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Detection and Polarization of Nuclear and Electron Spins using Nitrogen-Vacancy Centers

by

Claudia Esther Avalos

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy

in

Chemistry

in the

$\begin{array}{c} \mbox{GRADUATE DIVISION} \\ \mbox{ of the} \\ \mbox{UNIVERSITY OF CALIFORNIA, BERKELEY} \end{array}$

Committee in charge: Professor Alexander Pines, Chair Professor David Wemmer Professor Dmitry Budker

Fall 2014

Detection and Polarization of Nuclear and Electron Spins using Nitrogen-Vacancy Centers

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Abstract

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by

Claudia Esther Avalos

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Alexander Pines, Chair

Magnetic resonance spectroscopy is one of the most powerful spectroscopic tools for obtaining detailed information about molecular structure. It has also served as a remarkable tool for exploring interesting quantum phenomena in large spin ensembles. In this dissertation, we present investigations of the optically detected magnetic resonance of the NV⁻ center, a point defect in diamond that has gained notoriety in the magnetic resonance community due to its interesting and useful spin properties. In the past few years, the NV⁻ center has been used as a gyroscope, a magnetic sensor for investigating thin superconducting films and most recently, as a magnetometer for nanoscale magnetic resonance measurements. In this work, we explore the optically detected magnetic resonance of the NV^- center in a number of different contexts. In chapter 5 and 6 we investigate the coherence lifetime of the NV⁻ center and discover a novel method for probing nuclear quadrupolar interactions in the solid state. In chapter 7 we obtain detailed chemical information about defect centers neighboring the NV^- center via observation of cross-relaxation effects. In chapter 8 we find a method to sensitively control the polarization of nuclear spins neighboring the NV⁻ center in the diamond lattice. And in chapters 9 and 10 we use an ensemble of NV^- centers to probe small magnetic fields external to the diamond lattice.

To my family

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Symbols

Tensor product
Dot product
A ket vector in Hilbert space
A bra dual vector in Hilbert space
A density matrix describing ensemble quantum state
Hamiltonian, the total energy operator of a system
Spin-orbit Hamiltonian
Spin-spin Hamiltonian
Magnetic field vector
Amplitude of static magnetic field
Nuclear spin operators
Electron spin operators
Axial zero-field splitting
Transverse zero-field splitting
Hyperfine tensor
Zero-field splitting
Gyromagnetic ratio of spin
State symmetry: doubly degenerate state
State symmetry: singly degenerate state
NV ⁻ electron orbital states
Symmetry of NV ⁻ Triplet excited electronic state
Symmetry of NV ⁻ Triplet ground electronic state
Paramagnetic nitrogen defect in diamond
Negatively Charged Nitrogen-Vacancy Center
Nitrogen-Vacancy Center
Neutral Nitrogen-Vacancy Center
Microwave or radio frequency field
effective spin-lattice relaxation time
effective spin-spin relaxation time
spin-lattice relaxation time
spin-spin relaxation time
Spin magnetization
Magnetic field vector
Amplitude of the static magnetic field
Rabi nutation frequency
Offset frequency
Resonance frequency

Acronyms

ODMR	Optically detected magnetic resonance
ODESR	Optically detected electron spin resonance
ESR	Electron spin resonance
NMR	Nuclear magnetic resonance
RF	Radio frequency
CPMG	Carr Purcell Meiboom Gill
UDD	Uhrig dynamic decoupling
ESEEM	Electron spin echo envelope modulation
QIP	Quantum information processing
ZPL	Zero-phonon line
PB	Pulse blaster
AOM	Acousto optic modulator
ND	Neutral density
TTL	Transistor transistor logic
N.A.	Numerical aperture
ELWD	Extra long working distance
APD	Avalanche photodiode
OD	Outer diameter
ID	Inner diameter
PMMA	Polymethyl methacrylate
PDMS	Polydimethyl siloxane
PEEK	Polyether ether ketone
DPPH	2,2-diphenyl-1-picrylhydrazyl

Physical Constants

- *h* Planck constant, 6.626176×10^{-34} J· s
- \hbar Reduced Planck constant, $h/2\pi$
- k_B Boltzmann constant, 1.380662 times 10⁻²³ J/K
- e Electron charge, 1.602177×10^{-19} C
- m_e Electron rest mass, 9.109383 × 10⁻³¹ kg
- m_p Proton rest mass, 1.672622 × 10⁻²⁷ kg
- μ_0 Vacuum permeability, $4\pi \times 10^{-7} \text{ V} \cdot \text{s/(A} \cdot \text{m})$
- g_s Electron g-factor, -2.00231930436153 \pm 2.6 \times 10⁻¹³
- μ_B Bohr magneton, $e\hbar/(2m_e) = 9.274 \times 10^{-24} \text{ J/T}$
- μ_N Nuclear magneton, $e\hbar/(2m_p) = 5.051 \times 10^{-27} \text{ J/T}$

Chapter 1

Introduction

"To see the world for a moment as something rich and strange is the private reward of many a discovery." - Edward Mills Purcell

1.1 A Brief History

The history of nuclear magnetic resonance (NMR) is closely intertwined with that of electron spin resonance and the optical detection of magnetic resonance. Here we follow the series of events leading up to the discovery of NMR and optically detected magnetic resonance (ODMR) and we explore the role that some of the early ODMR experiments played in bringing ODMR research of nitrogen-vacancy (NV⁻) centers to where it is today. We provide this background so that the reader may better understand the significance of the work presented in this thesis and how it fits into place within the scientific goals espoused by the greater magnetic resonance community.

1.1.1 Magnetic Resonance

In the years leading up to the first measurement of nuclear magnetic resonance (NMR), the scientific community was hard at work building the foundations for understanding quantum mechanics, using both theoretical and experimental realizations at their disposal. Of particular interest to the community was the accurate measurement of nuclear magnetic moments. Molecular beam experiments were used to measure the magnitude and sign of the magnetic moments of atomic nuclei. In a molecular beam experiment, the spin state of a particle is changed as it passes through a highly inhomogeneous and poorly-defined static magnetic field and the deflection of the beam is measured. However, these measurements had a rather large margin of error ($\pm 5\%$) due to the uncertainty in the inhomogeneous magnetic field strength, and so a more accurate method was desirable. In a conversation with Isidor Rabi (a pioneer in molecular beam experiments and a professor at Columbia University at the time), C.J. Gorter¹ asked why resonant absorption was not used to change the particle spin state in his molecular beam experiments instead of an inhomogenous field [1]. Not long after, Rabi measured a deflection of a ⁷Li molecular beam after radio-frequency (RF) irradiation at a resonance condition [2, 3]. Inspired by Rabi's work and also that of C.J. Gorter's studies on paramagnetic relaxation [4], Zaviosky subsequently demonstrated the detection of electron spin resonance (ESR) via microwave absorption measurements of manganese salts [5,6].

Rabi's experiment, though non-trivial, had the distinct advantage of being done on a molecular beam composed of nearly completely uncoupled nuclear spins, and so spin relaxation time was not a significant concern. NMR measurements of coupled nuclear spins in bulk liquid and solids, however, would prove to be more technically challenging. After considerable effort in producing properly homogenous magnets, and developing the proper technical expertise, Purcell, Torrey and Pound detected the NMR signal from a solid block of paraffin, using RF absorption measurements [7, 8]. At around the same time, Bloch, Hansen and Packard detected an NMR signal from proton nuclei in water using inductive detection [9]. In the years that followed, scientists developed a greater understanding of how to use RF and microwave radiation to probe couplings between nuclear and electron spins [10–13]. This led to accurate measurements of hyperfine interactions and relaxation constants, thus enabling significant advances in the understanding of electronic structure, spin-lattice interactions and relaxation mechanisms in different types of materials [14].

It wasn't until two decades after the first NMR measurement that yet another crucial discovery would occur, (this one being more closely related to the topics of this thesis) which would eventually lead to a better understanding of smaller ensembles of electron and nuclear spins, reducing the minimum number of detectable spins to ~ 10^4 [15, 16].

1.2 Optically Detected Magnetic Resonance

In 1957, Hans Dehmelt predicted that optically polarized resonance radiation from alkali vapor could be observed to modulate in the presence of small oscillating magnetic fields [17]. Bell and Bloom confirmed this when they measured modulations in the light polarization transmitted through a gas of sodium atoms in the presence of an oscillating RF field [18]. Not long after, Geschwind, Collins and Schawlow measured paramagnetic resonance in a solid through observation of fluorescent reabsorption rates with and without the presence of resonant microwaves [19]. Optically detected magnetic resonance was also demonstrated in phosphorescent triplet states, where the emission intensity of the electron triplet state of

¹Gorter was the first to measure paramagnetic relaxation and may have been the first to recognize that this relaxation implied that the magnetic dipole transitions between Zeeman levels of spin systems could exhibit some resonance effect. Before Rabi's experiment, he had attempted to detect NMR in solid LiF by continuously irradiating the solid with radio waves and measuring the change in the solid's temperature as a function of magnetic field. He was unsuccessful, but he correctly attributed the negative result as due to the effect of long nuclear spin relaxation times. (At the time no one had any idea how long nuclear spin-lattice relaxation times were!) [1]

phenanthrene biphenyl crystals was found to be directly linked to changes in populations of Zeeman levels [20,21]. The expected modulation of phosphorescent emission from triplet states in a time dependent RF field was described in further detail in a paper by Charles Harris [15] where he points out that the absorption and emission of light will only occur at the Larmor frequency of the spin states involved if the electric dipole transition between these excited spin states and the ground state is of the same polarization. The results of these experiments led to the important discovery that light polarization, wavelength and intensity could be correlated with observables of a spin system.

In 1973, Breiland, Harris and Pines extended what was known about NMR sequences to the case of photo excited triplet states, where they showed that the spin dynamics of molecular-excited triplet states could be monitored point by point by applying pulses resonant with molecular spin state transitions. This meant that ODMR could be used to study coherence properties of strongly coupled spin systems, such as defects in solids, as well as the spin coherence properties of short-lived excited states typically inaccessible for study using inductive detection timescales [16]. Additionally, because ODMR is an optical technique, it is considerably more sensitive than inductive detection. Therefore, ODMR detection schemes introduced unprecedented access to the spin dynamics of small spin ensembles ($\sim 10^4$). In 1993, Wrachtrup used ODMR to make the first magnetic resonance measurement on a single molecule at 1.8 K [22].

1.2.1 Optical Detection of Nitrogen-Vacancy Centers in Diamond

It was in this scientific climate that van Oort, Manson, and Glasbeek, first measured the ground state ODMR spectrum of an ensemble of negatively charged nitrogen-vacancy centers, atomic defects found in nitrogen-rich (type I-b) diamond with an electron spin 1. At this point, it was known that the spin states of the NV⁻ center could be optically pumped and that the fluorescence from its zero phonon line (ZPL) was remarkably stable [23], however, little was known about the nitrogen-vacancy center's spin dynamics.² Using techniques established by Breiland et al. van Oort, Manson and Glasbeek measured relaxation dynamics of the NV⁻ ensembles at 1.4 K in the electronic ground state and explored the perturbative effects of magnetic and electric fields on the ground state of the NV⁻ center using stimulated echo measurements [25–28].

In 1997, Gruber et al. demonstrated optically detected magnetic resonance of single NV⁻ centers at room temperature [29]. Further investigation of the point defect's spin properties, made by Kennedy et al., revealed that NV⁻ centers exhibit significantly long coherence times for a solid state electron spin at room temperature [30]. The detection of a single NV⁻ spin using ODMR as well as the long coherence time of NV⁻ centers sparked interest in using this electron spin system to detect magnetic fields with high resolution and sensitivity [31].

²Understanding was also incomplete with respect to the full electronic structure of the NV⁻ center, however, by this point it was known that that the NV⁻ center has a metastable singlet, that the NV⁻ electronic transition is between a ³A ground state and ³E excited state [24], and also that the excited state exhibits more complicated fine structure than the ground state [23]

Nanoscale resolution of magnetic resonance was later demonstrated with NV⁻ centers [32,33] and the detection of single electron and nuclear spins using nitrogen-vacancy centers was proposed. At around the same time, polarization transfer between optically polarized NV⁻ centers and neighboring nuclear spins was observed [34,35]. This observation suggested that the NV⁻ center could potentially act as both a magnetometer and as a spin polarizing source.

Because of these remarkable properties, NV⁻ centers have been proposed for use in sensitive metrology, high resolution magnetic resonance imaging, spin polarization transfer and quantum information applications.

1.3 Recent Progress using Nitrogen-Vacancy Centers

A remarkable number of NV⁻ related research has been published in the past few years. Here we discuss a select few publications.

1.3.1 Magnetometry: Detection of Electron and Nuclear Spins

One of the most exciting aspects of NV⁻ ODMR is that it can be used to non-invasively obtain chemical information of nanoscale structures. Previous detection schemes that measured magnetic resonance at the nanoscale required extensive experimental efforts, requiring sub-Kelvin temperatures to operate [36]. Staudacher et al. recently demonstrated that a single NV⁻ center embedded 5 nm from the diamond surface could detect 10² protons in liquid and solid organic samples at ambient temperature within a $(5 \text{ nm})^3$ volume. A train of microwave pi pulses (akin to a CPMG sequence) applied to the NV⁻ center with equal spacing at τ acted as a filter of certain parts of the spin noise spectrum for any given τ . A decrease in the NV⁻ fluorescence signal was observed when the spacing τ matched half the period of the proton Larmor frequency period [37]. Using a slightly different method, Rugar et al. detected statistical polarization of proton spins using a single nitrogen-vacancy center embedded in an isotopically ¹²C enriched diamond layer 20 nm from the diamond surface. The statistical polarization of proton spins was detected in a PMMA substrate by inverting the nuclear spins with RF pulses during an NV⁻ spin-echo measurement and observing the change in the NV⁻ fluorescence intensity [38]. Most recently, Lorentz et al. implanted a diamond substrate with NV^- centers \sim 10 nm from the diamond surface and etched the diamond down placing the NV⁻ center < 3 nm from the diamond surface. The diamond was then coated with a thin film of ammonium hexafluorophosphate. Using the NV⁻ hyperfine field as an imaging gradient, Lorentz et al. were able to distinguish the NMR signal from a single proton spin in the thin film, and they determined the distance of the NV^{-} and single proton to be ~ 4 nm, the first such measurement of this kind [39].

Though the work described using single NV^- centers is indeed interesting and unprecedented, it is not the focus of the thesis that we have written here. Instead, we have chosen to focus on the interactions of NV^- centers in an ensemble. Rather than probe the nanoscale like single NV^- centers, NV^- ensemble magnetometers are used to probe a regime of nanometers to microns. The advantage of an NV^- ensemble is that it affords higher magnetic field



Figure 1.1: NV⁻ centers are first polarized using a 532 nm laser, a spin echo sequence is initiated with τ matching half the period of the Larmor precession frequency and the fluorescence output of the NV⁻ center is recorded. In the publications mentioned in the magnetometry section, a train of pi pulses is used to increase the NV⁻ coherence lifetime.

sensitivity. Single centers are limited to sensitivities of ~ 10 nT/ \sqrt{Hz} , while NV⁻ ensembles have achieved subnT/ \sqrt{Hz} magnetic field sensitivities³ [40]. In addition, NV⁻ ensemble magnetometers fill the gap in the availability of sensitive magnetometers that also have high spatial resolution, this is shown in Figure 1d of Ref. [41] and shown in Figure 1.2. As with single centers, chemically specific information about atoms inside and outside the diamond lattice can be determined using an ensemble of NV⁻ centers. For example, chemically specific information about neighboring electron defects (~ 8 nm away from NV⁻) within the diamond lattice can be measured via cross-relaxation effects observed in the NV⁻ ODMR spectrum, as we discuss in chapter 7 of this thesis [42]. Though it has not yet been demonstrated with ensembles, bulk detection of nuclear spin magnetization is certainly possible and we discuss a few possible experiments at the conclusion of this thesis.

Recently, Clevenson et al. demonstrated improved collection efficiencies of NV⁻ ensemble fluorescence, using an edge on collection configuration. [43]. And more recently, Wolf et al. demonstrated the first sub-picoTesla diamond magnetometer, reporting a sensitivity of 0.9 pT/\sqrt{Hz} using a ~ (9 um)³ NV⁻ sensor detection volume [41]. Wolf et al. maximized fluorescence collection efficiencies by adapting a lens on one end of the diamond magnetometer.

