetry properties, the spherical harmonics $Y_{\lambda \mu}[37]$

$$
\begin{equation*}
D_{m m^{\prime}}^{l}\left(\boldsymbol{n}_{i}, \omega_{i}\right)=\sum_{\lambda=0}^{2 l} \sum_{\mu=-\lambda}^{\lambda}(-i)^{\lambda} \frac{2 \lambda+1}{2 l+1} \chi_{\lambda}^{l}\left(\omega_{i}\right) C_{l m^{\prime} \lambda \mu}^{l m} \sqrt{\frac{4 \pi}{2 \lambda+1}} Y_{\lambda \mu}\left(\boldsymbol{n}_{i}\right), \tag{8.10}
\end{equation*}
$$

where the $Y_{\lambda \mu}\left(\boldsymbol{n}_{i}\right)$ are evaluated at the polar angles of the rotation axis vectors, $\lambda$ is the rank, and $\mu$ is the $m$-value. Note that the maximum value of $\lambda$ is twice the rank of $D^{l}$. Inserting this expansion into Eq. (8.9), using the selection rules for the Clebsh-Gordan coefficients, and canceling constants gives the following conditions for an isotropic pulse sequence

$$
\begin{gather*}
\sum_{i=0}^{n} \chi_{\lambda}^{l}\left(\omega_{i}\right) Y_{\lambda \mu}\left(\boldsymbol{n}_{i}\right)=0,  \tag{8.11}\\
k_{l}=\sum_{i=0}^{n} \frac{t_{i}}{t_{c}} \chi^{l}\left(\omega_{i}\right), \tag{8.12}
\end{gather*}
$$

where $\chi^{l}\left(\omega_{i}\right)$ is the trace of the rank- $l$ Wigner matrix, and the $\chi_{\lambda}^{l}\left(\omega_{i}\right)$ are so-called generalized characters [37].

Equation (8.11) implies that if the configuration rotation angle is constant (i.e. all points on the trajectory have the same distance from the origin) then the pulse sequence is guaranteed to isotropically scale the Hamiltonian if spherical harmonics up to twice the rank
of the interaction considered vanish when averaged over the distribution. Symmetries of distributions over which spherical harmonics of a given rank sum to zero are well known. For example a tetrahedral distribution of points ensures that the rank-1 and rank-2 spherical harmonics average to zero, while an icosahedral distribution averages up to rank-4 spherical harmonics to zero. Thus we can talk about tetrahedral sequences (isotropic for rank-1 Hamiltonians), and icosahedral sequences (isotropic up to rank-2 Hamiltonians) etc.

Equation (8.12) shows that the degree of the scaling induced by a given isotropic sequence is determined by the average of the traces of the rotation superoperators that take $H$ into the toggling frame. In other words the scaling is determined by the average distance from the origin of the trajectory $\left\{\left(\boldsymbol{n}_{i}, \omega_{i}\right)\right\}$.

### 8.3 Pulse Sequence for Rank-1 Decoupled $J$-Spectroscopy

In this Section we will derive a pulse sequence for decoupling a ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ system from external magnetic fields, while maintaining an isotropic, zero-field like, $J$-coupling between the spins. Any isotropic sequence, i.e. a sequence that conforms to Eq. (8.11), will leave the $J$-coupling unchanged. This is easily seen because $H_{J}$ is a scalar operator and commutes with all rotations. The Zeeman Hamiltonian is linear in each spin species meaning it corresponds to a rank-1 interaction and we therefore seek a pulse sequence that generates a configuration trajectory that has at least tetrahedral symmetry. Further, since we wish to remove the effect of the field on the spin evolution, i.e. we seek a decoupling sequence, $k_{1}$ should be 0 . The character of a rank- 1 Wigner matrix is $\chi^{1}(\omega)=1+2 \cos (\omega)$ which evaluates to zero for $\omega=2 \pi / 3$. This means that the sequence should have an average $\omega_{i}$ (distance from the origin in configuration space) of $2 \pi / 3$ according to Eq. (8.12).

The theory of isotropic scaling as developed in the preceding Section presumes that each pulse $P_{i}$ corresponds to a rotation of the total Hamiltonian. However, for a heteronuclear system at zero field this is in general not true, different spins rotate at different rates proportionally to their gyromagnetic ratios. But, as has been noted several times throughout this dissertation, for protons and carbon-13 (So far the most commonly used spin pair in zero-field NMR) $\gamma_{H} / \gamma_{C} \approx 4$. This means that a $2 \pi / 3$ rotation on carbon corresponds to a $8 \pi / 3=2 \pi / 3$ rotation on hydrogen. Thus any pulse sequence that both satisfies Eq. (8.11) and is made up of only $2 \pi / 3$ pulses (on carbon) will be isotropic for any ${ }^{13} \mathrm{C}-{ }^{1} \mathrm{H}$ spin-system. This suggests a straightforward way of constructing a pulse sequence that removes the effect of residual magnetic fields on both carbons and protons while leaving the isotropic $J$-coupling between them intact;

We first note that $\hat{R}\left(x, \frac{2 \pi}{3}\right) \times \hat{R}\left(x, \frac{2 \pi}{3}\right)=\hat{R}\left(x,-\frac{2 \pi}{3}\right)$ and $\hat{R}\left(x, \frac{2 \pi}{3}\right) \times \hat{R}\left(x, \frac{2 \pi}{3}\right) \times \hat{R}\left(x, \frac{2 \pi}{3}\right)=\mathbb{1}$. Three successive $2 \pi / 3$ rotations around the x -axis therefore generates a configuration trajectory of $\left\{\left(x, \frac{2 \pi}{3}\right),\left(-x, \frac{2 \pi}{3}\right),(0,0)\right\}$, which traces out a line in configuration space. Two more lines at right angles to the first one makes an octahedron (which has higher than tetrahedral


