

Ultra-Low and Truly Zero-Field Nuclear Magnetic Resonance

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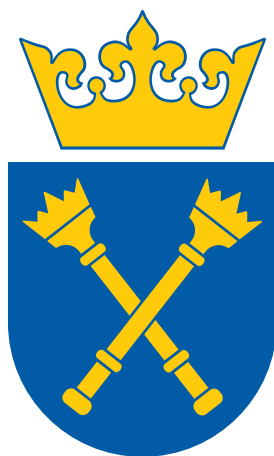
Doctor of Physics

by

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Piotr Put: *Ultra-Low and Truly Zero-Field Nuclear Magnetic Resonance* (2022)

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TO MY BELOVED ZUZIA

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Oświadczenie

Ja niżej podpisany **Piotr Put** (nr indeksu: 1089287), doktorant Wydziału Fizyki, Astronomii i Informatyki Stosowanej Uniwersytetu Jagiellońskiego oświadczam, że przedłożona przeze mnie rozprawa doktorska pt "Ultra-Low and Truly Zero-Field Nuclear Magnetic Resonance" jest oryginalna i przedstawia wyniki badań wykonanych przeze mnie osobiście, pod kierunkiem dr. hab. Szymona Pustelnego. Pracę napisałem samodzielnie. Oświadczam, że moja rozprawa doktorska została opracowana zgodnie z Ustawą o prawie autorskim i prawach pokrewnych z dnia 4 lutego 1994 r. (Dziennik Ustaw 1994 nr 24 poz. 83 wraz z późniejszymi zmianami). Jestem świadom, że niezgodność niniejszego oświadczenia z prawdą ujawniona w dowolnym czasie, niezależnie od skutków prawnych wynikających z ww. ustawy, może spowodować unieważnienie stopnia nabytego na podstawie tej rozprawy.

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ABSTRACT

This dissertation is concerned with the zero- and ultra-low field (ZULF) nuclear magnetic resonance (NMR). In contrast to conventional high-field NMR, where the coupling with the external magnetic field is the dominant interaction, the nuclear-spin evolution in this field regime is governed by the spin-spin (J) coupling. The thesis presents the latest developments in this technique, obtained by the author with the use of in-house-built ZULF spectrometers, based on the atomic magnetometry techniques also partially developed by author during PhD studies.

Firstly, a chemical analysis of compounds with ZULF NMR at natural isotopic abundance is shown. As zero-field signal relies on the presence of the heteronuclear coupling, zero-field spectroscopy is typically performed with labeled compounds. Here, organophosphorus compounds, with 100% natural abundance of spin- $1/2$ ^{31}P nuclei are studied. Compounds with naturally abundant ^{13}C (1.1%) and ^{15}N (0.3%) are also measured, yet in this case, the samples are hyperpolarized in zero-field with the use of parahydrogen.

The first-ever ZULF NMR studies of important biomolecules (metabolites, amino acids, and sugars) are also presented. Moreover, the ability to indirectly detect diluted compounds via ultra-low field relaxometry of solvent is demonstrated. The role of chemical exchange in zero-field NMR is also investigated in the context of biomolecules.

Finally, ZULF NMR is used to search for physics beyond the standard model. Specifically, constructed liquid-state nuclear comagnetometer is characterized and preliminary results of searching for the spin-gravity couplings are provided, already revealing the ability to improve the existing limits on the strength of this hypothetical interaction.

STRESZCZENIE

Rozprawa doktorska dotyczy zero- i ultra-niskopolowego rezonansu jądrowego (MRJ). W przeciwieństwie do konwencjonalnego MRJ, gdzie oddziaływanie z zewnętrznym polem magnetycznym jest dominujące, w tym reżimie pola ewolucja spinów rządzona jest przez oddziaływanie spin-spin (sprężenie J). W rozprawie przedstawione są ostatnie osiągnięcia w tej dziedzinie uzyskane przez autora tej pracy, przy użyciu technik magnetometrii atomowej, rozwijanych przez autora w ramach doktoratu.

W pracy przedstawiono analizę chemiczną z użyciem niskopolowego MRJ w związkach z naturalną abundancją izotopową. Jako, że zeropolowy sygnał wymaga obecności heteronuklearnego sprężenia, spektroskopia MRJ w tych warunkach prowadzona jest typowo z użyciem wzbogacanych izotopowo związków. Przedstawiono tutaj wyniki zeropolowej spektroskopii MRJ związków organicznych fosforu, z naturalnie występującym jądrem ^{31}P ze spinem $1/2$. Związki w naturalnej abundancji ^{13}C (1.1%) i ^{15}N (0.3%) zostały natomiast zmierzone w zeropolowych warunkach po hiperpolaryzacji z użyciem parawodoru.

Następnie w rozprawie zostały zaprezentowane pierwsze zarejestrowane spektra zeropolowego MRJ biomolekuł: metabolitów, aminokwasów oraz cukrów. Przedstawiono możliwość pośredniego wykrywania rozcieńczonych roztworów poprzez niskopolową relaksometrię rozpuszczalnika. Zbadano również rolę wymiany protonów w spektrum zeropolowym.

Niskopolowe sygnały MRJ zostały użyte wreszcie do szukania fizyki poza modelem standardowym. Skonstruowano jądrowy komagnetometr cieczowy, w którym uzyskano wstępne wyniki poszukiwań sprężenia spin-grawitacja, pokazując, że już na ten moment taki pomiar jest w stanie poprawić obecne limity na siłę tych hipotetycznych sprężeń.

CONTENTS

1	THEORETICAL PRELIMINARIES	1
1.1	Preface	1
1.2	Quantum mechanical states and their evolution	1
1.3	Evolution of the state	2
1.4	Wavefunction	3
1.5	Density matrix	3
1.6	Role of the environment	4
1.7	Angular momentum	5
1.7.1	Angular momentum as generator of rotations	5
1.7.2	Commutation relationship for rotation and angular-momentum operators	6
1.7.3	Direct product space- multiple spins	7
1.7.4	Addition of angular momenta	8
1.7.5	Rotation of states	8
1.7.6	Euler angles	9
1.8	Spin	9
1.8.1	Spin as intrinsic angular momentum	9
1.8.2	Nuclear spin	10
1.9	Visual representation of angular momentum states	10
2	INTRODUCTION TO (ZERO-FIELD) NMR	13
2.1	Nuclear magnetic resonance	13
2.1.1	Classical description of NMR experiment	13
2.1.2	Spin-1/2 in external magnetic field	17
2.2	Hamiltonian in NMR experiment	19
2.2.1	Spin Hamiltonian hypothesis	19
2.2.2	Zeeman interaction and chemical shift	20
2.2.3	Quadrupolar interaction	21
2.2.4	Dipole-dipole interaction	22
2.2.5	Electron-mediated J -coupling	23
2.2.6	Molecular motion and spin Hamiltonian	24
2.2.7	Interactions in isotropic media	24
2.2.8	Role of spin interactions in spin relaxation	27
2.2.9	Role of high field in truncating spin interactions	29
2.2.10	Summary of spin interactions	30
2.3	Role of the magnetic field in NMR	30
2.4	Different magnetic-field regimes in NMR	33
2.5	Zero-field NMR	35
2.5.1	Advantages of ZULF NMR	35
2.5.2	Brief history	36
3	ZERO-FIELD NMR EXPERIMENT	39
3.1	General NMR experimental sequence	40
3.2	Polarization preparation	40
3.2.1	Thermal prepolarization	41
3.2.2	Parahydrogen-induced polarization	45
3.2.3	Polarization in ZULF NMR experiment-conclusions	54
3.3	Detection of ZULF NMR	54
3.3.1	Introduction to detection of ZULF NMR	54
3.3.2	Atomic structure of alkali metals	55
3.3.3	General atomic magnetometry	56
3.3.4	Optical pumping	58
3.3.5	Optical properties of atomic medium	58

3.3.6	Sources of alkali-atom polarization relaxation	59
3.3.7	Nonlinear Magneto-Optical Rotation	61
3.3.8	Spin-Exchange Relaxation Free optical magnetometry	69
3.3.9	Comparison between NMOR and SERF magnetometers in ZULF NMR experiments	73
3.3.10	Ultra-low field NMR with the use of NMOR magnetometers	74
3.3.11	Signal detection - conclusions	77
3.4	Zero-field NMR signal	78
3.4.1	Generating zero-field NMR signals	78
3.4.2	Understanding ZF spectrum	84
3.4.3	Zero and ultra-low field NMR signals – conclusions	91
4	ZULF NMR IN PRACTICE- EXPERIMENTAL	93
4.1	Zero-field NMR spectrometer	93
4.2	Sample preparation	93
4.3	Sample polarization and transport to zero-field	94
4.3.1	Magnet for prepolarization	94
4.3.2	Sample transport in remote-prepolarization experiments	95
4.3.3	Bubbling system for parahydrogen-induced-polarization ex- periments	96
4.4	SERF magnetometer	98
4.5	Solenoid and coil assembly	100
4.6	Data acquisition and experimental control	103
4.7	Software for running zero-field NMR experiment	105
4.8	Data postprocessing and spectrum generation	106
4.9	Experimental-conclusions	107
5	ZERO-FIELD SPECTROSCOPY WITH NUCLEI AT NATURAL ABUNDANCE	109
5.1	<i>J</i> -spectroscopy of phosphorous compounds	110
5.1.1	Motivation	110
5.1.2	Organophosphorus compounds	111
5.1.3	ZULF NMR of organophosphorus compounds	111
5.1.4	Organophorus compounds - conclusions and outlook	113
5.2	Parahydrogen-induced polarization in zero-field NMR experiment	114
5.2.1	Introduction	114
5.2.2	Zero-field NMR experiments with parahydrogen-induced po- larization	115
5.2.3	Zero-field spectroscopy of naturally-abundant hydrogenatively- hyperpolarized samples	116
5.2.4	Reversible-exchange based polarization in zero-field	118
5.2.5	Conclusions and outlook on parahydrogen-induced polar- ization in ZULF NMR	120
6	ZERO-FIELD NMR OF BIOMOLECULES	123
6.1	Zero-field NMR as a tool for (bio-)chemical analysis	124
6.2	Spectrum structure in ZULF NMR	124
6.3	Zero-field spectra of metabolites, sugars and amino acids	126
6.4	Role of chemical exchange in zero-field spectra	129
6.5	Relaxometry at ultra-low magnetic field	133
6.6	Compact and mobile setup for zero-field NMR	136
6.7	ZULF NMR of biomolecules - conclusions	136
7	EXOTIC PHYSICS WITH ZERO-FIELD NMR	139
7.1	Motivation behind exotic physics searches	139
7.1.1	Standard model of particles	139
7.1.2	Table-top searches for new physics	139
7.2	ZULF NMR in precision measurements	140
7.3	Single-species nuclear spin comagnetometer	141
7.3.1	Energy structure of methanol at ultra-low magnetic field	141
7.3.2	Magnetometer and comagnetometer performance	143

7.4	Towards new spin-gravity coupling limits with ZULF NMR	144
7.4.1	Spin-gravity coupling effect on nuclear spin	144
7.4.2	Detection geometry	146
7.4.3	Preliminary results	147
7.5	Outlook on the spin-gravity-coupling search	148
8	CONCLUSIONS AND OUTLOOK	151
8.1	Summary	151
8.2	Some outlook on future ZULF NMR	151
A	DATA ANALYSIS AND SPIN SYSTEM SIMULATION CODE	167
A.1	Processing of experimental data	167
A.2	Zero-field spectra simulation	168
A.3	Zero-field spectra with chemical exchange: simulation	170
B	MEASUREMENT OPTIMIZATION	179
B.1	Magnetic pulse calibration	179
B.2	Piercing solenoid	179
B.3	Shimming zero-field spectrometer	180
C	EXPERIMENTAL DESIGNS	181
C.1	Permanent magnet assembly for prepolarization	181
C.2	Magnetometer holder for zero-field NMR assembly	181

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STRUCTURE OF THE DISSERTATION

Besides containing the summary of several years of scientific activities, an important aim of this dissertation is providing a detailed introduction into the realm of ZULF NMR. In this scope, the dissertation is divided into is organized into 8 chapters.

The first chapters (Chapters 1-3) provide the theoretical background for NMR, with particular focus on its ZULF incarnation. Thus, after a brief general introduction to relevant parts quantum mechanics, Chapter 2 presents the theory of NMR with the emphasis on different interactions that nuclei experience and analyzes them in a scope of isotropic liquid samples at ZULFs.

Chapter 3 follows a typical ZULF NMR experiment. It starts with the discussion of preparing a polarization of nuclear spins. Later the detection scheme, based on the atomic magnetometry is presented. Finally, an explanation of generating zero-field NMR spectra and its interpretation is provided. Chapter 4 contains discussion about the experimental details of research featured in this thesis.

Chapter 5 shows the experiments in chemical analysis of compounds at natural isotopic abundance with the use of zero-field spectroscopy. Chapter 6 is concerned with the detection of small biomolecules, while Chapter 7 discusses the use of ultra-low field NMR for searches of new physics.

Last chapter contains the summary of the dissertation as well as possible further directions of research in ZULF NMR.

1.1 PREFACE

This chapter introduces, in a concise manner, mathematical tools and physical theory used later to explain zero-field nuclear magnetic resonance (NMR). The reader can find a review of quantum mechanics (QM) in textbooks, such as [Sakurai and Commins \[1995\]](#). The basics of atomic polarization and atomic magnetometry (AM) are presented in a comprehensive fashion in [Auzinsh et al. \[2010\]](#), while the theory of NMR is extensively explained in [Levitt \[2013\]](#). This chapter starts with the description of a quantum-mechanical state via the state vector in the Hilbert space and through a density matrix. The theory of angular momentum is briefly introduced, as intrinsic angular momentum – spin – plays a central role both in AM and NMR, while the graphical representation of angular momentum states, used later in the thesis, is also introduced here.

1.2 QUANTUM MECHANICAL STATES AND THEIR EVOLUTION

The angular momentum of an atomic ensemble or the nuclear spins in molecules is described by quantum mechanics. A physical state of a system, according to quantum-mechanics postulates (see, for example, [Sakurai and Commins \[1995\]](#)), can be described using a state vector $|\alpha\rangle$ given in **Hilbert space**, where the ket state fully describes the physical system. A physical quantity observable in physical reality, for example, an alkali-atom polarization or nuclear-spin-ensemble magnetization, is represented by an operator $\hat{A}$ acting in the Hilbert space. Generally, an operator, acting on the ket state, produces yet another state in the Hilbert space:

$$\hat{A} |\alpha\rangle = |\beta\rangle. \quad (1.1)$$

However, there exists a set of states $|\alpha_n\rangle$, which are only scaled by a numerical factor when acted upon by the operator $\hat{A}$:

$$\hat{A} |\alpha_n\rangle = \alpha_n |\alpha_n\rangle, \quad (1.2)$$

where α_n are the **eigenvalues** of the operator $\hat{A}$ corresponding to **eigenvector** α_n . The set of eigenvalues of the operator can be complex. In quantum mechanics, however, operators corresponding to **observables** are expressed in terms of Hermitian operators, that is:

$$\hat{A} = \hat{A}^\dagger. \quad (1.3)$$

We can write down equations for the eigenvalues of the Hermitian operator and its Hermitian conjugate in a form:

$$\begin{aligned} \hat{A} |\alpha_1\rangle &= \alpha_1 |\alpha_1\rangle, \\ \langle\alpha_2| \hat{A}^\dagger &= \langle\alpha_2| \hat{A} = \alpha_2^* \langle\alpha_2|. \end{aligned} \quad (1.4)$$

If we multiply a top row of Eqs. 1.4 $\langle \alpha_2 |$ and the bottom row by $|\alpha_1\rangle$ respectively, we arrive at the following set of equations:

$$\begin{aligned}\langle \alpha_2 | \hat{A} |\alpha_1\rangle &= \alpha_1 \langle \alpha_2 | \alpha_1 \rangle, \\ \langle \alpha_2 | \hat{A}^\dagger |\alpha_1\rangle &= \langle \alpha_2 | \hat{A} |\alpha_1\rangle = \alpha_2^* \langle \alpha_2 | \alpha_1 \rangle.\end{aligned}\tag{1.5}$$

By subtracting formulas from Eq. 1.5, we arrive at the following condition:

$$(\alpha_1 - \alpha_2^*) \langle \alpha_2 | \alpha_1 \rangle = 0.\tag{1.6}$$

If we choose the eigenvectors to be the same, namely $|\alpha_1\rangle = |\alpha_2\rangle$, we arrive at the following condition:

$$\alpha_1^* = \alpha_1,\tag{1.7}$$

which ensures that the spectrum of the observable is real (as physical quantities measurable in experiments have to be real). By choosing the eigenvalues in Eqs. 1.6 to be different, we arrive at yet another condition:

$$\langle \alpha_1 | \alpha_2 \rangle = 0,\tag{1.8}$$

which means that the eigenvectors of the observable form an orthogonal basis.

1.3 EVOLUTION OF THE STATE

Among many physical observables, an energy operator, the Hamiltonian $\hat{\mathcal{H}}$, plays a crucial role in determining the evolution of a system. The nonrelativistic evolution of the state vector $|\Psi\rangle$ of the quantum state is governed by the **Schrödinger equation**:

$$\hat{\mathcal{H}} |\Psi\rangle = i\hbar \frac{d}{dt} |\Psi\rangle,\tag{1.9}$$

where $\frac{d}{dt}$ indicates the derivative over time. For the time-independent Hamiltonian, the Schrödinger equation can be solved, yielding a time evolution of the state $|\Psi\rangle(t)$:

$$|\Psi(t)\rangle = e^{-it\hat{\mathcal{H}}/\hbar} |\Psi(0)\rangle,\tag{1.10}$$

where $|\Psi(0)\rangle$ is the initial state of the system and **evolution operator** is given by:

$$\hat{U}(t) = e^{-it\hat{\mathcal{H}}/\hbar} = \hat{1} + \frac{-it}{\hbar} \hat{\mathcal{H}} - \left(\frac{t}{\hbar}\right)^2 \hat{\mathcal{H}}^2 + i \left(\frac{t}{\hbar}\right)^3 \hat{\mathcal{H}}^3 + \dots.\tag{1.11}$$

The eigenstates $|\psi_n(t)\rangle$ of the energy operator $\hat{\mathcal{H}}$ satisfy the relation:

$$\hat{\mathcal{H}} |\psi_n(t)\rangle = E_n |\psi_n(t)\rangle,\tag{1.12}$$

This means that during the evolution, an eigenstate acquires only a physically-insignificant phase shift:

$$|\psi_n(t)\rangle = e^{-itE_n/\hbar} |\psi_n(0)\rangle\tag{1.13}$$

and the **expectation value** of any observable measured in such a **stationary state**, is time-independent:

$$\langle \psi_n(t) | A | \psi_n(t) \rangle = \langle \psi_n(0) | A | \psi_n(0) \rangle = \langle A \rangle.\tag{1.14}$$

This discussion indicates that it is often convenient to express the state of the system in the eigenbasis of the Hamiltonian.

One can also derive an equation, which describes the evolution of the expectation value of the operator $\langle A \rangle$ in the quantum state $|\Psi\rangle$:

$$\begin{aligned} \frac{d\langle A \rangle}{dt} &= \frac{d}{dt} \langle \Psi | \hat{A} | \Psi \rangle = \frac{i}{\hbar} (\langle \Psi | \hat{\mathcal{H}} \hat{A} | \Psi \rangle - \langle \Psi | \hat{A} \hat{\mathcal{H}} | \Psi \rangle) + \langle \Psi | \frac{\partial \hat{A}}{\partial t} | \Psi \rangle \\ &= \frac{i}{\hbar} \langle [\hat{\mathcal{H}}, \hat{A}] \rangle + \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle, \end{aligned} \quad (1.15)$$

where we used the Schrödinger equation (and its complex conjugate) to arrive at the time evolution of the expectation value. In Chapter 2, we use Eq. 1.15 to analyze the semiclassical behavior of a magnetization operator.

1.4 WAVEFUNCTION

A particular representation of the ket state in basis of the position operator $\hat{x}$ is called a **wavefunction** $\psi(x)$:

$$\psi(x) = \langle x | \psi \rangle, \quad (1.16)$$

where $|x\rangle$ indicates the eigenstate of the position operator. The wavefunction of quantum mechanical system is a complex-valued function. In three dimensions, it takes the form

$$\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle, \quad (1.17)$$

where $|\mathbf{r}\rangle$ is an eigenstate of the position vector operator. We use this representation of a quantum-mechanical state to analyze how such a state transforms upon rotations in Cartesian coordinate system (see Sec. 1.7) and exchange of particles.

1.5 DENSITY MATRIX

So far, the state of the system was described by the state vector, which corresponds to a single physical system (a single atom or nuclei) or to a set of identical physical systems in the identically prepared state. The ensemble of particles, characterized by an identical vector state for all particles, is said to be **pure**. For this state, we can express the expectation value of the operator $\hat{A}$ as:

$$\begin{aligned} \langle \bar{A} \rangle &= \frac{1}{N} \sum_{i=1}^N \langle \psi_i | A | \psi_i \rangle = \langle \psi | A | \psi \rangle = \sum_m \langle \psi | \hat{A} | m \rangle \langle m | \psi \rangle = \sum_m \langle m | \psi \rangle \langle \psi | \hat{A} | m \rangle = \\ &= \text{Tr}(\hat{\rho} \hat{A}) = \text{Tr}(\hat{A} \hat{\rho}), \end{aligned} \quad (1.18)$$

where we insert an identity operator $\hat{\mathbb{1}} = \sum_m |m\rangle \langle m|$, with $|m\rangle$ being any complete set of normalized basis states and N being the number of particles. The operator $\hat{\rho} = |\psi\rangle \langle \psi|$ is called a **density operator**.

The density operator plays here a role similar to an averaged vector state of the ensemble state. Individual elements of the density operator form, in a given representation, elements of the density matrix:

$$\rho_{mn} = \frac{1}{N} \sum_{i=1}^N \langle m | \psi_i \rangle \langle \psi_i | n \rangle. \quad (1.19)$$

The diagonal elements of the density matrix

$$\rho_{mm} = \frac{1}{N} \sum_{i=1}^N \langle m | \psi_i \rangle \langle \psi_i | m \rangle = 1/N \sum_{i=1}^N |\langle m | \psi_i \rangle|^2, \quad (1.20)$$

correspond to the average probability of finding a system in the state $|m\rangle$ and are referred to as **populations**. The off-diagonal density-matrix elements, corresponding to the superposition of states, are called **coherences**.

The density matrix possess some useful properties. For instance, for a normalized set of states, the trace of the density matrix is equal to one (sum of populations is normalized to one):

$$\text{Tr } \rho = \sum_m \frac{1}{N} \sum_{i=1}^N \langle m | \psi_i \rangle \langle \psi_i | m \rangle = 1/N \sum_{i=1}^N \sum_m \langle \psi_i | m \rangle \langle m | \psi_i \rangle = 1/N \sum_{i=1}^N \langle \psi_i | \psi_i \rangle = 1, \quad (1.21)$$

while by construction the whole density operator is Hermitian ($\hat{\rho} = \hat{\rho}^\dagger$) and positive semi-definite (populations are always non-negative: $\rho_{mm} \geq 0$). Properties of the density matrix can be used to determine if a given state is pure, since for such a state the following relation occurs:

$$\hat{\rho}^2 = \hat{\rho}. \quad (1.22)$$

Moreover, the degree of the coherence has an upper bound connected to the population of the states it connects:

$$|\rho_{mn}| \leq \sqrt{\rho_{mm}\rho_{nn}}. \quad (1.23)$$

This relation becomes equality only for the pure states.

To find the time evolution of the density matrix, describing the state of the system, one can use the Schrödinger equation (Eq. 1.9) and its Hermitian conjugate version:

$$-i\hbar \frac{d}{dt} \langle \Psi | = \langle \Psi | \hat{\mathcal{H}}, \quad (1.24)$$

which gives:

$$\begin{aligned} i\hbar \frac{d}{dt} \hat{\rho} &= \frac{1}{N} \sum_{i=1}^N \left[i\hbar \left(\frac{d}{dt} |\psi_i\rangle \right) \langle \psi_i| + i\hbar |\psi_i\rangle \left(\frac{d}{dt} \langle \psi_i| \right) \right] \\ &= \frac{1}{N} \sum_{i=1}^N (\hat{\mathcal{H}} |\psi_i\rangle \langle \psi_i| - |\psi_i\rangle \langle \psi_i| \hat{\mathcal{H}}) = [\hat{\mathcal{H}}, \hat{\rho}]. \end{aligned} \quad (1.25)$$

Equation 1.25, called the **Liouville equation**, governs the coherent evolution of the density matrix. It is the basis of analytical and numerical calculation of the density matrix evolution in the case of atoms, constituting the magnetic-field sensor, and the nuclear spins measured under zero-field conditions.

It is worth noting that the introduction presented here, where each subsystem is characterized by a state vector (and, therefore, is a pure state), is unnecessarily strict. More generally, if there exists interaction between subsystems in the ensemble, it is generally impossible to assign a wavefunction to an individual subsystem. For example, this is a case in a spin ensemble in thermal equilibrium, where each individual spin is in the mixed state. To incorporate the description of such a state, the definition of the density operator is slightly modified to take into account the averaging over states in the ensemble:

$$\hat{\rho} = \sum_i P_i |\psi_i\rangle \langle \psi_i| \quad (1.26)$$

where P_i is a probability of state $|\psi_i\rangle$ existing in the ensemble.

1.6 ROLE OF THE ENVIRONMENT

So far, the evolution of the quantum system has been independent of any interaction from the rest of the universe, since we completely separated the system from the

environment. In reality, a system is coupled to its surroundings as well as interacts stochastically with itself. Those processes cause relaxation in the system. Despite their complexity, these behaviors can be phenomenologically described using the relaxation superoperator $\hat{\Gamma}$, acting on the density operator in the modified Liouville equation:

$$i\hbar \frac{d}{dt} \hat{\rho} = [\hat{\mathcal{H}}, \hat{\rho}] - i\hbar \hat{\Gamma} (\hat{\rho} - \hat{\rho}_0), \quad (1.27)$$

where $\hat{\rho}_0$ is a density operator under the steady-state condition or thermal equilibrium. Specific sources of relaxation are discussed in detail in the context of atomic vapors (Sec. 3.3.6) and nuclear spins in liquid (Sec. 2.2.8).

1.7 ANGULAR MOMENTUM

1.7.1 Angular momentum as generator of rotations

Understanding an angular momentum in quantum mechanics is crucial to the description of the evolution of the spin (acting like intrinsic angular momentum) in the case of both atomic and nuclear spin ensembles. In quantum mechanics, an operator $\hat{\mathbf{J}}$ is defined to be a generator of rotation when the following condition is satisfied:

$$\hat{R}_{\mathbf{e}_n}(d\phi) = \mathbb{1} - \frac{i\hat{\mathbf{J}} \cdot \mathbf{e}_n}{\hbar} d\phi, \quad (1.28)$$

where $\mathbf{e}_n$ is a unit vector along which rotation by an infinitesimal angle $d\phi$ is carried out. Arbitrary-angle rotation can be created by combining infinitely many infinitesimal rotations:

$$\hat{R}_{\mathbf{e}_n}(\phi) = \lim_{n \rightarrow \infty} (1 - (i\frac{\phi}{n} \hat{\mathbf{J}} \cdot \mathbf{e}_n)/\hbar)^n = \exp(-(i\phi \hat{\mathbf{J}} \cdot \mathbf{e}_n)/\hbar). \quad (1.29)$$

It can be shown that the operator $\hat{\mathbf{J}}$ corresponds to the angular-momentum operator. For simplicity, let us consider an infinitesimally small rotation of the vector $\mathbf{r} = (x, y, z)$ around the z -axis. For a system in the state $|\psi\rangle$ given in the Hilbert space, an associated wavefunction takes a form $\psi(\mathbf{r}) = \langle \hat{\mathbf{r}} | \psi \rangle$. Upon infinitesimally rotation, the value of the initial wavefunction transforms according to:

$$\psi'(\mathbf{r}') = \psi(\mathbf{r}) = \psi(R_z^{-1}(d\phi)\mathbf{r}'), \quad (1.30)$$

where $R_z(d\phi)$ describes the classical rotation. If we expand on the action of classic rotation onto the position vector $\mathbf{r}$, we get:

$$\hat{R}_z^{-1}(d\phi) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x + yd\phi \\ y - xd\phi \\ z \end{pmatrix}. \quad (1.31)$$

Therefore, an arbitrary wavefunction transforms in a following fashion:

$$\psi'(x, y, z) = \psi(x + yd\phi, y - xd\phi, z), \quad (1.32)$$

which, in a first order of the Taylor expansion in $d\phi$, yields:

$$\begin{aligned} \psi'(x, y, z) &= \psi(x, y, z) + d\phi \left(\frac{\partial}{\partial x} y - \frac{\partial}{\partial y} x \right) \psi(x, y, z) \\ &= \psi(x, y, z) - \frac{i}{\hbar} d\phi \left(\frac{\hbar \partial}{i \partial x} y - \frac{\hbar \partial}{i \partial y} x \right) \psi(x, y, z). \end{aligned} \quad (1.33)$$

Recalling a position representation of the momentum operator:

$$p_x = \frac{\hbar}{i} \frac{\partial}{\partial x}, \quad (1.34)$$

and, in analogous form to the rest of momentum components, we can immediately recognize the expression in the brackets in Eq. 1.33 as the operator of angular momentum along the z-axis. Comparing Eq. (1.33) with expression (1.28), we arrive at important conclusions: angular-momentum operator is the generator of rotations in the space of physical states.

1.7.2 Commutation relationship for rotation and angular-momentum operators

To derive commutation relations for the angular-momentum components, we first calculate the commutation of the rotation operators, where the rotation angle $d\phi$ is infinitesimally small. We first express rotation matrices along the x -, y -, z -axes, neglecting the terms higher than $d\phi^2$ as:

$$\hat{R}_x(d\phi) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(d\phi) & -\sin(d\phi) \\ 0 & \sin(d\phi) & \cos(d\phi) \end{pmatrix} \approx \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 - d\phi^2 & -d\phi \\ 0 & d\phi & 1 - d\phi^2 \end{pmatrix}, \quad (1.35)$$

$$\hat{R}_y(d\phi) = \begin{pmatrix} \cos(d\phi) & 0 & \sin(d\phi) \\ 0 & 1 & 0 \\ -\sin(d\phi) & \sin(d\phi) & \cos(d\phi) \end{pmatrix} \approx \begin{pmatrix} 1 - d\phi^2 & 0 & d\phi \\ 0 & 1 & 0 \\ -d\phi & 0 & 1 - d\phi^2 \end{pmatrix} \quad (1.36)$$

$$\hat{R}_z(d\phi) = \begin{pmatrix} \cos(d\phi) & -\sin(d\phi) & 0 \\ \sin(d\phi) & \cos(d\phi) & 0 \\ 0 & 0 & 1 \end{pmatrix} \approx \begin{pmatrix} 1 - d\phi^2 & -d\phi & 0 \\ d\phi & 1 - d\phi^2 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (1.37)$$

If we calculate the commutation of the matrices $\hat{R}_x(d\phi)$ and $\hat{R}_y(d\phi)$, neglecting terms $\mathcal{O}((d\phi)^3)$ and higher, we get:

$$[\hat{R}_x(d\phi), \hat{R}_y(d\phi)] \approx \begin{pmatrix} 0 & -d\phi^2 & 0 \\ d\phi^2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \approx \hat{R}_z(d\phi^2) - 1. \quad (1.38)$$

Following a similar procedure for other pairs of the Cartesian components of the rotation operators, we arrive at a general formula for the commutation of the rotation operators (for small angles):

$$[\hat{R}_i(d\phi), \hat{R}_j(d\phi)] = \epsilon_{ijk} [\hat{R}_k(d\phi^2) - 1]. \quad (1.39)$$

Following the commutation relationships for rotation operators (Eq. 1.39) and neglecting terms $\mathcal{O}(d\phi^3)$ and higher, we can write:

$$\begin{aligned} & \left[1 - \frac{i\hat{J}_x d\phi}{\hbar} - \frac{\hat{J}_x^2 d\phi^2}{2\hbar^2} \right] \left[1 - \frac{i\hat{J}_y d\phi}{\hbar} - \frac{\hat{J}_y^2 d\phi^2}{2\hbar^2} \right] - \left[1 - \frac{i\hat{J}_y d\phi}{\hbar} - \frac{\hat{J}_y^2 d\phi^2}{2\hbar^2} \right] \left[1 - \frac{i\hat{J}_x d\phi}{\hbar} - \frac{\hat{J}_x^2 d\phi^2}{2\hbar^2} \right] = \\ & = \frac{(\hat{J}_y \hat{J}_x - \hat{J}_x \hat{J}_y) d\phi^2}{\hbar^2} = -i \frac{\hat{J}_z d\phi^2}{\hbar}, \end{aligned} \quad (1.40)$$

we arrive at the commutation relationship for the angular-momentum operators:

$$[\hat{J}_x, \hat{J}_y] = i\hbar \hat{J}_z. \quad (1.41)$$

Similarly, commutation relations can be obtained for other angular momentum components:

$$\begin{aligned} [\hat{J}_y, \hat{J}_z] &= i\hbar \hat{J}_x, \\ [\hat{J}_z, \hat{J}_x] &= i\hbar \hat{J}_y. \end{aligned} \quad (1.42)$$

The operator $\hat{J}^2$, corresponding to square of total momentum, commutes with all the components of the angular-momentum operator:

$$\begin{aligned} [\hat{J}_x, \hat{J}^2] &= [\hat{J}_x, \hat{J}_x^2] + \hat{J}_y [\hat{J}_x, \hat{J}_y] + [\hat{J}_x, \hat{J}_y] \hat{J}_y + \hat{J}_z [\hat{J}_x, \hat{J}_z] + [\hat{J}_x, \hat{J}_z] \hat{J}_z = \\ &= 0 + i\hbar (\hat{J}_y \hat{J}_z + \hat{J}_z \hat{J}_y - \hat{J}_z \hat{J}_y - \hat{J}_y \hat{J}_z) = 0 = [\hat{J}_y, \hat{J}^2] = [\hat{J}_z, \hat{J}^2]. \end{aligned} \quad (1.43)$$

With the commutation relations, we can find a complete set of states in the so-called **Zeeman basis** (eigenstates of both $\hat{J}^2$ and $\hat{J}_z$ operators). The states are quantified by two quantum numbers J and m_J . One can show that the Zeeman states satisfy the following eigenproblems:

$$\begin{aligned} \hat{J}^2 |J, m_J\rangle &= \hbar^2 J(J+1) |J, m_J\rangle, \\ \hat{J}_z |J, m_J\rangle &= \hbar m_J |J, m_J\rangle. \end{aligned} \quad (1.44)$$

To simplify mathematical formulas in this thesis, from this point on, dimensionless angular-momentum operators are used by reassigning the operator according to $\hat{J}_i \rightarrow \hat{J}_i/\hbar$.

1.7.3 Direct product space- multiple spins

A quantum-mechanical state of two particles exists in the direct product space of two Hilbert spaces:

$$|\Psi\rangle_{12} = |\Psi\rangle_1 \otimes |\Psi\rangle_2. \quad (1.45)$$

Similarly, the density operator of such a two-atom system can be calculated using the tensor product:

$$\hat{\rho}_{12} = \hat{\rho}_1 \otimes \hat{\rho}_2, \quad (1.46)$$

where ρ_{12} is the density matrix of two particles. Finally, angular-momentum operators for individual particles can be expressed in the direct product space as:

$$\begin{aligned} \hat{J}_{j,1} &= \hat{J}_j \otimes \mathbb{1} \\ \hat{J}_{j,2} &= \mathbb{1} \otimes \hat{J}_j, \end{aligned} \quad (1.47)$$

where the j indicates a component of the angular momentum. A mixed operator, which is a product of the angular-momentum operators of particles 1 and 2, can also appear in the density matrix description of such a product state. The term $\hat{J}_{x,1}\hat{J}_{y,2}$ indicates a correlation between the angular-momentum component of particle 1 along the x -axis with the y -component of the angular momentum of the second particle (see, for example, [Levitt \[2013\]](#)). For a complete description of two coupled angular momenta, a total of 16 angular-momentum operators are needed: 6 so-called single-spin operators of form $\hat{J}_{j,1}$ or $\hat{J}_{j,2}$, 9 two-spin operators of a form $\hat{J}_{j,1}\hat{J}_{j,2}$ and the identity operator $\mathbb{1}$. A total density matrix of such two particle state can be expressed via the combination of such angular-momentum operators. This approach is especially useful in description of NMR experiments as the Hamiltonian describing evolution of the states can be expressed using angular-momentum operators (to be exact spin operators) and the evolution of parts of density matrix expressed via angular-momentum operators can be calculated in straightforward fashion.

For the important for this dissertation case of two ensembles of particles with angular momentum (spin) $1/2$, their collective state can be described using Zeeman states (eigenstates of angular momentum/spin operators): $\{|1/2, 1/2\rangle, |-1/2, -1/2\rangle, |-1/2, 1/2\rangle, |1/2, -1/2\rangle\}$, where the numbers correspond correspond to m_J quantum number for the first and the second spin respectively. Alternatively the different

set a basis, so-called **singlet-triplet** states, which can be expressed by the Zeeman states as:

$$\begin{aligned} |S_0\rangle &= |0,0\rangle = 1/\sqrt{2} (|1/2, -1/2\rangle - |-1/2, 1/2\rangle), \\ |T_0\rangle &= |1,0\rangle = 1/\sqrt{2} (|1/2, -1/2\rangle + |-1/2, 1/2\rangle), \\ |T_{+1}\rangle &= |1,1\rangle = |1/2, 1/2\rangle, \\ |T_{-1}\rangle &= |1,-1\rangle = |-1/2, -1/2\rangle. \end{aligned} \quad (1.48)$$

may be used. In chapters 2 and 3 we will see how Zeeman and singlet-triplet basis are the eigenstates of high- and zero-field spin hamiltonian respectively.

1.7.4 Addition of angular momenta

When we add two angular momenta in classical physics, the magnitude of the resulting momenta cannot be larger than the sum of magnitudes of compositing momenta, but neither it can be smaller than the absolute value of their difference. Analogous relation hold true in Quantum Mechanic:

$$|J - I| \leq F \leq J + I. \quad (1.49)$$

In quantum mechanics, the angular momentum is quantized, as it changes in steps of 1 (in $\hbar$ units). Projections along the z-axis of two angular momenta (m_J and m_I) can be added in a straightforward manner:

$$m_F = m_J + m_I, \quad (1.50)$$

while in general, two angular momenta when added can contribute to many total angular states:

$$|J, m_J, I, m_I\rangle = \left(\sum_{F, m_F} |F, m_F\rangle \langle F, m_F| \right) |J, m_J, I, m_I\rangle = \sum_{F, m_F} |F, m_F\rangle \langle F, m_F | J, m_J, I, m_I \rangle, \quad (1.51)$$

where we insert the identity operator ($\sum_{F, m_F} |F, m_F\rangle \langle F, m_F|$) = 1. The numerical coefficient relating angular momentum in tensors product bases and total angular momentum basis are called **Clebsch-Gordan coefficients**.¹ In a standard Condon-Shortley phase convention, the Clebsch-Gordan coefficients are real and satisfy various symmetry rules:

$$\begin{aligned} \langle J, m_J, I, m_I | F, m_F \rangle &= (-1)^{J-j_1-j_2} \langle J, -m_J, I, -m_I | F, -m_F \rangle = \\ &= (-1)^{J-j_1-j_2} \langle J, m_I, I, m_J | F, m_F \rangle. \end{aligned} \quad (1.52)$$

The numerical values of the Clebsch-Gordan coefficients are tabulated, but can also be calculated using built-in functions in various software packages.

The addition of angular momenta is crucial in explaining the energy-level structure of alkali metals that are used for magnetometry (Sec. 3.3.2), as well as, the zero-field spectrum of coupled nuclear spins (Sec. 3.4.2).

1.7.5 Rotation of states

In both NMR and AM, evolution in a magnetic field leads to rotation of quantum states. To calculate new states, one can express the density matrix of the state $\hat{\rho}$ as a weighted sum of angular-momentum operators and use a number of properties to see how the components of the density matrix evolve after such rotations.

¹ Note, that typically Clebsch-Gordan coefficient is defined as: $\langle J, m_J, I, m_I | F, m_F \rangle = \langle F, m_F | J, m_J, I, m_I \rangle^*$. In the standard convention, however, these coefficients are real, so the number in the main text is a regular Clebsch-Gordan coefficient.

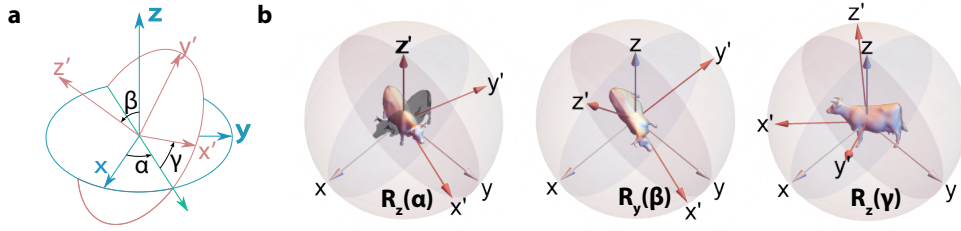


Figure 1.1: a) Graphical representation of Euler angles α, β, γ . The primed coordinates correspond to the body-fixed axes. The green lines indicate an axis created at the intersection of xy and $x'y'$ planes. b) Rotation of the object by Euler angles. Red arrows mark body-fixed axes.

Consider the expression $\hat{R}_i(\theta)\hat{L}_j\hat{R}_i(-\theta)$. When the angular-momentum-operator component is rotated around the direction it is pointing along:

$$\hat{R}_x(\theta)\hat{L}_x\hat{R}_x(-\theta) = e^{-i\theta\hat{L}_x}\hat{L}_xe^{i\theta\hat{L}_x} = \hat{L}_x, \quad (1.53)$$

as the operator L_x commutes with itself and therefore with $e^{i\theta\hat{L}_x}$ and the operator does not change its form. Analogous relations can be found for other angular momentum components. However, when the rotation is performed along different axes, the angular-momentum operator is:

$$\begin{aligned} \hat{R}_x(\theta)\hat{L}_y\hat{R}_x(-\theta) &= e^{-i\theta\hat{L}_x}\hat{L}_ye^{i\theta\hat{L}_x} \\ &= (\hat{L}_y - i\phi\hat{L}_x\hat{L}_y + \dots) (1 - i\phi\hat{L}_x + \dots) \\ &= \hat{L}_y \cos(\theta) + \hat{L}_z \sin(\theta). \end{aligned} \quad (1.54)$$

Similar relationships can be found for other pairs of angular momentum components again using the commutation relations 1.41 and 1.42. With this relationships in mind, one can easily find the transformation of the components of the density matrix upon action of the rotation operator.²

1.7.6 Euler angles

An arbitrary rotation in space can be characterized by the so-called **Euler angle**. The three angles describe the three consecutive rotations of the body-fixed z -, y - and z -axis:

$$R(\alpha, \beta, \gamma) = R_z(\alpha)R_y(\beta)R_z(\gamma), \quad (1.55)$$

where $\alpha, \gamma \in [0, 2\pi)$ and $\beta \in [0, \pi)$. Figure 1.1 illustrates the Euler angles (α, β, γ) with respect to the body-fixed axis of the object, as well as the series of rotations corresponding to the rotation by the Euler angles.

1.8 SPIN

1.8.1 Spin as intrinsic angular momentum

Atoms and nuclei are made up of fermions: electrons, protons, and neutrons, which are spin-1/2 particles. Spin, an intrinsic property of the particle itself, follows the same mathematical treatment as regular angular momentum, and it can couple with other angular momenta in the system forming a total angular momentum of a system.

² Notice that the relationship is analogous to a rotation of a regular vector, pointing along the y -axis around the x -axis by the angle θ . This correspondence gives an intuitive picture of the rotations of the angular-momentum components.

Spin plays a vital role both in AM (Sec. 3.3) as well as NMR (also its zero-field version, see Sec. 3.4.2). This is because the **magnetic moment** is associated with the intrinsic angular momentum of the particle. The physical quantity, relating magnetic moments $\hat{\mu}$ of a particle to its spin is called a **gyromagnetic ratio** and is expressed:

$$\hat{\mu} = \gamma \hat{S}. \quad (1.56)$$

For an isolated electron, the electron gyromagnetic ratio is given by:

$$\gamma_e = -\frac{e}{2m_e}g_e, \quad (1.57)$$

where g_e is an electronic g -factor, e is the electric charge of the electron, and m_e is the mass of the electron. Similarly for the nucleus, the nuclear gyromagnetic ratio γ_n is given by:

$$\gamma_n = \frac{e}{2m_p}g_n, \quad (1.58)$$

where g_n is the g -factor of the nucleon or nucleus. Since the gyromagnetic ratios scale inversely proportional to the mass of the particles, the gyromagnetic ratio is generally much larger for the electronic than nuclear system ($m_p/m_e \approx 1836$). For that reason, a combined gyromagnetic ratio for atomic system is still larger than that of the bare nucleus (e.g., for a ground state of ^{87}Rb atom and nuclear spin of ^1H the ratio is approximately 167). The strong field dependence ensures high sensitivity to magnetic field of the atomic system. The discrepancy in strength of coupling to magnetic field by nuclear and electronic systems may however prove challenging in adjusting the nuclear magnetic precession frequency and the AM response range.

1.8.2 Nuclear spin

As nuclei are composed objects made from protons and neutrons, both spin-1/2 particles, the nuclei can possess a non-zero spin. Nuclear spin can be determined using the **nuclear-shell model** (Mayer [1949]), which uses a deformed harmonic potential with spin-orbit coupling to model the energy structure of the nucleus. This early model of the nucleus describes the energy arrangement of nucleons analogously to that of electrons in atoms (atomic shells). As nucleons occupy nuclear shells, the way they fill the nuclear shells determines the total spin of the nucleus. For example, a single proton in ^1H occupies a $1s_{1/2}$ shell, contributing to the total spin of 1/2. In carbon ^{12}C , the 6 protons are paired in the $1s_{1/2}$ and $1p_{3/2}$ shells (see, for example, De-Shalit and Talmi [2013]) and all the 6 neutrons are paired in the same manner, giving rise to the total spin 0. The additional neutron in the ^{13}C nucleus occupies the $1p_{1/2}$ shell, giving rise to a total nuclear spin of 1/2. Similarly, in ^{31}P the unpaired protons occupy $2s_{1/2}$ shells resulting in spin-1/2, while in ^{14}N one unpaired proton and neutron in the $1p_{1/2}$ shell give rise to a total spin 1.

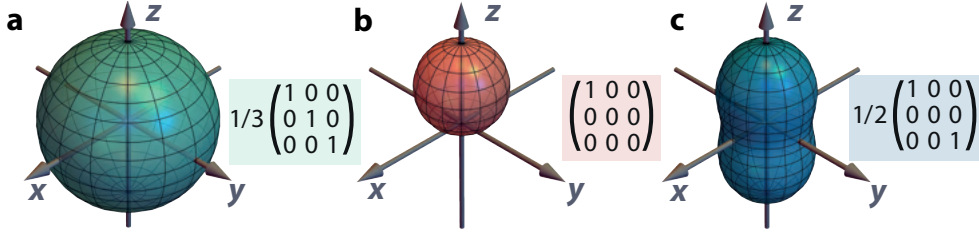
Since NMR relies on nuclear magnetic moment, it arises only in nuclei with non-zero nuclear spin. The tables with NMR active nuclei can be found in many NMR textbooks (see, for example, Levitt [2013]), while properties of the nuclei used in this thesis are Table 1.1.

1.9 VISUAL REPRESENTATION OF ANGULAR MOMENTUM STATES

Angular-momentum states can be visualized to provide an intuitive physical understanding of angular-momentum addition and state evolution.

Table 1.1: Summary of properties of nuclei studied with the use of zero-field NMR in this thesis. Values taken from [Levitt \[2013\]](#).

Isotope	Spin	Gyromagnetic ratio (MHz/T)	Abundance (%)
^1H	$1/2$	42.58	~ 100
^{13}C	$1/2$	10.71	1.10
^{14}N	1	3.08	99.60
^{15}N	$1/2$	-4.32	0.37
^{15}P	$1/2$	17.25	~ 100
^{35}Cl	$3/2$	1.68	75.77
^{37}Cl	$3/2$	1.405	24.23

**Figure 1.2:** Angular momentum probability surfaces for a number of example states in $F=1$ angular momentum manifold. Explicit forms of the density matrix are shown next to the corresponding AMPS. a) Unpolarized state. b) State polarized along z direction. c) Aligned state along z -axis.

One method used in this thesis to illustrate quantum states is based on **angular-momentum probability surfaces** (AMPS), first introduced in [Rochester and Budker \[2001\]](#). To demonstrate application of the technique, we first consider a density matrix spanning across the Zeeman sublevels of the total angular-momentum operator $\hat{F}$. If we determine a given maximal projection m_F along a chosen quantization axis, we get:

$$\langle Fm_F | \hat{\rho} | Fm_F \rangle = \rho_{m_F m_F}. \quad (1.59)$$

We then rotate the quantization axis and once again calculate ρ_{FF} . If we repeat the procedure for all possible spatial directions, we end up with a set of points constituting a 3D surface, which can be characterized by polar angles (θ, ϕ) :

$$\rho_{FF}(\theta, \phi) = \sum_{mm'} D_{mF}^*(\phi, \theta) \rho_{mm'} D_{m'F}(\phi, \theta), \quad (1.60)$$

where $D_{m'F}(\phi, \theta)$ are the Wigner D-functions. The reconstructed in this manner angular-momentum probability surface is a useful representation of density matrix. The surface contains as much information about the state as the density matrix and its symmetry properties mirror nonzero coherences present in the density matrix ([Alexandrov et al. \[2005\]](#)). Some angular-momentum surface are plotted in [Fig. 1.2](#). We will come back to this description when discussing nonlinear effects in alkali atoms ([Sec. 3.3.7](#)).

2

INTRODUCTION TO (ZERO-FIELD) NMR

2.1 NUCLEAR MAGNETIC RESONANCE

2.1.1 Classical description of NMR experiment

Nuclear magnetic resonance experiments exploit the magnetic properties of atomic nuclei, constituting molecules. Nuclei with non-zero spins have a non-zero permanent magnetic moment and therefore can interact with external magnetic fields. Being a source of microscopic magnetism, they may produce a macroscopic magnetization of a sample, the evolution of which is detected in NMR experiments.

Let us first consider a classical magnetic moment μ placed in an external magnetic field B . The energy of the system is given by (see, for example, [Jackson \[1999\]](#)):

$$E_{\text{magnetic}} = -\mu \cdot B. \quad (2.1)$$

The equation shows that the magnetic energy depends on the relative orientation of the magnetic moment and the magnetic field. Specifically, if the magnetic moment points along the magnetic field, its energy is the lowest, while the magnetic moment oriented opposite to the magnetic field has the highest possible energy. As the physical system tends towards the lowest-energy state, one would expect nuclear magnetic moments pointing along the magnetic field in the equilibrium state. However, the thermal energy of the environment is a constant source of excitation and in reality only a tiny fraction of microscopic magnetic moment point preferably along the magnetic field (see Sec. 3.2). This small excess in the magnetic moment orientation¹ produces, however, observable **macroscopic magnetization** M defined for a given volume V as:

$$\mu = \int_V M dV. \quad (2.2)$$

One can find ([Jackson \[1999\]](#)) that the torque is exerted onto the magnetic moment if its direction does not align with the magnetic field:

$$T = \mu \times B. \quad (2.3)$$

Assuming that the magnetic moment is proportional to the angular momentum L of a particle via $\mu = \gamma L$, we can write a classical equation of motion of magnetic dipole subject to the magnetic field:

$$\frac{d}{dt} L = T = \gamma (L \times B). \quad (2.4)$$

Based on the equation, one may introduce the time evolution of the magnetization $M = N_\mu \gamma L$, where N_μ is the density of magnetic moments. We start by multiplying both sides of Eq. 2.4 by a factor of $N_\mu \gamma$:

$$N_\mu \gamma \frac{d}{dt} L = (N_\mu \gamma) \gamma (L \times B), \quad (2.5)$$

which can be rearranged into:

$$\frac{d}{dt} (N_\mu \gamma L) = \gamma ((N_\mu \gamma L) \times B), \quad (2.6)$$

¹ One can show that in infinite temperature no magnetization is produced, and the NMR experiment is impossible.

to finally arrive at:

$$\frac{d}{dt}\mathbf{M} = \gamma (\mathbf{M} \times \mathbf{B}). \quad (2.7)$$

The magnetization vector precesses around the direction of the magnetic field with the characteristic frequency $-\omega = \gamma B$. This precession is called a **Larmor precession**, while the frequency of precession is referred to as the **Larmor frequency**. The Larmor frequency scales linearly with the applied magnetic field.

While Eq. 2.7 suggests continuous precession of magnetization. In reality, however, this process is disturbed by local magnetic-field fluctuations, caused by the thermal energy of the environment. Thereby, over time, the system is brought to thermal equilibrium, i.e., magnetization orients along the magnetic field. This relaxation of “along-the-field” (longitudinal) component occurs at the characteristic time called **the longitudinal relaxation time** T_1 . The equation of motion for relaxing magnetization is given by:

$$\frac{d}{dt}M_z = -\frac{M_z^0 - M_z(t)}{T_1}, \quad (2.8)$$

where M_z^0 is the magnetization in thermal equilibrium and we assume that the magnetic field $\mathbf{B}$ is aligned along the z -axis.

The transverse component of the magnetization also decays over time. Local magnetic-field fluctuations or field inhomogeneities modify precession frequencies of individual magnetic moments and hence the initially synchronized precession starts to dephase between different moments, eventually smearing over all possible orientations of magnetic moments in the transverse plane. This leads to a complete wash out of the transverse component of the magnetization. The process occurs with the characteristic **transverse relaxation time** T_2 and is characterized with the following relations:

$$\begin{aligned} \frac{d}{dt}M_x(t) &= -\frac{M_x(t)}{T_2}, \\ \frac{d}{dt}M_y(t) &= -\frac{M_y(t)}{T_2}, \end{aligned} \quad (2.9)$$

where M_x and M_y are the components of magnetization perpendicular (transverse) to the magnetic field and in thermal equilibrium both components vanish.

For molecules and conditions of experiments studied in this thesis, both T_1 and T_2 relaxation times are long, ranging from about a second to tens of seconds.

Combining relaxation equations (Eqs. 2.8 and 2.9) with the equation describing the Larmor precession (Eq. 2.7), we may write a set of classical equations describing evolution of magnetization of a spin ensemble in magnetic field, known as **the Bloch equations**:

$$\begin{aligned} \frac{d}{dt}M_x(t) &= \gamma [M_y(t)B_z(t) - M_z(t)B_y(t)] - \frac{M_x(t)}{T_2}, \\ \frac{d}{dt}M_y(t) &= \gamma [M_z(t)B_x(t) - M_x(t)B_z(t)] - \frac{M_y(t)}{T_2}, \\ \frac{d}{dt}M_z(t) &= \gamma [M_x(t)B_y(t) - M_y(t)B_x(t)] - \frac{M_z^0 - M_z(t)}{T_1}, \end{aligned} \quad (2.10)$$

where we assumed an arbitrary time-dependent magnetic field and the equilibrium polarization pointing along the z -axis. In general, the analytical solution of the Bloch equations may not be possible. However, one may find some interesting cases that can be solved analytically. Such a case is the magnetization initially oriented in the xy -plane (pointing along the x -axis) that evolves in the constant z -oriented

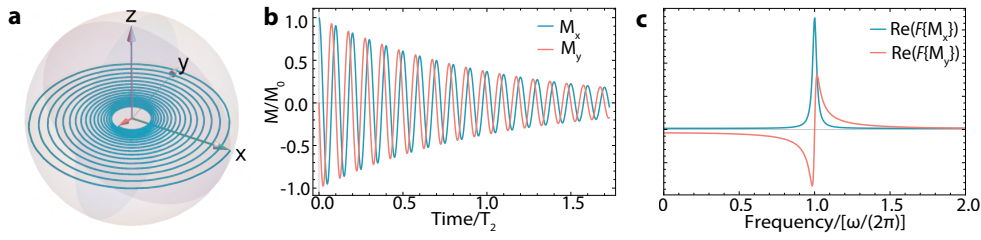


Figure 2.1: Evolution of the transverse magnetization subject to the static magnetic field oriented along the z -axis, calculated using the Bloch equations. The Larmor-precession period equals $T_2/10$. a) Magnetic precession of magnetization, initially oriented along the x -axis and b) corresponding evolution of x and y components of the magnetization (known in NMR as a FID signal). c) Real part of the Fourier transform of the x and y magnetization components (corresponding to the NMR spectrum).

magnetic field B . Then the transverse components of the magnetization are given by:

$$\begin{aligned} M_x(t) &= M_0 \cos(\omega t - \phi) e^{-t/T_2}, \\ M_y(t) &= M_0 \sin(\omega t - \phi) e^{-t/T_2}. \end{aligned} \quad (2.11)$$

These solutions to the Bloch equation are shown in the Fig. 2.1.

In a constant magnetic field, a transverse polarization precesses around the direction of the field. The oscillating components of the transverse magnetization are detected in conventional NMR experiments and the decaying signal corresponding to the magnetization is called a **free induction decay** (FID) (Fig. 2.1b). In NMR, the FID signals are rarely investigated directly but rather a spectrum of FID, called an **NMR spectrum**, is plotted (Fig. 2.1c) and analysed.

An important question in this discussion concerns means of tipping the magnetization from the thermal equilibrium (orientation along the magnetic field), to the transverse plane, where it precesses with the Larmor frequency. To illustrate this process let us consider a situation when a system of the magnetization, originally aligned along the static magnetic field (the z -axis), is subject to the transverse magnetic field, oscillating at the frequency Ω . In that case, the Bloch equations can be written as follows:

$$\begin{aligned} \frac{d}{dt} M_x(t) &= \gamma [M_y(t) B_0 - M_z(t) B_1 \sin(\Omega t)] - \frac{M_x(t)}{T_2}, \\ \frac{d}{dt} M_y(t) &= -\gamma M_x(t) B_0 - \frac{M_y(t)}{T_2}, \\ \frac{d}{dt} M_z(t) &= \gamma M_x(t) B_1 \sin(\Omega t) - \frac{M_z^0 - M_z(t)}{T_1}, \end{aligned} \quad (2.12)$$

where we assumed that the oscillating magnetic field with the amplitude B_1 points along the y -direction, while the static magnetic field B_0 is oriented along the z -axis. To find a solution to these equations, it is convenient to transfer the system into the frame of reference, rotating around the z -axis at the frequency Ω (the **rotating frame**). Then, the magnetization components in the rotating frame, denoted by rot , are related to the laboratory-frame components via:

$$\begin{aligned} M_x^{rot} &= \cos(\Omega t) M_x, \\ M_y^{rot} &= \sin(\Omega t) M_y, \\ M_z^{rot} &= M_z. \end{aligned} \quad (2.13)$$

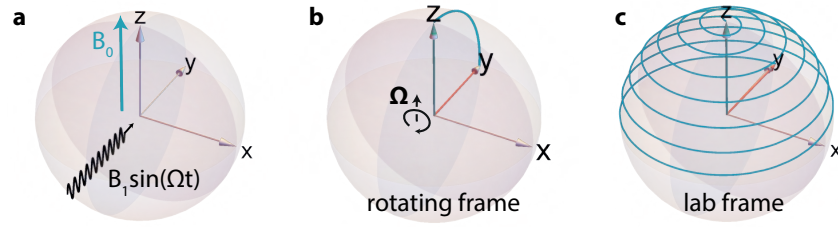


Figure 2.2: Effect of the resonant oscillating magnetic field on the dynamics of magnetization as predicted by Bloch equations. a) Geometry of the fields, static magnetic field B_0 points in z direction while the oscillating field with amplitude B_1 is applied along y direction. b) Nutation of the spins caused by the rotating component of the oscillating resonant field as seen in the rotating frame of reference. c) Dynamics of the spin in the stationary, laboratory frame of reference.

Using Eqs. 2.13, we can rewrite the Bloch equations into:

$$\begin{aligned} \frac{d}{dt} M_{xy}^{rot}(t) &= i(\Omega - \omega_0) M_{xy}^{rot}(t) + i\gamma \frac{B_1}{2} M_z^{rot}(t) e^{i\Omega t} (e^{-i\Omega t} - e^{i\Omega t}) - \frac{M_{xy}^{rot}}{T_2}, \\ \frac{d}{dt} M_z^{rot}(t) &= i\gamma \frac{B_1}{2} M_{xy}^{rot}(t) e^{i\Omega t} (e^{-i\Omega t} - e^{i\Omega t}) - \frac{M_z^0 - M_z^{rot}(t)}{T_1}, \end{aligned} \quad (2.14)$$

which describe evolution of the transverse magnetization $M_{xy}^{rot} = M_x^{rot} + iM_y^{rot}$ and the longitudinal magnetization M_z in the rotating frame. The factor $1/2$ arises from the **rotating-wave approximation** (RWA). This approximation can be used when the oscillating-field frequency is equal to the Larmor frequency $\Omega = \omega_0$ and it consists in neglecting the terms oscillating in Eq. 2.14 at 2Ω .² Within RWA we arrive at the set of simple equations, describing evolution of the magnetization in the rotating frame:

$$\begin{aligned} \frac{d}{dt} M_{xy}^{rot}(t) &= i\gamma \frac{B_1}{2} M_z^{rot}(t) - \frac{M_{xy}^{rot}}{T_2}, \\ \frac{d}{dt} M_z^{rot}(t) &= i\gamma \frac{B_1}{2} M_{xy}^{rot}(t) - \frac{M_z^0 - M_z(t)}{T_1}. \end{aligned} \quad (2.15)$$

This shows that the complex evolution of the system in the laboratory frame can be largely simplified in the rotating frame to the rotation of magnetization around the x -axis with the frequency $\omega_n = \gamma(B_1/2)$ called the **nutation frequency**.³ By taking real and imaginary parts of the transverse magnetization M_{xy} , one can retrieve equations for all Cartesian components of the magnetization:

$$\begin{aligned} \frac{d}{dt} M_x^{rot}(t) &= -\frac{M_x^{rot}}{T_2}, \\ \frac{d}{dt} M_y^{rot}(t) &= \gamma \frac{B_1}{2} M_z^{rot}(t) - \frac{M_y^{rot}}{T_2}, \\ \frac{d}{dt} M_z^{rot}(t) &= -\gamma \frac{B_1}{2} M_y^{rot}(t) - \frac{M_z^0 - M_z(t)}{T_1}. \end{aligned} \quad (2.16)$$

The classical analysis of evolution of the magnetization in the magnetic field (the Bloch equation) provides coarse description of NMR. To provide the more detailed insight into the effect, we now turn to a QM description of an ensemble of non-interacting spin-1/2 particles. We also show the correspondence of classical and QM descriptions.

² The off-resonant component of the oscillating magnetic field gives rise to a shift in the evolution frequency. The effect is known as the Bloch-Siegert shift (Bloch and Siegert [1940]) and was observed and analysed in NMR (Anderson and Freeman [1962]).

³ For the resonance condition $\Omega = \omega_0$, the axis of rotation is determined by the initial phase ϕ of the oscillating magnetic field $B_1 = B_1 \sin(\Omega t + \phi)$. In the case, the phase ϕ is the angle between the rotation and x -axes. This enables rotation around any direction even with the field oriented in a given transverse direction.

2.1.2 Spin-1/2 in external magnetic field

Let us consider an ensemble of identical, non-interacting nuclear spin-1/2 particles, characterized with the gyromagnetic ratio γ . The magnetic moment of each spin is given by the operator $\hat{\mu} = \gamma\hbar\hat{I}$ (the factor $\hbar$ comes from using dimensionless angular-momentum operators). By the analogy to the relation for the energy of the magnetic moment in the field (Eq. 2.1), we can show that in the Zeeman basis, the eigenvalues of the spin states in the magnetic field $\mathbf{B}$ of amplitude B_0 , oriented along the z -axis, $\mathbf{B} = \mathbf{e}_z B_0$ are given by:

$$E_{\pm} = -\gamma\hbar B_0 \langle I_z \rangle_{\pm} = \mp 1/2 \gamma\hbar B_0. \quad (2.17)$$

This energy difference between two Zeeman levels leads to a (small) fraction of spins preferably point along the direction of the magnetic field (see Sec. 3.2) as opposed to pointing in the reverse direction. We label this fraction as the nuclear polarization P_0 , which gives rise to a following form of the density operator $\hat{\rho}_0$:

$$\hat{\rho}_0 = (1/2 + P_0) |1/2, 1/2\rangle \langle 1/2, 1/2| + (1/2 - P_0) |1/2, -1/2\rangle \langle 1/2, -1/2|. \quad (2.18)$$

This density operator can be expressed using the angular-momentum operators for the spin-1/2:

$$\hat{\rho}_0 = \frac{1}{2} \mathbb{1} + P_0 \hat{I}_z, \quad (2.19)$$

where the z -component of angular momentum for spin 1/2 is equal to a third Pauli matrix $\hat{I}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$.

Let us now focus on the action of the oscillating magnetic field applied in transverse plane (as shown in classical considerations, this field causes nutation of the magnetic moment). To do that we first transform the thermal-equilibrium density operator (Eq. 2.19) using the rotation operator $\hat{R}_z$:

$$\hat{\rho}_0^{rot} = \hat{R}_z(-\Omega t) \hat{\rho}_0 \hat{R}_z(\Omega t) = e^{i\Omega t \hat{I}_z} \hat{\rho}_0 e^{-i\Omega t \hat{I}_z}, \quad (2.20)$$

where we used that $R_z^+(\phi) = R_z(-\phi)$. Since the density operator commutes with the spin operator $\hat{I}_z$, the density matrix has the same form in the laboratory and rotating frames:

$$\hat{\rho}_0^{rot} = \hat{\rho}_0 e^{i\Omega t \hat{I}_z} e^{-i\Omega t \hat{I}_z} = \hat{\rho}_0. \quad (2.21)$$

In the rotating frame, the evolution of the density matrix due to the oscillating magnetic field can be also calculated using the Liouville equation (Eq. 1.25):

$$i\hbar \frac{d}{dt} \hat{\rho}^{rot}(t) = [\hat{H}_1^{rot}, \hat{\rho}^{rot}(t)], \quad (2.22)$$

where the Hamiltonian $\hat{H}_1^{rot}$ describes interaction with the oscillating field in the rotating frame. The laboratory-frame Hamiltonian:

$$\hat{H}_1 = -\hbar\gamma B_1 \sin(\Omega t) \hat{I}_y + \omega_0 \hat{I}_z, \quad (2.23)$$

describing interaction with the magnetic field of the amplitude B_1 and the frequency Ω oscillating in the y -direction, can be transformed into the rotating frame through:

$$\hat{H}_1^{rot} = \hat{R}_z(-\Omega t) \hat{H}_1 \hat{R}_z(\Omega t) - \Omega \hat{I}_z. \quad (2.24)$$

Then the interaction with oscillating field can be presented as:

$$\hat{H}_1^{rot} = -\frac{\hbar\gamma B_1}{2} [(\hat{I}_x \cos(\Omega t) + \hat{I}_y \sin(\Omega t)) - (\hat{I}_x \cos(\Omega t) - \hat{I}_y \sin(\Omega t))] + \omega_0 \hat{I}_z.$$

(2.25)

Using RWA, we arrive at:

$$\hat{H}_1^{rot} \approx -\frac{\hbar\gamma B_1}{2} [\cos(\Omega t)\hat{I}_x + \sin(\Omega t)\hat{I}_y] + \omega_0\hat{I}_z. \quad (2.26)$$

Assuming a resonant oscillating magnetic field, i.e., $\Omega = \omega_0$, we can now calculate the form of the rotating-wave Hamiltonian $\hat{H}_1^{rot}$:

$$\hat{H}_1^{rot} = \hat{R}_z(-\Omega t) \left\{ -\frac{\hbar\gamma B_1}{2} [\cos(\Omega t)\hat{I}_x + \sin(\Omega t)\hat{I}_y] \right\} \hat{R}_z(\Omega t) = -\frac{\hbar\gamma B_1}{2} \hat{I}_x. \quad (2.27)$$

In the rotating frame, the oscillating-field Hamiltonian takes a time-independent form and is proportional to the angular-momentum operator.