We would like to note that the performance of a magnetometer based on electron spins is [44],

$$\delta B \simeq \frac{1}{g_s \mu_B} \frac{1}{R\sqrt{\eta}} \frac{1}{\sqrt{NtT_2^*}},\tag{1.1}$$

where δB is the minimum detectable field, μ_B is the Bohr magneton, g_s is the electron gfactor, R is the ODMR fluorescence measurement contrast, η is the fluorescence detection efficiency, N is the number of spin centers, t is the interrogation time, and T₂^{*} is the coherence lifetime of the NV⁻ center. In order to increase the sensitivity of the magnetometer one could increase the collection efficiency as demonstrated by Ref. [43], or increase the collection efficiency and the total number of NV⁻ centers that are being probed such as in Ref. [41]. Additionally one could devise a way to extend the coherence lifetime of a spin ensemble further using decoupling techniques, or using a method based on super irradiant masing as proposed by Ref. [45]. For a full review of the current state of NV⁻ magnetometery we direct the reader to Ref. [46].

1.3.2 Coherence Lifetimes of NV Centers

Understanding the dynamics and decoherence mechanisms of coupled spin systems is an important problem in nuclear magnetic resonance and quantum information processing (QIP). Decoupling techniques such as Carr-Purcell-Meiboom-Gill (CPMG) and Uhrig dynamical decoupling (UDD) are often employed to extend coherence lifetimes [52]. Lengthening the coherence lifetime allows for longer interrogation periods in spin systems leading to narrower line widths and thus improved sensitivity in the estimation of frequencies and

³The magnetic field per \sqrt{Hz} notation indicates the minimum magnetic field that a magnetometer can detect with a signal to noise ratio of one after 1 second of signal averaging.



Figure 1.2: Magnetic field sensitivity vs detector-sample distance, at room temperature [41]. References for the values shown are: for alkali vapor magnetometer [47] [48], squid magnetometer [49], single NV⁻ [39], [41], NV⁻ ensemble [41], hall probe sensors [50], Whispering Gallery Mode - Resonator [51].

small magnetic fields. Specifically, extending the coherence lifetime of a large number of spins is desirable for QIP and ultra sensitive magnetometry. Because of the ease with which we can tailor the dopants in diamond, the NV⁻ center is a particularly useful system for studying ensembles of coupled spins and exploring different decoherence mechanisms.

There have been a number of publications in the past few years that have extended our understanding of the sources of decoherence of the nitrogen-vacancy center, recently, Bar-Gill et al. showed that the form of the coherence decay in NV⁻ centers can be used to determine whether the primary decoherence mechanism is electron-spin or nuclear spin dominated [53]. And in chapter 5 we discuss a mechanism by which the coherence lifetime of an NV⁻ ensemble can be extended by two fold using a magnetic field perpendicular to the NV⁻ axis [54]. In addition, an ensemble of NV⁻ centers were shown to exhibit a coherence lifetime approaching 1 second in an isotopically pure ¹²C diamond lattice, Bar-Gil et al. reported a room temperature coherence lifetime of an ensemble of NV⁻ centers to be 600 ms [55].

And more recently, and something that is quite interesting, Jin et al. have proposed a method to increase the coherence time of an ensemble of NV^- centers (or any ensemble of spins in a solid) by orders of magnitude, [45], here they propose to exploit superradiant lasing to enhance the coherence times of spin ensembles by coupling them to a high-quality microwave cavity and driving the coupled system into superradiant masing.

1.3.3 Nuclear Spin Polarization with NV Centers

Detection of nuclear magnetic resonance relies on a population difference between nuclear spin states. Often this population difference is very small, less than .00001% of the total spin population.⁴ The population difference is often described in terms of a spin-polarization. For a spin 1/2, the polarization is defined as [56],

$$P = \frac{e^{\frac{\hbar\gamma B}{2k_BT}} - e^{\frac{-\hbar\gamma B}{2k_BT}}}{e^{\frac{\hbar\gamma B}{2k_BT}} + e^{\frac{-\hbar\gamma B}{2k_BT}}},$$
(1.2)

where γ is the gyromagnetic ratio of the spin of interest, B is the magnetic field, k_B is Boltzmann's constant, T is the temperature, and \hbar is the reduced Planck constant. There are several ways to increase the spin polarization. For example, one could use a 'brute force' method, where one increases the magnetic field and decreases the temperature. This will increase the equilibrium spin polarization. Alternatively, one could use hyperpolarization methods that rely on dynamic non-equilibrium spin polarization. These latter methods often require polarization transfer between spin systems that are at different spin-temperatures. In 1953, Overhauser demonstrated polarization transfer from electrons in metals to nuclear

⁴Though small, this population difference is detectable using inductive detection, however, it does make standard NMR an inherently insensitive technique. In standard techniques, often a very large number of spins is required in order to have a detectable signal with sufficient signal to noise in a reasonable amount of time.

spins, resulting in nuclear spin polarization enhancements of two orders of magnitude [12]. Since then, the NMR community has honed and polished dynamic nuclear polarization techniques, often using solutions filled with electron rich radicals and transferring electron polarization at cold temperatures and high magnetic fields to nuclear spins via microwave irradiation [57].

Recently there has been interest in using the electron spin system of the nitrogen-vacancy center to polarize nuclear spins at room temperature. In 2010, King et al. demonstrated polarization transfer from NV⁻ centers to neighboring ¹³C nuclear spins in the diamond lattice by optically irradiating a diamond sample that contained a high density of NV⁻ centers [34]. In chapter 8 we discuss another method of polarization transfer from NV⁻ centers to ¹³C nuclei in diamond that allows for sensitive control of the direction of nuclear spin polarization near the NV⁻ center ground state level anti-crossing regime [58]. Recently, Breinland et al. have demonstrated nuclear polarization transfer by optically irradiating NV⁻ centers at their excited state level anti-crossing of 50 mT, and shuttling to a high field magnet for inductively detected NMR measurements. They achieved a \sim 0.5% $^{13}\mathrm{C}$ spin polarization for spin active carbon nuclei in the diamond [59]. Though polarization of nuclear spins within the diamond lattice has been demonstrated in numerous publications, in order to generalize this technique to polarize other materials, we must polarize nuclear spins external to the diamond lattice, a feat that has yet to be demonstrated in the current literature. Abrams et al. have investigated effects of average NV⁻ center depth and nanoscale surface topology on the polarization transfer between shallow nitrogen-vacancy centers to nuclear spins on the surface of the diamond. In their calculations they find that it is possible to achieve high nuclear spin polarization at moderate magnetic fields if the diamond surface is engineered with a nanoscopic surface roughness [60].

1.3.4 Diamond Materials

Improved understanding of the formation of NV^- centers has led to a remarkable degree of control over the orientation, spatial positioning and coherence lifetime properties of this diamond defect⁵. This has allowed for the controlled formation of NV^- centers in diamond with properties tailored for particular experimental realizations [62], [63], [55].

As mentioned in one of the previous sections, NV^- centers were formed in isotopically enriched ¹²C diamond and were found to have a coherence lifetime 2 orders of magnitude greater than previously reported [55]. Recently, Fukui et al. demonstrated perfect orientational alignment of NV^- centers along the [111] axis of the diamond for NV^- centers incorporated into diamond during chemical vapor deposition (CVD) diamond growth [62]. When working with an ensemble of NV^- centers, there are four possible NV^- orientations

⁵Though it must be noted that having control over one of these properties often negates the control of the other property. Currently, the position of the oriented NV^- centers formed during CVD growth cannot be controlled. While for the case of implanted centers, it is the orientation that cannot be controlled. NV^- centers formed during CVD growth exhibit excellent coherence properties, while those that are implanted exhibit shorter coherence times than their CVD grown counterparts, though progress has been made in increasing these coherence times [61].

that one can work with. Often only one of these orientations is used for magnetometry measurements and so one of the NV^- orientations is spectrally separated from the other orientations by applying a magnetic field aligned along one of the [111] axes of the diamond. Preferential orientation of NV^- centers grown in diamond will simplify magnetic field alignment in magnetometry experiments and will also increase the magnetic field sensitivity.

For detecting electron and nuclear spins external to the diamond lattice (or perhaps polarizing nuclear spins) it is desirable to have NV^- centers close to the diamond surface in order to increase the coupling strength between the NV^- centers and the surface spins of interest. Ion implantation of nitrogen atoms into diamond affords control over the spatial positioning of NV^- centers in the diamond to within 10's of nm resolution, where the x-y resolution is limited by the size of the ion collimator [64] and the z-positioning is dependent on the spread of incoming beam energies of the nitrogen atoms, often resulting in a gaussian spread of the particle positions within the diamond. After the ion implantation, the diamond can then be etched down using oxygen plasma to leave nitrogen-vacancy centers very close to the surface [63]. The depth of the nitrogen-vacancy centers after the etching can be determined within 2.6 nm accuracy from the diamond surface to a diamond depth of 10 nm [65].

1.4 Motivation

In this dissertation, nitrogen-vacancy centers are explored in a number of different contexts. In general, we explore how an ensemble of nitrogen-vacancy centers couple to electron and nuclear spins in the diamond lattice. Specifically, we explore how we can exploit these interactions to use ensembles of nitrogen-vacancy centers as a more sensitive magnetometer, as a polarizing source, and for improving fundamental understanding of decoherence mechanisms in large strongly coupled spin systems. All with the goal in mind that this will lead to greater understanding of how we can use these systems for chemical detection, fundamental physics studies, and nuclear magnetic resonance signal enhancements.

Chapter 2

Spin Systems

There have been a number of subjects mentioned in the previous chapter that have not yet been properly introduced. For example, we have not yet discussed spin states or magnetic resonance, nor how we can use magnetic resonance to obtain chemical information about materials. Here we will present to the reader a brief introduction on these topics, and much of what we discuss is based on information found in Sakurai, [66], Keeler [67], Griffiths [68], Cohen-Tannoudji [69] and Levitt [56]. And for the reader that would prefer to first read a review on the physical properties and the spin dynamics of NV^- centers, we would recommend going straight to chapter 3.

2.1 Spin

In addition to mass and electric charge, electrons and nuclei have a property known as spin. Spin is an intrinsic property of subatomic particles that contributes to their total angular momentum. The total angular momentum of a particle characterizes its magnetic moment, and the magnetic moment defines the maximum torque experienced by the particle when placed in an external magnetic field.¹

The effects of spin were first observed in 1896, when Pieter Zeeman placed a sodium lamp in a strong magnetic field and recorded a splitting of the spectral lines in the sodium optical emission spectrum [70]. Since Zeeman's measurement, our understanding of spin has improved markedly, though it is still incomplete. An important step in our understanding of the electron spin occurred in 1928, when Dirac predicted the existence of electron spin 1/2 using his relativistic wave equation [71]. Dirac then theoretically determined the magnitude of the electron spin magnetic moment, a value that has since been refined using modern quantum electrodynamic theories [72]. Understanding and calculating nuclear spin, however, has proven to be a significantly more difficult task and the precise origin of the spin 1/2 of proton and neutron spin has yet to be determined [73, 74]. A more thorough discussion on

¹It is important to note that the angular momentum of subatomic particles is quantized and that spin is itself a purely quantum phenomenon, unobservable in macroscopic systems.

the nature of the proton and neutron spin and the subatomic particles that make them up is outside of the scope of this chapter. For now it will suffice to say that the proton and neutron have a spin of 1/2 and the spins of nuclei are formed by combining the spins of protons and neutrons. When combining two spins with spin quantum numbers J_1 and J_2 , the total angular momentum quantum number will take the following form [56],

$$J_3 = [|J_1 - J_2|, |J_1 - J_2| + 1, ..., |J_1 + J_2|].$$
(2.1)

It is possible to have nuclei of zero spin, half-integer spin and integer spin, where the rules determining how the proton and neutron spins combine to give the spin of an atomic nucleus may be understood using the nuclear shell model [75]. Protons and neutrons will pair as they combine in a given atomic nucleus and only unpaired protons or neutrons will contribute to the nuclear spin.

2.1.1 Magnetic Moment

The magnetic moment of a particle gives us information about the coupling strength between the particle and a magnetic field. The magnetic moment of the electron is a couple orders of magnitude larger than that of the proton and this has important implications with regard to the spin polarization of the electron versus that of the proton, we will discuss this later on in this chapter. As mentioned previously, the total angular momentum of a particle characterizes its magnetic moment. The spin magnetic moment of the electron is defined as,

$$\mu_{\mathbf{S}} = \mathbf{g} \frac{\mu_B}{\hbar} \mathbf{S},\tag{2.2}$$

where g is the Landé g-factor, μ_B is the Bohr magneton, \hbar is the reduced Planck constant and **S** is the electron spin. The Bohr magneton is defined as, $\frac{e}{2m_e}\hbar$, where e is the elementary charge, and m_e is the electron mass. In a general formulation of the electron magnetic moment, the electron g-factor is better expressed as a g-tensor. For a free electron, the g-tensor is isotropic and is close to a value of g_s , the electron g-factor, however, for electrons in radicals or inorganic complexes the tensor components can change and the g-tensor can become anisotropic. This is because the g-tensor is is a measure of the orbital contribution to the magnetic moment as well as the spin. It is usually negative if the centre has unpaired electrons and positive if it has unpaired holes associated with it. Anisotropy of the g-tensor is caused by spin-orbit coupling effects and often causes line broadening in isotropic electron spin resonance spectra. For example, for a free electron $g_s = -2.00231930436153 \pm 2.6 \times 10^{-13}$, while the g-factor of the NV⁻ center in the ground state has been measured to be just nearly isotropic, with values of $g_{gs}^{\perp} = 2.0031 \pm 0.0002$, and $g_{gs}^{\parallel} 2.0029 \pm 0.0002$ [76, 77]. Despite this small difference, we have used g_s for most of the calculations done in this thesis.

The nuclear spin magnetic moment is defined as,

$$\mu_{\mathbf{I}} = \frac{g_n \mu_N}{\hbar} \mathbf{I},\tag{2.3}$$

where μ_N is the nuclear magneton, g_n is the nuclear g-factor particular to each nucleus, and I is the nuclear spin. The nuclear magneton is defined as $\frac{e}{2m_p}\hbar$, where m_p is the mass of the proton. For convenience, the magnetic moment of an electron or nucleus is often written in terms of a gyromagnetic ratio,

$$\gamma_i = \frac{g\mu_i}{\hbar}.\tag{2.4}$$

Where the subscript 'i' indicates the relevant spin. Often we wish to discuss the gyromagnetic ratio in terms of Hz/T rather than rad/(s·T) and so the γ values included in this text refer more appropriately to the expression $\gamma/2\pi$, though in the work shown in chapter 6, this is made clear.