Figure 8.1: Illustration of the ${ }^{13} \mathrm{C}^{-1} \mathrm{H}$ rank-1 decoupling sequence presented in the text. The sphere represents the space of possible rotations. The red dots are the rotations $\hat{R}_{i}\left(\boldsymbol{n}_{i}, \omega_{i}\right)$ bringing the Hamiltonian into the toggling frame defined by Eq. (8.1) after each pulse in sequence $A$. The blue line is drawn to guide the eye to the tetrahedral symmetry of the sequence.
symmetry) $\left\{\left(x, \frac{2 \pi}{3}\right),\left(-x, \frac{2 \pi}{3}\right),(0,0),\left(y, \frac{2 \pi}{3}\right),\left(-y, \frac{2 \pi}{3}\right),(0,0),\left(z, \frac{2 \pi}{3}\right),\left(-z, \frac{2 \pi}{3}\right),(0,0)\right\}$. Such a configuration trajectory could be generated by 3 successive $2 \pi / 3$ rotations about the x-axis, followed by three around y and finally z. However, in order to effect decoupling we want the average rotation angle (i.e. the distance from the origin) of the trajectory to be $2 \pi / 3$. Conveniently, the vertices of the octahedron are already located at $\omega=2 \pi / 3$ by construction, meaning all we need to do is to drop the terms corresponding to the $(0,0)$ configurations from the average in Eq. (8.2). This is easily done by not allowing any free evolution between the pulses that take the trajectory from one line to the next, letting $t_{i} \rightarrow 0$ between those pulses. A possible pulse sequence that would generate such a trajectory, assuming delta function pulses, is

$$
x-(\tau / 2-x-\tau-x y-\tau-y-\tau-y z-\tau-z-\tau-z x-\tau / 2)_{n}-\bar{x} .
$$

We will call this pulse sequence A, the trajectory is shown graphically in Fig. 8.1. Since A generates a configuration trajectory that conforms to the conditions set out in Eqs. (8.11) and (8.12) the corresponding first order average Hamiltonian will have $k_{1}=0$ and $k_{0}=1$. i.e. terms linear in the spin operators are averaged to zero, while scalar couplings remain unchanged. Second rank bilinear terms, such as those arising from the magnetic dipoledipole interaction are not guaranteed to be scaled in any sensible way by this sequence, since an octahedral distribution of points does not average a fourth rank spherical harmonic to zero, c.f. Eq. (8.11).

### 8.3.1 Error Correction

The preceding arguments presume idealized, infinitely short pulses, which is not borne out in practice. The first point to note is that $\gamma_{H} / \gamma_{C} \approx 3.97$ which means that even a perfectly calibrated $2 \pi / 3$ pulse on ${ }^{13} \mathrm{C}$ will result in a $\sim 7.94 \pi / 3$ pulse on ${ }^{1} \mathrm{H}$, and of course, real pulses are not going to be perfectly calibrated. Second, real pulses necessarily have finite duration
which lead to higher order corrections to the average Hamiltonian. In addition, finite pulse lengths change the $k_{0}$ scaling factor even in first order, as we shall see. These effects all have to be taken into account in order to design an effective sequence.

Flip Angle Errors To deal with amplitude errors and the slight mismatch in gyromagnetic ratios we slightly modify the trajectory by replacing the $\alpha$ pulses by $2 \bar{\alpha}$ giving

$$
x-(\tau / 2-2 \bar{x}-\tau-x y-\tau-2 \bar{y}-\tau-y z-\tau-2 \bar{z}-\tau-z x-\tau / 2)_{n}-\bar{x}
$$

where the over-bar denotes a reversal of the direction of the pulse. In first order this modification eliminates both amplitude errors and errors due to the gyromagnetic ratio mismatch. This can be seen by noting that in the limit of $\tau \rightarrow 0$ each $2 \bar{\alpha}$ pulse is sandwiched by an $\alpha$ pulse which perfectly cancels the pulse evolution, assuming complete phase-control. The octahedral symmetry of the trajectory is retained and the distance from the origin is still $2 \pi / 3$. Second order corrections to the average Hamiltonian arising from finite $\tau$ can be corrected for as usual using an anti-palindromic expansion [39].

Non-zero Pulse Widths The ${ }^{13} \mathrm{C}$ and ${ }^{1} \mathrm{H}$ spin-vectors are not collinear during the pulses, even if the outcome of the rotation is the same for both spin-species. This means that nonzero pulse lengths may change the effective couplings between protons and carbons. Here we evaluate this effect.

The toggling frame Hamiltonian during the $i^{\text {th }}$ pulse of a cycle is given by

$$
\begin{equation*}
\tilde{H}_{P i}(t)=P_{1}^{\dagger} P_{2}^{\dagger} \ldots \mathrm{e}^{2 \pi \mathrm{i} H_{P i} t} H \mathrm{e}^{-2 \pi \mathrm{i} H_{P i} t} \ldots P_{2} P_{1}, \tag{8.13}
\end{equation*}
$$

and the contribution to the average Hamiltonian from evolution during the pulse is to first order [147, 148]

$$
\begin{equation*}
\bar{H}_{P i}^{1}=\frac{1}{t_{p}} \int_{0}^{t_{p}} \tilde{H}_{P i}(t) d t \tag{8.14}
\end{equation*}
$$