Using Eq. 2.27, we can calculate the effect of the oscillating field on the density matrix:

$$\hat{\rho}_0^{rot} = \exp\left(\frac{\gamma B_1 t \hat{I}_x}{2}\right) \hat{\rho}_0 \exp\left(-\frac{\gamma B_1 t \hat{I}_x}{2}\right). \quad (2.28)$$

In the rotating frame, the evolution operator under $\hat{\mathcal{H}}_1$ (Eq. 2.27) takes the form of rotation around the x -axis, corresponding exactly to the nutation of classical magnetization in the rotating frame of reference. To see that the analogy extends even further, let us introduce a magnetization operator with following transverse components:

$$\begin{aligned} \hat{M}_x &= N\hbar\gamma\hat{I}_x, \\ \hat{M}_y &= N\hbar\gamma\hat{I}_y. \end{aligned} \quad (2.29)$$

To see how the observable of macroscopic magnetization evolves, let us look at the time evolution of the expectation values of magnetization components:

$$\begin{aligned} \frac{d}{dt} \langle \hat{M}_x \rangle &= \frac{i}{\hbar} \langle [\hat{\mathcal{H}}, \hat{M}_x] \rangle, \\ \frac{d}{dt} \langle \hat{M}_y \rangle &= \frac{i}{\hbar} \langle [\hat{\mathcal{H}}, \hat{M}_y] \rangle, \\ \frac{d}{dt} \langle \hat{M}_z \rangle &= \frac{i}{\hbar} \langle [\hat{\mathcal{H}}, \hat{M}_z] \rangle. \end{aligned} \quad (2.30)$$

If we consider evolution of the expectation value in the rotation frame, according to the Hamiltonian given by Eq. 2.27, we arrive at a following set of equations:

$$\begin{aligned} \frac{d}{dt} \langle \hat{M}_x^{rot} \rangle &= -\frac{i\gamma B_1}{2\hbar} \langle [\hat{I}_x, \hat{M}_x^{rot}] \rangle = 0, \\ \frac{d}{dt} \langle \hat{M}_y^{rot} \rangle &= -\frac{i\gamma B_1}{2\hbar} \langle [\hat{I}_x, \hat{M}_y^{rot}] \rangle = \frac{\gamma B_1}{2\hbar} \langle \hat{M}_z^{rot} \rangle, \\ \frac{d}{dt} \langle \hat{M}_z^{rot} \rangle &= -\frac{i\gamma B_1}{2\hbar} \langle [\hat{I}_x, \hat{M}_z^{rot}] \rangle = -\frac{\gamma B_1}{2\hbar} \langle \hat{M}_y^{rot} \rangle. \end{aligned} \quad (2.31)$$

which are identical to the set of Bloch equations describing nutation of classical magnetization (Eq. 2.16), where the role of the classical magnetization is taken by the expectation values of magnetization operator.⁴ Similarly, we can show that the expectation values of the transverse components of the magnetization precess around the direction of the z -oriented magnetic field according to the Bloch equations:

$$\begin{aligned} \frac{d}{dt} \langle \hat{M}_x \rangle &= -\frac{i\gamma B_0}{\hbar} \langle [\hat{I}_z, \hat{M}_x] \rangle = \frac{\gamma B_0}{\hbar} \langle \hat{M}_y \rangle, \\ \frac{d}{dt} \langle \hat{M}_y \rangle &= -\frac{i\gamma B_0}{\hbar} \langle [\hat{I}_z, \hat{M}_y] \rangle = -\frac{\gamma B_0}{\hbar} \langle \hat{M}_x \rangle, \\ \frac{d}{dt} \langle \hat{M}_z \rangle &= -\frac{i\gamma B_0}{\hbar} \langle [\hat{I}_z, \hat{M}_z] \rangle = 0. \end{aligned} \quad (2.32)$$

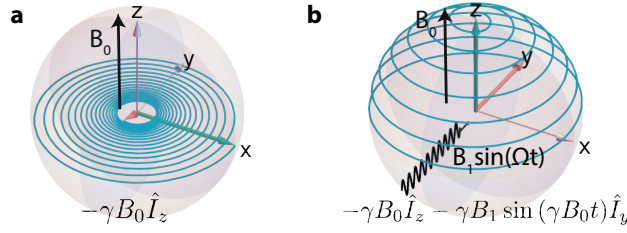


Figure 2.3: Behaviour of the expectation values of the magnetization operator under influence of a magnetic field. The calculation was performed using *Spin Dynamica* (Bengs and Levitt [2018]) package of *Wolfram Mathematica*. Notice that the evolution is identical to classical model derived from Bloch equations (Figs. 2.1a) and 2.2c)). a) Magnetization vector precession in a constant magnetic field along the z-axis given by Hamiltonian shown below. b) Nutation and precession of the spins caused interaction with static and oscillating magnetic field (as seen in laboratory frame).

In summary, we showed that the set of non-interacting spin-1/2 particles can be effectively described using a semi-classical model with the magnetization expectation value corresponding to the classical magnetization. The magnetization evolution is governed by the set of Bloch equations, with two characteristic decay times. This classical correspondence can also explain stages of a regular NMR experiment and explain appearance of FID signals. However, this semi-classical description is not sufficient to provide detailed explanation of NMR experiments. Namely, the role of inter- and intramolecular interactions is completely neglected (it is investigated in the next section). Moreover, the classical description is generally not adequate to describe the rise of zero-field NMR signals, which is similar to quantum beats between two eigenstate of the zero-field Hamiltonian (Sec. 3.4). Some semiclassical models (like vector model), however, can explain features of zero-field spectra, as shown, for example, in Butler et al. [2013b].

2.2 HAMILTONIAN IN NMR EXPERIMENT

2.2.1 Spin Hamiltonian hypothesis

To provide a complete description of a nuclear-spin system in a typically NMR sample, we need to describe an incredibly complex quantum system, consisting of an astronomical number of electrons and nuclei with a large number of degrees of freedom. The collective evolution of the state $\hat{\rho}_{total}$, evolving under the total Hamiltonian $\hat{\mathcal{H}}_{total}$ is given by:

$$\frac{d}{dt}\hat{\rho}_{total} = -\frac{i}{\hbar} [\hat{\mathcal{H}}_{total}, \hat{\rho}_{total}]. \quad (2.33)$$

To describe evolution of nuclear spins, an assumption that the evolution occurs only due to the spin-depended part of the total Hamiltonian. Under this, so-called, **spin Hamiltonian hypothesis** (see, for example, Levitt [2013]) the spin part of the density matrix evolves as:

$$\frac{d}{dt}\hat{\rho}_{spin} \approx -\frac{i}{\hbar} [\hat{\mathcal{H}}_{spin}, \hat{\rho}_{spin}], \quad (2.34)$$

where $\hat{\mathcal{H}}_{spin}$ is the spin Hamiltonian. Specifically, the NMR Hamiltonian only consists of the terms that depend on nuclear spins. The assumption, which is a basis of every NMR calculation, is founded at different energy and time scales of nuclear and electron interactions; electrons' motion is so fast, that nuclear spins effectively

⁴ Note that relaxation is neglected in Eqs. 2.31.

couple to average electric and magnetic fields of the electrons (see Secs. 2.2.2 and 2.2.3). Moreover, the excitation energy of nuclear spins is low enough and it does not affect the motion of the whole nuclei.⁵

We can generally divide the spin Hamiltonian into two parts, indicating whether the interaction of the nuclear spins occurs with external or internal electromagnetic fields:

$$\hat{\mathcal{H}}_{spin} = \hat{\mathcal{H}}_{external} + \hat{\mathcal{H}}_{internal}. \quad (2.35)$$

Below, we analyze specific interactions present in the Hamiltonian.

2.2.2 Zeeman interaction and chemical shift

In a (typical) NMR experiment, a sample is placed inside a magnetic field. The nuclear-spin interaction with a magnetic field was discovered in the context of atomic spectroscopy and named after Pieter Zeeman (the **Zeeman interaction**). For the a local magnetic field $\mathbf{B}$, the interaction takes the form:

$$\hat{\mathcal{H}}_{Zeeman} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} = -\hbar\gamma\hat{\mathbf{S}} \cdot \mathbf{B} = -\hbar\gamma(\hat{S}_x B_x + \hat{S}_y B_y + \hat{S}_z B_z), \quad (2.36)$$

where the magnetic moment $\boldsymbol{\mu}$ is related to a spin $\mathbf{S}$ by a gyromagnetic ratio γ . In a typical NMR experiment, the magnetic field is dominated by the applied field of the NMR spectrometer. However, the external magnetic field at the nucleus may be modified by the electrons present in a molecule. This is because an electronic cloud deforms due to the the external magnetic field, inducing additional field, which modifies the field at the nucleus. This interactions causes for example protons in water molecule to experience effectively different magnetic field than those experienced by the $-\text{CH}_3$ group in methanol, even if both samples are placed in the same external field. This local modification of the magnetic field, caused by the induced field, is called a **chemical shift** and is basis for analytical capabilities of conventional, high-field NMR. The induced field that is responsible for chemical shift is linearly proportional to the applied magnetic field B_0 :

$$\mathbf{B}_{CS} = \boldsymbol{\delta} \cdot \mathbf{B}_0, \quad (2.37)$$

where $\boldsymbol{\delta}$ is the rank-2 chemical-shift tensor:

$$\boldsymbol{\delta} = \begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{pmatrix}. \quad (2.38)$$

Since the chemical shift is a tensor, the induced magnetic field $\mathbf{B}_{CS}$ generally does not need to be aligned along the external-field direction.

It is noteworthy that the chemical shift is molecular-site specific. This means that same nuclei in the same molecule but at different sites may experience different magnetic field. In NMR, the nuclei experiencing the same chemical shift are called to be **chemically equivalent**.⁶ Chemical shift is typically weak and its magnitude lies between 1 and 1000 parts per million (ppm).

Usually the chemical-shift tensor is assumed to be symmetric, i.e., $\delta_{ij} = \delta_{ji}$, where $i \neq j \in \{x, y, z\}$.⁷ Thus one may find a set of spatial directions (base vectors) under

⁵ The motional degree of freedom of nuclei can affect its nuclear-spin energy as is evident in spin-lattice relaxation (relaxation of the longitudinal magnetization, see, for example, Levitt [2013]). This once again proves an approximately character of the relationship given by Eq. 2.34.

⁶ As shown in a later chapter, under the zero-field conditions, all nuclei experience same (zero) magnetic field, so such a distinction is not valid.

⁷ The antisymmetric part of the chemical-shift tensor plays a vital role in relaxation processes caused by chemical-shift anisotropy (Abragam [1961]). It may may be also (potentially) used in NMR to distinguish molecular enantiomers, as a chemical-shift antisymmetric part should differ for molecules of different chirality (Buckingham and Fischer [2006]).

which the chemical-shift tensor is diagonal. The set of these vectors, directly related to a molecular structure, is called **principal axes** (noted latter by X, Y, Z). The chemical-shift values along the axes are called the **principal chemical-shift values**:

$$\delta_{\text{symmetric}} = \begin{pmatrix} \delta_{XX} & 0 & 0 \\ 0 & \delta_{YY} & 0 \\ 0 & 0 & \delta_{ZZ} \end{pmatrix}. \quad (2.39)$$

Let us finally stress that the Zeeman interaction is the dominant interaction in high-field NMR experiments (0.2–10 T). The average strength of the Zeeman interaction in the frequency units lies between tens and hundreds of megahertz ($\langle \hat{\mathcal{H}}_{\text{Zeeman}} \rangle / h \approx 1 - 1000 \text{ MHz}$). In that regard, traditional NMR is an atypical spectroscopic technique, where the strongest measured interaction happens between the instrumentation and the sample.

2.2.3 Quadrupolar interaction

The electrostatic interaction energy between electrons charge distribution $\rho_e(\mathbf{r})$, and the electric charge of the nucleus $\rho_n(\mathbf{r})$ is given by (Jackson [1999]):

$$E_{\text{electric}} = \frac{1}{4\pi\epsilon_0} \int \int \frac{\rho_e(\mathbf{r}_e)\rho_n(\mathbf{r}_n)}{|\mathbf{r}_e - \mathbf{r}_n|} d^3r_e d^3r_n, \quad (2.40)$$

where the $\mathbf{r}_e$ and $\mathbf{r}_n$ are the position vectors of electronic and nuclear charge density. As generally charge distribution is not uniform, we can expand the denominator using a classical multipole expansion into spherical harmonics (Jackson [1999]):

$$\frac{1}{|\mathbf{r}_e - \mathbf{r}_n|} = \sum_{l=0}^{\infty} \frac{(r_n)^l}{(r_e)^{l+1}} \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{l,m}^*(\theta_e, \phi_e) Y_{l,m}(\theta_n, \phi_n), \quad (2.41)$$

where we expressed the reverse of relative-position vector using a series composed of the Legendre polynomials, which then were expressed using the spherical harmonics (given in the spherical coordinates of the electron and nuclear charge density). If we plug the expansion 2.41 into Eq. 2.40, we arrive at a following form of the electrostatic-interaction energy:

$$E_{\text{electric}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l A_{m,l} B_{m,l}^*, \quad (2.42)$$

where the terms $A_{m,l}$ and $B_{m,l}$ take a form: (Abragam [1961]):

$$\begin{aligned} A_{m,l} &= \sqrt{\frac{1}{\epsilon_0} \frac{1}{2l+1}} \int \rho_n(\mathbf{r}_n) r_n^l Y_{l,m}(\theta_n, \phi_n) d^3r_n, \\ B_{m,l} &= \sqrt{\frac{1}{\epsilon_0} \frac{1}{2l+1}} \int \rho_e(\mathbf{r}_e) r_e^{-(l+1)} Y_{l,m}^*(\theta_e, \phi_e) d^3r_e. \end{aligned} \quad (2.43)$$

It can be shown (see, for example, Abragam [1961]) that the corresponding Hamiltonian, which expectation value takes the form of energy shown in Eq. 2.42, can be written as:

$$\hat{\mathcal{H}}_{\text{electric}} = \sum_{l,m} \hat{A}_{l,m} \hat{B}_{l,m}^*, \quad (2.44)$$

where the operators $\hat{A}_{l,m}$ and $\hat{B}_{l,m}$ are expressed as:

$$\begin{aligned} \hat{A}_{l,m} &= \sqrt{\frac{1}{\epsilon_0} \frac{1}{2l+1}} \sum_j e_j \hat{\mathbf{R}}_j^l Y_{l,m}(\theta_{n,j}, \phi_{n,j}), \\ \hat{B}_{l,m} &= -e \sqrt{\frac{1}{\epsilon_0} \frac{1}{2l+1}} \sum_j \hat{\mathbf{r}}_j^{-(l+1)} Y_{l,m}(\theta_{e,j}, \phi_{e,j}), \end{aligned} \quad (2.45)$$

where $\hat{R}_j$ and $\hat{r}_j$ are the position operators for the nucleons in the nuclei and electrons respectively. Since the $\hat{A}_{l,m}$ and $\hat{B}_{l,m}$ operators transform upon rotations as spherical harmonics, matrix elements of the nuclear operator $\hat{A}_{l,m}$ (corresponding to the electric multipoles of the nucleus charge) can be expressed as:

$$\langle \chi, I', m_I' | \hat{A}_{l,m} | \chi, I, m_I \rangle = \langle I, l, m_I, m | I', m_I' \rangle \langle I, \chi | \hat{A}_l | I', \chi' \rangle, \quad (2.46)$$

where we used the **Wigner-Eckart theorem** (see e.g. [Sakurai and Commins \[1995\]](#)). The non-zero values of the **Clebsch-Gordan coefficients** $| \chi, I, m_I \rangle = \langle I, l, m_I, m | I', m_I' \rangle$ impose a following condition for non-zero elements of the matrix elements of nuclear operator:

$$|I - I'| \leq l \leq I' + I, \quad (2.47)$$

which, for a spins I , immediately gives an upper bound for non-zero elements of the nuclear electric-moment operator:

$$l \leq 2I. \quad (2.48)$$

$\hat{A}_0$ is a zeroth-order multipole, which is present for all nuclei, which shifts the energy of all spin level and does not contribute to the spin Hamiltonian. Until now, the permanent electric dipole term $\hat{A}_1$, which could exist for nuclei with spin $I > 1/2$, was not found (neither for protons nor neutrons) ([Griffith et al. \[2009\]](#)). For spins larger than $1/2$, however, higher-order terms (quadrupolar, octupole, etc.) exist and can affect nuclear dynamics. The next non-zero term in the expansion, corresponding to quadrupolar interaction, has a form ([Abragam \[1961\]](#)):

$$\hat{\mathcal{H}}_{quadrupolar} = \frac{eQ}{2I(2I-1)\hbar} \hat{\mathbf{I}} \cdot \mathbf{V}^{(2)} \cdot \hat{\mathbf{I}}, \quad (2.49)$$

where Q is a quadrupolar moment of the nuclei, while $\mathbf{V}^{(2)}$ is a electric gradient tensor:

$$V_{ij}^{(2)} = \frac{\partial^2 V}{\partial x_i \partial x_j}, \quad (2.50)$$

where V is the electric-field potential. The electric-field gradient exists in most molecules as electron-charge distribution is rarely symmetric in respect to nuclei position. As explained earlier, this interaction exists only for nuclei of spins larger than $1/2$. Specific examples of such nuclei, are naturally abundant and hence popular in NMR ^{14}N , ^2D , and ^{35}Cl , ^{37}Cl . The strength of the interaction depends of nucleus properties (**quadrupolar moment**) as well as electronic surroundings (electric-field gradient) and it can be substantial reaching tens of megahertz ($\langle \hat{\mathcal{H}}_{quadrupolar} \rangle / \hbar \approx 1 - 100 \text{ MHz}$).

Finally, it should be noted that higher electric moments (e.g., hexadecapole) exist for nuclei with even larger spins. However, they are typically weaker than quadrupolar interaction and hence are almost always neglected in calculation.

2.2.4 Dipole-dipole interaction

As a permanent magnetic dipole moment is associated with nuclear spin- $1/2$, the magnetic field created by a nuclear spins may effect evolution of nearby spins via the **dipole-dipole interaction**. The Hamiltonian, describing the dipole-dipole interaction between two spins $\hat{\mathbf{I}}_1$ and $\hat{\mathbf{I}}_2$ characterized with the gyromagnetic ratios γ_1 and γ_2 , respectively, can be introduced through the analogy to a classical magnetic dipole-dipole interaction ([Abragam \[1961\]](#)):

$$\hat{\mathcal{H}}_{dipole-dipole} = \frac{\mu_0 \gamma_1 \gamma_2 \hbar^2}{4\pi r^3} [3(\hat{\mathbf{I}}_1 \cdot \mathbf{r}_{12})(\hat{\mathbf{I}}_2 \cdot \mathbf{r}_{12}) - \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2], \quad (2.51)$$

where r is a distance between two nuclei and $\mathbf{r}_{12}$ is a unit vector connecting nuclei 1 and 2. As evident from Eq. 2.51, the strength of the dipole-dipole interaction depends on the relative orientation of interacting spins (it is minimal when they both spins are parallel) and the cube of the distance. The strong dependence of the dipole-dipole interaction on the distance is used in NMR for structural studies. The typical strength of the dipole-dipole interaction lies in the kilohertz regime ($\langle \hat{\mathcal{H}}_{dip-dip} \rangle / h \approx 1 - 100 \text{ kHz}$).

2.2.5 Electron-mediated J -coupling

Another interaction in a molecule is a coupling between nuclei mediated by bonding electrons (indirect coupling). It was discovered in NMR via observation of additional splitting of NMR lines observed in spectra of liquids (Gutowsky et al. [1951]). This indirect coupling between two spins takes a form (Levitt [2013]):

$$\hat{\mathcal{H}}_J = 2\pi\hbar \hat{\mathbf{I}}_1 \cdot \mathbf{J}_{12} \cdot \hat{\mathbf{I}}_2, \quad (2.52)$$

where $\mathbf{J}_{12}$ is the J -coupling rank-2 tensor. The J -coupling, being an effect induced by bonding electrons that changes local magnetic field, can be understood as a second-order hyperfine coupling. In this scheme, electronic energy levels in the molecule are affected by the interaction with the spin of first the nucleus. The electrons couple to the spin of the second nuclei again through the hyperfine coupling affecting its energy structure. This leads to effective coupling between two nuclei sharing an electronic cloud. The $\mathbf{J}_{12}$ -coupling tensor is proportional to the gyromagnetic ratios γ_1 and γ_2 of two coupled spins and can be written as:

$$\mathbf{J}_{12} = \frac{\hbar\gamma_1\gamma_2}{2\pi} \mathbf{K}_{12}, \quad (2.53)$$

where the so-called reduced J -coupling tensor $\mathbf{K}_{12}$ can be calculated from (Ramsey [1953]):⁸

$$\mathbf{K}_{12} = \frac{\partial^2 E_{\text{electronic}}(\boldsymbol{\mu}_1, \boldsymbol{\mu}_2, \dots)}{\partial \boldsymbol{\mu}_1 \partial \boldsymbol{\mu}_2} \Big|_{\boldsymbol{\mu}_1=0, \boldsymbol{\mu}_2=0}. \quad (2.54)$$

The reduced coupling tensor can be broken into four terms, as first introduced by Ramsey [1953]. The electron-mediated coupling can involve both electronic orbital momentum and electronic spin. Among the former group, there is the **paramagnetic spin-orbit coupling**:

$$k_1^{PSO} = \alpha^2 \sum_j \frac{\mathbf{l}_j}{r_{1,j}} = \alpha^2 \sum_j \frac{i \nabla \times \mathbf{r}_{1,j}}{r_{1,j}}, \quad (2.55)$$

where $\mathbf{l}_j$ is an orbital momentum of the j -th electron and $r_{1,j}$ is the distance between the electron and nucleus. This term couples the nuclear magnetic moment with the orbital angular momentum of the electrons. The other orbit-nucleus coupling is the **second order diamagnetic interaction**:

$$k_{12}^{DSO} = \alpha^4 \sum_j \frac{\mathbf{1}(\mathbf{r}_{1,j} \cdot \mathbf{r}_{2,j}) - \mathbf{r}_{1,j} \otimes \mathbf{r}_{2,j}}{r_{1,j}^3 r_{2,j}^3}, \quad (2.56)$$

which takes the form of the classical dipole-dipole interaction. The last two terms describe coupling between the nucleus and electronic spins can be written as:

$$k_1^{SPIN} = k_1^{SD} + k_1^{FC} = \alpha^2 \sum_j \left(\frac{3\mathbf{r}_{1,j}(\mathbf{r}_{1,j} \cdot \boldsymbol{\mu}_j)}{r_{1,j}^5} - \frac{\boldsymbol{\mu}_j}{r_{1,j}^3} \right) + \frac{8\pi\alpha^2}{3} \sum_j \delta(\mathbf{r}_{1,j}) \boldsymbol{\mu}_j, \quad (2.57)$$

⁸ Equation 2.54 is a basis for density-functional-theory calculations of J -coupling values (Barone et al. [2002]).

where the sum is carried over all the electrons in the molecule, μ_j is the magnetic moment of the electron, the $r_{1,j}$ describes the distance between the nucleus and the electron, while α denotes the fine-structure constant. Note that the spin-dependent term in the J -coupling k_1^{SPIN} takes a form of a classic dipole magnetic field produced by the electronic spin. The term k_1^{SD} is called the **spin-dipole interaction**, while the term k_1^{FC} is called the **Fermi-contact potential** and is non-zero only when the electron is at the position of the nucleus. The Fermi-contact contribution to the J -coupling is often dominant.

Generally, the J -coupling interaction is the weakest intramolecular interaction observable in NMR ($\langle \hat{\mathcal{H}}_J \rangle / h \approx 0 - 1000$ Hz).

2.2.6 Molecular motion and spin Hamiltonian

The form of the interaction presented in a previous section modifies when molecules in a sample have additional degrees of freedom. Since this thesis describes research with isotropic liquids, we will now discuss the effective spin Hamiltonian in such systems.

Molecules in a liquid are in constant motion (translation, rotation, and vibration). Molecular orientation, characterized by the time-dependent solid angle $\Theta(t)$, changes due to rotation. To describe the dynamics of the spin in the molecule under thermal motion we will introduce the time-averaged Hamiltonian (so called **motional averaging**):

$$\overline{\hat{\mathcal{H}}}_{spin} = \frac{1}{\tau} \int_0^\tau \hat{\mathcal{H}}_{spin}(\Theta(t)) dt, \quad (2.58)$$

where the integration time τ is much longer than the timescale of the rotation. Using **the ergodic hypothesis** (see for example [Neumann \[1932\]](#)), we can replace the time average with the ensemble average. Assuming distribution of molecular angle in the ensemble $p(\Theta)$, Eq. 2.58 can be rewritten to:

$$\overline{\hat{\mathcal{H}}}_{spin} = \int p(\Theta) \hat{\mathcal{H}}_{spin}(\Theta) d\Theta. \quad (2.59)$$

In an isotropic medium, all orientations are equally probable, i.e., $p(\Theta) = 1/N$, where N is the number of molecules in the ensemble, the Hamiltonian can be rewritten to:

$$\overline{\hat{\mathcal{H}}}_{spin} = \frac{1}{N} \int \hat{\mathcal{H}}_{spin}(\Theta) d\Theta. \quad (2.60)$$

Since the rotation considers only the internal motion of a single molecule, it averages out all the intramolecular interactions, including the chemical shift, quadrupolar coupling, dipole-dipole, and electron-mediated coupling.

Translations motion in liquid can be roughly divided into **diffusion**, where motion of neighbouring molecules is random, and **flow**, describing an ordered motion of the molecules in a particular direction. The diffusive motion over the timescale of an experiment leads to averaging of short-range intermolecular interaction to zero, while long-range intermolecular interaction may survive the diffusion averaging ([Levitt \[2013\]](#)). It should be also stressed that in zero-field NMR experiments diffusion may play an important role. Particularly, this may be a case if significant temperature gradient is present across a sample ([Ledbetter et al. \[2012\]](#)).

2.2.7 Interactions in isotropic media

Below, we consider various interactions present in molecules, constituting isotropic media.

Isotropic chemical shift

The chemical-shift part of the Zeeman interaction is averaged out by molecular motion as the induced magnetic field is characterized by a rank-2 tensor and therefore depends on the molecular orientation. We can express the chemical shift observed in a given direction, $\delta(\theta)$, by rotating the chemical-shift tensor defined in the principal-axis basis:

$$\delta(\theta) = R(\Theta) \begin{pmatrix} \delta_{XX} & 0 & 0 \\ 0 & \delta_{YY} & 0 \\ 0 & 0 & \delta_{ZZ} \end{pmatrix} R^{-1}(\Theta), \quad (2.61)$$

where $R(\Theta)$ is the rotation matrix, associated with the angle Θ between applied magnetic field and molecular orientation. If we assume that the applied magnetic field points along the z-axis, the full chemical-shift Hamiltonian is given by:

$$\hat{\mathcal{H}}_{CS}(\Theta) = -\hbar\gamma B_0 [\delta_{xz}(\Theta)\hat{I}_x + \delta_{yz}(\Theta)\hat{I}_y + \delta_{zz}(\Theta)\hat{I}_z], \quad (2.62)$$

where δ_{ij} are the specific components of the rotated chemical-shift tensor $\delta(\Theta)$ (Eq. 2.61). If we now assume an isotropic medium, we can write:

$$\overline{\hat{\mathcal{H}}_{CS}}(\Theta) = -\frac{\hbar\gamma B_0}{N} \int [\delta_{xz}(\Theta)\hat{I}_x + \delta_{yz}(\Theta)\hat{I}_y + \delta_{zz}(\Theta)\hat{I}_z] d\Theta. \quad (2.63)$$

We can find the averaged chemical-shift tensor, if we perform integration over the whole solid angle (all possible orientation). For convenience, we will do it using the Euler angles:

$$\bar{\delta} = \frac{1}{8\pi^2} \int_0^{2\pi} \left\{ \int_0^\pi \left[\int_0^{2\pi} R(\alpha, \beta, \gamma) \cdot \delta \cdot R^{-1}(\alpha, \beta, \gamma) d\alpha \right] \sin(\beta) d\beta \right\} d\gamma, \quad (2.64)$$

where the rotation matrix $R(\alpha, \beta, \gamma)$ is given by (Levitt [2013]):

$$R(\alpha, \beta, \gamma) = \begin{pmatrix} \cos(\alpha)\cos(\beta)\cos(\gamma) - \sin(\alpha)\sin(\gamma) & -\sin(\alpha)\cos(\gamma) - \cos(\alpha)\cos(\beta)\sin(\gamma) & \cos(\alpha)\sin(\beta) \\ \sin(\alpha)\cos(\beta)\cos(\gamma) + \cos(\alpha)\sin(\gamma) & \cos(\alpha)\cos(\gamma) - \sin(\alpha)\cos(\beta)\sin(\gamma) & \sin(\alpha)\sin(\beta) \\ -\sin(\beta)\cos(\gamma) & \sin(\beta)\sin(\gamma) & \cos(\beta) \end{pmatrix}. \quad (2.65)$$

Performing the integration (Eq. 2.64), we arrive at:

$$\bar{\delta} = \begin{pmatrix} \frac{\delta_{XX} + \delta_{YY} + \delta_{ZZ}}{3} & 0 & 0 \\ 0 & \frac{\delta_{XX} + \delta_{YY} + \delta_{ZZ}}{3} & 0 \\ 0 & 0 & \frac{\delta_{XX} + \delta_{YY} + \delta_{ZZ}}{3} \end{pmatrix}, \quad (2.66)$$

where the value at the diagonal is called the **isotropic chemical shift**:

$$\delta_{iso} = \frac{\delta_{XX} + \delta_{YY} + \delta_{ZZ}}{3} = \delta. \quad (2.67)$$

The isotropic chemical-shift value is often simply referred to as the chemical shift (this is true throughout this thesis).

When combined with the Zeeman term, the total spin interaction with applied magnetic field takes in isotropic medium a form of:

$$\hat{\mathcal{H}}_{Zeeman}^{iso} = -\hbar\gamma B_0 (1 + \delta) \hat{S}_z, \quad (2.68)$$

where we assume that the magnetic field with magnitude B_0 points along the z-axis.

Since the chemical shift is measured by the shift of resonance lines in an NMR spectrum with respect to the same type of nucleus in a reference compound (e.g., for ^1H nuclei the most common reference compound is tetramethylsilane) and is typically expressed in part per million (ppm). For simple compounds, one can find also shielding factor values describing absolute relative change in the strength on the applied field at the position of a given molecule.

Quadrupolar interaction in isotropic media

As explained in the previous section, for nuclei with spins larger than $1/2$, the quadrupolar interaction can be significant. In analogy to the chemical-shift consideration, we may express the electric-field gradient along the specific direction $V(\Theta)$ using the principle-axis values and rotation matrix:

$$V(\Theta) = R(\Theta) \begin{pmatrix} V_{XX} & 0 & 0 \\ 0 & V_{YY} & 0 \\ 0 & 0 & V_{ZZ} \end{pmatrix} R^{-1}(\Theta). \quad (2.69)$$

Then, following the previous discussion, it can be shown that in an isotropic medium, the electric-field-gradient tensor can be written as:

$$\bar{V} = \begin{pmatrix} \frac{V_{XX} + V_{YY} + V_{ZZ}}{3} & 0 & 0 \\ 0 & \frac{V_{XX} + V_{YY} + V_{ZZ}}{3} & 0 \\ 0 & 0 & \frac{V_{XX} + V_{YY} + V_{ZZ}}{3} \end{pmatrix}. \quad (2.70)$$

The electric-gradient components are constrained by the Gauss law:

$$V_{XX} + V_{YY} + V_{ZZ} = 0. \quad (2.71)$$

This leads to the conclusion that contrary to the chemical shift, the quadrupolar interaction (but also higher-order multipoles) disappears in isotropic media:

$$\hat{\mathcal{H}}_{quadrupolar}^{iso} = 0. \quad (2.72)$$

Isotropic dipole-dipole interaction

The dipole-dipole interaction depends on relative orientation of interacting spins. To calculate an ensemble-averaged dipole-dipole interaction in isotropic media, we first express dipole-dipole interaction in spherical coordinates:

$$\begin{aligned} \hat{\mathcal{H}}_{dip-dip} &= -\frac{\mu_0 \hbar^2 \gamma_1 \gamma_2}{4\pi r^3} [3(\hat{\mathbf{I}}_1 \cdot \mathbf{r}_{12})(\hat{\mathbf{I}}_2 \cdot \mathbf{r}_{12}) - \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2] \\ &= \frac{\mu_0 \hbar^2 \gamma_1 \gamma_2}{4\pi r^3} [\hat{I}_{1x} \hat{I}_{2x} + \hat{I}_{1y} \hat{I}_{2y} + \hat{I}_{1z} \hat{I}_{2z} - \\ &\quad 3(\hat{I}_{1x} \sin(\theta) \cos(\phi) + \hat{I}_{1y} \sin(\theta) \sin(\phi) + \hat{I}_{1z} \cos(\theta)) \\ &\quad (\hat{I}_{2x} \sin(\theta) \cos(\phi) + \hat{I}_{2y} \sin(\theta) \sin(\phi) + \hat{I}_{2z} \cos(\theta))] . \end{aligned} \quad (2.73)$$

Rewriting Eq. 2.73 in the matrix form, we obtain:

$$\hat{\mathcal{H}}_{dip-dip} = \frac{\mu_0 \hbar^2 \gamma_1 \gamma_2}{4\pi r^3} \hat{\mathbf{I}}_1 \cdot \mathbf{D} \hat{\mathbf{I}}_2, \quad (2.74)$$

where the dipolar coupling matrix $\mathbf{D}$ takes a form of:

$$\mathbf{D}(\phi, \theta) = \begin{pmatrix} 1-3\sin^2(\theta)\cos^2(\phi) & 3\sin^2(\theta)\sin(\phi)\cos(\phi) & 3\sin(\theta)\cos(\theta)\cos(\phi) \\ 3\sin^2(\theta)\sin(\phi)\cos(\phi) & 1-3\sin^2(\theta)\sin^2(\phi) & 3\sin(\theta)\cos(\theta)\sin(\phi) \\ 3\sin(\theta)\cos(\theta)\cos(\phi) & 3\sin(\theta)\cos(\theta)\sin(\phi) & 1-3\cos^2(\theta) \end{pmatrix}. \quad (2.75)$$

If we now consider the dipole-dipole interaction in an isotropic medium, we need to integrate the dipolar coupling matrix over all orientations:

$$\overline{\mathbf{D}(\phi, \theta)} = \frac{1}{4\pi} \int_0^\pi \left(\int_0^{2\pi} \mathbf{D}(\phi, \theta) d\phi \right) d\theta = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (2.76)$$

Based on Eq. 2.76, we may conclude that in the isotropic media, the dipole-dipole interaction averages out to zero:

$$\hat{\mathcal{H}}_{dip-dip}^{iso} = 0, \quad (2.77)$$

and hence it does not directly visible in NMR spectra.

Isotropic J -coupling

The indirect spin-spin coupling is specific for all molecular orientation as it is characterized by the J -coupling tensors J , having a symmetric and antisymmetric parts (Abragam [1961]):

$$J = J_{sym} + J_{anti}. \quad (2.78)$$

For the symmetric part of the J -coupling tensor, the matrix is diagonal along the principle axes:

$$J_{sym} = \begin{pmatrix} J_{XX} & 0 & 0 \\ 0 & J_{YY} & 0 \\ 0 & 0 & J_{ZZ} \end{pmatrix}. \quad (2.79)$$

In isotropic media, in a manner similar to the chemical-shift calculations, we can show that the J -coupling tensor averages to a diagonal matrix with an averaged values of the J -coupling on the diagonal. Then we can write the indirect spin-spin coupling as:

$$\hat{H}_J^{iso} = 2\pi\hbar\hat{\mathbf{I}}_1 \cdot \begin{pmatrix} J & 0 & 0 \\ 0 & J & 0 \\ 0 & 0 & J \end{pmatrix} \cdot \hat{\mathbf{I}}_2 = 2\pi\hbar J (\hat{I}_{1x}\hat{I}_{2x} + \hat{I}_{1y}\hat{I}_{2y} + \hat{I}_{1z}\hat{I}_{2z}) = 2\pi\hbar J \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2. \quad (2.80)$$

The antisymmetric part of the J -coupling tensor therefore averages out to zero in isotropic media (Ramsey [1953]):⁹

$$\begin{aligned} \overline{J_{anti}} &= \overline{\begin{pmatrix} J_{xx}^{anti} & J_{xy}^{anti} & J_{xz}^{anti} \\ -J_{xy}^{anti} & J_{yy}^{anti} & J_{yz}^{anti} \\ -J_{xz}^{anti} & -J_{yz}^{anti} & J_{zz}^{anti} \end{pmatrix}} = \\ &= \frac{1}{8\pi^2} \int_0^{2\pi} \left[\int_0^\pi \left(\int_0^{2\pi} R(\alpha, \beta, \gamma) \cdot J_{anti} \cdot R^{-1}(\alpha, \beta, \gamma) d\alpha \right) \sin(\beta) d\beta \right] d\gamma = \\ &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \quad (2.81)$$

The Hamiltonian 2.80, presenting the form of the J -coupling, is often referred to as the scalar coupling, while the isotopically averaged indirect spin-spin coupling constant is simply referred to as the J -coupling constant. The indirect-coupling constant can be both positive and negative and it is the basis for NMR spectroscopy under zero-field and ultra-low-field conditions.

2.2.8 Role of spin interactions in spin relaxation

A nuclear system brought out from equilibrium eventually reaches thermal equilibrium, i.e., a state in which coherences (in the eigenbasis of the spin Hamiltonian) and population follows the Boltzmann distribution. In isotropic media, relaxation is predominantly caused by the fluctuating magnetic and electric fields associated with thermal tumbling of molecules.

A specific source of relaxation is **chemical-shift anisotropy**. In this case, magnetic field, induced at a position of a nucleus, changes as the molecule rotates with

⁹ By aligning molecules, the antisymmetric part of the J -coupling can be in principle, observed in NMR. This fact is used in Blanchard et al. [2020a], where it is proposed that the electric field can enable observation of molecular parity non-conservation manifesting itself in the antisymmetric part of the J -coupling. Antisymmetric part of J -coupling tensors can also potentially be used to distinguish chiral molecules with the use of NMR (King et al. [2017]).

respect to the applied magnetic field (modification of shielding tensor). As a result, the spin evolution occurs in ever-fluctuating magnetic field, causing relaxation of the spin polarization, as the Larmor frequency of individual spin differ causing random dephasing. The rates of this relaxation are proportional to the average of square of amplitude of magnetic-field fluctuation, which leads to the quadratic scaling of the chemical-shift-anisotropy relaxation with the magnitude of applied magnetic field. This results in considerable effects in high-field NMR (Schwalbe [2017]), but in the context of research described in this dissertation, i.e., in zero and ultra-low fields, the relaxation is suppressed, including its complete disappearance at zero field.

In isotropic liquids, quadrupolar interaction averages out to zero, not contributing to NMR spectra. However, this interaction can lead to rapid relaxation of spin polarization for nuclei with spin larger than $1/2$ (Abragam [1961]). Contrary to the chemical-shift-anisotropy relaxation, this effect manifests itself also in zero field, where spins with a quadrupolar moment are typically not observed in an NMR spectrum. Exceptions to this rule are nuclei with relatively small dipole moments, e.g., ^2H (for zero-field spectra of deuterated compounds see Alcicek et al. [2021a]) or in highly symmetrical environments, the electric-field gradient averages to zero (see, for example, the NMR study of $^{14}\text{NH}_3$ $^{14}\text{NH}_4^+$ under zero-field conditions, Barskiy et al. [2020]). The fast quadrupolar relaxation also affects the lifetime of other nuclei coupled to the quadrupolar nuclei, as is discussed later in this section.

As evident from Eq. 2.73, the dipole-dipole coupling depends on the relative orientation of magnetic moments and distance between interacting nuclei. Therefore, molecular tumbling causes the fluctuation in the strength of the interaction that results in spin relaxation. As magnetic field from a dipole scales with the inverse of the distance cubed, $\propto r^{-3}$, the dipolar relaxation scales very strongly with the distance, $\propto r^{-6}$. This feature is extensively used in studies of molecular structures in liquids and is explored in such NMR techniques as NOESY and ROESY (Carver and Slichter [1953]). The dipolar relaxation can be suppressed at zero field, where a nuclear singlet state can be created between two heteronuclei (see, for example, Emondts et al. [2014]). As the magnetic field is increased, the singlet state is destroyed and the dipolar relaxation becomes important and shortens the lifetime of the spin polarization.

The electron-mediated indirect coupling, which in an isotropic medium, takes a form of the scalar J -coupling (Eq. 2.80), can also play a role in spin relaxation. Specifically, this can be the case, if one of J -coupled nuclei undergoes **chemical exchange** (see Chapter 6), i.e., attaches and reattaches to random molecules. With this exchange, the coupling constant fluctuates over time, introducing randomness into the spin dynamics and hence relaxation. This type of relaxation is often called **relaxation of the first kind** and it scales proportionally to the square of the coupling strength, $\sim J^2$. The effect of the exchange-induced scalar relaxation on zero-field NMR spectra may be significant and was studied in detail by Barskiy et al. [2019b] (it is also investigated in Chapter 6). If the J -coupling exists between nuclei out of which one is a quadrupolar nucleus, additional relaxation, called **relaxation of the second kind**, arises. Specifically, if one spin undergoes fast quadrupolar relaxation, it acts as an effective **polarization sink**, shortening the lifetime of spin polarization of the molecule. Scalar relaxation of the second kind manifests itself in the zero-field NMR spectrum by broadening of the lines. The effect was studied in detail under the ultra-low-field conditions in Tayler and Gladden [2019], where it was found that coupling to quadrupolar nuclei with relatively small quadrupolar moments (^2D) causes faster relaxation than coupling to the high quadrupolar-moment nuclei (e.g., $^{79}\text{Br}/^{81}\text{Br}$ or $^{35}\text{Cl}/^{37}\text{Cl}$). This behaviour is opposite to the scalar relaxation of the second kind in high-field, where higher quadrupolar moment causes faster relaxation of coupled nuclei.

2.2.9 Role of high field in truncating spin interactions

So far, the interactions described by the spin Hamiltonian were discussed in a general terms. However, in high-field NMR, the Zeeman interaction dominates spin evolution, which allows to introduce simplifications into the spin-system description. Generally, by separating the total spin Hamiltonian into dominating part $\hat{A}$ and part $\hat{B}$, describing weaker interactions, we can neglect terms in $\hat{B}$, so that $\hat{B}$ becomes block diagonal in the eigenbasis of $\hat{A}$:

$$\hat{B} = \sum_n b_{nn} |n\rangle \langle n| + \sum_{m \neq n} b_{nm} |n\rangle \langle m|, \quad (2.82)$$

where $|n\rangle, |m\rangle$ describe eigenstates of the $\hat{A}$. The off-diagonal terms b_{nm} of $\hat{B}$ do not survive the approximation if (Levitt [2013]):

$$|b_{nm}| \ll |a_n - a_m|, \quad (2.83)$$

where a_n, a_m label the eigenvalues of $\hat{A}$. In other words, the terms may be neglected if the energy corrections they introduce to the transition between states m and n are much smaller than the energy differences of the states. This approach is often undertaken in high-field NMR experiments and is known in literature as the **secular approximation**.

Below, the effect of the secular approximation on different molecular interactions is discussed in detail.

Dipole-dipole interaction in secular approximation

In the case of two identical spins of different chemical shifts, the Zeeman Hamiltonian takes the form:

$$\hat{\mathcal{H}}_{Zeeman}^{homonuclear} = \hbar \gamma_1 B_0 [(1 + \delta_1) \hat{I}_{1z} + (1 + \delta_2) \hat{I}_{2z}]. \quad (2.84)$$

Then, the secular part of the dipole-dipole interaction is given by (Levitt [2013]):

$$\hat{\mathcal{H}}_{dip-dip}^{homonuclear} \approx \frac{\mu_0 \hbar^2 \gamma_1 \gamma_2}{4\pi r^3} \left(\frac{3 \cos(\Theta_{12}) - 1}{2} \right) (3 \hat{I}_{1z} \hat{I}_{2z} - \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2), \quad (2.85)$$

where Θ_{12} is the angle between the internuclear vector $\mathbf{r}$ and the direction of applied magnetic field. For the heteronuclear dipole-dipole coupling, the Zeeman interaction energy difference between different nuclear species is large, and therefore, the transverse spin operators can be neglected, which gives the Hamiltonian:

$$\hat{\mathcal{H}}_{dip-dip}^{heteronuclear} \approx \frac{\mu_0 \hbar^2 \gamma_1 \gamma_2}{4\pi r^3} \left(\frac{3 \cos(\Theta_{12}) - 1}{2} \right) 2 \hat{I}_{1z} \hat{I}_{2z}. \quad (2.86)$$

Although in isotropic media the dipole-dipole interaction averages out to zero, both in the high-field case (when the secular approximation is adequate) and at zero field (where this simplification is not applicable), the residual dipolar interaction is present in partially oriented media, and can be detected in NMR experiment. Specifically, under the ZULF conditions parts of the dipolar interaction normally truncated in NMR by large magnetic field affects spin dynamics. For example, for a uniaxial system, with an anisotropy axis along the z direction, the heteronuclear dipolar coupling takes a form of:

$$\hat{\mathcal{H}}_{dip-dip}^{zero-field} = \frac{\mu_0 \hbar^2 \gamma_1 \gamma_2}{4\pi r^3} \left(\frac{3 \cos(\Theta) - 1}{2} \right) (3 \hat{I}_{1z} \hat{I}_{2z} - \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2), \quad (2.87)$$

where θ is the angle between the internuclear vector and the anisotropy axis. This Hamiltonian is truncated in high field under secular approximation to:

$$\hat{\mathcal{H}}_{dip-dip}^{high-field} \approx \frac{\mu_0 \hbar^2 \gamma_1 \gamma_2}{4\pi r^3} \left(\frac{3 \cos(\Theta) - 1}{2} \right) 2 \hat{I}_{1z} \hat{I}_{2z}. \quad (2.88)$$

The untruncated part of the dipolar interaction under ZULFs was measured in [Blanchard et al. \[2015\]](#). In the study, the extra terms in zero-field Hamiltonian, given by Eq. 2.87, the so-called “flip-flop” terms, normally unobservable in NMR, contribute to new lines in zero-field spectra. This demonstrates that operation at zero and ultra-low fields enables probing normally not-measurable parts of the spin interactions.

Secular J -coupling

The electron-mediated J -coupling is also truncated by the strong magnetic field. In the scalar approximation, the scalar part of the coupling (Eq. 2.80) between two heteronuclei takes the form:

$$\hat{\mathcal{H}}_J^{\text{heteronuclear}} \approx 2\pi\hbar J_{12} \hat{I}_{1z} \hat{I}_{2z}. \quad (2.89)$$

To the contrary, in the homonuclear case, when the Zeeman energy difference is small, the whole part of the scalar interaction survives:

$$\hat{\mathcal{H}}_J^{\text{homonuclear}} = 2\pi\hbar J_{12} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2. \quad (2.90)$$

Equations 2.89 and 2.90 show that at high field a long-lived singlet states can be created between homonuclei but not between heteronuclei. The situation is different at ZULFs, when there is no magnetic field to truncate the scalar interaction. Then the J -coupling Hamiltonian, even for heteronuclei, has a form identical to the secular form of the secular for homonuclear J -coupling (Eq. 2.90). Under such conditions, the heteronuclear singlet (and triplets states) are naturally created in the experiment, and their very long lifetimes ([Emondts et al. \[2014\]](#)) can be used for high-resolution spectroscopy ([Blanchard et al. \[2013\]](#)).

2.2.10 Summary of spin interactions

In this section, we introduced the spin Hamiltonian based on the spin-Hamiltonian hypothesis and considered several interactions present in molecular systems. The discussion of motional averaging in isotropic liquids was provided and relaxation processes were discussed. The high-field truncation of the spin Hamiltonian was introduced and confronted with the zero- and ultra-low-field case. The results of these discussions are summarized in Table 2.1.

2.3 ROLE OF THE MAGNETIC FIELD IN NMR

The progress in the magnetic-resonance spectroscopy has been directly associated with going to ever higher magnetic fields in search to improve on inherently low sensitivity of the technique. Starting from initial experiments at micro- and militesla magnetic fields (1950s), through the era of strong field up to 2 T, produced by poled electromagnets (since 1960s) (see [Becker \[1993\]](#)), to the field ranging up to tens of tesla produced by superconducting magnets, the strong magnetic field was used to improve chemical information and spatial resolution with the use of **magnetic resonance imaging** (MRI). Current commercial systems for imaging can reach up to 10 T, while spectrometer for analytical purposes recently crossed 1 GHz barrier for protons (23.5-T field), with even stronger field produced in the pulsed-field experiments (up to 100 T). To understand motivation behind going for such strong fields, we now discuss how magnetic-field strength affects NMR experiments.

The three main drives for a strong magnetic field are:

Polarization

As explained in the previous section, NMR signals are determined by macroscopic magnetization generated by nuclear magnetic moments. To obtain non-zero mag-

Table 2.1: Summary of the interaction in the spin Hamiltonian. Form of the interaction and its averaged form in isotropic media is provided. Typical strength for the high-field NMR and type of the interaction is provided. The relaxation mechanism is also indicated.

Spin interaction				
	Hamiltonian	Strength (Hz)	Type	Isotropic average
Zeeman	$-\gamma\hbar\hat{S} \cdot \mathbf{B}$	10^8 - 10^{10}	External	$-\gamma\hbar B_z \hat{S}_z$
Chemical Shift	$-\gamma\hbar\hat{S} \cdot \boldsymbol{\delta} \cdot \mathbf{B}$	10^2 - 10^5	Intra-	$-\gamma\hbar B_z \delta \hat{S}_z$
Quadrupolar	$\frac{eQ}{2I(2I-1)\hbar} \hat{\mathbf{I}} \cdot \mathbf{V}^{(2)} \cdot \hat{\mathbf{I}}$	10^4 - 10^7	Intra-	0
Dipolar	$\frac{\mu_0 \hbar^2 \gamma_1 \gamma_2}{4\pi r^3} \hat{\mathbf{I}}_1 \cdot \mathbf{D} \cdot \hat{\mathbf{I}}_2$	10^3 - 10^5	Intra-/inter-	0
Electron mediated	$2\pi\hbar \hat{\mathbf{I}}_1 \cdot \mathbf{J}_{12} \cdot \hat{\mathbf{I}}_2$	10^0 - 10^3	Intra-	$2\pi\hbar J_{12} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2$
				Fast, Scalar Relaxation of the Second Kind
				Field inhomogeneity Chemical Shift Anisotropy ($\propto B^2$) Fast, Scalar Relaxation of the Second Kind
				Fast, ($\propto r^{-6}$) Scalar Relaxation of the Second Kind

netization, a sample with a non-zero nuclear spin is placed inside a magnetic field and allowed to reach thermal equilibrium. Since the magnetic field splits the energy level via the Zeeman interaction (Sec. 2.2.2), the small fraction of spins populates more favourably lower energy levels. For an ensemble of spins-1/2 at room temperature, this fraction (also called the **nuclear polarization** P_0) is (roughly) proportional to the magnetic-field strength B_0 and gyromagnetic ratio γ , while being inversely proportional to temperature T :

$$P_0 \approx \frac{\hbar\gamma B_0}{2k_B T}. \quad (2.91)$$

This linear dependence of polarization is first key to understand going to stronger magnetic fields, as a number of spins contributing to the signals scales linearly with the magnetic-field magnitude.

Its worth pointing out that the polarization obtained by this approach is minuscule, reaching only 100 ppm for the strongest magnetic fields (see Fig. 3.1a). This is one of the reason for the inherent poor sensitivity of the NMR technique. However, this limitation is not fundamental. The hyperpolarization techniques (see Sec. 3.2) can provide polarization at a level of tens percent, even without the use of a strong magnetic field.

An important exception to the extremely low thermal polarization is the case when the number of magnetic moments (spins) is no longer macroscopic. One can find that the statistical polarization is proportional to the square root of number of magnetic moments involved ($\sqrt{N}$), which can be exploited in microscopic NMR experiments (Glenn et al. [2018]). The extreme end of this is measuring a single spin which can be always assumed to be polarized (Lovchinsky et al. [2016]).

Detection

Measurement of the precessing magnetization (NMR signal) is typically performed using electromagnetic coils. Since the precessing magnetization $M(t)$ gives rise to a time-dependend magnetic flux $\Phi(t)$, the voltage induced on the coil $V(t)$ follows the **Faraday induction law**:

$$V(t) = -\frac{d\Phi(t)}{dt} = -\omega_0 M(t) = -\gamma B_0 M(t), \quad (2.92)$$

where ω_0 is the frequency of precession (Larmor frequency). Although here, we only calculate voltage over the coil, not taking into the account important technical consideration of detection such as filling or Q factors of the coils, there is (approximately) a linear scaling of the signal amplitude with the magnetic field. This is the second motivation for higher magnetic fields.

To further quantify the scaling of the NMR signal with magnetic field, we now consider an important figure of merit for any technique, i.e., the **signal-to-noise ratio** (SNR). If we limit ourselves only to considerations of coil thermal noise, i.e., noise caused by thermal excitation of electrons inside a coil material, we can estimate noise using the Johnson–Nyquist formula (Nyquist [1928]):

$$\text{noise} = \sqrt{4k_B T R \Delta f}, \quad (2.93)$$

where the T is the temperature of the conductor, Δf is the measurement bandwidth and R is the conductor (coil) resistance. The resistance R in a model, cylindrical conductor grows with the square root of the frequency of current ω_0 , as the skin effect restricts the effective cross section of the wire (Jackson [1999]):

$$R \propto \sqrt{\omega_0}. \quad (2.94)$$

Combining Eqs. 2.91–2.94, we arrive at a following scaling of signal-to-noise ratio with the strength of the magnetic field:

$$\text{SNR} \sim (\gamma B_0)^{7/4}. \quad (2.95)$$

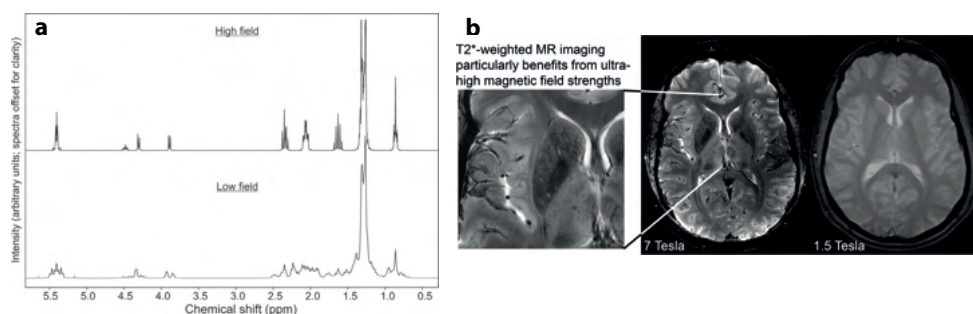


Figure 2.4: Comparison of NMR experiments performed with different strength of magnetic field. a) ^1H NMR spectrum of oil measured in low-field (1.4 T) and high-field spectroscopy (7 T) spectrometers. Image taken from [Parker et al. \[2014\]](#) b) MRI images of brain obtained with the use of T_2 contrast as obtained in 7 and 1.5 T MRI scanners. The increased resolution caused by relaxation dispersion and higher SNR is clearly visible in high-field image. Image taken from [Ladd et al. \[2018\]](#).

Using the relation, one may show that increasing the field strength by an order of magnitude leads to over 50-times increase in SNR. This can be further translated into about 3000-times shortening of signal acquisition to get the same SNR.

Despite these arguments, the quality of the acquired signal is not the only reason to use higher magnetic fields in NMR.

Better resolution

Nuclear magnetic resonance is used to obtain chemically-specific information about unknown samples, structural information about molecules, as well as, high-resolution, non-invasive images with the use of MRI.

At high field, the spectroscopic information is typically inferred from the chemical shift. Thus, it is crucial to split NMR resonances beyond their linewidths. In fact, the stronger the field, the better spectral resolution may be achieved (Fig. 2.5).

Outside of spectroscopic applications, MRI often relies on a contrast of relaxation times to distinguish between different parts of the image. As a high magnetic field can lead to an increase in the longitudinal relaxation time T_1 , as well as, the increase in the transverse relaxation time T_2 , due to an effect associated with magnetic susceptibility, higher fields may also be preferred in imaging ([Ladd et al. \[2018\]](#)).

In turn, application of high magnetic field is driven by better spectral and spatial resolution.

2.4 DIFFERENT MAGNETIC-FIELD REGIMES IN NMR

Although in NMR going toward larger magnetic field is typically beneficial, an opposite trend of performing NMR experiments in low magnetic fields has also emerged (see, for example, [Blanchard et al. \[2021a\]](#)). The transition from the high-field regime to the low- or ultra-low-field regime is presented, for example, in [Appelt et al. \[2010\]](#), when the analysis of simple heteronuclear coupled-spin systems under changing magnetic-field strength (ranging several orders of magnitude) was performed. Since this thesis specifically deals with experiments under ultra-low and zero field, it's good to define high, low, ultra-low and zero-field NMR.¹⁰

¹⁰ In this thesis a scalar J -coupling strength marks a division point between different fields regimes since we only consider NMR of isotropic liquids. Analogous field boundaries can be found for system where quadrupolar or dipolar coupling is a dominant internal interaction.

High-field NMR

High-field NMR is a conventional incarnation of the technique. Under such conditions, the Zeeman interaction dominates the spin dynamics and predetermines the positions of NMR resonances in a spectrum. One can define the conditions of high-field NMR by:

$$B_{high} > \left| \frac{J_{homo}}{2\pi\gamma(\delta_1 - \delta_2)} \right|, \quad (2.96)$$

where J_{homo} is the coupling strength between two homonuclei (with the same gyromagnetic ratios γ) with different chemical shifts δ_1 and δ_2 . This means that, in the high-field regime, the difference in the chemical shifts of two nuclei is larger than the scalar coupling between the nuclei. In this case, positions of spectral lines are determined by the chemical shifts, i.e., the eigenstates of the spin Hamiltonian are, in a good approximation, those of the Zeeman basis, and the J -coupling just perturbs (shifts or splits) the energy levels, hence lines number and positions. The typical magnetic field range of this regime spans between roughly 0.1 T to tens of tesla.

Low-field NMR

The low-field regime arises when the interaction with an external magnetic field (the Zeeman interaction) dominates the heteronuclear couplings J_{hetero} :

$$\left| \frac{J_{homo}}{2\pi\gamma(\delta_1 - \delta_2)} \right| > B_{low} > \left| \frac{J_{hetero}}{2\pi(\gamma_1 - \gamma_2)} \right|, \quad (2.97)$$

where γ_1 and γ_2 are the gyromagnetic ratios of coupled heteronuclei. In the low-field regime, the coupling between the same nuclei species is larger than the corresponding chemical-shift difference. This regime typically stretches from 100 nT up to 100 mT, and hence it covers the NMR experiments at the Earth magnetic field (30-50 μ T), see, for example, [Appelt et al. \[2006\]](#). The magnetic field in this regime is created with the use of regular electromagnets, which significantly reduces the size and cost of spectrometers. At the same time, this occurs at the expense of reduced chemical resolution ([Appelt et al. \[2006\]](#)).

Ultra-low-field NMR

Ultra-low-field (ULF) NMR is considered when interaction with an external magnetic field no longer dominates the inter/intramolecular couplings:

$$\left| \frac{J_{hetero}}{2\pi(\gamma_1 - \gamma_2)} \right| > B_{ultra-low} > \left| \frac{1}{2\pi\gamma T_{relax}} \right|, \quad (2.98)$$

where T_{relax} is the characteristic relaxation time, which determines the linewidth of the NMR resonances. In this regime, the Zeeman interaction is just a small correction or at most comparable to the J -coupling; hence, the eigenstates of the spin Hamiltonian are approximately given by zero-field coupled states. In that context, the lower limit provided by Eq. 2.98 can be understood as the minimal field, for which the Zeeman splitting of the NMR lines starts to be visible in the spectrum. This ULF regime was investigated in detail in [Ledbetter et al. \[2011\]](#), where the application of a small magnetic field was introduced to modify and simplify the analysis of a zero-field NMR spectrum. This NMR regime is used in this thesis for both chemical analysis (Chapter 6) and comagnetometry (Chapter 7).

Zero-field NMR

The zero-field regime arises when the Zeeman interaction no longer affects the spectrum, i.e., any splitting is negligible with respect to the NMR resonance linewidth:

$$B_{\text{zero-field}} < \left| \frac{1}{2\pi\gamma T_{\text{relax}}} \right|. \quad (2.99)$$

Under the zero-field condition, the position of the spectral lines is entirely determined by the J -coupling. The field range for the zero-field NMR regime stretches from zero up to couple of nanotesla, although to operate in zero-field spectrometers are usually magnetically shimmed below a 0.5-nT level.

It is worth pointing out that magnetic-field values provided for different regimes are not general, depending both on the coupling strength between nuclei, as well as, gyromagnetic difference between two couple nuclei. One should also note that for molecules without the J -coupling the above classification does not apply. For instance, NMR peaks of water protons moves linearly with the magnetic field in whole field range, eventually contributing only to quasistatic magnetization at zero magnetic field. Even in the case of compounds with no coupled spins, the terms *low* or *weak* magnetic field is still often used. This is because going to lower magnetic fields will results in many practical benefits (see next section) and change in relaxation properties (Sec. 2.2.8, see also [Bodenstedt et al. \[2021\]](#)), although a structure of NMR spectrum does not change in any meaningful way.

2.5 ZERO-FIELD NMR

2.5.1 Advantages of ZULF NMR

Analyzing the motivation for the high-field application in NMR, one may wonder about the reasons for performing such experiments at ultra-low magnetic fields. Despite some apparent, but not necessarily ultimate limitations of operation under such fields, ZULF NMR may also offer important benefits and research opportunities unavailable to its high-field counterpart. The motivation for such measurements is discussed below.

Technical aspects

The first group of benefits of ZULF NMR is associated with the technical aspects of the method. As strong magnetic fields are generated by superconducting magnetic coils, they require cryogenic cooling. Going to low and ultra-low fields, one can alleviate the problem of cryocooling. Cryogenic-free operation significantly reduces the footprint of ZULF NMR spectrometers as they do not require bulky and expensive cryostats.¹¹ In turn, ZULF NMR spectrometers can be small and light, therefore portable, as shown, for example, in [Put et al. \[2021\]](#) and discussed in Chapter 6. They may also be orders of magnitude cheaper than their high-field counterparts. Moreover, operation at low and ultra-low fields reduces the dangers of the technique associated with applicability to people without pacemakers and metallic orthoprosthesis.

¹¹ It is worth pointing out that benefits of getting rid of cryogenics, are not reserved for ultra-low-field setups, as both low and high-field setups (so-called benchtop NMR spectrometers) can be realized either with regular, room-temperature electromagnetic coils or with arrays of permanent solid-state magnets. Still, ZULF NMR setups can be both significantly less bulky and cheaper, while offering capabilities unobtainable to high-field NMR.

Spin physics

Another set of benefits is related to the difference in spin evolution under the ZULF Hamiltonian. As explained in Chapter 2.2.1, in the ZULF regime, the internal interaction dominates over the Zeeman interaction. This leads to a rich-in-information NMR spectrum of intermolecular interactions (the *J*-spectroscopy), which allows chemical identification (see, for example, Blanchard et al. [2013]). Moreover, some of the parts of the interactions, truncated by a high field, can be directly probed under zero-field conditions (Blanchard et al. [2015]). The relaxation properties at ultra-low fields are also completely different. First, it is easy to obtain very high field homogeneity by enclosing a sample inside a magnetic shielding and compensating residual fields with a set of Helmholtz coils. This stems from the fact that although the relative homogeneity of the field cannot match sophisticated high-field setups, scaling the total field down by several orders of magnitude scales down the absolute homogeneity of the fields determining the width of the peaks. Moreover, as mentioned in Sec. 2.2.8, the ULF conditions suppresses chemical-anisotropy relaxation and can suppress the dipolar relaxation, which are two main sources of relaxations of a spin-1/2 in liquids. This results in ZULF NMR resonances with a width of about 10 mHz and the ability to determine the line position at the sub-mHz level (Wilzowski et al. [2017]). Moreover, relaxation dispersion is different at ULF, which offers a potential for relaxometry studies (Tayler and Gladden [2019]) and increased contrast in MRI. As frequency of the signal and magnetic-field pulses used for spin manipulations goes down with the strength of the magnetic field. This means that a slowly oscillating NMR signal can be easily picked up from inside metallic shells and containers, since the skin effect is no longer an issue. This feature was used to image objects inside metallic sheets (McDermott et al. [2004]) and to monitor the chemical reaction inside metallic reactors with the use of zero-field NMR spectroscopy (Burueva et al. [2020]). Zero- and ultra-low fields finally eliminate the problem of magnetic-susceptibility mismatches and enable probing of inhomogeneous samples (Burueva et al. [2020]).

2.5.2 Brief history

Although the development of NMR followed the direction of ever-higher magnetic fields, the ULF experiments also have a rich history (see, for example, Blanchard et al. [2021a] and references therein). Shortly after the discovery of the NMR phenomena, an experiment using Earth's magnetic field was carried out (Packard [1954]). The precession of hydrogen spins was measured, following a sudden switch of the 10-mT prepolarizing coil. Such measurements found their application in geophysical surveys, where the precession of a large volume of the ground occurs at the Earth magnetic field (Waters [1955]). Some development was carried out in the field of low-field MRI, where the homogeneity of the Earth magnetic field was used to perform dispersion and diffusion measurements of liquids in porous materials (Callaghan et al. [2007]; Altobelli et al. [2019]).

Zero-field conditions entered NMR experiments with a set of seminal experiments performed in the 1980s in the group of Alexander Pines at the University of California at Berkeley. In an initial work, the zero-field condition was used to resolve dipolar coupling patterns in polycrystalline samples (Weitekamp et al. [1983]), which produce broad unresolved spectra at a high field. This is because the truncated dipole-dipole interaction depends on the orientation of the molecules with respect to the applied magnetic field (Eq. 2.86). In turn, differently oriented crystals manifest in NMR spectra with peaks at different positions (leading to resonance broadening). As discussed in Sec. 2.2.1, under the zero-field conditions there is no preferred spatial direction, so dipolar-coupling patterns in all crystallites are equivalent. The evolution in zero field resulted in NMR spectra with a resolution vastly improved, comparable to that of a spectrum of a single crystal. This and

similar experiments (see, for example, Zax et al. [1985]) were performed using a field cycling, i.e., sample was initially prepolarized in the superconducting magnet and then was shuttled out of the magnet. As the sample left the magnet, it was transferred to a weaker, but still dominant magnetic field. Then the ~ 10 -mT field was suddenly compensated to zero (shielding of Earth's magnetic field) and spins evolve in zero field under dipole-dipole coupling. After a given time, the field was suddenly switched back on, and the sample was adiabatically transported to the superconducting magnet for detection. The time of evolution in the zero field could be varied, providing an additional dimension in NMR experiments. Pulsed techniques were also developed for the selective averaging of the spin Hamiltonians in the zero-field conditions (Lee et al. [1987]). It should be noted that a similar shuttling approach between high and zero fields was recently exploited in multidimensional NMR experiments with liquid samples (Zhukov et al. [2020]).

Initial zero-field NMR experiments were time consuming, as the spin evolution in zero-field conditions was acquired in a point-by-point manner. This stemmed from the necessity to detect signals at high magnetic field, as inductive detection is not suitable to detect NMR signals at low frequencies. To circumvent this problem, other magnetic-field sensors replaced inductive coils. Initial experiments were based on the application of superconducting quantum interference devices (SQUIDs) and were realized in collaboration between Alexander Pines and John Clarke, a pioneer in superconducting magnetometry. This solution pushed NMR to a militesla regime with enough resolution to measure chemical shifts (Wong-Foy et al. [2002]). Further development led to experiments in microtesla ranges, capable of resolving the J -couplings in liquids (McDermott et al. [2002]), as well as, some first ULF NMR experiments with *in-situ* detection (Trabesinger et al. [2004]). SQUID detection also contributed greatly to the field of low-field imaging with images of phantoms inside metallic covers or anatomical images (for a comprehensive overview of the subject, see Kraus et al. [2014]).

The next chapter in ZULF NMR is associated with the development of atomic magnetometers (Budker and Kimball [2013]) in the early 2000s.¹² The application of these new non-inductive and non-cryogenic sensors in ULF NMR was pioneered by Alexander Pines and Dmitry Budker. Initial experiments aimed to measure the relaxation of hyperpolarized gases (Yashchuk et al. [2004]) and perform remote polarization MRI (Xu et al. [2006, 2008]). The next step of the research was the J -spectroscopy at truly zero magnetic field (Ledbetter et al. [2008, 2009]). In the latter context, hyperpolarization techniques were used in J -spectroscopy (Theis et al. [2011, 2012]), making **the NMR without magnets** a reality. The most recent chapter of ZULF NMR was written in Europe in groups in Mainz, Barcelona, and Kraków. During that period, zero-field setups became more approachable (Blanchard et al. [2020b], Put et al. [2021]), while the technique was further developed for chemical analysis (Wilzewski et al. [2017], Burueva et al. [2020], Barskiy et al. [2020], Alcicek et al. [2021a]), as well as, fundamental-physics experiments (Jiang et al. [2018], Wu et al. [2019]). Some of these recent developments in this field are presented in the following chapters.

¹² Note that nuclear magnetization of hyperpolarized gas was first detected with optically-pumped atoms by Cohen-Tannoudji et al. [1969] many years earlier.

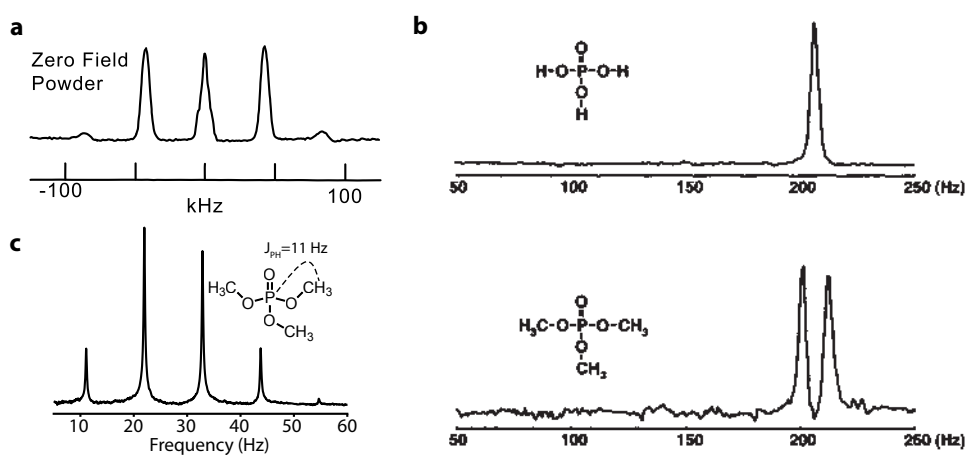


Figure 2.5: Developments in ZULF NMR spectroscopy. a) Zero-field spectrum of barium chlorate hydrate powder as obtained by Weitekamp et al. [1983] by the method of magnetic-field cycling. b) Low-field (μT range) spectra of phosphorus-containing liquid as measured *in-situ* with the use of the SQUID detectors. Adapted from McDermott et al. [2002]. c) NMR spectrum of trimethyl phosphate measured under the zero-field conditions. Adapted from Alcicek et al. [2021b].