2.2 Spin States

The number of available spin states for a particle with total spin S is, 2S+1. With the possible states being [-S, -S+1, ..., +S]. Hence, the total number of spin states for a spin 1/2 particle is two: -1/2 and +1/2, while the total number of states for a spin 1 particle is three, with states: -1, 0, 1. We would now like to explore the mathematical representation of a spin state, but to do so we must first introduce a few concepts. The state of a particle can be represented by a wave function. Wave functions satisfy the conditions for abstract vectors and so we can mathematically represent the state of the particle using a complex vector space. The dimensionality of the vector space is specified according to the number of accessible states in the system, and thus for the case where spin is the only degree of quantum mechanical freedom, the number of spin states of the system defines the dimensionality of the vector space. In the notation of Dirac, the vector that represents the state is called a ket and a ket is represented as $|\psi\rangle$. For a spin 1/2 system the state vectors (ket) can be written as,²

$$|\alpha\rangle = \begin{pmatrix} 1\\0 \end{pmatrix},\tag{2.5}$$

and,

$$|\beta\rangle = \begin{pmatrix} 0\\1 \end{pmatrix}. \tag{2.6}$$

These kets constitute the basis kets of the spin 1/2 system which can be represented as a two-dimensional vector space. Using the basis kets we can describe the wavefunction as a linear combination of the basis kets that span this two-dimensional vector space, for example,

$$|\psi\rangle = a|\alpha\rangle + b|\beta\rangle, \qquad (2.7)$$

²Technically, a spin state is better represented by a spinor. Both vectors and spinors transform linearly with respect to a rotation operation, however, the spinor transformation depends on the ordering of the rotation. The difference in the outcome between identical rotational operations acting on a spinor versus a vector is observed in the form of a geometric phase factor, this quantum mechanical effect is known as Berry's phase and has been observed in magnetic resonance measurements [78]

where, a and b are complex scalars with the normalization relation of,

$$a|^2 + |b|^2 = 1. (2.8)$$

We can simplify the representation of $|\psi\rangle$ as,

$$|\psi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}. \tag{2.9}$$

It is important to note that we are using the framework of abstract vectors to represent a physical system with physical observables, hence we must have a way to define what the 'length' of a vector means in this vector space in terms of a physical quantity.³ For this to be the case, the vectors in the vector space must be orthonormal, meaning that,

$$\langle m|n\rangle = \delta_{mn},\tag{2.10}$$

where δ_{mn} is the Kronecker delta, equal to 1 for m = n and equal to 0 for $m \neq n$. So if we have a ket defined as seen in Eq. 2.7, we can use the orthonormality property of the basis vectors to specify 'how much' of each of these basis vectors contributes towards the final vector, $|\psi\rangle$, i.e.,

$$a = \langle \alpha | \psi \rangle. \tag{2.11}$$

In equation 2.11 we have used the notion of a previously undefined 'bra space'. In quantum mechanics, it is postulated that corresponding to every ket $|\psi\rangle$ there exists a bra $\langle\psi|$ such that,

$$\langle \psi | = |\psi\rangle^{\dagger} = \begin{pmatrix} a^* & b^* \end{pmatrix}, \qquad (2.12)$$

where $|\psi\rangle^{\dagger}$ is the conjugate transpose of $|\psi\rangle$ and * indicates the complex conjugate. The 'bra space' is often referred to as a space that is 'dual' to the ket space.

As a final note, for the case of working with two or more spins, (for example if we would like to explore a system that includes an electron spin 1/2 and a nuclear spin 1/2) we can form a new vector space by taking the tensor product of the two spaces. Using the expressions for α and β defined in equations 2.5 and 2.6, we would have,

$$|\alpha\rangle \otimes |\alpha\rangle = \begin{pmatrix} 1\\0\\0\\0 \end{pmatrix}, |\alpha\rangle \otimes |\beta\rangle = \begin{pmatrix} 0\\1\\0\\0 \end{pmatrix}, |\beta\rangle \otimes |\alpha\rangle = \begin{pmatrix} 0\\0\\1\\0 \end{pmatrix}, |\beta\rangle \otimes |\beta\rangle = \begin{pmatrix} 0\\0\\0\\1 \end{pmatrix}.$$
(2.13)

The new vector space is now a four dimensional space rather than a two dimensional space with basis kets of, $|\alpha\alpha\rangle$, $|\alpha\beta\rangle$, $|\beta\alpha\rangle$, and $|\beta\beta\rangle$.

So how do we obtain any useful information from these spin state representations? For that we require operators that correspond to observables of the spin system.

³The need for these requirements is a bit more obvious once we move away from two-dimensional vector spaces to large multi-dimensional vector spaces. In three dimensions we can easily visualize 3 axes that are perpendicular to one another and thus use common geometric notions to describe the projection of a vector onto any of these axes. The basis for this space is made up of these 3-axes, and a vector can be described as a linear combination of these axes. The same ideas apply to multi-dimensional spaces, but they only apply if all of the 'axes' of the system are orthonormal.

2.3 Operators

Observables such as momentum or spin components can be represented by operators acting on kets. A ket $|\psi\rangle$ is said to be an eigenket of operator **A** if the operation of **A** on ket $|\psi\rangle$ yields the same ket multiplied by a scalar:

$$\mathbf{A}|\psi\rangle = a|\psi\rangle. \tag{2.14}$$

The scalar 'a' is then said to be an eigenvalue of operator **A** and it corresponds to the mean value of the observable A. The expectation value of observable A for a normalized ket $|\psi\rangle$ is,

$$\langle A \rangle = \langle \psi | \mathbf{A} | \psi \rangle = \begin{pmatrix} a^* & b^* \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}.$$
(2.15)

The expectation value gives the predicted mean value⁴ of an observable A.

Operators do not, in general, commute [68]. This means that $\mathbf{AB}|\psi\rangle$ does not give the same result as $\mathbf{BA}|\psi\rangle$. The amount that these operators fail to commute is determined by the commutator, which is written out as

$$[\mathbf{A}, \mathbf{B}] = \mathbf{A}\mathbf{B} - \mathbf{B}\mathbf{A}.\tag{2.16}$$

For commuting observables (operators), $[\mathbf{A}, \mathbf{B}] = 0$. For non-commuting observables, $[\mathbf{A}, \mathbf{B}] \neq 0$. For a pair of observables whose operators do not commute, they are called incompatible observables. Incompatible observables do not share a complete set of eigenfunctions $|\psi\rangle$ (though they may share a subset of eigenfunctions). Compatible observables do share a complete set of eigenfunctions.⁵. What exactly does this mean? The wave function describes our system. We represent the wave function in terms of a ket space and dual bra space. If the wave function is not an eigenstate of both of the operators that are acting on the state it is impossible to make both measurements without disturbing the initial state of the system. This has important implications regarding what we can know about our spin system and is commonly referred to as the uncertainty principle.

2.3.1 Spin Angular Momentum Operators

We would now like to discuss the form of spin angular momentum operators and some of their properties. As mentioned previously, spin contributes to the total angular momentum of a particle. We can define the spin operators S_x , S_y , S_z which represent the three Cartesian components of spin angular momentum. We can also define a spin angular momentum vector,

$$\mathbf{S} = \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}.$$
 (2.17)

⁴It is important to note that the tools provided by quantum mechanical theory predict the statistical means of observables (e.g. momentum, position, spin state), not the result of a single measurement.

⁵Here we make a distinction between eigenfunctions and eigenvectors. An eigenfunction is an eigenvector that is also a function, but an eigenvector is not necessarily an eigenfunction.

The commutation relations of these operators are,

$$[S_x, S_y] = i\hbar S_z,$$

$$[S_y, S_z] = i\hbar S_x,$$

$$[S_z, S_x] = i\hbar S_y.$$

(2.18)

The square of the spin angular momentum vector is the operator

$$\mathbf{S}^2 = S_x^2 + S_y^2 + S_z^2. \tag{2.19}$$

From this we have the additional commutation relations of

$$[\mathbf{S}^2, S_x] = [\mathbf{S}^2, S_y] = [\mathbf{S}^2, S_z] = 0.$$
(2.20)

Of these spin operators, we see from equation 2.18 that we cannot measure any of the three Cartesian components of the spin angular momentum simultaneously, however, we can measure the squared magnitude of the spin angular momentum and one of the Cartesian components of the spin angular momentum operators simultaneously. We can also define raising and lowering operators for spin angular momentum. These are defined as

$$S_{\pm} = S_x \pm i S_y, \tag{2.21}$$

where we have the following commutation relations,

$$[S_{+}, S_{z}] = -\hbar S_{+}, [S_{-}, S_{z}] = \hbar S_{-}.$$
(2.22)

The spin angular momentum operators are nearly always represented in the Zeeman basis (direction of applied magnetic field defines z). Spin states are often represented as a ket $|s, m_s\rangle$, where s is the total spin and m_s is the spin state. For a spin with total spin s, the number of spin states is 2s+1, with $m_s = [-s, -s+1, ..., s]$. As mentioned previously, the dimensionality of the vector space that represents the spin system is determined by the total number of spin states, hence for a spin 1, we would represent the spin operators as 3x3 square matrices. For a spin 1 the Cartesian spin angular momentum operators are,

$$S_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, S_y = \frac{1}{\sqrt{2}i} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}, S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$
(2.23)

and the ladder operators are,

$$S_{+} = \sqrt{2} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, S_{-} = \sqrt{2} \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$
(2.24)

We can now see how these operators act on the spin state $|s, m_s\rangle$,

$$\begin{aligned} \mathbf{S}^{2}|s, m_{s}\rangle &= \hbar^{2}s(s+1)|s, m_{s}\rangle \\ S_{z}|s, m_{s}\rangle &= \hbar m_{s}|s, m_{s}\rangle \\ S_{\pm} &= |s, m_{s}\rangle = \hbar m_{s}|s, m_{s}\rangle \end{aligned}$$
(2.25)

These spin operators are used throughout the text. We can use the operators presented to describe spin-spin interactions as well as a number of other interactions that will be introduced in chapter 3 of this thesis.

2.3.2 Hamiltonian

The operator that we will use the most in this text is the Hamiltonian, \mathcal{H} . The Hamiltonian is an operator that corresponds to the total energy of a system. It is generally composed of several other operators that represent particular interactions within the system (e.g. spin angular momentum operators). The eigenstates of the Hamiltonian are the energy eigenstates of the system. And the eigenvalues of these eigenstates gives the energy levels of the system. We can express this as the time-independent Schrödinger equation,

$$\mathcal{H}|\alpha\rangle = E_{\alpha}|\alpha\rangle. \tag{2.26}$$

In addition to calculating the eigenstates of the spin system at time zero, often we wish to obtain information about a spin state $|\psi\rangle$ after it has evolved for some time t. For this purpose we can use the time-dependent Schrödinger equation,

$$-i\hbar\frac{\partial}{\partial t}|\psi\rangle = \mathcal{H}|\psi\rangle. \tag{2.27}$$

If we solve the time-dependent Schrödinger equation for both the bra and ket we arrive at the following expression,

$$|\psi(t)\rangle\langle\psi(t)| = e^{-i\mathcal{H}t}|\psi(0)\rangle\langle\psi(0)|e^{i\mathcal{H}t}.$$
(2.28)

The expression $e^{-i\mathcal{H}t}$ is often referred to as the propagator of the system and the expression $|\psi(t)\rangle\langle\psi(t)|$ is referred to as the outer product and is the formal definition of a density operator.

2.4 Density Operator

At this point, we have only considered systems that have a well defined, pure state $|\psi\rangle$. The reality of the situation is that we hardly ever have a quantum system that can be described as a pure state. Instead we have a mixed state. So what is the difference? When we compute the expectation value of an observable A for a pure state case, we must only consider the probability that the known state $|\psi\rangle$ will give observable A. With the case of mixed states, not only must we consider the probability that a state ψ will give observable A, we must also consider the probability of state $|\psi\rangle$ being in some state $|\psi\rangle$ or perhaps any number of other states $|\psi_k\rangle$ [69]! In addition, these different states can interact and produce interference terms. The formalism that we described in the previous section is not sufficient to describe this interference effect, we must introduce a way to describe statistical mixtures of states.⁶

In the context of electron and nuclear magnetic resonance we often deal with mixed states, thus we must include the effects described above. This can be done using density operator formalism. For simplicity, we will develop the formalism for the case of a pure state. We can describe a state vector as,

$$|\psi(t)\rangle = \sum_{n} c_n(t)|u_n\rangle.$$
(2.29)

The formal definition of the density operator is

$$\rho(t) = |\psi(t)\rangle\langle\psi(t)|. \tag{2.30}$$

We can insert equation 2.29 into equation 2.30 to give,

$$\langle u_p | \psi(t) \rangle \langle \psi(t) | u_n \rangle = c_n^*(t) c_p(t).$$
(2.31)

The density operator can be represented as a matrix with the elements:

$$\rho_{pn}(t) = \langle u_p | \rho(t) | u_n \rangle = c_n^*(t) c_p(t).$$
(2.32)

Let us now consider an observable A with matrix elements,

$$\langle u_p | A | u_p \rangle = A_{np}. \tag{2.33}$$

Using equation 2.29 we find that the mean value of A at time t is

$$\langle A \rangle(t) = \langle \psi(t) | A | \psi(t) \rangle = \sum_{n,p} c_n^*(t) c_p(t) A_{np}.$$
(2.34)

We can now express the expectation value of observable A using a density matrix as,

$$\langle A \rangle(t) = \sum_{n,p} \langle u_p | \rho(t) | u_n \rangle \langle u_n | A | u_p \rangle,$$

$$= \sum_p \langle u_p | \rho(t) A | u_p \rangle,$$

$$= Tr[\rho(t)A]$$

$$(2.35)$$

⁶A common misconception is that a mixed state can be described as a linear combination of pure states, this is not the case. A mixed state is only fully described if you include the interactions between the states that make up the mixed state.
Equation shows the expectation value for a pure state. For the case of a mixed state the expression is,

$$\langle A \rangle = Tr[\rho A], \tag{2.36}$$

where

$$\rho = \sum_{k} p_k \rho_k. \tag{2.37}$$

 ρ is the average of the density operators $\rho_k = |\psi_k\rangle \langle \psi_k|$ that make up the system, where p_k is a probability factor. Though it is not quite obvious here, this expression is quite powerful for determining how different states in a spin system are linked. The derivation can be found in Ref. [69].

And lastly, using equation 2.27 we find that the time evolution of the density matrix obeys the equation [69]:

$$i\hbar \frac{d}{dt}\rho(t) = [H(t), \rho(t)].$$
(2.38)

2.4.1 Populations and Coherences

The elements of the density matrix including diagonal and off diagonal elements (we are considering the case of mixed states) can be expressed as [66] [79],

$$\rho_{nm} = \langle n | \rho | m \rangle = \sum_{k} \langle n | \psi_k \rangle \langle \psi_k | m \rangle = \sum_{k} \sum_{n,m} c_n^k (c_m^k)^* = \overline{c_n c_m^*}, \qquad (2.39)$$

where overbars indicate a statistical average over the ensemble and c_n^k is a complex, timedependent amplitude coefficient for the component of basis state $|n\rangle$ that makes up state $|\psi_k\rangle$. Diagonal elements of the density matrix ρ give the average probability of occupying one of the pure states $|n\rangle$, and these elements are commonly referred to as spin population. The coefficients of the diagonal elements are,

$$\rho_{nn} = \overline{c_n^2}.\tag{2.40}$$

Off-diagonal elements of the density matrix express the interference effects between states $|n\rangle$ and $|m\rangle$. ρ_{mn} is an average of these interference terms taken over all possible states of the mixture. The coefficients of the off-diagonal elements of the density matrix are,

$$\rho_{mn} = \overline{c_n c_m^*}.\tag{2.41}$$

The off-diagonal elements are called coherences. Why are these terms called coherences? The element ρ_{mn} doesn't really tell us how much interference is happening between each state in the mixture, but rather how these different interference interactions sum to give some average. Hence, the elements that make up ρ_{mn} might all be non-zero, but ρ_{mn} can still be zero. When coherence exists between states the interference does not cancel across the average, hence a coherent state!

2.4.2 Time evolution of density matrix

We can also consider how the elements of the density matrix change with time using equation 2.38. The results are,

$$i\hbar \frac{d}{dt}\rho_{nn}(t) = 0,$$

$$i\hbar \frac{d}{dt}\rho_{mn}(t) = (E_n - E_m)\rho_{mn}.$$
(2.42)

Solving equation 2.42 we obtain the following expressions [69]:

$$\rho_{nn}(t) = constant,$$

$$\rho_{mn}(t) = e^{\frac{i}{\hbar}(E_m - E_n)t}\rho_{mn}(0).$$
(2.43)

Here we see that populations remain the same over time, but the coherences oscillate at (E_m-E_n) . This energy splitting is the energy difference between the eigenvalues of the states that are in a superposition, $|n\rangle$ and $|m\rangle$. For a completely isolated spin system, the coherence lifetime of a superposition of quantum states should continue indefinitely. However, when we consider for example, an ensemble of NV⁻ centers in a superposition state, the coherence lifetime will be limited by the interaction of the NV⁻ centers and the spin environment of the diamond lattice. Any magnetic field fluctuations that occur at the transition frequency of the states that are in a superposition state will result in a decrease in the coherence lifetime. The loss of coherence (or decoherence) is commonly referred to as dephasing. We will explore the sources of decoherence in more detail in chapters that follow.

2.5 Magnetic Resonance

We will now discuss some of the principles of magnetic resonance and the physical response of an ensemble of spins to a static and an oscillating field.