Let the ${ }^{13} \mathrm{C}$ rotation angle be $\theta$ such that $B \gamma_{C} t=\theta$. Then the proton rotation angle is $\theta_{H} \approx 4 \theta$. We can now calculate the effect of a pulse along the x -axis on the $J$-coupling as

$$
\begin{align*}
\bar{H}_{P}^{1} & =\int_{0}^{2 \pi / 3} \mathrm{e}^{2 \pi\left(4 \theta K_{x}+\theta S_{x}\right)} \boldsymbol{K} \cdot \boldsymbol{S} \mathrm{e}^{-2 \pi\left(4 \theta K_{x}+\theta S_{x}\right)} d \theta  \tag{8.15}\\
& =K_{x} S_{x}+\int_{0}^{2 \pi / 3}\left[\left(\cos (4 \theta) K_{y}+\sin (4 \theta) K_{z}\right)\left(\cos (\theta) S_{y}+\sin (\theta) S_{z}\right)\right. \\
& \left.+\left(\cos (4 \theta) K_{z}-\sin (4 \theta) K_{y}\right)\left(\cos (\theta) S_{z}-\sin (\theta) S_{y}\right)\right] d \theta  \tag{8.16}\\
& =K_{x} S_{x} \tag{8.17}
\end{align*}
$$

So for a $2 \pi / 3$ pulse on a ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ system the components of the $J$-coupling that are not parallel to the pulse average to zero, while the component parallel to the pulse remain unchanged.

The integral goes to zero for a $4 \pi / 3$ pulse as well. It follows that if the duration of the pulses is non-zero, with length $t_{p}$, the evolution under each pulse along the $\alpha$ direction will give a contribution to $\bar{H}^{1}$ of $\left(t_{p} / t_{c}\right) K_{\alpha} S_{\alpha}$, where $t_{c}$ is the total cycle time including the pulses. Since the sequence A' contains three pulses in each direction we obtain the following modified expression for the heteronuclear rank 0 scaling factor as a function of the pulse spacing $\tau$ and pulse duration

$$
\begin{equation*}
k_{0}=\frac{6 \tau+3 t_{p}}{6 \tau+9 t_{p}} \tag{8.18}
\end{equation*}
$$

Equation (8.18) assumes that the pulse amplitude, not the duration, is doubled in order to obtain $4 \pi / 3$ pulses. For the homonuclear couplings the situation is different, in this case the spin vectors do remain collinear during the pulse rotations and consequently the effective couplings remain unchanged. The result is that as the ratio $t_{p} / t_{c}$ changes from 0 in the limit of delta function pulses to $1 / 9$ in the limit of a windowless sequence, the scaling factor for heteronuclear couplings goes from $k_{0}=1$ to $k_{0}=1 / 3$, while homonuclear couplings are unchanged. This scaling could potentially be useful if employed deliberately but the main take-away is that short, delta function like, pulses are preferable in most cases, especially for systems with both homo- and heteronuclear couplings.

### 8.4 J-Decoupling

In Chapter 7 we introduced a method for obtaining homonuclear $J$-spectra by decoupling proton-carbon $J$-couplings using a modified version of the XY4 pulse sequence [138]. A pulse sequence that averages $H_{J}$ to zero can not be a true isotropic scaling sequence since $H_{J}$ is a scalar operator and therefore rotationally invariant. But a heteronuclear $J$-coupling interaction $\boldsymbol{I} \cdot \boldsymbol{S}$ is linear if considered with respect to only one of the spin-species. Since $\pi$ pulses on carbon leave proton spins approximately unchanged a pulse sequence built on such pulses decouples heteronuclear $J$-couplings if it averages rank-1 interactions to zero. The fact that XY4 averages first-rank interactions to zero when considered with respect to only the spins that rotate during the pulses can be understood within the framework of isotropic scaling [140, 141].

The pulse sequence we used in Chapter 7 is reproduced here for convenience

$$
\left(\begin{array}{llllllll}
x y \bar{x} \bar{y} & \bar{x} \bar{y} x y & \bar{x} y x \bar{y} & x \bar{y} \bar{x} y & \bar{y} x y \bar{x} & y \bar{x} \bar{y} x & \bar{y} \bar{x} y x & y x \bar{y} \bar{x})_{n}, \tag{8.19}
\end{array}\right.
$$

where the pulses were calibrated to effect a $\pi$ rotation of the ${ }^{13} \mathrm{C}$ spins and there is equal spacing between each $\pi$ pulse (the fact that some pulses have spaces between them is simply to ensure clarity of presentation). We have also made explicit the antipalindromic expansion. The pulse sequence can be stopped and free evolution resumed after each 4-pulse block. In other words the full super cycle has 8 sampling points. This Section contains initial analysis as to why this particular phase cycle scheme works well for decoupling ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C} J$-couplings.


Figure 8.2: Plots of the heteronuclear decoupling fidelity obtained by different pulse sequences as function of pulse error and the number of applied pulses. (a) XY4, (b) XY8, (c) XY16, (d) Sequence (8.19).

### 8.4.1 Error Correction

Flip-angle Errors A perfectly calibrated $\pi$ pulse on ${ }^{13} \mathrm{C}$ corresponds to a $\sim 3.97 \pi$ pulse on ${ }^{1} \mathrm{H}$, which complicates the simple analysis above, which assumes that the proton remains stationary as the carbon spin rotates. We use numerical simulations to demonstrate the robustness of Sequence (8.19) to slight miscalibrations of the pulse amplitudes. We ignore relaxation and define the fidelity [149] of a pulse sequence as

$$
\begin{equation*}
F=\frac{\left|\operatorname{Tr}\left\{U_{\text {ideal }} U_{\text {actual }}^{\dagger}\right\}\right|}{\sqrt{\operatorname{Tr}\left\{U_{\text {ideal }} U_{\text {ideal }}^{\dagger}\right\}} \operatorname{Tr}\left\{U_{\text {actual }} U_{\text {actual }}^{\dagger}\right\}}, \tag{8.20}
\end{equation*}
$$

where $U_{\text {ideal }}=\mathrm{e}^{-\mathrm{i} \bar{H}_{\text {des }} n t_{c}}$ is the propagator for desired average Hamiltonian, and $U_{\text {actual }}$ is the actual propagator for all the (miscalibrated) pulses and free evolution intervals. We use $1-{ }^{13} \mathrm{C}$-propionic acid as our model system. The Hamiltonian is given by Eq. (7.10) and $\bar{H}_{\text {des }}={ }^{3} J_{\mathrm{HH}} \boldsymbol{K} \cdot \boldsymbol{L}$. If $F=1$ the evolution induced by the pulse sequence exactly corresponds to evolution under only the homonuclear coupling term.