3

ZERO-FIELD NMR EXPERIMENT

The results presented in this chapter have been previously published as the following peer-review articles:

1. **Piotr Put**, Kacper Popiołek, and Szymon Pustelny. “Different sensitivities of two optical magnetometers realized in the same experimental arrangement.” *Scientific Reports* 9.1 (2019): 1-9.
2. **Piotr Put**, Wcislo Piotr, Wojciech Gawlik and Szymon Pustelny “Nonlinear magneto-optical rotation with parametric resonance.” *Physical Review A* 100.4 (2019): 043838.

3.1 GENERAL NMR EXPERIMENTAL SEQUENCE

Nuclear-magnetic-resonance experiments in zero-field follow an experimental sequence not different from regular NMR experiments. The experiment starts with establishing macroscopic nuclear magnetization, which evolution is detected at a later stage. In high-field experiments, this step is usually done by simply keeping a sample in high field for sufficiently long time (several times characteristic T_1 time) to establish thermal equilibrium. This produces a tiny nuclear polarization and hence measurable magnetization of the sample. Operation at ZULF may require application of this approach, which is discussed in detail in Sec. 3.2.

As the nuclear spins start to evolve in magnetic field (typically after being tipped by a pulse), their evolution is measured by the NMR apparatus. In high field detection is often done with the use of coils, generating and detecting a field in the direction perpendicular to a strong magnetic field B_0 . As the precessing magnetization produces a time-dependent magnetic flux through the coils, a Faraday induction law (Eq. 2.92) guarantees a rise of voltage in the detection circuit. After careful amplification, the voltage signal is detected in a phase-sensitive manner and the down-converted analog signal is digitized with the use of analog-to-digital converter (ADC). The signal is then post-processed and the Fourier transform is performed to generate the NMR spectrum. As the frequency of the zero-field NMR signals is very low (typically < 1 kHz) one cannot rely on inductive detection. In Sec. 3.3, means of detecting zero-field NMR are presented.

To perform a NMR experiment, a detectable NMR signal must be generated. We discussed in Sec. 2.1.2, how a resonant with Larmor frequency, oscillating magnetic-field pulse produces a magnetization precessing in the transverse plane. In the zero-magnetic field, however, we do not rely on the Larmor precession, i.e., other interaction inducing time dependence of magnetization must be present. We present means of generating zero-field NMR signals in Sec. 3.4.

3.2 POLARIZATION PREPARATION

Nuclear magnetic resonance relies on the detection of nuclear magnetization of a sample. We can define a nuclear magnetization operator simply as:

$$\hat{M} = \frac{\hbar}{V} \sum_i \gamma_i \hat{I}_i, \quad (3.1)$$

where V is the sample volume and γ_i and $\hat{I}_i$ are the gyromagnetic ratio and the spin operator of the i -th nuclei, respectively. In NMR experiments, specific components of magnetization are detected. We can now consider a completely unpolarized ensemble characterized by the density matrix:

$$\hat{\rho}_{unpolarized} \sim \mathbb{1}, \quad (3.2)$$

We can now calculate the expectation value of the magnetization associated with such a state:

$$\langle \hat{M} \rangle = \text{Tr}(\rho \hat{M}) \sim \text{Tr}(\mathbb{1} \hat{M}) = \frac{\hbar}{V} \sum_i \gamma_i \text{Tr}(\hat{I}_i) = 0, \quad (3.3)$$

as the angular momentum operators, being rotation generators, are traceless. Equation 3.3 shows that the unpolarized state generates no observable magnetization. Such a state will also not change under the influence of the spin Hamiltonian. In particular, a magnetic pulse cannot generate observable magnetization in unpolarized samples. To observe NMR signals, one needs therefore to polarize the nuclear ensemble.

3.2.1 Thermal prepolarization

When an ensemble of nuclear spins I is placed in a magnetic field, the Zeeman interaction lifts the degeneracy of $2I + 1$ magnetic sublevels, as the corresponding energy of the state will depend on the magnetic number m_I :

$$E_{m_I} = -\hbar\gamma B_0 m_I. \quad (3.4)$$

Under thermal equilibrium, the magnetic sublevel m_I is populated according to the Boltzmann distribution:

$$\rho_{m_F} \propto e^{\frac{-E_{m_F}}{k_B T}} = e^{\frac{\hbar\gamma B_0 m_F}{k_B T}}, \quad (3.5)$$

where T is the temperature of the sample. At thermal equilibrium, all the coherences are averaged out to zero. We can concisely write the density matrix at the thermal equilibrium $\hat{\rho}_{th}$ as:

$$\hat{\rho}_{th} = \frac{1}{\mathcal{Z}} e^{\frac{-\hat{H}}{k_B T}}, \quad (3.6)$$

where $\mathcal{Z}$ is the thermodynamical partition function:

$$\mathcal{Z} = \text{Tr} \left(e^{\frac{-\hat{H}}{k_B T}} \right). \quad (3.7)$$

If we now substitute the general Hamiltonian with the Zeeman Hamiltonian, we get the following matrix:

$$\hat{\rho}_{th} = \frac{1}{\mathcal{Z}} e^{\frac{-\hat{H}_{Zeeman}}{k_B T}} \propto \frac{1}{(2I+1)^N} e^{\frac{\hbar B_0 \sum_i^N \gamma_i \hat{I}_z^i}{k_B T}} \approx \frac{1}{(2I+1)^N} \left(\mathbb{1} + \frac{\hbar B_0 \sum_i^N \gamma_i \hat{I}_z^i}{k_B T} \right). \quad (3.8)$$

Here we assumed an ensemble of N nuclei of spin I , while individual spins are characterized by the gyromagnetic ratio γ_i . The approximation of the exponential with the first two terms of the Taylor series of exponent functions is often used in NMR, as typically $\gamma B / (k_B T) \ll 1$. In fact, it works for all the cases presented in this thesis. As evident by Eq. 3.3, only a second term in Eq. 3.8 can give rise to observable magnetisation, as it corresponds to nuclear polarization.

To develop intuition regarding the polarization level achievable with a static magnetic field, we consider an ensemble of identical spins-1/2. For such an ensemble, we can calculate the normalized difference of the population, i.e., the polarization P_0 , which is given by:

$$P_0 = \frac{\rho_{1/2,1/2} - \rho_{1/2,-1/2}}{\rho_{1/2,1/2} + \rho_{1/2,-1/2}} = \frac{e^{\frac{\hbar\gamma B_0}{2k_B T}} - e^{-\frac{\hbar\gamma B_0}{2k_B T}}}{e^{\frac{\hbar\gamma B_0}{2k_B T}} + e^{-\frac{\hbar\gamma B_0}{2k_B T}}} = \tanh \left(\frac{\hbar\gamma B_0}{2k_B T} \right) \approx \frac{\hbar\gamma B_0}{2k_B T}, \quad (3.9)$$

where once again only the terms up to the linear term of the Taylor series are kept. Figure 3.1a) shows the thermal nuclear polarization P_0 as a function of the magnetic field for some of the popular NMR isotopes. The key observation is that even in the very high magnetic field of today's top-of-the-line spectrometers, the thermal polarization does not exceed 100 parts per million (10^{-4}). This level of thermal polarization is sufficient to obtain NMR signals; however, it is also responsible for

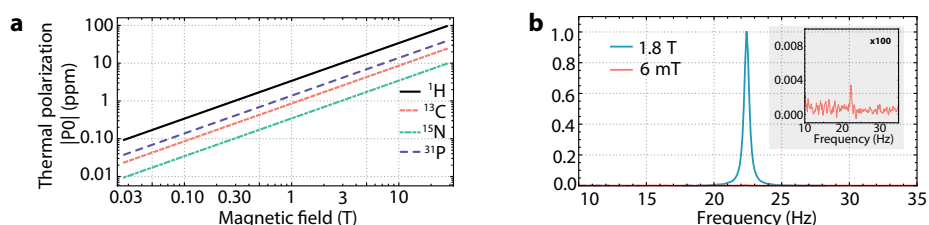


Figure 3.1: Nuclear polarization level achievable with thermal polarization. a) Level of thermal polarization of room-temperature (300 K) spin-1/2 nuclear ensemble versus magnetic-field magnitude for nuclei investigated within this thesis. b) Low-field (~ 500 nT) spectra of water, providing comparison of two approaches of thermal prepolarization in ZULF NMR. The blue trace corresponds to the spectrum of the sample remotely prepolarized with a permanent magnet (1.5 T) and the red trace (inset) correspond to the signal measured with the sample prepolarized *in-situ* with a solenoid field of 6 mT. The blue trace is a result of single-shot experiment, while the red trace was acquired by averaging of 16 transients.

intrinsically poor sensitivity of the technique. The polarization level also depends on the gyromagnetic ratio, i.e., the higher the ratio, the higher the polarization.

Thermal polarization of the sample can be used to prepare nuclear spins in ZULF NMR experiments. The sample can be either polarized outside of the ZULF region, i.e., inside a strong magnetic field, or *in situ* with the use of the polarizing coil. In the following section, we explore the pros and cons of both approaches.

Remote prepolarization

In the remote prepolarization scheme a sample is initially held inside a strong magnetic field and then physically transported to a zero-field region. The idea for this prepolarization is identical to the field cycling, performed in the very beginning of zero-field NMR (Zax et al. [1985]). The sample spends a multiple of T_1 (typically tens of seconds) in a strong magnetic field and next is transported into the ZULF region (into a magnetic field) over time that should be $\ll T_1$ (typically hundreds of milliseconds). Since the regions of strong and zero field are spatially separated, the magnetic field can be created using schemes in which turning off of the field is hard to achieve, e.g., in bores of superconducting magnets or inside permanent magnet assemblies. These schemes allow for generation of magnetic fields reaching 10 T in the case of superconducting magnets or up to 2 T with permanent-magnet assemblies. This translates to several ppm levels of polarization (see Fig. 3.1).

Superconducting magnets used for such a field cycling were typically bores of NMR spectrometers. The magnets offer exceptional field homogeneity and stability; however, these parameters are not relevant to the prepolarization field, as they have little influence on the signal level. In principle, smaller and cheaper superconducting magnets may be used for prepolarization purposes, while still offering large (for thermal prepolarization) polarization levels. To avoid cryogenic operation and reduce cost, a permanent-magnet ensembles are often paired with ZULF NMR spectrometers. The field produced inside such systems can reach up to 2 T. The most widely used configuration is the so-called Halbach cylinder, where magnetisation direction of permanent magnets arranged around a circle follow magnetic dipole lines (Fig. 3.2) (Halbach [1980]). Such an array can be readily assembled with the use of 3D-printed parts and cheap permanent magnets (Tayler and Sakelariou [2017]). In fact, different permanent magnet arrays (Fig. 3.2) were used to perform ZULF NMR experiments presented in this dissertation.

Because the high-field and ZULF regions are spatially separated, an NMR sample has to be transported between them. This can be achieved in many ways, e.g., by flowing liquid samples (see for example Xu et al. [2006]). As the samples studied in this thesis are enclosed in vacuum-sealed 5-mm glass NMR tubes, their transport

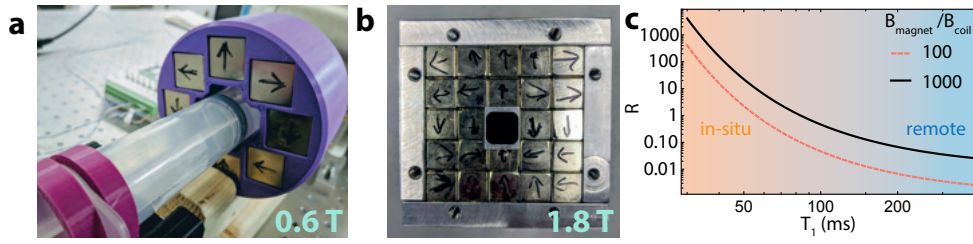


Figure 3.2: Assemblies of permanent magnet used for thermal prepolarization in ZULF NMR experiments presented in the thesis. a) Photo of a Halbach array assembled inside the 3D-printed holder, where metallic cubes are neodymium magnets with the direction of the magnetization marked by hand-drawn arrows. The assembly produced a magnetic field of 0.6 T inside the bore. b) Pseudo-dipolar magnet assembly used in the Kraków's ZULF NMR spectrometer. The designed is based on Tayler and Sakellariou [2017]. The arrows on the exposed neodymium magnets (cover not yet put onto the assembly) indicate the directions of magnetization of individual permanent magnets. With this magnet, a field of 1.8 T is obtained in the volume of $12 \times 12 \times 50 \text{ mm}^3$. c) Comparison of NMR signal acquired per square root of time with the use of prepolarizing coil and remote polarization, based on approximate relation Eq. 3.10. The ratio of signal amplitudes is plotted as a function of sample's T_1 for two relative strength of magnetic fields and somewhat realistic transport times (400 ms) and experimental times ($10T_1$). Notice that for relaxation time $> 100 \text{ ms}$ the remote prepolarization is a preferred method, while in-situ polarization is optimal for short T_1 .

is realized with the use of either pneumatic or mechanical shuttling. The sample arrives in the ZULF region 400-700 ms after leaving the magnet.¹ The delay between polarization and detection may be the weakness of remote propolarization schemes. Particularly, for short T_1 , the transfer may prevent observation of NMR signals. On the other hand, the advantage of this approach is the comparable polarization level of the NMR samples in comparison to conventional high-field experiments. In fact, remote prepolarization is the most popular way of sample polarization in ZULF NMR and was explored in most of the studies presented in this dissertation.

In-situ thermal polarization

An electromagnetic coil can be used to polarize the samples right in the ZULF region. The prepolarizing coils often take a form of a solenoid stretching either the whole length of the inner layer of a magnetic shield (providing ZULF conditions) or piercing the shield so that the field leakage outside the solenoid is minimized (the latter configuration acts as an infinitely long solenoid not producing outside field). The field produced by the coil is in the millitesla range, which is two to three orders of magnitude lower than the field produced with remote polarization with permanent magnets. As shown in Fig. 3.2c), this yields proportionally smaller NMR signals of samples with long T_1 . However, for samples with short T_1 (e.g., in the millisecond range), the *in-situ* polarization can offer an advantage. We can try to quantify this advantage by comparing a registered NMR signal with both remote and in-situ polarization, for a sample with a characteristic polarization lifetime T_1 . As the averaging improves the signal-to-noise ratio of the registered signal we normalize the signal amplitudes by the square root of time. The ratio R of such

¹ Faster shuttling is possible, however, for that one needs to provide a strong guiding magnetic field between the regions to provide adiabatic conditions of the transfer. With a faster transfer, the concern also is a structural integrity of the sample. Nonetheless, such fast sample transport is achievable, for example, in conventional field-cycling experiments.

normalized signal acquired with the use of in-situ and remote polarization can be estimated as:

$$R \approx e^{-\frac{t_{transport}}{T_1}} \frac{B_{coil}}{B_{magnet}} \sqrt{\frac{T_{exp} + T_{shuttling}}{T_{exp} + T_{deadtime}}} \quad (3.10)$$

where $T_{shuttling}$ is the shuttling time in remote prepolarization, T_{exp} is the total length of the experimental sequence (polarization and detection), $T_{deadtime}$ is the delay between excitation of the signal and its detection (see Sec. 3.3) and B_{coil} and B_{magnet} are magnetic-field strengths used for *in-situ* and remote polarization, respectively. In Fig. 3.2, the ratio of signals (Eq. 3.10) has been plotted for realistic experimental conditions. As shown, the advantage of *in-situ* polarization clearly manifests itself for polarization lifetime below 100 ms.

The *in-situ* polarization was successfully implemented in measurement of relaxation processes at ultra-low and low magnetic fields in samples characterized by relaxation times up to ~ 30 ms (Bodenstedt et al. [2021]). It is worth noting that principally it can be used to detect signals from samples of even shorter T_1 , as the coils switching time can reach μ s level, but until now such studies are limited due to dead time of the sensor used for NMR detection (see Sec. 3.3).

Finally, it should be noted that this approach requires some considerations. Since ZULF experiments are typically preformed inside magnetic shielding, the polarizing field is produced inside the shield. The field of 1-100-mT is sufficient to magnetize a mu-metal (Jiles [2015]), which is the material the shield is typically made of. This magnetization may lead to uncompensated residual magnetic field inside the shield. In the worst-case scenario, the strong magnetic field saturates the material, which deteriorates the shielding factor and hence negatively affect quality of zero-field spectrum. The use of the inner ferrite layer in magnetic shielding may remedy the problem, as ferrite is a hard magnetic material with much higher saturation field (Jiles [2015]).

As discussed here, the prepolarization in a strong magnetic field is a preferred method of polarization, as the J -coupling energy is insufficient to create a measurable signal. For example, a typical 100-Hz coupling produces nuclear polarization on the level of 10^{-11} . In this scope, the prepolarization method is universal, cost-efficiently and easily implementable into ZULF NMR experiment. That is the reason why majority of the results presented in this thesis use this method of polarization (Chapters 6 and 7). For long relaxation times, remote polarization in tesla-level field, produced by a permanent magnet, is preferable while to studies rapidly decaying signal, the *in-situ* polarization in a millitesla field is better. No matter the implementation, however, the thermal polarization levels are in order of ppm and less, resulting in poor sensitivity. That is why other methods of obtaining nonequilibrium nuclear polarization were also used in the research on ZULF NMR presented in this dissertation.

Nuclear hyperpolarization

The set of techniques use to obtain high (reaching tens of percent) nuclear polarization is referred to as **hyperpolarization**. This nonequilibrium nuclear polarization can be obtained in a number of ways.

For example it can exploit high-electronic polarization obtained by process of optical pumping. In this technique (**Spin Exchange Optical Pumping (SEOP)**) optically polarized alkali atoms transfer their polarization to nuclear spins of noble gas nuclei via collision, resulting in the large nuclear polarization. The technique since found it use e.g. in MRI to obtain high-resolution images of lungs (normally lacking detectable nuclear spins) (see for example Mugler III and Altes [2013]). The SEOP has found it use in ZULF NMR from the very beginning (Cohen-Tannoudji et al. [1969]) but also in later reemergence of this NMR modality (see for example: Yashchuk et al. [2004] and Ledbetter et al. [2012]).

The other popular incarnation of hyperpolarization schemes in **Dynamic Nuclear Polarization (DNP)**. While this technique is based on a number of physical mechanisms, it always involves transferring a electron spin polarization (due to high gyromagnetic ratio much larger than corresponding nuclear polarization at the same temperature and magnetic field) to nuclear spins. One incarnation of the technique (dissolution DNP) found a wide use in polarizing ^{13}C nuclei in relevant biomolecules (see for example [Ardenkjaer-Larsen \[2016\]](#)). This technique has also recently find a use in zero-field experiments as shown in [Barskiy et al. \[2020\]](#) and [Picazo-Frutos et al. \[2022\]](#), while the chemically-induced DNP was also investigated under ZULF conditions ([Sheberstov et al. \[2021\]](#)).

While the hyperpolarization techniques can rely on the electronic polarization, they can also rely on an easily prepared, highly ordered nuclear spin state of hydrogen, which we will describe in more detail in a following section.

3.2.2 Parahydrogen-induced polarization

Parahydrogen - molecular singlet state of hydrogen

Parahydrogen is a singlet nuclear state of molecular hydrogen. Considering factorability of a nuclear wavefunction, a total nuclear state of molecular hydrogen can be written as:

$$|\Psi_{\text{nuclear}}\rangle = |\Psi_{\text{transl}}\rangle |\Psi_{\text{vib}}\rangle |\Psi_{\text{rot}}\rangle |\Psi_{\text{spin}}\rangle, \quad (3.11)$$

where we factored out the total nuclear state $|\Psi_{\text{nuclear}}\rangle$ into a product of translation part $|\Psi_{\text{transl}}\rangle$, part describing molecular vibrations $|\Psi_{\text{vib}}\rangle$ and rotation $|\Psi_{\text{rot}}\rangle$, and the spin-depended part $|\Psi_{\text{spin}}\rangle$. The total nuclear wavefunction describes a pair of fermions (protons) and hence must be antisymmetric upon the exchange of particles ([Sakurai and Commins \[1995\]](#)). As the translation part describes movement of the center of mass of symmetric molecule, it is symmetric. The vibrational states of molecular hydrogen can be approximated as the solution to quantum harmonic oscillator, with the ground state wavefunction given by:

$$\langle \hat{x} | \Psi_{\text{vib}}^{\text{ground}} \rangle = \Psi_{\text{vib}}^{\text{ground}}(x) \propto e^{-\frac{m\omega x^2}{2\hbar}} \quad (3.12)$$

which is symmetric. As the energy of the vibrational-state excitation (4342 cm^{-1} [Linstrom and Mallard \[2001\]](#)) is more than order magnitude larger that room-temperature thermal energy, the symmetrical vibrational ground state is occupied. Lastly, the rotational wavefunction for molecular hydrogen can be found as solutions to a quantum-rigid-rotor problem ([Sakurai and Commins \[1995\]](#))

$$\langle \hat{x} | \Psi_{l,m}^{\text{rot}} \rangle = \Psi_{l,m}(\phi, \theta) \propto e^{-im\phi} P_l^{|m|} \cos(\theta) \quad (3.13)$$

where P_l are the Legendre polynomials. The rotational states are therefore symmetric for even l and antisymmetric for odd l , where l enumerates the molecular states. The energy associated with the rotational state is given by:

$$E_l = \frac{\hbar^2 l(l+1)}{2I} \quad (3.14)$$

where $I = 1.39 \times 10^{-47} \text{ kg m}^2$ is the moment of inertial of the hydrogen molecule. As the energy separation is smaller than thermal energy at room temperature, all rotational states are occupied.

As two protons in a hydrogen molecule are chemically equivalent, the spin-depended part of the nuclear state can take the form of homonuclear antisymmetric singlet state called **parahydrogen** or the triplet state, called **orthohydrogen** (see for

example [Green et al. \[2012\]](#)). As the total nuclear wavefunction has to be antisymmetric, we can make an important observation regarding spin states of molecular hydrogen. Namely, the molecular-hydrogen nuclear spin state depends on the rotational state of the molecule. Specifically, if the molecule is the even rotational state, hydrogen is the nuclear spin singlet state, while the molecule in the odd rotational state its nuclear spin state must be triplet. We can calculate the fraction of hydrogen molecules in parastate as ([Green et al. \[2012\]](#)):

$$\chi_{para} = \frac{\sum_{l_{even}} (2l + 1) \exp \left[-\frac{\hbar^2 l(l + 1)}{2Ik_B T} \right]}{\sum_{l_{even}} (2l + 1) \exp \left[-\frac{\hbar^2 l(l + 1)}{2Ik_B T} \right] + \sum_{l_{odd}} (2l + 1) \exp \left[-\frac{\hbar^2 l(l + 1)}{2Ik_B T} \right]}, \quad (3.15)$$

where we used the Boltzmann distribution to obtain populations in even and odd rotational states. The dependence of the parahydrogen fraction as the function of temperature is plotted in Fig. 3.3a). In a high-temperature limit, i.e., when $\hbar^2 l(l + 1)/(2Ik_B T) \ll 1$, we can show that $\chi_{para} = 1/4$. This means that all spin states (one of parahydrogen and three of orthohydrogen) are occupied with the same probability. As seen in Fig. 3.3a) this condition is well satisfied at room temperature, as fraction of parahydrogen is 25%, and the polarization is negligible. As the temperature decreases, the fraction of parahydrogen increases, reaching 51% at 77 K (boiling temperature of liquid nitrogen), and plateaus below 30 K, when all thermal-equilibrium hydrogen is parahydrogen.

Generation of parahydrogen

As seen from Eq. 3.15 and Fig. 3.3, we can obtain high level of parahydrogen by cooling molecular hydrogen down. This is the principle behind production of parahydrogen used to perform NMR experiments. It is noteworthy that Eq. 3.15 holds true for thermal equilibrium. However, in normal conditions, as hydrogen cools down it converts to parastate very slowly (in weeks). This is a result of a forbidden transition between singlet and triplet states. Hence to efficiently generate parahydrogen in cold finger a paramagnetic catalyst (breaking symmetry of hydrogen nuclear state) is used. On the other hand, if stored in nonmagnetic container, the parastate can be preserved for for a long time (days, weeks).

The home-built system developed for the research described in this thesis is shown in Fig. 3.3. It is based on a number of previous designs (see for example: [Theis \[2012\]](#)). The high-purity hydrogen gas (99.99999%) at 200 bars is passed through a regulator where its adjusted to an appropriate pressure levels (initial pressure is set to around 2 bars and is slowly increased until the parahydrogen cylinder is filled up to 6 bars). The gas then passed through a spiral-shaped cold finger, filled with the catalyst for ortho-para conversion, placed inside the liquid nitrogen dewar. The portion of gas is initially held in the cold finger as it cools down after being submerged in liquid nitrogen. Then (typically after 20 min) the outlet valve is then opened and the needle valve controls the flow of a gas to the aluminium storage tank. After the pressure equalizes in the line and the parahydrogen tank, the pressure on the regulator is slowly increased. The total filling time of the tank to the pressure of 6 bars takes at least two hours. The parahydrogen is typically used in experiments up to two days. Before parahydrogen production the whole line is vacuumed below 1×10^{-4} mbar. After initial assembly, or every time the cold finger is exposed to air, the catalyst is reactivated by heating it above 100 °C and pulling vacuum for couple of hours. This procedure desorbs water vapor and other contaminants from the surface of the catalyst, and is crucial to obtain high conversion efficiency. The catalyst– Hydrated, Catalyst grade, Iron(III) oxide, 30-50 mesh (Sigma Aldrich, CAS number: 20344-49-4)– is used for conversion and the nonmagnetic aluminium diving tank is used for the storage and transport of parahydrogen between generator and the zero-field spectrometer.

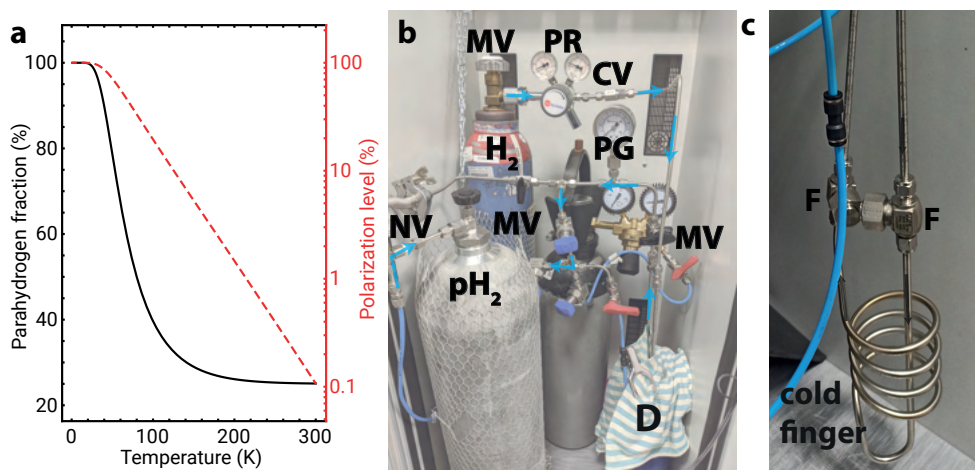


Figure 3.3: a) Parahydrogen level in the molecular hydrogen under thermal equilibrium as a function of temperature. Red plot, corresponding to right (red) axis shows the corresponding polarization parameter. b) Home-built parahydrogen generator operating in Kraków and used for experiments described in this dissertation. Various components of the gas manifold are highlighted and labelled. The high-purity (99.99999%) hydrogen gas (H_2) is supplied from a gas cylinder and exposed to the rest of the system by opening a manual valve (MV). Outlet pressure of the gas is controlled with the pressure regulator (PR). The check valve (CV) is installed after pressure regulator to protect the system from backpressure build-up (as for example not-vacuumed cold finger warms up from liquid nitrogen to room temperature). The gas passes through a cold finger, shown in c), submerged in liquid nitrogen dewar (D). When the cylinder for parahydrogen (pH_2) is prepared for filling, a MV is opened, while the pressure is monitored with the pressure gauge (PG). The flow into the tank and through the catalyst inside the cold finger is controlled through the use of needle valve (NV). c) Close-up of the cold finger filled with catalyst for conversion of orthohydrogen to parahydrogen. The cold finger is filled with the catalyst up to the $50\ \mu\text{m}$ sized filters F, which ensure that the iron oxide does not contaminate other parts of the setup.

Parahydrogen-induced polarization

So far, we discussed generation of the singlet state of molecular hydrogen. However, parahydrogen is not directly detectable in NMR experiments (both at high and zero fields), as it corresponds to the total spin $S = 0$, not producing magnetization. To exploit parahydrogen for spin polarization, one needs to break the symmetry of hydrogen nuclei in the parastate, which can be done using chemical reaction (irreversible hydrogenation or reversible exchange in the presence of a catalyst).

Hydrogenative parahydrogen hyperpolarization

We can express the density-matrix operator of parahydrogen molecule using spin operators:

$$\hat{\rho}_{para} = |S_0\rangle \langle S_0| = \frac{1}{4} \mathbb{1} - \hat{\mathbf{I}} \cdot \hat{\mathbf{S}}, \quad (3.16)$$

where $\hat{\mathbf{I}}$ and $\hat{\mathbf{S}}$ are the spin operators of two hydrogen nuclei. To break a symmetry of this state and successively generate magnetization, we can perform a hydrogenative reaction of parahydrogen with a given molecule. Different schemes of parahydrogen-induced polarization are:

- **Hydrogenation at high field**

If hydrogenation is performed with the use of parahydrogen molecule in high magnetic field, the parahydrogen state should be considered in the Zeeman basis. In this basis, the parahydrogen density matrix takes the form:

$$\hat{\rho}_{para} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1/2 & -1/2 & 0 \\ 0 & -1/2 & 1/2 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \quad (3.17)$$

After hydrogenation, the evolution of two hydrogen nuclei from the parahydrogen molecule under the magnetic-field interaction, in the rotating frame, is given by:

$$\hat{\mathcal{H}}_{para} = -\hbar\gamma_H B_0 (\sigma_I \hat{\mathbf{I}} + \sigma_S \hat{\mathbf{S}}), \quad (3.18)$$

where σ_I and σ_S are the chemical shifts of two hydrogen nuclei attached to the target molecule but originating from the same parahydrogen. If chemical shifts of the protons are identical, i.e., they are chemically equivalent, the state does not evolve under the high-field Hamiltonian (Eq. 3.18). If, however, the nuclei end up in different chemical environments and hence are characterized with the different chemical shifts, the non-diagonal terms of $\hat{\rho}_{para}$ evolve due to magnetic field. Beginning of the evolution is random, as the attachment of the hydrogen to the molecule is a statistical process. Accounting for the huge number of molecules leads to incoherent averaging of the coherences in the density matrix 3.17, resulting in the state given by:

$$\hat{\rho}_{para}^{PASADENA} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \\ 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \frac{1}{4} \mathbb{1} - \hat{I}_z \hat{S}_z, \quad (3.19)$$

which describe a state aligned along the z-axis.

The described scheme is the basis of the, so-called, **PASADENA** (Parahydrogen and Synthesis Allows Dramatically Enhanced Nuclear Alignment) experiment (Bowers and Weitekamp [1987]), which allows to induce high-field NMR signals (after application of a 45° pulse). In that case, the spectrum consists of

pairs of antisymmetric (180° out of phase) peak doublets. As hydrogenation can be performed inside a high-field spectrometer, it is often implemented with conventional NMR experiments.²

- **Hydrogenation at low field**

In low magnetic field, the hydrogen parastate is approximately given by the eigenstate of the Hamiltonian 3.18. In this case, the density matrix survives incoherent averaging, as it is diagonal in the basis of spin hamiltonian, and the state, given by Eq. 3.17, survives the hydrogenation. This is the basis of **ALTADENA** (Adiabatic Longitudinal Transport After Dissociation Engenders Net Alignment) technique, where a hydrogenated sample is transported to a high-field NMR spectrometer in adiabatic fashion, resulting in the density matrix of a following form (written in the high-field basis):

$$\hat{\rho}_{para}^{ALTADENA} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \frac{1}{4}\mathbb{1} - \hat{I}_z\hat{S}_z - \frac{1}{2}(\hat{I}_z - \hat{S}_z). \quad (3.20)$$

With respect to the PASADENA state, the ALTADENA density matrix carries the extra term $\hat{I}_z\hat{S}_z$ which can be used to obtain measurable NMR signal and results in different signal generation by pulses.

The state given by Eq. 3.20 can be used to generate a detectable NMR signal (using the 90° pulse). ALTADENA signal arises due to magnetic inequivalence of two parahydrogen-originating protons as opposed to chemical inequivalence that is used in the PASADENA experiment. As a result, a pair of phased doublets, antiphased in respect to each, other is produced (Pravica and Weitekamp [1988]).

- **Hydrogenation in zero field**

In zero magnetic field, the parastate of hydrogen is the eigenstate of the spin hamiltonian dominated by J -coupling (Eq. 2.80). Then, upon addition to the molecule, the quantum state of parahydrogen starts to evolve under the zero-field Hamiltonian. In particular, the density matrix of a single hydrogenated molecule (Eq. 3.17) transforms as:

$$\hat{\rho}(t) = \exp\left(\frac{-i\hat{H}_{zero}t}{\hbar}\right)\hat{\rho}(0)\exp\left(\frac{i\hat{H}_{zero}t}{\hbar}\right). \quad (3.21)$$

To obtain a density matrix of a macroscopic number of molecules, we need to account for molecules, whose evolution started at different times:

$$\bar{\rho} = \frac{1}{t} \int_0^t dt' \exp\left(\frac{-i\hat{H}_{zero}t'}{\hbar}\right)\hat{\rho}(0)\exp\left(\frac{i\hat{H}_{zero}t'}{\hbar}\right). \quad (3.22)$$

It has been shown (Theis et al. [2011]) that the resulting averaged density matrix takes a form:

$$\bar{\rho}(t) = \sum_{ik} a_{i \neq k}(t) \hat{I}_i \cdot \hat{I}_k, \quad (3.23)$$

which is a sum of pairwise couplings, leading to creation of heteronuclear singlet states. The averaged density matrix is diagonal in the zero-field basis, i.e., off-diagonal coherences average out in a course of reaction and the time-dependent weights $a_{ik}(t)$ reach steady-state values. Finally, the singlet order is spread across whole molecule. A DC magnetic field pulse is then used to convert singlet order to an observable magnetization (Butler et al. [2013a]).

² It should be noted that the chemical-shift difference is not strictly necessary to obtain hyperpolarized signals using parahydrogen. This was demonstrated with hydrogenation of symmetric molecules at high-magnetic field (Zhivonitko et al. [2013]).

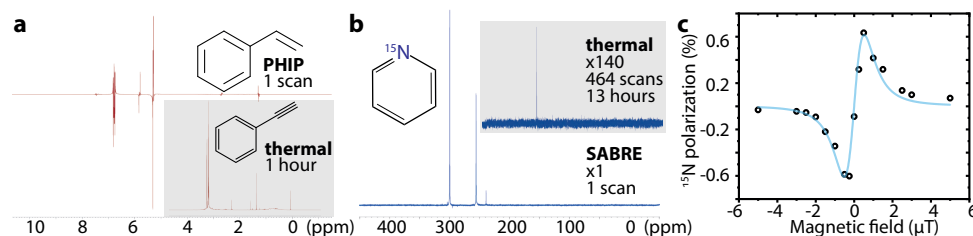


Figure 3.4: NMR signals obtained with the various hyperpolarization techniques of parahydrogen-based hyperpolarization at different conditions. The results were obtained by the author using a 600 MHz Bruker NMR spectrometer. a) ^1H NMR spectrum of styrene obtained by hydrogenation of phenylacetylene using parahydrogen. Inset shows a thermal spectrum of precursor (phenylacetylene) with 1 hour of averaging. The hyperpolarized spectrum was obtained using OPSY sequence (Aguilar et al. [2007]), filtering thermal signals. Notice the greatly enhanced antiphased peaks in the hyperpolarized spectrum. b) Spectrum of ^{15}N -labeled pyridine hyperpolarized with parahydrogen using the reversible-exchange mechanism. The spectrum was obtained after hydrogenation in 6-mT field, matching the LAC condition (see the main text). Inset shows the spectrum of the pyridine obtained over a night-long averaging. Additional peaks in the hyperpolarized spectrum correspond to the spectrum of pyridine bounded to the metalorganic SABRE catalyst. c) Pyridine NMR signal hyperpolarized at ultra-low field using the reversible exchange. The pyridine polarization level is plotted as a function of magnetic field, in which the exposition to hydrogen took place. Sum of two symmetrically positioned Lorentzians with extremes at $\approx \pm 0.4 \mu\text{T}$ (matching the LAC condition for heteronuclear case), are plotted matching adequately experimental data.

The polarization via hydrogenation not only pioneered use of parahydrogen in NMR but also found numerous NMR applications (Kovtunov et al. [2018]), but it is also used for example to generate hyperpolarized MRI contrasts (Goldman et al. [2005]). The main advantage of the technique is high polarization level achieved with this method (reaching tens of percent Knecht et al. [2021]; Blanchard et al. [2020b]). The signal increase due to parahydrogen polarization is demonstrated in Fig. 3.4 a), where the thermal spectrum is compared to one obtained with hydrogenative hyperpolarization with pH_2 . Due to its high-polarization levels, relatively simple sample preparation, and natural compatibility with zero-field experiments, parahydrogen-induced polarization was used in ZULF NMR at its early stage (Theis et al. [2011]) and it was continued to be used since then (Blanchard et al. [2020b]). However, as the technique works with samples prone to hydrogenation, its scope is hence limited. This limitation is tackled by other parahydrogen-based techniques, which do not rely on hydrogenation reaction.

Non-hydrogenative parahydrogen hyperpolarization

The advent of nonhydrogenative parahydrogen-induced polarization started with the work of Adams et al. [2009], where the reversible exchange of parahydrogen and target molecule on an organometallic catalyst gave rise to non-equilibrium polarization of the target molecule (see Fig. 3.5b). The technique was called **signal amplification by reversible exchange (SABRE)**. Similarly to the hydrogenative reaction, the reversible exchange can take place at different magnetic field. Below, we discuss this hyperpolarization technique at different magnetic-field regimes:

- **Reversible exchange at high magnetic field**

Similarly to the previously described experiments, a prerequisite for obtaining nuclear polarization with the use of parahydrogen using the reversible exchange is breaking the symmetry of two protons constituting the molecule. This is achieved by a temporary addition of the protons to a metalloorganic

complex (Adams et al. [2009]). The rest of the complex is reversibly bonded to a target molecule. As both parahydrogen protons and target molecule form a temporary complex, they act a coupled-nuclear-spin system. In the high-field regime (defined in Sec. 2.4), cross-relaxation between hyperpolarized protons and the nuclei on the target molecule may lead to polarization of the latter (Barskiy et al. [2019a]). This allows for hyperpolarization of the target molecules in high-field spectrometers³), although efficiency of the transfer can be greatly improved by exploiting highly coupled spin-system under low and ultra-low field magnetic field conditions (Eills et al. [2019]).

- **Reversible exchange in low and ultra-low magnetic field**

Under the low-field conditions, the set of target nuclear spins and protons from a parahydrogen molecule compose of a strongly coupled system, where the J -coupling interaction dominates over the Zeeman energy shifts. This occurs in the low-field conditions for homonuclear systems and at ultra-low fields for heteronuclear systems. The strong J -coupling leads to a polarization transfer, which is magnetic-field depended. The field dependence may be explained using the **level anticrossing** (LAC) phenomenon (see for example Barskiy et al. [2019a]). Such process arises when energy levels of unperturbed Hamiltonian are crossing, but due to additional perturbation, mixing of levels is introduced, and the levels repeal themselves. In turn, the levels do not cross. The level anticrossing occurs when the perturbation energy matches the energy difference between the levels of unperturbed Hamiltonian. When the system is brought adiabatically through the level anticrossing, population is transferred directly from one state to another. This is exploited in continuous SABRE experiments under low-field conditions (Truong et al. [2015]).

When we consider a system of two protons from a parahydrogen molecule (labelled A and A') and target nuclei (B), LAC can be used to transfer system from the singlet state $|S_0, \alpha\rangle$ to the specific triplet state $|T_{+1}, \beta\rangle$, where the state of parahydrogen is shown in singlet-triplet basis, while the state of target nuclei is indicated by spin up α and spin down β Zeeman states. This transfer process corresponds to a flip of one the parahydrogen protons and target nuclei. The condition for this level anticrossing is given by:

$$|v_A - v_B| \approx |J|, \quad (3.24)$$

where the frequency difference in the Zeeman evolution of spins A and B matches the J -coupling between hydrogen spins⁴. For a simple three spin system AA'B system, Eq. 3.24 can be rewritten to the form:

$$\begin{aligned} B_{LAC}(\sigma_A - \sigma_B) &= \pm J_{AA'} \\ B_{LAC} &= \frac{\pm J_{AA'}}{(\sigma_A - \sigma_B)}, \end{aligned} \quad (3.25)$$

which typically results in the magnetic field B_{LAC} in a millitesla range. This resonance condition is used to perform SABRE experiments under low magnetic-field conditions, where the polarization is very effectively transferred to protons in the target molecule (reaching tens of percent Rayner et al. [2017]).

In the heteronuclear case the condition given by Eq. 3.24 takes a form:

$$\begin{aligned} B_0(\gamma_A - \gamma_B) &= \pm J_{AA'} \\ B_0 &= \frac{\pm J_{AA'}}{(\gamma_A - \gamma_B)}, \end{aligned} \quad (3.26)$$

³ Application of electromagnetic radiation may greatly improve polarization efficiency in high fields (Pravdivtsev et al. [2014])

⁴ More generally an effective J -coupling in the system is typically an algebraic combinations of couplings between A, A', B spins in the system, see: Barskiy et al. [2019a].

which, in the case of ^1H and ^{15}N , typically results in a resonant magnetic field of couple of microtesla. The typical dependence on the field in hydrogenation in the heteronuclear case is shown in Fig. 3.4c).

It is worth pointing out that the analysis presented here is greatly simplified. To begin with, the more realistic scenario than considered here would include an AA'XX' spin system. This is so because the target molecule is attached to multiple sites on the catalyst. This leads to modification of Eq. 3.24, as a single J -coupling strength becomes a combinations of multiple J -couplings. Moreover, multiple LAC conditions can exist, modifying field dependence of polarization transfer in SABRE (Barskiy et al. [2019a]). Finally, the level-anticrossing approach is just an useful approximation of reversible-exchange dynamics, which may hold valid under constant magnetic field hydrogenation. However, more optimal polarization transfer yet can be achieved with the use of time-depended magnetic fields (Eriksson et al. [2021]).

• Reversible exchange at zero magnetic field

Looking at the resonance condition given by Eq. 3.26 and the measured field dependence shown in Fig. 3.4c), one could be concerned at feasibility of obtaining hyperpolarization with reversible exchange at zero field, as two symmetrically positioned LAC resonances cancel each other out. The non-equilibrium polarization, hence an enhanced NMR signal, can be, however, obtained, as the singlet-order of form $\hat{I} \cdot \hat{S}$ is spread over the target molecule (in contrast to creating a polarization on a target nuclei, typically ^{15}N or ^1H). This non-equilibrium, singlet-order state can be used to observe ZULF NMR signals that arises shortly after a DC pulse, as first demonstrated in Theis et al. [2012]. As described therein, an effective density matrix of the hyperpolarized target molecule can be described as a sum of two-spin singlet terms:

$$\hat{\rho}_{\text{SABRE}}^{\text{zero}} = \sum_i c_i \hat{I} \cdot \hat{S}_i, \quad (3.27)$$

where $\hat{I}$ corresponds to a heteronucleus (e.g., ^{15}N) and $\hat{S}_i$ to proton spins, coupled to this nuclei with c_i . Via numerical simulations, the authors of Theis et al. [2012] found that in the case of hydrogenation of ^{15}N at zero-field only three coefficients are independent because of the symmetry of the molecule. Moreover, only two coefficients contribute to the initial density matrix. Whatever may be the symmetry of the non-equilibrium density matrix after hydrogenation, the presence of heteronuclear singlet-order terms will give rise to zero-field NMR signals.

The parahydrogen-induced polarization based on the reversible exchange found its place in NMR experiments (see for example Kovtunov et al. [2018] and references therein). Moreover, since it naturally works at ultra-low and zero-field conditions, it found its application in ZULF NMR. The polarization levels obtained via this mechanism can be really large, up to 10%, while the reversible nature means that the experiments can be repeated many times (up to hours, see for example Blanchard et al. [2021b]). This approach allows for straightforward parameter optimization. Moreover, it may be used for replacing thermal remote prepolarization with highly-efficient *in-situ* polarization, offering additional ability of repeating the experiment many times. The direct SABRE mechanism, however, is limited to a number of molecules, because an appropriate catalyst must be found and optimized to ensure efficient polarization transfer.

Even more general approach to hyperpolarization based on parahydrogen can be implemented and adapted to a large number of target molecules. The approach is described below.

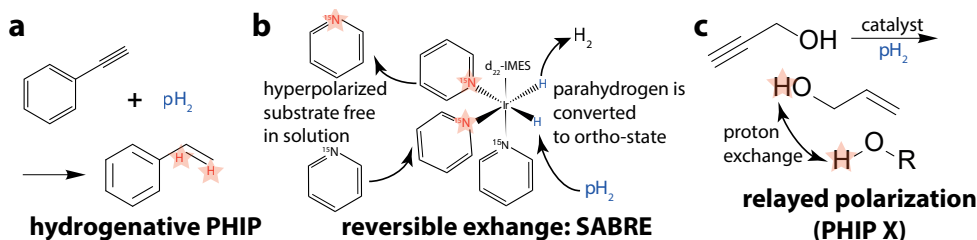


Figure 3.5: Chemical mechanisms of parahydrogen-induced-polarization reactions. Stars indicated (hyper-) polarized nuclei a) Hydrogenative reaction of phenylacetylene with parahydrogen, leading to hyperpolarization of styrene (the NMR spectrum of the hyperpolarized styrene is shown in Fig. 3.4 a). b) Mechanism of polarization transfer using reversible exchange with SABRE, enabling hyperpolarization pyridine. The parahydrogen and substrate is reversibly bounded to an iridium-based catalyst (the high-field NMR spectrum of hyperpolarized pyridine is shown in Fig. 3.4 b). c) Parahydrogen-induced polarization relayed with exchangeable proton (PHIP-X mechanism). Propargyl alcohol reacts with parahydrogen producing hyperpolarized allyl alcohol. The polarized proton in OH-group exchanges with protons in the target (alcohol) molecules.

Relayed parahydrogen hyperpolarization

It was recently demonstrated that parahydrogen-induced polarization can be applied to molecules, which neither react with parahydrogen nor reversibly bind to an appropriate catalyst. Starting from Iali et al. [2018], an idea of **relaying polarization from one substrate polarized via SABRE mechanism to the target molecule** (dubbed SABRE-relay) has been investigated. In the reversible-exchange mechanism, this can be achieved in two ways. First, one can introduce a second metallorganic catalyst to which both a relay and target molecules bind reversibly (Roy et al. [2018]). Specifically, the relay molecule first binds reversibly to a regular SABRE catalyst, where it gets polarized by parahydrogen, and then it attaches to a second metallic center, where it transfers polarization to the reversibly-bounded target molecule. This was successfully used to polarize a number of organophosphorus compounds (Roy et al. [2018]).

The other SABRE-relay approach relies on chemically exchanging protons with the relay molecule (Iali et al. [2018]). Specifically, the relay molecule is first polarized by the SABRE and then a hyperpolarized, chemically exchangeable proton is transferred from the relay molecule to the target compound. This results in highly-enhanced NMR signals from the target molecule. Moreover, other nuclei also are getting polarized in the process, as evident by results presented in Iali et al. [2018].

Yet another approach recently emerged with the use of hydrogenative parahydrogen induced polarization (Them et al. [2021]). In this technique (called **PHIP-X**), a relay molecule is first polarized with the use of parahydrogen hydrogenation. Then an exchangeable proton is transferred to a target molecule (see Fig. 3.5). Similarly to the SABRE-relay case, not only an exchangeable proton gets polarized in target molecule, but the polarization also spreads to other nuclei.

The most important parameter for all the methods is the efficiency of hyperpolarization. The PHIP-X mechanism was studied numerically from fields ranging from the Earth magnetic field up to couple of mT (Them et al. [2021]). The analysis seems to indicate that the polarization transfer to the exchangeable proton is crucial for the process. It is affected by both magnetic-field strength and chemical-exchange rate. In particular, it was found that the transfer efficiency is growing linearly with the field strength and maximizes at about 80 mT (independent on the exchange rate) for a range of small target molecules. This dependence suggests a general approach toward PHIP-X-based ZULF NMR. Specifically, a sample should be first hydrogenated in a millitesla-field (either produced *in-situ* or outside of ZULF region) and then the zero-field conditions should be reached (either by reducing the

field or shuttling the sample). In the case of SABRE-relay, a hydrogenation should take place in millitesla field (to satisfy LAC), which maximizes the polarization of the exchangeable proton in the relay molecule. Also in this case, the sample should first experience the stronger field and then ZULF conditions should be reached to perform NMR measurements.

The creation of singlet order in the target molecule before detection of ZULF NMR signals, is also of essence. In principle, the polarization of only the exchanging proton is sufficient to see coupled evolution at zero field, as long as the exchange rate is not much faster than the relevant J -coupling. If the proton exchange is faster (as for example in case of most alcohols) transfer of polarization to other (non-exchanging) nuclei is crucial to obtain ZULF NMR spectra.

The strength of SABRE-relay and PHIP-X approaches lies in a fact that a large number of relevant biomolecules have exchangeable protons. This means that molecules that were not polarizable with conventional approaches can be hyperpolarized using chemical exchange of protons. Particularly, SABRE-relay and PHIP-X were used to hyperpolarized alcohols and some amino acids (Roy et al. [2018]; Them et al. [2021]). Very recently, the zero-field signals of methanol and ethanol were measured following a relayed polarization in mT-field to a ZULF region for NMR detection (Van Dyke et al. [2022]). Moreover, many metabolites (e.g., urea, see Chapter 6) can be in principle hyperpolarized using these approaches. Finally, it should be stressed that presence of the exchangeable proton in the measured molecule can strongly affect the zero-field spectra (see Chapter 6 and Barskiy et al. [2019b] for more details). This is a factor that needs to be taken into account while planing ZULF NMR experiments.

3.2.3 Polarization in ZULF NMR experiment-conclusions

As we saw in this section, the thermal-equilibrium polarization at zero-magnetic field is not sufficient to generate nuclear magnetization and hence detect NMR signals. Because of that one needs to prepare a non-equilibrium nuclear state, which can be done by either prepolarizing a sample at strong magnetic field or by using a hyperpolarization method, among which parahydrogen-induced polarization is one that offers large polarization level. After addressing a problem of inherently low polarization at ZULF, we turn our attention to another challenge of zero-field NMR, i.e., detection of low-frequency oscillating magnetic fields.

3.3 DETECTION OF ZULF NMR

3.3.1 Introduction to detection of ZULF NMR

Zero-field NMR signals in liquids typically arises between 0 all the way up to 1000 Hz. Detection of such a low-frequency field becomes challenging, if possible at all, with electromagnetic-induction-based methods (see Eq. 2.92). This implies the use of other magnetometric methods. As seen in the section dedicated to history, the problem was initially solved using field-cycling methods, where the detection in a high field followed evolution in a zero field. This way, the zero-field evolution was indirectly probed. Some time after that, non-inductive sensors (SQUIDS) were used to probe the ULF signals. Such low-frequency measurements were possible due to femtotesla sensitivity of the devices near DC fields. In particular, such measurements find its applications in low-field imaging (Kraus et al. [2014]). As the SQUID sensors operate with the use of superconductors, a cryogenic cooling of the magnets is required. This significantly increases the spectrometer cost and footprint. In recent years, the alternative magnetometric scheme that is sensitive at low frequencies, i.e., **atomic magnetometry**, emerged and found its application in ZULF

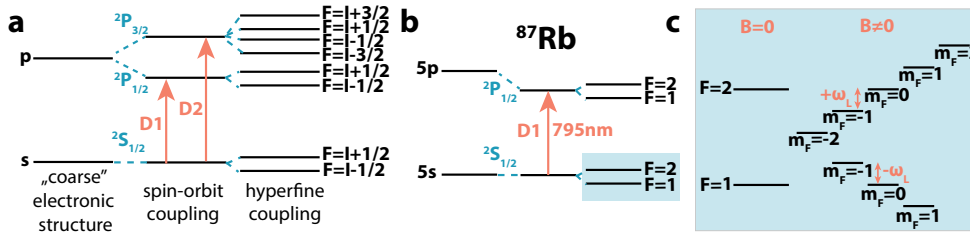


Figure 3.6: General electronic energy-level structure of alkali atoms. a) General structure of the energy levels presenting orbital levels, as well as fine and hyperfine structures. The vertical arrows indicate D1 and D2 lines in the atoms. b) Energy-level structure of ^{87}Rb , which is used in magnetometers presented in this thesis. The coarse energy transition is indicated with the wavelength of resonant light. c) Ground-state energy-level structure of ^{87}Rb (highlighted in blue in part b)) in zero and non-zero magnetic field. Notice opposite Zeeman splitting of magnetic sublevels in different ground-state hyperfine levels.

NMR.⁵ The first use of such sensors to detect low-magnetic field signals, goes back to Cohen-Tannoudji et al. [1969], where a ultra-low frequency precession signals from hyperpolarized ^3He sample contained in a glass cell, was detected with the use of a nearby sample of rubidium atoms. Over the years, atomic magnetometers found their use in zero-field spectrometers (Tayler et al. [2017]), as its small physical footprint, low-energy requirements, and noncryogenic operation make them a perfect match for ZULF NMR.

In the following sections, atomic magnetometry is described in details and its implementation to ZULF NMR extensively discussed.

3.3.2 Atomic structure of alkali metals

An atomic magnetometer typically use an **alkali-metal vapor** to detect weak magnetic fields. To discuss the magnetometer operation, the energy-level structure of such atoms and their interaction with light and external magnetic fields must be first understood.

The alkali-metal electronic structure is rather simple to explain as the system can be approximated by a system consisting of a single valence electron that orbits nuclear “core” (combination of nucleus charge shielded with inner-shell electrons). Such a hydrogen-like-atom approximation can provide a coarse energy-level structure of alkali atoms. The alkali-atom transition energies between the lowest energy s and p orbitals lay in the visible or near infrared range and hence can be easily addressed (and coherently driven) with laser light. The energy-level structure is further affected by the coupling of the valence-electron spin and the electron angular momentum. The electronic spin- $1/2$ couples to the orbital angular momentum modifying the energy of electrons. This **spin-orbit coupling** takes the form of:

$$\hat{\mathcal{H}}_{\text{spin-orbit}} \propto \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \quad (3.28)$$

and results in **the fine structure** of the alkali atoms. For the ground s orbital, the angular momentum is zero, $L = 0$, giving a single fine level characterized by the term symbol $^2S_{1/2}$. The higher-energy p orbital couples to two different electronic total momenta J , $J = 1/2$, $J = 3/2$, labelled by the term symbols $^2P_{1/2}$ and $^2P_{3/2}$. For historic reason the transition to the lower $^2P_{1/2}$ state is called the D1 line, while the transition to the $^2P_{3/2}$ state is referred to as the D2 line.

The energy levels are further split by the coupling to the nuclear spin of the atoms (**the hyperfine interaction**), leading to the hyperfine structure of the levels. As all

⁵ Such techniques use optically-polarized alkali-metal vapors for field sensing thus the devices are often referred to as **optically-pumped magnetometers**. Moreover, since detection of the signals, providing magnetic-field information, is optical, they are also called **optical magnetometers**.

the alkali atoms have non-zero nuclear spins, the coupling give rise to additional splitting. It can be shown from the Wigner-Eckart theorem (see for example [Sakurai and Commins \[1995\]](#)), that the ground state splits into two levels with $I \pm 1/2$, where I is the nuclear spin of the alkali atom. Figure 3.6a) shows the hyperfine energy-levels in the s and p states of the alkali atoms. Finally, the hyperfine levels have Zeeman sublevels ranging between $m_F = -F$ to $m_F = 1$ by 1. These sublevels are degenerated at zero field, but in nonzero magnetic field, the hyperfine levels split. If we consider the hyperfine and Zeeman interactions, we get a following interaction Hamiltonian:

$$\hat{\mathcal{H}}_{alkali} = \frac{2\hbar\omega_{hf}}{2I+1} \hat{\mathbf{I}} \cdot \hat{\mathbf{J}} + g_s \mu_B \hat{\mathbf{J}} \cdot \mathbf{B} - g_I \mu_N \hat{\mathbf{I}} \cdot \mathbf{B}, \quad (3.29)$$

where μ_B and μ_N are the Bohr and nuclear magnetons, respectively, and g_s and g_I are Landé g factors for the electron and nucleus, respectively. One can find the energy of the hyperfine levels by diagonalization of the Hamiltonian. Then, the energies of the hyperfine magnetic sublevels in a ground state are given by:

$$E(F = I \pm 1/2, m_F) = \frac{\hbar\omega_{hf}}{(2I+1)} - g_I \mu_n m_F B \pm \frac{\hbar\omega_{hf}}{2} \sqrt{1 + \frac{4m_F x}{2I+1} + x^2}, \quad (3.30)$$

where $x = (g_s \mu_B + g_I \mu_n) B / (\hbar\omega_{hf})$. Equation 3.30 is known as **the Breit-Rabi formula**. For weak magnetic fields, which is the case considered withing this dissertation, the Breit-Rabi formula can be expanded into the Taylor series and only the lowest terms are taken into account:

$$E(F = I \pm 1/2, m_F) \approx \hbar\omega_{hf} \left(\frac{-1}{2(2I+1)} \pm 1/2 \right) + \left(-g_I \mu_n \pm \frac{g_s \mu_B + g_I \mu_n}{2I+1} \right) \frac{B}{\hbar}. \quad (3.31)$$

From the equation, we can see that the linear Zeeman splitting has opposite sign in two ground-state hyperfine levels at weak fields when, the effective gyromagnetic ratio takes an approximate form of:

$$-g_I \mu_n \pm \frac{g_s \mu_B + g_I \mu_n}{2I+1} \approx \pm \frac{g_s \mu_B}{2I+1}. \quad (3.32)$$

So far, we described a generic electronic energy-level structure of alkali atoms. Let us now consider an example of particular alkali metal, rubidium-87, which is used for magnetometry in this thesis. The ^{87}Rb is one of two stable isotopes of rubidium with a natural abundance of 27.8% (the metal used in vapor cell for magnetometry purposes are typically isotopically enriched). Both D1 and D2 line are accessible by lasers emitting near-infrared radiation. Specifically, for ZULF NMR measurements, the atoms were excited at the D1 line (795 nm). The ^{87}Rb nuclei has spin $I = 3/2$, which couples to the electronic angular momentum, resulting in two hyperfine ground states of $F = 1$ and $F = 2$ and two lowest-energy excited-state hyperfine levels of $F = 1$ and $F = 2$. Figure 3.6 b) shows the structure along with four available optical transitions. The $F = 1$ level has three and the $F = 2$ state has five Zeeman sublevels, which splits in non-zero magnetic field in opposite direction (Fig. 3.6c). The effective Larmor frequency in weak magnetic fields is equal to:

$$\omega_L / B \approx \pm \frac{g_s \mu_B}{2I+1} = \pm \frac{1}{4} 28 \frac{\text{GHz}}{\text{T}} = \pm 7 \frac{\text{GHz}}{\text{T}} = \pm 700 \frac{\text{kHz}}{\text{G}}. \quad (3.33)$$

This strong energy dependence on the external field plays a fundamental role in atomic magnetometry.

3.3.3 General atomic magnetometry

Although atomic magnetometry encompasses many different techniques, they all share some common elements. For example, in all presented atomic-magnetometry

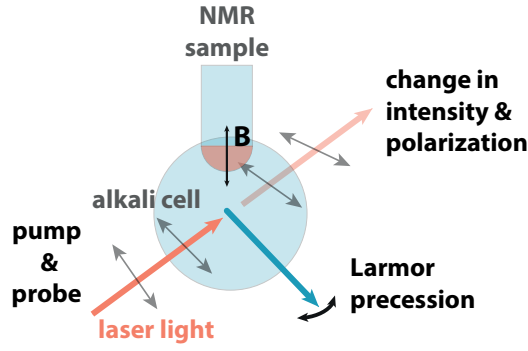


Figure 3.7: Generic scheme of an atomic magnetometer. The alkali-metal vapor cell (center) is subjected to a weak magnetic field from the NMR sample. The atomic polarization (indicated by the blue arrow) created by the resonant laser light (red arrows) undergoes Larmor precession in the magnetic field. This evolution is then measured by monitoring of the intensity or the polarization state (indicated by gray arrows) of the laser light passing through the cell. The pumping and probing here is done by a single light beam, as in case of all of the magnetometers presented in this thesis.

techniques, light is used to prepare the electronic state of the system as well as to observe evolution of the state in the magnetic field.

In this context, the magnetic-field-detection process of the atomic magnetometer can be divided into three stages:

1. **Optical pumping**, where an angular momentum is transferred from resonant light to the atomic medium. The process results in non-equilibrium spin polarization of the ground state.
2. **Evolution in the magnetic field**, in which a created ground-state polarization undergoes the Larmor precession in the magnetic field, modifying optical properties of the atoms.
3. **Probing of the optical properties of the medium**, in which the magnetic-field-determined medium's optical properties affect the properties of light (polarization state or intensity). In turn, detection of light provides the quantitative information about the field.

A general scheme of the atomic magnetometry is illustrated in Fig. 3.7. It should be noted that all three stages occur at the same time (with a notable exception of the pulsed magnetometer, see for example [Limes et al. \[2020\]](#)). Moreover, the process of optical pumping and probing can be realized by two laser beams, but also with a single laser.

One of the crucial parameters of a magnetic-field sensor is its **sensitivity**. We can derive a quantum-mechanical limit for such sensitivity by investigating the uncertainty of the measuring spin-orientation angle. Measurements of the spin ensemble for the time T_2 , where T_2 is the transverse relaxation rate, results in the uncertainty in the determination of the precession angle on the order of 1 rad. In atomic ensemble, such measurements is “repeated” over N atoms interacting with light, reducing uncertainty by the factor of $\sqrt{N}$. This leads to a following fundamental limit of sensitivity:

$$\delta B_{\text{atomic}} \approx \frac{1}{\gamma} \sqrt{\frac{1}{NT_2}}, \quad (3.34)$$

where the magnetic sensitivity is given in $\text{T}/\sqrt{\text{Hz}}$, i.e., it is normalized to roughly 1-s measurement time, and the gyromagnetic ratio acts as a conversion factor between spin-orientation precision and the magnetic field. This so-called **spin-projection**

noise sensitivity limit is valid for measurement times $\tau \gg T_2$ (see for example Auzinsh et al. [2004]). Equation 3.34 provides important insights into optimizing the performance of the atomic magnetometer. As the gyromagnetic ratio is determined by the atoms chosen for field measurements, two experiment parameters that may affect fundamental sensitivity of the magnetometers are: the ground-state relaxation rate and the number of atoms. In Sec. 3.3.6 different sources of relaxation are discussed and ways of extending relaxation times, hence improving performance of the magnetometers, are presented. The dependence on the number of atoms indicates that atomic-magnetometer performance should improve at higher concentration (provided the relaxation rate is not affected).

It should be also stress that atomic shot noise is not the only contribution to the noise in atomic magnetometry. Another contribution comes from photon shot noise, related with fundamental fluctuation in the number of photons used for probing. Finally, there is **the back-action noise contribution**, which is also associated with fluctuation in the photon number, that introduces uncertainty in spin precession via the AC Stark shift. This is all three contributions fundamentally limit the sensitivity of magnetic-field measurements with atomic magnetometers.

Despite the fundamental limits, it is more likely that technical noise limits the performance of the atomic magnetometer. Specific factors that may introduce such uncertainty are light-parameter fluctuations (light power, frequency and polarization fluctuations), electronic noise in detection, and environmental magnetic noise.

The highest sensitivity ever achieved with atomic magnetometer in near DC field measurements was $160 \text{ aT}/\sqrt{\text{Hz}}$, (Dang et al. [2010]), while the sensitivity of magnetometers used in the work lays in the range between $10 - 100 \text{ fT}/\sqrt{\text{Hz}}$.

3.3.4 Optical pumping

Optical pumping is a process, in which photons absorbed by an atomic medium transfers angular momentum to the atoms. The transfer of momentum leads to nonequilibrium distribution of the populations between Zeeman sublevels, resulting in polarization of both ground and excited states.⁶ The ground-state polarization is a results of selective excitation by laser light and the spontaneous repopulation from selectively populated excited-state sublevels. The process of optical pumping can achieve polarization level on the order of unity, which is roughly 7 orders of magnitude larger than thermal polarization of atoms in the Earth magnetic field. The strong polarization of the atoms greatly enhances their sensitivity to magnetic fields.

3.3.5 Optical properties of atomic medium

The propagation of electromagnetic wave (light) through the medium can be calculated using the Maxwell equations:

$$\begin{aligned}\nabla \cdot \mathbf{D} &= \rho_c, \\ \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t}, \\ \nabla \cdot \mathbf{B} &= 0, \\ \nabla \times \mathbf{H} &= \mathbf{j} + \frac{\partial \mathbf{D}}{\partial t},\end{aligned}\tag{3.35}$$

where the electric components of the electromagnetic wave are determined by $\mathbf{E}$ and $\mathbf{D}$ and magnetic field component by $\mathbf{H}$ and $\mathbf{B}$. Assuming that the charge density ρ_c and free current density $\mathbf{j}$ both equal zero (dielectric medium), we can find

⁶ In most cases, the excited-state relaxation is so fast that the population of the state is negligible.

the formula describing propagation of the wave (time dependence of electric and magnetic fields) by:

$$\nabla^2 \mathbf{E} - \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = \frac{\partial^2 \mathbf{P}}{\partial t^2}, \quad (3.36)$$

where the medium polarization $\mathbf{P}$ gives rise to a source term in the wave equation. For monochromatic light of frequency ω

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r})e^{-i\omega t}, \quad (3.37)$$

propagating along z , we can rewrite Eq. 3.36 to the Helmholtz equation with the source term proportional to the medium polarization:

$$\frac{\partial^2 \mathbf{E}}{\partial z^2} + k^2 \mathbf{E} = -k^2 \mathbf{P}, \quad (3.38)$$

where a wavenumber $k = \frac{\omega}{c}$. The total polarization can be expressed by four polarization components P_i , which can be written in a compact form (Auzinsh et al. [2010]):

$$\mathbf{P} = \text{Re} \left\{ e^{i(kz - \omega t)} \frac{1}{\sqrt{2}} \left[(P_1 - iP_2)(\mathbf{e}_x + i\mathbf{e}_y) + \frac{1}{\sqrt{2}}(P_3 - iP_4)(\mathbf{e}_x - i\mathbf{e}_y) \right] \right\}, \quad (3.39)$$

describing the medium polarization in terms proportional to rotating components of light (spherical basis). The change in properties of light propagating through such a medium can be expressed via this polarization components (see for example: Auzinsh et al. [2010]). Specifically, the light absorption during propagation dE_0/dl and polarization rotation during the propagation $d\alpha/dl$ are given by:

$$\begin{aligned} \frac{dE_0}{dl} &= \frac{2\pi\omega}{c} [\sin(\alpha)(-P_1 \sin \epsilon + P_4 \cos \epsilon) + \cos \alpha(P_2 \cos \epsilon + P_3 \sin \epsilon)], \\ \frac{d\alpha}{dl} &= \frac{2\pi\omega}{c} \frac{1}{\cos 2\epsilon} [\cos(\alpha)(P_1 \sin \epsilon + P_4 \cos \epsilon) - \sin \alpha(P_2 \cos \epsilon - P_3 \sin \epsilon)]. \end{aligned} \quad (3.40)$$

The medium polarization vector can be expanded in terms of dependence on the electric field:

$$\mathbf{P} = \sum_n \chi^n \mathbf{E}^n, \quad (3.41)$$

where χ^n is n -th order electric susceptibility tensor. In gas media (such as atomic vapor), only even order terms in electric susceptibility tensor are non-zero. The lowest order corresponds to linear optical effects as the wave equation Eq. 3.38 becomes linear. The higher-order terms correspond to non-linear optical properties of the medium.

3.3.6 Sources of alkali-atom polarization relaxation

The ground-state polarization is subject to a number of relaxation processes limiting sensitivity of the atomic magnetometer (see Eq. 3.34).

The alkali atoms in the atomic magnetometers are typically hold in a glass vapor cell at temperature between 20-200°C. The average thermal velocity of atoms at such temperature can be calculated from the Maxwell-Boltzmann distribution:

$$\overline{v_{\text{thermal}}} = \sqrt{\frac{8k_B T}{\pi m}}, \quad (3.42)$$

where m is atomic mass, and for ^{87}Rb for example, at room temperature reach 270 m s^{-1} while at 200°C reach 350 m/s .

Below, relaxation processes in alkali vapor contained in glass cell are reviewed in more details.