2.5.1 Thermal Equilibrium and Spin Magnetization

The sum of all of the magnetic moments of a spin ensemble is called the spin magnetization. As we discussed in the first section of this chapter, the magnetic moment of a particle is dependent on the spin state of the particle. Since the density matrix that we just described gives us this information, we can use the density operator to determine the magnetization of an ensemble of spins at thermal equilibrium. The density operator of a system in thermodynamic equilibrium is [69],

$$\rho = \frac{e^{-\mathcal{H}/k_B T}}{Z},\tag{2.44}$$

where \mathcal{H} is the Hamiltonian operator, k_B is the Boltzman constant and Z is the partition function, $Z = Tr[e^{-H/k_BT}]$. It is interesting to note what the diagonal and off-diagonal matrix elements of the density matrix look like, we find,

$$\rho_{nn} = \frac{e^{E_n/k_B T}}{Z},\tag{2.45}$$

and

$$o_{mn} = \frac{e^{-E_m/k_B T}}{Z} \langle n|m\rangle = 0.$$
(2.46)

At thermal equilibrium there are no coherences, the system is completely dephased. We only have spin populations. Using the formalism that we described in the previous section we can calculate the spin magnetization along a given Cartesian coordinate. For a spin 1/2 system, the expectation value of the magnetic moment along z can be represented as,

$$\langle \mu_z \rangle = \gamma Tr[\rho S_z]. \tag{2.47}$$

This is also the representation for the system spin polarization. As we mentioned in the first section, the gyromagnetic ratio of the electron is 2 orders of magnitude larger than the proton gyromagnetic ratio. From Eq. 3.9 we see that this is directly reflected in the spin magnetization.

2.5.2 Resonance

So now that we have established these equilibrium parameters, and have shown how to calculate the spin magnetization let's consider the case where a spin 1/2 is placed in a magnetic field B_0 with an applied oscillating field B_1 . The Hamiltonian of this system is [69],

$$\mathbf{H}(t) = -\gamma S \cdot [B_0 + B_1(t)].$$
(2.48)

Though we have shown the Hamiltonian of the system above, for the purposes of this discussion we will use a semi-classical description of the effects observed in a magnetic resonance measurements, for a more rigorous discussion we would refer the reader to [69]. Let us represent our spin system as a classical system with total angular momentum S and with some magnetic moment $\mathbf{m} = \gamma S$. This system will interact with a static magnetic field in the following way,

$$\frac{d\mathbf{m}(t)}{dt} = \gamma \mathbf{m}(t) \times B_0. \tag{2.49}$$

From Eq. 2.49 we see that $\mathbf{m}(t)$ will rotate about B_0 with an angular velocity ω_0 of $-\gamma B_0$. If we then apply an oscillating field B_1 with perpendicular to B_0 the magnetic moment will begin to precess/rotate about some effective field that is the vector sum of B_1 and B_0 which we will call B_{eff} . However, the direction of B_1 changes with respect to time, because the B_1 vector is also rotating about B_0 with angular velocity ω . This complicates the equation of motion of $\mathbf{m}(t)$, so instead we switch to a rotating frame to remove the time dependence of the effective field. Now we can describe the motion of $\mathbf{m}(t)$ as a precession about a static field B_{eff} . With the equation [69],

$$\left(\frac{d\mathbf{m}(t)}{dt}\right)_{Rot} = \mathbf{m}(t) \times [\Delta \omega \hat{z} - \omega_1 \hat{x}], \qquad (2.50)$$

where,

$$\begin{aligned} \Delta \omega &= \omega - \omega_0, \\ \omega_1 &= -\gamma B_1. \end{aligned} \tag{2.51}$$

For the equation described above B_{eff} has the form,

$$B_{eff} = \frac{1}{\gamma} [\Delta \omega \hat{z} - \omega_1 \hat{x}]. \qquad (2.52)$$

The effect of the oscillating field B_1 on the motion of **m** is most pronounced when ω is almost the same value as ω_0 . When this happens B_1 can have the effect of inverting the motion of **m**. Let us now consider the quantum case. In a quantum spin system the static magnetic field has the effect of splitting the $m_s = \pm 1/2$ spin states by the Zeeman term γB_0 , where γ is the gyromagnetic ratio of the spin of interest, this term is known as the Larmor precession frequency and it determines the frequency at which the spin will precess about the magnetic field B_0 . The 'motion' of an ensemble of spins interacting with a static and oscillating magnetic field is quite analogous to the classical description above, if we ignore relaxation effects. The idea of a resonance condition is also quite analogous. If a B_1 field is applied at a frequency of approximately ω_0 to the spin system perpendicular to the static field, the ensemble spin magnetization will periodically invert at a frequency,

$$\Omega = \sqrt{\Delta \Omega^2 + {\Omega_1}^2},\tag{2.53}$$

where $\Delta\Omega$ is the frequency offset $\gamma B_0 - \gamma B_1$ and Ω_1 is γB_1 . This is known as the Rabi nutation frequency.

In a magnetic resonance experiment, the oscillation at the Larmor precession frequency is detected using inductive detection, we can think of this as a rotating magnet inducing current in a solenoid due to the changes in the magnetic flux through the coil. Often there is not just one Larmor precession frequency, but several, due to microscopic variations in the magnetic field in a spin system. These microscopic variations in the magnetic field are sometimes related to the electron density distributions in molecules. Nuclear magnetic resonance exploits this property to obtain chemical information about materials at high magnetic fields.

2.5.3 Bloch Equations

We used the classical example in the previous section to provide a tangible description of how spin magnetization behaves in a magnetic field. In practice, the Bloch equations are used to describe the evolution of an ensemble of spins via a semi-classical method. The Bloch equations are equations of motion for the spin magnetization, they were first introduced by Felix Bloch as a phenomenological tool to describe the evolution of spin magnetization in the presence of relaxation effects. The Bloch equations are

$$\frac{dM_x}{dt} = \gamma \cdot M_y \cdot B_0 - \frac{M_x}{T_2},$$

$$\frac{dM_y}{dt} = \gamma \cdot M_x \cdot B_0 - \frac{M_y}{T_2},$$

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}.$$
(2.54)

In Eq. 2.54 M_0 is the equilibrium spin magnetization, and M_x , M_y , M_z are the Cartesian components of the spin magnetization. T₂ and T₁ are relaxation terms associated with coherence decay. We use these equations in great detail in Chapter 9 of this thesis.

2.6 Relaxation processes

At thermal equilibrium only diagonal elements of the density matrix are present. When the spin system is perturbed by some radio frequency pulse coherences can be created. After the system has been moved away from its equilibrium state there is a relaxation time associated with the system returning back to its equilibrium spin magnetization. In magnetic resonance we often encounter two types of relaxation. Spin-lattice relaxation, T_1 and spinspin relaxation T_2 . Spin-lattice relaxation is associated with the recovery of spin populations, while spin-spin relaxation is associated with the decay of coherences.

2.6.1 Sources of Relaxation and Spectral Density

Local and environmental magnetic field fluctuations acting on the spin ensemble are the primary sources of relaxation. Often these fluctuations come in the form of dipole-dipole spin interactions or magnetic field inhomogeneities that cause different spins in the ensemble to precess at different frequencies. We can approximately describe the magnitude of some of these fluctuations using a random fluctuating field model. It is a model that is qualitative in nature since it only considers sources of relaxation that are not a part of the spin system. The fluctuating field model describes the magnitude of relaxation inducing field fluctuations using a mean square field, [56]

$$\langle B_x^2(t) \rangle \neq 0, \tag{2.55}$$

and we can describe the frequency of these fluctuations using an autocorrelation function, [56]

$$G(\tau) = \langle B_x(t)B_x(t+\tau) \rangle \neq 0.$$
(2.56)

 $G(\tau)$ can be expressed as $\langle B_x^2 \rangle e^{-\tau/\tau_c}$, where τ_c is the correlation time of the field fluctuation. We can use the correlation function to describe the spectral density of a system, a function that plays a very important role in determining sources of relaxation. The spectral density is often represented as a 'normalized spectral density' and is described as,

$$J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2}.$$
(2.57)

In Eq. 2.57, ω is the frequency of the noise fluctuation and τ_c is the correlation time. In our studies, we are mostly concerned with relaxation effects on coherences. The spectral density is a nice tool to explore these effects. For example, let us consider a spin 1/2 system with kets $|\alpha\rangle$ and $|\beta\rangle$. Suppose that the spin states experience some fluctuating field that places $|\alpha\rangle$ into a new state $|\alpha'\rangle$, and places $|\beta\rangle$ into a new state $|\beta'\rangle$. We can describe the transition probability between these states as,

$$W_{-} = \frac{\overline{\langle \beta | \alpha' \rangle^2}}{\tau},$$

$$W_{+} = \frac{\overline{\langle \alpha | \beta' \rangle^2}}{\tau}.$$
(2.58)

Transitions between $|\alpha\rangle$ and $|\beta\rangle$ will induce relaxation processes. W₋ and W₊ can be expressed in terms of the spectral density,

$$W_{-} = W_{+} = \frac{1}{2}\gamma^{2} \langle B_{x}^{2} \rangle J(\omega^{0}).$$
(2.59)

If $|\alpha\rangle$ and $|\beta\rangle$ are placed in a coherent state the coherence decay will be related to the magnitude of the spectral density at the $|\alpha\rangle \leftrightarrow |\beta\rangle$ transition frequency. Additional discussions on relaxation mechanisms can be found in Ref. [56].

There are many aspects of magnetic resonance that we have not covered here, and for those who would like to read more, we would recommend the following references, [80], [81], [82]. We will now proceed to explore the NV⁻ electron spin system in more detail in the following chapter.

Chapter 3

The Nitrogen-Vacancy Center

3.1 Background

The negatively charged nitrogen-vacancy (NV⁻) centre in diamond has been exploited in optically detected magnetic resonance (ODMR) experiments because of its favorable properties including spin-dependent fluorescence [83], spin coupling to the magnetic environment [84] and its long polarization lifetime as compared with other similar substrates [32], even at room temperature. The electron spin of the NV⁻ center can be highly polarized to the $m_s = 0$ state via optical pumping, [85] and its spin-state-dependent fluorescence intensity allows convenient optical readout of the spin state of the electron spin with high fidelity at room temperature [86]. Because the NV⁻ spin-coherence lifetimes can be as long as milliseconds in an isotopically pure diamond lattice, [87] the system is an ideal platform for experimental quantum information science. Among such devices are precision magnetometers that have applications as industrial sensors, probes of magnetic materials, and as detectors of magnetic resonance.

In the following, we present a review of the optical properties and electronic structure of the NV^- system. We also include the effect of magnetic and electric field perturbations on the spin states of the NV^- as well as the perturbations caused by NV^- spin-bath interactions. A more thorough discussion of the NV^- center's optical and electronic properties can be found in an excellent review by Doherty et al. and also Maze et al. [76,88].

For those that wish to skip the gritty (albeit important) details, we would suggest starting at the "NV⁻ Optical Dynamics" section of this chapter and continuing through the experimental chapter.

3.2 Physical Structure and Formation

The nitrogen-vacancy center is a point defect in diamond that consists of a substitutional nitrogen atom at a carbon lattice site and a vacancy that is adjacent to the nitrogen atom. Surrounding the vacancy are three carbon atoms with dangling bonds that also contribute



Figure 3.1: (a) Nitrogen-Vacancy in Diamond (b)From left to right: clear <1 ppb Nitrogen Diamond, yellow ~100 ppm Nitrogen Diamond, purple ~100 ppm Nitrogen Diamond and ~10 ppm NV centers after electron irradiation and annealing.

to the properties of the NV center. The NV axis is along the [111] direction of the crystal lattice, and has C_{3V} symmetry. NV centers are formed by producing vacancies in diamond using electron or ion irradiation followed by annealing above 800 C°. The nitrogens and vacancies in the diamond lattice then form an energetically favorable complex during the annealing time [89]. Centers can also be formed via nitrogen ion implantation or ambient nitrogen incorporation during the diamond growth process [90].

3.3 Optical Properties

NV centers exist in two known charge states¹, here denoted as NV^- and NV^0 . NV^- has a characteristic zero-phonon line (ZPL) at 637 nm, while the NV^0 has a ZPL at 575 nm. Both forms of the NV center have defined vibronic bands extending from their respective ZPL, associated with NV-phonon coupling. This electron-phonon coupling turns out to play an important role in the spin dynamics of the NV center.

The optical absorption (not shown) and emission spectrum in figure 3.2b, can be explained by modeling the ground state and excited state vibrational wave function as a quantum mechanical oscillator. Using a low temperature approximation, we assume that the lowest vibrational state is preferentially populated and that only electrons in the lowest vibrational state are excited into the electronic excited state vibrational states. As a result, the lowest excitation energy that can be used to excite the NV⁻ or NV⁰ is its ZPL transition

¹Though apparently there is speculation about an NV⁺ charge state [91].



Figure 3.2: (a) Harmonic oscillator model of NV^- vibrational states in ground state and excited state (b) Optical emission spectrum of nitrogen-vacancy center at room temperature, NV^- ZPL at 637 nm, NV^0 ZPL at 575 nm

energy. However, higher energy excitation can be used to excite these centers as long as the excitation energy is within the bandwidth of NV-phonon coupled states. This means that an off-resonance laser can be used for fluorescence spectroscopy of NV^- centers (a practical advantage when setting up experiments). Variations in absorption are seen in the spectrum because the transition probability is proportional to the square of the overlap integral between the ground state vibrational wave function and the vibrational wave function of the excited state, this is in accordance with Franck-Condon rules [92].

Once in the excited state, we can assume that the electrons decay into the lowest vibrational state of the excited state, so we would only expect emission from this state. Emission will place population in any number of different vibrational states in the ground state, where the ZPL is the highest emission energy and the electron-phonon transitions are all lower energy.

Another important optical feature of the NV center, related to the NV optical stability and localized nature of the NV wave function, is that the NV ZPL is exceptionally sharp, meaning that the NV defect levels that are associated with these optical transitions are buried in the diamond band gap, limiting interaction between these defect levels and valence and conduction bands of diamond [93,94]. However, interconversion between NV⁻ and NV⁰ is known to occur, and is thought to be mediated by paramagnetic nitrogen (N_S) in the lattice that has energy levels near the defect levels in the band gap [95].

3.4 Electronic Structure

For the remainder of this discussion on NV centers we will focus on the electronic structure of the NV^- charge state in detail, as the majority of this thesis involves investigations of this charge state. The experiments described in this thesis are all done at room temperature, involve NV ensembles and primarily involve studies of the ground state structure of the NV^- center. However, here we will describe the electronic structure in both the ground state and excited states, as it gives a more complete picture of the interactions that lead to the observed spin dynamics of the NV^- center.

To fully understand the NV structure and dynamics it is quite vital to understand how the orbital and spin parts of the NV^- wave function couple to give the observed eigenstates in the ground state and excited state. Understanding of the orbital part for each electron configuration gives details of how the electron density is distributed among the nitrogen, carbons, and vacancy in the ground state and excited states of the NV^- . This distribution and its coupling to the spin part of the NV^- wave function has important implications with regards to the origin of the hyperfine coupling, the intersystem crossing branching ratios, selection rules, and the re-polarization rates of the NV^- center [88].

3.4.1 Electron Orbitals

The NV⁻ system is a six electron system, with two unpaired electrons, where the three surrounding carbon atoms contribute three electrons, the nitrogen lone pair contributes two and another electron is contributed by the lattice. The atomic orbitals of the NV⁻ center can be labeled as $\{\sigma_1, \sigma_2, \sigma_3 \sigma_N\}$, as depicted in figure 3.3, where the $\sigma's$ represent sp³ hybridized orbitals of the carbon atoms and the σ_N represents the sp³ hybridized nitrogen orbital. The orbital part of the NV⁻ wave function can be determined via projection of the carbon and nitrogen atomic orbitals onto the NV⁻ C_{3V} irreducible representation. We can form linear combinations of these atomic orbitals such that the combinations will transform as the group C_{3v}. The final form and the ordering of these states can then be determined by considering the coulomb interaction energy between the two unpaired electrons, or two holes, within the constructed orbitals [88]. The resulting ordering of orbitals is shown in figure 3.3. The form of the molecular orbitals in the C_{3V} basis is shown below,

$$e_x = \frac{2\sigma_1 + \sigma_2 + \sigma_3}{\sqrt{6}} \qquad e_y = \frac{\sigma_2 - \sigma_3}{\sqrt{2}},$$

$$a_1 = V\sigma_N + V' \frac{\sigma_1 + \sigma_2 + \sigma_3}{3} \qquad a'_1 = V \frac{\sigma_1 + \sigma_2 + \sigma_3}{3} + V' \sigma_N \qquad (1 + 1)$$

where the terms V and V' are related to the Coulomb interaction energy between electrons in different molecular orbitals, the full form and a derivation of these values is shown in Maze's work in ref. [88], where the Coulomb interaction terms are labeled as α and β respectively in the reference's appendix A.