Various compensated versions of the ( $x y x y \equiv \mathrm{XY} 4$ ) exist. Here we evaluate the performance of our decoupling sequence against two common ones, XY8/16 [150]. These sequences are particularly relevant as comparisons because at zero-field it is challenging to correctly calibrate pulses with arbitrary phases as required for many more advanced compensation schemes. A pulse that is not along either the $\mathrm{x}, \mathrm{y}$, or z -axes require current in two or three coils simultaneously, and since the coils are not exactly identical this is challenging to do accurately. In the simulation the ${ }^{13} \mathrm{C}$ flip angle is varied from $0.97 \pi$ to $1.03 \pi$ to simulate a miscalibration of the pulse amplitudes. To match the experiment in Chapter 7 each pulse is assumed to be $200 \mu$ s long and the interpulse spacing is 2 ms . The actual propagator is compared to the target propagator every 4 pulses, meaning the evolution through a total of 800 pulses is simulated. The results in Fig. 8.2 show clearly how Sequence (8.19) outperforms
the conventional XY4/8/16 sequences when it comes to heteronuclear $J$-decoupling in terms of robustness to flip angle errors. In fact for XY4/8 the mismatch induced by the ratio of gyromagnetic ratios not being exactly four is enough to immediately bring the fidelity below 0.9. In all cases optimal performance is actually seen for a ${ }^{13} \mathrm{C}$ flip angle of $\sim 1.008 \pi$ as opposed to $\pi$. This can be understood by noting that this is the rotation angle which maximizes the phase difference between the ${ }^{13} \mathrm{C}$ and ${ }^{1} \mathrm{H}$ spins after each pulse.

Non-zero Pulse Widths We can also consider the effect of evolution during the pulses with non-zero width analytically. We evaluate Eq. (8.16) for the case of positive and negative ${ }^{13} \mathrm{C} \pi$ pulses along the x - and y -axes and obtain

$$
\begin{align*}
\bar{H}_{x} & =\frac{2}{3}\left(-I_{z} S_{y}+I_{y} S_{z}\right)+I_{x} S_{x},  \tag{8.21}\\
\bar{H}_{\bar{x}} & =\frac{2}{3}\left(+I_{z} S_{y}-I_{y} S_{z}\right)+I_{x} S_{x},  \tag{8.22}\\
\bar{H}_{y} & =\frac{2}{3}\left(-I_{x} S_{z}+I_{z} S_{x}\right)+I_{y} S_{y},  \tag{8.23}\\
\bar{H}_{\bar{y}} & =\frac{2}{3}\left(+I_{x} S_{z}-I_{z} S_{x}\right)+I_{y} S_{y} . \tag{8.24}
\end{align*}
$$

Next we use these results together with Eq. (8.13) and calculate the first order average Hamiltonian for each 4-pulse subcycle in Sequence (8.19)

$$
\begin{align*}
\bar{H}_{x y \bar{x} \bar{y}} & =\frac{4}{3}\left(I_{z} S_{y}-I_{z} S_{x}\right),  \tag{8.25}\\
\bar{H}_{\bar{x} \bar{y} x y} & =\frac{4}{3}\left(-I_{z} S_{y}+I_{z} S_{x}\right),  \tag{8.26}\\
\bar{H}_{\bar{x} y \bar{x} \bar{y}} & =\frac{4}{3}\left(-I_{z} S_{y}-I_{z} S_{x}\right),  \tag{8.27}\\
\bar{H}_{x \bar{y} \bar{x} y} & =\frac{4}{3}\left(I_{z} S_{y}+I_{z} S_{x}\right) . \tag{8.28}
\end{align*}
$$

The contribution to the average Hamiltonian from finite pulse lengths is thus zero to first order across the full super-cycle in Sequence (8.19).

### 8.5 Results and Discussion

### 8.5.1 Rank-1 Decoupling Results

To demonstrate effectiveness of the rank-1 decoupling pulse-sequence derived above we used $1-{ }^{13} \mathrm{C}$-acetic acid as a model system. In zero-field the Hamiltonian for this molecule is given by

$$
\begin{equation*}
H_{J}=2 \pi J \boldsymbol{S} \cdot \boldsymbol{K} \tag{8.30}
\end{equation*}
$$



Figure 8.3: Zero and ultralow field spectra of $\left[{ }^{13} \mathrm{C}\right]$-acetic acid.
where $\boldsymbol{K}$ is the sum of the proton angular momentum, as in Chapters 6 and 7. The corresponding $J$-spectrum is shown in Fig. 8.3a and consists of one peak at $J$ and one at $2 J$. To simulate operation in a shield-less environment [146] we applied an 80 nT magnetic field perpendicular to the detection axis (which is denoted $z$ ) using the $y$-shim. The effect of such a field on a zero-field $A X_{3}$ spin-system is treated in detail in [24]. The Hamiltonian is given by

$$
\begin{equation*}
H=2 \pi J \boldsymbol{S} \cdot \boldsymbol{K}-B_{y}\left(\gamma_{C} S_{y}+\gamma_{H} K_{y}\right) \tag{8.31}
\end{equation*}
$$

The near zero-field spectrum obtained by evolution under $H$ is a doublet at $J$ and a sextet at $2 J$ (plus additional peaks close to zero). In the experimental data in Fig. 8.3 b we clearly see a doublet with a splitting of $\sim 4 \mathrm{~Hz}$ at $J$, consistent with an 80 nT field, but we resolve only four peaks at $2 J$. There is also a small residual peak at $J$, this arises due to the detection axis being slightly tilted relative to the ideal case [31].