1. This large thermal velocity leads to very frequent collision of alkali atoms with cell walls. As the alkali atoms bumps into the glass surface it gets absorbed for a short time (10^{-7} – 10^{-5} s, [De Freitas et al. \[2002\]](#)). During that time it experiences large local electric and magnetic fields produced by the ions and atoms on the glass surface. These fields cause a random evolution of the atoms, which leads to a full randomization of the ground-state polarization during the absorption time. If not suppressed, such a wall collision may become a dominant source of relaxation, as the collision lead to a magnetic-line broadening Δf_{wall} ([Seltzer \[2008\]](#)):

$$\Delta f_{wall} \approx \frac{1}{2\pi} \frac{\overline{v_{thermal}} A}{4V}, \quad (3.43)$$

where A and V indicate a surface area and volume of the vapor cell. For the cells used in the work presented within this dissertation, The linewidth limited by wall collision is > 12 kHz (for a 2 cm spherical cell at room temperature) and > 70 kHz for microcell heated up to 180°C , more than two orders of magnitude larger than magnetic linewidths in the corresponding magnetometers. The depolarization caused by frequent collisions with the cell walls can be suppressed in two ways. First, the surface of the glass inner walls can be **coated** with a special layer suppressing depolarization. Often used coating material is paraffin, which consists of long chains of hydrocarbons. As discovered by [Bouchiat and Brossel \[1966\]](#), the paraffin has very low polarizability, leading to much smaller local electric field than the surface of the glass. Moreover, the low adsorption energy (≈ 0.1 eV) leads to short absorption time. As a consequence, an atom undergo even up to a 10^6 collision with the coated wall without depolarization ([Balabas et al. \[2010\]](#)). The other approach relies on the introduction of a **buffer gas** into the vapor cell. The dense buffer gas (noble gas like helium, or a chemically inert molecule like N_2) significantly limits the frequency of the collision with glass walls, as the alkali atoms undergo a diffusive motion. The rate of such collision scales as ([Seltzer \[2008\]](#)):

$$\Delta f_{wall}^{buffer} \approx \frac{D}{l^2}, \quad (3.44)$$

where l is a characteristic cell length, while D is a diffusion constant of alkali atoms in the vapor cell, revealing inverse dependence on the pressure of the buffer gas. This diffusive motion in the buffer-gas atmosphere leads to narrowing of the wall-collision magnetic linewidth by at least 3 orders of magnitude.

2. A different type of relaxation is connected to collisions between alkali atoms and alkali or buffer-gas atoms. The rate for such collisions is given by (see for example [Seltzer \[2008\]](#)):

$$R_{col} = n\sigma\overline{v_{rel}}, \quad (3.45)$$

where n is density of other gas species (buffer gas or alkali), while σ indicates the cross-section for the collisions. The relative average thermal velocity $\overline{v_{rel}}$ is given by a formula similar to Eq. 3.42, where the mass of the alkali is replaced by the reduced mass of two colliding atoms. We can classify the collision processes into two groups: collisions not-preserving total angular momentum of alkali atoms (the so-called spin-destruction collisions) and collisions preserving total angular momentum of alkali atoms, the so-called spin-exchange collisions.

The spin-destruction collisions may occur when alkali collides with other alkali atom or with the buffer-gas atom (if such is used). The collision transfers the spin of the alkali atom to the rotational angular momentum of the pair of

colliding atoms, and depends on the strength of the magnetic dipole-dipole interaction. The cross-section for the spin-destruction collisions was measured for a range of alkali atoms and the buffer gasses (see for example [Demtröder \[2013\]](#)). As the spin-destruction collisions randomize the electronic spin, they lead to the decay of the ground-state polarization. For the vapor used in most of the experiments presented in this thesis (rubidium vapors at 200 °C), the spin-destruction collisions between rubidium atoms limit the rubidium ground-state relaxation rate to roughly 170 Hz (the contribution from buffer gas collisions is roughly 6 times smaller).⁷

In the other collisional process, i.e., during **the spin-exchange collisions**, the total spin of the pair of two colliding atoms is preserved. The process can lead to the exchange of the electron spin state between the atoms. This is associated with the fact that during the alkali-atom collisions, two colliding atoms form a short-lived molecule and the initial states of the independent atoms lead to the superposition of the singlet and triplet molecular states. The large energy splitting between the singlet and triplet states in such alkali dimer leads to phase shift in the molecular superposition, which, after the molecule splits into two atoms, can result in the exchange of electron-spin states of the atoms. As the collisions may lead to electron-spin flips, the spin-exchange collisions redistribute populations among the hyperfine and Zeeman levels. As evident from Eq. 3.33, the two hyperfine ground states have an opposite sign of the Zeeman splitting, leading to the opposite Larmor precession in the two states. In turn, the collisions introduce decoherence and deterioration of the ground-state polarization. The cross section for the spin-exchange collisions is orders of magnitude larger than for the corresponding spin-destruction collisions, hence the process may dominate over other relaxation sources (if the alkali density is high).⁸ For example, for ⁸⁷Rb contained in a vapor cell at 180 °C, the spin-exchange collisions (in the limit of high-magnetic field) lead to magnetic line broadening of about 8 kHz. Luckily, the spin-exchange relaxation can be strongly suppressed as discussed in Sec. 3.3.8.

3.3.7 Nonlinear Magneto-Optical Rotation

One of the physical phenomena used to measure magnetic fields with alkali atoms is **nonlinear magneto-optical rotation (NMOR)**. Discovered by [Gawlik et al. \[1974\]](#), the effect allowed to observe ultra-narrow magnetic-field-dependent optical signals. It is based on the light-intensity- and magnetic-field-dependent rotation of the polarization plane of resonant light traversing a medium subject to an external magnetic field. The rotation originates from optical pumping of atoms and successive reorientation of the polarization is the effect of the external magnetic field.

It can be shown that solving the Liouville equation (Eq. 1.25) that for a model, two-level system with $F = 1$ in the ground state and $F = 0$ in the excited state, the medium polarization depends on the density-matrix elements as ([Auzinsh et al. \[2010\]](#)):

$$P \sim \text{Re} \left[(\tilde{\rho}_{0',-1} - \tilde{\rho}_{0',1}) \mathbf{e}_x + i(\tilde{\rho}_{0',-1} - \tilde{\rho}_{0',1}) \mathbf{e}_y + \sqrt{2} \tilde{\rho}_{0',0} \mathbf{e}_z \right], \quad (3.46)$$

where we used $P = N_d \text{Tr}(\rho d)$. Eq. 3.46 relates the density-matrix elements with the medium polarization. In Eq. 3.46, we assumed x -polarized light propagating along the z direction and $\tilde{\rho}_{0',-1}$, $\tilde{\rho}_{0',1}$, $\tilde{\rho}_{0',0}$ are the density-matrix elements given in RWA. From Eqs. 3.40 and 3.46 the atomic-polarization quadratures that affect

⁷ As the buffer-gas pressure increases the rate of wall collision decreases (diffusion constant scales with pressure), while the rate of spin-destruction collisions increases. One can find an optimum buffer-gas pressure to minimize total relaxation associated with these two processes.

⁸ The alkali density in the vapor is controlled by temperature. Specifically, the vapor density is strongly depended on the temperature: for ⁸⁷Rb for example, the density doubles roughly every 10 °C.

light properties depend on the coherences created in the atoms. For example, the polarization rotation is given in the considered case by:

$$\frac{d\alpha}{dl} = \frac{2\pi\omega}{c} P_4, \quad (3.47)$$

can be rewritten to:

$$\frac{d\alpha}{dl} = -\frac{6\Gamma\omega_L}{DL} \left\{ 8\omega_L^2 \left[8\omega_L^2 + \Gamma^2(\kappa_2 + 2) - 8\Delta^2 \right] + \gamma \left[4\gamma(\Gamma^2 - 4\Delta^2) - \Gamma^3\kappa_2(\kappa_2 + 2) \right] \right\}, \quad (3.48)$$

where the Liouville equations were solved in the steady state, $\dot{\rho} = 0$. In Eq. 3.48, Γ denotes the relaxation rate of the excited state, Δ is the optical detuning from the resonant frequency, and the κ_2 is the saturation parameter, given by:

$$\kappa_2 = \frac{\Omega_R^2}{\Gamma\gamma}, \quad (3.49)$$

quantifying the strength of the interaction with the resonant light and Ω_R and γ are the Rabi frequency and the relaxation rate of the ground state, respectively.

Using Eq. 3.48 we can plot the polarization rotation as a function of the magnetic field (Fig. 3.8). We can look at the different contribution to observed optical rotation as a function of light power (saturation parameter). The linear effect (effectively taking $\kappa_2 \rightarrow 0$) gives rise to a broad optical feature observed in the magnetic-field domain. This feature is characterized by the excited-state relaxation rate Γ and can be understood as splitting of two overlapping resonances, corresponding to two circular components of linearly polarized light. Since the individual resonances are dispersively shaped, their difference in not-too-strong field gives the dispersive curve centered around $B = 0$. The introduction of non-zero saturation parameter κ_2 results in the appearance of a narrow dispersive feature centered around the $B = 0$ and with width (in Larmor frequency units) comparable to ground state polarization relaxation rate γ . This central feature in optical polarization rotation signal is light-intensity depended (plotted for different κ_2 in Eq. 3.48) while the steep dependence on the magnetic field (with width determined by the relaxation of the ground state) is the basis for sensitive magnetometry techniques.

Evolution of the density matrix in NMOR can be presented using AMPS surfaces (Sec. 1.9). To do so, we focus on the ground-state density matrix, as, in most cases, excited-state population is negligible. Based on the three-stage approach described above, we can analyze evolution of the density matrix in a similar manner. First, an atomic alignment is created in atoms via optical pumping with linearly polarized light. This corresponds to the density-matrix shape, being peanut-like shape which axis is oriented along the light-polarization direction (Fig. 3.8). Such polarization of the medium leads to linear dichroism. Specifically, for the x -polarized light, the light is just weakly absorbed, but at the same time y -polarized light is strongly absorbed (both cases assume the steady state of the medium). In effect, the atomic vapor prepared in such a state acts as a linear polarized, rotating the angle of polarization through linear dichroism. It also explains why the optical rotation is zero for $B = 0$. In the next state, the aligned state starts to evolve around the magnetic field, leading to the precession of atomic alignment. The processes of precession, relaxation, and repumping lead to effective rotation of the anisotropy axis away from the original direction. This can be visualized as the precession of the peanut-like shape of the density matrix around the magnetic field by a finite angle. In the last stage of magnetometric measurement, weak light (may be the same beam used for the optical pumping) is affected by this rotated dichroism and its polarization plane is being rotated.

A representative NMOR signal is shown in Fig. 3.8. The three regions of polarization rotation versus the magnetic field can be distinguished. Below, we discuss them in more detail:

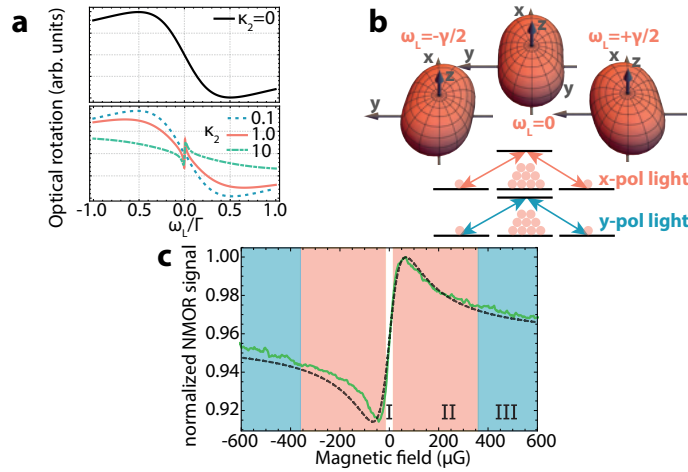


Figure 3.8: a) Calculated optical rotation under the steady-state conditions as a function of the Larmor frequency ω_L . The simulation was performed for following parameters: $\gamma = 0.005$, $\Gamma = 1$, $\Delta = 0$. Upper plot (black, solid line) shows the rotation for a saturation parameter $\kappa_2 \rightarrow 0$, where the rotation is an effect of circular dichroism of the medium (the linear regime). Lower plot, an optical rotation plotted for several non-zero saturation-parameter values. Notice the rise of the narrow feature near zero magnetic field, of the width γ , associated with NMOR. The amplitude of the signal first grows with κ_2 (compare $\kappa_2 = 0.1$ with $\kappa_2 = 1$) but then deteriorates with the increase in saturation parameter ($\kappa_2 = 10$). b) AMPS surfaces plotted for a state pumped with x -polarized light propagating in the direction of the magnetic field (z), for three values of magnetic field $\omega_L = \pm 0.5\gamma$ and $\omega_L = 0$. The saturation parameter $\kappa_2 = 1$, while $\gamma = 0.005$, $\Gamma = 1$. Below a schematic representation of the energy levels with population marked by red balls. The non-equilibrium population is an effect of optical pumping. The arrows indicate the transitions probed by the linearly polarized light. c) Measured (solid green line) and simulated NMOR (dashed gray line) signals in ^{87}Rb vapor contained in paraffin-coated cell. Three region of the magnetic-field dependence are indicated by background colors and Roman numbers and are discussed in the main text. The constant offset seen in the signal is a results of application of elliptical polarization. Figure c) is adapted from [Put et al. \[2019b\]](#).

- I At a zero field (white region in Fig. 3.8 c), the medium polarization is the strongest, but, as the Larmor precession is negligible, the axis of the medium optical anisotropy is aligned with light polarization. Hence, no polarization rotation is observed for such condition.
- II When a non-zero yet not-too-strong magnetic field is applied (red region in Fig. 3.8c), polarization rotation is observed. This is so because the magnetic field induces rotation of anisotropy of the medium. However, in the case of continuous-wave (CW) optical pumping, the Larmor precession of different atoms are not synchronized. Since larger precession angles requires more time, and relaxation is always present in the system, a number of atoms with a given orientation depends on the precession angle. In turn, the net (ensemble-averaged) orientation of the medium anisotropy strongly depends on the magnetic-field strength. Specifically, a quasi-linear dependence of NMOR on the magnetic field, used for magnetometry purposes, is observed in this region.
- III If the magnetic field becomes even stronger (blue region in Fig. 3.8c), fast precession and continuous pumping washes out transverse polarization of the medium, hence reducing its anisotropy. This is why for such fields, the NMOR signal drops with the magnetic-field increase. In turn, this region is not used for magnetometry purposes and it limits the “dynamic range” of the sensor.

Analysis of NMOR signals features (Fig. 3.8) shows that the phenomenon can be used for magnetic field sensing.

DC magnetometry

The NMOR phenomenon described above leads to magnetic-field-dependent optical rotation near the zero field (the rotation disappears for higher fields). Such magnetometry, however, is limited to very weak (< 50 nT) fields. This requires careful shimming and can hinder some experiments (i.e., ultra-low-field NMR measurements). Moreover, the NMOR signal (rotation of polarization plane) is static, hence it may be strongly affected by low-frequency and technical noise. For this reason, a number of techniques were invented to perform the NMOR-based magnetometry in finite magnetic fields. In particular, the techniques are based on phase-sensitive detection of oscillating optical signals, where the oscillation is either introduced externally or via interaction with atoms. The latter case is possible, for example, through the so-called **synchronous optical pumping**. In this technique, the pumping rate, modulated by frequency or amplitude modulation of light, is synchronized with the Larmor precession of atoms, preserving atomic polarization/alignment and resulting in the NMOR signal at the harmonics of Larmor frequency of alkali atoms (Gawlik et al. [2006], Acosta et al. [2006]).

Another approach to measure stronger (above 50 nT) magnetic fields is not based on the modulation of light parameters, but rather the parameters of the atoms. For example, this can be done by modulation of the relaxation rate of atoms, which can be, for example, done by time-dependent longitudinal (along the light propagation direction) magnetic field. If the change of the relaxation rate coincides with the Larmor frequency, or its specific harmonic, a dynamic optical anisotropy can be generated in the medium and hence strong time-dependent optical rotation signals can be observed. This phenomenon, known as **parametric nonlinear magneto-optical rotation (PNMOR)**, can be also used for atomic magnetometry (Put et al. [2019b]).

The specific mechanism of generation of medium anisotropy in PNMOR depends on the strength of the magnetic field to be measured. Specifically, the first regime arises when the field is much smaller than the ground-state relaxation rate $\omega_0 < \gamma$. An oscillating magnetic field, with amplitude significantly larger than the static components ($\Delta\omega_L \gg \omega_0$) is applied. Under such conditions, demodulation of the optical signal at the first harmonic of the oscillating-field frequency gives rise to a magnetically-dependent signal centered at $B = 0$ (Fig. 3.9a). The appearance

of the resonance at the field can be understood via the analysis of the evolution of the ground-state density matrix of atoms (Fig. 3.9b), which is done based on numerical solution of the Liouville equations (simulated signals are visible next to experimental results in Fig. 3.9):

$$\dot{\hat{\rho}} = -\frac{i}{\hbar} [\hat{\mathcal{H}}, \hat{\rho}] + \hat{\Gamma}(\hat{\rho}) + \hat{\Lambda}, \quad (3.50)$$

where $\hat{\mathcal{H}}$ is the total system Hamiltonian (which includes interaction with light and the magnetic field), $\hat{\Gamma}(\rho)$ is the relaxation operator of the system and Λ is the density matrix in thermal equilibrium conditions. For simplicity we use a two level system with ground state characterized by total angular momentum $F = 1$ and excited state with $F = 0$, which sufficiently captures dynamics of NMOR. After calculation a density matrix evolution (which visualized with the use of AMPS in Fig. 3.9 b,d)), nonlinear magneto-optical rotation φ is calculated as (Auzinsh et al. [2010]):

$$\varphi \propto \frac{1}{\varepsilon} \text{Re}(\tilde{\rho}_{-1,0'} - \tilde{\rho}_{1,0'}), \quad (3.51)$$

where $\tilde{\rho}_{-1,0'}$ and $\tilde{\rho}_{1,0'}$ describe slowly varying envelopes of optical coherences of between the ground sublevels and excited state, while ε describes the amplitude of the electric field of resonant light (for detailed derivation see Pustelny et al. [2011]). As the experiment uses a lock-in detection at the harmonics of oscillating field we multiply simulated oscillating NMOR signals by cos and sin functions at the harmonics of the field modulation and then integrate numerically over a period of evolution (pseudo lock-in detection).

In case of low-field PNMOR, optical pumping leads to generation of ellipsoidally-shaped AMPS, which, due to the action of the oscillating magnetic field, tilts back and forth (Fig. 3.9). Specifically, for the first part of the modulation period the shape rotates in one direction, then it turns back at π/ω_m and precesses in the opposite direction. To observe the strongest rotational, the modulation frequency ω_m is chosen such that $\Delta\omega_L/\omega_m \approx \pi/4$. To understand this condition, we first recall that the strongest polarization rotation is observed when the axis of optical dichroism of the medium is oriented at $\pi/4$ with respect to the incident light polarization. We can now argue that in order to obtain maximal rotation, the phase accumulated between two turning points should be equal to $2\pi/4 = \pi/2$. The magnetic-precession phase $\Delta\phi(t_2, t_1)$, accumulated from time t_1 to time t_2 , is equal to:

$$\Delta\phi(t_1, t_2) = \int_{t_1}^{t_2} \Delta\omega_L \cos(\omega_m t) dt = \frac{\Delta\omega_L}{\omega_m} [\sin(\omega_m t_2) - \sin(\omega_m t_1)], \quad (3.52)$$

By imposing the condition that $\Delta\phi(\pi/(2\omega_m), 3\pi/(2\omega_m)) = \pi/2$ we get that the most efficient pumping of the atomic ensemble happens when the $\Delta\omega_L/\omega_m \approx \pi/4$. It worth pointing out that by applying an oscillating magnetic field we shifted the point of operation of our NMOR-based magnetometer to higher frequencies (e.g., to 10 kHz as the results seen in Fig. 3.9).

The PNMOR signals can be also observed at stronger magnetic fields, $\omega_0 \gg \gamma$. In that case, the PNMOR resonance is observed when the oscillating magnetic-field frequency matches twice the Larmor frequency (Fig. 3.9c).⁹ Similarly as in the previous case, we can understand this process via the numerical analysis of the density-matrix evolution (Fig. 3.9d). In contrast to the low-field case, however, in this case, the ellipsoidal AMPS precesses in the same direction during whole evolution (as long as the field modulation amplitude does not exceed the static magnetic-field strength, i.e., $\Delta\omega_L \ll \omega_0$). Under such condition the precession is not happening at a constant rate. Particularly, when the modulation frequency coincides with twice the Larmor frequency, the optical anisotropy is not completely

⁹ The factor of 2 stems from the fact that the alignment created by the (nearly) linearly polarized light is symmetric upon the rotation by π around magnetic field.

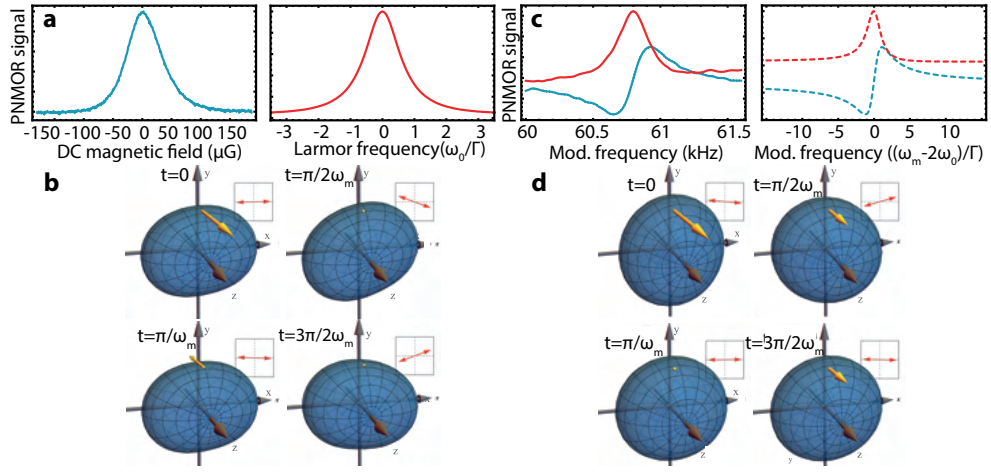


Figure 3.9: a) Measured (blue) and simulated (red) PNMOR signal at a weak, static magnetic field. b) Ground-state density-matrix evolution, visualized using AMPS, at zero magnetic field. c) Measured (left panel) and simulated (right panel) components of the demodulated PNMOR signal at a strong, static magnetic field. The red curve indicates quadrature and blue curve is the in-phase lock-in signal at the modulation frequency. d) Evolution of the corresponding ground-state density matrix. The yellow arrow present in b) and d) indicate an instantaneous magnetic field, while the insets show the instantaneous optical-anisotropy direction of initially x -polarized light. All figures adapted from Put et al. [2019b].

washed out because of the CW pumping, as in regular (CW) NMOR at higher fields, but survives the process. This is so because the atoms spend more time with their polarization oriented along the light-propagation direction than in any other direction. In turn, most newly-pumped atoms contribute constructively to the preexisting atomic polarization, while efficiency of generation other orientations is smaller. Thereby, the medium becomes anisotropic and its axis precess around the field in the xy -plane. In fact, the PNMOR resonance can be observed with either sweeping magnetic field or controlling modulation frequency, as long as the resonance condition, $\omega_m \approx 2\omega_L$, is fulfilled.

Polarization rotation can be also used to detect oscillating magnetic fields. This phenomenon, known as **radio-frequency (RF) NMOR** (although the magnetometer often operates far from radio-frequency range), is usually realized with linearly polarized light propagating through an alkali-metal vapor perpendicularly to the static magnetic field that coincides with the light polarization. If the frequency of a weak oscillating field (nT), applied orthogonal to both the light propagation direction and the static magnetic field, coincides with the Larmor frequency of the static field, the polarization rotation is observed (Fig. 3.10b).

To better understand the foundations of the technique, we again investigate evolution of the ground-state density matrix in such a system. In the analysis, it is convenient to consider the system evolution in the rotating frame at the frequency of the oscillating field. As explained in Sec. 2.1.1, RWA consists in neglecting the component of the magnetic field counter-rotating with respect to the Larmor precession of alkali polarization. The total magnetic field experienced by the atoms in the frame is given by:

$$\mathbf{B} = \frac{\omega_L - \omega_m}{g\mu_B} \mathbf{e}_z + \frac{\Delta\omega}{2g\mu_B} \mathbf{e}_x. \quad (3.53)$$

In the rotating frame, the field is tilted away from the z axis causing rotation of the anisotropy of the medium. In contrast to NMR, however, in this scheme, the atoms are constantly repolarized, which does not allow the polarization to be tilted at all, but rather rotate by some angle with respect to the z -axis (a situation similar to conventional NMOR). The evolution of the density matrix under such conditions

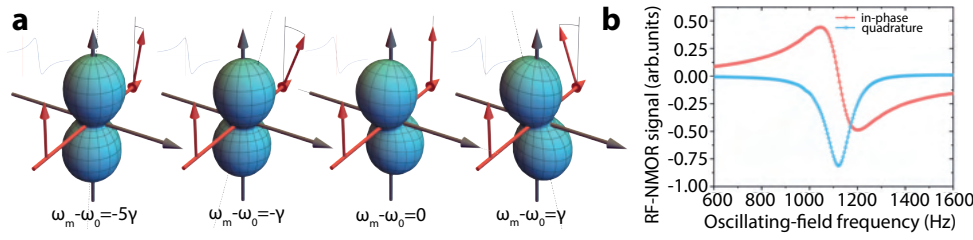


Figure 3.10: a) Evolution of the ground-state density matrix undergoing RF NMOR. The evolution of the AMPS is plotted in the rotating frame at ω_m . The horizontal red arrow indicates incoming laser light, with polarization indicated by the perpendicular shorter red arrow. The rotation of the polarization plane is exaggerated to be easily observed. The evolution of the density matrix is static in the rotating frame and was plotted for a number of detuning from the resonance condition (the saturation parameter was set to $\kappa_2 = 10$, while the oscillating field Larmor frequency (strength of the oscillating field) was set to $\Omega_{rf} = 0.5\gamma$). Notice that the angle on the horizontal plane is a relative phase between the anisotropy-axis evolution and the magnetic field. As the AMPS are obtained at the same moment of time in relative to magnetic field (as they are shown in the rotating frame), the instantaneous value of optical rotation for resonant condition is equal to zero (while in fact amplitude of oscillating polarization rotation is maximum for $\omega_m = \omega_0$). The demodulated, in-phase signal is shown in the insets. b) Measured NMOR resonance in a paraffin-coated ^{87}Rb vapor cell with the use of weak oscillating field. Both the quadrature components are plotted versus the frequency of the oscillating-field frequency. The signal were obtained in the magnetometer described in Sec. 3.3.10.

is shown in Fig. 3.10a). The ground-state polarization rotates at the frequency of the oscillating magnetic field, and the angle of the rotation is maximal when the frequency of oscillating field matches the Larmor frequency of alkali atoms (the effective magnetic field in a rotating frame points in the x direction). The quadrature components of the RF-NMOR signal are shown in Fig. 3.10b). The in-phase component of the signal may be used for sensitive magnetometry of static magnetic field.

AC magnetometry schemes

The amplitude of the RF NMOR signal strongly depends on the oscillating field frequency and amplitude, as illustrated in Fig 3.11a). This can be used for sensitive measurements of oscillating magnetic fields. In such a scheme, the oscillating field is completely turned off and the NMOR is induced by the oscillating field to be detected. In this case, the magnetometer needs to be “tuned” to the desired frequency by adjustment of the static magnetic field. To use this method for detection of the ultra-low-field NMR, one need to design an experiment with independently adjusted magnetic field for the nuclear-spin sample and the field-sensing alkali-vapor cell. This is needed because of the different geomagnetic ratios of alkalis and nuclear spins, i.e., the strong field detunes the magnetometer from the field emitted by Zeeman-precessing nuclei and the detection does not work.

Despite the ability to use RF NMOR to detect static and oscillating magnetic field in the same experimental conditions, the detection of the oscillating fields is significantly more sensitive than its quasi-DC counterpart (Put et al. [2019a]) (with sensitivity reaching sub fT Hz⁻¹ levels). The difference stems from lower noise floor (AC magnetometer operates at higher light powers, decreasing photon-shot noise) but more importantly from **a larger response to an equivalent magnetic field**. In the AC-mode magnetometer is kept under the resonance condition, and when the frequency of the oscillating field coincides with the Larmor frequency an effect of even a small perturbation can accumulate, leading to significant modification of properties of a whole medium.

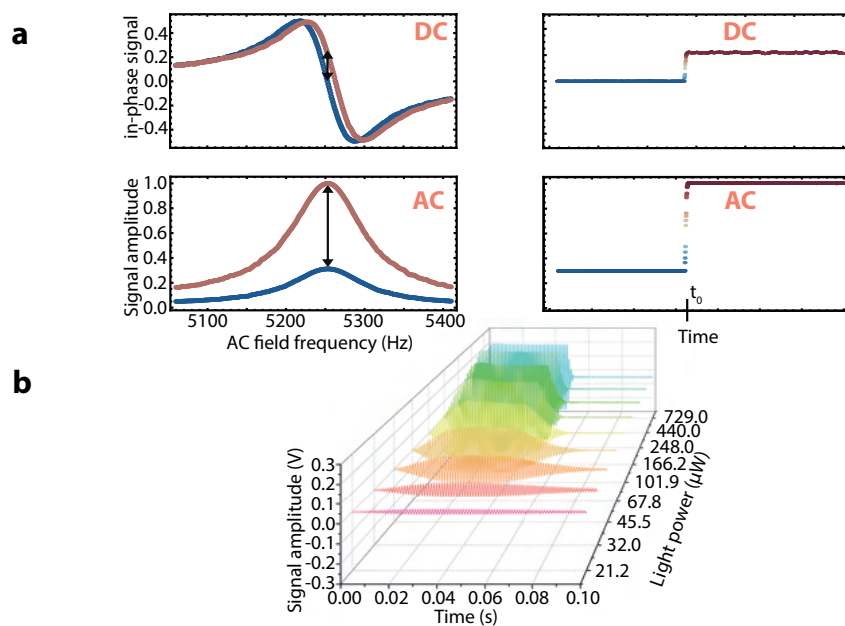


Figure 3.11: a) In-phase components of the RF NMOR signals versus the modulation frequency, demonstrating the signal response of the signal to the static (top) and oscillating (bottom) magnetic-field change (left). Right parts of the plots show the temporal trace of the signal for in-resonance conditions. The DC and AC fields were changed by the same amount (1.5 nT) at t_0 change in the signal (in resonance). b) The raw optical-rotation signal after applying a 50-ms long pulse, oscillating at the Larmor frequency (the 1-nT amplitude pulse). Notice that for the small light powers the response builds up and dies out slowly. As the power increases the response to the pulse starts to closer resemble the original test pulse. The control over light power allows for increase in bandwidth (and decrease in the response time of the magnetometer). Adapted from [Put et al. \[2019a\]](#).

Beside the sensitivity another important parameter of the magnetic-field sensor is its bandwidth. For a passive atomic magnetometers (as those described in this thesis), the bandwidth of the magnetometer is comparable to the linewidth of the NMOR resonance, used for field sensing (Włodarczyk et al. [2012]). On one hand the relaxation rate γ , determining the linewidth, depends on various characteristics of the experimental system/atoms, including concentration, temperature, means of prolongation of the relaxation time (wall-coating or buffer gas), etc. However, the rate can be also affected by light power, as the strong repumping limits the lifetime of the transverse polarization. While typically one wants to keep the light power low, not to reduce sensitivity of the measurements, higher intensities can be used to increase the bandwidth of the magnetometer, hence shorten the response time of the device, (Fig. 3.11b)). This may be used to efficiently detect rapidly decaying signals.

NMOR-base magnetometry found in use in NMR. Specifically it was used to detect ULF NMR and MRI signals (Xu et al. [2006]) and was also used to measure signals from nuclear spins precessing at the Earth's magnetic field (Savukov et al. [2020]).

3.3.8 Spin-Exchange Relaxation Free optical magnetometry

In parallel to the development of NMOR-based atomic magnetometers, a different approach to atomic alkali-vapor magnetometry was pursued to obtain zero-field NMR spectra presented in this dissertation. As the temperature of the vapor cell increases, the sensitivity of atomic magnetometry initially rises. This is because the atomic number density increases (see Eq. 3.34). However, as the density increases further, the spin-exchange collisions, which, at low temperature/concentrations, leads to negligible relaxation, becomes more frequency, eventually becoming a dominant source of relaxation. The additional relaxation counteracts the rise of the concentration and in fact, the overall sensitivity of the measurements does not improve further.

As mentioned in Sec. 3.3.6, due to the spin-exchange collision, the atom changes its hyperfine (ground) state. This leads to a change in a direction of precession and hence to extra relaxation. Moreover, frequent spin-exchange collisions redistribute polarization among ground-state levels. In a case of spin-exchange collision rate exceeding other relaxation mechanisms and the Rabi frequency (the pumping rate) the populations follow the so-called **spin-temperature distribution** (Walker and Anderson [1993]):

$$\rho(F, m_F) \propto e^{m_F \ln \left(\frac{1+P}{1-P} \right)}, \quad (3.54)$$

where P is the atomic polarization. As the parameter $\ln \left(\frac{1+P}{1-P} \right)$ is always positive, this leads to an excess of populations in the sublevels with larger m_F . It should be also noted that there is no population difference between the sublevels of the same m_F belonging to the different hyperfine states. In turn, there is larger population in the hyperfine level of the larger F . One may expect that as the vapor density increases, the spin-exchange relaxation also increases. This is true just in a limited range of concentration/temperatures. In fact, it was discovered by Happer and Tam [1977] that at very high-densities (corresponding to temperatures of about 160-200 °C) the relaxation due the spin-exchange collisions is strongly suppressed. At high concentration when spin-exchange relaxation is high and the magnetic field is low ($R_{SE} \gg \omega_L$), the atoms acquire just a small phase between successive spin-exchange collision. This results in the atoms sampling both hyperfine states over times much shorter than the Larmor period. The time present in a specific magnetic sublevel is weighed by population of the sublevel (Eq. 3.54), so that atoms effectively spends more time in hyperfine state $I + 1/2$, which leads to an effective precession

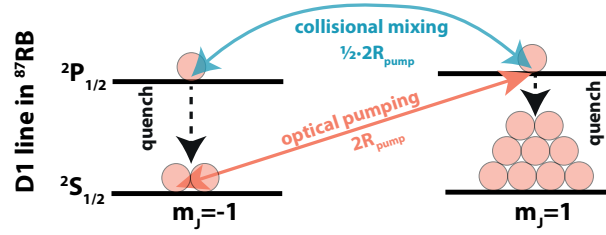


Figure 3.12: Schematic representation of optical pumping in dense ^{87}Rb vapor under SERF conditions. The red arrows show interaction with the strong, circularly polarized laser beam (pump beam) tuned to the D1 transition. The collisional mixing with the buffer gas quickly equalizes the population in the upper state (indicated by the blue arrow), while the populations of the excited state is quickly quenched to the ground state by collisions with the buffer gas present in the vapor cell. Rates of optical pumping and collisional mixing (assuming total mixing) are indicated next to corresponding arrows. Figure based on Walker and Happer [1997].

in one direction and strong suppression of relaxation. This phenomenon allow the atomic magnetometers to operate at high-alkali densities yet the atoms used for field sensing are characterized by long coherence times. This results in very high sensitivity of the field sensing (Eq. 3.34). As a matter of fact, such **spin-exchange relaxation free (SERF) magnetometers** (Allred et al. [2002]) offer the highest near DC sensitivity ever achieved (Dang et al. [2010]).

As the high pressure of the buffer gas results in frequent collision with alkali atoms and strong relaxation which leads to the overlap of optical transition from the two ground-state hyperfine levels. This somewhat simplifies our considerations so that we can neglect hyperfine interaction and only consider the fine structure of alkali atoms. As the result, the atoms are characterized with the electronic total angular momentum J and the corresponding magnetic quantum numbers m_J . The principle behind optical pumping in dense ^{87}Rb vapor interacting with σ^+ circularly polarized light tuned to the D1 line is shown in Fig. 3.12 (see also Seltzer [2008]). Under the SERF conditions, when interacting with circularly polarized light (here chosen to be σ^+), the atoms are pumped into the $m_J = 1/2$, being the dark state (the state is inaccessible to light) of the system. The populations in the excited state are quickly equalized due to collisional mixing with buffer gas and quenched to the ground state as indicated in Fig. 3.12. The change in the population of two ground states can be calculate with the rate equations:

$$\begin{aligned} \frac{d}{dt}\rho_{-1/2} &= -R_{\text{pump}} \rho_{-1/2}, \\ \frac{d}{dt}\rho_{+1/2} &= R_{\text{pump}} \rho_{-1/2}, \end{aligned} \quad (3.55)$$

where we assume that the collisional mixing is total (the probability of the optically excited state decaying to either ground state is equal to each other). The time-depended change of the total-spin projection along the z direction can be calculated as:

$$\frac{d}{dt}\langle \hat{S}_z \rangle = \frac{1}{2} \frac{d}{dt} (\rho_{+1/2} - \rho_{-1/2}) = \rho_{-1/2} = \frac{1}{2} (1 - 2\langle \hat{S}_z \rangle), \quad (3.56)$$

which results in a built-up of population of spin state, corresponding to a positive projection in an exponential fashion (for σ^+ -polarized light). If we now account for the relaxation of the spin created in the ground state, Eq. 3.56 needs to be rewritten as:

$$\frac{d}{dt}\langle \hat{S}_z \rangle = \frac{1}{2} (1 - 2\langle \hat{S}_z \rangle) - \gamma \langle \hat{S}_z \rangle, \quad (3.57)$$

where γ is the relaxation rate of the spin polarization. This equation can be directly integrated, and assuming initially unpolarized atoms, $\langle \hat{S}_z(0) \rangle = 0$, we arrive at:

$$\langle \hat{S}_z(t) \rangle = \frac{R_{pump}}{R_{pump} + \gamma} \left(1 - e^{-(R_{pump} + \gamma)t} \right) = P \left(1 - e^{-(R_{pump} + \gamma)t} \right), \quad (3.58)$$

where P called the equilibrium spin polarization used in the spin-temperature distribution (Eq. 3.54).

We can now turn into considering the behaviour of atomic ensemble in magnetic field. The polarization generated in the ground state by optical pumping evolves in the external magnetic field. Under the SERF conditions, the evolution can be effectively described by the Bloch equations (Savukov and Romalis [2005]), first introduced in this thesis in the context of NMR (Sec. 2.1.1). Including both the optical pumping along the z -axis with σ^+ polarized light and relaxation we get:

$$\frac{d}{dt} \langle \hat{S} \rangle = \gamma \mathbf{B} \times \langle \hat{S} \rangle + \frac{R_{pump}}{2I + 1} (1/2 \mathbf{e}_z - \langle \hat{S} \rangle) - \frac{1}{T_2(2I + 1)} \langle \hat{S} \rangle. \quad (3.59)$$

When the magnetic field is static, the stationary (time independent) solutions to the Bloch equations are given by:

$$\begin{aligned} \langle \hat{S}_x \rangle &= P \frac{\beta_y + \beta_x \beta_z}{1 + \beta_x^2 + \beta_y^2 + \beta_z^2}, \\ \langle \hat{S}_y \rangle &= P \frac{-\beta_x + \beta_y \beta_z}{1 + \beta_x^2 + \beta_y^2 + \beta_z^2}, \\ \langle \hat{S}_z \rangle &= P \frac{1 + \beta_z^2}{1 + \beta_x^2 + \beta_y^2 + \beta_z^2}, \end{aligned} \quad (3.60)$$

where we use a reduced magnetic field $\beta = \frac{g(2I + 1)}{R_{pump} + 1/T_2} \mathbf{B}$. The spin-polarization components perpendicular to the pumping-light propagation direction strongly depend (for a small total field approximately linearly) on the transverse magnetic field components. We can measure this components of the atomic polarization with weak, perpendicular to the pump beam, probe light. Obtained in this manner optical signal (rotation of polarization plane, absorption, etc.) is sensitive to magnetic field components, which is the basis of SERF optical magnetometry.

Similarly to the NMOR-based magnetometry, in the SERF magnetometry it is also beneficial to measure oscillating signals (instead of static signal) and thus limit effect of low-frequency technical noise. For example, this goal can be achieved by modulating polarization of the probe beam (Jiang et al. [2019]). However, in this thesis, a scheme based on the application of oscillating magnetic field, periodically modulating optical signal, was employed (Shah and Romalis [2009]). Moreover, in the developed scheme, a single light beam was used for both pumping and probing atomic medium, which allowed simplify the experimental setup. The physical foundations for such a magnetometer operation are described below.

In the magnetometer used for the detection of ZULF NMR signals presented withing this thesis, a single beam, propagating along the x -axis, was used. An oscillating magnetic field was typically applied in the z direction. The dynamics of atomic polarization can be once again described by the Bloch equation, but this time with the time-dependend magnetic field $\mathbf{B} = \mathbf{B}_0 + B_1 \cos(\omega_1 t) \mathbf{e}_z$. The analytical solution to the Bloch equations can be obtained and the component oscillating at the frequency of the modulation ω_1 takes a form of (Cohen-Tannoudji et al. [1970]):

$$\langle S_x(\omega_1) \rangle = \frac{2R_{pump}\gamma B_z}{(\gamma^2 B_z^2) + (R_{pump} + 1/T_2)^2} J_0 \left(\frac{\gamma B_1}{(2I + 1)\omega_1} \right) J_1 \left(\frac{\gamma B_1}{(2I + 1)\omega_1} \right) \sin(\omega_1 t), \quad (3.61)$$

where the J_0 and J_1 are the Bessel function of the first kind of the 0th and 1st order, respectively. The quantity $J_0\left(\frac{\gamma B_1}{(2I+1)\omega_1}\right) J_1\left(\frac{\gamma B_1}{(2I+1)\omega_1}\right)$ depends on the ratio of modulation strength and the modulation frequency and is maximal at ≈ 1.082 . Operating at this condition guarantees the highest spin-polarization amplitude and hence the optimal magnetometric sensitivity.¹⁰ We can calculate an optical signal generated by the evolving spin polarization. The effects induced in the atomic vapor are predominantly linear, so we can limit our consideration to the lowest order in Eq. 3.41 (the polarizability tensor χ^0). Then, the polarization rotation signal takes a form of (Seltzer [2008]):

$$\alpha(\omega_1) = \frac{\pi \nu l}{c} (n_+(\nu) - n_-(\nu)) = \frac{\pi \nu l}{c} (\chi_+^0(\nu) - \chi_-^0(\nu)) \approx \frac{\pi l n_{\text{cr}}}{2} \text{Im}(V(\nu - \nu_0)) \langle S_x(\omega_1) \rangle \propto B_z(\omega_1 t), \quad (3.62)$$

where $\text{Im}(V(\nu - \nu_0))$ indicates the Voigt optical line profile (see Demtröder [2013]). This relation shows that the polarization rotation oscillates at the modulation frequency with the amplitude proportional to the component of the magnetic field along the modulation direction. Similarly, a transmission of the circularly polarized light (σ_+) can be calculated, giving rise to the following relation for the transmitted light intensity:

$$\begin{aligned} I &= \frac{1}{\sigma(\nu) T_2} W\left(\sigma(\nu) I(0) T_2 e^{\sigma(\nu) I(0) T_2 - n\sigma(\nu) l}\right) \approx I_0 (1 - n\sigma(\nu) l) \\ &= I_0 \left(1 - \frac{\pi l n_{\text{cr}}}{2} \text{Re}(V(\nu - \nu_0)) (1 - 2 \langle S_x(\omega) \rangle)\right), \end{aligned} \quad (3.63)$$

where we kept only the terms linear in $\sigma(\nu) T_2$ in the Lambert W-function. Looking at a oscillating component of the light intensity we arrive at:

$$I(\omega_1) \approx I_0 \pi l n_{\text{cr}} \text{Re}(V(\nu - \nu_0)) \langle S_x(\omega_1) \rangle \propto B_z \sin(\omega_1 t). \quad (3.64)$$

As in the polarization-rotation case, the transmission of light is modulated at the magnetic-field modulation frequency ω_1 with the amplitude proportional to B_z component of the magnetic field.

In principle, one could use either optical rotation or light transmission signal for magnetometric purposes. If the optical pumping and probing is to be done with the same laser beam, however, there are some key differences between two arrangements. First, the optical rotation measurements require a laser beam to have a linear polarization components. To perform pumping and probing with the same beam an elliptically polarized beam needs to be used (Shah and Romalis [2009]). In case of measuring absorption, the circularly polarized laser beam is used. The second difference stems from the dependence of both optical signals on the light-frequency detuning. While the contrast in transmission signal is maximal when light is tuned to the center of optical line (in the typical SERF conditions the linewidth is broadened to the multigigahertz range due to collisions with buffer-gas atoms), the maximal optical rotation is obtained for detunings equal to half of the width of the optical transition. At the same time, for such a detuning, the circularly-polarized component of the light leads to a significant AC-stark shift (known also as light shift) acting as an effective magnetic field along the light-propagation direction (Shah and Romalis [2009]). This leads to extra broadening of the resonance, as the spin-exchange collision starts to contribute to relaxation. If the beam profile is homogeneous in the volume of the cell this light-shift contribution can be compensate

¹⁰ Notice that because the response depends of the ratio, pushing the modulation frequency to higher frequencies range to limit low-frequency noise, requires increase of the modulation amplitude. In the SERF magnetometer, however, the stronger modulation leads to additional relaxation, as the system is no longer under the SERF regime. This additional relaxation scales as B_1^2 , which puts an upper limit on the modulation strength and the modulation frequency.

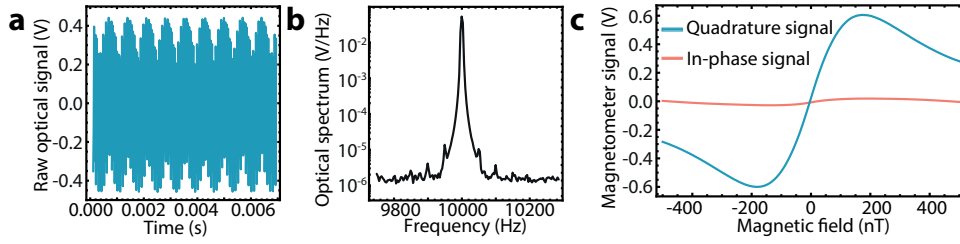


Figure 3.13: a) Raw optical signal of the SERF magnetometer with the magnetic-field modulation as obtained for zero-magnetic field (DC components is cut by a high-pass filter). The largest components of the signal oscillates at the second harmonic of the magnetic-field modulation frequency, as we are in the center of the dispersion curve shown in panel b). The spectrum of the optical signal around the modulation frequency (10 kHz) operating at a zero ambient magnetic field. The response at the modulation frequency is visible as large central peak, while the magnetic signals are visible as symmetric sidebands around the modulation frequency. In the presented example no ZULF NMR signal is measured, the visible sidebands correspond to the power-line magnetic noise. c) Demodulated at the magnetic field modulation frequency, optical signal used for the magnetometry purposes. The presented signals are measured with the SERF magnetometer constructed within this dissertation.

by applying an opposing magnetic field. This applied magnetic field is, however, problematic for zero-field NMR experiments, as the magnetic field used to optimize the performance of the sensor affects the nuclear spins. For this reason, and the overall technical simplicity (using a single photodiode instead of a polarimeter), the absorption-based modulated SERF magnetometer was used to obtain results presented in this thesis.

A representative SERF magnetometer signal is shown in Fig. 3.13. The raw signal (intensity of transmitted light) is shown in Fig. 3.13a) and its Fourier transform is shown in Fig. 3.13b). The large DC components has been cut from the optical signal. The largest component to oscillation is the response on twice the Larmor frequency, (not seen in the Fourier spectrum of the signal), while the residual response at the modulation frequency (10 kHz) is seen as a large peak in spectrum of the signal Fig. 3.13b). The symmetric sidebands around the modulation frequency are a results of magnetic field noise at power line harmonics. If measured ZULF NMR signal will appear as such sidebands in the raw optical signal. The demodulated quadrature signal is shown in Fig. 3.13c). The quadrature (90° out of phase with modulation signal) component has a dispersive shaped centered around a zero magnetic field and is used for magnetometry. The slope of the linear part of the resonance is equal to 7.5 mV/nT which, with a measured noise floor of $450 \text{ nV Hz}^{-1/2}$, results in magnetic sensitivity of $60 \text{ fT Hz}^{-1/2}$.

3.3.9 Comparison between NMOR and SERF magnetometers in ZULF NMR experiments

NMOR and SERF magnetometers can both reach $\text{fT}/\sqrt{\text{Hz}}$ sensitivity level for near-DC magnetic fields. In fact, both techniques were successful used to detect ZULF NMR signals (Xu et al. [2008], Bevilacqua et al. [2019]; Ledbetter et al. [2007]; Jiang et al. [2019]).

The experimental arrangements and many elements of both types of magnetometers discussed above are similar and based on the same optical components. One of the most noticeable differences between the techniques is the temperature of the vapor (the density of atoms in in SERF the magnetometer is typical 3-4 orders of magnitude larger than in a typical NMOR magnetometer). This results in following differences between the magnetometers:

- Higher density of the alkali atoms is achieved through heating up a cell containing alkali metal droplet. In the SERF magnetometer, the vapor cell is kept at a temperature of 160 – 200 °C. At the same time, the temperature of the vapor cell in the NMR magnetometers is 30 °C – 50 °C. The higher temperature of the vapor cell in the SERF magnetometer requires a heating system, which does not magnetically interfere with the output of magnetometer. Moreover, from the standpoint of NMR measurements, the cells needs to be placed in the vicinity of NMR samples, which may be problematic in the latter case due to the dissipation of heat.
- In our research, the NMOR magnetometer employed a paraffin-coated cell for field sensing, while in the SERF case the buffer-gas cell was used. Absence of the buffer-gas results in atoms freely bouncing of the walls in the first case and thermalization and diffusion of atoms in the second. This means that in the NMOR magnetometer, the detected magnetic field is averaged over the whole volume of the cell, while in the buffer-gas SERF cell the magnetic field is averaged only across the optically path. As the field from NMR sample decays quickly with the distance (approximately like a dipole with the inverse of cubed distance r^{-3}) averaging of the magnetometer readout in paraffin coated cell may lower the detected signal levels.
- To achieve high sensitivity, the NMOR magnetometry must rely on large cell than in the case of the SERF magnetometer (assuming the necessity of keeping the paraffin-coated-cell temperature low). In fact, the SERF magnetometers can use smaller vapor cells or even so-called microcells (Jiménez-Martínez and Knappe [2017]). Specifically, the paraffin-coated cell used in the NMOR-based magnetometer presented in this thesis is a cylinder with 1-cm radius and 1-cm length, while the SERF magnetometer used a cubic microcell of 4x4x2 mm³. Thereby, a point-like magnetic dipole, placed 3 mm from the cell, produces about four times larger field in the smaller cell than in the larger cell. This also means that the volume needed for NMR detection with magnetometer needs to significantly smaller in the latter case.

The NMOR magnetometers presented in this dissertation has been develop to perform ZULF NMR experiments. Those initial experiments are described in the next section. For the reasons mentioned above, the development of the SERF-based spectrometer soon started and the results presented in Chapter 5 and 6. were obtained using this atomic magnetometry approach. Some of the results presented in Chapter 6 and Chapter 7 were obtained using a commercial magnetometer, which is also based on the SERF phenomenon.

3.3.10 Ultra-low field NMR with the use of NMOR magnetometers

Following section describes the initial ZULF NMR experiments performed with the used of NMOR-based optical magnetometer. Results obtained with SERF-based systems are presented in Chapters 5-7.

NMOR based NMR spectrometer

As mentioned previously, a first ZULF NMR spectrometer presented here used an oscillating-field NMOR magnetometer. The schematic of the experimental setup is shown in Fig. 3.14. The NMR sample, housed in a 2-ml plastic shell vial, is shuttled pneumatically between the prepolarizing magnet and the detection region. The evolution of the nuclear spins takes place inside a four layer cylindrical mu-metal shield (Twinleaf MS-2). The two-layered solenoid, wound back and forth and piercing the whole length of the shield, provide the magnet field for the nuclear sample, simultaneously not affecting the magnetometer performance (a relative field leakage of

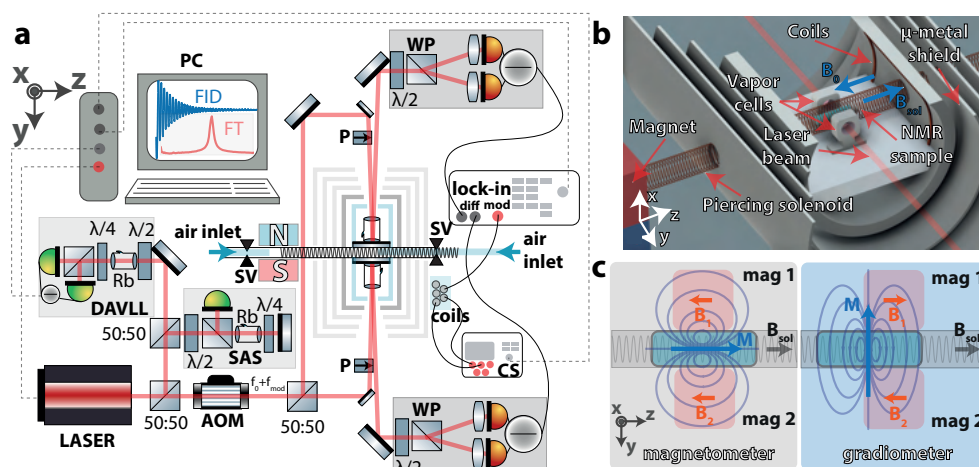


Figure 3.14: a) Schematic of the NMOR-based ULF NMR spectrometer. **SAS** indicates Saturation Absorption Spectroscopy (SAS), (**DAVLL**) Dichroic Atomic Vapor Laser Lock optical system, while (**AOM**) denotes acousto-optical modulator. The light polarization is prepared with a crystalline polarizer (**P**) with the polarization axis aligned with the z direction. The light then enters magnetic shield (illustrated with the rectangular shape with optical access holes), passing through a cylindrical vapor cell and bounces back on the thin, dielectric mirror passing again through the atomic vapor. The light is guided to the polarimeter setup (gray highlight), consisting of the Wollaston prism (**WP**) and two photodiodes. The optical setup is mirrored in the other arm of the gradiometer. The differential signals are connected to the lock-in amplifier at demodulated at the modulation frequency of the magnetic field. Same lock-in supplies an oscillating magnetic field (if operating in DC mode). The 3 channel precise current source (**CS**) is used to shim transverse field and provide a guiding field B_0 as well as powering the solenoid providing a magnetic field B_{sol} . The samples is shuttled through a plastic tube with the piercing solenoid wrapped across the whole width of the magnetic shield. The air flow causing shuttling is controlled with the use of two solenoid valves (**SV**). The sample is prepolarized in the solid-state permanent magnet. The experiment is controlled with the use of a computer (**PC**). Optical components drawings shown in this dissertation are taken from ComponentLibrary by Alexander Franzen (licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported License). b) Inside of the NMOR-base spectrometer. The key components for the NMR experiment are indicated. The blue arrows mark the directions of the bias field for detection B_0 and the solenoid field B_{sol} for the nuclear spin. c) The NMR sample (blue rectangle) positions in different detection schemes. Left: sample symmetrically placed in respect to two magnetometer cells (mag 1 and mag 2) in "magnetometer" arrangement. Right: sample placed asymmetrically in respect to vapor cells, allowing for differential detection (the direction of the magnetic field in two vapor cell, indicated by red arrows is opposite to each other). The blue arrow marks the direction of the nuclear magnetization M .

less than 10^{-4}). The magnetic shield has a set of internal coils used for generation of a guiding field for the magnetometer and zeroing the transverse fields. The fields are controlled with a low-noise, stable current source (DM Technologies). The coils are also used to provide a weak oscillating field when the magnetometer is operated in the DC mode. Magnetic-field pulses to manipulate the nuclear spins are also applied with the use of these internal coils. The magnetic shield houses two paraffin-coated vapor cells filled with isotopically-enriched ^{87}Rb and placed opposite each other on both sides of the solenoid. Magnetic-field sensing is based on NMOR, i.e., via analysis of polarization of light traversing the vapor.

Optical pumping and probing of the field-sensing atoms is performed with a single laser-light beam (Toptica DL100) tuned to the $F = 2 \rightarrow F = 1$ transition of the D1 line of ^{87}Rb . The laser frequency is locked to this transition with the use of dichroic atomic vapor laser lock (Wasik et al. [2002]). When locked, the laser frequency is stable at a level of ± 10 MHz over hours (long enough to perform NMR experiments). The laser light passes through an acousto-optical modulator and the first-order diffraction of light is directed to the experiment. The light intensity can be changed by adjusting the amplitude of the acoustic wave (driving voltage) at the modulator. The size of the laser beam is adjusted by a diaphragm, and the light is linearly polarized. Next, the light is split and used to independently illuminate the cells placed inside the shield. Inside the shield, the beams propagate along the shield axis, perpendicular to the static-field direction. After passing the vapor cells, mounted in custom-made 3D-printed frames, they bounce off thin dielectric mirrors placed between the cells and the solenoid and, after crossing the cells again, leave the shield at small angles in respect to the incident beams. The cell is heated with the hot air to a temperature of about $\sim 50^\circ\text{C}$ to increase vapor density and boost sensitivity of the sensor. The double-pass configuration also increases the signals (by doubling the interaction paths). Finally, the polarization of the laser beams is detected with balanced polarimeters. In the polarimeters, each beam is split with a high-quality crystal polarizer into two beams that are detected with differential photodiodes (Thorlabs PDA100A). The differential signals from the photodiodes are demodulated with a lock-in amplifier (Zurich Instruments HF2LI). The in-phase signal is used at the magnetometer readout. The lock-in provides the oscillating magnetic field to the coil in case of operating DC mode. The lock-in amplifier is also used to control the pneumatic shuttling of the sample and the timing of the pulses. The experiment is controlled with the program written in LabView. The gradiometric configuration used in this scheme allows to improve signal-to-noise ratio of detection by suppressing common-mode noise in both magnetometer channels.

Ultra-low NMR signals detected with NMOR

Figure 3.15 shows the measured field, corresponding to static magnetization aligned with the magnetic field. The initial jump in the signal is caused by the sample arriving in the detection region. The following exponential decay of the signal indicates relaxation of the magnetization. Although this signal carries no chemically-specific information (all nuclear Larmor frequencies are centered at zero), the ability to measure static signals allows for the T_1 measurements in a single shot, while in a typically in ZULF NMR measurement the longitudinal relaxation is measured in a series of measurements. The amplitude of this longitudinal magnetization can be changed by applying a short DC pulse prior to the acquisition. The pulse rotates the nuclear spins and affects the length of measured longitudinal component of the nuclear magnetization. The measured signal amplitude follows a sinusoidal dependence on the pulse angle (insert in Fig. 3.15a)).

If the nuclear spins are tipped from the direction of the magnetic field, they undergo Larmor precession. The sample for this measurement is positioned such the transverse magnetization produces a field along the sensitive axis of magnetome-

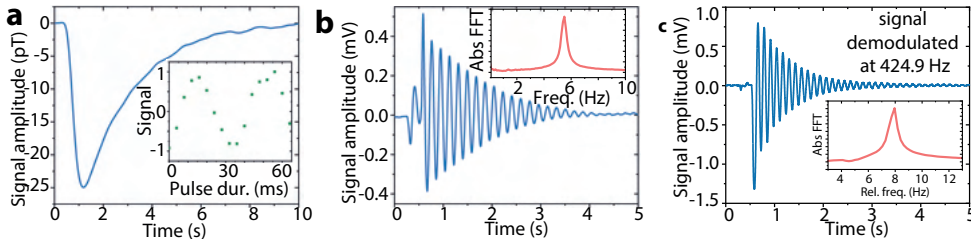


Figure 3.15: a) A quasi-static magnetization signal from prepolarized nuclear spins in a water sample. The NMR sample enters the sensing volume after 0.5 s and then the signal decays with the longitudinal relaxation rate of $T_1 = 2.8$ s. The vertical scale indicates the magnetic field generated by the 4-ml sample. The inset shows the signal amplitude of the recorded static-magnetization signal after applying a transverse magnetic-field pulse, generating rotations up to 3π . The shown time trace is a result of 4 averages. b) An ULF precession of protons in a transverse field of ~ 130 nT. The initial period, where no signal is recorded, corresponds to the saturation of the magnetometer by a strong magnetic-field pulse, which is followed by the built-up of the signal as the magnetometer recovers. The inset shows the spectrum of the signal. The signal was measured in the in the gradiometric configuration explained in the main text. c) NMR signals from precessing proton spins detected at the field ~ 10 μ T with the AC-magnetometer. The signal is demodulated at the Larmor frequency. The inset shows the spectrum of signal. The increased width (0.9 Hz with respect to 0.5 Hz) is likely a result of the inhomogeneities of the solenoid field.

ter (Fig. 3.15b)). The oscillating signals detected by two magnetometers are of an opposite signs, so subtraction of the signals reduce common-mode noise, while increasing the amplitude of the signal of interest. The precessing signal can be also picked up when operating the magnetometer in AC-mode (Fig. 3.15c). The magnetic field is applied along the piercing solenoid, while the spins are tipped away to transverse plane by a resonant AC pulse (akin to high-field NMR experiment). The oscillating signal stemming from precessing magnetization is measured and demodulated at the reference frequency by a lock-in amplifier (local oscillator of the lock-in provides oscillating field used in NMR pulse). In both cases (detection by DC and AC magnetometer) an oscillating signal is detected with enhanced sensitivity compared to the quasi-static DC signal.

3.3.11 Signal detection - conclusions

As shown in this section, low-frequency NMR signals under the ultra-low and zero-field conditions can be detected with atomic magnetometers. The magnetometers rely on the modification of optical properties of alkali-metal vapor induced by magnetic field. The operation of atomic magnetometer can be understood in three stages: optical pumping to polarized ground state of alkali atoms, evolution in the magnetic field and detection of optical properties (rotation of polarization plane or absorption), while sensitivity of the magnetometer is fundamentally limited by the number of atoms used for probing (atomic density and probing volume) and the relaxation time of the ground polarization (limited by wall collisions and collisions with other alkali atoms or buffer gas atoms/molecules). The two popular schemes for atomic magnetometry rely on Nonlinear Magneto-Optical Rotation or Spin-Exchange Relaxation Free operation. We show that modulation of the longitudinal magnetic field leads to strong NMOR resonances, which can be used for a sensitive magnetometry at zero- and large magnetic fields (Parametric NMOR). We also show that the applying a transverse oscillating magnetic field can be used to detect small magnetic fields with the use of RF-NMOR phenomena. The same setup can be used to detect oscillating magnetic field resonant with the Larmor frequency of alkali atoms with even better sensitivity. The NMOR-based NMR spectrometer

using the gradiometer detection was also introduced. The example signals and spectra obtained with its use were presented. This initial setup was then superseded by the SERF-magnetometer-based spectrometer. The SERF magnetometry used to obtain ZULF spectra in the next chapters of this thesis, relies on high-density alkali vapor placed in ultra-low magnetic field, where the spin-exchange collision stop contributing to relaxation processes. This combined with high density of atoms allow for unprecedented sensitivity in small cell volumes. Important differences between these two approaches to magnetometry in context of detecting NMR signals were also discussed. As we showed how to solve the issues of nuclear polarization in zero-field and detection of ultra-low frequency field signals from nuclear spins lets turn our attention to generation and interpretation of zero-field NMR signals.

3.4 ZERO-FIELD NMR SIGNAL

As this thesis describes ZULF NMR experiments, it is necessary to analyze mechanisms giving rise to appearance of such NMR signals and describe means of their interpretation. As described in Sec. 2.1.1, conventional high-field signals are generated, when polarization of thermally polarized samples is tipped off to the transverse plane with a resonant magnetic-field pulse and it subsequently precesses in a nonzero magnetic field (the magnetization precession is detected with a pick-up coil). Same principle applies for experiments at ULFs, where spin polarization of samples with no heteronuclear couplings but spins-1/2 precess in non-zero static magnetic field, being detected with non-inductive sensors. The situation changes when such a coupling is present, in particular, when it dominates over the Zeeman interaction. Then the dynamics of the spin evolution becomes more complicated and interplay between two interactions is observed. At a truly zero magnetic field, the Zeeman interaction disappears, but the heteronuclear spin coupling may produce time-dependend magnetic moment, which can be also detected with non-inductive magnetometers.

3.4.1 Generating zero-field NMR signals

Signals detected in ZULF NMR experiments are often determined by a specific component of the nuclear magnetization $\hat{M}$ (Eq. 3.1). We can therefore limit our discussion to the analysis of the non-zero expectation value of magnetization $\langle \hat{M} \rangle$ and its temporal evolution.

Thermally polarized, high-field hamiltonian eigenstate

Let us start by discussing signals produced in a generic heteronuclear two, spin-1/2 nuclei system. The system is thermally polarized to the level $P_i = \frac{\hbar B_0 \gamma_i}{4k_B T}$ and evolves under the zero-field Hamiltonian (expressed here and after in units of $\hbar$):

$$\hat{\mathcal{H}}_0 = 2\pi J \hat{I} \cdot \hat{S}. \quad (3.65)$$

We can write the polarized state in a following form:

$$\begin{aligned} \hat{\rho}_{sudden} = \frac{1}{4} \left(\mathbb{1} + \frac{\hbar B_0 \gamma_I}{2k_B T} \hat{I}_z + \frac{\hbar B_0 \gamma_S}{2k_B T} \hat{S}_z \right) = \\ \frac{\mathbb{1}}{4} + \frac{\hbar B_0}{8k_B T} [(\gamma_I + \gamma_S) (\hat{I}_z + \hat{S}_z) + (\gamma_I - \gamma_S) (\hat{I}_z - \hat{S}_z)], \end{aligned} \quad (3.66)$$

where we separated the non-identity part of the density matrix into two terms proportional to the sum and the difference of the spin operators along the z-axis. $\hat{I}_z$ and $\hat{S}_z$ indicate z-components of the single-spin operators, represented by 4×4

matrices. The first term, $(\hat{I}_z + \hat{S}_z)$, is the z component of the total spin, i.e., $\hat{F}_z$, which commutes with the Hamiltonian $\hat{H}_0$:

$$[\hat{H}_0, \hat{F}_z] = [2\pi J \hat{\mathbf{I}} \cdot \hat{\mathbf{S}}, \hat{F}_z] = [2\pi J (\hat{F}^2 - \hat{I}^2 - \hat{S}^2), \hat{F}_z] = 0, \quad (3.67)$$

as the $\hat{F}_z$ operator commutes with the squares of the spin operators. This means that this term does not evolve under the zero-field Hamiltonian and only contribute to the static magnetization (not carrying spectral information). The second term, however, does not commute with the Hamiltonian, i.e., it evolves in the zero field. Calculating its evolution we get:

$$\frac{d}{dt} (\hat{I}_z - \hat{S}_z) = -\frac{i}{\hbar} [(\hat{I}_z - \hat{S}_z), \hat{H}_0] = -2\pi J (\hat{I}_x \hat{S}_y - \hat{I}_y \hat{S}_x), \quad (3.68)$$

where we used commutation rules first introduced in Sec. 1.7. We can equivalently calculate the time evolution of this part of the density matrix as:

$$(\hat{I}_z - \hat{S}_z)(t) = e^{-it\hat{H}_0} (\hat{I}_z - \hat{S}_z) e^{it\hat{H}_0}. \quad (3.69)$$

We can turn into calculating expected magnetization signal as:

$$\begin{aligned} \langle \hat{M}_i(t) \rangle &= \frac{1}{4} \text{Tr} (\mathbb{1} \hat{M}_i) \\ &+ \frac{\hbar B_0}{8k_B T} \text{Tr} \left(\hat{M}_i (\gamma_I + \gamma_S) e^{-it\hat{H}_0} (\hat{I}_z + \hat{S}_z) e^{it\hat{H}_0} \right) \\ &+ \frac{\hbar B_0}{8k_B T} \text{Tr} \left(\hat{M}_i (\gamma_I - \gamma_S) e^{-it\hat{H}_0} (\hat{I}_z - \hat{S}_z) e^{it\hat{H}_0} \right). \end{aligned} \quad (3.70)$$

One can evaluate Eq. 3.70 for three Cartesian components of the magnetization:

$$\begin{aligned} \langle \hat{M}_x(t) \rangle &= 0, \\ \langle \hat{M}_y(t) \rangle &= 0, \\ \langle \hat{M}_z(t) \rangle &= N h \frac{B_0}{8k_B T} \left((\gamma_I + \gamma_S)^2 + (\gamma_I - \gamma_S)^2 \cos(2\pi J t) \right). \end{aligned} \quad (3.71)$$

It is clear from Eqs. 3.71 that polarization of the sample aligned along z , if suddenly transferred to the zero field, is preserved (still aligned along the axis). This magnetization has two time components: one static and one oscillating at the J -coupling constant. The zero-field evolution under the J -coupling can be illustrated by drawing the expectation values of the angular momentum and magnetization operators (Fig. 3.16a). As shown, the spin component along z undergoes quantum beats and is transferred between two nuclei (the total spin is conserved as it commutes with the zero-field Hamiltonian). Similarly, the magnetization associated with individual spins oscillates back and fourth, but here in contrast to the total spin, the total magnetization, for two heteronuclei (different gyromagnetic ratios), is not conserved and oscillates back and forth and the J -coupling frequency. This instantly points us to more general conclusion: **to observe a zero-field spectrum at the characteristic coupling frequencies, the molecules must contain at least two different nuclear species to produces time-dependend signal**, as evident by Eq. 3.71. This considerations showcase the first way to generate a zero-field NMR signal, i.e., by transferring the thermally-prepolarized sample suddenly to the zero-field magnetization, where it starts to evolve without the need for any magnetic-field pulses. In fact, this approach is often used with nuclei of opposite sign of the gyromagnetic ratios, as in that case the $(\gamma_I - \gamma_S)^2$ term is maximized.