Figure 3.3: (a) Atomic Orbitals, looking down on defect, where $\sigma_{1,2,3}$ is an sp³-orbital from the carbon atom, σ_N is an sp³-orbital from the nitrogen atom (b) NV⁻ ground state configuration - e² and excited state configuration- ae, the a'_1 orbital is not considered to play a role in the dynamics of the NV⁻ center because it lies within the valence band of the lattice [96]. Note that changes in the electron configuration will also change the relative energies of the orbital states, this is not reflected in the diagram.

The molecular orbitals are filled according to the first of Hund's rules, which states that the most stable configuration of a state is one with the highest spin multiplicity. When electrons are distributed in different orbitals electron shielding from the nucleus is reduced, producing a more stable configuration. From this picture we can identify the ground state and excited state configurations (see figure 3.3). The ground state configuration shows that the electron density is largest in the orbitals e_x and e_y , while the excited state configuration has the largest electron density in the orbitals a_1, e_x , and e_y . This has important implications for the relative strengths of the NV⁻-¹⁴N hyperfine coupling between the ground state and excited state. Since the a_1 orbital is in part localized onto the nitrogen atom, while the e_x and e_y orbitals have no overlap with the nitrogen atom, one would expect to see a larger hyperfine coupling term in the excited state; this is indeed observed [97].

3.4.2 Total Wave Function

The total electronic wave function is built by considering both orbital and spin parts and taking appropriate symmetric combinations to give the form shown in tables 3.1 and 3.2. Electronic structures for the excited and ground state triplet are shown in figures 3.5 and 3.4. The symbols A, E, indicate how the particular state transforms in C_{3V} . Note that the ${}^{3}A_{20}, {}^{3}A_{2+}, {}^{3}A_{2-}$ states indicated in the tables are labeled by their spin state $m_{s} = 0$, $m_{s} = +1$ and $m_{s} = -1$ throughout this thesis. Once we know the symmetry of a state we can determine which terms in a given Hamiltonian will affect that state solely on symmetry considerations. This greatly simplifies calculations.

	$ \alpha \rho / - \downarrow /$		
Angular Momentum	Total Wave function	State Label	State Symmetry
	$ e_x e_y - e_y e_x\rangle \otimes \alpha \alpha\rangle$	${}^{3}A_{2+}$	$E_1 + E_2$
L=0, S=1	$ e_x e_y - e_y e_x \rangle \otimes \beta\beta\rangle$	$^{3}A_{2-}$	E1-E2
	$ e_x e_y - e_y e_x\rangle \otimes \alpha\beta + \beta\alpha\rangle$	${}^{3}A_{20}$	A_1
	$ e_x e_x - e_y e_y\rangle \otimes \alpha\beta - \beta\alpha\rangle$	${}^{1}E_{1}$	E_1
L=1, S=0	$ e_x e_y + e_y e_x\rangle \otimes \alpha\beta - \beta\alpha\rangle$	${}^{1}E_{2}$	E2
	$ e_x e_x - e_y e_y\rangle \otimes \alpha\beta - \beta\alpha\rangle$	${}^{1}A_{1}$	A_1

 $|\alpha\beta\rangle = |\uparrow\downarrow\rangle$

Table 3.1: NV⁻ Ground State

$ E_{\pm}\rangle = a_1e_{\pm} - e_{\pm}\rangle, \ e_{\pm} = \mp (e_x \pm ie_y), \ \alpha\beta\rangle = \uparrow\downarrow\rangle$			
Angular Momentum	Total Wave function	State Label	State Symmetry
	$ E_{-}\rangle \otimes \alpha\alpha\rangle - E_{+}\rangle \otimes \beta\beta\rangle$	A_1	A_1
	$ E_{-}\rangle \otimes \alpha\alpha\rangle + E_{+}\rangle \otimes \beta\beta\rangle$	A_2	A_2
L=0, S=1	$ E_{-}\rangle \otimes \beta\beta\rangle - E_{+}\rangle \otimes \alpha\alpha\rangle$	E_1	E_1
	$ E_{-}\rangle \otimes \beta\beta\rangle + E_{+}\rangle \otimes \alpha\alpha\rangle$	E_2	E_2
	$(E_{-}\rangle + E_{+}\rangle)/2 \otimes \alpha\beta + \beta\alpha\rangle$	E_y	E_1
	$(E_{-}\rangle - E_{+}\rangle)/2 \otimes \alpha\beta + \beta\alpha\rangle$	E_x	E_2
	$ a_1e_x + e_xa_1\rangle \otimes \alpha\beta - \beta\alpha\rangle$	$^{1}E_{x}$	E_1
L=1, S=0	$ a_1e_y + e_ya_1\rangle \otimes \alpha\beta - \beta\alpha\rangle$	${}^{1}E_{y}$	E_2

Table 3.2: NV^- Excited State: The orbital averaging mechanism that occurs at higher temperatures enables the ³E orbital doublet to be treated as an effective orbital singlet system, see the Orbital Averaging section.

3.4.3 Spin-Spin and Spin-Orbit Interactions

In this section we will summarize the effects of spin-orbit and spin-spin coupling on the ground and excited states of the NV⁻ center and comment on the relevance of this interaction on the NV⁻ electronic structure. Although derivations of these interactions are outside the scope of this chapter, the interested reader can find them in the following references [88,98].

Spin-Orbit

The spin-orbit interaction has the effect of lifting multiplet degeneracy for non-zero spin states. It also has the effect of mixing spin states through spin-orbit coupling. The degree of mixing is dependent on the strength of the spin-orbit interaction and also the energy separation between the states that are interacting. The spin-orbit Hamiltonian in terms of angular momentum operators is [99],

$$\mathcal{H}_{SO} = L \cdot S = \sum_{i} \lambda_{xy} (l_i^x s_i^x + l_i^y s_i^y) + \lambda_z l_i^z s_i^z, \qquad (3.1)$$

where *i* is the *i*th electron, λ_{xy} is the non-axial and λ_z is the axial strength of the spinorbit interaction, and s_i and l_i are the corresponding spin and orbital angular momentum operators for each electron. The axial spin-orbit interaction has the effect of splitting the ${}^{3}E$ spin triplet into three two fold degenerate states, $\{A_1, A_2\}$, $\{E_x, E_y\}$ and $\{E_1, E_2\}$ states by λ_z and linking the following states: $A_1(ae) \leftrightarrow^1 A_1(e^2)$, $E_{1,2}(ae) \leftrightarrow^1 E_{1,2}(e^2)$, and $E_{x,y}(ae) \leftrightarrow^1 E_{x,y}(ae)$ as seen in figure 3.4. λ_z links states with zero spin projection to states with the same electron configuration and spin-projection, while λ_{xy} links states with non-zero spin projections to singlets in different electron configurations. This can be seen more clearly by looking at the non-axial part of the spin-orbit interaction: $\lambda_{xy}(L_+S_- + L_-S_+)$. This term will only mix states with different electron configurations because of the L_+ and $L_$ operators. How these states are linked, as well as the transition rates involved, is shown in figure 3.6.

The spin-orbit coupling allows non-spin conserving transitions to occur via intersystemcrossing, a property of the point defect that is necessary for the spin-state read out and optical polarization of the NV^- center.

Spin-Spin

The spin-spin interaction is a dipolar coupling between the two unpaired electrons of the NV^- center. The general spin-spin Hamiltonian can be written as,

$$\mathcal{H}_{SS} = -\frac{\mu_0 \gamma_1 \gamma_2 h^2}{16\pi^3} [3(S_1 \cdot \hat{r})(S_2 \cdot \hat{r}) - (S_1 \cdot S_2)], \qquad (3.2)$$

where μ_0 is the vacuum permeability constant, γ is the gyromagnetic ratio of the spin in question, and r is the separation between spins 1 and 2. The spin-spin interaction has the effect of splitting ${}^{3}A_{20}$ and ${}^{3}A_{2\pm}$ ground states by a factor D_{gs} , known as the axial zerofield splitting (ZFS). In the excited state the spin-spin interaction splits the $\{E_x, E_y\}$ and $\{A_1, A_2\}, \{E_1, E_2\}$ manifolds by D_{es} , mixes the following states $\{E_x, E_y\} \leftrightarrow \{E_1, E_2\}$ and splits the $\{A_1, A_2\}$ states by Δ' , see figure 3.4. The form of Δ' and Δ'' is not included here, but can be found in the following references [88, 98].

Orbital Averaging

Up until now, the electronic structure for the NV⁻ has been described for the low temperature case <150 K. At temperatures above 150 K much of the complicated fine structure in the excited state disappears². At higher temperatures, the width of the NV⁻ ZPL line

²Recent evidence has suggested that orbital averaging effects are apparent at temperatures as low as 22 K. The effects come in the form of changes in the intersystem crossing rates of the excited state levels A_1 , E_1 , E_2 [101]



Figure 3.4: NV⁻ Excited state triplet as seen for the low strain, low temperature <150K case. λ_z is the axial spin-orbit term, D_{es} is the excited state axial zero-field splitting term and δ' , δ'' are spin-spin coupling terms. At high strain the E₁, E₂ and E_x, E_y degeneracy is lifted to give two orbital branches [100] (not shown here).



Figure 3.5: NV⁻ Ground state triplet. D_{gs} is the ground state axial zero-field splitting term.

increases from ten's of GHz to thousand's of GHz as optical transitions mix with lattice vibrations of slightly different energies. Because vibrations interact with electronic orbits but not with electron spin, an increase in temperature has the effect of averaging the orbital parts of the wave function [102]. This results in a quenching of the axial spin-orbit interaction λ_z , as well as the Δ' spin-spin term that splits the A_1 and A_2 levels [102]. At cold temperatures the excited state is an orbital doublet and at higher temperatures it can be treated as an orbital singlet. Any splitting due to orbital interactions is averaged out, and so the only term that remains is the D_{es} spin-spin term, which splits the zero spin and non-zero spin states by 1.42 GHz in the excited state as seen in figure 3.6. For the remainder of this chapter, we will only consider the spin dynamics and state perturbations on the NV⁻ at room temperature.

3.5 NV⁻ Optical Dynamics

The ability to optically read the spin-state of the NV⁻ center coupled with the ability to optically pump the NV⁻ center into the $m_s = 0$ spin state makes the NV⁻ defect useful for a number of applications in metrology, nuclear spin polarization and quantum information science. Here we discuss the origin of spin-dependent fluorescence and optical spin polarization of the NV⁻ center.

3.5.1 Inter-System Crossing and Optical Pumping

Rate constant	Value (10^6 s^{-1})
$k_{0\to 0'} = k_{\pm\to\pm'}$	77
$k_{0' \to s} = k_{\pm' \to s}$	30
$k_{0' \rightarrow s}$	0
$k_{s \to 0}$	3.3
$k_{s \to \pm}$	0
$k_{0\to\pm'} = k_{\pm\to0'}$	1.5

Table 3.3: NV⁻ Transition Rates: -,+,0 are the $m_s = -,+,0$ ground states and -',+',0' are excited states, s indicates the singlet state (this includes ${}^{1}A_{1}$ and ${}^{1}E$ structure.)

The NV⁻ center can be optically excited with a beam energy that falls within its vibronic absorption band (~480-640 nm)³. Since the electric dipole operator does not act on spin but rather on the orbital component, the spin state of the NV⁻ will be conserved upon optical excitation [104]. However, once in the excited state, NV⁻ in the $m_s = +1$ or $m_s = -1$ spin state will decay with some probability via a non-radiative pathway to a ground state singlet

 $^{^{3}}$ This allows for a range of illumination sources to be used for NV⁻ fluorescence based magnetometry, providing nice flexibility when setting up experiments



Figure 3.6: The ground state triplet and singlet and also the excited state triplet and singlet manifolds are shown here. Though the exact ordering of ${}^{1}A_{1}$ and ${}^{1}E_{1,2}$ is still a point of contention, we have ordered the states based on symmetry considerations and the observed intersystem crossing decay paths shown here. The high probability of intersystem-crossing between the ${}^{3}E |\pm\rangle$ state and the singlet state seems to suggest that the singlet that is closes in energy to the ${}^{3}E$ manifold is of the same symmetry E. State lifetimes are shown next to the respective state symbol and the values were obtained from Ref. [103]. Transitions relevant to NV⁻ spin dynamics are shown, where the dashed lines indicate weaker transition rates. The transition rates are listed in table 3.3, where $k_{0\to0'}$ indicates the rate for a transition from the $m_s = 0$ ground state to the $m_s = 0$ excited state, and $k_{s\to0}$ indicates the transition rates.

 ${}^{1}A_{1}$ and subsequently into the ground state triplet state ${}^{3}A_{2}$, $m_{s} = 0$, see figure 3.6, [88,104]. Because of this property, NV⁻ exhibits spin-dependent fluorescence and can be optically pumped into the $m_{s} = 0$ spin state, such that 80% of the electron population will be in the $m_{s} = 0$ state after several optical cycles [85].

An inter-system crossing (ISC) occurs because the non-axial part of the spin-orbit interaction links the ${}^{3}E$, $m_{s} = \pm 1$ states to the ${}^{1}E$ singlet state⁴. The spin-orbit interaction mixes singlets and triplets with the same symmetry, suggestive of ${}^{1}E$ as the state that is mixing with the ${}^{3}E$, $m_{s}=\pm 1$ states. In order to flip the electronic spin from the ${}^{3}E$ to ${}^{1}E$ state, phonon emission is required to maintain energy conservation, therefore, the intersystem crossing indicated in figure 3.6 is thought to be mediated by a one-phonon spin-orbit coupling interaction [101]. If this were the only mechanism governing the triplet—singlet pathway one would expect for 100% of NV⁻ to eventually be optically pumped into the m_{s} = 0 state, this is thought to be unobserved because the non-axial spin-orbit coupling weakly mixes the $m_{s} = 0$ and $m_{s}=\pm 1$ states, weakly allowing transitions from the ${}^{3}A_{2}$, $m_{s} = 0$ to ${}^{3}E$, $m_{s}=\pm 1$ states [104].

The optical transition rates and state lifetimes are shown in figure 3.6 and table 3.3. The rates in 3.3 are taken from Ref. [104]. By considering the transition rates listed in this table we can calculate the expected fluorescence emission behavior from an ensemble of NV^- centers. The explicit form of the rate equations is shown in the simulation code in Appendix A.

Within the first few microseconds⁵ of laser irradiation, the $m_s = 0$ spin state of the NV⁻ ensemble becomes preferentially populated and an increase in fluorescence emission is observed. The decay following the increase of emission is due to NV⁻ population being stored in singlet state, this reduces the observed emission. Other causes of emission decay that can be observed over time are due to NV⁻ to NV⁰ photoionization [104].

For the remainder of this chapter we will only consider the ODMR of the NV⁻ ground state.

3.6 ODMR of NV⁻ Ensemble

The spin-state of an NV⁻ center is correlated with its optical emission. Changes in the spin state distribution of an ensemble of NV⁻ centers will result in changes in the fluorescence intensity. Since the selection rules for magnetic dipole transitions are $\Delta m_s = \pm 1$, $\Delta m_I = 0$, the $m_s = 0$ to $m_s = +1$ or $m_s = -1$ transition can be driven by a microwave field perpendicular to NV⁻ axis. When NV⁻ population cycles into the $m_s = \pm 1$ states, some of the NV⁻ centers cycle through the inter-system crossing, and so a decrease in emission is observed as seen in figure 3.8. When a small magnetic field is applied along the NV⁻ axis the $m_s = \pm 1$ levels split by $\gamma_e B_z m_s$, where γ_e is the electron gyromagnetic ratio, equal to 1.761×10^{11}

⁴As mentioned previously, the ordering of the singlets is still a point of contention as spin-decay rates and symmetry considerations contradict the calculated ordering of these levels [88]

⁵The polarization time is dependent on the laser pump intensity.