We obtained the zero-field $J$-spectrum of $1-{ }^{13} \mathrm{C}$-acetic acid in the presence of a 80 nT magnetic field using the heteronuclear isotropic rank-1 decoupling sequence A'. To deal with the issue of magnetometer dead-time as described in Section 3.2.6 we used 2D-detection [2]. The sample is allowed to evolved under the effective Hamiltonian, $\bar{H}$ imposed by the pulse sequence for a time $t_{1}$, after which the signal, $S$ is monitored during a period of free evolution as a function of time, $t_{2} . S\left(t_{1}, t_{2}\right)$ is subject to a 2 D fast Fourier transform, giving the spectrum of the average Hamiltonian induced by the pulse sequence, $\bar{H}$, along the y-axis (F1) and the spectrum of the unmodified Hamiltonian, $H$, along the x-axis (F2). For the case of the pulse sequence A' we have $\bar{H}^{1}=k_{0} H_{J}$. Evolution was initiated using a DC pulse calibrated to effect a $\pi$ pulse on the ${ }^{13} \mathrm{C}$ spin, see Section 2.3.3, after which the pulse sequence A' was repeated between 0 and 150 times, sampling the signal every other cycle. The pulse duration was $200 \mu \mathrm{~s}$ and the time between pulses was 2 ms .


Figure 8.4: Rank-1 decoupled $J$-spectrum of ${ }^{13} \mathrm{C}$-acetic acid in a magnetic field acquired using pulse sequence A'. The left-hand side panel is experimental data and the right-hand side is a numerical simulation.

The 2D Fourier transform of the resulting data is shown is Fig. 8.4a. Along F2 we see the full near zero-field spectrum corresponding to $H$, though we resolve only three of the peaks at $2 J$. Along F1 however, peaks occur at only two positions, corresponding to the zero-field spectrum of $H_{J}$. There are no cross-peaks between peaks belonging to the $1 J$ and $2 J$ multiplet, since the correspond to different values of total proton angular momentum, see Chapter 6. The red traces are 1D decoupled spectra constructed by taking slices along F2. The peaks occur at 6.4 Hz and 12.8 Hz , which corresponds to slightly lower frequencies than what would be expected based on the unscaled $J$-coupling constant ( 6.8 Hz ). According to Eq. (8.18) $k_{0}$ is 0.913 , which should give a scaled $J$-coupling constant of 6.2 Hz , which is lower than experimentally observed value of 6.4 Hz .

The results of Fig. 8.4 demonstrates the success of the pulse sequence $A^{\prime}$ in decoupling protons and carbons separately from external fields, while preserving the heteronuclear isotropic couplings that are the core of $J$-spectroscopy. However, one of the attractive features of $J$-spectroscopy are the narrow linewidths, but the $J$-spectrum obtained at 80 nT using rank-1 decoupling is significantly broader than the intrinsic linewidth of $1-{ }^{13} \mathrm{C}$-acetic acid. Simulations shown in the right hand panel in Fig. 8.4 do not reproduce the broadening, and we therefore assign it to imperfections in the pulse-shape, and an imbalance between the amplitudes of the positive and negative pulses due to asymmetry in the linear amplifiers.


Figure 8.5: Top panel: Full $J$-spectrum of ${ }^{13} \mathrm{C}_{2}$-acetic acid. Bottom panel: Homonuclear $J$-spectrum of ${ }^{13} \mathrm{C}_{2}$-acetic acid consisting of a single peak at the carbon-carbon coupling frequency.

### 8.5.2 J-Decoupling Results

To demonstrate the effectiveness of the new pulsing hardware we obtained the homonuclear $J$-spectrum of ${ }^{13} \mathrm{C}_{2}$-acetic acid using the same protocol presented in Chapter 7. However, since the pulses were shorter and more accurate, we obtained good results even though the largest frequency in this spin-system was 10 x larger than for $1-{ }^{13} \mathrm{C}$-propionic acid, which is the sample we used in Chapter 7 . We used $30 \mu$ s pulses and the inter pulse spacing was $300 \mu \mathrm{~s}$, giving a cycle time of $1.32 \mathrm{~ms} .1 / t_{c}$ is thus 760 Hz , while the largest frequency in the system is 280 Hz (see Fig. 6.5). The cycle time is thus faster, but not that much faster, than the interaction we are trying to average, and we can expect errors due to higher order corrections to $\bar{H}$.

The Hamiltonian for this spin-system is

$$
\begin{equation*}
H=2 \pi\left({ }^{1} J_{\mathrm{CH}} \boldsymbol{S}_{\mathrm{A}} \cdot \boldsymbol{K}+{ }^{2} J_{\mathrm{CH}} \boldsymbol{S}_{\mathrm{B}} \cdot \boldsymbol{K}+{ }^{1} J_{\mathrm{CC}} \boldsymbol{S}_{\mathrm{A}} \cdot \boldsymbol{S}_{\mathrm{B}}\right), \tag{8.32}
\end{equation*}
$$

where $\boldsymbol{K}$ and $\boldsymbol{S}_{\mathrm{A} / \mathrm{B}}$ are angular momentum operators for the proton group and carbons respectively. During application of the heteronuclear decoupling sequence the evolution is described by the average Hamiltonian $\bar{H}^{1}=2 \pi^{1} J_{\mathrm{CC}} \boldsymbol{S}_{\mathrm{A}} \cdot \boldsymbol{S}_{\mathrm{B}}$. That is, the only frequency in the decoupled spectrum is the carbon-carbon coupling frequency.