Adiabatic transfer to zero-field

In the previous section, we discussed the case of the sudden transfer to the zero field, where oscillating magnetization is generated. Alternatively, the high-field

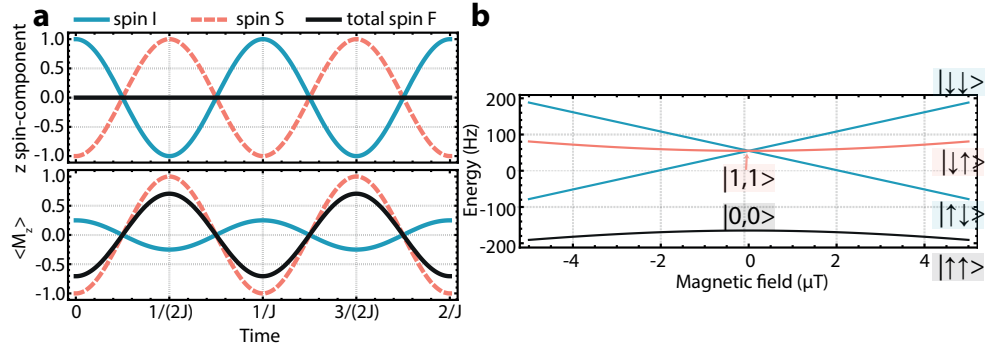


Figure 3.16: a) Temporal evolution of expectation values of the z-component of the spins I and S of the heteronuclear coupled spin system along with the total spin component F_z and corresponding magnetizations. For simplicity only part of the matrix proportional to $(I_z - S_z)$, evolving under J -coupling is considered. The spins I and S undergo evolution under the J -coupling with the spin component oscillating between two nuclei. Notice that the total-spin component along z is constant. At the same time, magnetization along z of the whole system oscillates at the J -coupling frequency giving rise to the zero-field NMR signal. The relative scales of oscillation are taken for a coupled system of ^1H and ^{13}C nuclei following sudden transfer of the system to zero-field. b) The energy levels for the ^1H - ^{13}C system as a function of magnetic field. During adiabatic transfer, the system is always in the eigenstate of the system and the Zeeman state populations are transferred to triple-singlet basis as indicated by the state label and written explicitly in the main text. The coupling strength is set to 220 Hz.

polarization can be **transferred adiabatically** to the zero field. In that case, the density matrix remains in the eigenstates of the instantaneous spin Hamiltonian, i.e., at all time, it contains population.

First, we can find eigenenergies of our model two-coupled-spin system versus the magnetic field. This can be done by diagonalization of the Hamiltonian containing both interaction terms. The dependence of the eigenenergies on the field are shown in Fig. 3.16b). As shown in Fig. 3.16b), the populations of high-field Zeeman states $\rho_{1/2,1/2}$, $\rho_{-1/2,1/2}$, $\rho_{1/2,-1/2}$, $\rho_{-1/2,-1/2}$, are converted to the populations of singlet-triplet states respectively $\rho_{1,1}$, $\rho_{1,0}$, $\rho_{0,0}$, $\rho_{1,-1}$. Based on the form of the density matrix, we can write populations after transfer to the zero field:

$$\begin{aligned}
 \rho_{1,1} &= \frac{1}{4} + \frac{\hbar B_0}{8k_B T}(\gamma_I + \gamma_S), \\
 \rho_{1,0} &= \frac{1}{4} + \frac{\hbar B_0}{8k_B T}(\gamma_I - \gamma_S), \\
 \rho_{0,0} &= \frac{1}{4} - \frac{\hbar B_0}{8k_B T}(\gamma_I - \gamma_S), \\
 \rho_{1,-1} &= \frac{1}{4} - \frac{\hbar B_0}{8k_B T}(\gamma_I + \gamma_S).
 \end{aligned} \tag{3.72}$$

We can therefore write the density matrix after adiabatic transfer to zero field as (following Emondts et al. [2014]):

$$\begin{aligned}
\hat{\rho}_{ad} &= \left[\frac{1}{4} + \frac{\hbar B_0}{8k_B T} (\gamma_I + \gamma_S) \right] \left(\frac{1}{4} + \frac{\hat{I}_z + \hat{S}_z}{2} + \hat{I}_z \hat{S}_z \right) \\
&+ \left[\frac{1}{4} + \frac{\hbar B_0}{8k_B T} (\gamma_I - \gamma_S) \right] \left(\frac{1}{4} + \hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y - \hat{I}_z \hat{S}_z \right) \\
&+ \left[\frac{1}{4} - \frac{\hbar B_0}{8k_B T} (\gamma_I - \gamma_S) \right] \left(\frac{1}{4} - \hat{\mathbf{I}} \cdot \hat{\mathbf{S}} \right) \\
&+ \left[\frac{1}{4} - \frac{\hbar B_0}{8k_B T} (\gamma_I + \gamma_S) \right] \left(\frac{1}{4} - \frac{\hat{I}_z + \hat{S}_z}{2} + \hat{I}_z \hat{S}_z \right) \\
&= \frac{1}{4} + \frac{\hbar B_0}{8k_B T} (\gamma_I + \gamma_S) (\hat{I}_z + \hat{S}_z) + \frac{\hbar B_0}{4k_B T} (\gamma_I - \gamma_S) (\hat{\mathbf{I}} \cdot \hat{\mathbf{S}} - \hat{I}_z \hat{S}_z),
\end{aligned} \tag{3.73}$$

where we expressed the population in singlet-triplet basis by the angular momentum operator. Since the density matrix is diagonal in the eigenbasis of the Hamiltonian, it does not evolve in time. Therefore, the adiabatic density matrix $\hat{\rho}_{ad}$ does not produce the time-dependent magnetization, but only a static magnetization along the z direction:

$$\langle \hat{M}_z \rangle_{ad} = N \hbar \frac{B_0}{8k_B T} (\gamma_I + \gamma_S)^2. \tag{3.74}$$

We can now analyze the role of pulses to generate the oscillating signals from this initial state.

Pulses in zero-field NMR

As the spin evolution under zero-field conditions is happening at low-frequencies (typically < 1 kHz) the DC magnetic field pulses can (and typically are) used to manipulate nuclear spins. We can distinguish two cases based on the direction of the pulse in respect to the nuclear-polarization axis:

- **Longitudinal-pulse**

The action of the magnetic pulse oriented along the z-axis can be calculated using the Hamiltonian:

$$\hat{\mathcal{H}}_{pulse}^z = B_{pulse} \tau (\gamma_I \hat{I}_z + \gamma_S \hat{S}_z), \tag{3.75}$$

where τ is the pulse length and B_{pulse} is its amplitude. The density matrix after adiabatic transfer to zero-field following the z pulse takes the form:

$$\begin{aligned}
\hat{\rho}_{ad}^z &= \frac{1}{4} + \frac{\hbar B_0}{8k_B T} (\gamma_I + \gamma_S) (\hat{I}_z + \hat{S}_z) \\
&+ \frac{\hbar B_0}{4k_B T} (\gamma_I - \gamma_S) [\hat{I}_x \cos(B_p \gamma_I \tau) - \hat{I}_y \sin(B_p \gamma_I \tau)] [\hat{S}_x \cos(B_p \gamma_S \tau) - \hat{S}_y \sin(B_p \gamma_S \tau)] \\
&+ \frac{\hbar B_0}{4k_B T} (\gamma_I - \gamma_S) [\hat{I}_y \cos(B_p \gamma_I \tau) + \hat{I}_x \sin(B_p \gamma_I \tau)] [\hat{S}_y \cos(B_p \gamma_S \tau) + \hat{S}_x \sin(B_p \gamma_S \tau)] \\
&= \frac{1}{4} + \frac{\hbar B_0}{8k_B T} (\gamma_I + \gamma_S) (\hat{I}_z + \hat{S}_z) \\
&+ \frac{\hbar B_0}{4k_B T} \{ \hat{I}_x \hat{S}_x [\sin(B_p \gamma_I \tau) \sin(B_p \gamma_S \tau) + \cos(B_p \gamma_I \tau) \cos(B_p \gamma_S \tau)] + \\
&\hat{I}_y \hat{S}_y [\sin(B_p \gamma_I \tau) \sin(B_p \gamma_S \tau) + \cos(B_p \gamma_I \tau) \cos(B_p \gamma_S \tau)] \} \\
&+ \frac{\hbar B_0}{4k_B T} (\hat{I}_x \hat{S}_y - \hat{I}_y \hat{S}_x) [\sin(B_p \gamma_I \tau) \cos(B_p \gamma_S \tau) - \sin(B_p \gamma_S \tau) \cos(B_p \gamma_I \tau)],
\end{aligned} \tag{3.76}$$

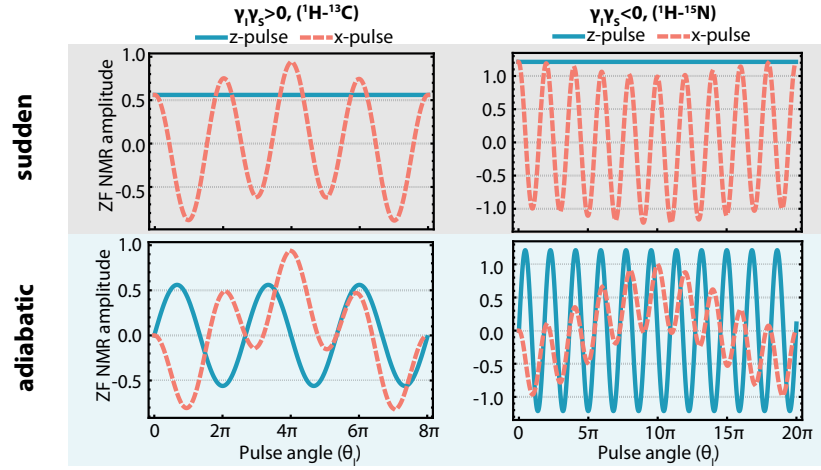


Figure 3.17: Zero-field NMR signal amplitude as a function of the tilting-pulse phase corresponding to ^1H rotation. The top row shows signal the evolution after the sudden transfer and corresponds to the pulse along x or z . Notice that the z -pulse has no influence on the signal following sudden transport. The left column shows the signal dependence for two nuclei with the same sign of the gyromagnetic ratio, where the optimal pulse along x can increase the amplitude of the signal in comparison with the sudden transfer. The opposite is true for a pair of nuclei with the opposite sign of gyromagnetic ratio (left column). The bottom row shows the signal following an adiabatic transition to zero-field and subsequent pulse. Here, evolution during the z pulse follows relation Eq. 3.77, while the x -pulse evolution follows more complicated dependence Eq. 3.80. For nuclei with the same sign of the gyromagnetic ratios (left side), the optimal transverse pulse can produce higher signal, while for nuclei with opposite sign the z pulse allows for larger zero-field NMR signals.

where three initial terms commute with the zero-field Hamiltonian and therefore contribute only to a static magnetization. The last term, however, leads to an oscillating terms in the magnetization. Hence, we can write down the formula for the expectation value of the z -magnetization as:

$$\langle \hat{M}_z(t) \rangle_{ad}^z = N h \frac{B_0}{8k_B T} \left[(\gamma_I + \gamma_S)^2 + (\gamma_I - \gamma_S)^2 \sin((\gamma_I - \gamma_S) B_p \tau) \sin(2\pi J t) \right], \quad (3.77)$$

where the first term is static magnetization (it does not depend on the z -pulse), while the second term describes the magnetization oscillating at the J -frequency. **The amplitude of the oscillating signal depends on the relative angle of rotation between spins I and S , and is maximized when said relative angle is equal to $\pi/2$.** The amplitude of oscillating field after the z pulse is plotted in Fig. 3.17. Notice that for a relative angle of $\pi/2$, the magnetization produced after the z pulse is the same as the magnetization after the sudden transfer with the exception of $\pi/2$ in the phase of the oscillating component.

If we consider an action of the z -pulse on the density matrix following the sudden transfer, we can immediately conclude that such a pulse has no effect on the observable magnetization as the pulse Hamiltonian commutes with the sudden-transfer density matrix $[\hat{\rho}_{sudden}, \hat{\mathcal{H}}_{pulse}^z] = 0$. To affect the nuclear state after sudden (and also adiabatic) transfer to zero-field we can apply pulses transverse to the initial polarization direction.

- **Transverse pulse,**

When the magnetic-field pulse is applied perpendicular to the initial magnetization, the dynamics of the system is different. We can calculate the action

of such a non-oscillating pulse, by considering evolution under the following Hamiltonian:

$$\mathcal{H}_{pulse}^x = B_p \tau (\gamma_I \hat{I}_x + \gamma_S \hat{S}_x), \quad (3.78)$$

where we assumed (without the loss of generality) a pulse along the x -axis. Hence, we can calculate the new form of the adiabatic density matrix, which, after the x -pulse, is:

$$\begin{aligned} \hat{\rho}_{ad}^x = & \frac{\mathbb{1}}{4} + \frac{\hbar B_0}{8k_B T} (\gamma_I + \gamma_S) [\hat{I}_z \cos(B_p \gamma_I \tau) + \hat{S}_z \cos(B_p \gamma_S \tau)] \\ & + \frac{\hbar B_0}{8k_B T} (\gamma_I - \gamma_S) \{ \hat{I}_x \hat{S}_x + [\hat{I}_y \cos(B_p \gamma_I \tau) + \hat{I}_z \sin(B_p \gamma_I \tau)] \\ & [\hat{S}_y \cos(B_p \gamma_S \tau) + \hat{S}_z \sin(B_p \gamma_S \tau)] \}, \end{aligned} \quad (3.79)$$

where only the second term contributes to the magnetization along the z -axis:

$$\begin{aligned} \langle \hat{M}_z(t) \rangle_{ad}^x = & Nh \frac{B_0}{16k_B T} \left\{ (\gamma_I + \gamma_S)^2 [\cos(B_p \gamma_I \tau) + \cos(B_p \gamma_S \tau)] \right. \\ & \left. + (\gamma_I - \gamma_S)(\gamma_I + \gamma_S) [\cos(B_p \gamma_I \tau) - \cos(B_p \gamma_S \tau)] \cos(2\pi Jt) \right\}, \end{aligned} \quad (3.80)$$

where the first term corresponds to the static magnetization, while the second describes magnetization oscillating at the J -coupling frequency. The maximal value of static magnetization is exactly equal to the static magnetization components following the sudden and adiabatic transfer to the zero field. The oscillating component of the magnetization is maximized when:

$$[\cos(B_p \gamma_I \tau) - \cos(B_p \gamma_S \tau)] = 2, \quad (3.81)$$

and its amplitude is plotted for different nuclei as function of the pulse phase in Fig. 3.17. When the oscillating component of the magnetization is maximized with the proper magnetic-field pulse, the static component completely vanishes as evident from Eq. 3.80. The ratio of the maximum signal amplitude obtained after the adiabatic transfer to the zero field, followed by the optimal z and x pulses is equal to:

$$\frac{M_z^{osc,x}}{M_z^{osc,z}} = \frac{\gamma_I + \gamma_S}{\gamma_I - \gamma_S}. \quad (3.82)$$

The x pulse can also modify the density matrix following the sudden transfer to the zero field:

$$\begin{aligned} \hat{\rho}_{sudden}^x = & \mathbb{1}/4 \\ & + \frac{\hbar B_0}{8k_B T} (\gamma_I + \gamma_S) [\hat{I}_z \cos(B_0 \gamma_I \tau) - \hat{I}_y \sin(B_0 \gamma_I \tau) + \hat{S}_z \cos(B_0 \gamma_S \tau) - \hat{S}_y \sin(B_0 \gamma_S \tau)] \\ & + \frac{\hbar B_0}{8k_B T} (\gamma_I - \gamma_S) [\hat{I}_z \cos(B_0 \gamma_I \tau) - \hat{I}_y \sin(B_0 \gamma_I \tau) - \hat{S}_z \cos(B_0 \gamma_S \tau) + \hat{S}_y \sin(B_0 \gamma_S \tau)], \end{aligned} \quad (3.83)$$

which gives rise to the z -magnetization:

$$\begin{aligned} \langle M_z \rangle_{sudden}^x = & Nh \frac{B_0}{16k_B T} (\gamma_I + \gamma_S)^2 [\cos(B_0 \gamma_I \tau) + \cos(B_0 \gamma_S \tau)] + \\ & Nh \frac{B_0}{16k_B T} (\gamma_I + \gamma_S)(\gamma_I - \gamma_S) [\cos(B_0 \gamma_I \tau) - \cos(B_0 \gamma_S \tau)] + \\ & Nh \frac{B_0}{16k_B T} (\gamma_I + \gamma_S)(\gamma_I - \gamma_S) [\cos(B_0 \gamma_I \tau) - \cos(B_0 \gamma_S \tau)] \cos(2\pi Jt) + \\ & Nh \frac{B_0}{16k_B T} (\gamma_I - \gamma_S)^2 [\cos(B_0 \gamma_I \tau) + \cos(B_0 \gamma_S \tau)] \cos(2\pi Jt), \end{aligned} \quad (3.84)$$

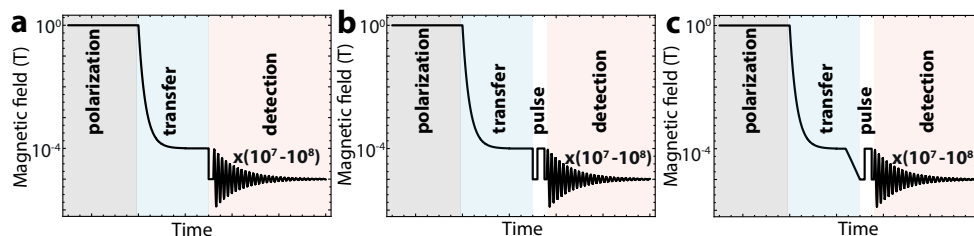


Figure 3.18: Magnetic-field trajectories implemented in different schemes in ZULF NMR experiments exploiting remote prepolarization: a) sudden transfer to the zero field, b) sudden transfer, followed by a magnetic field pulse, and c) adiabatic transfer to the zero field accompanied by a subsequent magnetic-field pulse. The amplitude of the zero-field signal has been enlarged for visibility (in typical experiments the amplitudes of such signals are on the order of 1-10 pT). The different stages of the experiment are highlighted.

where the first two terms describe the static component of the magnetization, while the last two describe the components oscillating at the J -coupling frequency. The amplitude of this oscillating part is plotted in Fig. 3.17 (top row). The maximum amplitude of the oscillating component of the signal, following the x -pulse, that is achievable with sudden and adiabatic transfer, is exactly the same.

To summarize, in a zero-field NMR experiment a magnetic-field component produced by a nuclear magnetization is detected.¹¹ In typical experimental geometries, a detectable component of the magnetic field coincides with magnetization along the same direction. The oscillating magnetization, carrying information about the J -coupling between nuclei, can be generated in a number of ways. For example, the oscillating signal is obtained when the sample is transported suddenly from high-magnetic field to the zero field. This is achieved in experiments with remote thermal prepolarization by applying switching of a guiding magnetic field in time scales much shorter than the relevant J -coupling. The zero-field NMR signal can be also acquired after the adiabatic transfer to the zero field and subsequent application of longitudinal or transverse magnetic-field pulses. The transverse pulse can be also applied after a sudden transition to the zero field to affect the amplitude of the generated zero-field NMR signal. These three approaches to generate the zero-field signals are shown schematically in Fig. 3.18.

3.4.2 Understanding ZF spectrum

In the previous section, we described how a zero-field NMR signal can be generated. Below, we show how to understand the zero-field spectrum obtained in such experiments.

Note on the spin-system notation

To denote specific spin coupling patterns under zero-field conditions we rely on the labeling convention introduced in a previous works (see for example Theis et al. [2013]). In a simplest studied system a set of n equivalent spin labelled A_n is coupled strongly to a heteronuclei X constituting XA_n spin system. If another not chemically equivalent spin is strongly coupled to a system it would be labelled XA_nB , while in case of weak coupling to spin B we would put a parenthesis around the strongly coupled part like $(XA)_nB$. The same nuclei which are not magnetically equivalent (have different couplings) will be denoted with a apostrophe like A and A' .

¹¹ Sometimes detection of more than one component of the magnetic field may be beneficial as shown, for example, in Blanchard et al. [2020a].

General selection rules for transitions observable in zero-field NMR

From a theoretical perspective, determination of an NMR spectrum involves calculating eigenenergies of the zero-field Hamiltonian and identifying the transition frequencies between specific energy levels. However, not all transitions are visible in zero-field NMR. As mentioned in the previous section, the observable signal stems from the nuclear magnetization. If we limit our observables to the z-component of the magnetization, we can find a transition rate between two sublevels in the structure of the total spin :

$$\langle F, m_F, \chi | \hat{M}_z | F', m_F', \chi' \rangle = \langle F, m_F, 1, m_m | F', m_F' \rangle \langle F, \chi | \hat{M}_z | F', \chi' \rangle, \quad (3.85)$$

where we used the Wigner-Eckart theorem to express the transition rate as a product of the reduced-matrix element $\langle F, \chi | \hat{M}_z | F', \chi' \rangle$ and the Clebsch-Gordan coefficient, and χ denotes remaining quantum numbers. Based on that we can introduce the selection rules (for which an appropriate Clebsch-Gordan coefficient is non-zero):

$$\begin{aligned} \Delta F &= F' - F = 0, \pm 1, \\ \Delta m_F &= m_{F'} - m_F = 0, \end{aligned} \quad (3.86)$$

where the second selection rules stems only from choosing the quantization axis to be along the sensitive direction (the z -axis). Note also that in the spin systems with additional symmetries (for example groups of equivalent spins) additional selection rules may apply. Moreover, the use of the oscillating, resonant magnetic-field pulses to excite observable magnetization can restrict excitable transmission for both oscillating and rotating magnetic fields (Sjolander et al. [2016]).

Direct calculation

For a certain, simple spin systems, one can find an analytical expression for an observed zero-field spectra. To demonstrate that, we can start with the XA_n system, which was extensively studied in the zero-field NMR context (see for example Theis et al. [2013]). For such a spin system, we can write down the scalar-coupling Hamiltonian in a form of:

$$\hat{\mathcal{H}}_{XA_n} = 2\pi J \left(\hat{I} \cdot \sum_i \hat{S}_i^n \right) = 2\pi J (\hat{I} \cdot \hat{K}) = \pi J (\hat{F}^2 - \hat{I}^2 - \hat{K}^2), \quad (3.87)$$

where we introduced the total spin $\hat{K}$ of n equivalent X spins and the total spin of the whole system $\hat{F} = \hat{I} + \hat{K}$. The energy levels of this zero-field Hamiltonian are characterized by the I , K , and F quantum numbers:

$$\hat{\mathcal{H}}_{XA_n} |F, m_F, I, K\rangle = \pi J [F(F+1) - I(I+1) - K(K+1)] |F, m_F, I, K\rangle. \quad (3.88)$$

In the XA_n system, an additional, i.e., beyond these given above, selection rule apply to the transitions. As the $\hat{K}^2$ operator commutes with the zero-field Hamiltonian (Eq. 3.87) and the pulse Hamiltonian (Eq. 3.78), the magnetic-field pulse cannot change the state of a total spin of equivalent spins:

$$\Delta K = 0, \quad (3.89)$$

as both $\hat{I}^2$ and $\hat{K}^2$ are conserved during evolution. Looking back at the energy-level structure, we see that different values of K give us energy-level manifolds within in which the possible transition are observed (as $\Delta K = 0$). If we take for example a common situation where both the A spins and the X spin are equal to $1/2$, we get two possible states characterized with $F, F+1$ quantum numbers for each value of K , apart from the possible manifold $K = 0$, where only one F state is possible and

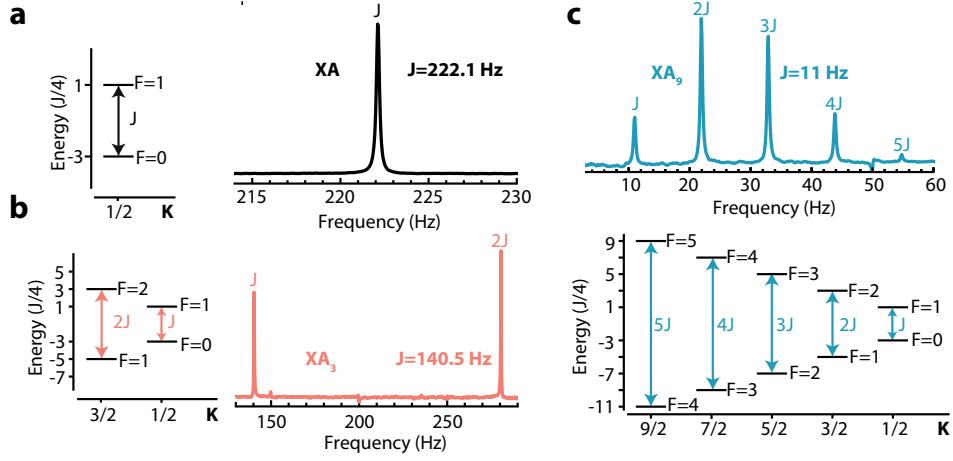


Figure 3.19: Experimental NMR spectra of simple XA_n obtained under zero-field magnetic field conditions. The corresponding energy levels are shown in the units of relevant J -coupling. The energy levels are shown for as a function of total spin K of n equivalent A spins. The Zeeman sublevels are not shown for clarity (as they are degenerate at zero-magnetic field). a) The experimental spectrum of $[^{13}\text{C}]$ -formic acid representing effective XA system (as the hydroxyl proton undergoes fast chemical exchange decoupling it effectively from other spins in the molecule). The single line is observed at the $J = 221.1$ Hz. b) The experimental spectrum of $[^{13}\text{C}]$ -methanol representing a simple XA_3 spin system. The spectral lines are seen at 1 and 2 time the coupling frequency $J = 140.5$ Hz. c) The experimental zero-field NMR spectrum of trimethyl phosphate which constitutes an XA_9 spin system. The 5 spectral lines are visible at multiples of coupling frequency $J = 11$ Hz. The small features at multiples of 50 Hz are harmonics of power line magnetic noise leaking into the detection region. Part c) has been adapted from [Alcicek et al. \[2021b\]](#).

no visible transitions are observed at zero-field. We can straightforward calculate the frequency for such transition:

$$\Delta f_{XA_n} = 1/(2\pi) \left(\langle F+1, m_F, 1/2, K | \hat{H}_{XA_n} | F+1, m_F, 1/2, K \rangle - \langle F, m_F, 1/2, K | \hat{H}_{XA_n} | F, m_F, 1/2, K \rangle \right) = (F+1)J. \quad (3.90)$$

For a system with odd number of equivalent spins A the takes values from $1/2, 3/2$ up to $N/2 - 1, N/2$, corresponding to even values of F : $F = 1, F = 2, F = 3 \dots$. This in turn results in the spectral lines at the multiple of J -coupling frequencies:

$$\Delta f_{XA_{2n+1}} = J, 2J, \dots, nJ, (n+1)J. \quad (3.91)$$

This means that XA spin system has a single line at J -frequency, XA_3 system two lines at J and $2J$ etc. Spectra of such example systems and the corresponding energy diagram are shown in Figure 3.19.

For a system with even number of A -spins the observable transitions happen at odd multiples of $J/2$:

$$\Delta f_{XA_{2n}} = 3/2J, 5/2J, \dots, (2n-1)/2J, (2n+1)/2J. \quad (3.92)$$

This means that XA_2 spin system has a single line at $3/2J$ -frequency, XA_4 system two lines at $3/2J$ and $5/2J$ etc.

The relative amplitudes of subsequent NMR can be also analytically calculated for XA_n spin systems. The transition probability between two states $|m\rangle$ and $|n\rangle$ is given as:

$$(\langle n | \hat{M}_z | m \rangle)^2 = \left(\sum_{m_K, m_I} (\gamma_A m_K + \gamma_I m_I) \langle K, I, m_K, m_I | F, m_F \rangle \langle K, I, m_K, m_I | F', m_{F'} \rangle \right)^2.$$

(3.93)

Example experimental spectra of XA_n spin system are shown in Fig. 3.19 showcasing equally spaced (every J) spectral lines as explained by theoretical analysis presented here.

Perturbation theory approach

Although an XA_n -system spectrum is easy to interpret, the real molecules, due to abundance of couplings, are rarely characterized with such a simple structure and hence produce the simple spectrum. In some cases, where such additional interactions as weak J -coupling to different nuclei or weak Zeeman interaction at ULFs perturbs a simple system, **the perturbation theory can be effectively used to calculate the spectrum**. Below, we consider several examples in which the perturbative approach can be implemented.

- **System with additional weak J -couplings**

The perturbative approach was used in a number of zero-field studies (see for example Theis et al. [2013]). In many cases, even a first-order correction to the energy levels is sufficient to not only describe the system qualitatively but also quantitatively explain the zero-field spectrum.

We first consider an $(XA_n)B_m$ system, where n equivalent spins A are coupled to the heteronucleus X , and both of those spins are only weakly coupled to the a set of m equivalent spins B . We can write a zero-field nuclear-spin Hamiltonian for such a system as:

$$\hat{\mathcal{H}} = 2\pi J_{XA} \hat{I} \cdot \hat{K}_A + 2\pi J_{XB} \hat{I} \cdot \hat{K}_B + 2\pi J_{AB} \hat{K}_A \cdot \hat{K}_B, \quad (3.94)$$

where a $\hat{K}_A$ describes the total spin of the spins A , while $\hat{K}_B$ corresponds to the total spin of the spins B . We can divide the the Hamiltonian into two parts:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1 = 2\pi J_{XA} \hat{I} \cdot \hat{K}_A + (2\pi J_{XB} \hat{I} \cdot \hat{K}_B + 2\pi J_{AB} \hat{K}_A \cdot \hat{K}_B), \quad (3.95)$$

where the $\hat{\mathcal{H}}_0$ describes the interactions in the XA_n system, while the $\hat{\mathcal{H}}_1$ part includes couplings to the spins B . As the couplings to the B spins are much weaker than those between X and A spins, $J_{XA} \gg J_{XB}, J_{AB}$, we can treat the effect of $\hat{\mathcal{H}}_1$ as a small correction to eigenenergies of $\hat{\mathcal{H}}_0$. Thereby, we can use the perturbation theory to obtain subsequent corrections to the energy levels and calculate transitions observed in the zero-field spectrum. This approach was extensively used in Butler et al. [2013b], where the first-order correction to $\hat{\mathcal{H}}_1$ takes a form of:

$$\hat{\mathcal{H}}_1^{(1)} = 2\pi \left(J_{XB}^{(1)} + J_{AB}^{(1)} \right) \hat{F}_A \cdot \hat{K}_B, \quad (3.96)$$

where the $\hat{F}_A = \hat{I} + \hat{K}_A$ describes the total spin of XA_N subsystem. The modified coupling strength $J_{XB}^{(1)}, J_{AB}^{(1)}$ are given by (Butler et al. [2013b]):

$$\begin{aligned} J_{XB}^{(1)} &= J_{XB} \frac{F_A(F_A + 1) + I(I + 1) - K_A(K_A + 1)}{2F_A(F_A + 1)}, \\ J_{AB}^{(1)} &= J_{AB} \frac{F_A(F_A + 1) - I(I + 1) + K_A(K_A + 1)}{2F_A(F_A + 1)}. \end{aligned} \quad (3.97)$$

We can now calculate the first-order correction to eigenenergies of the AX_n system:

$$\begin{aligned} \hat{\mathcal{H}}_1^{(1)} &= \pi \left(J_{XB}^{(1)} + J_{AB}^{(1)} \right) \left(\hat{F}^2 - \hat{F}_A^2 - \hat{K}_B^2 \right), \\ E^{(1)} &= \pi \left(J_{XB}^{(1)} + J_{AB}^{(1)} \right) [F(F + 1) - F_A(F_A + 1) - K_B(K_B + 1)], \end{aligned} \quad (3.98)$$

where the energy levels are labelled with the total spin F , the total spin F_A of the A nuclei in the XA_n subsystem, and the total spin K_B of the B spins. The equivalence of B spins results in an additional selection rule

$$\Delta K_B = 0, \quad (3.99)$$

and combined with the previously-discussed selection rules and the energy-level structure of the system allows to obtain approximate zero-field spectra of $(XA_n)B_m$ system. The example of a spectrum of such a $(XA_n)B_m$ system, along with the corresponding energy diagram, both calculated within the first-order perturbation theory, is shown in Fig. 3.20a).

- **XA_n system in the ultra-low magnetic field**

When a magnetic field is applied, the total spin Hamiltonian for the XA_n system can be written as:

$$\hat{\mathcal{H}}_{AX_N}^{ULF} = 2\pi J \hat{\mathbf{I}} \cdot \sum_i^N \hat{\mathbf{S}}_i + \left(-\gamma_I B_0 \hat{I}_z - \gamma_S B_0 \sum_i^N \hat{S}_{i,z} \right) = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1. \quad (3.100)$$

For ultra-low magnetic fields, we can treat the characteristic energies of the Hamiltonian H_1 as much smaller than those of the H_0 Hamiltonian and calculate resulting energy levels with the use of the perturbation theory. In the first-order perturbation calculation, the energy levels of zero-field Hamiltonian H_0 are shifted depending on the m_F value. In Fig. 3.20, a representative ultra-low field spectrum of the XA_N system is shown with the approximate energy levels.

Presence of the magnetic field may affect the selection rules for observed transitions. If the z -component of the magnetization, $\hat{M}_z$, is detected, the z -magnetic field does not modify the selection rules, i.e., $\Delta m_F = 0$. If, however, we apply a field in a x or y direction, it is convenient to orient the coordinate system along the magnetic-field direction, so that the magnetic field shifts the levels not inducing transitions between them. The selection rules for observing $\hat{M}_z$ component of magnetization in this new rotated frame of reference now take a form of $\Delta m_F = \pm 1$, resulting in lines splitted around the J and $2J$ frequencies, as shown in Fig. 3.20b).

Numerical simulations of spin systems at zero field

As the complexity of the spin system increases and the number of couplings grows, the analytical approach based on exact calculation or calculation of perturbative corrections to a known energy structure is no longer sufficient to predict the zero-field spectrum. The energy-level structure and the resulting observable transitions can be, however, calculated with the use of numerical diagonalization of the zero-field Hamiltonian. This approach has been used to explain the zero-field NMR spectrum since the beginning of the technique, and compared to perturbative methods in Theis et al. [2013].

A number of approaches was used for numerical simulations of ZULF NMR spectra throughout this thesis. For example, the Mathematica Spin Dynamica package (Bengs and Levitt [2018]) used for the high-field spin simulations has been successfully used to simulate and understand zero-field spectra (see for example Put et al. [2021] and code shown in Appendix A). The package is the useful tool to represent spin operators in an arbitrary basis and provides means to visualize the expectation values of such operators, which can be especially helpful in understanding zero-field NMR dynamics. The package, however, is well suited for relatively small systems, and in practice calculations with more than six spins in the system are impractical.

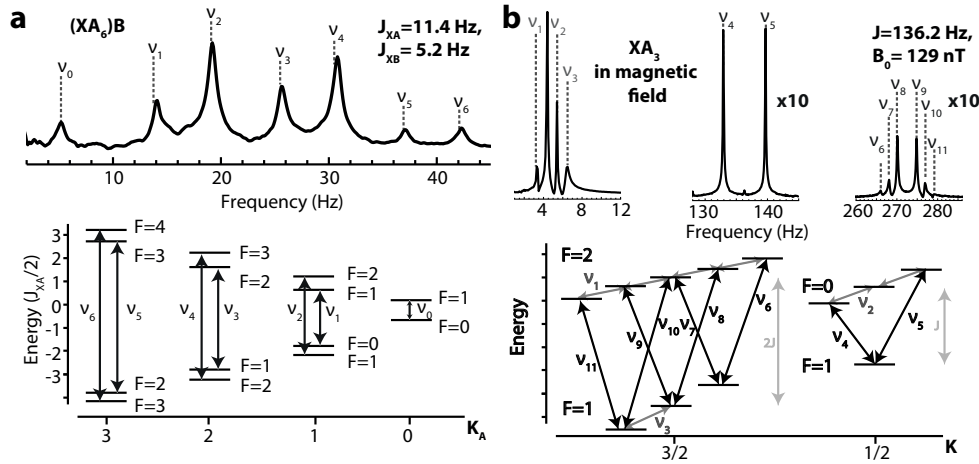


Figure 3.20: a) Zero-field spectrum of dichlorvos, i.e., a compound of the $(XA_6)B$ spin topology, and the corresponding energy-level structure. The relevant J -couplings in the system are also indicated. The dashed vertical lines show the position of lines calculated with the first-order perturbation theory. Different manifolds are labelled by the total spin of A subsystem. The individual levels are labelled by the total spin number F . Only the selected transitions are indicated for clarity. b) Experimentally measured ULF NMR spectrum of $[2-^{13}C]$ -acetonitrile and corresponding XA_3 spin system at a perpendicular field of ~ 129 nT. The spectrum is divided into three regions: low-frequency peaks, corresponding to the transitions between m_F sublevels, two peaks around J -frequency corresponding to transitions in the $K = 1/2$ manifold, and the six peaks around $2J$ -frequency corresponding to transitions in $K = 3/2$ manifold. The largest low-frequency peak around 4.5 Hz does not originate from XA_3 system but from the residual water in the sample. The schematic energy diagram of the ultra-low field Hamiltonian for the XA_3 system based on the first-order perturbation calculations. The manifolds are labelled with the total spin of the A spins. The transitions are indicated with red arrows and labelled to show the relevant peaks position in the above experimental spectrum. The relevant energy levels are labelled by the total spin of the system, while individual sublevels correspond to different values of m_F . Figure a) adapted from [Alcicek et al. \[2021b\]](#).

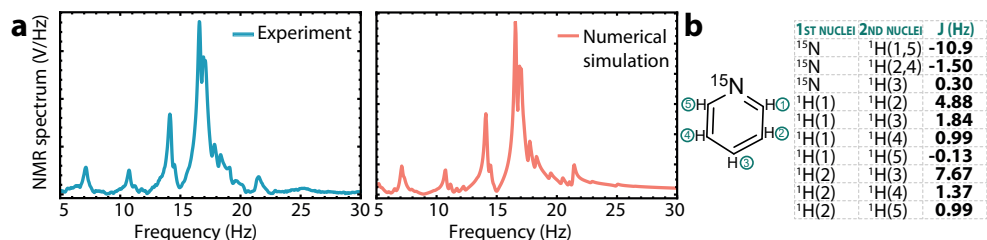


Figure 3.21: a) Measured (left) and simulated (right) zero-field spectra of ¹⁵N-pyridine. The simulation was performed with Spintrum Python package, assuming the uniform relaxation rate $T_2 = 1.7$ s and the J -coupling values taken from literature (Theis et al. [2012]). The peaks in the zero-field spectrum are grouped around ~ 17 Hz, approximately corresponding to a sum of two strongest coupling in the system and spans of 20 Hz (low-frequency peaks are cut from the spectra as excess noise in that region prevent peak identification). The features of the experimental spectra are the results of the spectral overlap of many transitions and are well-reproduced by numerical simulations. b) The structure of ¹⁵N-pyridine and used in the simulations values of scalar couplings between the nuclei in the molecule.

The numerical calculations based on the action of superoperators on the vectorized density matrices can be also used more efficiently calculating the evolution of spin in zero-field conditions (see for example Barskiy et al. [2019b]). As the calculations of the results in the Liouville space are faster, the memory restrictions are more severe requiring use of sparse matrix methods (as the evolution operators resulting from two-spin J -coupling produce such matrices). Thankfully such performance and memory optimizations are implemented in popular scientific-computing software, such as MATLAB. Within this thesis, the custom MATLAB code was used to obtain zero-field spectra under the chemical exchange (see Alcicek et al. [2021a] and Chapter 6), while other NMR-dedicated packages can be used to efficiently calculate the zero-field spin evolution with the use of MATLAB (among them especially highly efficient SPINACH (Hogben et al. [2011])). The example code for simulating spins under zero-field chemical exchange is provided in Appendix A.

The efficiency of the zero-field spectra simulations has been previously tackled in Wilzewski et al. [2017]. The authors reduced complexity of calculation of density-matrix evolution by expressing both the density matrix and the detection operator in the eigenbasis of the zero-field Hamiltonian. In the article, the authors created a Python-based package, called Spintrum (Afach [2018]), with a specific goal of high-efficiency zero-field spectra simulations and fitting of experimental data. The use of low-level programming accelerated with the use of low-level programming routines for linear algebra operations (open BLAS library) results in the so-far unmatched simulations speed of zero-field spectrum of large spin systems. The Spintrum library was used to simulate a significant portion of zero-field spectra presented in this thesis. An example spectrum calculated with the use of this package is shown in Fig. 3.21, while the example code can be found in Appendix A.

Even for spin systems which can be exactly or approximately solved using perturbation methods, the numerical simulations provide means for a quantitative analysis of couplings, based on the spectra fitting (see for example Wilzewski et al. [2017]). For that reason numerically simulated spectra routinely accompany the experimental ZULF NMR results. On the other hand however, numerical simulations of the zero-field spectra on their own lack an obvious interpretation or prediction for determining such generated spectra. Moreover, simulations of zero-field Hamiltonian are unfortunately resource heavy, as even with the optimized packages the simulation of the small molecule, consisting of eleven spins takes up to twenty minutes on the modern 16-core CPU. The simulations of large, biorelevant molecules are not feasible with current approaches. Complexity of zero-field spin spectra calculation even attracted attention from quantum-computing community. In a recent

experiment (Seetharam et al. [2021]), the zero-field spectra of simple spin systems were calculated using a quantum computer operating on a chain of trapped ions. The zero-field NMR simulation was chosen as being an example of classically hard problem. Such techniques may eventually lead to effective simulations of zero-field evolution of large-spins systems.

3.4.3 Zero and ultra-low field NMR signals – conclusions

Zero- and ultra-low-field NMR signals can be generated by thermal polarization and transferring the system from high- to zero-field region. We discussed two important cases of the sudden and the adiabatic transfer. In the former, the rate of change of the Larmor frequency is much shorter than the J -coupling frequency: $\left(\frac{d}{dt}\omega_L\right)\tau \gg J$, which results in non-adiabatic change between high-field and J -coupling basis. In turn, the density matrix of the thermally prepolarized state, diagonal in the high-field Hamiltonian basis, has non-zero off-diagonal elements in the basis of the zero-field spin Hamiltonian. This leads to generation of oscillating magnetization (zero-field NMR signal) without the need for the magnetic field pulse. In case of adiabatic transport, the system is continuously in the eigenbasis of the instantaneous magnetic-field-dependent Hamiltonian of the system. Then, the thermally prepolarized state leads to imbalance in populations of singlet and triplet states observed at the zero field, but no coherences are present in the system, so to initiate the ZULF NMR signals, magnetic-field pulses can be used. A transverse or longitudinal magnetic-field pulses generate coherences with different selection rules, also leading to different amplitudes of the zero-field NMR signals.

The zero-field NMR signals have both a static and the oscillating components. The oscillating component carries information about the spin-system coupling pattern as well as strengths of specific couplings. The relative amplitudes of both static and oscillating components are specific for the state preparation and the gyromagnetic ratios of the coupled spins.

In the presented analysis, the interpretation of the zero-field NMR spectra was also provided. The appropriate selection rules for observable NMR transitions in zero field were introduced. It was shown that for a simple XA_n system, one can find the eigenergies of the zero-field Hamiltonian and the corresponding observable transitions. Hence one can calculate the corresponding spectra with resonance occurring at multiples of the J -coupling or odd multiples of $J/2$. For more complicated spin systems or additional interactions present, one can modify the approach by treating the weak interactions perturbatively. This allows to introduce corrections to the energies of levels of the system and hence determine position of ZULF NMR resonances. In many cases, however, due to complexity of spin systems numerical-simulation methods need to be used to explain zero-field spectra.

4 | ZULF NMR IN PRACTICE - EXPERIMENTAL

4.1 ZERO-FIELD NMR SPECTROMETER

In the previous section, we discussed the key stages of a ZULF NMR experiment, i.e., sample polarization, NMR signal generation and detection, and interpretation of the zero-field NMR spectra. This chapter describes the experimental implementations of these stages. Beside the NMOR-based ZULF spectrometer (Sec. 3.3.10), two other ZULF NMR spectrometers were constructed within the thesis realization. The first type is based on a home-built SERF magnetometer and was used in a system used for measurements with thermal prepolarization. The second setup is based on commercial atomic magnetometers and was explored in various experiments using thermal prepolarization, as well as, hyperpolarization techniques. Such a spectrometer was first constructed during the thesis's author stay at the University of California at Berkeley and incorporated into a portable zero-field setup (see Chapter 6 and Put et al. [2021]). The second incarnation of the system was later built in Kraków and used in many experiments described in this dissertation (Chapters 5, 7). Below, the setups, as well as general experimental procedures in zero-field NMR experiments are discussed in more detail.

4.2 SAMPLE PREPARATION

The liquid samples for the zero-field NMR experiments are held in standard 5-mm NMR tubes (Wilmad-LabGlass WG-1000-7 NMR). The neat liquid samples are transported directly to the NMR tube, while the solid samples are dissolved in the appropriate solvent. It should be stressed that since at the zero field uncoupled spins only produce a static magnetic field, there is no need to use deuterated solvents for ZULF NMR spectroscopy. This is a significant distinction of this incarnation of NMR with respect to its high-field counterpart.¹

Sample for thermal polarization

Samples for thermal measurements are typically flame sealed. As the oxygen dissolved in the liquid can be a significant source of paramagnetic relaxation of the NMR signals (Abragam [1961]), the NMR samples are degassed before sealing. The process of degassing is done with the use of the short Schlenk line (Fig. 4.3a). The sample is held pressure tight with the use of a special manifold (Wilmad 5 mm NMR Tip-Off Manifold). The container with liquid nitrogen or the mixture of acetone and dry ice is then brought close to the NMR tube and the sample is frozen (in many cases, the sample can just rest in the vapor and freeze without submerging in the liquid). While the sample is frozen, the valve on top of the tip-off manifold is opened and the air above the sample is pumped out. Next, the valve is closed and the sample is thawed. As the sample melts, the residual gases previously dissolved in the liquid come to the gas phase (as the pressure above the liquid is significantly lower). This **freeze-pump-thaw cycle** is then repeated 3-4 times, until the pressure over the liquid is below 10^{-4} mbar. The typical volume of the NMR sample used in

¹ Note that while in high fields deuterated solvents are popular they are not always used.

zero-field NMR ranges 200 and 300 mL. The sample volume affects the signal amplitudes registered by the atomic magnetometer. As dipolar in nature, the magnetic field of the polarized NMR sample quickly decays with the distance only a small liquid volume contributes to the signal. The small sample volume (see Fig. 4.2a)) is also beneficial as the zero-field NMR spectroscopy often requires working with neat, isotopically enriched liquids. Such liquids are expensive or hard to obtain in large quantities.

Sample for parahydrogen induced polarization experiments

Samples for parahydrogen experiments are typically prepared by dissolving the appropriate metalloorganic catalyst and the desired target molecule in the solvent. Typically, in the experiments described within this thesis, sample volumes of such experiments are larger and lie in the range of 400-600 mL. There is a threefold reason for that. First, larger samples produce higher magnetization and thus larger NMR signals detected with the magnetometer. Second, the amount of the labelled substance in the samples is either very small or zero, so larger samples can be readily prepared without significant expense.² Lastly, the process of bubbling of parahydrogen through the sample tends to accelerate the evaporation of the sample, which means that larger samples allow for longer ZULF NMR experiments using this hyperpolarization technique.

After chemical preparation, the samples for parahydrogen experiments are put in 5-mm NMR tubes, but, instead of flame sealing them, the tubes are connected to the bubbling system described in Sec. 4.3.3. The teflon 1/4-inch tubing is stretched over the top part of the NMR tube, providing a sealed connection. This way the tube can withstand up to 10-bar pressure, but in a typical parahydrogen experiment presented here, gas pressure did not exceed 6 bars.

4.3 SAMPLE POLARIZATION AND TRANSPORT TO ZERO-FIELD

4.3.1 Magnet for prepolarization

In most spectroscopic experiments presented in this dissertation, NMR samples are thermally prepolarized in the magnet outside of the measurement (ZULF) region. The magnets used to obtain presented results were either a commercial Halbach cylinder array, producing up 1.5-T homogeneous field inside the bore or a home-made assembly of magnets arranged in a pseudo-Halbach dipolar array (Taylor and Sakellariou [2017]). The home-made system was assembled from 24 cuboid neodymium (NdFeB) magnets (N48 or N50 material) with external dimensions of 50x15x15 mm³. The magnets were not sorted based on the field strength or magnetization alignment. The magnets were placed inside an aluminium frame, through an aluminium shield, exposing only one slot in the magnet assembly, providing safety of the construction. The magnets in the complete arrangements are held only by friction. The inside bore walls of the magnet is made of aluminium and are thin to ensure maximum size of the bore. In the constructed system, it enabled installation of an 11-mm outer-diameter solenoid (piercing solenoid) in the bore. The field inside the bore was 1.6 T for the N48 magnets and 1.9 T with the N50 magnets. The magnet assembly is surrounded by a steel shield to minimize a leakage of the magnetic field outside of the magnet. While this enables placement of the magnet close to the magnetic shield, one still needs to be cautious not to saturate the outer-most layer of the shield. Such magnetization would affect the magnetic-shield performance. The photo showcase the magnet during assembly as well a technical

² Labelled substances are much more expensive than their naturally-abundant counterparts.

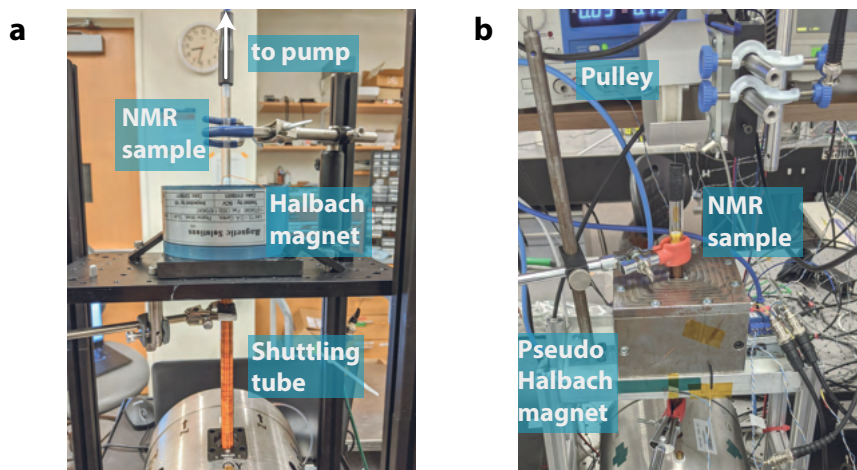


Figure 4.1: The upper part of the ZULF spectrometer. a) mobile spectrometer, b): home-built SERF-based ZULF spectrometer. The crucial parts of the prepolarization and the transport system are highlighted. The setup on the left is using a pneumatic shuttling, with the vacuum line attached to the top and the Halbach magnet (Magnetic Solutions). The sample shuttles inside the tube onto which the solenoid is wrapped. The setup depicted on the right uses a mechanical shuttling with the pulley while the sample is prepolarized in the pseudo-Halbach array assembly.

drawing of the parts of the magnet holder can be found in Appendix C. When using the unshielded Halbach magnet (see mobile spectrometer in Chapter 6), the magnet was placed on the steel board to minimize the field at the position of the mumetal shield as seen in Fig. 4.1 a).

4.3.2 Sample transport in remote-prepolarization experiments

In the remote-prepolarization scheme, samples need to be transported between the high-field prepolarization region and the ZULF detection region. This transport has to occur in times much shorter than the longitudinal relaxation time T_1 of the nuclear spins of the measured samples. In the spectrometer presented here, the samples move along the vertical path between the magnet, placed above the magnetic shield, and the shield. In all experiments, the samples were only transported up, while transport downward occurs in a free fall. The transport up was done either pneumatically or mechanically. In the former case, samples were sucked up with by a vacuum attached to the top of the shuttling tube (see Fig. 4.2a)). A teflon spacer was typically placed around the glass NMR tube to center the tube inside the shuttling tube and maximize the pulling force on the tube. This enables application of a small air flow to lift the sample. The pneumatic-shuttling system was burdened with some problem. It repeatably required some adjustments. First, it was found that the pressure of vacuum housed to labs fluctuates, causing, in the extreme cases, interruption in shuttling of the samples. The compact vacuum pump was used to remedy this problem, but the disadvantage of this solution was noise produced by the pump. Another disadvantage of pneumatic system was that the air flow had to be adjusted for each sample, as the movement is affected by the total mass of the NMR sample. Nonetheless, such a scheme was used to obtain the results with the compact ZULF NMR spectrometer (Chapter 6). A particular advantage of the pneumatic system was that when well adjusted, it enabled minimization of mechanical vibrations in the measurement system. Alternatively, mechanical transport was used (see Fig. 4.2b)). It was realized by attaching a thin string (a plastic fishing line worked well) to the NMR tube. The other end of the string was wrapped around a pulley attached to a stepper motor placed above the prepolarizing magnet. Motion of the stepper motor was controlled through an Arduino interfaced with the

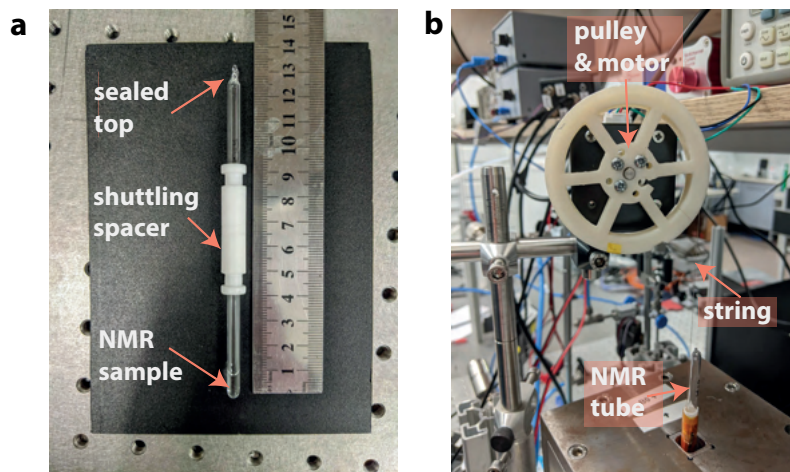


Figure 4.2: a) A typical NMR sample used in the thermal prepolarization experiments. The liquid takes about 1 cm of the bottom of the sample, the top is sealed up following degassing. The teflon spacer can be used to position sample in the shuttling tube. b) Mechanical system for transporting sample in prepolarization experiments. System consists of stepper motor and 3D printed pulley, while the NMR tube is attached to the system with the string.

LabView programme running the whole experiment. The motor moved fast when transporting the samples back to the ZULF NMR region, effectively allowing the free fall of the sample. After the measurements, the motor spins in the reverse direction moving the sample from the detection region. The mechanical transport allowed for thousands of experiment repetitions without the loss of consistency in shuttling, while the compact size of the shuttling setup was also its advantage. As the stepper motor can produce significant mechanical vibration when accelerating and stopping, special care had to be taken, however, to mechanically separate the magnetometer from the stepper-motor system. Top parts of ZULF spectrometers (mobile and featuring home-built SERF magnetometer) are shown in Fig. 4.1, where both the shuttling system components and the magnets used for prepolarization are highlighted.

4.3.3 Bubbling system for parahydrogen-induced-polarization experiments

In zero-field NMR experiments using parahydrogen-induced polarization, the sample magnetization was created inside the magnetic shielding, i.e., without the need for moving the NMR samples. For this purpose, however, the samples had to be saturated with parahydrogen. This was accomplished with the use of a small capillary tube ($1/4$ inch of the outer diameter, 0.012 inch of inner diameter) submerged in the samples, responsible for a creation of small parahydrogen bubbles near the bottom of the NMR tube. The gas inlet and the outlet were connected to the bubbling system (Fig. 4.3b), designed similarly to one presented in Theis [2012]. The bubbling system had two inlets. One of them was for the nitrogen gas, which was used for purging the system from oxygen. The second one is used to supply parahydrogen. The outlet of the system was connected through a needle valve and the mass flow controller to ventilation. The bubbling rate was controlled by adjusting the needle-valve or the mass-flow-controller set points. The inlets could be directly connected to the outlet, bypassing the tube through two short lines. The first short line, controlled by a manual valve, was opened while connecting gas to the manifold. This allowed to immediately equalize the pressures across the inlet and outlet, which prevented the samples from being sucked into the outer tubes. During the experiments, the manual short line was closed. The second short line was operated with the solenoid valved controlled with computer software. During bubbling, the

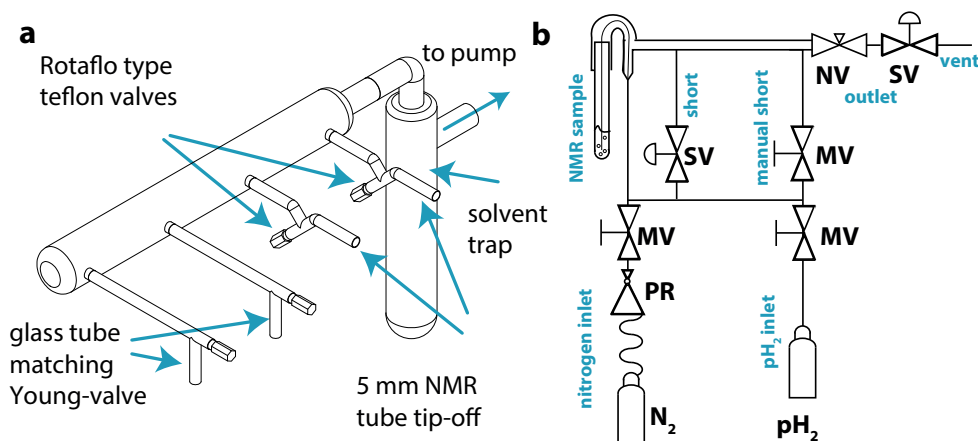


Figure 4.3: a) Schematics of the Schlenk line used to prepare NMR samples for thermal prepolarization. The vacuum pumped is protected by the solvent trap submerges while in operation in liquid nitrogen. The Schlenk line has 4 ports, each one with the separate valve. Two of them can be used to connect Young-valve tubes (not used in the work presented here), while the other two end with the tip-off manifolds for 5 and 10 mm NMR tubes for flame sealing under vacuum. b) Diagram of the bubbling system gas manifold. The system has inlets for the purging gas (N_2) and parahydrogen. Those manifolds can be cut from the rest of the system with the use of manual valve (MV). The pressure of nitrogen is reduced with the use of pressure regulator (PR) to the 4-5-bar level. With both of the short lines (marked in the figure), one operating with MV and the other with the solenoid valve (SV), the gas can flow through the small capillary submerged in the liquid sample. The used gas is directed towards the outlet line, where a needle valve (NV), or mass-flow controller (not shown here) controls the flowrate of gas through the NMR sample. The outlet can be opened or closed to ventilation with the use of a solenoid valve.

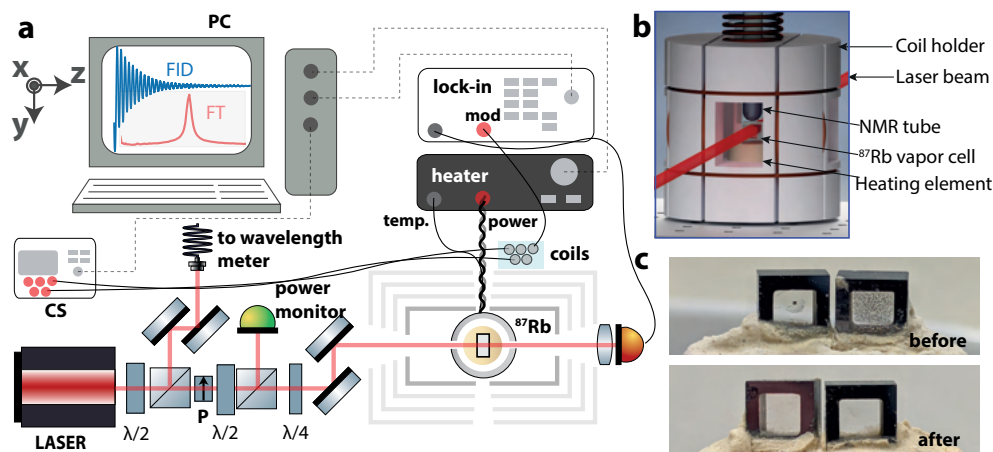


Figure 4.4: a) Schematics of the SERF magnetometer used in one of the ZULF NMR spectrometers constructed within this dissertation. The laser was tuned to center of pressure broadened ^{87}Rb D1 line and was monitored with the wavelength-meter. Circularly polarized light of an adjusted intensity (linear polarizer and waveplates) was directed to the four-layer magnetic shield (indicated with the grey lines), where it illuminated the vapor cell inside the oven. The laser beam passes there through the oven (with optically transparent windows) and the vapor cell mounted on the ceramic pedestal heated resistively (indicated by the yellowish circle in a diagram). The laser beam intensity is measured with the photodiode. The optical signal is demodulated by the lock-in amplifier. The lock-in provides the oscillating voltage signal connected through resistors and the high-pass filter to x coil. The heater controller and the lock-in amplifier is controlled with the use of computer. The multi-channel low-noise current source is used to zero the magnetic field inside the shield. b) The "heart" of the atomic magnetometer: vapor cell placed on the ceramic pedestal residing inside the oven. The NMR sample is stopped right above (within 2 mm) the vapor cell (for clarity the separating upper piece of oven is not shown). c) Vapor microcells used in the SERF magnetometer. The top picture shows a rubidium droplet and "metallic mirror" formed on the side of the vapor cell blocking partially the laser beam. The metallic deposition onto the optical windows resulted from the failure in the heating system and subsequent temperature gradient. The bottom pictures shows the same vapor cell after "curing" where the air around them was heater to $\sim 200^\circ\text{C}$ while the ceramic pedestal they are cemented onto were cooled by water. The whole curing process took 10 days. Path of the laser beam was marked with the red line.

short line was closed, sending the gas through the sample. When the bubbling was supposed to stop, the short-line solenoid valve was opened, which completely stops bubbling within about 100 ms. During the bubbling, the gas flows through the tube to the capillary and bubbles through the sample, while the used gas flows through a larger tube to the outlet of the bubbling system. The outlet solenoid valve was also controlled via software, i.e., the valve was open during the bubbling stage and closed during the measurements. The outlet valve also remained open when purging the system with nitrogen gas before the experiment and venting the system out of hydrogen before changing the sample.

4.4 SERF MAGNETOMETER

As mentioned previously, one of the ZULF NMR setups used in this work was based on the home-made single-beam SERF magnetometer. The schematic of this magnetometer setup is presented in Fig. 4.4. The magnetometer used a single laser beam tuned to the center of the pressure-broadened D1 line of rubidium (795 nm).

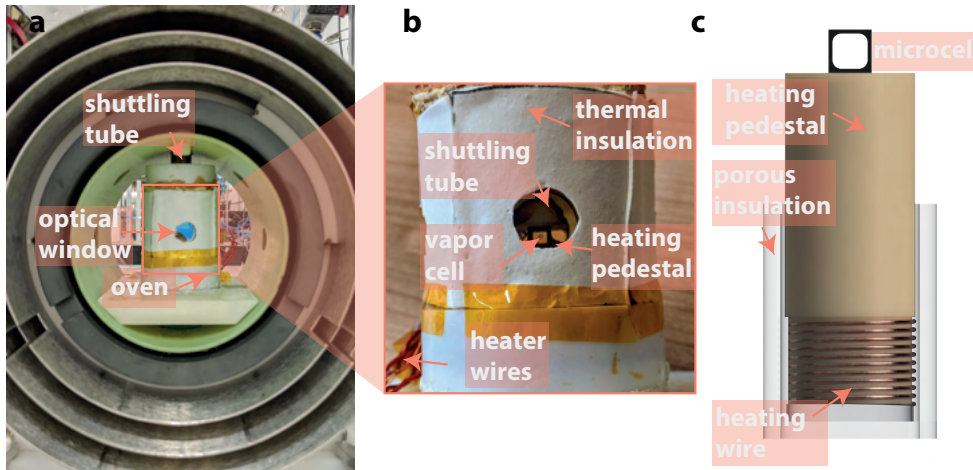


Figure 4.5: Vapor cell oven used in the homebuilt SERF magnetometer. a) View of the oven inside the magnetic shielding (endcaps taken off for the photo). The optical window (one of four) is visible. b) Close-up of the oven, showcasing the vapor microcell on the heating pedestal visible through optical windows. The end of the shuttling tube as well as the leads of the heating wire are also visible. c) Render of the heating system used for most of studies with home-built SERF-base spectrometer. The microcell rests on heating element enclosed in the porous cerami insulation. The pedestal conducts heat generated by running AC current through the heating wires (at the bottom of the pedestal).

The light beam interacting with the rubidium atoms was circularly polarized with the use of a high-quality crystal polarizer and a quarter waveplate. The wavelength and intensity of the laser light was monitored independently (no active stabilization of the laser parameters was used) using a photodiode (Thorlabs PDA36A) and the wavelength meter (HighFinesse Wavelength Meter). The laser beam illuminated the whole volume of a vapor cell (Twinleaf VC 4x4x2 mm) filled an isotopically enriched sample of ^{87}Rb and 700 torr of molecular nitrogen as a buffer gas. The vapor cell was placed inside and custom-made oven made of a high-temperature plastic (seen in Fig. 4.5, and was resistively heated. The 300-kHz AC current was used to reduce magnetic noise (modulation was strongly outside of the magnetometer bandwidth). A temperature sensor (PT1000) was used to monitor and control the temperature of the vapor. The second task was accomplished by controlling a power output of the oven current driver using a PID controller (Twinleaf TCHF-50V). The cell was completely enclose in the oven with four optical access points (windows with an anti-reflective coating) visible in Fig. 4.5. Intensity of light traversing the vapor cell placed inside the shield was measured with a photodiode in a transimpedance arrangement (Thorlabs PD100A). The photodiode voltage signal was connected to the input of the lock-in amplifier (Zurich Instruments MFLI) and demodulated at the first harmonic of the modulation frequency of the x -oriented magnetic field (Fig. 4.4). The signal from the amplifier was high-pass filtered (reduction of the noise outside of the magnetometer bandwidth) and then digitized with the ADC converted built in the lock-in amplifier. A multichannel current source (DM Technologies) was used to shim the magnetic field inside the ZULF region. The computer was used to control the heater, lock-in amplifier, and the current source.

In the home-made SERF magnetometer, the vapor microcell was used (visible in 4.5b). To provide high concentration and operation under the SERF regime, the cell had to be heated to the temperature above 160°C . As mentioned above, the heating was done resistively with high-frequency AC current. In the first iteration of the spectrometer, the heating was done through the thermally conductive ceramic pedestal, as shown in Fig. 4.5. The further-from-the-cell end of the pedestal was wounded with a double-twisted wire, which reduced the inductance and the

magnetic field from the current. The high-temperature cement (Omegabond 400) was used to mount the cell onto the pedestal and provide a good thermal interface to the heating element (pedestal). Many different wires were tested for heating purposes. Many of them failed due to the high-temperature operation that led to burning of the electric insulation and subsequent shorting of the wires. Even the high-temperature insulation (made from kapton or teflon) failed after couple of days of continuous heating. Another consideration for the wire is the material. The most popular heating material (nichrome) is magnetic, which would hinder the performance of the magnetometer by introducing stray magnetic fields inside the magnetic shielding. Finally, a phosphor bronze wire with high-temperature enamel isolation was used to heat the cell through the ceramic element (a total resistance of $20\ \Omega$). One could use also a copper wire with high-temperature enamel isolation (here copious testing were performed to find the one with the most mechanically and temperature resistant insulation), keeping in mind that operating with a small load ($2\ \Omega$) would increase the heat generation in the heater amplifier, which may lead to its eventual failure. The heating employing this last solution failed after running constantly for about a year.

It should be noted that heating using the ceramic element has some disadvantages. After failure of the heating system and a subsequent sudden fall of the cell temperature, the rubidium droplets formed on the optical windows of the cell, blocking the optical access for the laser beam. It is believed that this was caused by the temperature gradient across the cell. As the silicon rim of the cell provides thermal conduction to the heating element, after the heating failure, the sapphire windows become cold spots and hence the center of rubidium-vapor condensation. As the rubidium deposit hinders the performance of the optical magnetometer had to be cured before putting them back in the setup. This was accomplished by once again placing the cell on the ceramic tubes and inside the oven, but this time heating the air around the cell to 200°C and cooling the ceramic element by placing it in cool water. After 10 days, such curing process removed the rubidium deposits from the cell (Fig. 4.4c).

After many problems with wire heating, the heating scheme in the SERF magnetometer was changed. In this new incarnation, the heater resistors were installed inside the oven, next to the cell to heat up the vapor cell. The heaters were low-inductance, so that a tightly wound electric paths cancel the magnetic field effectively. Moreover, a pair of heaters were used pressed against each and connected such that the magnetic fields are cancelled effectively. This solution eliminated the problem of rubidium droplet formation. In this case, care needed be taken to avoid burning of the heater support material³ or detaching of the soldered wire from the resistor due to high temperature.

4.5 SOLENOID AND COIL ASSEMBLY

To manipulate the spins, various magnetic fields need to be used. These fields need to be generated and often dynamically controlled, so various magnetic-field coils are installed in the ZULF NMR system.

For example, in our experiments, a tube connecting the high-field and ZULF regions and hence providing the pathway for NMR samples, was wrapped with a **solenoid**. This solenoid-generated guiding field ensured a specific orientation of the nuclear polarization of the samples when reaching the ZULF region. Moreover, it was also used to provide the field during experiments with parahydrogen-induced polarization. The solenoid can either end just before the detection region (Fig. 4.6c), or stretch the whole length of the magnetic field (Fig. 4.6d). The latter solution, called a **piercing solenoid**, minimizes the leakage of

³ In one of our experiment, kapton heaters did fail for that reason within a couple of days.