Figure 3.7: The fluorescence emission from the NV⁻ during a 532 nm optical pulse changes over time. The initial rise in the fluorescence emission is due to an increase in the electron spin population in the $m_s = 0$ state. The subsequent decrease in emission is due to electron spin population being stored in the metastable singlet state.

 $s^{-1}T^{-1}$ and B_z is the strength of the magnetic field applied along the NV⁻ axis. Most fluorescence based magnetometry to date is based on applying microwaves and reading out the changes in the emission of the NV⁻ center as an indicator of local magnetic field, using either pulsed or continuous wave ODMR methods [41, 105, 106]⁶. The NV⁻ Hamiltonian is given approximately as,

$$\mathcal{H}_{NV^{-}} = D_{gs}S_z^2 + E_{gs}(S_x^2 - S_y^2) + \gamma_e \mathbf{B} \cdot \mathbf{S}, \qquad (3.3)$$

where the axial ($D_{gs} \sim 2.87 \text{ GHz}$) and transverse (E_{gs} , ~ 2 to ~ 5 MHz for most diamond samples in this thesis)⁷ zero-field splitting (ZFS) parameters can be determined from the spectra at ambient magnetic field, **S** is the electron spin of the NV⁻ centre with the electron gyromagnetic ratio of γ_e , **B** is the external magnetic field aligned along one of the NV⁻ symmetry axes, and z is defined along the direction of the NV⁻ axis. The hyperfine interaction with nuclear spins in the diamond lattice (¹⁴N/¹⁵N and ¹³C) is much smaller than the axial ZFS, and so these terms are not included in this Hamiltonian. Though these interactions are small, they can affect the NV⁻ ODMR spectra in noticeable ways. We will discuss these interactions and their effects on the ODMR spectra in the 'Diamond Spin Bath' section of this chapter.

The NV⁻ ODMR spectrum is obtained by sweeping the applied microwave frequency under continuous laser irradiation, as shown in figure 3.12. At earth's field, figure 3.12, the crystal strain term in the NV⁻ Hamiltonian splits the $m_s=+1$ and $m_s=-1$ resonances by 2E, and has the effect of mixing these two states. As mentioned previously, a magnetic field applied along the NV⁻ axis will split the $m_s=+1$ and $m_s=-1$ states by γ_e B_z m_s. In the case of an ensemble measurement, 8 NV⁻ resonances are observed, as seen in figure 3.8 corresponding to the $m_s=0 \leftrightarrow m_s=-1$ and $m_s=0 \leftrightarrow m_s=+1$ transitions for each NV⁻ orientation, with D_{gs} = 2.87 GHz, and a magnetic field applied of ~ 50 G. Additional features due to the hyperfine interaction terms are obscured due to microwave power broadening.

A noticeable feature of figure 3.8 is that the decrease in the emission due to resonant microwaves is different for two pairs of orientations. This can be explained as follows: When working with an ensemble of NV⁻ centers, the fluorescence collected includes fluorescence emitted from the four NV⁻ orientations found in the diamond lattice. The fluorescence emission from each center will vary depending on the incoming light polarization [83], since the maximum light absorption occurs when the optical electric dipole moment is along the axis of the NV⁻ center. The effect that the incoming light polarization has on the ODMR spectrum is shown in figure 3.9. In addition, because the strength of the driving frequency supplied by the microwaves is dependent on the direction of the microwave B_1 field with respect to the NV⁻ center, not all four orientations will experience the same microwave field strength. Therefore, the contrast at resonance is dependent on the NV⁻ orientation relative to the laser polarization and B_1 direction.

⁶Magnetometry based on absorption at 1042 nm is also used, in which the change in NV^- spin distribution is readout by measuring the trapped NV^- population in the singlet state. This technique is less susceptible to ambient temperature fluctuations that may reduce the sensitivity of the magnetometer. [107]

⁷The transverse ZFS is a crystal strain splitting particular to each diamond sample



Figure 3.8: Optically detected magnetic resonance spectra of an ensemble of NV⁻ centers at a magnetic field strength of ≈ 50 G. 8 resonances are observed, corresponding to the m_s $= 0 \leftrightarrow m_s = \pm 1$ transitions of NV⁻ centers experiencing different projections of the applied magnetic field due to their fixed orientation in the diamond lattice.



Figure 3.9: Effects of incoming light polarization on NV⁻ ODMR spectrum.

Additional features that are often present in an NV⁻ ensemble ODMR spectrum, but are not shown in figure 3.8, include ODMR resonances belonging to NV⁻ centers that are coupled to a neighboring ¹³C or N_S center (also known as P1 center) [108]. Examples and interpretation of ODMR spectra showing some of these features are found in the 'Diamond Spin-Bath' section of this chapter, see figure 3.12.

We will now explore the effect of external perturbations on the NV⁻ center ODMR spectrum.

3.6.1 Electric Field Effects

For simplicity we will consider only the electron spin part of the NV⁻ Hamiltonian, with an applied axial field B_z ,

$$H_{NV} = (D_{gs} + d_{gs}^{\parallel} \varepsilon_z) S_z^2 + (E_{gs} + d_{gs}^{\perp} \varepsilon_x) (S_x^2 - S_y^2) + \gamma_e B_z,$$
(3.4)

where d_{gs}^{\perp} and d_{gs}^{\parallel} are the electric field-NV⁻ coupling constants listed in table 3.5 and ε_x and ε_z are electric fields along x and z, where z is defined by the NV⁻ axis.

The matrix form of the Hamiltonian in equation 3.4 can be written in the $m_s = 0, +1,$



Figure 3.10: A static magnetic field aligned 54.5 degrees with respect to all 4 of the possible NV⁻ axes will produce the ODMR spectrum shown in blue. For this case, the $m_s = \pm 1$ states of the 4 NV⁻ orientations are degenerate. A static magnetic field aligned along the NV⁻ axis produces the ODMR spectrum shown in green. Where the outermost peak corresponds to one NV⁻ orientation and the innermost peak corresponds to 3 NV⁻ orientations.

-1 basis as,

$$H_{NV} = \begin{pmatrix} D_{gs} + d_{gs}^{\parallel}\varepsilon_z + B_z & 0 & 2d_{gs}^{\perp}\varepsilon_x \\ 0 & 0 & 0 \\ 2d_{gs}^{\perp}\varepsilon_x & 0 & D_{gs} + d_{gs}^{\parallel}\varepsilon_z + B_z \end{pmatrix},$$

where we see that the axial electric field has the effect of changing the energy separation between $|0\rangle$ and $|\pm 1\rangle$ eigenstates by $\pm d_{gs}^{\parallel}\varepsilon_z$, and the transverse electric field acts much like the crystal field strain, it mixes the $|+1\rangle$ and $|-1\rangle$ states and separates them by $\pm \frac{(d_{gs}^{\perp}\varepsilon_x)^2}{(\gamma_e B_z)}$. In the ODMR spectrum we would observe a shift in the center frequency of the spectrum and an additional energy splitting between the $|0\rangle \leftrightarrow |-1\rangle$ and $|0\rangle \leftrightarrow |+1\rangle$ resonances.

3.6.2 Temperature Effects

In addition to the orbital averaging effects already mentioned, changes in temperature affect the zero-field splitting D_{gs} by a factor dD/dT = -78.6 kHz/K related to the crystal lattice expansion [109], [110],

$$\frac{1}{D}\frac{dD}{dT} \approx \frac{1}{D}\frac{d\langle (r_{12}^2 - 3z_{12}^2)/r_{12}^5 \rangle}{dR}\frac{dR}{dT},$$
(3.5)

where r_{12} is the displacement between two spins, z_{12} is the r_{12} component along NV⁻ symmetry axis and R is the separation distance between carbon nuclei in diamond. The change in the spin-spin coupling constant D_{gs} with respect to temperature has been the basis for a number of thermometry applications [110, 111], where the temperature sensitivity using single NV⁻ defects has been reported to be 5 mK/ \sqrt{Hz} for low frequency temperature fluctuations <1 Hz.

3.6.3 Pressure Effects

Strain transforms the same way in C_{3V} as an electric field does and so has similar effects on the NV⁻ electronic structure. An increase in the pressure will result in linear shifts of the center frequency of the ODMR spectrum, with dD(P)/dT = 14.58 MHz/GPa [112] related to the increased localization of the NV⁻ molecular orbitals and a change in the electron spin density about the vacancy site. This effect was modeled by Doherty et al. in reference [112]. Pressure shifts the center of the ODMR spectrum to higher frequency and also has the effect of blue shifting the ZPL line of the NV⁻. Above 60 GPa the NV⁻ center can no longer be optically excited using 532 nm light.

3.7 Diamond Spin-Bath

There are a number of electron and nuclear spins in the diamond lattice that can interact with the NV⁻ center and influence the observed ODMR spectrum and NV⁻ spin dynamics.

Description	Symbol	Value	Reference
Axial SO	λ_z	5.5 GHz	[88]
Transverse SO	λ_{xy}	7.3 GHz	[88]
Axial ZFS	D_{es}	1.42 GHz	
Transverse ε -Field	d_{es}^{\perp}	$600 \text{ kHz} (\text{V/cm})^{-1}$	[100]
Transverse Strain	$ ilde{d}_{es}^{\perp}=d_{es}^{\perp}/g_{\parallel,\perp}$	$2.5 \times 10^3 \text{ THz/unit-strain}$	[113]
Piezoelectric Constant	$g_{\parallel,\perp} = \partial \epsilon_{\parallel,\perp} / \partial E_{\parallel,\perp}$	$2.4 \times 10^{-10} (V/cm)^{-1}$ ·unit-strain	[88, 113]

Table 3.4: **NV⁻ Coupling Constants for the Excited State** - The spin-orbit values are calculated values, as well as the piezoelectric constant. Note that ϵ is a given strain component, ε is electric field applied.

Here we discuss the NV⁻ interaction with the $^{14}\rm N$ spin, $^{13}\rm C$ spin, as well as with the of $\rm N_S$ and $\rm NV^0$ centers.

3.7.1 ¹⁴N

The terms in the NV Hamiltonian that pertain to the ¹⁴N nucleus are,

$$H = \mathbf{S} \cdot A \cdot \mathbf{I} + Q \cdot \left[(I_z)^2 - (\mathbf{I})^2 / 3 \right] + \gamma_{^{14}N} \mathbf{B} \cdot \mathbf{I}, \qquad (3.6)$$

where I is the ¹⁴N nuclear spin, $\gamma_{^{14}N}$ is the ¹⁴N nucleus gyromagnetic ratio, A is the hyperfine tensor, and Q is the quadrupolar term. The axial part of hyperfine coupling can be resolved in an NV⁻ ODMR spectrum, as shown in figure 3.11. Since the ZFS is so large, the nonaxial part of the hyperfine coupling is truncated. Precise values for the ¹⁴N hyperfine were determined in reference [77] via EPR measurements. Felton et al. found the following form for the ¹⁴N hyperfine tensor, shown here in units of MHz,

$$A = \begin{pmatrix} 2.3 & 0 & 0\\ 0 & 2.3 & 0\\ 0 & 0 & 2.1 \end{pmatrix}.$$

The axial quadrupolar term was also determined in [77], with a value of -5.01(6) MHz.

In addition to affecting the ODMR spectra, hints of $NV^{-.14}N$ coupling can be observed in NV^{-} Electron Spin Echo Envelope Modulation (ESEEM) measurements. The quadrupolar coupling is manifest as a modulation on top of the coherence decay curve, for an explicit case where a magnetic field transverse to the NV^{-} quantization axis is applied. A more thorough explanation is presented in chapter 5.



Figure 3.11: The hyperfine interaction between the NV^- electron spin and ¹⁴N nuclear spin is observed in the ODMR spectrum of an NV^- ensemble. The resonance shown here is for the case where a static magnetic field is aligned along one of the NV^- orientations in the ensemble.

Description	Label	Coupling	Reference
Axial ZFS	D_{gs}	2.87 GHz	[109]
Transverse ZFS	E	$\sim MHz$	[44]
Axial ε -Field	d_{gs}^{\parallel}	$0.35 \text{ Hz } (\text{V/cm})^{-1}$	[113]
Transverse ε -Field	d_{gs}^{\perp}	$17 \text{ Hz} (\text{V/cm})^{-1}$	[113]
Axial Strain	$\widetilde{d}_{gs}^{\parallel}$	5.46 GHz/unit-strain	[113]
Transverse Strain	$\widetilde{d}_{gs}^{\perp}$	19.63 GHz/unit-strain	[113]
Piezoelectric Constant	$g_{\parallel,\perp} = \partial \epsilon_{\parallel,\perp} / \partial E_{\parallel,\perp}$	$2.4 \times 10^{-10} (V/cm)^{-1}$ ·unit-strain	[88, 113]
Temperature on ZFS	dD(T)/dT	-78.6 kHz/K	[110]
Axial Pressure on ZFS	dD(P)/dT	14.58 MHz/GPa	[112]

Table 3.5: **NV⁻ Coupling Constants for the Ground State** - Unlike for the excited state constants table, here the axial and transverse strain coupling constants were experimentally measured.

3.7.2 ¹³C

The NV⁻ center couples to the ¹³C nuclear spins through the hyperfine interaction, where the interaction scales with the proximity of the 13 C nucleus to the NV⁻ center. 1.1% of carbon nuclei in the diamond lattice are ¹³C spin active nuclei that can interact with the electron spin of the NV⁻ center. 1.1% corresponds to $\sim 10^4$ ppm 13 C concentration. This means that >96% of the NV⁻ centres do not have a direct ¹³C neighbor, that is, a ¹³C within the first shell. Most often only the ¹³C in the first shell is considered, as the hyperfine splitting due to the nearest neighbor 13 C can be easily seen to be ~ 130 MHz in the ODMR spectra shown in figure 3.12. A table that includes the ground state hyperfine coupling for numerous shells can be found in the following references: [96, 114, 115]. We have reproduced a similar table with the hyperfine values from Ref. [115]. Dreau et al. measured 400 single NV⁻ defects and recorded the observed ¹³C hyperfine splittings in the ODMR spectra. Note that the capital letters A-O in table 3.6 make reference to ¹³C lattice positions with respect to the NV⁻ center. Ref. [114] shows the diamond structure and ¹³C lattice positions labeled A-O. The 130 MHz hyperfine term is not included in table 3.6. The first column in 3.6 indicates the lattice site in which the relevant ${}^{13}C$ resides. Column 2 indicates the measured ${}^{13}C$ hyperfine interaction at 20 Gauss where $A_C^{20} = \sqrt{A_{xz}^2 + A_{yz}^2 + A_{zz}^2}$. Column 3 indicates the ¹³C hyperfine interaction at 510 Gauss where $A_C^{510} = \sqrt{A_{xz}^2 + A_{yz}^2 + (A_{zz} - \gamma_{14}_N B)^2 + \gamma_{14}_N B}$. The last column indicates the polarization estimate for nuclear spins at a particular lattice site when at the excited state level crossing, 510 G, where the parentheses indicates the standard deviation from the mean. Details about the polarization measurement can be found in Ref. [115]. And a full discussion on the hyperfine interactions can be found in Ref. [115].

¹³ C Label	A_C^{20} [MHz]	$A_C^{510}[MHz]$	P [%]
А	13.78	13.69	52 (20)
В	12.8	12.73	53(13)
С	-9.0	-8.9	-56(8)
D	-6.6	-6.55	-65 (10)
E, F	4.12	4.21	43(6)
G	2.55	2.54	34(6)
Η	2.09	2.15	54(4)
Ι	1.13	1.20	0(1)
J	-1.03	-0.99	-3(1)
Κ	0.95	0.92	60(8)
L	0.85	0.86	1(1)
Μ	-0.70	-0.69	-4(4)
Ν	0.56	0.52	2(4)
0	0.43	0.40	13(7)

Table 3.6: $^{13}\mathrm{C}$ hyperfine interaction for a magnetic field aligned along NV^– axis at 20 G and 510 G.