The corresponding homonuclear $J$-spectrum is presented in Fig. 8.5. As expected the decoupled spectrum has a single peak corresponding to ${ }^{1} J_{\mathrm{CC}}=56 \mathrm{~Hz}$, thus demonstrating successful decoupling. However, the peak is significantly broader than in the fully coupled


Figure 8.6: Left hand panel: Homonuclear ${ }^{1} \mathrm{H}$-decoupled $J$-spectrum of ${ }^{13} \mathrm{C}_{2}$-acetic acid acquired using the pulse sequence in Fig. 7.1. The stick spectra on the axes are the transition frequencies predicted based on numerical diagonalization of the Hamiltonian. Right hand panel: A full numerical simulation of the experiment.
spectrum, indicating that the averaging is not complete. We can obtain some insight into the origin of the broadening by comparing the full 2D spectrum (c.f. Chapter 7) with a numerical simulation. The data is presented in Fig. 8.6a. All peaks are clearly resolved in F2, while in F1 peaks occur only at a single frequency, consistent with the 1D decoupled spectrum.

As in the case of the rank-1 decoupling sequence the simulation assumes perfectly square, perfectly calibrated pulses of the exact length that was entered into the spectrometer at the time of the experiment. The spacing between the pulses is also assumed to be exact. The initial condition of the spin-system was assumed to be magnetization along the z-axis. In spite of these assumptions the simulation in Fig. 8.6b reproduces the experimental data very well. Since even the various imperfections are reproduced by the simulation, this indicates that we are not limited by pulse amplitude calibrations, pulse shapes, or mismatches between positive and negative pulses (since all these things are perfect in the simulation) but rather that the decoupling efficiency is set by higher order corrections to the average Hamiltonian due to the cycle time being too long.

### 8.6 Conclusions

In this chapter we have demonstrated zero-field $J$-spectroscopy in the presence of an 80 nT magnetic field. We used coherent averaging to isolate the coupled spins from the external field while retaining the isotropic $J$-couplings between carbons and protons. This technique will enable high-resolution zero-field $J$-spectroscopy without bulky mu-metal shielding. The resonance frequency of protons in the earth's field is $\sim 2 \mathrm{kHz}$, which is comparable to the interactions involved in solid state line narrowing sequences. Therefore there is no reason in principle why this technique should not extend all the way to earth's field, at which point $J$-spectra could be obtained without even electromagnetic coils to screen the ambient field.

We have also shown that an improved pulsing setup expands the scope of homonuclear $J$-coupling spectroscopy to molecules with $J$-couplings larger than 100 Hz . This will enable more facile acquisition of chemically informative spectra of isotopomer mixtures. The ability to selectively turn on and off heteronuclear couplings in zero-field experiments may also have other applications, for example as a 'polarization valve' in parahydrogen experiments, or in quantum simulation experiments.

## Chapter 9

## Conclusions and Outlook

In this dissertation we have outlined how to build and set up a state-of-the-art zero-field NMR spectrometer and use it to acquire $J$-spectra of simple molecules in the liquid state. Further, we have introduced a number of new possibilities for spin control and excitation beyond broad band, one dimensional pulse-acquire spectroscopy. We have also shown in detail how to acquire and interpret two-dimensional $J$-spectra. We have introduced the concept of multiple-quantum zero-field NMR and shown how it can be used to simplify assignment of crowded $J$-spectra. Finally we have shown how coherent control may be used to obtain both homonuclear $J$-spectra and zero-field $J$-spectra in the presence of magnetic fields. These methods have been presented with an eye towards applications in chemical analysis, however it must be stressed that the techniques themselves are agnostic about the particularities of their deployment.

In the end there are many outstanding challenges if zero-field NMR is to become a mainstay of portable chemical analysis. Chief among them is the same specter that haunts all low-field NMR - the sensitivity issue. The spectra in this work were acquired using pure $100 \%$ isotopically enriched liquids, and the averaging times were still orders of magnitude longer than in a 'normal' high-field experiment. However, if this problem can be overcome, and that is admittedly a big if, zero-field NMR holds promise as a spectroscopic modality that circumvents the trade off between spectral resolving power and magnetic field strength (and therefore instrument bulk and size).

How then might one go about attaining such a sensitivity boost? The most straightforward, yet elusive, answer is hyperpolarization. When it works, it works really well, but no one has yet developed a technique that is both cheap and general. The second point is better sensors. The magnetometer used in this work has a sensitivity of $\sim 30 \mathrm{fT} / \sqrt{\mathrm{Hz}}$, however it is possible to construct vapor cell magnetometers with sensitivities down to $1 \mathrm{fT} / \sqrt{\mathrm{Hz}}$ without sacrificing bandwidth. This would mean a factor of 900 in averaging time. There are also different sensors available. NV- centers can be brought to within nanometers of a target molecule and on the single molecule level spin-polarization becomes irrelevant, which is obviously quite an advantage. Finally, we point out that while in a standard high-field experiment the sensor surrounds the sample, in zero-field NMR the detector sees what is
essentially a dipolar field emanating from the sample tube. It is not obvious that the current geometry, where the detector is placed right below the sample, is optimal. It would be interesting to study the effect on sensitivity by placing the sample in different positions around the cell.