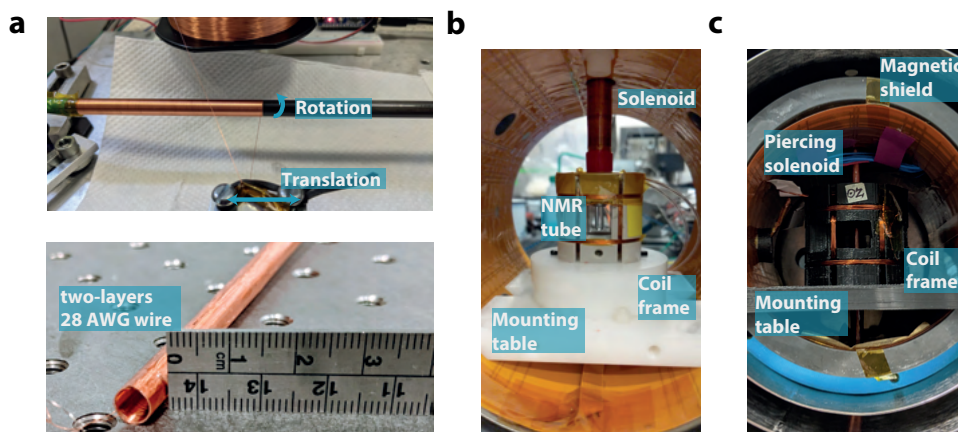


Figure 4.6: a) Process of winding the solenoid coil with the use of two programmable, stepper motors. b) Close up of the wound piercing solenoid (this time with the support tube removed). The whole solenoid with a length of 30 cm is wound with two-layers of a 28 AWG wire (0.126 mm). The inside of the solenoid has a diameter of ~ 5.5 mm large enough to enable free shuttling of 5 mm NMR tube. c) The coil frame, holding three pairs of Helmholtz coils inside magnetic shielding, with the solenoid leading to the of the assembly. The frame also holds the commercial magnetometer (here taken out not to obscure the view). As seen the the NMR sample was measured outside the solenoid, while during operation the sensor package was brought in contact with the tube to minimize the distance between sensing volume and the sample. The assembly is part of the mobile ZULF spectrometer featured in Chapter 6. d) The coil frame and support for the commercial magnetometer (not inserted for clarity) used in the ZULF NMR spectrometer with the piercing solenoid going through the whole width of the magnetic shield. The sensor is normally placed in a way its package touches the solenoid to minimizes the distance between the magnetometer and NMR sample. The assembly is part of the one of two ZULF NMR spectrometers operating in Kraków that were used to obtain results presented in Chapters 5 and 7.

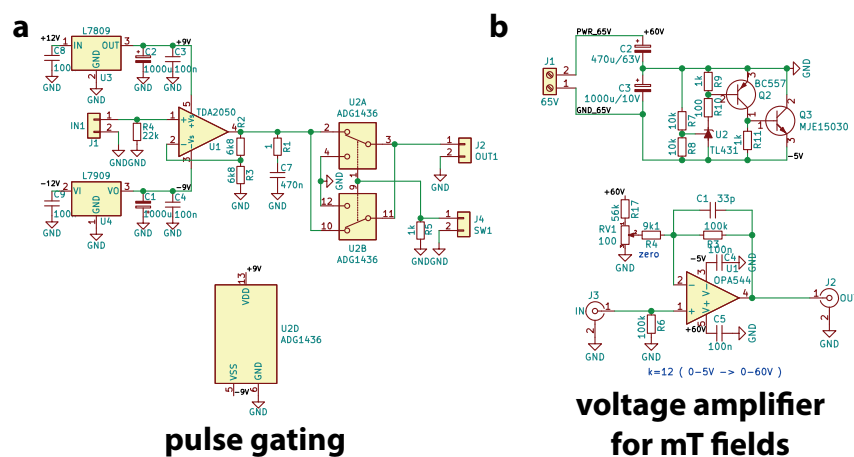


Figure 4.7: a) Diagram of the electronic circuit used for generating DC magnetic-field pulses with a submicrosecond precision. The setup is based on a pair of dual-channel single-pole double throw analog switches. b) Electrical diagram of the voltage amplifier, providing current for the solenoid in experiments that required mT fields. The circuit, which was supplied with a 60-V voltage, is linearly amplifying the voltage of the function generator.

the solenoid field to the magnetometer placed close to the sample. This allows the operation at finite magnetic fields without hindering sensitivity or completely saturating the atomic magnetometer. The piercing solenoid should be wound with a thin wire and made out of two layers wound back and forth to fully reduce the leakage field.

As a manual winding of the solenoid is impractical, the solenoids used in ZULF spectrometers were wound using a simple built coil-winding system. It consisted of two stepper motors, where one motor spun the coil holding the tube, while the other guided the wire across the length of the support tube (winding process shown in Fig. 4.6a). The wire unwinds itself from the large spool rotating around the central post, while the rubber band is used to provide tension and adjust to changes in the strain as the spool unwinds. Both motors are controlled with stepper motor drivers connected to Arduino Nano controlled with the use of LabView software. The layers of the solenoid were glued together using epoxy to prevent unwinding. The outer layer was additionally protected from mechanical damage (e.g., scratches) with the kapton tape. The two-layer solenoid wound from 0.125-mm copper wire (0.140-mm thickness with insulation) produced fields up to 6 mT applied exclusively to NMR samples.

The nuclear polarization state can be manipulated with the use of magnetic-field pulses. Specifically, in most of zero-field experiments, non-oscillating (DC) pulses are used. To provide a full control over the nuclear spins, arbitrarily oriented magnetic-field pulses need to be generated. This was achieved with **a set of three orthogonal coils**. In our ZULF spectrometers the pulses were generated with three orthogonal Helmholtz coils incorporated directly onto the holder for the atomic magnetometer (Fig. 4.6 c) and d). The coil-holder design allowed to mount the sensor right next the NMR sample or the piercing solenoid. The frame was 3D printed, as the outside of the sensor is relatively cool, while example design of the coil frame can be found in Appendix C. The coil frame and sensor holder is placed on the mounting table inside 4-layer magnetic shielding. The coils were used for generating “sharp” DC pulses (typical $\pi/2$ pulse for ^1H taking $\sim 50\ \mu\text{s}$) and to tip the spins along the sensitive axis, providing the field up to $100\ \mu\text{T}$.

To control the magnetic field produced by the solenoid and the guiding coil, a set of optocoupler relays was used. Their states were controlled with logic (TTL) signals (0 and 5 V). They were used to switch off the coils in less than 1 ms. This

was sufficient for the ZULF NMR experiments presented within this dissertation. For example, it was fast enough to satisfy the sudden-transfer condition discussed in Chapter 3. The relays also ensured that, with the magnetic fields turned off, electrical noise of the sources did not affect the performance of the magnetometer (by introducing additional magnetic-field noise). The voltage to this coils was either provided by laboratory power supplies or by an arbitrary-wave generator. The latter solution was used to create specific magnetic-field profile. Specifically, a linear ramp-down of the field for the adiabatic transfer to the zero field⁴ or to change the direction of the spins were implemented.

To generate short magnetic-field pulses, one cannot rely on the optocoupler relay, as their opening time is too long. Instead, a custom system, enabling switching on the coils within roughly 10 ns was constructed.⁵ The electrical diagram of the system is shown in Fig. 4.7a). The trigger pulses gated the voltage provided to the input channel and the resulting gated pulses are passed onto the Helmholtz coils. Both the voltage reference and the gating signals can be created with the use of arbitrary-waveform generators but also even by such modules as Arduino, where a trigger signal, connected to a specific pins of the module, starts a preprogrammed sequence of square pulses (with the time resolution better than 1 μ s).

For some zero-field experiments, a field in the mT regime has to be provided. This is done to either thermally prepolarize the sample *in situ*, or to provide an appropriate magnetic field for efficient polarization using parahydrogen based polarization. Such a large fields were typically supplied to the solenoid, which, however, required higher voltages and currents than those provided by a typical arbitrary-waveform generator. For that reason the generator output needed to be amplified. In this work, it was done by an electronic circuit shown in Fig. 4.7b). The circuit is powered by a 60-V laboratory power supply and can provide linear amplification of electric signals to the inductive loads. This way an arbitrary field profile can be created with the maximum amplitude of 6 mT.

4.6 DATA ACQUISITION AND EXPERIMENTAL CONTROL

As ZULF NMR signals are low frequency (< 1 kHz), a direct sampling of the magnetometer signal is used to acquire ZULF NMR signals and hence observe the ZULF NMR spectra.

Data acquisition, in the case of the commercial magnetometers used in this work (QuSpin QZFM), was performed with the use of a data acquisition card (DAQ), providing a sampling rate of analog signals at a level of 1-2 kS/s. The same card supplied logic signals used to switch off the relay connected to the solenoid and guiding coil, gate the magnetic pulses, trigger the generation of arbitrary magnetic fields, and sample shuttling. It was also used to control the solenoid valves in parahydrogen experiments. A representative experimental sequences for both the thermal and parahydrogen-induced polarization are shown in Fig. 4.8a) and b), respectively. While the example exploited the sudden-transfer approach, more complicated sequences were also realized with various delays introduced using logic signals. As soon as the spin evolution starts to take place e.g., right after suddenly switching field or/and applying a pulse, the more precise, hardware triggered timing (with sub- μ s precision) is used to ensure exactly the same spin evolution. This precise timing is also used to trigger data acquisition, so that the measured NMR signal is consistent between repeats of the sequence. Rest of the logic inputs (con-

⁴ In that case, the voltage at the solenoid was first ramp down and after reaching zero, the relay is switched off. The adiabatic decrease in the magnetic-field strength can also be achieved by adding capacitors to the solenoid coils, such that a sudden switch of the relay causes an exponential decay of the voltage across the solenoid with a characteristic time dependent on the capacitance and resistance.

⁵ In the portable spectrometer, an alternative system, based on high-voltage, ultra-fast relay (Willamette High Voltage MHVSW), was used to gate short DC magnetic pulses.

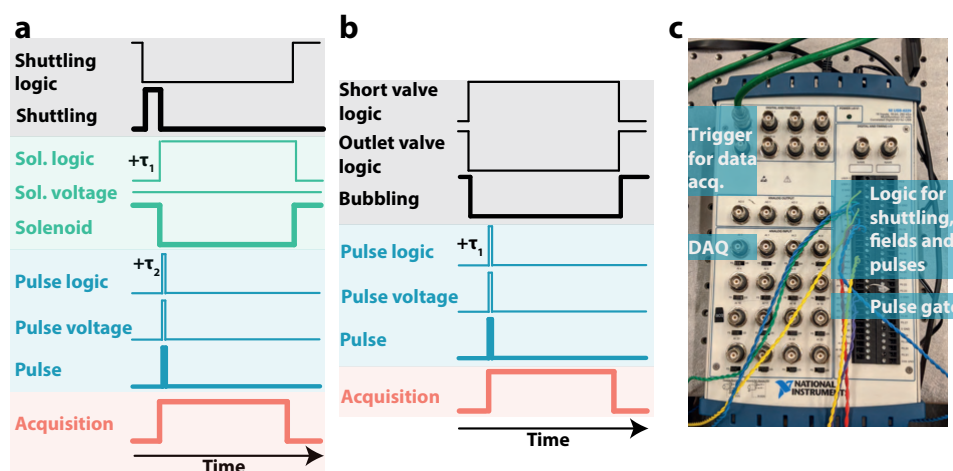


Figure 4.8: a) Timing diagram for the example zero-field NMR experiment with thermal pre-polarization. The zero-field field experiment involves shuttling from the prepolarizing magnet to zero-field, sudden transition to zero-field through a rapid turning off the guiding field of the solenoid and subsequent DC magnetic field pulse. The left columns shows different channels used in the experiment, while the left column shows schematic signal shapes. The shuttling logic channel change of state starts the sequence, as the sample shuttles to zero-field. Then after time τ_1 (taken to be larger than shuttling time, typically ~ 500 ms) the solenoid field is switched off (the logic signal gates relay and cuts the constant voltage supplied to the solenoid). The magnetic field follows after an additional time delay τ_2 . The pulse is hardware triggered on the edge of solenoid logic signal with controllable delay and timed with sub μ s precision. The edge of the solenoid logic signals also triggers data acquisition. After the measurement period, the solenoid field is turned by on and the sample is shuttled back to the magnet. b) The timing diagram for the example zero-field NMR experiment with parahydrogen induced polarization. The bubbling of parahydrogen through the NMR sample at zero magnetic field is followed by DC pulse and data acquisition. The bubbling is controlled with two valves steered by two logic-signal. During bubbling short solenoid valve is closed, while the outlet valve is open. As the bubbling stops, right prior to data acquisition, the short valve is opened while the outlet closes. The magnetic field pulse follows, while the edge of this pulse is used as a hardware trigger to start data acquisition. c) The DAQ card used in the mobile NMR spectrometer used to obtain results in Chapter 6. Different section of the card used for different purposes in zero-field NMR sequence are highlighted. The digital channels (middle right) are used for sample shuttling and guiding field switching, while the timed PFI (bottom right) channels are used to hardware timed logic for NMR pulses. The timing inputs (top left) are used as a trigger for the start for data acquisition, and the analog input channels (middle and bottom left) are used to registered the analog outputs from atomic magnetometer (here not connected).

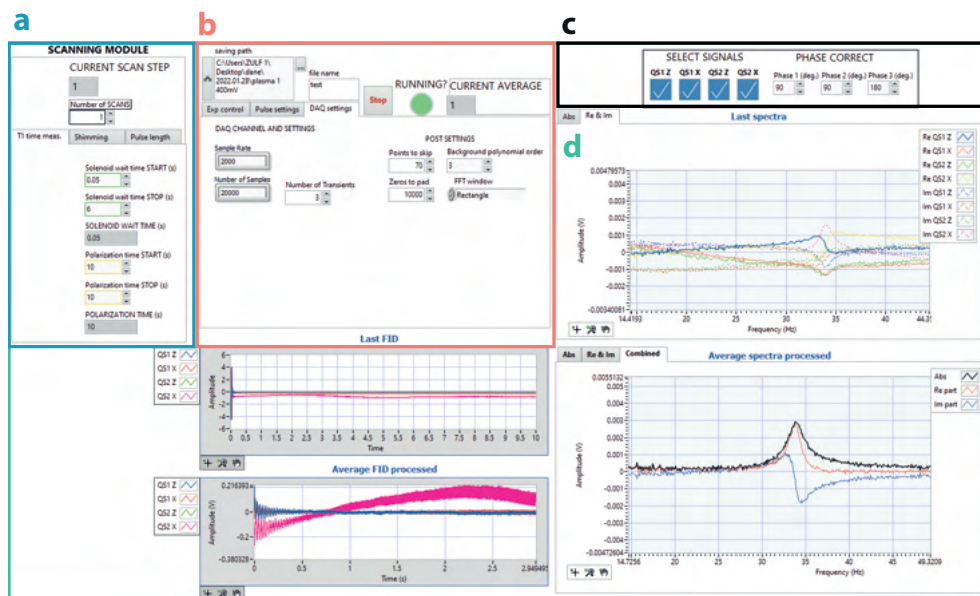


Figure 4.9: Front panel of the custom coded LabView program, running zero-field NMR experiments, exploiting thermal prepolarization. a) Module used to control measurement parameters, e.g., waiting time, prepolarization time, magnetic-field shimming and time for magnetic-field pulses. b) Additional settings, including the filename and directory for saving data (top), experimental timings (first tab), pulse parameters (second tab) and the data-acquisition setting (third tab). c) The panel used to choose channel for acquiring signal, when operating with multi-channel and multisensor setup. The user can choose a phase correction of signal obtained by each sensor to create proper combined spectrum. d) Graphs showing the latest and average FID (time signal) and the resulting spectrum.

trolling sequence before nuclear spin evolution) could be software synchronized as jitters in the timing were not affecting the signal.

While the ZULF NMR spectrometer employing commercial magnetometers used the DAQ card, in the home-built spectrometer, a lock-in amplifier (Zurich Instruments MFLI) was used to detect and acquire the signals. Moreover, through the use of built-in digital channels, the lock-in provided logic signals for controlling the experiment, so that it fully controlled the system. Despite the hardware differences, a typical experimental sequence in that setup was similar to the one shown in Fig. 4.8.

4.7 SOFTWARE FOR RUNNING ZERO-FIELD NMR EXPERIMENT

The NMR experiments presented in this thesis were controlled with the use of software written in LabView. The front panel of the program (user interface) is shown in Fig. 4.9. The interface was split in multiple sections. The first section allowed the user to specify the parameters of the experiment. The specific parameters were: data acquisition parameters, the logic channels used for triggering magnetic-field pulses and shuttling, and the magnetic-field pulse timings. The user also had an option to specify the location and filename of files to save data. Additionally, the panel allowed to automatically vary parameters of the measurement, e.g., storage and prepolarization times for relaxometry measurements, pulse lengths and shimming currents to optimize the ZULF NMR signals. The user also had the ability to specify which channels were used for data acquisition (in case of multichan-

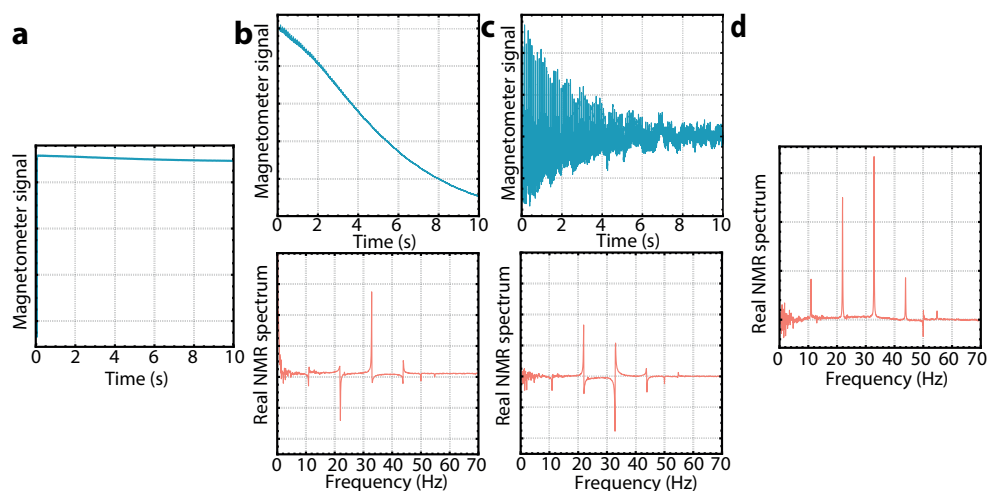


Figure 4.10: Different stages of postprocessing of a zero-field signal from trimethyl phosphate. a) Raw signal measured directly by the magnetometer. The initial large feature at the very beginning of the signal stems from saturation of the magnetometer, by a guiding magnetic field and subsequent magnetic-field pulse. The non-corrupted part of time-signal lays on the nonlinear background. b) Magnetometer signal with a removed initial corrupted part and corresponding NMR spectrum. The clearly visible nonlinear background in the magnetometer signal is clearly visible, as is the oscillating signal from the nuclear spins. c) Signal and corresponding spectrum after background subtraction and reconstruction of initial corrupted points. d) Final zero-field NMR spectrum after additional windowing with exponentially decaying envelope, zero-filling and phase correction. The spectrum shows five peaks at multiples of J -coupling frequency. The power-line harmonics come from the residual magnetic field, leaking into the detection region.

nel or/and multisensor operation). The latest FID signal and its spectrum were displayed on the panel. The averaged/postprocessed time signal and the resulting spectrum were also shown. In case of multichannel operation, a combined spectrum (with a phase manually adjusted by the user) was also produced and plotted. The program itself was based on a number of subroutines (subVis) controlling particular aspects of the experiment: experimental timing, data acquisition, data postprocessing (cutting initial corrupted points and subtracting the background from the time signal), producing and plotting Fourier transform of the signal, as well as, saving the data. During the advancement of the ZULF NMR research, new measurement capabilities were needed so that the program grew in its functionality. The modular characteristic of the subroutines allowed for straightforward changes in code, while the use of LabView allowed for hassle-free adaptation of new hardware into the experimental sequence. The software shown in Fig. 4.9 was used for the ZULF spectrometer based on commercial sensors. A similar program was used in experiments exploiting parahydrogen-induced polarization.

4.8 DATA POSTPROCESSING AND SPECTRUM GENERATION

The data measured directly in the zero-field NMR experiment required processing to obtain a high-quality NMR spectrum. The oscillating magnetic field signal was produced by the nuclear spins as soon as the leading field was switched off or the magnetic pulse was applied. The same strong magnetic field, however, saturated the atomic magnetometer, which, after going back to the zero field, needed time to revive its operation. This **magnetometer dead time**, closely related with the mag-

netometer bandwidth, resulted in corruption of about 30-80 ms of initial data (Fig. 4.10 a). To address the problem, **the initial points needed to be cut off from the raw FID**, before further data processing (Fig. 4.10 b). The magnetometer **signal in zero-field NMR experiment often resides on a large, nonlinear background**. The origin of this background can be different: the sample itself produces a quasi-static decaying magnetization (see chapter), presence of the sample can affect the temperature of the vapor cell causing large drift in the magnetometer signal, while in some commercial sensors strong magnetic field right before detection causes the internal temperature PID loop to misbehave causing a large, slow changes in magnetometer output. This **background was determined by fitting a polynomial function (typical with order of 11-13)** to the magnetometer signal which was then **subtracted from the experimental data** (Fig. 4.10 c). **The initially corrupted points cut from the time-signal can be also reconstructed using signal backprediction methods**. If used, an initial part of the magnetometer signal (typically 1 s) reversed in time used to predict the cut part of the signal with the use autoregressive method, while the coefficient in linear model are estimated using *TimeSeriesModelFit[]* function in Wolfram Mathematica. As the time acquisition parameter was not matched to the optimal signal-to-noise in the resulting zero-field spectrum, the additional multiplying experimental signal by an exponential decaying envelope is used. This procedure effectively weighted down the later points in the time signal, where the noise normally suppresses the NMR signal. Optionally, additional zeros were added at the end of the time signal to increase the number of points in the resulting spectrum. The phase correction (zero and first order) was applied to the resulting NMR spectrum to obtain peaks with absorptive shape. As shown in Fig. 4.10d) the postprocessing resulted in a much clearer and easy to interpret zero-field NMR spectrum. Reader can find the example Mathematica code used to postprocess zero-field NMR data and generate spectrum in Appendix A.

4.9 EXPERIMENTAL-CONCLUSIONS

In this chapter, a hardware used to construct multiple ZULF NMR spectrometers were presented. The role and requirements of key elements of the systems (magnetometer, coils, pulse generation etc.) were explained and specific solution implemented in the spectrometers were presented. The typical experimental sequence was also shown, while the last section provided insights into the data postprocessing, providing clear zero-field spectrum. While the home-built spectrometer was constructed on a standard optical table, a more compact version of the system is feasible (see for example Chapter 6). The reader can also notice that most of the key functions of the ZULF spectrometer can be realized with inexpensive hardware, showcasing one of the key practical advantages of this NMR regime.

Results presented in this chapter were previously published as the following peer-review articles:

1. Alcicek, Seyma, **Piotr Put**, Vladimir Kontul, and Szymon Pustelny. "Zero-Field NMR J-Spectroscopy of Organophosphorus Compounds." *The Journal of Physical Chemistry Letters* 12, no. 2 (2021): 787-792.

Moreover, a part of the material presented here is being prepared for publication under the title:

1. **Piotr Put**, Alcicek, Seyma, Oksana Bondar, Łukasz Bodek, Simon Duckett and Szymon Pustelny. "Zero-field NMR Detection of Pyridine Derivatives by SABRE Hyperpolarization"

5.1 J -SPECTROSCOPY OF PHOSPHOROUS COMPOUNDS

5.1.1 Motivation

Zero-field NMR spectroscopy is based on the J -coupling between spin-1/2 heteronuclei. Often, one of the nuclei of the investigated molecule is abundant, for example ^1H reaches nearly 100% of all hydrogen isotopes, while the abundance of the other isotope is low, such as in the case of ^{13}C that accounts for just 1.1% of all carbon isotopes or ^{15}N , whose natural abundance is 0.36%. The ZULF NMR signals obtained with prepolarization techniques are weak and the corresponding magnetic fields, detected by a near-by magnetometer, rarely exceed 1 pT. Therefore, to obtain high-quality spectra with thermal polarization, isotopically enriched compounds need to be used. Making the ZULF NMR technique a true analytical modality of NMR requires that its limitation be addressed.

One solution to the single-strength problem is to rely on naturally abundant nuclei. Outside of ^1H , the other abundant spin-1/2 nuclei are ^{19}F and ^{31}P . The former was previously studied in ZULF NMR (Tayler et al. [2016]). The authors of that study used difluoroacetic acid, which was measured in the zero field. During the research they encountered another problem of ZULF NMR in the ^1H - ^{19}F system. Specifically, despite being popular in conventional high-field NMR, one encounters the problem of small gyromagnetic-ratio difference of the proton and fluorine nucleus, $\gamma_{^{19}\text{F}} = 0.94\gamma_{^1\text{H}}$. Although high values of the gyromagnetic ratios make these two nuclear attractive objects of study of conventional high-field NMR experiments (see for instance Eq. 2.95), a small difference between them hinders the zero-field signals (see 3.84). For example, for the XA spin system, composed of ^{19}F and ^1H , an optimal magnetic-field pulse (see Chapter 3) produces signals approximately an order of magnitude smaller than the signals generated in the same topology, yet with ^{13}C , replacing ^{19}F as evident by:

$$\frac{(\gamma_{^1\text{H}})^2 - (\gamma_{^{19}\text{F}})^2}{(\gamma_{^1\text{H}})^2 - (\gamma_{^{13}\text{C}})^2} \approx 0.12. \quad (5.1)$$

The other problem of using nuclei with similar gyromagnetic ratios is manipulation of the spin state to achieve the highest possible ZULF NMR signal. This requires rotation of one spin with respect to the other by π and hence, in such a case, customary DC magnetic-field pulses become impractical to implement. In particular, pulses flipping the respective spin orientations are either long or strong, so that their imperfections or decoherence during the pulse diminish the sample polarization. This problem was addressed by the authors by manipulating spin not at the zero field but at a strong magnetic field, where the difference in the Larmor frequencies becomes large enough and one can selectively inverse the orientation of a given spin (akin to regular high-field NMR). Next, the nuclear sample is adiabatically transferred to the zero field. When a resonant AC field with a half-sine envelope is applied, the spins inversion occurs, and the enhanced zero-field signal is observed.

Here, we present the first zero-field NMR study of compounds containing ^{31}P . As the gyromagnetic ratio of phosphorus nuclei is significantly different than that of ^1H , quality zero-field spectra can be readily obtained. In the presented study, a group of organophosphorus compounds were investigated using the zero-field J -spectroscopy, which allowed for chemical identification of even similarly structured compounds. This was possible because the characteristic J -coupling frequencies of the compound were different enough (about 0.5 Hz) to produce detectable shifts of the resonance position in ZULF NMR spectra. An analytical calculation (also based on a perturbative approach) as well as numerical simulations were used to explain zero-field spectra, providing an excellent agreement with the experimental results. Among the many investigated compounds, one had the strongest J -coupling ever detected in ZULF NMR.

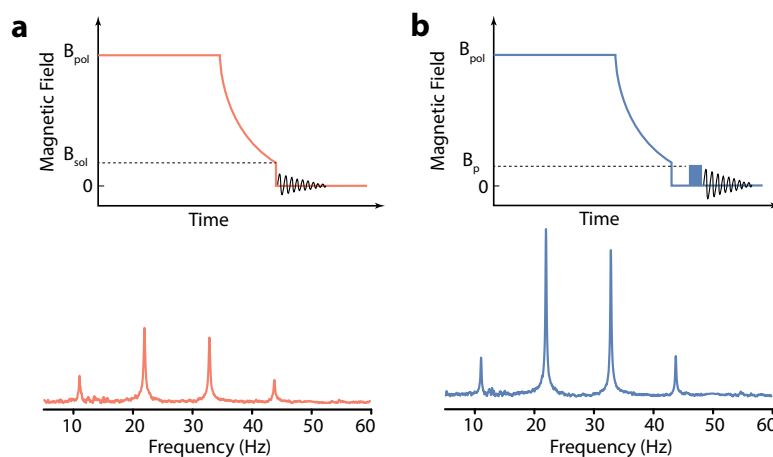


Figure 5.1: a) (Bottom) Zero-field NMR signal of trimethyl phosphate following sudden transport to zero-field. (Top) Schematic profile of the magnetic field in the zero-field experiment. b) (Bottom) Spectrum of trimethyl phosphate following the sudden transfer to zero-field and the optimal pulse, resulting in enhanced signal amplitude. (Top) Field profile for this experimental sequence. Each spectrum is a result of averaging 32 transients. The optimal pulse significantly increases the amplitude of the signal. Figure adapted from [Alcicek et al. \[2021b\]](#) (SI).

5.1.2 Organophosphorus compounds

Organic compounds containing phosphorus, so-called **organophosphorus compounds**, play an important role in human biology. In particular, they are crucial for metabolism and cell structuring ([Corbridge \[2013\]](#)). The conventional, high-field NMR techniques were used to study both inorganic phosphate and organic phosphorus-containing compounds (e.g., adenosine triphosphate - ATP), providing information about cellular metabolism and intracellular pH conditions ([Liu et al. \[2017\]](#)). Within the same group of compounds, however, there are toxic chemicals, which are widely used as pesticides, insecticides and fungicides ([Tajti and Keglevich \[2018\]](#)). In fact, improper handling of organophosphorus-based pesticides may lead to significant contamination of the environment. This implies the necessity of implementation of sensitive, yet robust techniques of detection and monitoring of the compounds (see for example [Kumar et al. \[2013\]](#)).

5.1.3 ZULF NMR of organophosphorus compounds

Within this dissertation, organophosphorus compounds were investigated both experimentally and theoretically with the use of zero-field NMR spectroscopy. Starting from two large XA_n spin systems, we demonstrated the analytical capabilities of the technique. Next, we proceeded to the investigation of the spin systems with a range of coupling strengths and explain the observed zero-field spectra with the use of perturbation theory and numerical simulations. Details of the study are presented below.

The signal for the pair of coupled ^1H - ^{31}P nuclei can be generated after following a sudden transfer for zero-field (see Fig. 6.1b). Moreover, an additional pulse can be used to generate the coherences (Chapter 3). For the ^1H - ^{31}P pair, the optimal pulse, flipping the spin of one nuclei with respect to the other, rotates the proton by 5π . The enhancement of the signal from such an optimal pulse is (Sec. 3.4.2):

$$\frac{\gamma_{1\text{H}} + \gamma_{^{31}\text{P}}}{\gamma_{1\text{H}} - \gamma_{^{31}\text{P}}} \approx 2.4. \quad (5.2)$$

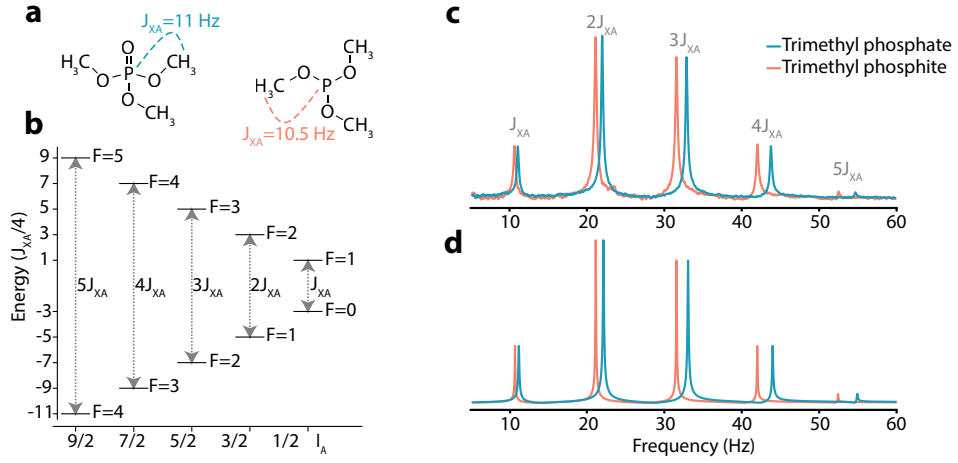


Figure 5.2: a) Molecular structure of two ^{31}P -containing XA_9 spin systems: trimethyl phosphate (left) and trimethyl phosphite (right). The relevant J -couplings are indicated by the dashed line and their values are shown. b) Schematic representation of the energy-level structure of the spin systems at the zero field. The manifolds are labelled by the total proton spin I_A . The transitions observable in the system are indicated by dashed arrows. c) Experimental zero-field NMR spectra of trimethyl phosphate (blue) and trimethyl phosphite (red). The line positions are indicated by multiples of the heteronuclear J -coupling strengths. Due to the unique environment (different J -couplings) and narrow linewidths, the two spin systems are clearly discernible. Each spectrum is a result of averaging 128 transients. d) Simulated zero-field spectra of the trimethyl phosphate (blue) and trimethyl phosphite (red) calculated using Spintrum package (see Sec. 3.4.2 and also code provided in Appendix A). The positions and relative strengths of the NMR lines match the experimental results shown in c). Figure adapted from Alciček et al. [2021b].

The zero-field spectra of trimethyl phosphate after the sudden zero-field transfer with and without the optimal pulse are shown in Fig. 6.1c), demonstrating the significant enhancement of the signal when the pulse is used.

In liquid samples under the zero magnetic field, the total spin Hamiltonian takes the form:

$$\hat{\mathcal{H}} = 2\pi \sum_{i>j} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j, \quad (5.3)$$

where the specific coupling strength is characteristic for a given spin pair, bond type, and geometry. In the compounds studied here, the J -coupling between hydrogen and phosphorus nuclei is relevant. For instance, in the case of a single-bond coupling, the strength of the interaction reaches hundreds of hertz while the three-bond coupling is almost two orders of magnitude weaker. Simultaneously, coupling to quadrupolar nuclei, which may be present in such molecules due to the presence of ^{35}Cl or ^{37}Cl , is neglected in the analysis as such nuclei relax fast enough not to be visible in zero-field spectra. We also did not include coupling to nuclei that have low abundance (e.g., ^{13}C). We started our investigation with the study of two XA_9 spin systems. Molecular structures of the studied trimethyl phosphate and trimethyl phosphite are shown in Fig. 5.2a). Both molecules consist of 9 magnetically equivalent hydrogen nuclei coupled to the central ^{31}P nucleus. The total Hamiltonian of such a system (Eq. 5.3) can be reduced to:

$$\hat{\mathcal{H}} = 2\pi \sum_i J_i \hat{\mathbf{S}} \cdot \hat{\mathbf{I}}_i = 2\pi J_{XA} \hat{\mathbf{S}} \cdot \sum_i \hat{\mathbf{I}}_i = 2\pi J_{XA} \hat{\mathbf{S}} \cdot \hat{\mathbf{I}}_A, \quad (5.4)$$

where the energy eigenlevels are characterized by the total proton spin $\hat{\mathbf{I}}_A$ and the total coupled spin $\hat{\mathbf{F}} = \hat{\mathbf{S}} + \hat{\mathbf{I}}_A$ as shown schematically in Fig. 5.2b). Applying the

selection rules for the observable magnetic transitions in zero-field (Sec. 3.4.2), the spectrum of such a XA_9 system consists of five lines at J_{XA} , $2J_{XA}$, $3J_{XA}$, $4J_{XA}$ and $5J_{XA}$ (see also Sec. 3.87), as seen in the experimental data shown in Fig. 5.2c). The difference in the J -coupling strengths, stemming from the unique electronic environment enabled unambiguous identification of similar (these and others) compounds, even though they have the same spin topology, demonstrating the capabilities of ZULF NMR for chemical fingerprinting.

The next stage of the study were the analysis of molecules with multiple heteronuclear coupling strengths to the ^{31}P nucleus. As an example we presents here the studies of molecules with XA_nB_m spin topology, whose zero-field spectrum can be explained using the perturbation theory. One such a spectrum of an organophosphorus molecule– dichlorvos– of the $(XA_6)B$ topology, was is shown in Fig 3.20a). Eq. 3.96 describes the first-order energy correction to the relevant XA_n topology and provides and insight into the structure of the zero-field NMR spectrum.

Dichlorvos molecule contains a single ^{31}P spin coupled to six equivalent protons with three bond couplings (11.4 Hz) and a single ^1H spin through a four bond coupling with strength of 5.2 Hz. The weak, six-bond proton-proton couplings are neglected in the analysis. The zero-field spectrum of dichlorvos shown in Fig. 3.20a) consists of 6 lines resulting from the additional weak coupling splitting energy levels of the simple XA_6 system, as seen in the schematic energy diagram shown in Fig. 3.20a). The low-frequency transitions (< 3.5 Hz) with $\Delta F_T = \pm 1$ are spectrally overlapping (6 transitions within 2 Hz-wide span) are not evident in the measured spectrum, due to the excess low frequency noise. The transitions with $\Delta F_T = 0$ due to low-relative amplitude an spectral overlap are also hard to distinguish in the spectrum. The width of the spectral peaks in the dichlorvos spectrum in general is significantly (~ 2.5 -times) larger those observed in trimethyl phosphate and phosphite which may be caused the longer rotation correlation time of a large molecule (Harris and McVicker [1976]).

A representative organophosphorus $(XA)B_6$ spin system, dimethyl phosphite (Fig. 5.3a) was measured using zero-field NMR. In the molecule, a pair of ^1H and ^{31}P spins in the molecule are J -coupled with a strong coupling strength (a single-bond coupling of 695 Hz). The three-bond coupling between CH_3 protons and the ^{31}P nucleus is also present in the molecule and its strength is 11.7 Hz. Very weak four-bond couplings, arising between inequivalent spins, were neglected in the theoretical analysis. Because of this clear hierarchy of couplings, the zero-field NMR spectrum consists of lines concentrated in two spectral regions: the low-frequency region below 25 Hz and the high-frequency region between 670 and 720 Hz. The ranges are determined by the strengths of the three-bond and single-bond couplings, respectively. The structure of the zero-field spectrum can be understood qualitatively using the first-order perturbation theory (Sec. 3.4.2). The weaker interaction changes the energy levels of the XA spin system, leading to multiple levels and transitions (Fig. 5.3b). Notably, the first-order perturbation did not produce additional splittings of the levels. Taking into account the higher-order perturbation can solve that issue. At the same time, numerical simulations of the total spin system provide an adequate match to experimental results (Fig 5.3c). Interestingly, the presented spectrum of dimethyl phopshite demonstrates the measurement of a molecule with the strongest J -coupling ever measured in ZULF NMR. In this scope, it should be noted that, due to a finite bandwidth of the magnetometer used for measurements, the device suffered from the loss of sensitivity at higher frequencies, which manifested by approximately 4-times higher noise observed in this frequency range (worse SNR).

5.1.4 Organophorus compounds – conclusions and outlook

With the study on organophorous compounds, we demonstrated the application of zero-field NMR spectroscopy for highly-sensitive, chemically-specific sensing of molecules with naturally abundant ^{31}P and ^1H . The research demonstrated a good

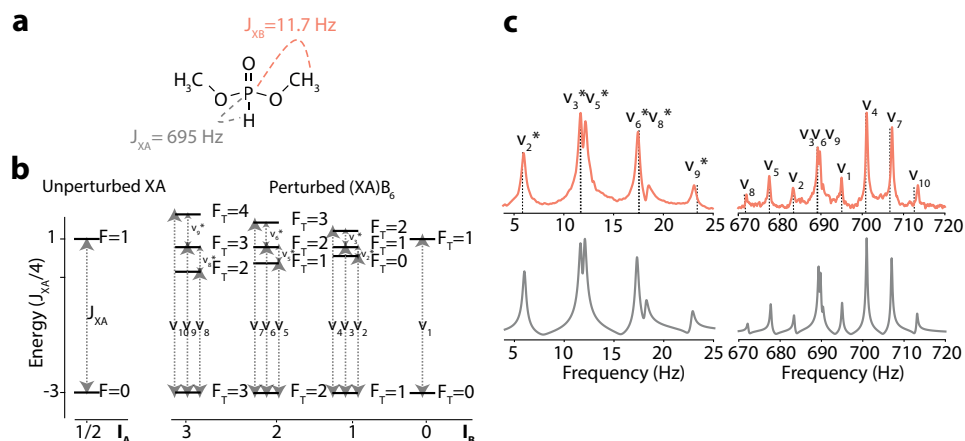


Figure 5.3: a) Molecular structure of ^{31}P containing $(\text{XA})\text{B}_6$ spin system: dimethyl phosphite. The relevant value of the J -couplings is indicated by the dashed line. b) Energy-level structure of the unperturbed XA system (left) and the spin-system with an additional weak coupling to six equivalent spins, i.e., the $(\text{XA})\text{B}_6$ spin system (right). The manifolds in the perturbed system are labelled by the total proton spin I_A and the total spin of the B spins respectively. The transitions observed at the zero field are indicated by the gray dashed arrows. c) Experimental (top) and simulated (bottom) zero-field NMR spectra of dimethyl phosphite. The line positions of the lines, calculated using the first-order perturbation theory, are indicated by the vertical dashed lines, which are labelled with the corresponding frequencies shown in the energy-level structure. Two regions presented in the spectra correspond to low-frequency transitions, determined by the three-bond coupling, and high-frequency transitions, which correspond to the single-bond coupling. Figure adapted from [Alcicek et al. \[2021b\]](#).

agreement between the experimental and simulated data, even if the first-order perturbation theory was used. We also demonstrated the ability to directly detect high-frequency J -couplings, which is relevant for the detection of strongly-coupled phosphorus- or fluorine-containing compounds. Importantly, all the studies were performed using thermal prepolarization, which was possible due to the high abundance of ^{31}P and ^1H . This enables construction of portable, low-cost detection ZULF NMR spectrometers that hold promise of chemically specific detection of phosphorus compounds in a number of environments. For example, this may be interesting in environmental studies, while the same technique can be used in biological sciences to investigate biorelevant molecules such as phosphocreatine, ATP, and phospholipids.

5.2 PARAHYDROGEN-INDUCED POLARIZATION IN ZERO-FIELD NMR EXPERIMENT

5.2.1 Introduction

The other approach to performing zero-field NMR spectroscopy on samples without isotopic enrichment is to replace thermal prepolarization with hyperpolarization techniques. Although ZULF NMR experiments may be based on multiple repetitions of the measurements, such studies of molecules with low-abundance nuclei may be long or even impossible. At the same time, a great improvement in polarization levels using hyperpolarization makes measurements of such molecules feasible. Specifically, ZULF NMR spectroscopy with parahydrogen-induced polarization (Sec. 3.2.2) enabling investigations of molecules with low-abundant nuclei,

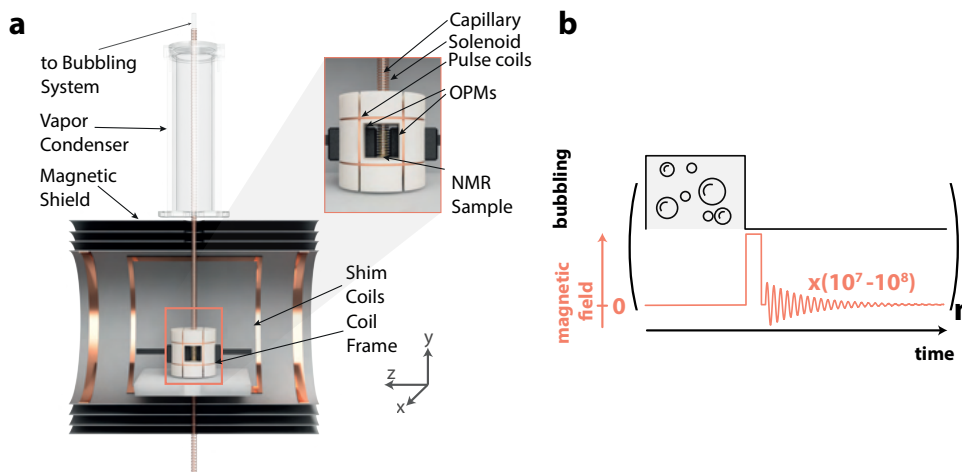


Figure 5.4: a) Illustration of the key-components of the zero-field spectrometer used to perform zero-field NMR experiments with the use of parahydrogen-induced polarization. A long NMR tube was connected from the top to the bubbling system described in Sec. 4.3.3. The top of the NMR tube can be held inside a 3D-printed vapor condenser chamber, and cooled down with the cold nitrogen vapor. This significantly slowed down the evaporation of the sample, as the liquid vapor was carried out with the used hydrogen. The condenser was used in experiments with many repetitions (see Sec. 5.2.4), as the sample loss was especially acute in long measurements. The tube was placed inside the piercing solenoid, spanning the whole length of the magnetic shield. The bottom of the NMR tube, which typically contained about 500 μL of liquid sample, was placed in the 3D-printed coil frame housing two commercial atomic magnetometers. The sample was positioned as close as possible to both sensors, measuring magnetic field along the z-axis. b) Experimental sequence used to obtain zero-field NMR spectrum following parahydrogen-induced polarization presented in this thesis. Top trace shows the bubbling sequence, which was switched off before generation and detection of ZULF NMR signal. Bottom trace shows profile of magnetic field during experiment, which was divided into several stages: initial bubbling at zero magnetic field, a sharp DC magnetic field pulse, and subsequent detection of NMR signal in zero-magnetic field. As indicated the sequence could be repeated if the hyperpolarization was sustained through many hydrogenation cycles.

^{13}C (1.1 %) or ^{15}N (0.36 %), was performed within this dissertation and is presented below.

5.2.2 Zero-field NMR experiments with parahydrogen-induced polarization

All zero-field NMR experiments with parahydrogen-based polarization started with the preparation of the parahydrogen gas in the setup described in Sec. 3.2.2. Parahydrogen was collected in the 10-l aluminium diving tank and the generation of parahydrogen stopped when the gas pressure reached 6 bar. The cylinder was then physically transported from the chemical laboratory, where the generator was installed, to the nearby laboratory where the zero-field spectrometer was located. In the lab, the parahydrogen tank was connected to the bubbling system, described in Sec. 4.3.3. The liquid sample (typically 500 μL) of the investigated compound was placed inside a long NMR tube (made out of two 7-inch standard NMR tubes) which is connected to the bubbling system with the use of a teflon tube. The NMR tube was placed inside the a piercing solenoid stretching the whole length of 4-layer magnetic shielding, such that the sample was positioned inside the zero-field region in the close proximity of two commercial atomic magnetometer. The magnetometer and solenoid were held inside a 3D-printed frame, which also supports three pairs of Helmholtz coils used for magnetic-field pulses. Larger coils, mounted at

the inner surface of innermost layer of the shield, were used to shim the magnetic field to zero at the position of the NMR sample. The vapor condenser, consisting of a 3D-printed chamber that was cooled with cool nitrogen vapor (from the gently heated liquid nitrogen container), could be placed around the top of the NMR tube (above the magnetic shield) to minimize evaporation of the liquid. Evaporation affects the composition of the sample, leading to change in the spectrum (Blanchard et al. [2021b]) as the concentration of the target molecules increases and also to the loss of the polarization efficiency. In extreme cases the evaporation may lead to the precipitation of sample constituents and clogging of the capillary tube.

A typical experimental sequence used to hyperpolarize samples for ZULF measurements is shown in Fig. 5.4 b). Parahydrogen was bubbled through the liquid sample in the zero field (residual fields were smaller than 0.1 nT after the shimming procedure). After stopping the bubbling, a sharp magnetic-field pulse, corresponding to the $\pi/2$ angle for protons, was used to generate a zero-field NMR signal. The bubbling time was adjusted for a specific experiment. In particular, in hydrogenative PHIP the bubbling time was long, exceeding 10 s. As the chemical reaction and hence the polarization transfer were not reversible processes, the long bubbling time ensured that most of the compound reacted with hydrogen and got polarized. In turn, hydrogenative PHIP signals were typically visible only in the first three repetitions of the experiment (every time the sample was bubbled for 20 s and then measured). No signal was observed later, suggesting that all of the substrate reacted with hydrogen. For nonhydrogenative SABRE-based hyperpolarization (Sec. 5.2.4), a bubbling was shorter (typically 6 s) and the reversible polarization allowed for hundreds of repetitions of the experimental sequence (Fig. 5.6).

5.2.3 Zero-field spectroscopy of naturally-abundant hydrogenatively-hyperpolarized samples

As explained in Sec. 3.2, the simplest way to use the parahydrogen-induced polarization in NMR experiments is by directly attaching a hydrogen molecule to an organic molecule with a triple/double bond. This hydrogenation reaction may eventually enable the polarization from parahydrogen to be transferred to the target substance.

Here, we present the results exploiting the attachment of parahydrogen to a group of organic molecules at the zero magnetic field. It resulted in hyperpolarization of the ^{13}C - ^1H group and hence the ability to observe molecules with natural abundance of carbon. The zero-field NMR spectra with molecules polarized in such a manner are shown in Fig 5.5. The Fig. 5.5a) shows a zero-field signal produced after the attachment of parahydrogen to dimethyl acetylenedicarboxylate, producing a hyperpolarized dimethyl maleate (the relevant chemical reaction is shown above the spectrum). Similar experiments were used to demonstrate the parahydrogen-induced polarization in the zero field (Theis et al. [2011]). Moreover, the addition of parahydrogen to dimethyl acetylenedicarboxylate was recently used to demonstrate in-line chemical reaction monitoring (Burueva et al. [2020]), where a zero-field NMR signal was used to monitor the concentration of dimethyl maleate and dimethyl succinate. Importantly, the reaction occurred inside a metal container, demonstrating the important advantage of zero-field NMR. In the results presented in this thesis, the hydrogenation reaction was performed in an acetone solution, while the Rhodium based catalyst ($[\text{Rh}(\text{dppb})(\text{COD})]\text{BF}_4$) was used for hydrogenation of the 2-M solution of naturally abundant dimethyl acetylenedicarboxylate. The measured zero-field spectrum was the equal-weight sum of spectra of $[1\text{-}^{13}\text{C}]$ -dimethyl maleate and $[2\text{-}^{13}\text{C}]$ -dimethyl maleate (any contribution from $[1,2\text{-}^{13}\text{C}]$ -dimethyl maleate isotopomer was two orders of magnitude smaller and was not observed in the experiment). The explanation of the zero-field spectrum obtained after hydrogenation of dimethyl acetylenedicarboxylate, can be found in Butler et al. [2013a]. The $[2\text{-}^{13}\text{C}]$ -dimethyl maleate spectrum consisted of antiphased peaks around the strongest single-bond coupling (167 Hz) and a single low-frequency peak. The zero-

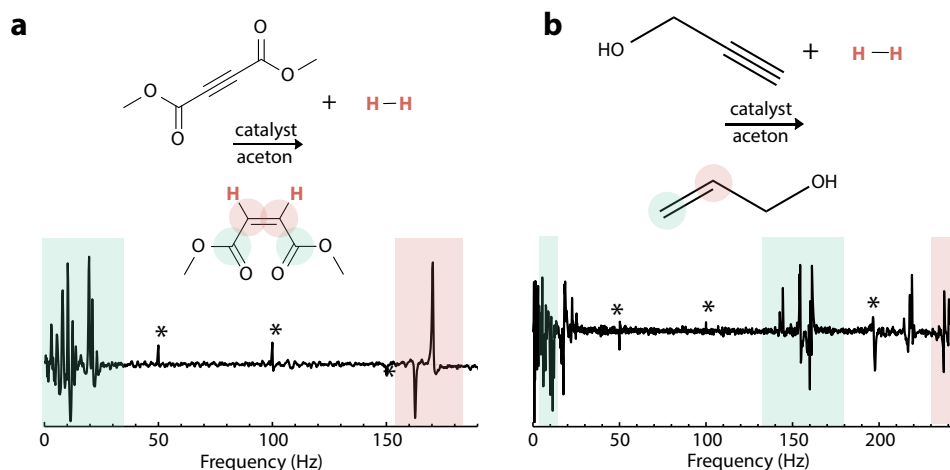


Figure 5.5: Zero-field spectroscopy of molecules of naturally-abundant nuclei obtained with the use of hydrogenative parahydrogen-induced polarization. a) Zero-field NMR spectrum of hydrogenated dimethyl acetylenedicarboxylate. The experimental spectrum is a result of averaging three transients, following successive hydrogenations of a single NMR sample. The chemical reaction is shown above the spectrum. Due to the use of naturally abundant ^{13}C , the NMR spectrum contains contributions from hyperpolarized $[1-^{13}\text{C}]$ -, and $[2-^{13}\text{C}]$ -dimethyl maleate isotopomers, as indicated by green and red highlights in the spectrum. b) Zero-field NMR spectrum obtained based on hydrogenation of propargyl alcohol with parahydrogen. The inset at the top shows the chemical reaction. The hyperpolarized NMR spectrum is once again a sum of contribution from two different isotopomers: $[2-^{13}\text{C}]$ -, and $[3-^{13}\text{C}]$ -allyl alcohol, as indicated by highlighting colors. In both spectra stars indicate noise contribution from residual magnetic field leaking into the detection region.

field spectrum of $[1-^{13}\text{C}]$ -dimethyl maleate gave rise to several low-frequency peaks < 25 Hz because only weak, two- and three-bond couplings were present in the molecule. To obtain the experimental spectrum presented in Fig. 5.5a), a single sample was used, while the signal is the average first three transients in the experiment (only there the PHIP signal was clearly visible). Similarly, a zero-field NMR spectrum after propargyl-alcohol hydrogenation is shown in Fig. 6.1b) along with the corresponding chemical reaction (solvent, catalyst, and target concentrations remained identical as in dimethyl acetylenedicarboxylate hydrogenation). Propargyl alcohol hydrogenative hyperpolarization was previously exploited in a number of studies, although its use in ZULF NMR was demonstrated for the first time in this dissertation.¹ Compared to the hyperpolarized spectrum of dimethyl maleate, the zero-field spectrum of allyl alcohol (Fig. 5.5b)) is more complex, as the molecule is less symmetric, leading to peak splittings by nonequivalent spins. The resultant spectrum, obtained at natural abundance, was once again a sum of zero-field spectra of two isotopomers, i.e., $[2-^{13}\text{C}]$ -allyl alcohol and $[3-^{13}\text{C}]$ -allyl alcohol. In the spectrum shown in Fig. 6.1b), contributions from both isotopomers are indicated in red and green. Despite a richer spectrum and additional exchanging proton, which contributes to spin relaxation (see Chapter 6), the zero-field spectrum of hydrogenated propargyl alcohol is clearly visible after only 3 transients. This demonstrates a high-degree polarization obtained under the zero-field conditions.

Hydrogenative or non-hydrogenative polarization transfer under ultra-low or zero-field conditions naturally complements ZULF NMR technique, as the polarization and detection conditions are the same, and due to high-polarization levels enabled the detection of suitable compounds with natural abundance of ^{13}C in

¹ It should be also noted that hydrogenative polarization of propargyl alcohol was recently used in a related research, where a proton polarization first created by a PHIP mechanism was then transferred to another molecule by chemical exchange of polarization protons (Them et al. [2021]).

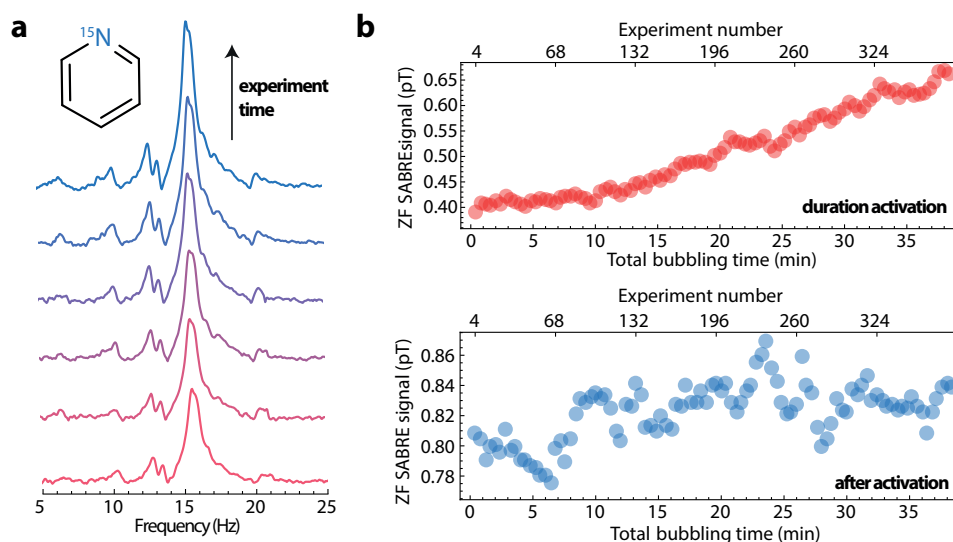


Figure 5.6: Continuous SABRE experiment at zero magnetic field a) Zero-field NMR spectrum of ^{15}N -pyridine following a hyperpolarization with SABRE technique. The individual spectra shown here are a results of averaging 4 transients, and are positioned in order of experimental time (the upper spectra are taking longer into the continuous SABRE experiment). The spectral features are similar to a thermal spectrum of pyridine (see Fig. 3.21), while the amplitude of a signal grows as the SABRE catalyst activates. b) The total amplitude of the zero-field signal of ^{15}N -pyridine in a continuous SABRE experiment. The top graph (red points) show an experiment where the catalyst is activating during the experiment leading to a increase of the SABRE signal in time. The bottom graph (blue points) shows analogous experiment but with sample which was activated prior to the experiment by running a large flow of parahydrogen through it for 10 min. Zero-field signal in that case is a stable through the 300+ experimental repeats. The signal was calculate by integrating over the peaks from pyridine in the NMR spectrum (all the spectral features in the spectrum of pyridine scale by the same amount as the experiment progress). Following initial activation signal is stable over tens of minutes of bubbling, and hundreds of experimental transients. Eventually solvent evaporation leads to modification of spectrum and signal decay, but the vapor condenser efficiently slows down the process so that in a studied experimental time the efficiency of polarization is not affected.

single-shot NMR experiments. Although the technique is limited to certain compounds with unsaturated bonds undergoing hydrogenation reaction, ZULF NMR already demonstrated its usefulness both in the generation of hyperpolarized contrast agents (Knecht et al. [2021]) and in the monitoring of chemical reaction (Buruева et al. [2020]). The results presented here were a first step in implementation of a relayed polarization scheme (PHIP X) into ZULF NMR. The transfer of a proton polarization to propagyl alcohol under ZULF conditions aims at polarizing small target molecules that undergo chemical exchange (such as water, methanol, urea, etc.). This is a topic of ongoing research (see Alciček [2022]).

5.2.4 Reversible-exchange based polarization in zero-field

Instead of relying on the one-way reaction (hydrogenation) to create a hyperpolarized NMR signal, we can turn to the reversible-exchange method (SABRE) to observe enhanced signals at the zero field. To illustrate the main advantage of continuous polarization in a zero field, we performed multiple polarization sequences of pyridine and its derivatives. Figure 6.1 shows successive zero-field spectra of ^{15}N -pyridine. The zero-field spectrum following SABRE polarization is similar to the spectrum of thermally prepolarized pyridine, with a slight difference in cou-

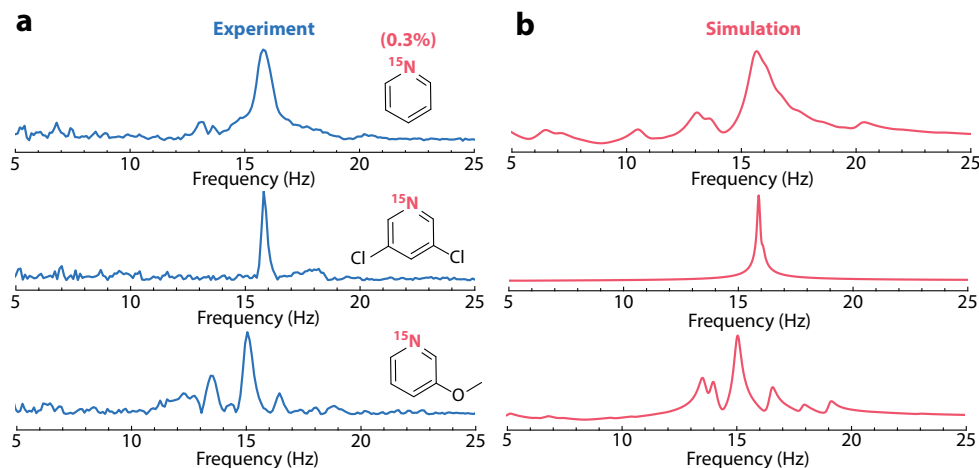


Figure 5.7: SABRE experiment at zero field performed with natural abundance of ^{15}N . a) Experimental zero-field NMR spectra of pyridine and its derivatives following a SABRE hypolarization. Front the top a zero field spectrum of: pyridine, 2,5-dichloropyridine and 3-methoxypyridine. Each spectrum is a result of averaging 128 subsequent transients (6s bubbling in each transient). The spectra are taken with target substance at their natural isotopic abundance. Insets shows the molecular structures of hyperpolarized compounds. The reduced complexity of 2,5-dichloropyridine and increased complexity of 3-methoxypyridine when compared to pyridine spectrum is a results of a smaller and larger number of coupled spins $1/2$ (protons). The zero-field NMR spectra of each pyridine-derived compounds is characteristic for each spin system enabling chemical differentiation. b) The simulated, zero-field spectrum of pyridine derivatives.

pling strength, originating from the solvent environments (methanol versus neat pyridine). All the spectral features hyperpolarized pyridine are also in-phase, consistent with the initial density matrix proposed in Theis et al. [2012]. An amplitude of the zero-field pyridine signal is plotted in a successive experiment in Fig. 5.6 b). As shown, the signal amplitude initially increased as the SABRE catalyst (Crabtree's catalyst: $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{Py})]\text{PF}_6$) activated. If catalyst activation was performed prior to the experiment, the signal amplitude was stable over time (Fig. 5.6b), i.e., the hyperpolarized pyridine signal was clearly visible after hundreds of experimental repetitions (and tens of minutes of total bubbling). It is worth pointing out that, as noted in Blanchard et al. [2021b], the signal of continuous SABRE polarized samples eventually die out, as the solvent evaporates and the increased pyridine concentration affects the efficiency of polarization transfer. Here, however, the condenser efficiently reduced the evaporation rate of solvent and allowed for hundreds of repetitions without visibly affecting the sample composition and the resulting zero-field spectrum.

The ability to continuously produce large nuclear polarization at zero-magnetic field with the use of SABRE mechanism can be exploited to performs zero-field NMR experiment at natural isotopic abundance. For that we studied a number of pyridine derivatives, containing a natural abundance of ^{15}N (0.3%). The experimental zero-field spectra and the corresponding simulated spectra are presented in Fig. 6.1. Each sample was prepared in a similar fashion: 2 M of pyridine substrates and 25 mM of catalyst, $\text{IrCl}(\text{COD})(\text{IMes})$, were dissolved in 500 μL of methanol. The SABRE catalyst was activated outside of the zero-field setup by continuously purging a hydrogen through the sample until the sample changed color (from yellow to transparent). This typically lasted for about 10 min. The sample was then placed in the zero-field region and following a bubbling in zero-field and a DC pulse, a zero-field NMR signal was acquired. The experimental spectra presented in Fig. 6.1a) are a result of averaging 128 transients. It is noteworthy that the spectrum of hyperpolarized pyridine (top) was broader when compared to thermal spectra due to

solvent effects. The spectrum of 2,5-dichloropyridine is significantly simpler than that of pyridine, as the couplings to hydrogen nuclei in ortho-positions were not presented. Due to a large quadrupolar moment, the couplings to Cl nuclei are not visible in the spectrum, although the large quadrupolar moment of the Cl did not significantly contribute to line broadening, as the scalar-relaxation of the second kind in zero magnetic field is less severe for nuclei with large quadrupolar moment, as studied in [Tayler and Gladden \[2019\]](#). As a result, the zero-field NMR spectrum of 2,5-dichloropyridine consists of closely spaced, overlapping spectral lines concentrated around 16 Hz, corresponding to $3/2$ two-bond J -coupling between ^{15}N and ^1H nuclei. The lines splitting are a result of an additional weak coupling to the hydrogen nuclei in para position (opposite to ^{15}N nucleus). The spectrum of 3-methoxypyridine on the other hand is more complex, as the extra protons in the methoxy group coupled to the ^{15}N and ^1H spins in the aromatic part of the molecule. This leads to additional peaks in the zero-field spectrum at lower and higher frequencies than the frequency of the dominant peak (at ~ 15 Hz), which originates from the two-bond coupling between ^{15}N and orthoprotons. The results presented here were the first demonstration of application of SABRE to polarize and measure molecules other than pyridine at a zero magnetic field. Despite somewhat broad spectral lines, each molecule produces a characteristic zero-field spectra enabling chemical identification. The high polarization levels and the ability to continuously polarize and measure under the zero-field conditions enable efficient detection of samples, containing ^{15}N at natural isotopic levels.

5.2.5 Conclusions and outlook on parahydrogen-induced polarization in ZULF NMR

Parahydrogen-induced polarization at zero-magnetic field provides nuclear magnetization enabling observation of ZULF NMR spectra of molecules with natural abundance of ^{13}C and ^{15}N . Specifically, we used PHIP technique to measure hyperpolarized spectra of compounds with unsaturated carbon-carbon bonds after hydrogenation with pH_2 . The boost in the signals is significant enough so that the good quality spectra from a sample at natural isotopic abundance of ^{13}C can be observed in just three averages. We hope that upon further optimization, large polarization of some of the PHIP targets (like propargyl alcohol studied here) can be relayed by a chemical exchange to a broader range of molecules undergoing chemical exchange (water, alcohols, urea, etc.). This would result in the technique being suitable for the hyperpolarization of a wide range of relevant molecules. The reversible polarization offered by the SABRE technique was also exploited to obtain zero-field NMR spectra. We studied the polarization levels during SABRE catalyst activation using zero-field NMR spectra and obtained stable, reversible polarization over hundreds of experimental repeats by condensation of solvent vapor to ensure a stable sample composition and efficient polarization transfer. We also expanded zero-field SABRE studies to a new group of molecules (pyridine derivatives) and measured several spectra of molecules at the natural isotopic abundance of ^{15}N nuclei. The characteristic zero-field spectra of such compounds enable chemical identification, while the ability to work without isotopically labeled compounds broadens the scope of chemicals detectable in zero-field NMR. Moreover, reversible hyperpolarization at zero-magnetic can also be a source of hyperpolarized NMR signal used in the precision physics experiments (see for example, Chapter 7 and [Garcon et al. \[2019\]](#)), while the very recent developments in relaying polarization created in SABRE process to obtain zero-field spectra ([Van Dyke et al. \[2022\]](#)) can prove useful to polarize even larger number of molecules under ZULF conditions.

The parahydrogen-induced hyperpolarization is a natural match for zero-field NMR technique: it is cheap to perform compared to other hyperpolarization methods and does not require strong magnetic fields (in fact, it can work optimally under exactly zero-field conditions). The increase in the polarization levels of het-

eronuclei, such as ^{13}C and ^{15}N , can alleviate one of the zero-field problems, which is the dependence on heteronuclear coupling. This allows one to perform zero-field experiments on samples with natural isotopic compositions, bringing the zero-field NMR closer to real-world, practical applications.

The results presented in this chapter were previously published in the following peer-review articles:

1. **Put, P.**, Pustelny, S., Budker, D., Druga, E., Sjolander, T. F., Pines, A., Barskiy, D. A. (2021). Zero-to ultralow-field NMR spectroscopy of small biomolecules. *Analytical Chemistry*, 93(6), 3226-3232.
2. Alcicek, S., **Put, P.**, Barskiy, D., Kontul, V., Pustelny, S. (2021). Zero-Field NMR of Urea: Spin-Topology Engineering by Chemical Exchange. *The Journal of Physical Chemistry Letters*, 12(43), 10671-10676.

6.1 ZERO-FIELD NMR AS A TOOL FOR (BIO-)CHEMICAL ANALYSIS

As NMR spectroscopy provides chemically specific information about the molecular structures and transformations that the molecule undergoes, the technique found its application in chemical and biochemical laboratories as a powerful analytical tool. However, the analytical capabilities of the technique come at the cost of expensive and bulk infrastructure, which is needed for high-field, high-resolution spectroscopy. Recently, ZULF NMR emerged as a complementary incarnation of conventional NMR, providing high-resolution chemically specific information (see for example [Blanchard et al. \[2015\]](#)) and the ability to determine spin couplings with unrivalled submillihertz precision ([Wilzewski et al. \[2017\]](#)). These developments eventually led to the application of ZULF NMR in chemical research. For example, ZULF NMR was used to study chemically-exchanging systems ([Barskiy et al. \[2020\]](#)) and to monitor chemical reactions ([Burueva et al. \[2020\]](#)). Moreover, ZULF NMR can be performed under much less demanding experimental conditions. As shown in previous chapters, a typical zero-field NMR spectrometer (see for example [Tayler et al. \[2017\]](#)) relies on an atomic magnetometer, offering very high sensitivity, operating at ambient temperature, having small power consumption and almost no maintenance. As the rest of the hardware (magnetic shielding, prepolarization scheme, electronic devices for pulses, experiment control, and data acquisition) is typically low cost, the zero-field NMR has the potential to really lower the barrier of entry into NMR-based chemical analysis.

In this chapter, we present the developments in the use of zero-field NMR as analytical spectroscopic tools with potential application in bioscience. This was done by analyzing spectra of important groups of biomolecules, including sugars, metabolites, and amino acids. We study the molecules with a number of experimental techniques developed for ZULF NMR. In particular, the techniques are: ULF NMR precession experiments (relaxometry), ULF NMR spectroscopy, and the zero-field J -spectroscopy. We demonstrate the spectroscopic capabilities of the techniques with the use of a home-built spectrometer, as well as a portable ZULF NMR spectrometer put together with off-the-shelf commercial components.

6.2 SPECTRUM STRUCTURE IN ZULF NMR

The NMR experiment performed at ZULF provides information complementary to that achieved in high-field NMR experiments. The general structure of ZULF NMR has been explained in Sec. 3.4. Specifically, in a typical ultra-low field NMR spectrum of a simple molecule, two groups of resonances can generally be identified. The first group arises because of the interaction of nuclear spins with an ultra-low magnetic field. In this case, individual spins undergo Larmor precession, akin to high-field NMR experiments, although at a rate given by the combination of the gyromagnetic ratios of coupled spins. A typical range of frequencies of such signals ranges from 0 to tens of hertz. The second group of resonances, usually observed at higher frequencies, is a direct effect of spin evolution under the spin-spin J -couplings. As shown in Sec. 3.4.2, the number, positions, and strengths of the resonance depend on the nuclear-spin topology and coupling strengths. The presence of residual magnetic field additionally splits the resonance lines as explained in Sec. 3.4.2.