The NV⁻¹³C Hyperfine Hamiltonian is,

$$H_{HF} = \mathbf{S} \cdot A'' \cdot \mathbf{K} + \gamma_{^{13}C} \mathbf{B} \cdot \mathbf{K}, \qquad (3.7)$$

where K is the ¹³C nuclear spin⁸ (K=1/2), $\gamma_{^{13}C}$ is the ¹³C nucleus gyromagnetic ratio and A" is the hyperfine tensor of a ¹³C in the first NV⁻ shell. The hyperfine tensor, in units of MHz, is expressed as

	(123)	0	$0 \rangle$	
A'' =	0	123	0	.
	0	0	205/	

Note that since the ¹³C does not lie along the same axis as the NV⁻, if one were to calculate the eigenstates of the NV⁻ Hamiltonian the hyperfine tensor shown above would require a coordinate transformation on the ¹³C to match the NV⁻ coordinate system, where the NV⁻ axis is the z-axis. The transformation one uses will of course depend on which carbon shell the ¹³C is in with respect to the NV system. For the first shell, from [108], the separation between the two ¹³C related resonances should be separated from the main NV⁻ m_s = 0 \leftrightarrow m_s = ± 1 transition by -56.9(1) MHz and 127.6(2) MHz, where the asymmetry about the main NV⁻ resonance is due to the anisotropic terms of the hyperfine interaction.

In addition, signatures of the 13 C hyperfine interaction can be observed in the ODMR coherence decay of the NV⁻ center, as seen in figure 3.13. The frequency of the NV⁻

⁸For chapter 8 of this thesis the ¹³C nuclear spin is labeled as I and not K as it is indicated here.



Figure 3.12: The ODMR spectrum shows the hyperfine interaction between the NV⁻ electron spin and the nuclear spin of ¹³C found in the first shell. The ODMR resonances on either side of the main NV⁻ peaks are the NV⁻ resonances for NV⁻ centers that are coupled to ¹³C nuclear spins in the first shell.



Figure 3.13: Electron spin echo envelope modulation experiment for an NV⁻ ensemble with less than 1 ppb of NV⁻ centers. The echo train observed is due to the strong dependence of the ¹³C nuclear spin state on the electron spin state. The frequency of the modulation is the Larmor precession frequency of the ¹³C nuclear spins.

coherence revival in figure 3.13 is that of the Larmor precession frequency of the ¹³C nuclei.⁹ The hyperfine interaction leads to an electron spin dependent magnetic field acting on the ¹³C nucleus. Thus, when the electron spin magnetization is inverted during a spin-echo sequence, neighboring ¹³C nuclei will suddenly experience an equal and opposite field from the electron spin, this leads to an effect that mimics that of a radio frequency π pulse acting on the ¹³C nuclei.

Another interesting feature of the coupling between the NV⁻ center and ¹³C nuclei is that this coupling can be exploited to transfer polarization between the NV⁻ electron spin system to the ¹³C nuclear spin [58, 116, 117]. This is of particular interest to the quantum information and NMR scientific communities. We discuss one of these methods in Chapter 8 of this thesis.

3.7.3 The N_S Center

For I-b diamonds with a high concentration of nitrogen ~ 100 ppm, the nitrogen N_S center is the primary defect. It is an uncharged neutral nitrogen defect in diamond¹⁰ that

 $^{^9{\}rm This}$ effect is only observed in diamond NV⁻ samples in which $^{13}{\rm C}$ nuclei provide the primary NV⁻ decoherence mechanism.

 $^{^{10}\}mathrm{Also}$ known as the P1 center

forms when substitutional nitrogen displaces a single carbon in the diamond lattice. Like the NV⁻ centre, it also has four possible orientations due to the static Jahn-Teller distortion from T_d to C_{3v} symmetry [118].

In the spin-1/2 electronic ground state, the Hamiltonian of the N_S centre is given by [119–121],

$$H_{N_s} = \gamma_e \mathbf{B} \cdot \mathbf{S}' + \mathbf{S}' \cdot \mathbf{A}' \cdot \mathbf{I}' - \gamma_{^14N} \mathbf{B} \cdot \mathbf{I}' + Q' \cdot [(I'_z)^2 - (\mathbf{I}')^2/3], \qquad (3.8)$$

where **S**' is the electron spin of the N_S centre (S' = 1/2), **I**' is the ¹⁴N nuclear spin (I' = 1) with the nuclear gyromagnetic ratio γ_{14_N} , **A**' is the hyperfine interaction tensor, given by its axial ($A'_{\parallel} = 113.982$ MHz) and transverse ($A'_{\perp} = 81.345$ MHz) components, and Q' = -3.971 MHz is the quadrupole coupling parameter. Here only the ¹⁴N isotope is considered because the natural abundances of ¹⁴N and ¹⁵N are 99.634% and 0.366%, respectively.

The N_S center can perturb the ODMR spectrum of the NV⁻ center in a number of interesting ways. In Ref. [108], Simanovskaia et al. observed side resonances that were displaced from the unperturbed NV^{-} resonance by an amount corresponding to energies of transitions within the N_S center. The appearance of these resonances can be understood by considering the magnetic dipole-dipole interaction between NV^- and N_S centers. This interaction mixes the NV^- - N_S eigenstates and leads to simultaneous electron spin flips, which then leads to the observed shifts in the NV⁻ resonance. At earth's field, the N_S states are two-fold degenerate and separated by {18.4, 130.2, 148.2} MHz [42], as seen in Ref. [108]. This leads to sidebands in the ODMR spectrum that are separated by $\{36.8, 260.4, 296.4\}$ MHz. The separation in the N_S values mentioned above were calculated using the spin Hamiltonian in Eq. 3.8. Measurements performed in Ref. [108] determined the sidebands to be separated by $\{36\pm 2, 258\pm 2, 296\pm 2\}$ MHz, which is in agreement with our calculated values. In this thesis, we present a related observation where the hyperfine structure of the N_S center can be determined via observation of the NV⁻ ODMR spectrum at RF frequencies, this is explored in chapter 7. RF applied at the N_S transition frequencies induces N_S spin flips which indirectly interact with the NV⁻ center via cross-relaxation effects.

In addition to affecting the ODMR spectrum of the NV⁻ center, the N_S center can also dramatically affect the coherence lifetime of the NV⁻ center. Due to a high spinflip probability at low magnetic fields, the N_S ensemble in the diamond lattice produces a fluctuating magnetic field that can perturb the NV⁻ center coherence. As the magnetic field is increased, however, this spin-flip probability decreases (since the mixing of states goes as the square of the energy separation between the states). This leads to a prolonged coherence time of the NV⁻ center [84]. The change in the coherence lifetime of the NV⁻ center in the presence of an electron dominated spin-bath is further explored in chapter 5.

3.7.4 The NV^0 centre

The electronic structure of the NV⁰ centre is less well-understood than that of the NV⁻ or N_S centers. The proposed spin-1/2 ²E ground state has not been observed by EPR, probably because it is either obscured by other paramagnetic defects or broadened by the dynamic

Jahn-Teller distortion [122]. A recent optically excited EPR experiment has assigned the observed transitions of a trigonal nitrogen-containing defect in diamond to the spin-3/2 $^{4}A_{2}$ excited state of the NV⁰ centre, which should have relatively low energy and a long lifetime. The Hamiltonian of the NV^0 centre is given by [122-124],

$$H_{NV^{0}} = D^{0} \cdot (S_{z}^{0})^{2} + \gamma_{e} \mathbf{B} \cdot \mathbf{S}^{0} + \mathbf{S}^{0} \cdot \mathbf{A}^{0} \cdot \mathbf{I}^{0} - \gamma_{14_{N}} \mathbf{B} \cdot \mathbf{I}^{0} + Q^{0} \cdot [(I_{z}^{0})^{2} - (\mathbf{I}^{0})^{2}/3], \quad (3.9)$$

where D^0 is the axial zero-field splitting parameter with the value determined as $D^0 \approx$ 1685(5) MHz, S⁰ is the electron spin of the NV⁰ centre (S⁰ = 3/2), I⁰ is the ¹⁴N nuclear spin $(I^0 = 1)$ of the NV⁰ centre, A^0 is the hyperfine interaction tensor given by its axial $(A^0_{\parallel} =$ -35.7 MHz) and transverse ($A^0_{\perp} = -23.8$ MHz) components [122], and $Q^0 = -4.654$ MHz is the quadrupole coupling parameter [124]. The spin Hamiltonian parameters were determined using >95% ¹⁵N enriched NV⁰ and are used here with reasonably good approximation [122].

The effects of the NV⁰ center on the ODMR spectrum are often seen in the form of a decrease in NV⁻ ODMR contrast. Since the NV⁰ also fluoresces, it can contribute to unwanted background fluorescence in the ODMR signal. This background can be reduced by using a long-pass or band-pass filter that excludes the NV⁰ ZPL and phonon band. In addition, NV⁻ centers can often be ionized into the NV⁰ charge state during ODMR experiments, though certain steps can be taken to optimize the NV⁻ steady state population. Aslam et al. found recently that the steady state population of NV⁻ is always $\leq 75\%$ under continuous laser irradiation in the 450-610 nm band. They also found that the largest NV^{-} steady state population occurs under laser irradiation in the 510-540 nm band, with the lowest steady state population occurring at 593 nm laser irradiation. These measurements have important implications about the NV⁻ absorption cross-section as a function of wavelength, in fact, Aslam et al. note that the saturation intensity for the NV^- center is not inversely proportional to the NV⁻ absorption cross-section as one would expect. Instead, the saturation intensity is dependent on the NV⁰ saturation intensities and absorption cross sections as well, leading to a new expression for the NV⁻ saturation intensity shown in the paper's appendix A [125].

In chapter 7, we shed additional light onto the nature of the NV^0 defect. We obtain detailed information about the hyperfine structure NV^0 by exploiting cross-relaxation effects between the NV⁰ center and the NV⁻ that change the NV⁻ ODMR spectrum at RF frequencies.

As the reader can observe, the NV⁻ center in diamond is a system rich with interesting spin physics, and we hope that this introduction has provided the reader with sufficient background to understand the nature of the NV⁻ experiments that will be discussed in this thesis.

Chapter 4

Experimental

In this chapter we will start with descriptions of the hardware and software used to run experiments. We will then discuss how continuous and pulsed ODMR experiments are done. As there were two different setups used for the experiments described in the pages that follow, we will distinguish the two as NV-1 and NV-2. The experiments discussed in chapters 7 and 8 were performed on the NV-2 setup, while the experiments discussed in chapters 5, 6, 9 and 10 were performed on the NV-1 setup.

4.1 NV-1 Overview

The NV-1 setup is configured for continuous wave and pulsed ODMR measurements of nitrogen-vacancy centers. Accurate and precise magnetic field control, phase control and pulse timing is important for proper experimental implementation and detection. The full optical configuration is shown in figure 4.1.

4.1.1 Optical Components

A 532±2 nm optically pumped semiconductor laser (Coherent Verdi G5) with a beam waist of 2.25 mm is passed through an optical isolator (Newport Faraday Isolator - ND4-532). The optical isolator consists of a strong, confined ~ 1 Tesla axial field that rotates the input polarization of the beam by 45 degrees via the Faraday effect [126]. Any back reflections are then rejected by the input polarizer. This prevents back reflections from re-entering the laser head and potentially damaging the laser. The beam then passes through a series of lenses that adjust the beam size to ~ 250 μ m before entering the acoustic optic modulator (AOM) shown in figure 4.1. The AOM (Isomet 1201E-1) is on a rotation mount and is attached to an RF driver (Isomet 521C-2) that is switched on and off via a transistor-transistor logic (TTL) pulse provided by the timing control pulse blaster board (Spin Core Inc. 400 MHz PB), see figure 4.7. When the RF driver is switched on, an acoustic wave propagates through dense flint glass within the AOM and changes the index of refraction of the glass, this produces 0th, 1st and higher order diffraction modes. The 1st order mode is used for beam alignment



Figure 4.1: NV-1 Spectrometer : Optical setup

since it can be turned on and off with the RF driver and TTL pulses. Because it takes time for the acoustic wave to propagate through the flint glass, the rise time of the laser pulse from the AOM is dependent on the incoming beam size as well as the incoming beam direction. A beam size of ~ 250 μ m should give a laser pulse rise time of ~ 46 ns.

A beam splitter that follows the AOM in figure 4.1 sends a beam to another NV setup that will not be described here. A 532 nm notch filter removes any pump beam used in the semiconductor laser pumping process. The beam then passes through a half wave plate, that has the effect of rotating the polarization vector of the incoming light. A wave plate is constructed out of bifringent material, such that the index of refraction of light varies depending on the direction of its polarization vector. A wave plate has two perpendicular axes: a fast axis and a slow axis. The index of refraction is lower along the fast axis compared to the slow axis. This results in a phase difference between components of light traveling along the fast axis or slow axis, and subsequently this produces a change in the polarization vector. The laser beam that we use exits the laser head linearly polarized perpendicular to light propagation axis, when it encounters the wave plate the light's polarization vector will be rotated by 2θ , where θ is the angle between the incoming light's polarization vector and the fast axis of the wave plate. Beam splitter B, as indicated in figure 4.1, then splits the beam in preparation for setting up a gradiometer configuration. A series of mirrors well separate the two beams leading up to the microscope objective. Iris 1 and Iris 2 isolate either one of the two incoming beams in case only a single beam is desired.

Before entering the microscope objective, the beam is expanded to match the size of the input aperture, this way the full numerical aperture of the objective can be used. The microscope objective (Nikon, 0.4, ELWD) has a numerical aperture of 0.4 N.A., and magnification of 20x with a working distance of 11 mm. The objective focuses the two beams onto the diamond plane, with the two beams separated by only ~ 300 μ m and with a spot size of ~ 1 μ m. The diffraction limited spot size is,

$$d = 1.22\lambda [(\frac{n_0}{N.A.})^2 - 1]^{1/2}, \tag{4.1}$$

where n_0 is index of diffraction of the medium (for air $n_0 = 1.000293$), N.A. is the numerical aperture of the objective and λ is the wavelength of the diffracted light. From this we find that for 532 nm light going through our microscope, we get a diffraction limited spot size of 1.48 μ m. The NV⁻ fluorescence is collected back through the microscope objective and passes through a dichroic mirror and through a low pass filter (Semrock 633RS-2S) with a cut off at 633 nm to prevent any green excitation light from getting to the detector. The fluorescence is then focused onto two nearly identical avalanche photo diodes (APD 110A) and the output voltage is sent to either the data acquisition (DAQ) card or lock-in amplifier, see section 4.1.5, for processing.

4.1.2 Microwave Components

Microwaves from a frequency synthesizer (HP8664A, HP8673C) are sent through a phase shifter (Waveline Inc. DPS 1150), an amplifier (Minicircuits ZX60-33LN-S+) and a mi-



Figure 4.2: AOM and RF Driver



Figure 4.3: Phase Shifter Box

crowave switch (CMC S0947a-C2). The phase shifter has 1.4° resolution and a maximum phase shift of 358.6°. To set the microwave pulse phase, the phase shifter has eight input channels that are connected via a 100-150 Ω ribbon cable to the pulse blaster as indicated in figure 4.3. Channels 13-20 of the pulse blaster (see section 4.1.4) are used to set the desired microwave pulse phase. Because the insertion loss due to the phase shifter is 8 dB, a low noise amplifier is placed before the phase shifter and the microwave switch. The microwave switch has a <2 ns switching time and is switched on and off with a TTL pulse from the pulse blaster. Following the microwave switch, microwaves pass through a 16 W amplifier (Minicircuits ZHL-16W-43-S+) to a microwave stripline on a printed circuit board with a 1.5mm diameter copper loop, as shown in figure 4.4. The diamond sample rests above the loop and is optically irradiated through a hole drilled into the microwave board. The circuit is terminated using a 50 Ω connector. The microwave stripline was designed to minimize back reflections at a broad range of microwave frequencies. Its properties were checked using a vector network analyzer (HP8713C), and it was found that the reflected power was minimal. It should also be noted that all microwave connections were made with rigid and semi-rigid coaxial cables equipped with SMA connectors.

The microwave stripline was fabricated using photolithography and copper etching pro-


Figure 4.4: Microwave Board

cedures. First, a thermoset microwave material laminate (Roger Corp. TMM10i), was obtained. The laminate is 0.381 mm thick and has a 17 μ m thick copper layer that has been electrodeposited on both sides. The copper coated laminate was then cleaned with acetone, isopropanol and distilled water. The laminate was then dried using nitrogen gas. One side of the laminate was then coated with a positive photoresist (S1818) using a spin coater. The laminate was placed on the spin coater and a small amount of S1818 was poured on the center of the laminate. The spin coater was run at a speed of 500 rpm, with an acceleration of 100 rpm/s for 10 seconds. This was followed by a 30 second run at 2500 rpm with an acceleration of 300 rpm/s. This procedure produced a nice even coating of S1818 on the copper laminate. The laminate was then heated on a hot plate at ~ 120°C for approximately 30 seconds. This 'pre-baking' procedure was done to drive off any excess solvent left over from the photoresist solution.