Another possibility would be to return to indirect high-frequency inductive detection, which offers particular synergies with the various decoupling techniques presented here. Since we have to rely on 2D detection of coherently averaged spectra in zero-field anyway, one dimension is already 'wasted'. Replacing it with a much more sensitive high-field detection period would leave the information content of the decoupled spectrum unchanged but speed up the experiment significantly. This could be done to improve the spectral resolving power or flexibility of portable permanent magnet systems, which are still more sensitive NMR detectors than rubidium magnetometers in practice, but lack the resolution available at zero-field. One could also imagine using a super-conducting magnet for detection, in which case the goal would obviously not be portability, but one could still obtain complementary spectral information. For example in situations where the high-field spectrum exhibits strong roofing effects it might be convenient to go to a first order picture by simply turning off the field (if increasing it further is not feasible). Other cases where zero-field evolution (with or without zero-field detection) could prove complementary to high-field spectroscopy is the study of heterogeneous materials. In addition to the absence of magnetic anisotropy effects the fact that the dipolar Hamiltonian is not truncated at zero-field should enable one to obtain all the elements of the order tensor, and thus define in more detail e.g. pore shapes. Finally, it has been suggested that $J$-coupling tensors in zero-field may report on the chirality of the molecule.

Faced with all these possibilities for how to develop zero-field NMR as a tool for (portable or not) chemical analysis we should remember that Rabi never intended for Nuclear Magnetic Resonance to be a chemical analysis tool in the first place. Perhaps the future of zero-field NMR does not lie in that direction at all. There are already papers in the literature using zero-field NMR for quantum simulation, as well as proposals for how the Hamiltonian symmetry of a zero-field NMR experiment enables the study of parity non-conserving fundamental interactions. When it comes to a technique that has not received very much attention it is always quite possible that an entirely different application is going to be 'the thing'. In any case, for as long as people will perform magnetic resonance experiments in the regime of zero magnetic field, there will be a need for spin control methods that work in that regime.

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## Appendix A

## A Zero-Field NMR Spectrometer

This Appendix concerns the practical operation of the zero-field NMR spectrometer, and its current (as of writing) state. It also contains a detailed overview of the software used to operate the spectrometer.

An important point to note is that the axis convention used in this Appendix differ from those in the rest of this dissertation. This is a consequence of the fact that in the vapor-cell community it is customary to refer to the axis of atomic spin-polarization (i.e. the pump axis) as the z -axis.

The spectrometer has been reviewed previously under the title

- Instrumentation for nuclear magnetic resonance in zero and ultralow magnetic field by Tayler, Theis, Sjolander, Blanchard, Kentner, Pustelny, Pines, and Budker [63].


## A. 1 Hardware

The following photos (A.1-A.4) show an overview of the spectrometer as it looks in the lab. All optical paths are enclosed in boxes for safety reasons. The box in Fig. A.1a contains the laser used for optical pumping of the rubidium cell, and the box in Fig. A.1b contains the polarimeter used to record the optical rotation signal. The polarimeter employs a Photo-Elastic-Modulator (PEM) in conjunction with a lock-in amplifier and schematics of the optical paths are shown in Fig. 3.4a/c. There are two BNC cables connecting the


Figure A.1: Optics boxes and shields (a) Box containing optics for the pump laser. (b) Box containing optics for the polarimeter setup used to measure the optical rotation signal. (c) The outer mu-metal shield layer used to screen out ambient magnetic fields and ensure a zero-field environment.
polarimeter box. One of them is the output of the photodiode and is connected to an amplification circuit shown in Fig. A.2b. The other BNC cable is the output of the PEM controller (Fig. A.3b), and connects to the PEM. The output of the amplification box goes to the lock-in amplifier shown in Fig. A.3c, which is referenced to the second output of the PEM controller. For a description of how the polarimeter works see Section 3.2.5.

Figure A.2a shows the data acquisition card that is used to operate the spectrometer. The analogue input 17 is connected to the output of the lock-in amplifier and carries the magnetometer response in real time. The digital output cable connects to the valve controlling the pneumatic shuttling, and the four analogue outputs are not used in the current configuration, but they can be connected to amplifiers for use with non-square pulses, see Chapter 5, or connected directly to the shim-coils to generate low-amplitude pulses, see Chapter 4. Figure A.2c shows the connectors for the shim-coils used to apply low-amplitude fields inside the magnetometer. Normally they connect to the DC current sources shown in Fig. A.3a, in which case they are used for shimming the residual field. We have found that shimming with linear fields only is enough to reach relaxation limited spectral resolution.


Figure A.2: Data acquisition and electronics boxes. (a) NI-DAQ card used to operate the spectrometer, read in data, and send out pulses. (b) Signal amplification box - to amplify the photo-current from the photodiodes in the polarimeter. (c) Access point to the shimming coils.

Note that the axes $x, y$, and $z$ refer to the probe path, the shuttling path, and the pump path respectively. This is distinct from the convention used in the main body of this Dissertation and is a legacy feature of this particular instrument.


Figure A.3: Shimming and polarimeter electronics. (a) DC current sources used for shimming the field inside the mu-metal shields. (b) Controller for the PEM used in the polarimeter setup see Section 3.2.5. (c) Lock-in amplifier used in the polarimeter setup.

Figure A. 4 shows the TTL amplification circuits used increase the high state of the PulseBlaser ESR pro board to $\sim 4 \mathrm{~V}$, which is required to trigger the switches in the pulsing circuit.

The circuit is described in more detail in Section 3.4.3. The Pulse-Blaster card is mounted in a PCI slot in the computer, and BNC cables take the signals to the amplification circuit. There are 6 switches (positive and negative pulses along 3 axes), so there are 6 BNC cables going from the computer to the amplification boxes.


Figure A.4: Pulse-Blaster signal amplifiers.