Figure 6.1a) presents simulated ZULF spectra of a simple XA spin system. The spectra are simulated at a non-zero magnetic field with different J -coupling strengths between the nuclei. The top spectrum, which presents a case of uncoupled spins, consists of just two low-frequency resonances. Resonances arise due to the Larmor precession of the ^1H and ^{13}C nuclei, while the relative strength of the lines

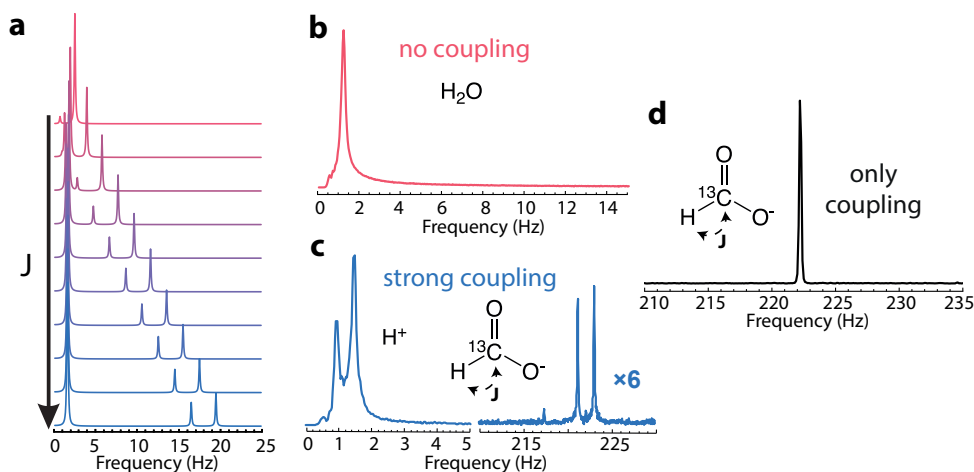


Figure 6.1: a) Simulated zero-field spectrum of the XA spin system (coupled ^1H and ^{13}C nuclei) subject to a ultra-low field (50 nT). The spectra are plotted as a function of the J -coupling strength in a range from 0 to 18 Hz. b) Experimentally measured ULF NMR spectra of proton in a water sample, where no heteronuclear coupling is present, resulting in a single peak at the Larmor frequency. Shown spectra is obtained in a single transient with the transverse field of 28 nT. c) Experimental ULF NMR spectrum of ^{13}C -formic acid, constituting the XA spin system, with a large (compared to the Larmor frequency) J -coupling of 222.2 Hz. The spectrum represent the strong-coupling regime, where the high-frequency resonances are centered around the J -coupling frequency and the splitting comes from the Zeeman interaction in 35-nT field. In the low-frequency region of a spectrum a single peak from the XA system at the average Larmor frequency of ^1H and ^{13}C is seen, while the additional peak at the proton Larmor frequency come from the OH^- which undergoes rapid chemical exchange in the sample and is effectively decoupled from the rest of the molecule. d) Experimental spectrum of ^{13}C -formic acid in the zero-field condition. A single peak at the J -coupling frequency is seen in the spectrum. The low-frequency peaks are now centered at 0 Hz frequency as the quasi-static components of magnetization decays to zero without undergoing additional evolution. Results were obtained with the portable ZULF NMR spectrometer built within this dissertation. The figure adapted from [Put et al. \[2021\]](#).

scales with the total magnetization of each nuclei (for thermal prepolarization, the resonance amplitude scales as γ^2). The presence of the J -coupling modifies the spectra. Specifically, instead of two Larmor-precession peaks, a single resonance is observed at the average Larmor frequency of the coupled spins. Moreover, a pair of split resonances are observed at higher frequencies. These resonances become more pronounced and arise at higher frequencies as the coupling increases. They are centered around the J -coupling frequency with their splitting given by the sum of the Larmor frequencies of the coupled nuclei.

Experimental spectra for the cases, corresponding to the no-coupling and strong-coupling regimes, are shown in Figs. 6.1b) and c). The water spectrum (Fig. 6.1b), taken at the 28-nT field, shows a single peak at low frequency (1.2 Hz), while the spectrum of ^{13}C -formic acid, consisting of two peaks at low frequencies (one from the XA couple system and the other from the exchanging OH^- proton) and the high-frequency resonance doublet centered around the J -coupling. (222.2 Hz). Figure 6.1d) shows yet another case, when the spectrum of the XA system is measured in a truly zero field. Under such conditions, the single peak at the J -frequency is seen, while the low-frequency resonance is not visible at all (the resonance should arise at 0 Hz, corresponding not to the Larmor precession but to the quasistatic magnetization).

Both the zero-field and ULF regimes have applications. The experiment using precessing magnetization at the ZULF conditions can be performed in a straightforward fashion without relying on the presence of the heteronuclear coupling. Although the chemical information in that case is not directly accessible, since the chemical shift in this field range is beyond the detection capabilities, the relaxation properties of the system can be explored. This may, for example, give information the sample concentration based on the solvent NMR signal, as we demonstrate later in this chapter. The presence of a magnetic field also changes in a controllable manner the NMR spectrum, which may be used for, i.e., for easier peak analysis for chemical identification as demonstrated in Ledbetter et al. [2011]. The zero-field J -spectroscopy offers chemically specific information while providing excellent spectral resolution. Although the precession signals are generally stronger than those due to the spin-spin J -coupling (due to scaling with the square of the gyromagnetic ratio, rather than the difference of gyromagnetic ration), the zero-field spectroscopy typically relies on spectral peaks in a higher frequency range, where the noise floor of the magnetometer is lower. This helps improve the signal-to-noise ratio and hence increases sensitivity of the measurements. The background magnetic field used for the precession experiment can also hinder the performance of the SERF magnetometer, which is used in research. Therefore, operation below background fields of 100 nT is advised or suppression of the detection field at the position of the magnetometer must be implemented (e.g., by using compensation coils and piercing solenoid geometry).

6.3 ZERO-FIELD SPECTRA OF METABOLITES, SUGARS AND AMINO ACIDS

While we showed the usefulness of the zero-field NMR in chemical identification in Chapter 5, here, we present spectra of small (containing several nuclei with non-zero spin) biomolecules that were observed under the zero-field conditions. The investigated molecules were thermally polarized and the ZULF NMR signals were generated on the basis of the sudden transfer approach (Sec. 3.4), without the application of the magnetic-field pulse. Before the measurement campaign, the magnetic field inside the shield was zeroed using the shimming procedure described in more detail in Appendix B. As the presence of heteronuclear coupling is necessary to obtain a zero-field spectrum (Sec. 3.4), the work presented in this chapter was carried

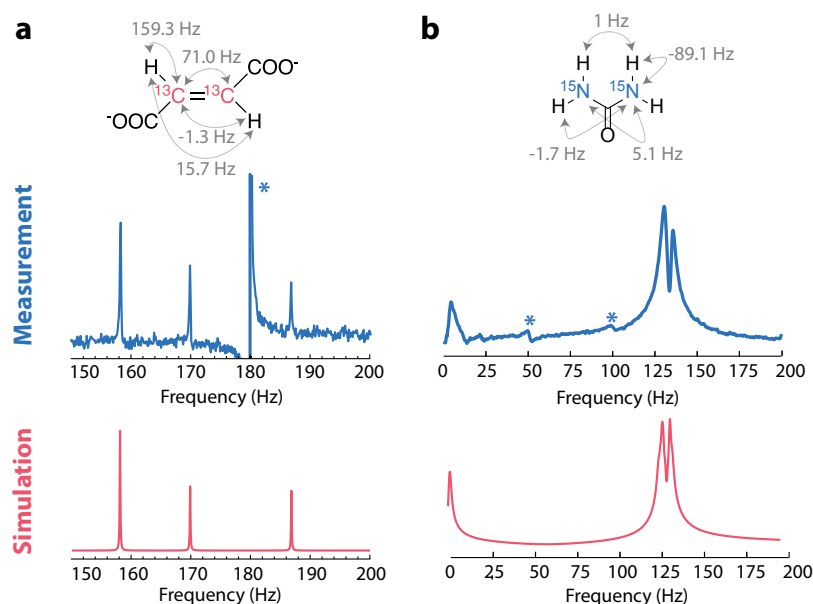


Figure 6.2: Zero-field spectrum of metabolites. a) The structure (top), experimental (blue curve) and the simulated (red curve) zero-field spectrum of $[2,3-^{13}\text{C}]$ -fumarate. The spectrum of fumarate dissolved in deionized water is a results of 1024 averages. The spectrum was simulated with the used of SpinDynamica package in Wolfram Mathematica. Adapted from Put et al. [2021]. b) Structural formula (top), experimental (blue) and simulated (red) zero-field spectrum of $[^{15}\text{N}_2]$ -urea. The urea sample was dissolved in deionized water. The experimental spectrum was obtained by averaging 2048 transients, while the simulated spectrum was obtained using Spintrum package under Python. Adapted from Alcicek et al. [2021a].

out with isotopically enriched samples (near 100% concentration of ^{13}C or ^{15}N). The solid samples were dissolved either in deionized water or in an appropriate solvent and then enclosed in the evacuated flame-sealed standard 5-mm NMR tube.

Two important metabolites ($[2,3-^{13}\text{C}_2]$ -fumarate and $[^{15}\text{N}_2]$ -urea) were investigated. Fumarate is a key substance in human metabolism, since it is converted to malate in a specific stage of the Krebs cycle. For that reason, fumarate is frequently used, as in preclinical MRI as a probe of cell necrosis (Mignon et al. [2014]). Hyperpolarized fumarate can be obtained cost-effectively by parahydrogen-induced polarization performed under ZULF conditions (Knecht et al. [2021]). The $[2,3-^{13}\text{C}_2]$ -fumarate molecule constitutes an $\text{XX}'\text{AA}'$ spin system, the spectrum of which contains three main lines around the dominant ^{13}C - ^1H J -coupling (Fig. 6.2a). The position and relative strength of the lines agree with the numerical simulations of such spin systems, which were performed by numerical diagonalization of the system's Hamiltonian (see Sec. 3.4.2) (Fig. 6.2b). The coupling is shown in the structure of fumarate (Fig. 6.2a). The spectral lines are narrow (~ 0.3 Hz), matching the long-lived 4-spin singlet state obtained in trans- $[2,3-^{13}\text{C}_2]$ -fumarate (Stevanato et al. [2015]).

Urea is another small biomolecule that plays a crucial role in human metabolism. It enables the exertion of nitrogen from the body. Meanwhile, hyperpolarized urea molecules are promising candidates for contrast in MRI, as they are highly biocompatible markers of liver and kidney functions (see for example Taylor and Vadgama [1992]). The urea molecule is made up of two $-\text{NH}_2$ groups joined with the carbonyl part. For $[^{15}\text{N}_2]$ -urea, this leads to the spectral lines being concentrated around the $3/2J_{\text{NH}}$ (133.7 Hz), as characteristic of individual XA_2 spin systems composed of the $-\text{NH}_2$ group. Weaker, homo- and heteronuclear couplings presented between the $-\text{NH}_2$ groups lead to additional splitting of the resonance and the appearance of low-frequency peaks in the spectrum. Figure 6.2c) shows experimentally measured

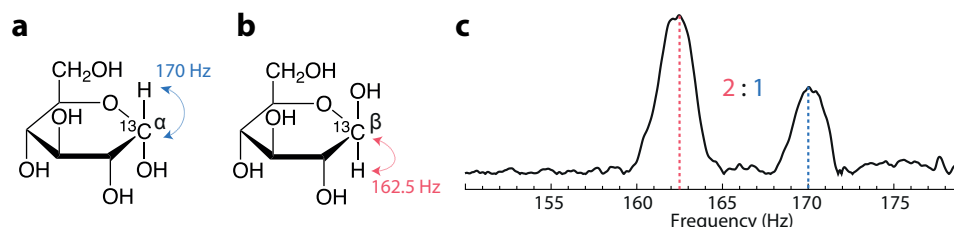


Figure 6.3: a) Structural formula of α -[^{13}C]-glucose with the strongest one-bond J -coupling between ^1H and ^{13}C . b) Corresponding structure of β -[^{13}C]-glucose. c) Zero-field NMR spectrum of [^{13}C]-glucose in a water solution. The vertical dashed lines indicate dominant coupling in α - (blue) and β - (red) forms of glucose. The ratio between the peaks integral (2:1) matches the ratio of glucose forms in water solution at room temperature, further confirming the assignment of spectral features. Adapted from Put et al. [2021].

and simulated zero-field spectra of [$^{15}\text{N}_2$]-urea in water solution. Instead of multiple narrow peaks around 133.7 Hz, two broad features were visible. This was the result of a significant broadening of the spectral lines. This broadening is caused by the chemical exchange of protons that make up the $-\text{NH}_2$ groups and consequent scalar relaxation of the first kind (see Sec. 2.2.8). We analyze the effect of the chemical exchange on the zero-field spectrum in the next section. The mere fact that the zero-field signals were visible under these conditions indicates that the chemical exchange rate is slower than the spin evolution (governed in zero magnetic field by the strength of the J -coupling). This is consistent with the chemical-exchange rate of urea in water at a natural pH of 1.9 s^{-1} (Vold et al. [1970]) that is significantly slower than the dominant coupling in the system.

We also looked at the possibility of detecting simple sugars with the use of zero-field NMR. The J -spectrum of [$1-^{13}\text{C}$]-glucose is shown in Fig. 6.3c). This isotopomer of a glucose molecule consists of a single carbon atom and eight nonequivalent coupled protons, which are responsible for the energy-level structure and a number of possible transitions between the levels. As the single-bond ^{13}C - ^1H coupling dominates the zero-field Hamiltonian, we expected the spectral line to be centered around this coupling value. In the measure spectra, we observe two broad ($\sim 0.3\text{ Hz}$) featureless structures around 168 Hz and 170 Hz. The centers of these structures corresponded to the dominant one-bond coupling between ^{13}C and ^1H , which is present in both the α and β glucose forms (Fig. 6.3a) and b). Moreover, the corresponding integrals under the peaks gave a ratio of approximately 2:1 consistent with the ratio of the β - and α -glucose form in neutral solution at 25 °C. The large width of the spectral features is the result of the spectral overlap of many zero-field transitions broadened through the chemical exchange of protons in glucose. This makes zero-field detection challenging as the amplitude of zero-field spectral lines is low, which is evident from the presented results, which required averaging over 2000 transients. However, recently developed hyperpolarization schemes (such as SABRE-relay and DNP) make the ability to distinguish between isomeric forms of sugar in solution by ZULF NMR in a compact, inexpensive, and portable spectrometer especially promising.

We also investigated the zero-field NMR spectra of amino acids, i.e., small organic molecules, which are building blocks of proteins and larger macromolecules, which play a seminal role in multiple processes in living organisms. Among the 20 different amino acids present in living organisms, we measured ZULF NMR spectra of one of them (glycine)¹. [$1-^{13}\text{C}$]-glycine makes up an effective XA_2 spin system, with two protons coupled to the ^{13}C nuclei through two-bound J coupling (see Fig. 6.4. The ^{14}N nuclei were not visible in the zero-field spectrum due to rapid quadrupolar relaxation. However, its presence can contribute to the line broadening (0.5-Hz

¹ For more spectra of amino acids obtained since under zero-field condition see Alciček [2022].

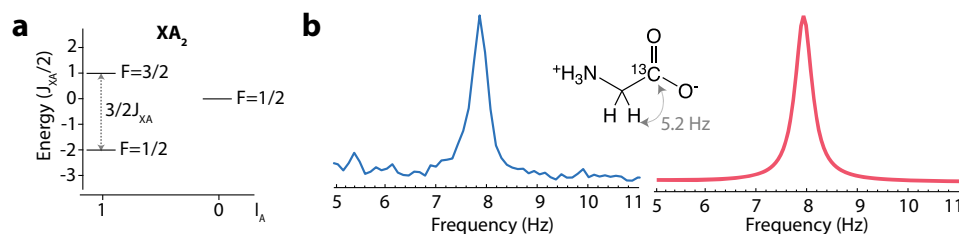


Figure 6.4: a) Energy level diagram of the zero-field Hamiltonian in the XA_2 spin system. Manifolds are characterized by the total spin I_A of equivalent A spins. The single detectable zero-field transition at $3/2 J_{XA}$ frequency is indicated by the vertical arrow. b) Experimental measured (left, blue curve) and simulated (right, red curve) of $[1-^{13}\text{C}]$ -glycine. The inset shows the structure of the amino acid with the J -coupling indicated. Adapted from Put et al. [2021].

width) via second-kind scalar relaxation (see Sec. 2.2.8). The experimental zero-field spectrum contains a single line at $3/2 \times 5.2 \text{ Hz} = 7.8 \text{ Hz}$ as expected from the calculations (Fig. 6.4b). Recently, the zero-field spectrum of $[1-^{13}\text{C}]$ -glycine was measured following hyperpolarization (with Dynamic Nuclear Polarization technique), producing an enhanced, but otherwise identical zero field spectrum (Picazo-Frutos et al. [2022]).

Obtaining a zero-field spectrum of amino acid required long measurement times. This can be remedied with the use of hyperpolarization techniques (see for example Pravdivtsev et al. [2021]). Although in this thesis, parahydrogen-induced hyperpolarization techniques are described, different approaches can also be used (Picazo-Frutos et al. [2022]).

6.4 ROLE OF CHEMICAL EXCHANGE IN ZERO-FIELD SPECTRA

Proton exchange between the protons of the molecule and the protic solvent can cause extra relaxation of the nuclear magnetization. The effect is relevant for many biomolecules, having exchangeable protons (for example, protons in sugars, amid groups in amino acids, and the NH_2 group in urea). This means that the NMR spectra (also obtained under zero-field conditions) of such molecules depend on the solvent. This is illustrated in Fig. 6.5, showing zero-field spectra of two isotopologues of urea: $[^{15}\text{N}_2]$ - and $[^{13}\text{C}, ^{15}\text{N}_2]$ -urea. The relevant structural formulas and couplings are shown in Figs. 6.5a) and b). The spectrum, as explained in Sec. 3.4.2, is a result of a range of transitions around the $3/2 J_{\text{NH}_2}$ -coupling, dominating the interactions in the molecule. Additional couplings lead to the presence of low-frequency peaks. For instance, the relatively strong ^{13}C - ^{15}N coupling gives rise to a wider span of low- and high-frequency peaks. The top row of the Fig. 6.5c) shows the simulated zero-field spectrum of both isotopologues of urea. In the middle row, an experimental zero-field spectrum taken in an aprotic solvent (DMSO), is shown. The results reveal a good agreement between the experimental and simulated data. The spectrum at the bottom presents the results obtained in water, which is a protic solvent. As shown, the observed resonances were roughly three times broader than in the aprotic solvent, which clearly demonstrates the effect of proton exchange on the relaxation properties.

The proton exchange influences both the T_1 relaxation time of nuclear polarization and the coherence relaxation time T_2 . Both of these rates affect zero-field spectra in thermal prepolarization experiments (Barskiy et al. [2020]). When the sample in the zero-field experiment leaves the prepolarization magnet, the generated magnetization starts to decay to zero, which is thermal equilibrium at a zero field. The

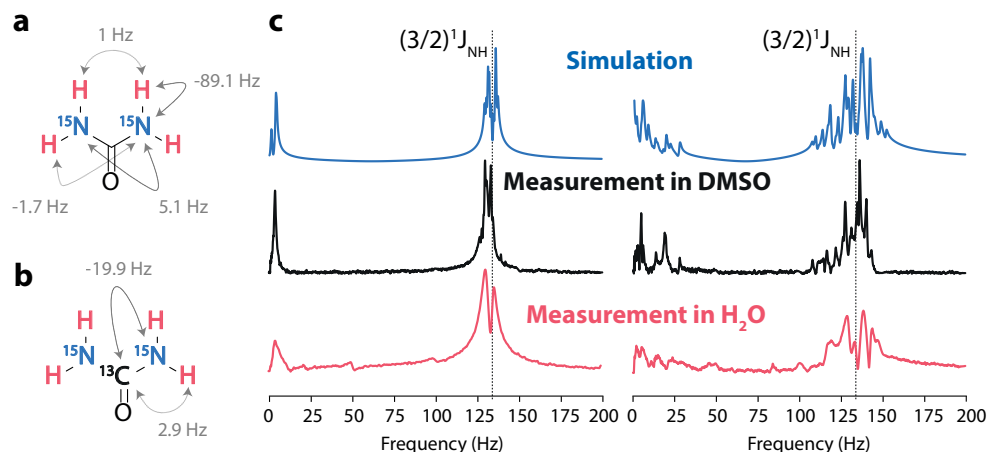


Figure 6.5: a) Structural formula of $^{15}\text{N}_2$ -urea, with the couplings (and their values) indicated in gray. b) Structure of $^{13}\text{C}, ^{15}\text{N}_2$ -urea with labelled couplings. Coupling values taken from Kuchel et al. [2014] and Steinhof et al. [2014]. c) Effects of the chemical exchange on the zero-field spectrum. Top: simulated zero-field spectrum of $^{15}\text{N}_2$ -urea (left) and $^{13}\text{C}, ^{15}\text{N}_2$ -urea (right) showing the observable-zero field transitions. Middle: experimental spectrum of urea isotopologues as taken in aprotic solvent–DMSO–closely matching the simulated spectrum. Bottom: Experimental spectrum of urea in protic solvent –water– showing the broadening of the spectral peaks resulting from the proton exchange in the solution. Adapted from Alcicek et al. [2021a]

rate of this decay, related to the relaxation time T_1 , depends on the spin environment. Specifically, for small molecules, the decay times are often long (seconds if not tens of seconds). In contrast, the proton relaxation rate in a solution is typically an order of magnitude larger. Protons leaving the molecule into the solution undergo quick thermalization, causing, outside of the strong field, their depolarization. As the unpolarized or partially polarized protons attach back to the molecule, the overall polarization of the target substance decreases. The more frequent the exchange, the faster the relaxation of the protons in the molecule. The polarization of other nuclei in the molecule is also affected by chemical exchange, as the scalar spin-spin interaction leads to transfer of polarization from other nuclei to the exchanging protons, where it is destroyed. In the scope of this discussion, it is clear that depolarization is weaker and therefore T_1 is larger in systems with slow exchange rates $R_{ex} \ll J$. For very large exchange rates, i.e., when $R_{ex} \gg J$, the exchangeable protons are effectively decoupled from the molecule and the polarization of the other nuclei is weakly affected. This enables to reach long T_1 s that may reach times on the order of seconds. For example, this is the case for formic acid (see for example Emondts et al. [2014]). For intermediate exchange rates, relaxation is severe, which could lead to complete deterioration of sample polarization before it reaches the zero-field region (Barskiy et al. [2019b]).

Chemical exchange also affects the coherence of spins evolving in a zero field. As exchangeable protons are J -coupled to the rest of the nuclei in a molecule, every time the proton detaches, the effective spin system changes. This changes the energy structure and hence the evolution frequencies in the molecule. As the proton reattaches to the molecule, the spin-evolution changes once again. These changes in the energy structure correspond to sudden jumps in the phase of otherwise coherent evolution. As the chemical exchange occurs randomly in the molecules in the ensemble, these random jumps in the phase of oscillations lead to overall relaxation of the coherence. This relaxation leads to significant broadening of zero-field lines, as seen in the zero-field spectrum of the aqueous solution of glucose (Fig. 6.3c) and urea (Fig. 6.5c).

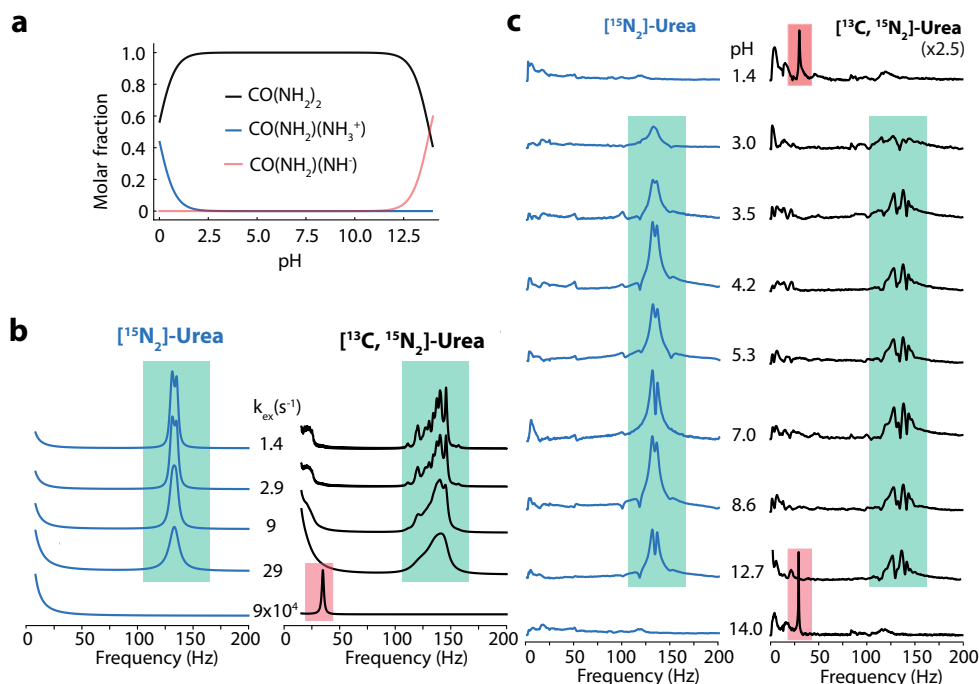
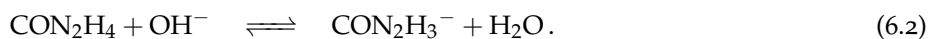
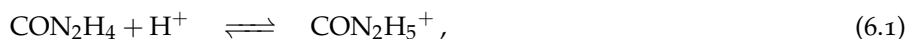


Figure 6.6: a) The molar fractions of different forms of urea in solution as a function of pH. The relative molar fractions were used in simulations of zero-field spectrum of urea (part b). b) Numerical simulation of zero-field spectrum of $[\text{^{15}N}_2]\text{-Urea}$ and $[\text{^{13}C}, \text{^{15}N}_2]\text{-Urea}$. c) Experimental zero-field spectrum of urea isotopologues at different pH conditions. The green boxes mark the high-frequency peaks disappearing and broadening in acidic and basic conditions. The red highlights low-frequency, narrow peaks emerging in the spectra in highly-acidic and highly-basic conditions. Figure adapted from [Alcicek et al. \[2021a\]](#).

In this dissertation, the effect of chemical exchange on the zero-field spectrum of urea was studied in detail. The proton exchange in urea is pH dependent. To demonstrate that the spectra shown in Fig. 6.6c) were recorded for different pH values. Interestingly, in urea the exchange is both acid and base catalysed as evident by two exchange mechanisms ([Bell et al. \[1943\]](#)):



Concentration of different forms of urea is shown in Fig. 6.6a) as function of pH.

As seen in Fig. 6.6c), the increase in the proton exchange rate, both under acidic and basic conditions, leads to a decrease in the amplitude of the high-frequency lines in the zero-field spectrum of urea. As the rate becomes much higher than the dominant J -coupling, NH_2 protons are effectively decoupled from the rest of the molecule, leading to the complete disappearance of high-frequency resonances. This disappearance is similar to an effect seen recently in the study of zero-field NMR of ammonium under highly acidic conditions ([Barskiy et al. \[2019b\]](#)), where the disappearance was caused by depolarization of protons during transport to the zero-field region.

The effect of depolarization in the transport is less pronounced when the guiding field is increase as evident by Fig. 6.7. Operating with stronger guiding undergoing chemical exchange may lead to higher-amplitude signals, which can be especially relevant for techniques which use a proton exchange to carry hyperpolarized signal, as in SABRE-relay ([Van Dyke et al. \[2022\]](#)).

Although chemical exchange leads to faster decay of polarization, and hence NMR line broadening, it can be also used to effectively change a spin system

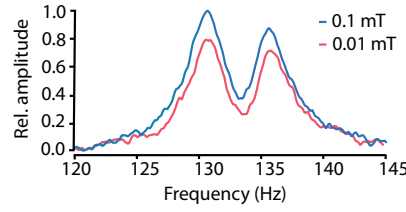


Figure 6.7: Zero-field spectrum of $[^{15}\text{N}_2]$ -urea as acquired after suddenly switching of the guiding field of 0.01 and 0.1 mT. The higher magnetic field during transfer leads to slightly higher signal. Adapted from [Alcicek et al. \[2021a\]\(SI\)](#).

and simplify the zero-field NMR spectrum. This is illustrated by the spectra of $[^{13}\text{C}, ^{15}\text{N}_2]$ -urea in highly acidic and highly basic solutions (Fig. 6.6c). Under such rapid chemical exchange, the protons become effectively decoupled from the other spins in the molecule, leading to an effective XA_2 spin system composed of ^{13}C - $^{15}\text{N}_2$ nuclei. In the zero-field spectrum, instead of broad and complicated spectra, a much narrower single peak was observed. By taking advantage of chemical exchange, we modified the zero-field spectra of the compound, resulting in an easier-to-interpret spectrum with a larger, yet narrower, dominating resonance. The simplified spectrum still depends on the specific coupling of the molecule between the nuclei. In turn, chemical identification is still possible under these favorable detection conditions.

The experimentally observed effects of chemical exchange on the zero-field NMR spectrum were also studied using numerical calculations, the results of which are presented in Fig. 6.6b). To calculate the signals, we follow the procedure introduced in [Barskiy et al. \[2019b\]](#). We start by writing down the kinetic equations for both mechanisms of chemical exchange in urea:

$$\begin{aligned}\frac{d}{dt}[A] &= -k_a^A[A][\text{H}^+] + k_d^C[C], \\ \frac{d}{dt}[C] &= k_a^A[A][\text{H}^+] - k_d^C[C], \\ \frac{d}{dt}[A] &= -k_d^A[A][\text{OH}^-] + k_a^D[D], \\ \frac{d}{dt}[D] &= k_d^A[A][\text{OH}^-] - k_a^D[D],\end{aligned}\tag{6.3}$$

where square brackets indicate the concentration, while we labeled urea $\text{CO}(\text{NH}_2)_2$ as subsystem A, $\text{CO}(\text{NH}_2)(\text{NH}_3^+)$ as subsystem C, and $\text{CO}(\text{NH}_2)(\text{NH}^-)$ as subsystem D. Kinetic constants labelled with letter k correspond to association and dissociation of system A (k_a^A and k_d^A), dissociation of system C (k_d^C) and association of system D (k_a^D). Equations 6.3 can be written in a compact matrix form:

$$\frac{d}{dt} \begin{pmatrix} [A] \\ [C] \\ [D] \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(-W_a^A - W_d^A) & \frac{1}{2}k_d^C & \frac{1}{2}k_a^D \\ W_a^A & -k_d^C & 0 \\ W_d^A & 0 & -k_a^D \end{pmatrix} \times \begin{pmatrix} [A] \\ [C] \\ [D] \end{pmatrix},\tag{6.4}$$

where we introduced the following kinetic constants: $W_a^A = k_a^A[\text{H}^+]$, $W_d^A = k_d^A[\text{OH}^-]$. To calculate a zero-field spectrum, we introduced a total state vector, describing the subsystems A, B, and D:

$$\rho(t) = \begin{pmatrix} \rho_A(t) \\ \rho_C(t) \\ \rho_D(t) \end{pmatrix},\tag{6.5}$$

where the density matrices ρ_A , ρ_C , and ρ_D , describing the corresponding subsystems, were vectorized (see for example [Petrosky and Prigogine \[1996\]](#)). We can now

develop the description of the collective-state evolution using a superoperator $\hat{M}$, following the equation:

$$\frac{d}{dt} \begin{pmatrix} \rho_A(t) \\ \rho_C(t) \\ \rho_D(t) \end{pmatrix} = \hat{M} \begin{pmatrix} \rho_A(t) \\ \rho_C(t) \\ \rho_D(t) \end{pmatrix}. \quad (6.6)$$

The superoperator matrix is given by:

$$\hat{M} = \begin{pmatrix} \frac{1}{2}(-W_a^A - W_d^A)\mathbb{1}_A + \mathbb{L}_A & \frac{1}{2}k_d^C\mathbb{T}_B & \frac{1}{2}k_a^D\mathbb{D}_B \\ W_a^A\mathbb{D}_B & -k_d^C\mathbb{1}_C + \mathbb{L}_C & 0 \\ W_d^A\mathbb{T}_B & 0 & -k_a^D\mathbb{1}_D + \mathbb{L}_D \end{pmatrix}, \quad (6.7)$$

The operators in the superoperator $\hat{M}$ have the following interpretation. The operator T_B corresponds to a partial trace on the subsystem B, which can be interpreted as the removal of the H^+ or OH^- protons from the molecule. The superoperator T_B describes the directional matrix product with the subsystem B and corresponds to a proton attaching to the molecule. The operators L_i govern the evolution of the corresponding subsystems under the spin Hamiltonian $\hat{\mathcal{H}}_i$, and hence it takes the form $\mathbb{L}_i = i(\mathbb{1} \otimes \mathcal{H}_i - \mathcal{H}_i \otimes \mathbb{1})$.

Equation 6.6 is solved in discrete steps of size Δt :

$$\rho(t + \Delta t) = e^{M\Delta t}\rho(t), \quad (6.8)$$

while evaluating an observable magnetization at each step: $M_z = \langle \hat{M}_z | \rho \rangle$. A magnetization signal obtained this way was then Fourier transformed to simulate an NMR spectrum. As the amount of each form of urea (Fig. 6.6a)) changes with pH, the molar fraction of each possible spin system is used to define nuclear magnetization M_z .²

The simulated spectra are plotted in Fig. 6.5b). They are in qualitative agreement with the experimental results shown in Fig. 6.5b). This confirms the adequate description of the process. Specifically, the simulations predict the disappearance of high-frequency peaks in highly basic or highly acidic conditions. It also shows that, in case of $[^{13}C, ^{15}N_2]$ -urea, the fast exchange leads to simplification of the spin system to the XA_2 spin topology where a single, narrower peak in the zero-field spectrum is observed. It should be noted however, that the model did not agree in all detail with the experimental results. For example, in simulations the line broadening is much more significant than observed experimentally. This may stem from the simplifications that were introduced in the calculations. First, we only considered the linear kinetics with respect to the concentrations, which is true only for dilute urea solutions. For the purpose of zero-field experiments, however, concentrated (~ 8 M) solutions were used. Moreover, in the model we assumed a total depolarization of the protons while leaving the urea molecule. Alternative approaches to simulations, such as Monte Carlo calculations, could resolve this issue and produce better quantitative agreement with the observed results. However, despite those problems, the simple model developed in this thesis captures all crucial effects of chemical exchange on the evolution of spin systems at a zero field.

6.5 RELAXOMETRY AT ULTRA-LOW MAGNETIC FIELD

As is the case in high-field NMR, ZULF NMR also offers the ability to investigate spin relaxation times. This modality was studied in a number of works (Tayler et al.

² Simulations shown in Fig. 6.5b) were performed on a regular 8-core PC in Matlab, using the MOIN library and the Matlab function `expmv`, directly calculating the action of the matrix exponential on the vector to deal with the memory restriction. The code used to generate zero-field spectra under chemical exchange is provided in Appendix A.

[2016], Tayler and Gladden [2019] and most recently in Bodenstedt et al. [2021]). In this dissertation, such measurements were developed in parallel to the spectroscopic measurements at zero-magnetic field. Relaxometry measurements under ULF conditions are typically performed in a series of measurements, where the sample is held for a variable time after polarization in a set of magnetic fields ³. After the storage, the field is switched off, possibly a magnetic field pulse is applied, and the spins start to evolve in a zero or ultra-low field. The amplitude of the detected signal is then plotted versus the storage time and the longitudinal relaxation time is determined. The corresponding T_2 time can be derived from the width of the peaks in the spectrum.

Examples of such measurements are shown in Fig. 6.8a),b), where the results of measurements of $[^{13}\text{C}]$ -formic acid, i.e., a standard zero-field NMR sample, and $[^{15}\text{N}]$ -methylpyridinium are presented. The formic-acid spectra were obtained in the presence of a small transverse detection field of 35 nT (Fig. 6.8a)). Under such ULF conditions, the spectrum of the XA spin system that corresponds to formic acid contains a single low-frequency peak at average of the Larmor frequency of the coupled spins, $2\pi\nu_1 = 1/2(\gamma_H + \gamma_C)B$, and two peaks centered around the J coupling constant with splitting proportional to the sum of gyromagnetic ratios, $2\pi(\nu_3 - \nu_2) = (\gamma_H + \gamma_C)B$ (Fig. 6.8b)). The additional peak visible in the low-frequency part of the spectrum is centered at the proton Larmor frequency and comes from residual water protons uncoupled from the rest of the spins. The decay of the amplitude of each peak is shown in Fig 6.8b) as a function of the storage time at a field of 1 μT . This dependence can be fitted with the single exponential decay with characteristic longitudinal time T_1 .⁴ The measured relaxation time of the high-frequency peaks was $5.81 \pm 0.14\text{s}$ that is with agreement the previously published results for formic acid containing residual amount of water (Emondts et al. [2014]). Interestingly, both low-frequency peaks decay faster, with the same relaxation time ($\sim 5\text{s}$). This is a somewhat surprising result, as one peak came from the coupled-spin system, while the other corresponded to practically uncoupled spin. The equality of relaxation mechanisms for different chemical groups under has been supported by recent results (Tayler and Gladden [2019]) suggesting a dominant contribution to T_1 by pair-correlated relaxation mechanisms.

Relaxation measurements can also be performed under low-field conditions, where the Zeeman interaction dominates over the scalar coupling. This is illustrated in the low-field spectrum of $[^{15}\text{N}]$ -methylpyridinium obtained under a magnetic field of $\sim 790\text{nT}$, where the two broadened peaks centered around the proton frequency are visible (Fig. 6.8c)). The broad structure is the result of an overlapping of several low-field resonances. Pyridinium-derived compounds are often investigated due to the very long (hundreds of second) lifetime of ^{15}N nuclei which may prove useful as MRI imaging contrasts (see for example Platas-Iglesias et al. [2004]), especially when hyperpolarized with the use of parahydrogen-based techniques (Jagtap et al. [2019]). The low-field signal decays (Fig. 6.8d)) exponentially with the T_1 time of $2.35 \pm 0.05\text{s}$ for a range of fields between 5 μT and 500 μT . In principle, the signal from long-lived nuclear species (^{15}N) can be detected and measured under the same-field condition (the low-frequency contribution is not visible for the spectra, as the magnetic field tilting nuclei away from the detection field is equal to $\pi/2$ for protons).⁵

³ Longitudinal relaxation of magnetization can be measured directly in a single-shot experiment with the DC magnetometer (see for example Fig. 3.15a)).

⁴ For the XA spin system stored in ULF, an amplitude of the signal versus the storage time may follow a bi-exponential, corresponding to the so-called fast decay associated with the lifetime of the triplet state and the slow decay related to the relaxation of the singlet state (Emondts et al. [2014]). In the work presented in this dissertation, the spectrum was measured following a transverse pulse to measure the equalization of populations in triplet state, so the signal decay is determined by a single longitudinal relaxation time T_1 .

⁵ The amplitude of nitrogen peaks in low-field regime (with only residual coupling) would be approximately 100 times smaller than the peaks from hydrogen using a thermal prepolarization.

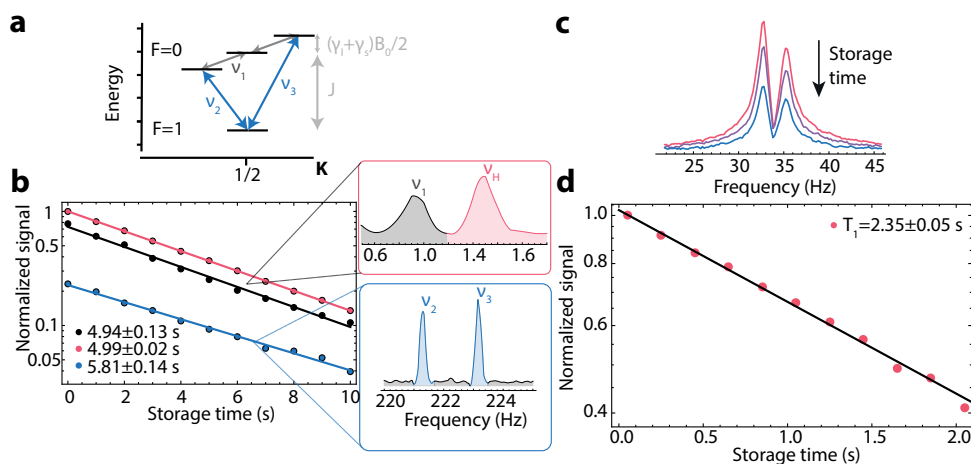


Figure 6.8: a) Energy-level structure of the XA spin system, with indicated transitions, under ULF condition. The field splitting the Zeeman sublevels was assumed to be perpendicular to the detection axis. (b). Amplitude of the NMR resonance spectral lines in the ultra-low field spectrum of ^{13}C -formic acid (see inset) plotted versus storage time at $1\ \mu\text{T}$. The extracted T_1 times for each group of peaks is shown in the bottom left corner. Figure adapted from Put et al. [2021]. c) Low-field spectrum of ^{15}N -methylpyridinium as measured in a field of $\sim 790\ \text{nT}$. The broad peaks, centered around proton frequency, come from the overlap of many transitions present in low-field spectrum of ^{15}N -methylpyridinium as a results of many couplings between nonequivalent nuclear spins in the molecule. d) The amplitude of the ^{15}N -methylpyridinium low-field signal as plotted versus the storage time at $1\ \mu\text{T}$. The extracted T_1 time of the protons is shown in the top right corner.

The method of polarization measurement presented here can be used to study the relaxation dispersion from zero field up to millitesla field range (as also explored in recent work Bodenstedt et al. [2021]). This enables measurements in the range that until now was not accessible to NMR relaxometry.

As ULF detection of NMR signals does not rely on the presence of heteronuclear couplings, such studies can be performed without the need for isotope labeling. Moreover, molecules can be potentially studied in an indirect manner, i.e., by investigating their influence on the relaxation properties of other molecule, e.g., effect of biomolecules on water relaxation. In particular, low-concentration molecules with naturally abundant isotopes can be indirectly probed in this way. To investigate this possibility, we studied the relaxometry properties of the glucose water solution at concentrations up to $10\ \text{mM}$ (see Fig. 6.10). The decay of the ULF NMR signal, after storing in a $1\text{-}\mu\text{T}$ field, followed a monoexponential decay (Fig. 6.10a). The characteristic decay time T_1 is plotted versus the D-glucose concentration, showing a clear dependence of the relaxation time of the solvent on the glucose concentration (Fig. 6.10c).

While the results presented in this dissertation clearly demonstrate the dependence of the relaxation properties of water protons on concentrations of biorelevant glucose, further studies with the use of biological fluids, such as plasma, serum, or whole blood, are needed to possibly identify a correlation between the relaxation time and glucose levels in these biofluids (most likely using relaxation dispersion properties in a range of storage fields). Such correlations between metabolic syndromes and nuclear spin relaxation times were shown in conventional NMR at the low-field regime (Robinson et al. [2017]). Ultra-low field NMR relaxometry apparatus, such as the one presented here, can therefore hasten development of compact, portable, and inexpensive spectroscopic tools for blood testing and metabolic screening (Mishra et al. [2018], Patel et al. [2018]).

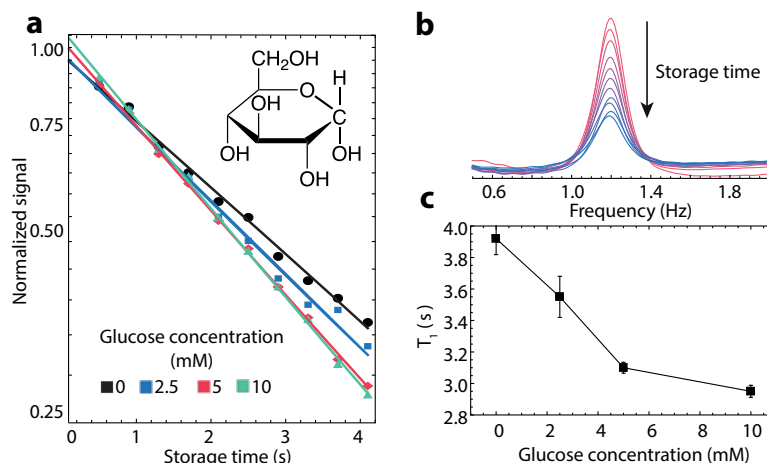


Figure 6.9: a) Ultra-low field relaxometry of aqueous solution of D-glucose. The amplitude of low-field solvent peak plotted as a function of storage time at 1 μ T for different concentrations of glucose. b) Proton signal measured at 50 nT shown for increasing storage times. c) Relaxation times T_1 extracted from water proton signals at different concentrations of glucose. Adapted from Put et al. [2021].

6.6 COMPACT AND MOBILE SETUP FOR ZERO-FIELD NMR

The zero-field NMR setup, used to obtain results presented in this chapter, was based on the commercial atomic magnetometer (QuSpin-QZFM). The sensor was enclosed in a small mu-metal shield (Twinleaf MS1). Rest of the components used to run an experiment (Halbach magnet, switches, power supplies current source, and data acquisition card are easily available). The setup itself is modular, as the components can be easily removed or replaced. This facilitates the transformation from thermal prepolarization to hyperpolarization using parahydrogen-based hyperpolarization. The setup was placed on the mobile card, while the solid-package construction of the sensor prevents misalignment and performance degradation. The small footprint of the device and its modular character made it possible to transport or rebuild the setup with minimal effort (see Fig. 6.10).⁶ Zero-field spectrometer as presented here opens up this modality of NMR to a range of investigation, as the technique no longer requires prior experience with atomic physics, the detection geometry can be easily adapted to a range of measurement while the portability make proof useful for situation where the measurement has to be performed in the field (e.g. reaction and environmental monitoring). Further development in this regard is warranted, as the ZULF NMR may become more widely used spectroscopic tool.

6.7 ZULF NMR OF BIOMOLECULES – CONCLUSIONS

In this chapter we investigate a range of small biomolecules with the use of ultra-low and zero-field NMR for the very first time. Different measurement schemes (measurement at zero and precession in the transverse ultra-low magnetic field), were explored and the rational behind them was explained. In zero-field we measured the spectra of molecules representing important groups of biorelevant substances: metabolites, aminoacids and sugars. We also explored quantitatively the role of the chemical exchange in the observed spectra, omnipresent in biomolecules. For the molecules without the measurable heteronuclear J -coupling, a relaxometry measurement can be performed in low and ultra-low range of field. For instance

⁶ As the atomic magnetometer became recently more available, similar zero-field setups (see for example Blanchard et al. [2020b]) were recently constructed.

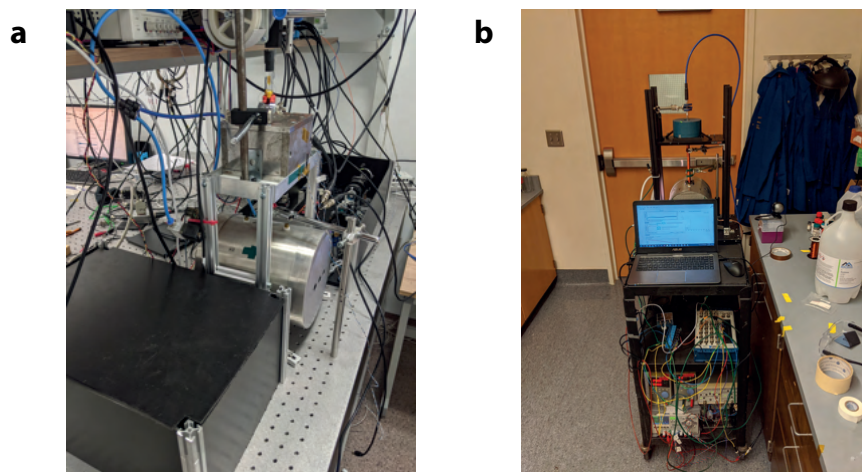


Figure 6.10: a) Home-made zero-field NMR spectrometer. The mu-metal shield (in the center) housed the vapor cell used to magnetic field detection. The black boxes accommodated the optical elements used to perform atomic magnetometry, while the necessary electronics was stashed on the shelves above. The whole setup was mounted onto the optical table. The setup was used to obtain zero-field spectra of urea, presented in this chapter. b) Mobile, zero-field spectrometer used to obtain zero-field spectra of biomolecules. The setup was based on the commercial magnetometer, housed inside a small, mu-metal shield, where the zero-field evolution of spins took place. The setup was built from off-the-shelf components and built in a modular fashion onto a movable cart. The use of commercial parts implies that eventually no prior atomic-physics knowledge would be required, while the setup could transported easily to suit different potential applications (here in the “wet lab”).

an indirect measurement of target compound concentration through the relaxation properties of the solvent can be performed, as shown here for dilute glucose solutions. While some of the results showcased in this chapter were obtained with in-house-built spectrometer, the portable, compact setup relying on commercial sensor was also constructed, pointing into the adaption of zero-field NMR technique outside of the physics lab.

So far, experimental results presented in this thesis show the use of ZULF NMR in chemical and biochemical analysis. Here, we report on the use of nuclear spin evolution under ULF conditions to probe the existence of “new physics”. Specifically, we discuss searches for the spin-gravity interaction.

7.1 MOTIVATION BEHIND EXOTIC PHYSICS SEARCHES

7.1.1 Standard model of particles

The current theory that describes matter and fundamental interactions (all except gravity), the so-called **standard model** (SM) of particles, has been extremely successful in predicting numerous physical phenomena (Patrignani et al. [2016]). These predictions were tested with unprecedented accuracy, revealing excellent agreement between the theory and the observations (see for example Hasert et al. [1974], Aubert et al. [1974], Hanneke et al. [2008], Aad et al. [2012]). Despite its undeniable success, there are several experimental observations that cannot be explained within the SM framework. Among them, there is an observed imbalance between matter and antimatter, unexplained nature of hypothesized dark matter, and an accelerated rate of the Universe expansion induced by the so-called dark energy (for more details, see for example Bull et al. [2016]). Additionally, so far no theory offers the ability to include all fundamental interactions (i.e., including gravity) in one self-consistent theory. All of these discrepancies lead to a number of searches to find yet undiscovered physics beyond SM.

7.1.2 Table-top searches for new physics

Although a large fraction of searches beyond SM is carried out with high-energy (TeV) experiments (Rappoccio [2019]), competing smaller-scale experiments were also developed for such a purpose. A prime example of such tabletop experiments is atomic, molecular, and optical (AMO) physics experiments, exploring high-precision atomic (quantum) sensors (atomic magnetometers, clocks, and interferometers) (see for example Safronova et al. [2018] and references therein).

Atomic magnetometry for exotic physics

As mentioned above, precise atomic magnetometry (Sec. 3.3), which was explored in all studies presented in this dissertation, was used to search for physics beyond SM. For example, atomic magnetometers were used to search for dark matter (Pospelov et al. [2013]). Such a search is possible if hypothesized dark-matter particles induce torque on spins. In this case, the interaction can be detected in the same manner as the detection of a magnetic field in atomic magnetometers. A specific example of the particles that may induce the torque are ultra-light bosons (e.g., axions). These particles can form topological defects or large astronomical objects, which would induce transient effects on optical magnetometers. Yet, to avoid false-positive signals, arising due to ever-present noise, the magnetometers were arranged in a global network composed of synchronized atomic magnetometers (Pustelny et al. [2013]).

Recently, this scheme has been explored to search for domain structures of axion-like fields (Afach et al. [2021]).

Nonlinear magneto-optical rotation, described in detail in Sec. 3.3.7, was also used to search for “new physics”. In Kimball et al. [2013], the Larmor precession of rubidium atoms was used to search for a long-range spin-mass coupling, also known as the **spin-gravity** coupling. The spin-gravity interaction consists of coupling of the gravitational field to the atomic angular momentum. In turn, the frequency of the Larmor precession in a given magnetic field would depend on the magnetic-field orientation with respect to the gravitational field. Since field fluctuations can lead to systematic effects mimicking the gravitational-field effect, the measurements were performed using comagnetometry based on two isotopes of rubidium (^{85}Rb and ^{87}Rb). This scheme allowed us to establish a new limit on the coupling of the gravitational field to protons (Kimball et al. [2017]).

Searches for new particles with the use of NMR

Being a very sensitive probe to spin interactions, NMR was also employed to search for exotic spin-dependent interaction. An example of an experiment searching for the interaction is the cosmic axion spin precession experiment (CASPER) (Budker et al. [2014], Garcon et al. [2017]). CASPER is based on the assumption that ultra-light bosons can interact with nuclear spins, producing time-varying (oscillating) coupling. Such an oscillating field, if resonant with the Larmor frequency of the nuclei, can induce a precession of nuclear magnetization, tipping it away from the original orientation. In this sense, then experiment is analogous to conventional high-field NMR (Sec. 2.1.1), where the Zeeman interaction with the oscillating field is replaced by the oscillating coupling to dark-matter particles (for more details see Aybas et al. [2021]).

7.2 ZULF NMR IN PRECISION MEASUREMENTS

Soon after the emergence of atomic-magnetometry-based zero-field NMR, the evolution of nuclear spins under ultra-low magnetic field was used for precise metrology. In Ledbetter et al. [2012], the authors analyzed the NMR spectra of a liquid mixture of pentane and hexafluorobenzene in an experimental scheme similar to that described in Chapter 3. Since in both compounds the heteronuclear J -coupling is absent, the precession of ^1H and ^{19}F spins were measured in ULFs (600 nT). Due to the very long coherence (T_2) time of these compounds at ULFs (~ 14 s for ^1H and ~ 21 s for ^{19}F), the authors were able to determine the frequency of precession with nHz resolution. Moreover, by taking a ratio of precession frequencies of two compounds, the authors demonstrated strong suppression of magnetic-field sensitivity, while still remaining the sensitivity to nonmagnetic couplings (spin-gravity coupling or permanent electric dipole moments). In the same work, a similar comagnetometer was constructed of a sample containing liquid ^{129}Xe and pentane. Polarization of xenon nuclei was obtained by hyperpolarization, that is, spin-exchange optical pumping, while protons in pentane were cross-polarized by the nuclear Overhauser effect (see for example Navon et al. [1996]). This part of the work pointed towards hyperpolarizing samples as a means of boosting the SNR of the comagnetometer readout and further improving the spectral resolution obtained in such systems.

The ZULF NMR comagnetometer, using a single-compound sample, was proposed in Wu et al. [2018]. In this work, $[2\text{-}^{13}\text{C}]\text{-acetonitrile}$ NMR was measured under ULF conditions (~ 100 nT). As acetonitrile is a XA_3 spin system (Sec. 3.4.2), the ULF NMR spectrum consists of two groups of resonances arising at the J and $2J$ (see Sec. 3.4.2). They correspond to the $F = 0 \rightarrow F = 1$ and $F = 1 \rightarrow F = 2$ transitions and the splitting is determined by specific combinations of the ^1H and ^{13}C gyromagnetic ratios. The authors of Wu et al. [2018] showed strong suppression

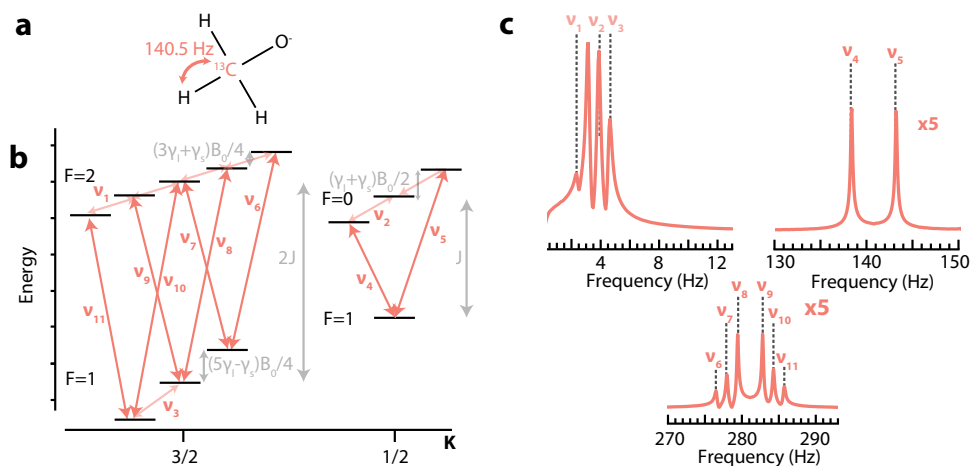


Figure 7.1: a) Structural formula of ^{13}C -methanol with the heteronuclear coupling indicated by the red arrow. b) Ultra-low-field energy diagram of the XA_3 spin system. Each energy manifold is characterized by the total spin K of equivalent protons. The red arrows indicate transitions observed in our experiment. c) Experimentally measured ULF spectrum of ^{13}C -methanol. All eleven transitions from the XA_3 spin systems are labelled. In the low-frequency region of the spectrum, the peak with the highest amplitude corresponds to the proton from OH^- -group, which is effectively decoupled from the rest of the molecule due to chemical exchange.

of the magnetic-field effect, while still preserving the sensitive to exotic couplings. Moreover, application of a single compound allowed for the limitation of systematic effects that were present in the different-compound comagnetometer. Particularly, while the authors of [Ledbetter et al. \[2012\]](#) discovered that magnetic-field gradients led to a systematic effect, mimicking the gravitational-field effect, this effect is absent in the single-species comagnetometer. This enabled the authors to consider schemes to establish new limits on spin-gravity coupling to protons. Although the analysis of the 15-hour long measurement showed that such a measurement can principally match the current limit on the interaction, the implemented experimental configuration did not allow for real measurements (wrong geometry). However, the same comagnetometer was used to obtain new limits on the interaction of spins with dark matter in the form of axion-like particles ([Wu et al. \[2019\]](#)).

The work presented in this chapter is based on the idea of the single-species nuclear comagnetometer. We implement a ZULF NMR spectroscopy to obtain a comagnetometer signal with the hope of probing spin-gravity coupling energies below current experimental limits. The details of the study are presented below.

7.3 SINGLE-SPECIES NUCLEAR SPIN COMAGNETOMETER

7.3.1 Energy structure of methanol at ultra-low magnetic field

In our research, we used a single-species ZULF NMR comagnetometer. In the comagnetometer, a sample of neat ^{13}C -methanol was used (the energy-level structure of ^{13}C -methanol is shown in Fig. 7.1a). This spin system has three equivalent protons J -coupled to a single carbon nucleus, thus it is XA_3 .¹ Although in Sec. 3.4.2, we explained the spectrum of the XA_n system using the perturbation theory, the NMR spectrum of such a system can be exactly calculated in arbitrary magnetic field (see

¹ The proton of the OH^- -group undergoes a fast chemical exchange and can be neglected from the analysis of spin dynamics.

Appelt et al. [2010]). To precisely understand the structure of the spin system used as a comagnetometer, we use this approach.

The energy-level diagram of the XA_3 spin system in the ultra-low magnetic field is shown in 7.1b). In the system, there are two independent manifolds, labeled by the total spin K of three equivalent X protons. For each value of K , two different possible values of F of $K \pm 1/2$ are possible. In the presence of a magnetic field, each manifold is divided into $2F + 1$ magnetic sublevels. The approximated splittings depend on the combination of the gyromagnetic ratio of ^1H and ^{13}C are indicated in Fig. 7.1b). The red arrows mark the transitions observable in a zero field, assuming that the quantization axis is parallel to the magnetic field, yet perpendicular to the sensitive direction ($\Delta F = 0, \pm 1$, $\Delta K = 0$, and $\Delta m_F = \pm 1$ (for more details, see Sec. 3.4.2). In turn, there are six high-frequency transitions in the $F = 1 \rightarrow F = 0$ manifold, two high-frequency transitions in the $F = 1 \rightarrow F = 0$ manifold, and six and two low-frequency transitions in the manifolds, yet some of these transitions are degenerate (four, two, and two times).

The spectrum of $[^{13}\text{C}]$ -methanol in a weak transverse magnetic field is shown in Fig. 7.1c). As discussed above, it consists of eleven lines corresponding to the XA_3 spin system and labeled by $\nu_1 - \nu_{11}$ and a single line from the decoupled proton of the OH^- group. The energy levels of the spin Hamiltonian (in units of h) for the XA_n spin system placed in a magnetic field B can be expressed as (Appelt et al. [2010]):

$$E_{\text{XA}_3}(B, J) = -m_F \gamma_A B - \frac{J}{4} + F_s \sqrt{\left(K + \frac{1}{2}\right)^2 J^2 - 2m_F J (\gamma_X - \gamma_A) B + (\gamma_X - \gamma_A)^2 B^2}, \quad (7.1)$$

where J indicates the strength of the heteronuclear J -coupling, γ_X and γ_A are the gyromagnetic ratios for the spins X and A, and F_s is a number defined such that $F_s = F - K$.

The spectral region around the J -coupling frequency consists of two peaks, corresponding to transitions in the $K = 1$ manifold. As for comagnetometry purposes, we are interested in the magnetic-field-induced splitting, and we can characterize these transitions by the splitting and average position of the lines. It can be shown from Eq. 7.1 that the splitting around the J frequency scales with magnetic field B as:

$$\Delta\nu_1 = \nu_5 - \nu_4 = B(\gamma_C + \gamma_H), \quad (7.2)$$

where we replaced the general parameters for the X and A spins with the parameters for ^1H and ^{13}C . Simultaneously, we can show that the center of the lines is given by:

$$\bar{\nu}_1 = \frac{1}{2} (\nu_5 + \nu_4) = \frac{1}{2} \left(J + \sqrt{J^2 + B^2 (\gamma_C + \gamma_H)^2} \right) \approx J + \frac{B^2 (\gamma_H - \gamma_C)^2}{4J}. \quad (7.3)$$

Equation 7.2 shows that the splitting of the line scales linearly with the field, while the central position of the lines is also magnetic-field dependent, shifting with the field toward the higher frequencies.

At approximately $2J$, three pairs of lines are visible. Once again, it is convenient to characterize the lines by their centers and splittings. For the innermost line pair, we obtain (Eq. 7.1):

$$\Delta\nu_2 = \nu_9 - \nu_8 \approx B \frac{\gamma_H + 3\gamma_C}{2} + \frac{3B^3 (\gamma_H - \gamma_C)^3}{64J^2}, \quad (7.4)$$

for the splitting and:

$$\bar{\nu}_2 = \frac{(\nu_8 + \nu_9)}{2} \approx 2J + \frac{3B^2 (\gamma_C - \gamma_H)^2}{32J}, \quad (7.5)$$

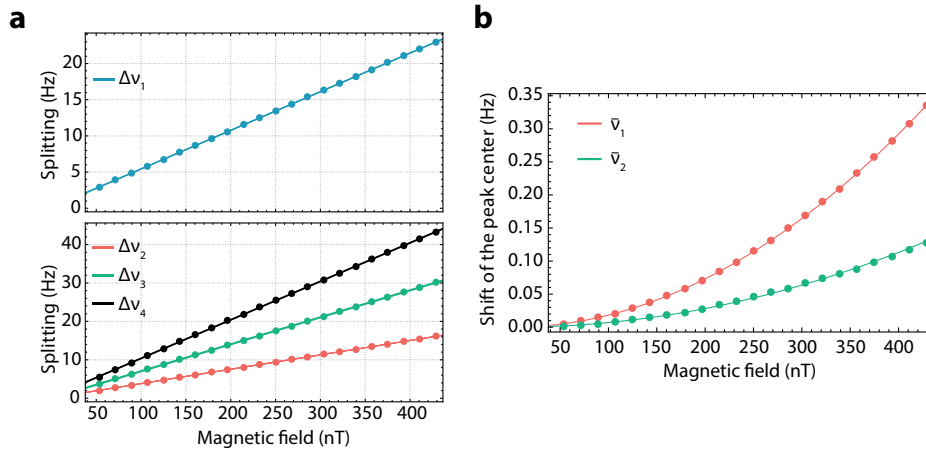


Figure 7.2: a) Experimentally measured splittings of the NMR lines in ULF NMR spectrum of $[^{13}\text{C}]$ -methanol. The experimental uncertainties are smaller than the data points on the graph. b) Experimentally measured shifts of the central positions of the resonance pairs in the ULF NMR spectrum of $[^{13}\text{C}]$ -methanol. The solid lines show the dependencies calculated based on Eqs. 7.3-7.7.

for the average position. The line positions for the middle pair of the lines can be calculated from:

$$\begin{aligned}\Delta v_3 = v_{10} - v_7 &\approx \frac{B(5\gamma_H - \gamma_C)}{2} + \frac{3B^3(\gamma_H - \gamma_C)^3}{64J^2}, \\ \bar{v}_3 = \frac{1}{2}(v_7 + v_{10}) &\approx 2J + \frac{7B^2(\gamma_H - \gamma_C)^2}{32J},\end{aligned}\quad (7.6)$$

while the transition frequencies of the most split lines are:

$$\begin{aligned}\Delta v_5 = v_{11} - v_6 &\approx \frac{B(3\gamma_H + \gamma_C)}{2} + \frac{3B^3(\gamma_H - \gamma_C)^3}{64J^2}, \\ \bar{v}_5 = \frac{(v_6 + v_{11})}{2} &\approx 2J + \frac{7B^2(\gamma_H - \gamma_C)^2}{32J}.\end{aligned}\quad (7.7)$$

The center of these lines also shifts to higher frequencies with the magnetic field, while the splitting has a nonlinear term contributing to scaling with the field.

Figure 7.2 shows the positions and splittings of the spectral lines determined based on the measured ULF NMR spectra of $[^{13}\text{C}]$ -methanol in a range of magnetic fields (50-450 nT). The parameters were determined by fitting a sum of complex Lorentzians to the NMR spectra, each of which was the result of 128 averages (the overall SNR of more than 1000). The splitting for the range of investigated fields and the experimental uncertainty scales linearly with the magnetic field for all pairs of lines, as the nonlinear corrections scale only as B^3 (see for example Eq. 7.4). As shown in Fig. 7.2b), the centers of the resonances shift to higher frequency at a quadratic rate, which is consistent with Eqs. 7.3, 7.5, 7.5, and 7.7.

7.3.2 Magnetometer and comagnetometer performance

As evident from Eq. 7.2 and 7.4, by measuring the splitting of lines in the ULF NMR spectra of methanol, we gain precisely information about the magnetic field value. This is illustrated in Fig. 7.3, where measurements of 128 successive transients of the magnetic field alternating between opposite field orientations are presented. As, due to residual fields, the reversal was not completely symmetric, the field strength changed by about 4.3 nT between two field orientations.

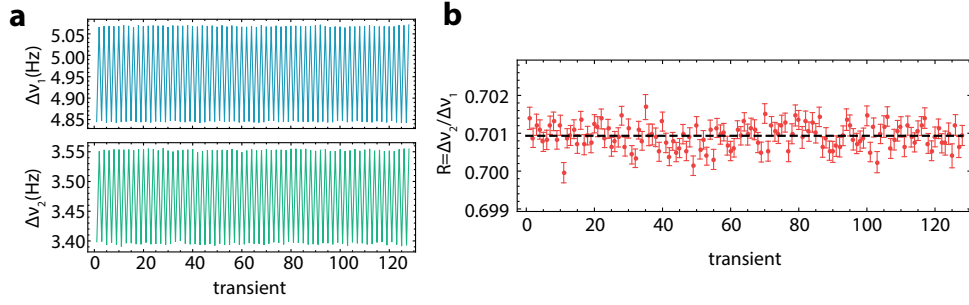


Figure 7.3: a) Splitting in the lines around the J and $2J$ frequency as extracted from successive measurements, when the magnetic field was imperfectly reversed, with a field modulation of ~ 4.3 nT. The splitting closely follows the magnetic-field magnitude change. b) Comagnetometer signal (ratio of splitting) for the same experiment as shown in a). Despite the field modulation, there is no obvious modulation of the comagnetometer signal.

The splitting measurements can then be used for comagnetometry. If we take a ratio of the splittings ν_1 and ν_2 (different pairs can also be considered), we get the following relation:

$$R = \frac{\nu_2}{\nu_1} \approx \frac{\gamma_H + 3\gamma_C}{2(\gamma_H + \gamma_C)} + \frac{3B^2(\gamma_H - \gamma_C)^3}{64J^2(\gamma_H + \gamma_C)}. \quad (7.8)$$

The ratio of frequencies is therefore, neglecting the residual (under ULF conditions) non-linear term, is insensitive to magnetic field fluctuation. This was experimentally verified (Fig. 7.3b), where the splitting ratio R was plotted for the same modulation of the magnetic field, as in Fig. 7.3a). The ratio R , used for comagnetometry, shows no clear dependence on the magnetic field, while its value is consistent with the theoretical value for ^{13}C -methanol:

$$R_{\text{methanol}} = 0.70093 + R_{\text{non}}(B), \quad (7.9)$$

where the constant term was evaluated using the gyromagnetic ratios for ^{13}C and ^1H given in Table 1.1, modified by the shielding factors measured for methanol (-137 ppm for ^{13}C , -29 ppm for ^1H as measured in Makulski [2008]). For the measurement where a magnetic field of 80 nT was used, the nonlinear term $R_{\text{non}}(80 \text{ nT})$ is equal to:

$$R_{\text{non}} = 0.000009. \quad (7.10)$$

This term gives the overall dependence of the ratio on the magnetic field and needs to be taken into account when the signals are precisely measured.

7.4 TOWARDS NEW SPIN-GRAVITY COUPLING LIMITS WITH ZULF NMR

7.4.1 Spin-gravity coupling effect on nuclear spin

The liquid-state nuclear comagnetometer described in this thesis was employed to probe for the hypothetical spin-gravity coupling. A review of theories that discuss possible spin-gravity can be found, for example, in Safronova et al. [2018]. The coupling to the nuclear spins in the NMR sample subject to Earth's gravitational acceleration g can be written as (following Kimball et al. [2013]):

$$\hat{\mathcal{H}}_{\text{spin-gravity}} = \sum_i \chi_i \hat{I}_i \cdot g, \quad (7.11)$$

where χ_i is the so-called **gyrogravitational ratio** which describes the strength of the coupling of the i -th spin to the gravitational field. The form of the Hamiltonian is completely analogous to the Zeeman Hamiltonian (Sec. 2.1.1), i.e., the spin-gravity coupling mimics the action of the magnetic field. At the same time, since the effect of the hypothetical spin-gravity coupling is at most orders of magnitude smaller than the J -coupling present in the molecule, we can use a perturbation theory to calculate the correction to the energy levels of the spin system at ZULF (see also Wu et al. [2018]):

$$\begin{aligned}\delta E_{SG}(F, m_F, K, S) &= \langle F, m_F | \hat{\mathcal{H}}_{spin-gravity} | F, m_F \rangle \\ &= \sum_{m_S, m_K} \langle K, m_K, S, m_S | F, m_F \rangle^2 g (\chi_X m_S + \chi_A m_K),\end{aligned}\quad (7.12)$$

where we assumed that the effect of the Zeeman interaction is a small correction to the J -coupling. We also assumed that the gravitational field coincides with the direction of the magnetic field (the z -axis), while the Clebsch-Gordan coefficient in Eq. 7.12 comes from changing the decoupled-spin basis to the coupled-spin basis.

Following formula Eq. 7.12, we can relate the measured comagnetometric signal with the strength of hypothetical spin-gravity coupling. The gyrogravitational ratios of the nuclei can be expressed by the strength of the coupling to the nucleons (protons and neutrons). Following the approach presented in Wu et al. [2018], we can write:

$$\begin{aligned}\chi_X &= \chi_C = -1/3\chi_n, \\ \chi_A &= \chi_H = \chi_p,\end{aligned}\quad (7.13)$$

where χ_n and χ_p refer to the gyrogravitational ratio of the neutron and proton, respectively, and we set the values of the ratios in the context of the XA_3 spin system. We can now calculate the effect of the spin-gravity coupling on the splittings in the ULF used for comagnetometry. We neglect here the nonlinear, B^2 -depended term in the comagnetometer readout (last term in Eq. 7.8).

$$\Delta v_1^{SG} = B(\gamma_H + \gamma_C) \pm \frac{g}{\hbar} (-1/3\chi_n + \chi_p), \quad (7.14)$$

and

$$\Delta v_2^{SG} \approx B(\gamma_H + 3\gamma_C) \pm \frac{g}{\hbar} (-\chi_n + \chi_p), \quad (7.15)$$

where we considered only the resonance pair of the smallest splitting (innermost resonance pair). The $\pm$ factor arising in the equations accounts for the magnetic field being along or opposite to the gravitational field. The ratio R , used for comagnetometry, is then equal to:

$$R_{SG} = \frac{\Delta v_2^{SG}}{\Delta v_1^{SG}} \approx \frac{\gamma_H + 3\gamma_C}{2(\gamma_H + \gamma_C)} \left[\frac{1 \pm (-\chi_n + \chi_p) \frac{g}{\hbar B (3\gamma_H + \gamma_C)}}{1 \pm (-1/3\chi_n + \chi_p) \frac{g}{\hbar B (\gamma_H + \gamma_C)}} \right], \quad (7.16)$$

Equation 7.16 can be further simplified by assuming that $g\chi_{n/p}/\hbar \ll B\gamma_C, B\gamma_H$, and expanding in the series with up to a linear term in g . Moreover, we can express the gyromagnetic ratios of ^1H and ^{13}C by nuclear magneton μ_N , leading to (Wu et al. [2019]):

$$R_{\pm} \approx \frac{\gamma_H + 3\gamma_C}{2(\gamma_C + \gamma_H)} \left[1 \mp \frac{g(4\chi_n + 5\chi_p)}{100\mu_N B} \right], \quad (7.17)$$

where $R_{\pm}$ indicates the ratio taken with the magnetic field aligned with and opposite to the gravitational field. From the expression, we can see that by taking

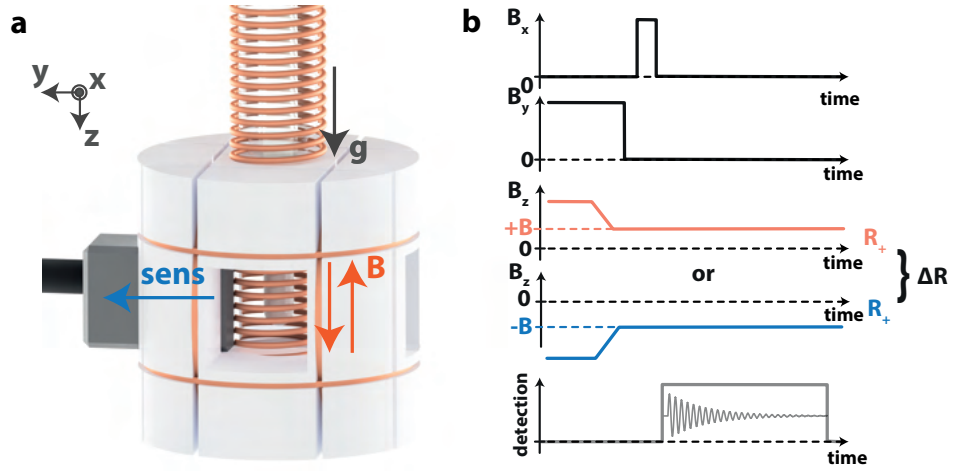


Figure 7.4: a) Geometry of the experiment searching for the spin-gravity coupling. The sensitive direction of the magnetometer is indicated by the blue arrow. The magnetic field B is marked with the red arrow and, during the experiment, was aligned with or opposite to the gravitational field g . b) Magnetic-field sequence after the sample left the prepolarization region and the corresponding ULF NMR signal.

successive measurements with the field aligned along and opposite to the gravitational field, we can subtract the comagnetometer readout and obtain the following ratio difference:

$$\Delta R = R_- - R_+ = \frac{3\gamma_C + \gamma_H}{\gamma_C + \gamma_H} \frac{g(4\chi_n + 5\chi_p)}{100\mu_N B}, \quad (7.18)$$

which constitutes a signal insensitive (to the first order) to magnetic fields but still sensitive to the postulated spin-gravity coupling. Notice, that the nonlinear correction we neglected in the analysis here scales as B^2/J . Upon complete field reversal, the contribution of this term to R_- and R_+ would be identical and would not affect the signal ΔR used to look for spin-gravity coupling.

7.4.2 Detection geometry

The ULF NMR spectrometer (comagnetometer), used to search for spin-gravity coupling, is based on the design presented in Chapter 4. The system was similar to the one used for the nuclear-spin comagnetometry presented in [Ledbetter et al. \[2012\]](#) and [Wu et al. \[2018\]](#), with three notable differences. First, an experimental configuration enabled us to actually search for spin-gravity coupling, as the detection axis was perpendicular to Earth's gravitational field, while the magnetic field could be applied along the gravitational field. Second, a commercial atomic magnetometer was used, which allowed for the correct geometrical measurement and limited the temperature gradient of the sample.² Finally, the NMR tube was kept inside a piercing solenoid allowing to apply a magnetic field exclusively to the NMR sample, i.e., the field was applied without deterioration of the sensitivity of the magnetometer. This increased SNR of the recorded NMR signals and decreases the statistical uncertainty in the comagnetometer readout. Moreover, this configuration allowed us to apply a much stronger field, which was used to precisely determine the line positions in the ULF spectra of methanol (Fig. 7.2).

The experimental geometry and the magnetic-field sequence are shown in Fig. 7.4. The gravitational acceleration g coincides with the z-axis and the direction of the magnetic field B present during spin evolution. The magnetometer was sensitive along the y-axis. After the sample left the prepolarization region, it was shuttled to

² The surface of the commercial magnetometer, placed in proximity to the NMR sample, was kept below 40 °C.

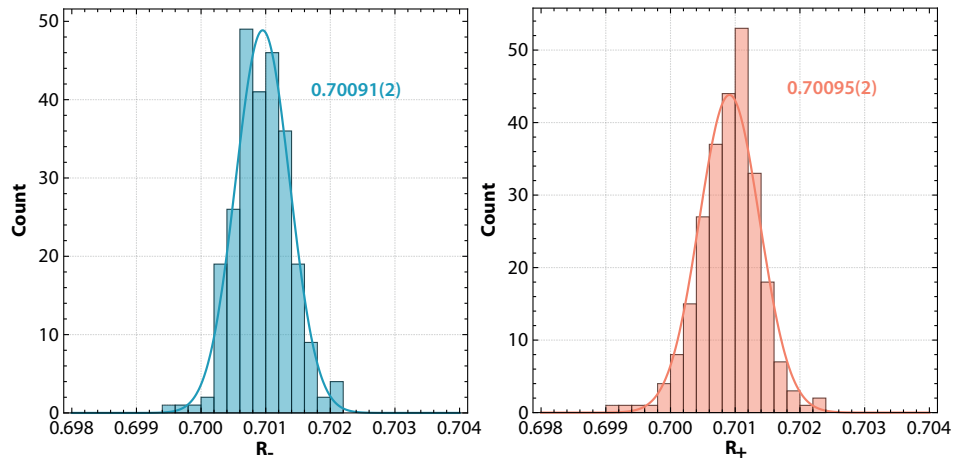


Figure 7.5: Histogram of extracted ratio from the preliminary comagnetometer measurements. From every measurement R_- or R_+ was determined. Inset shows extracted mean value, and the standard deviation of the mean, while the solid line shows an estimated Gaussian distribution of the statistics.

the ZULF region within the z -oriented guiding field of the piercing solenoid. After reaching the final position, the guiding field was turned off adiabatically in a weak field oriented in the y -direction, so that the spins ended up being oriented along the axis. The field was then suddenly switched off and the pulse was applied in the x -direction to boost the ULF NMR signal (for details see Sec. 3.4). The pulse triggered data acquisition. The direction of the B field present during the measurement, as well as, the direction of the guiding solenoid field, was reversed in every iteration. From two successive measurements, the value ΔR was determined, which, according to Eq. 7.18, provides information that was not affected by the magnetic field. Simultaneously, the value could probe the spin-gravity coupling. We now will show an example measurement probing this hypothetical interaction.

7.4.3 Preliminary results

In the preliminary measurement to probe for the spin-gravity coupling with the nuclear-spin comagnetometer the 512 successive measurements were performed. The NMR sample was prepolarized in the magnet for about 30 s and measured under the ULF conditions for another 30 s. Every other iteration, the magnetic field (with the magnitude of 83 nT) was reversed as shown in Fig. 7.4. The raw NMR signals were then preprocessed. Although the full preprocessing procedure is described in Chapter 4, here we limited the preprocessing to cutting off initial (corrupted by the magnetic-field pulse) points and subtracting the varying background. The double-sided (including negative frequencies) NMR spectra were then obtained, and the low-frequency and high-frequency (both at J and $2J$) spectral lines were fitted by a sum of Lorentzians (with the phase of each peak as a free parameter). The positions, amplitudes, and widths of the resonances were then used as starting parameters for the next fit, which consisted of fitting the FID to the sum of the multiple decaying exponentials. Fitting the raw data freed the analysis from any systematic errors that may be introduced by preprocessing. In particular, cutting off the initial part of the signals introduces a frequency-dependent phase shift. To avoid this problem, we introduced backprediction, enabling reconstruction of the initial part of the signal. Although this should eliminate the frequency-dependent phase shift, this process is not perfect and systematic errors may still be introduced. In the case of ultra-precise spectroscopy, which is a necessity in the spin-gravity searches, the systematic effects may distort the measurement results, potentially leading to the effects that mimic the spin-gravity coupling.

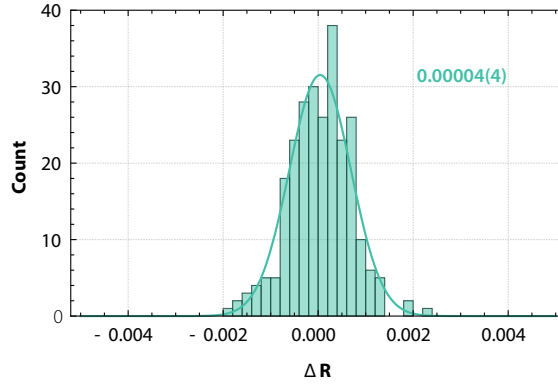


Figure 7.6: a) Histogram of the ratio difference ΔR extracted from the preliminary comagnetometer data. The results show the effect of measuring 512 successive transients (256 pair of data points). From every pair of measurement R_- or R_+ was measured and ΔR shown here was extracted. The inset shows the extracted mean value and the standard deviation of the mean, while the solid line shows an estimated Gaussian distribution.

Fig. 7.5 shows a histogram of ratios R_- and R_+ (being comagnetometer read-outs) extracted from 512 successive measurements. The mean value in both cases is consistent with theoretical value withing statistical uncertainty. Figure 7.6 presents the histogram of the extracted values of the ratio difference ΔR , used to probed for spin-gravity coupling, along with the Gaussian fitting to the dependence. The estimated mean value of ΔR is equal to:

$$\Delta R = 0.00004(4), \quad (7.19)$$

and within the statistical uncertainty consistent with zero. The statistical uncertainty on the level of $4 \cdot 10^{-5}$ can be translated to the statistical upper limit of the spin-gravity coupling to protons:

$$\chi_p \lesssim \frac{1/2}{0.70093} \frac{100\mu_n \cdot 83 \text{ nT}}{9 \cdot 9.81 \text{ m s}^{-2}} \lesssim 1.4 \cdot 10^{-33} \text{ g cm}, \quad (7.20)$$

where we assumed the proton and neutron contributions to be the same. Compared to the current upper limit on the proton spin-gravity coupling (Kimball et al. [2017])

$$\chi_p^{lit} \leq 5.6 \cdot 10^{-33} \text{ g cm}, \quad (7.21)$$

we see that the liquid-state nuclear comagnetometer can already probe spin-gravity coupling beyond the current experimental limits.

7.5 OUTLOOK ON THE SPIN-GRAVITY-COUPLING SEARCH

In this chapter, we presented the liquid-state single-species ULF NMR comagnetometer and discussed the preliminary measurements on the spin-gravity coupling. Based on the statistical uncertainties obtained in the 9-hour measurement, the comagnetometer was already capable of probing such a hypothetical coupling below current limits for the proton. Despite these promising results however, systematic studies of the effect, particularly aiming at identifying systematic errors of the measurements, need to be performed. We also plan to perform longer measurements for several field values. The improved statistics may reveal new systematic errors that need to be taken into account. Additional measurements will also be performed with an alternative XA_3 spin system ($[2-^{13}\text{C}]$ -acetonitrile) to cross-check the consistency of the comagnetometer results.

It should be noted that the comagnetometer presented in this chapter does not have to be based on ^{13}C - ^1H spin systems. Specifically, by changing the heteronuclei experiencing J -coupling, we can probe systems with different neutron and proton contributions.

Finally, the statistical uncertainty of the presented measurements was limited by the SNR of a single ULF NMR measurement. The ratio suffers from the low nuclear polarization obtained in 1.6-T field. The application of hyperpolarization has the potential to significantly reduce this uncertainty. In this context, a reversible way of polarizing the XA_3 spin system is needed. In that context, a recent work (Van Dyke et al. [2022]), employing the SABRE-relay scheme to repeatedly hyperpolarize ^{13}C -methanol, combined with NMR measurements at ULF, is especially promising. Whether the said technique can be adapted for measuring hyperpolarized concentrated samples yielding a much improved ULF signal has yet to be verified.

8.1 SUMMARY

In this dissertation, we analyze the evolution of the nuclear-spin system at zero- and ultra-low magnetic fields under the dominant scalar spin-spin coupling. We investigated how evolution under such conditions leads to the generation of low-frequency magnetic signals and described means of detecting the signals with the use of atomic magnetometers, many of which were developed during the PhD of the author. The theoretical background of ZULF NMR was also provided and detailed descriptions of various contributions to the spin dynamics were analyzed. Specifically, we showed the pivotal role of the heteronuclear J -coupling to observe ZULF NMR signals.

Theoretical investigations were accompanied by the results of numerous experiments. The experimental results were obtained with the use of multiple ZULF spectrometers built by the author. Among various systems, the state-of-the-art spectrometer, operating with the highly-sensitive, wide-bandwidth home-made atomic magnetometer was presented. The modular and portable spectrometer, employing a commercial magnetic sensor was also described. In the experimental analysis, we discussed the solution to the necessity of the existence of heteronuclear scalar coupling. In low abundance nuclei this typically requires isotopic labeling of compounds. Herein, the problem was addressed by working with naturally abundant nuclei, i.e., ^{31}P , which is a nucleus previously not explored in ZULF NMR. Beside its scientific value, the study of organophosphorus compounds also showed the chemical identification capabilities of ZULF NMR. The second solution to the problem, applicable to the low-abundance system, was hyperpolarization using parahydrogen. With the use of various parahydrogen-based hyperpolarization techniques, we demonstrated the ability to increase the amplitudes of the ZULF NMR signals by several orders of magnitude, enabling the detection of molecules undetectable with thermal polarization. We also studied small biomolecules, where the metabolites, amino acids, and sugars were investigated with the use of zero-field NMR for the first time. Using biologically relevant molecules, the effect of chemical exchange was also quantitatively investigated. We showed that small amounts of dilute analytes (such as glucose) can be indirectly studied by looking at the relaxation properties of the solvent. Finally, we used the zero-field NMR to look for physics beyond the standard model of particles. For this purpose, a single species, liquid-state nuclear comagnetometer was developed, and first promising results were presented.

Despite the discussed developments and significant progress of the field during the last couple of years, ZULF NMR still remains a novel technique with a number of challenges and opportunities. Some of the envisioned opportunities are described below.

8.2 SOME OUTLOOK ON FUTURE ZULF NMR

ZULF MRI

While the developments in ZULF NMR using atomic magnetometers were mostly limited to spectroscopy, the other widely used incarnation of NMR – magnetic res-

onance imaging – remained largely unexplored with the sensors (with notable exceptions of experiments presented in Xu et al. [2008] and Savukov and Karaulanov [2013]). Low-field imaging has found wider use in the development of mT-range imaging techniques with inductive detection (Sarracanie et al. [2015]), while μ T-range imaging is actively explored with the use of SQUID sensors (see Kraus et al. [2014] and references therein). In fact, imaging with atomic magnetometers at ULFs is challenging because of the deterioration of the performance of the sensors with the strength of the field and mismatch between atomic and nuclear gyromagnetic ratios. These problems can be addressed by point-by-point imaging. We propose for example that the field gradient, which completely saturates the magnetometer, is turned on only in the spatial encoding phase and the rest of the evolution and detection take place under a homogeneous ULF field. Another approach, we envision could be based on the idea of rotating-frame imaging (see, for example, Hoult [1979]). In this case, spatial information is encoded in an inhomogeneous magnetic-field pulse and evolution and detection occur without the presence of the field gradient. This idea was first explored in the NMOR-based setup presented in Chapter 3 (the results are described in Nędza [2020]), but its incorporation into different spectrometers (MRI scanner) is warranted. While point-by-point imaging is considerably slower, it retains full chemical information about the system. This can result in obtaining not only spatial but also spectroscopic information thanks to a high-resolution fingerprint-like spectrum. As for applications of such imaging, one possible direction would involve MRI of batteries, where the ULF conditions eliminate problems of sample inhomogeneity and presence of conductive elements. In fact, atomic magnetometers were already used to probe Li-ion batteries (Hu et al. [2020]).

It should be noted that the development of atomic magnetometry is strongly driven by rapidly advancing field of magnetoencephalography (Xia et al. [2006]). As the MEG devices based on SQUID has been combined with low-field MRI, maybe the same fate awaits AM based MEG systems, which while costing a fraction of SQUID counterparts, allow for non-cryogenic operation and can be worn while freely moving (Boto et al. [2018]).

Hyperpolarization to enhance ZULF NMR capabilities

As described in Chapter 3, NMR in general, but particularly its ZULF version, is severely hindered by poor sensitivity. Thus hyperpolarization seems like a natural solution to the problem, although a cheap and widely applicable technique is still missing. In this context, one promising approach may rely on parahydrogen-induced polarization to target molecules via chemically exchanging protons. Very recently, such an approach was shown with SABRE-relay-enhanced zero-field spectroscopy (Van Dyke et al. [2022]). An alternative to the technique is PXIP-X-based polarization combined with ZULF NMR spectroscopy. This is a subject of ongoing research in Kraków (see Alcicek [2022]). The technique can be naturally combined with ZULF NMR and can be used to polarize metabolites, amino acids, and sugars (see Chapter 6). It may also help with searches for physics beyond the standard model, as it would minimize the statistical uncertainty in liquid-state comagnetometry.

Handheld ZULF NMR spectrometer

Although ZULF spectrometers can already be made portable (Chapter 6), even smaller systems can be developed. As closed-package atomic sensors can be smaller than 2 cm^3 , the further decrease in system size can be achieved by miniaturizing the magnetic shield (as only the sensor and 1-cm^3 NMR sample must fit inside the shield), the prepolarizing magnet (or hyperpolarization system), and electronics. One can easily envision the whole experiment run by the use of a microcontroller

(see, for example, [Bodenstedt et al. \[2021\]](#)), which, combined with low-power requirements of the sensor, can be better operated. We can speculate that the size of such a portable spectrometer in the near future can be comparable to that of a standard suitcase, with a small enough weight, so it can be carried around and deployed in the field.

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DATA ANALYSIS AND SPIN SYSTEM SIMULATION CODE

A.1 PROCESSING OF EXPERIMENTAL DATA

Below, a Wolfram Mathematica code is provided. The code is used to postprocess a raw zero-field NMR signal, particularly, cutting initial corrupted points, subtracting background from the signal, and backpredicting missing initial points. It also allows for phase correction, exponential apodization and zero-filling of the signal to produce a clearer zero-field spectrum. The details of the procedure are described in Chapter 4.

```
In[1]:= (*Imports data*)
In[2]:= file=FileNames["*.dat",NotebookDirectory[]]
In[3]:= data=Table[Import[file[[i]]],{i,Length[file]};
In[4]:= (*Defines one-sided fourier transform*)
In[5]:= fte[data_,dt_]:=Module[{},
ft=2/Sqrt[Length[data]]*Fourier[data];
ft=Drop[ft,-Length[data]/2];
y=Table[(1/(Length[data]*dt))*(j-1),{j,Length[data]/2}];
ft=Transpose[{y,ft}]
In[6]:= (*Imports first two columns (can be adjusted)*)
In[7]:= coldata=Table[data[[i]][[All,1;;2]],{i,Length[data]};
In[8]:= (*Cuts intial corrupted data points, plots FIDs and spectrum*)
In[9]:= ListLinePlot[{(dropdata=Table[Drop[coldata[[i]],80],{i,Length[
  ↳ coldata]}][[8]]},PlotRange->{{0,10},All},Frame->True,Axes->False
  ↳ ,FrameStyle->Directive[Black,FontSize->16,FontFamily->"Myriad_
  ↳ Pro"],FrameLabel->{"time_(s)","magnetometer_signal_(V)"},
  ↳ ImageSize->Medium]
In[10]:= ListLinePlot[Abs[fte[dropdata[[8,1;;Length[dropdata
  ↳ [[2]]],2]],1/1000]],PlotRange->{{5,60},{-0.00003,0.00005}},
  ↳ PlotTheme->"Detailed",Frame->True,FrameStyle->Directive[Black,
  ↳ FontFamily->"Myriad_Pro",FontSize->16],FrameLabel->{"Frequency_(
  ↳ Hz)","Amplitude_(V)"}]
In[11]:= ListLinePlot[Re[fte[dropdata[[8,1;;Length[dropdata
  ↳ [[2]]],2]],1/1000]],PlotRange->{{0,60},{-0.00001,0.00001}},
  ↳ PlotTheme->"Detailed",Frame->True,FrameStyle->Directive[Black,
  ↳ FontFamily->"Myriad_Pro",FontSize->16],FrameLabel->{"Frequency_(
  ↳ Hz)","Amplitude_(V)"}]
In[12]:= (*Defines background polynomial and subtract it from the signal
  ↳ *)
In[13]:= polynomial[vars_List,n_Integer,coeff_]:=#.Array[coeff,Length@
  ↳ #]&@DeleteDuplicates[Times@@@Tuples[Prepend[vars,1],n]]

Clear[a]
In[15]:= backgroundmodel=Table[NonlinearModelFit[dropdata[[i]],
  ↳ polynomial[{x},11,a],Table[a[i],{i,22}],x],{i,Length[data]};
In[16]:= backgroundlist=Table[backgroundmodel[[i]]/@dropdata[[i,All
  ↳ ,1]],{i,Length[dropdata]};
In[17]:= backgroundsub=Table[dropdata[[i,All,2]]-backgroundlist[[i]],{i,
  ↳ Length[dropdata]}];
```

```

In[18]:= ListLinePlot[backgroundsub[[8]],PlotRange->All]
In[19]:= (*Backpredict the initial cut points, can be adjusted or turned
↪ off*)
In[20]:= tsm=Table[TimeSeriesModelFit[Reverse[backgroundsub[[i
↪ ,1;;1000]]],{"AR",100}],{i,Length[backgroundsub]}]
In[21]:= ListLinePlot[{(tsm[[9]])["TemporalData"],TimeSeriesForecast[tsm
↪ [[8]],{80}]}],PlotRange->All,Frame->True]
In[22]:= ListLinePlot[(databp=Table[Join[Reverse[Flatten[Normal[
↪ TimeSeriesForecast[tsm[[i]],{0}]],1][All,2]]],backgroundsub[[i
↪ ]],{i,Length[backgroundsub]}]),PlotRange->All]
In[23]:= (*Apply phase correction, apodization and zero-padding*)
In[24]:= Manipulate[{xb={lin,zero,decay,zeropadd},ListLinePlot[Transpose
↪ [{fte[PadRight[databp[[8]],zeropadd],1/1000][All,1]],Re[
↪ MapIndexed[E^(-I*(#2[[1]]*lin/1000+zero))*#1&,fte[MapIndexed[E
↪ ^(-#2[[1]]*decay/2000))*#1&,PadRight[databp[[8]],zeropadd
↪ ]],1/1000][All,2]]]}],PlotRange->{{0,60},All},Frame->True,
↪ PerformanceGoal->"Speed"]],{{lin,0},-\[Pi],\[Pi],0.001\[Pi]},{{
↪ zero,0},-\[Pi],\[Pi],0.01\[Pi]},{decay,0,5},{zeropadd
↪ ,10000,50000,1000}]
In[25]:= (*Produce final spectrum*)
In[26]:= ProcessedFFT=Transpose[{fte[PadRight[databp[[8]],xb
↪ [[4]]],1/1000][All,1]],Re[MapIndexed[E^(-I*(#2[[1]]*xb
↪ [[1]]/1000+xb[[2]]))*#1&,fte[MapIndexed[E^(-#2[[1]]*xb[[3]]/2000)
↪ *#1&,PadRight[databp[[8]],xb[[4]]],1/1000][All,2]]]}];
In[27]:= ListLinePlot[ProcessedFFT,PlotRange
↪ ->{{2,45},{-0.000001,0.000002}},PlotTheme->"Detailed",Frame->{{
↪ False,False},{True,False}},FrameStyle->Directive[Black,FontFamily
↪ ->"Myriad_Pro",FontSize->16],FrameLabel->{"Frequency_(Hz)",
↪ Amplitude_(V)},LabelStyle->Directive[Black,FontFamily->"Myriad_
↪ Pro",FontSize->16],AspectRatio->1/2,PlotStyle->Black]

```

A.2 ZERO-FIELD SPECTRA SIMULATION

Numerical simulations often accompany the experimental zero-field spectrum allowing for peak allocation and extracting of coupling constants (as explained in Sec ref). The simulations presented in this thesis are done using a Spintrum packaga developed in Wilzewski et al. [2017]. A sample code showing simulation of dimethyl phosphite is provided (as seen in Alcicek et al. [2021b]):

```

#import packages
import spintrum
import math
import matplotlib.pyplot as plt
import numpy as np
import time

#define gyroamgnetic ratios and multiplicity (spin)
gammas = [4257.7e4,4257.7e4,4257.7e4,4257.7e4,
↪ 4257.7e4,4257.7e4,4257.7e4,1723.5e4]
multips = [2,2,2,2,2,2,2,2]

#define the coupling matrix
jCouplings = [
↪ [0,0,0,0,0,0,0,695],

```

```

    [0,0,0,0,0,0,0,11.7],
    [0,0,0,0,0,0,0,11.7],
    [0,0,0,0,0,0,0,11.7],
    [0,0,0,0,0,0,0,11.7],
    [0,0,0,0,0,0,0,11.7],
    [0,0,0,0,0,0,0,11.7],
    [0,0,0,0,0,0,0,11.7],
    [0,0,0,0,0,0,0,0]
]

#define exp parameters
BThermal = 1.8e0
T2 = 1
sampleRate = 2e3
T= 1/sampleRate
points = 80000
gammah = 2*math.pi*4257.7e4

#Apply an optional pulse, define magnetic fields during detection, set
↪ sensitive axis
spinOp = spintrum.SpinOperations()
spinOp.add_operation(
    ↪ spintrum.SpinOperations.OPERATION__THERMAL_POPULATE,
        {'Bx': 0, 'By': 0, 'Bz': BThermal, 'T': 300})
spinOp.add_operation( spintrum.SpinOperations.OPERATION__TIP_SPINS,
    {'direction': 'y', 'BVstArea': 5*math.pi/gammah})
spinOp.add_operation(spintrum.SpinOperations.OPERATION__SET_HAMILTONIAN,
    {'Bx': 0, 'By': 0, 'Bz': 0})
spinOp.add_operation(
    ↪ spintrum.SpinOperations.OPERATION__INIT_TIME_INDEPENDENT_EVOLUTION,
        {'samplingRate': sampleRate,
         ↪ 'measurementDirection': 'z'})
spinOp.add_operation(
    ↪ spintrum.SpinOperations.OPERATION__EVOLVE_TIME_INDEPENDENT,
        {'points': points, 'threads': 8})

#simulate zero-field signal
start_time = time.time()

signal = spintrum.simulate(gyromagneticRatios=gammas,
                           jCouplings=jCouplings,
                           spinMultiplicities=multips,
                           spinOperations=spinOp)

signal = signal - np.mean(signal)
signal = [signal[i]*math.exp(-i/sampleRate/T2) for i in
    ↪ range(len(signal))]

#show the zero-field FID
print("Simulation lasted: " + repr(time.time()-start_time) + "s")
plt.plot(signal)
plt.show()

#plot and save the zero-field spectrum
fft = spintrum.FFTSpectralDensity(signal, sampleRate)
plt.plot(fft['x'], fft['y'])

```

```

plt.xlim(4,25)
plt.ylabel("signal")
plt.xlabel("frequency (Hz)")
plt.savefig('DMHP_simulated_spectra.pdf')
plt.show()

fft = spintrum.FFTSpectralDensity(signal, sampleRate)
plt.plot(fft['x'], fft['y'])
plt.xlim(670,720)
plt.ylabel("signal")
plt.xlabel("frequency (Hz)")
plt.savefig('DMHPHigh_freq_simulated_spectra.pdf')
plt.show()

```

A.3 ZERO-FIELD SPECTRA WITH CHEMICAL EXCHANGE: SIMULATION

Following code has been written in Matlab to calculate the zero-field spectra of chemically exchanging systems, and used to performed simulation feature in Chapter 6 and [Alcicek et al. \[2021a\]](#). The code uses an approach based on Liouville space superoperators to calculate effect of proton deattachment and reattachment to the spin system during evolution, as introduced in [Barskiy et al. \[2019b\]](#). The mathematical details of calculations are shown in Chapter 6, here the code for simulating a zero-field NMR spectrum in fully labelled urea is provided.

```

function [A, B] = ZULF_UREA_full13CN15()
% For questions - piotr.put@doctoral.uj.edu.pl
% A + B <--> C
% A + B <--> D EXCHANGE (modeling base and acid catalyzed exchange in
%   ↪ UREA)
% where the spin state of B is included into relaxation superoperator

% Dissosiation constants for urea
pH = [7];
pKa = 0.1;
pKb = 13.83;
lista = zeros(1,length(pH))
tic
for j=1:length(pH)
% Kinetic constants
WaA_2 = 9* 10^6* 10^(-pH(j)); % forward exchange rate constant [s^(-1)]
kdC_2 = 9* 10^6* 10^(pKa); % backward exchange rate [s^-1]
WdA_2 = 2* 10^6* 10^(-(14-pH(j)));
kaD_2 = 2* 10^6* 10^(-(14-pKb));
% Molar fractions in equilibrium
XA = 1/(1+(WaA_2/kdC_2)+(WdA_2/kaD_2))
XC = (WaA_2/kdC_2)/(1+(WaA_2/kdC_2)+(WdA_2/kaD_2))
XD = (WdA_2/kaD_2)/(1+(WaA_2/kdC_2)+(WdA_2/kaD_2))
%XA=1;
%XC=0;
%XD=0;

% Chemical kinetics operator

```

```

K = [-(WaA_2+WdA_2)/2 kdC_2/2 kaD_2/2; WaA_2 -kdC_2 0; WdA_2 0 -kaD_2];

% ZULF acquisition parameters
Bz = 0; % [T]
Bstorage=1.0e-5; % [T]
% Gyromagnetic ratios
g_1H = 267.522*1e6; % [rad/(T*s)]
g_13C = 67.283*1e6; % [rad/(T*s)]
g_15N = -27.126*1e6; % [rad/(T*s)]

%Pulse duration and FFT parameters
Bandwidth=500;
FWHH=1;

% J-couplings and coupling topology
J_couplings_A = [0, -19.9, -19.9, 2.9 2.9 2.9 2.9; 0 0 5.1 -89.1 -89.1
↳ -1.7 -1.7; 0 0 0 -1.7 -1.7 -89.1 -89.1; 0 0 0 0 0 1 1; 0 0 0 0 0 1
↳ 1; 0 0 0 0 0 0 0; 0 0 0 0 0 0 0];
J_couplings_C = [0, -19.9, -19.9, 2.9 2.9 2.9 2.9 2.9; 0 0 5.1 -89.1
↳ -89.1 -1.7 -1.7 -1.7; 0 0 0 -1.7 -1.7 -89.1 -89.1 -89.1; 0 0 0 0 0
↳ 1 1 1; 0 0 0 0 0 1 1 1; 0 0 0 0 0 0 0 0; 0 0 0 0 0 0 0 0; 0 0 0 0 0
↳ 0 0 0];
J_couplings_D = [0, -19.9, -19.9, 2.9 2.9 2.9; 0 0 5.1 -89.1 -89.1
↳ -1.7; 0 0 0 -1.7 -1.7 -89.1; 0 0 0 0 0 1; 0 0 0 0 0 1; 0 0 0 0 0
↳ 0];
N_spins_A = 7; N_spins_C = 8; N_spins_D = 6;

% Spin operators for A,C,D
[Lx_A, Ly_A, Lz_A] = Spin_Operator(N_spins_A);
[Lx_C, Ly_C, Lz_C] = Spin_Operator(N_spins_C);
[Lx_D, Ly_D, Lz_D] = Spin_Operator(N_spins_D);

% Zeeman Hamiltonian terms
H_A = -g_13C*Lz_A{1}*Bz -g_15N*Lz_A{2}*Bz -g_15N*Lz_A{3}*Bz
↳ -g_1H*Lz_A{4}*Bz -g_1H*Lz_A{5}*Bz -g_1H*Lz_A{6}*Bz
↳ -g_1H*Lz_A{7}*Bz;
H_C = -g_13C*Lz_C{1}*Bz -g_15N*Lz_C{2}*Bz -g_15N*Lz_C{3}*Bz
↳ -g_1H*Lz_C{4}*Bz -g_1H*Lz_C{5}*Bz -g_1H*Lz_C{6}*Bz -g_1H*Lz_C{7}*Bz
↳ -g_1H*Lz_C{8}*Bz;
H_D = -g_13C*Lz_D{1}*Bz -g_15N*Lz_D{2}*Bz -g_15N*Lz_D{3}*Bz
↳ -g_1H*Lz_D{4}*Bz -g_1H*Lz_D{5}*Bz -g_1H*Lz_D{6}*Bz;

% Zeeman Hamiltonian terms during storage
H_Ast=-g_13C*Lz_A{1}*Bstorage -g_15N*Lz_A{2}*Bstorage
↳ -g_15N*Lz_A{3}*Bstorage -g_1H*Lz_A{4}*Bstorage
↳ -g_1H*Lz_A{5}*Bstorage -g_1H*Lz_A{6}*Bstorage -g_1H*Lz_A{7}*Bstorage;
H_Cst=-g_13C*Lz_C{1}*Bstorage -g_15N*Lz_C{2}*Bstorage
↳ -g_15N*Lz_C{3}*Bstorage -g_1H*Lz_C{4}*Bstorage
↳ -g_1H*Lz_C{5}*Bstorage -g_1H*Lz_C{6}*Bstorage
↳ -g_1H*Lz_C{7}*Bstorage -g_1H*Lz_C{8}*Bstorage;
H_Dst=-g_13C*Lz_D{1}*Bstorage -g_15N*Lz_D{2}*Bstorage
↳ -g_15N*Lz_D{3}*Bstorage -g_1H*Lz_D{4}*Bstorage
↳ -g_1H*Lz_D{5}*Bstorage -g_1H*Lz_D{6}*Bstorage;

% Whole Hamiltonian with J couplings terms
for s=1:N_spins_A
    for p=1:N_spins_A

```

```

        H_A = H_A + (J_couplings_A(s,p))*(Lx_A{s}*Lx_A{p} +
        ↪ Ly_A{s}*Ly_A{p} + Lz_A{s}*Lz_A{p});
    end
end

for s=1:N_spins_C
    for p=1:N_spins_C
        H_C = H_C + (J_couplings_C(s,p))*(Lx_C{s}*Lx_C{p} +
        ↪ Ly_C{s}*Ly_C{p} + Lz_C{s}*Lz_C{p});
    end
end

for s=1:N_spins_D
    for p=1:N_spins_D
        H_D = H_D + (J_couplings_D(s,p))*(Lx_D{s}*Lx_D{p} +
        ↪ Ly_D{s}*Ly_D{p} + Lz_D{s}*Lz_D{p});
    end
end

% Whole Hamiltonian with J couplings terms DURING STORAGE
for s=1:N_spins_A
    for p=1:N_spins_A
        H_Ast = H_Ast + (J_couplings_A(s,p))*(Lx_A{s}*Lx_A{p} +
        ↪ Ly_A{s}*Ly_A{p} + Lz_A{s}*Lz_A{p});
    end
end

for s=1:N_spins_C
    for p=1:N_spins_C
        H_Cst = H_Cst + (J_couplings_C(s,p))*(Lx_C{s}*Lx_C{p} +
        ↪ Ly_C{s}*Ly_C{p} + Lz_C{s}*Lz_C{p});
    end
end

for s=1:N_spins_D
    for p=1:N_spins_D
        H_Dst = H_Dst + (J_couplings_D(s,p))*(Lx_D{s}*Lx_D{p} +
        ↪ Ly_D{s}*Ly_D{p} + Lz_D{s}*Lz_D{p});
    end
end

% Initial state (thermal prepolarization at HF), B unpolarized
rho_A = (-g_13C*Lz_A{1} -g_15N*Lz_A{2} -g_15N*Lz_A{3}
    ↪ -g_1H*Lz_A{4} -g_1H*Lz_A{5} -g_1H*Lz_A{6} -g_1H*Lz_A{7})/g_1H;
rho_B = 0.5*eye(2);
rho_C = (-g_13C*Lz_C{1} -g_15N*Lz_C{2} -g_15N*Lz_C{3} -g_1H*Lz_C{4}
    ↪ -g_1H*Lz_C{5} -g_1H*Lz_C{6} -g_1H*Lz_C{7} -g_1H*Lz_C{8})/g_1H;
rho_D = (-g_13C*Lz_D{1} -g_15N*Lz_D{2} -g_15N*Lz_D{3} -g_1H*Lz_D{4}
    ↪ -g_1H*Lz_D{5} -g_1H*Lz_D{6})/g_1H;
rho_initial = [rho_A(:); rho_C(:); rho_D(:)];

%Construction evolution superoperator L
% Liuvillian superoperators
L_A = sparse(kron(eye(2^N_spins_A),H_A) -
    ↪ kron(transpose(H_A),eye(2^N_spins_A)));
L_C = sparse(kron(eye(2^N_spins_C),H_C) -
    ↪ kron(transpose(H_C),eye(2^N_spins_C)));

```

```

L_D = sparse(kron(eye(2^N_spins_D),H_D) -
    ↪ kron(transpose(H_D),eye(2^N_spins_D)));
% Construction evolution superoperator Lst
L_Ast = sparse(kron(eye(2^N_spins_A),H_Ast) -
    ↪ kron(transpose(H_Ast),eye(2^N_spins_A)));
L_Cst = sparse(kron(eye(2^N_spins_C),H_Cst) -
    ↪ kron(transpose(H_Cst),eye(2^N_spins_C)));
L_Dst = sparse(kron(eye(2^N_spins_D),H_Dst) -
    ↪ kron(transpose(H_Dst),eye(2^N_spins_D)));

% Direct Product Superoperators
S_dpC = sparse(SuperProduct(2^N_spins_A, rho_B));
S_dpA = sparse(SuperProduct(2^N_spins_D, rho_B));
% Partial Trace Superoperators
S_ptC = 1/5*(TraceSuper1(4, size(rho_C,1))+TraceSuper1(5,
    ↪ size(rho_C,1))+TraceSuper1(6, size(rho_C,1))+TraceSuper1(7,
    ↪ size(rho_C,1))+TraceSuper1(8, size(rho_C,1)));
S_ptA = 1/4*(TraceSuper1(4, size(rho_A,1))+TraceSuper1(5,
    ↪ size(rho_A,1))+TraceSuper1(6, size(rho_A,1))+TraceSuper1(7,
    ↪ size(rho_A,1)));
% Zero matrix
A0(1:4^N_spins_D,1:4^N_spins_C) = 0;
A0=sparse(A0);
% Generalized Superoperator
L = sparse([-1i*L_A+K(1,1)*speye(4^N_spins_A) K(1,2)*S_ptC
    ↪ K(1,3)*S_dpA; K(2,1)*S_dpC -1i*L_C+K(2,2)*speye(4^N_spins_C) A0.';
    ↪ K(3,1)*S_ptA A0 -1i*L_D+K(3,3)*speye(4^N_spins_D)]);
Lst = sparse([-1i*L_Ast+K(1,1)*speye(4^N_spins_A) K(1,2)*S_ptC
    ↪ K(1,3)*S_dpA; K(2,1)*S_dpC -1i*L_Cst+K(2,2)*speye(4^N_spins_C)
    ↪ A0.'; K(3,1)*S_ptA A0 -1i*L_Dst+K(3,3)*speye(4^N_spins_D)]);
% Detection state
coil_A = XA*rho_A;
coil_C = XC*rho_C;
coil_D = XD*rho_D;
coil=[coil_A(:); coil_C(:); coil_D(:)];

% Building propagator
time_step=1/Bandwidth;
L=sparse(L);
Lst=sparse(Lst);

% Simulation: evolution in storage field
rho = rho_initial;
nsteps = Bandwidth; % number of steps in the storage field (1s)
for n=1:nsteps
    rho=expv(time_step,Lst,rho);
end
% Simulation: evolution in ZF
rho = rho;
nsteps = 512; % number of steps in the simulation
fid=zeros(nsteps,1); % preallocate the array
for n=1:nsteps
    fid(n)=coil'*rho;

```

```

        rho=expv(2*pi*time_step,L,rho,1.0e-2);
    end

    % Apodization
    fid_time=nsteps*time_step; % time of fid recording (s)
    time=0:time_step:fid_time-time_step;

    window_function=exp(-(FWHH*pi)*time)';
    fid=fid.*window_function;
    fid=fid-movmean(fid,10);
    % Fourier transform with zerofilling
    SI=2^15;
    spectrum=abs(fftshift(fft(fid, SI)));

    x=-Bandwidth/2:Bandwidth/SI:Bandwidth/2-1/SI;
    fy=flipud(spectrum);

    % Plotting
    plot(x, flipud(spectrum)); hold on;

end
toc
end
%-----
% Portion of code below contains definitions of Pauli matrices, direct
% → product and partial trace superoperators. The code for the expv
% → function used to quickly calculated the propagation of the
% → vectorized density matrix is provided.
%-----
% Calculates spin operators on the basis of N_spins (1/2)
function [Lx, Ly, Lz] = Spin_Operator(N_spins)

% Pauli matrices
unit = eye(2);
sigma_x = 0.5*[0 1; 1 0];
sigma_y = 0.5*[0 -1i; 1i 0];
sigma_z = 0.5*[1 0; 0 -1];

% Define cell arrays
Lx = cell(1, N_spins); Ly = cell(1, N_spins); Lz = cell(1, N_spins);

% Define spin operators

for n=1:N_spins
    Lx_current=1; Ly_current=1; Lz_current=1;
    for k=1:N_spins
        if k==n
            Lx_current = kron(Lx_current,sigma_x);
            Ly_current = kron(Ly_current,sigma_y);
            Lz_current = kron(Lz_current,sigma_z);
        else
            Lx_current = kron(Lx_current,unit);
            Ly_current = kron(Ly_current,unit);

```



```

        if (m1+(j-1)*P==x) && (n1+(j-1)*P==y)
            % B4(m,n,x,y)=1;
            B2(K,L)=1;
        end
    end
end
end
end
end
B2=sparse(B2);
end

function [w, err, hump] = expv( t, A, v, tol, m )

[n,n] = size(A);
if nargin == 3,
    tol = 1.0e-7;
    m = min(n,30);
end;
if nargin == 4,
    m = min(n,30);
end;

anorm = norm(A,'inf');
mxrej = 10; btol = 1.0e-7;
gamma = 0.9; delta = 1.2;
mb = m; t_out = abs(t);
nstep = 0; t_new = 0;
t_now = 0; s_error = 0;
rndoff= anorm*eps;

k1 = 2; xm = 1/m; normv = norm(v); beta = normv;
fact = (((m+1)/exp(1))^(m+1))*sqrt(2*pi*(m+1));
t_new = (1/anorm)*((fact*tol)/(4*beta*anorm))^xm;
s = 10^(floor(log10(t_new))-1); t_new = ceil(t_new/s)*s;
sgn = sign(t); nstep = 0;

w = v;
hump = normv;
while t_now < t_out
    nstep = nstep + 1;
    t_step = min( t_out-t_now,t_new );
    V = zeros(n,m+1);
    H = zeros(m+2,m+2);

    V(:,1) = (1/beta)*w;
    for j = 1:m
        p = A*V(:,j);
        for i = 1:j
            H(i,j) = V(:,i)'*p;
            p = p-H(i,j)*V(:,i);
        end;
        s = norm(p);
        if s < btol,
            k1 = 0;

```

```

    mb = j;
    t_step = t_out-t_now;
    break;
end;
H(j+1,j) = s;
V(:,j+1) = (1/s)*p;
end;
if k1 ~= 0,
    H(m+2,m+1) = 1;
    avnorm = norm(A*V(:,m+1));
end;
ireject = 0;
while ireject <= mxrej,
    mx = mb + k1;
    F = expm(sgn*t_step*H(1:mx,1:mx));
    if k1 == 0,
err_loc = btol;
        break;
    else
        phi1 = abs( beta*F(m+1,1) );
        phi2 = abs( beta*F(m+2,1) * avnorm );
        if phi1 > 10*phi2,
            err_loc = phi2;
            xm = 1/m;
        elseif phi1 > phi2,
            err_loc = (phi1*phi2)/(phi1-phi2);
            xm = 1/m;
        else
            err_loc = phi1;
            xm = 1/(m-1);
        end;
    end;
if err_loc <= delta * t_step*tol,
    break;
else
    t_step = gamma * t_step * (t_step*tol/err_loc)^xm;
    s = 10^(floor(log10(t_step))-1);
    t_step = ceil(t_step/s) * s;
    if ireject == mxrej,
        error('The requested tolerance is too high.');
```

end;

```

    ireject = ireject + 1;
end;
end;
mx = mb + max( 0,k1-1 );
w = V(:,1:mx)*(beta*F(1:mx,1));
beta = norm( w );
hump = max(hump,beta);

t_now = t_now + t_step;
t_new = gamma * t_step * (t_step*tol/err_loc)^xm;
s = 10^(floor(log10(t_new))-1);
t_new = ceil(t_new/s) * s;

err_loc = max(err_loc,rndoff);
```

```
    s_error = s_error + err_loc;  
end;  
err = s_error;  
hump = hump / normv;  
end
```

B.1 MAGNETIC PULSE CALIBRATION

To manipulate spins under ZULF conditions, DC magnetic-field pulses were used. The coils are initially calibrated to apply a proper pulse rotation. This was typically done in ULFs by observing the precession of protons (e.g., in water) and plotting the amplitude of the proton peak versus the pulse length or amplitude (Fig. B.1). Since the amplitude of the signal depended on the flip angle, fitting the dependence with the absolute value of the sine function allowed us to calibrate exact pulse amplitude and hence set the pulse parameters for the zero-field experiments.

B.2 PIERCING SOLENOID

In some ZULF experiments presented in this thesis, a piercing solenoid was used to provide a guiding field to an NMR sample without affecting the atomic magnetometer. During measurements performed at ZULF, the solenoid was powered by a low-noise current source. The solenoid was calibrated by measuring proton-precession signals in low magnetic fields. The center of the resonance was recalculated using a gyromagnetic ratio to the magnetic-field units and plotted versus the current that flows through the solenoid (Fig. B.2). The measured calibration factor agreed with the estimation based on the assumptions of an infinitely long solenoid of a given winding density:

$$C = 2\mu_0 \frac{1}{0.14 \text{ mm}} = 180 \frac{\text{G}}{\text{A}}, \quad (\text{B.1})$$

where factor 2 comes from the fact that the solenoid had two layers, while 0.14 mm is a measured width of the solenoid wire (with insulation).

The field leaking outside of the piercing solenoid was measured with the atomic magnetometer and in such a way at a level of at most 10^{-4} . This means that detection fields leading to proton frequencies up to 400 Hz (upper limit of the bandwidth of the atomic magnetometer) introduce only up to 1 nT at the position of the sensor. This lied well within the dynamic range of the sensor. It indicated that no further shimming of the solenoid field in ZULF volume was required.

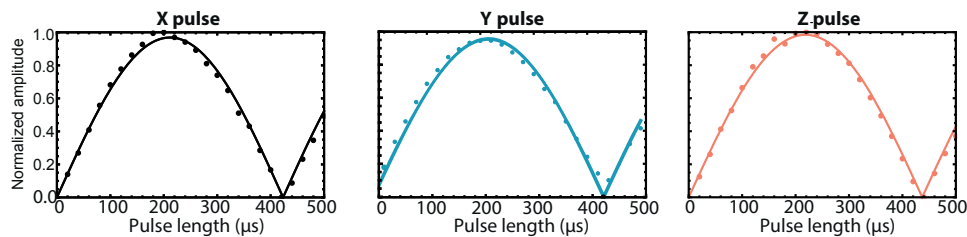


Figure B.1: Normalized amplitude of ULF NMR proton signal versus the pulse length in three orthogonal directions. The signals were used for calibrating the coils in all three directions. Adapted from the Supplemental Information in [Put et al. \[2021\]](#).

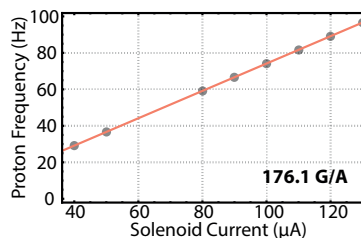


Figure B.2: Calibration of the piercing solenoid based on the proton precession frequency at ULFs. Linear fit was used to obtain the solenoid calibration factor.

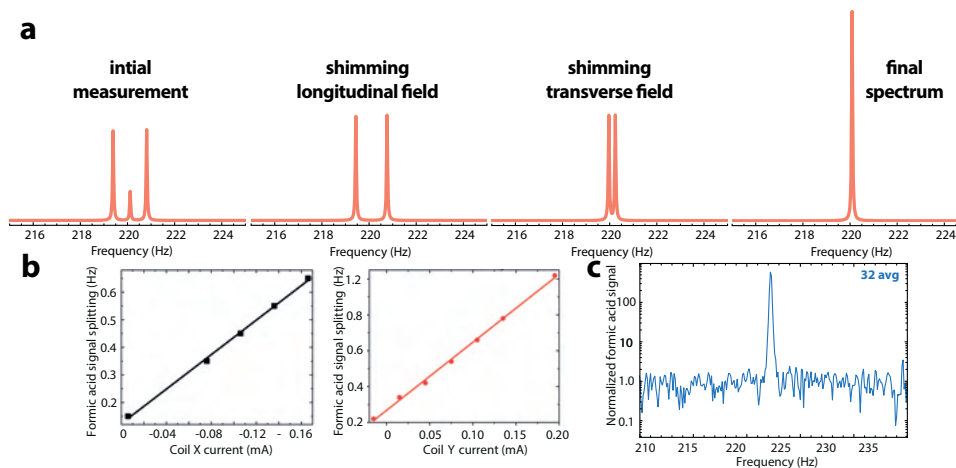


Figure B.3: a) Schematics of residual magnetic-field shimming process in ZULF NMR spectrometer, based on the formic acid spectrum (The procedure is described in the main text.) b) Splitting of the formic acid resonance at J as a function of transverse-field components. The solid lines show the calculate, theoretical lines splitting in the XA spin system. c) Typical zero-field NMR signal of reference sample ($[^{13}\text{C}]$ -methanol) after magnetic-field shimming. Parts b) and c) adapted from Supplemental Information of Put et al. [2021].

B.3 SHIMMING ZERO-FIELD SPECTROMETER

To obtain a quality zero-field spectrum, a residual field inside a magnetic shield (typically 10-20 nT) had to be compensated for. The field compensation was done with the built-in coils, providing a field in three spatial directions (the gradient coils were wound but were not used in the measurements presented in this thesis). The shimming was based on the measurement of the ULF spectrum of the XA spin system ($[^{13}\text{C}]$ -formic acid). The procedure used here followed Sjolander et al. [2016] and is illustrated schematically in Fig. B.3a). When no compensation was applied, a spectrum of formic acid typically consisted of three peaks centered around the J -coupling value, as the residual field had components in the sensitive and transverse directions. By compensating the field along the sensitive axis of the sensor, we made the central peak disappear. Following that, the transverse fields were adjusted so that two splitted peaks overlapped, i.e., formic acid spectrum consisted of a single, narrow peak. The compensation of the field was relatively simple since the splitting scaled linearly with the total transverse field, as evident from Fig. B.3 b). As the natural linewidth of formic acid in ZULF conditions is very small (see, for example, Emondts et al. [2014]) the residual fields could be shimmed below 0.5-nT levels, producing quality zero-field spectra (Fig. B.3c).

C.1 PERMANENT MAGNET ASSEMBLY FOR PREPOLARIZATION

A permanent magnetic assembly was constructed to provide a strong magnetic field for the prepolarization of the NMR samples. The assembly was based on the design presented in [Tayler and Sakellariou \[2017\]](#). It contained 24 neodymium magnets ($15 \times 15 \times 50 \text{ mm}^3$) in an aluminum casing, where they were held in place by friction (no adhesive was used). The bore of the magnet was large enough to house a solenoid, inside which 5- or 10-mm NMR tubes were moving. The magnets were inserted into their dedicated position through the jig piece, displacing an aluminum dummy with identical dimensions. In this way, the magnet could be put together safely, without the danger of the magnet flying out of the assembly while placing the new magnet in place. The completed magnet is shown in Fig. 3.2b) with arrows indicating the direction of magnetization in individual magnets, while the magnet during assembly (after placing the initial 8 magnets) is shown in Fig. C.1. After all the magnets were put in place, the bottom and top covers of the aluminum shield were installed. Eventually, the whole structure was placed inside the steel box, providing magnetic shielding. The assembly schematics are provided in Fig. C.2. Two magnet assemblies, one with a magnetic induction of 1.5 T (made of N48 magnets) and the other with a magnetic induction of 1.8 T (made of N50 magnets) were constructed and used in separate ZULF spectrometers.

C.2 MAGNETOMETER HOLDER FOR ZERO-FIELD NMR ASSEMBLY

As explained in Chapter 4, commercial magnetometers are held around the solenoid in the ZULF region using a plastic holder. The frame also provides support for a set of three orthogonal Helmholtz coils used for magnetic-field pulses. The schematics of the assembly, which were later 3D-printed and used in experiments featured in Chapters 5 and 7 of this dissertation, are shown in Fig. C.3. The circular opening allowed the installation of the piercing solenoid, while the sensor was fitted inside through the side windows. Before installing the frame inside the spectrometer, the Helmholtz coils were wound with a 0.4-mm-thick wire (typically 10 turns per each coil in a pair). While this particular assembly was designed to work with QuSpin QZFM sensors, the design can be easily adjusted for other sensor geometries.

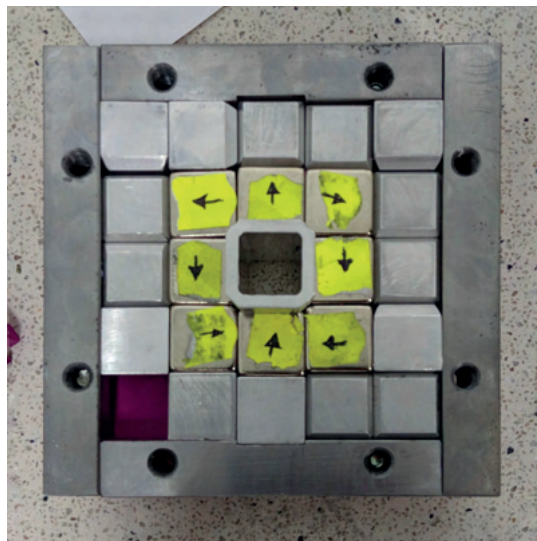
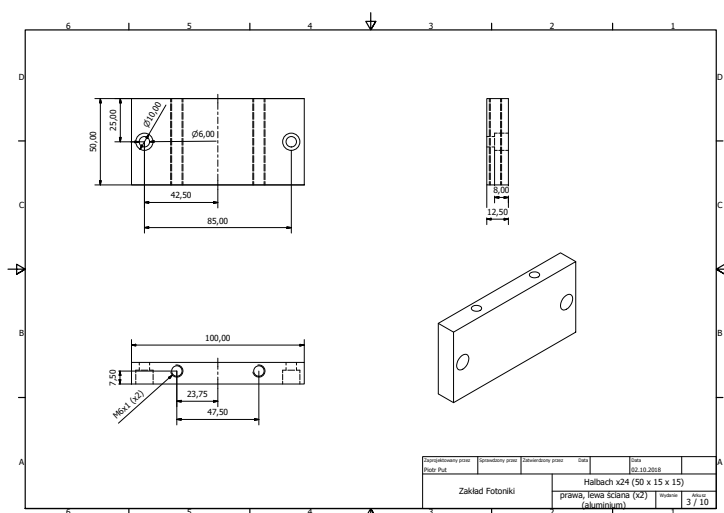
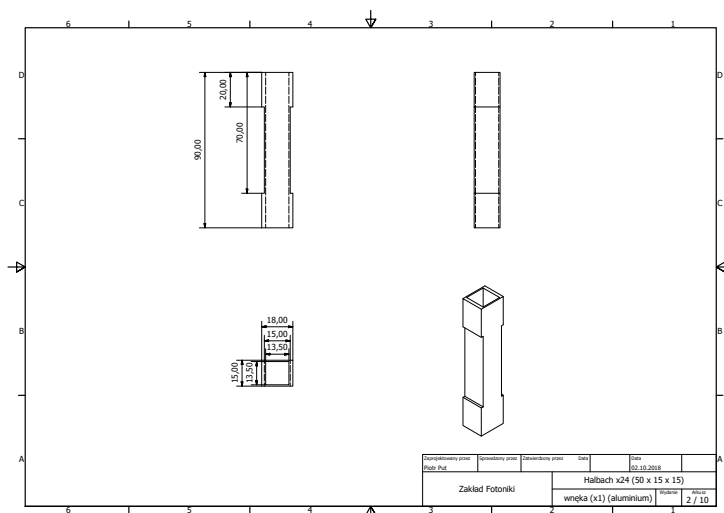
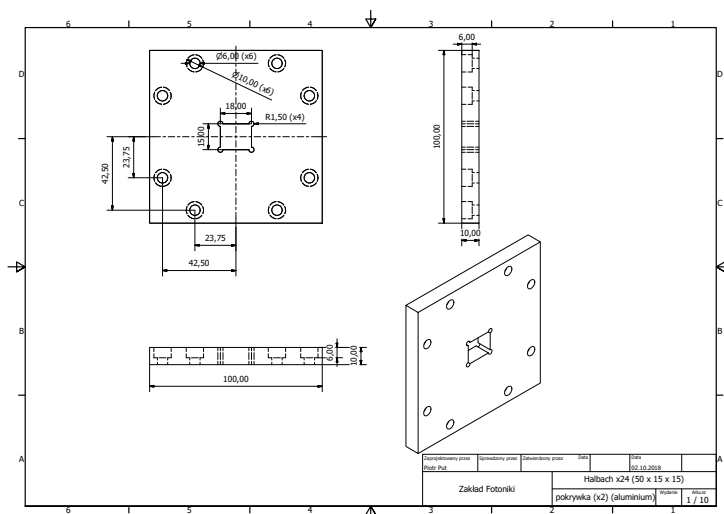
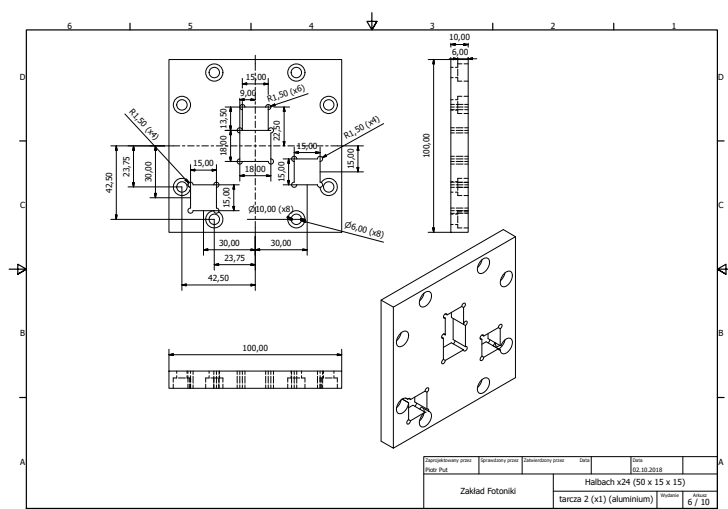
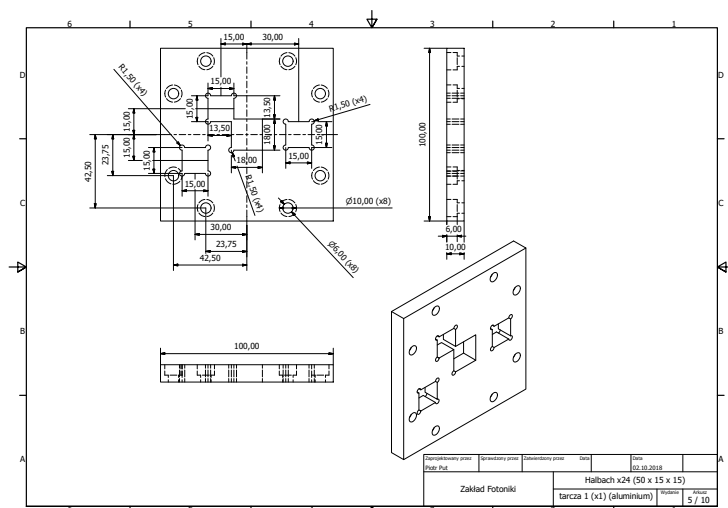
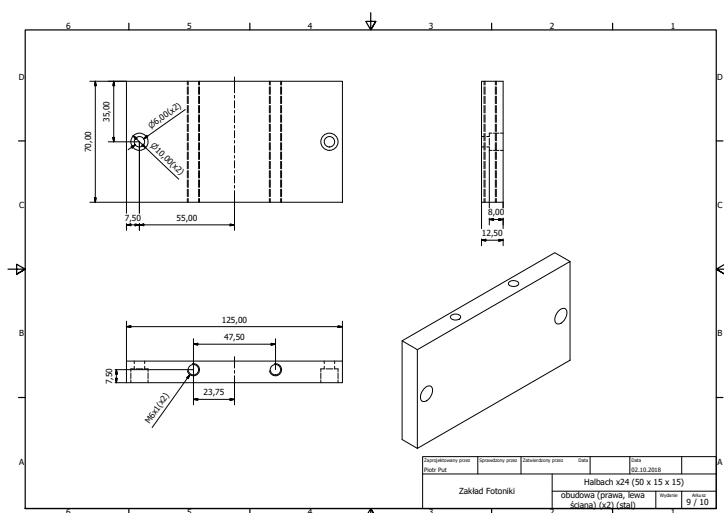
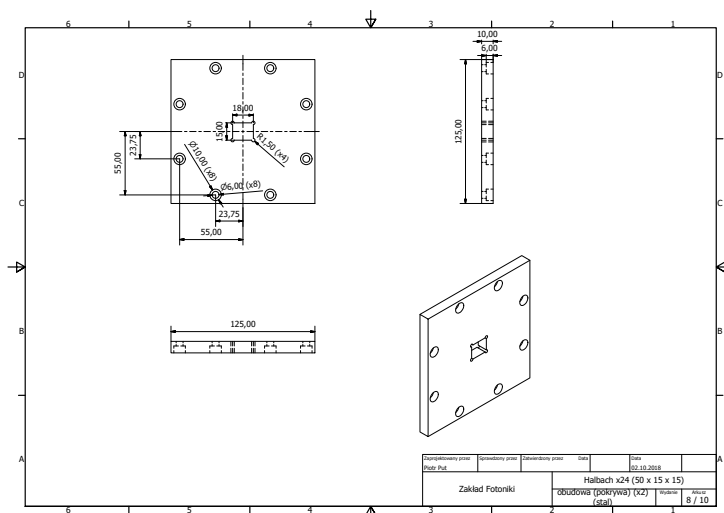
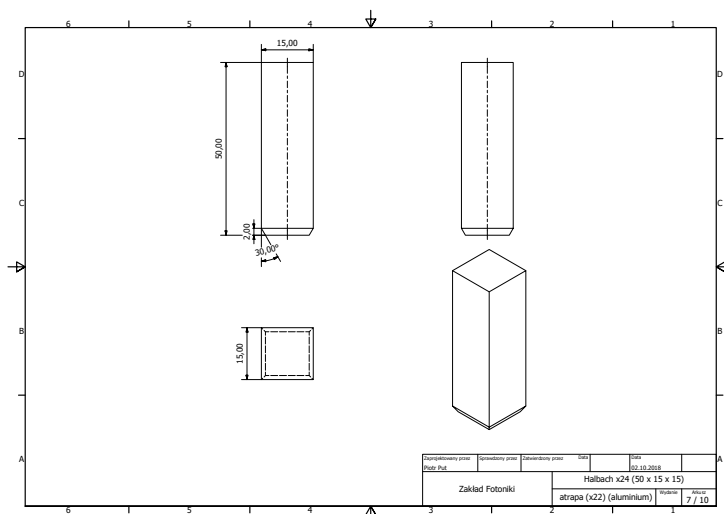


Figure C.1: (Pseudo-)Halbach magnet during assembling. First 8 magnets were placed around the bore, by displacing aluminium dummies through the jig pieces (not shown here). Arrows indicate directions of the magnetization in each neodymium magnet.







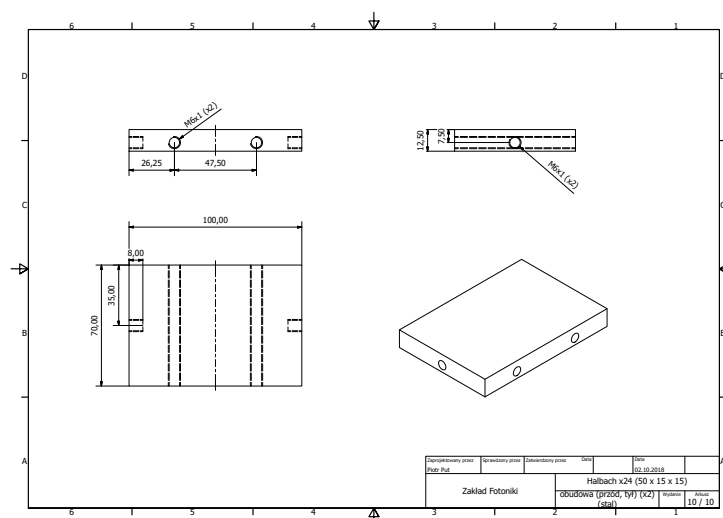


Figure C.2: Technical drawings of magnet assembly used in the ZULF spectrometers featured in this dissertation. The elements in order are: top/bottom aluminium covers, aluminium bore, aluminium side walls, jigs used to put magnets in placed during assembly, aluminium magnet dummies, steel enclosure working as magnetic shielding.

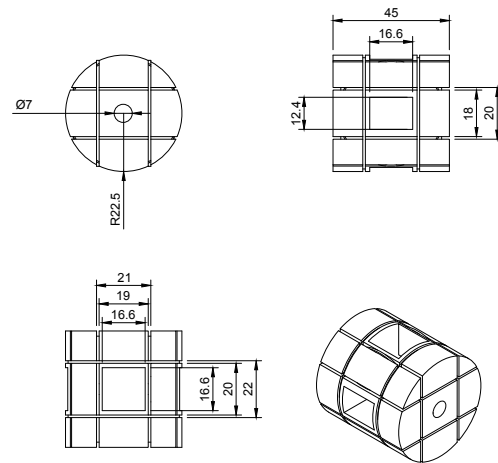


Figure C.3: Technical drawing of the coil frame. This system was designed for using a commercial magnetometer(s) to detect ZULF NMR signal. The circular opening on the top was prepared for the solenoid, piercing the whole shield.