## A. 2 Software

This section describes the operation and functionalities of the LabVIEW program used to operate the spectrometer. The program was custom written in order to enable the various pulsed experiments described herein and is available as part of this dissertation. We will only outline the front panel here, which is all that is required to perform experiments. If further customization is desired the program is commented.

1D Experiment The most important input settings are shown in Fig. A.5. Green buttons start data acquisition. The large green button starts a basic 1D experiment. The inputs are separated into preparation (labeled "Pulse") and acquisition (labeled "Acquisition").

To start an experiment one most first chose a folder to save the data to and a filename. The FID will be saved in .txt format with 2 columns. One for time, the second for voltage data. Second a pulse sequence must be entered. This is done in the large matrix labeled "Pulse sequence". Each row corresponds to one event, the duration of which (in units of milliseconds) is given by "Time". X, Y, and Z corresponds to the probe axis, the detection axis, and the pump axis respectively. In the current configuration (using DC power supplies for pulsing) these entries can take three values, $+1,0,-1$, where a positive 1 opens the + switch for the designated duration, 0 indicates the switch is closed, and - opens the - switch for the designated duration. The pulse amplitude is set by changing the voltages under 'amplifier


Figure A.5: Start panel
voltage' (this can also be done manually on the power supplies). All pulse sequences should be plotted using the "Plot Pulse Sequence" button before running the experiment. The result will show up in the "Digital Waveform Graph" window. Note that under no circumstances may both the + and - switch along the same axis be open simultaneously. This will lead to the amplifiers shorting. Always leave a small delay between pulses.

The basic cycle of an experiment goes as follows: The sample is kept in the permanent magnetic for a time given by "Polarization time". After that a trigger causes the sample to start falling. After a time given by "Shuttling time" the spectrometer starts playing out the chosen pulse sequence (most commonly a simple excitation pulse). Note that "Shuttling time" simply specifies the delay between the shuttling trigger and the start of the pulse sequence, in order to control the physical shuttling time one needs to manually adjust the vacuum connection to the tube. After the pulse sequence the DAQ card will start to record the magnetometer signal. The sampling rate is conveniently kept at $1000 \mathrm{~Hz}(500$ Hz bandwidth), and the acquisition time should be tailored to the relaxation time of the particular sample and the desired Fourier resolution. After the acquisition the sample will automatically be shuttled back up into the magnet. The process will be repeated 'Number of transients" times and the resulting FIDs are automatically added together.

Multiple Pulse Experiments To execute a multiple experiment with more than 5 or 6 pulses it is recommended to use the "loop" functionality. A loop is indicated by writing "loop" in the fifth column of the "Pulse Sequence" matrix. The effect of this will be to play out the pulse sequence indicated in the "Loops" matrix to the left (see Fig. A.6) at this time point. If no phase cycling is desired simply enter the events as normal in the matrix. If phase cycling is desired (e.g. an $(x y \bar{x} \bar{y} \bar{x} \bar{y} x y)_{n}$ sequence) this is entered by incrementing the


Figure A.6: Multiple pulse inputs.
button "Phase Cycle Dim" in both the time column and the pulse sequence matrix. The same notation is done if more than one "loop" entry is desired in the original pulse sequence.

For long sequences this input step can be ardous. The button "Load Pure Proton Sequence" automatically fills in the matrices with inputs corresponding to the heternoculear $J$-decoupling sequence (Eq. (7.2)) presented in Chapter 7, using the provided inputs as parameters. The pulse sequence has 8 steps corresponding with an anti-palindromic expansion [39]. If further cases of hard-coded pulse sequences are desired the can be added as extra 'cases' in the code that the button points to.

The number of times to repeat a loop is given by the "Repeat Loop xN times" button in Fig. A.5. Each row refers to a seperate loop (use the first row if only one loop is in effect). The "Phase cycle x Times" entry refers to the number of separate phase cycling steps in the pulse sequence. Enter 8 for the hard-coded pure proton sequence. Remember to plot the sequence and make sure that everything looks the desired way.

Once the pulse sequence has been entered the remaining inputs for a 2D experiment are shown in Fig. A. 7 under the heading "Coherent Averaging Parameters". A 2D experiment consists of a pulse sequence (which can be something as simple as a wait time) being repeated between $l$ and $k$ times, acquiring a maximum of $k$ data points. "Loops to increment" denotes which of the loops is being incremented during the 2 D experiment.

Finally to start the experiment press the small green button "Start Coherent Averaging Scan".

Pulse Calibrations The pulses generated by the DC power supplies have a fixed amplitude. This amplitude is set by the voltage controls "Set $\pm \mathrm{X} / \mathrm{Y}$ amplifier voltage", which should not be changed during an experiment. The flip-angle for a given pulse is instead


Figure A.7: Further settings panel.
tuned by changing the duration of the pulse. Nutation curves are obtained by choosing a voltage (the default values are fine) and changing the duration of the pulse. The relevant inputs are shown in Fig. A. 7 under "Flip Angle Calibration Settings".


Figure A.8: Output screens.

Outputs Figure A. 8 shows the output spectrum produced by an experiment. The top central panel shows the Fourier transform (either phased or in magnitude) of the most
recently acquired spectrum. The bottom panel affords the possibility of loading a spectrum of choice (chose the desired .txt file generated by this program during an acquisition). There is also the opportunity to request zero-filling and dropping initial corrupted data points (see Section 3.6) during the loading process but more sophisticated data analysis should be performed elsewhere.


Figure A.9: Spectrum analyzer.
Figure A. 9 shows the built-in spectrum analyzer functionality of the program. Press the green start button to monitor the power spectrum of the magnetometer in real time, and the stop button to stop. This program can not be run simultaneously with the data acquisition part. It is primarily used to optimize the magnetometer (by measuring the response at the test-signal frequency in response to various tweaking operations).