A photolithography mask containing the microwave stripline design was placed in a photolithography aligner¹. UV light is shined through the mask onto the S1818 coated laminate. The laminate was exposed to a UV lamp with an intensity of 18.4 mW/cm² for 6.6 seconds. The laminate was then heated on a hot plate again at ~ 120°C for approximately 1 minute

¹Masks used were designed using AutoCad and designs were sent to a printing company for high resolution mask printing.

and 30 seconds. In this case, this 'post-exposure-baking' is done to smooth any spatially periodic patterns in the formation of the carbonic acid which can occur due to standing waves present during UV exposure. This post-exposure-baking becomes more critical when the features on the mask are separated by less than a few microns, something that we actually don't run into here. The coated laminate was then placed in a 1:1 solution of Microposit developer concentrate (Microdev) and distilled water for 1 minute and 30 seconds. When positive photoresist is exposed to UV light diazonaphthaquinone (DQ) in the resist undergoes a photo reaction that produces indene carboxylic acid. The carboxylic acid is soluble in aqueous solutions, while the DQ is not.

The laminate is then thoroughly washed with distilled water to remove any residual carboxylic acid. The uncoated side of the laminate is then covered in tape (3M Scotchcal 220 68701) to prevent scratching or etching of the copper layer that is to serve as the microwave ground plane. The laminate is then placed in a bath of ferric chloride for ~ 30 minutes. The ferric chloride etches away any exposed copper that is not covered with the positive photoresist and leaves a copper trace with the microwave stripline design. The laminate is then rinsed thoroughly to remove any remaining copper particulates and cut into separate stripline boards using a diamond or aluminum bandsaw. A hole is drilled through the center of the copper loop for the purpose of optical illumination and SMA connectors are then soldered onto either end of the boards to serve as input and output connectors for the microwaves.

4.1.3 Magnetic Field Control

A 3-axis Helmholtz coil set is used to control the magnetic field at the diamond sample. The base of the coils was made by drilling holes into an aluminum pipe and screwing on thin aluminum plates to create an inset in which to wind the copper wire. Each coil in a pair was wound with a base layer of 3/16" copper tubing for water cooling, followed by 100 turns of 14 gauge wire. The Z coils have a 6" inner diameter and 9" outer diameter and are separated by 6". The X coils similarly have a 6" inner diameter and 9" outer diameter, separated by 12". The Y coils have a 7.5" inner diameter and 11" outer diameter and are separated by 12". From these values it is clear that the configuration we used is a pseudo-Helmholtz coil configuration, despite this, the homogeneity of the field at the optical irradiation point on the diamond was sufficient, as seen in figure 4.6. The maximum magnetic field that can be generated using these coils before encountering heating issues is ~ 100 Gauss. The field precision was found to be ~ \pm 0.1 Gauss.

Each coil pair is connected to a stable power supply (HP 6553A) set to constant current mode. The HP6553A current output can be controlled by applying a voltage of 0-5 V on the back terminal of each of the units. This voltage is supplied by a national instruments analog output card (PCIe-6323) that can be controlled using a lab view software, see section 4.1.6. In addition to having control over the strength of the magnetic field produced, full control of the magnetic field direction was also desired. This was achieved by adding a mechanical switch at the power supply current output that can be switched to change the polarity of



Figure 4.5: 3-Axis Helmholtz Coil

the magnetic field for each Helmholtz pair. The Helmholtz coils were cooled using a chiller (VWR 1162A). The copper tubing was equipped with hose connectors that are attached to a manifold that equally distributes the chilled water among the coils in order to prevent non-uniform temperature distributions between the coils. Calibration of the magnetic field produced by the coils was done by monitoring the output voltage from a hall probe (Ametes MFS-3A) and additionally by monitoring the position of the ODMR $m_s = 0 \leftrightarrow m_s = \pm 1$ transitions in an NV⁻ ensemble as the HP6553A output current was changed.

4.1.4 Timing Controls

All timing control was done using a 400 MHz PulseBlaster-ESR-PRO (Spin Core inc.). The pulse blaster has 24 digital output channels with a minimum pulse time of 2.5 ns. The control designations for each channel are shown in figure 4.7. Channels 1, 2, 3 and 4 are dedicated to controlling pulse sequence initialization, AOM switching, microwave switching and detection triggering respectively. Channels 13-20 are dedicated to programming the phase shifter parameters. Channels 22-24 must be set to high to run programs that last more than 6 clock cycles. The other pulse channels are unused. Pulse programs were implemented using LabView subroutines provided by Spin Core Inc.

Upon receiving a digital TTL command each component switch will have some charac-



Figure 4.6: X, Z-Magnetic Field Uniformity, x axis in cm. A hall probe was placed on an xyz stage and the magnetic field along x and z was measured as a function of position. The figures show the field homogeneity for a 50 G field, 54.5 deg about the y-axis in the x-z plane.



Figure 4.7: TTL Pulse Timing Control Diagram

teristic response time. This requires the inclusion of time delay compensation in the pulse programming. In order to characterize the time delay of each component, input TTL and output responses were monitored on an oscilloscope. An APD was placed at the AOM output and the APD voltage was monitored on the oscilloscope. A microwave power detector (Minicircuits ZX47-40-S+) was placed at the output of of the microwave stripline, and was also connected into an oscilloscope. As mentioned previously, in order to switch the laser on and off a TTL command is sent to an RF driver that is connected to the AOM. The driver then sends an acoustic wave to the AOM and this subsequently turns on the AOM switch. This order of events results in some delay between when the TTL pulse arrives at the RF driver and when the AOM actually turns on. It was found that the AOM switches on 1.48 μ s after the TTL pulse is received by the RF driver. In the case of the microwave switch, a delay of 50 ns was recorded. For proper timing, if a microwave pulse is to immediately follow a laser pulse, the TTL pulse controlling the microwave switch should follow 1.42 μ s after the AOM TTL pulse.

In addition to the switching time, rise times were also determined using oscilloscope measurements. The laser pulse was measured to have a rise time of ~ 70 ns, while the microwave pulse was found to have a rise time of ~ 2 ns. Pulse correction due to time delay should be repeated for any new system configurations (e.g. if additional components are added to system).

4.1.5 Detection

NV⁻ fluorescence was detected using an APD and the APD output voltage was either processed by a lock-in amplifier (SR830) or data acquisition card (Compuscope Gage Razor 1622). The lock-in amplifier was used for continuous wave measurements, while the data acquisition card was used for both continuous and pulsed measurements.

The lock-in amplifier takes the APD output voltage, multiplies it by a reference frequency, and integrates this product over a specified averaging time. This integrated product is output as a DC signal, the magnitude of which reflects the part of the APD output voltage that is at the same frequency as the reference.² In our experiments with NV⁻ ensembles, we modulated the microwave frequency at a chosen reference frequency as we swept the microwaves through the $m_s = 0 \leftrightarrow m_s = \pm 1$ resonances. This modulates the NV⁻ fluorescence at the reference frequency we have chosen and therefore modulates the APD output voltage. The APD signal is sent to the lock-in and multiplied with the reference signal. The DC output as a function of microwave frequency is then recorded in a LabView program using General Purpose Interface Bus (GPIB) communication with the lock-in. This results in a derivative ODMR spectrum as indicated in figure 4.8. A more detailed description of these kinds of experiments, as well as the physical effects of microwave and magnetic field modulation on an ensemble of NV⁻ centers can be found in Chapter 10 of this thesis.

The APD output voltage from APD1 and APD2 is sent to a DAQ card with two input channels, Ch 1 and Ch 0. The DAQ card is configured to collect data only after it receives a trigger signal from channel 4 of the pulse blaster (Figure 4.7). Once the trigger is received, the DAQ card begins to collect data for a time specified by the sampling rate, usually 200 megasamples/sec (MS/s), and number of points 'per segment'. These segments are stored on the DAQ card 'on board memory' and are downloaded to the CPU memory at a 200 MB/s transfer rate³. Once in CPU memory, the data points in each segment are then processed according to the experiment that was run. The sequence of events in a pulsed experiment, including the detection event, is indicated in figure 4.25. Additional data processing is discussed in detail in section 4.6 of this chapter.

4.1.6 Software and Signal Processing

The programming language used for timing and equipment control was LabView Visual programming language.⁴ There are two main programs associated with the NV-1 Setup, an

 $^{^{2}}$ In addition to supplying the magnitude of a particular frequency component in the signal, the lock-in also supplies information about the phase of the input signal relative to the reference signal. The lock-in also provides a range of filter functions for noise reduction.

³The DAQ has an on board sample acquisition memory of 128 MS with a 200 MB/s transfer rate. In future iterations of this detection scheme we would suggest a larger on board memory as well as a larger transfer rate. Because the DAQ is using PCI communication rather than PCI express our transfer rate was slower than desired and cost us a significant amount of experimental time.

⁴As a healthier alternative we would recommend using LabWindows, a script based programming interface, instead.



Figure 4.8: CW ODMR Derivative Spectrum for the case where a magnetic field is aligned along one NV⁻ axis (smaller peak). The derivative peak with the larger amplitude is from the $m_s = 0 \leftrightarrow m_s = -1$ resonance for unaligned NV⁻ orientations.

electron spin resonance program (Main ESR v2.vi) that programs simple pulse and continuous wave measurements and then the main decoupling program (Main Decoupling v2.vi) that programs more complicated pulse sequences such as CPMG, UDD and XY-N sequences, see section 4.6 for more details about these sequences. Within these main programs are nested numerous subroutines associated with establishing remote communications with instruments and also associated with programming any timing or acquisition cards that are interfaced with the CPU.

Software for Instrument and Card Programming

For the NV-1 setup, the frequency synthesizer and lock-in amplifier were controlled using GPIB communication via a National Instruments GPIB-USB adapter. GPIB communication could be established and commands could be sent using the LabView subroutine: Instrument I/O. The current supplied to the 3-axis Helmholtz coils was controlled using an analog output channel of a PCIe-6323 card. The PCIe-6323 card, along with the DAQ card and pulse blaster card have supporting LabView software provided by National Instruments, DynamicSignals LLC and Spin Core Inc. respectively. All of the main programs were written using supporting subroutines (or "sub VI's") from each of the companies described.

The Main ESR v2.vi interface can be seen in figure 4.9. Each of the tab controls leads to a different experiment. For each pulse sequence, a different set of time compensated pulse instructions are sent to the pulse blaster. Figure 4.10 shows how the pulse blaster is programmed. This program allows control of every aspect of the pulse blaster board. The number of pulse pattern instructions can be set, the length of each pulse can be adjusted, the green buttons indicate high or low TTL, the operation code indicates the flow of instructions after the pulse pattern has been executed (loop, continue, end loop, etc.), and the instruct data acts as an address for a given pulse pattern. Main ESR v2 first loads a pulse blaster program and then executes it once an internal trigger is received. The "SpinCore Pulse-Blaster Labview Extension Manual" on the Spin Core Inc. website provides all additional pulse blaster software information.

The magnetic field control block (shown in the upper right corner of figure 4.9) programs three analog output channels of the PCIe-6323 card. These channels will send different voltage values to each of the power supplies controlling the 3-axis Helmholtz array.

The DAQ control block is shown in figure 4.11. The total number of averages (number of records) can be set, as well as the acquisition parameters, trigger parameters and input channel parameters. The segment size and depth control the card memory dedicated to the acquisition and the total number of samples to acquire. The threshold value indicated in figure 4.11 determines the acquisition window as indicated in figure 4.12. The "CompuScope SDK for LabVIEW Manual" on the Dynamic Signals LLC website provides all additional DAQ Gage Razor software information.

The Main Decoupling v2.vi interface and software control is nearly identical to the Main ESR program with the exception of the type of programs sent to the pulse blaster board.

4.1. NV-1 OVERVIEW



Figure 4.9: Screen Shot of Main ESR v2.vi interface. The magnetic field control panel is on the upper right hand corner of the screen shot. The top right graph shows real-time data, the graph in the center shows the results of an ODMR measurement at earth's field.



Figure 4.10: Screen Shot of Pulse Blaster input commands - The number of pulse pattern instructions can be set, the length of each pulse can be adjusted, the green buttons indicate high or low TTL, the operation code indicates the flow of instructions after the pulse pattern has been executed, and the instruct data acts as an address for a given pulse pattern.

4.1. NV-1 OVERVIEW



Figure 4.11: Screen Shot of Gage input commands - this tab includes the control panel for the frequency synthesizer and the control panel for the data acquisition card. The window on the left hand side shows the fluorescence signal during an optical pulse.



Figure 4.12: NV⁻ Fluorescence during a probe pulse. The threshold values, offset bins and number of bins are indicated here and are described in the text. These 'bins' should really be called 'points', since a single bin here is equivalent to a single data point and we simply write the label here as it is written into the program.

Software for General Signal Processing

To see how the NV^- spin population changes when we apply a given sequence of microwave and optical pulses we must use a reference measurement that detects the fluorescence signal when the NV^- centers are completely optically polarized.⁵ Then once we've polarized the NV^- center we apply a microwave pulse sequence and then detect the $NV^$ fluorescence using a probe pulse that is short enough that it does not completely polarize the NV^- centers. The reference and probe fluorescence signals are then subtracted and

 $^{^{5}}$ The best polarization that has been demonstrated for NV⁻ centers has been 80% polarization. For the case of an ensemble, it is difficult to achieve even 80% because of the laser intensities required to fully saturate the system.

normalized to give the relative change in NV⁻ spin populations.⁶

Figure 4.12 shows the NV⁻ fluorescence signal detected by the DAQ card during the laser probe pulse. For data processing, a detection threshold value is set and only a small number of points after this threshold value are processed. This is done in order to avoid measuring NV⁻ centers that have been re-polarized. The program has two values, number of offset bins and number of bins. The number of offset bins shift the data processing window by a few time steps in order to avoid collection of fluorescence at the probe pulse rise time. The number of bins determines how many data points are collected after the offset bins have been accounted for These data points are then summed and averaged to give the average fluorescence value for each measurement.

The type of signal processing varied according to the type of experiment, detailed information about signal processing for each ESR experiment is included in section 4.6 of this chapter. All signal processing related to the lock-in was done on the SR830, and we would refer the reader to the SR830 manual for additional details regarding lock-in operation.

4.2 NV-2 Overview

The NV-2 setup was used for continuous wave ODMR experiments and also for the continuous wave double resonance experiments that are discussed in Chapter 5.

4.2.1 Optical Components

A 532 nm diode laser (OEM Laser Systems Inc.) with a fixed power of ~ 500 mW and beam size of ~ 2 mm is passed through a neutral density filter wheel to control the laser power incident on the NV⁻ ensemble. An AOM (Isomet 1205C-3) and RF driver (522C-2) were used to control the laser switching. After the AOM the laser is directed through a half wave plate for controlling laser polarization. The beam is focused onto the diamond through a microscope objective (MO) with N.A. = 0.7 to give a diffraction limited spot size of 662 nm. Unlike the NV-1 setup, that has a mechanical stage, the NV-2 setup has a piezo controlled xyz stage used for positioning the diamond sample with high precision (~ 50 nm). The fluorescence is collected through the MO and sent through a dichroic mirror to an avalanche photodiode (APD 110A).

4.2.2 Microwave Components

Microwaves from a frequency synthesizer (HP8673C) are sent through a microwave switch (ZYSW-2-50DR) followed by a choice of microwave amplifier (1-500 MHz: RF Empower 1079-BBM1C3K7G; 500-1000 MHz: Minicircuits LZY-2+; 800-2000 MHz: Minicircuits ZHL-10W-2G+; 2000-8000 MHz: Minicircuits ZVE-3W-83+). The variety of amplifiers was

⁶As mentioned previously, the NV⁻ ensemble exhibits spin-dependent fluorescence and NV⁻ centers in $m_s = \pm 1$ states exhibit lower fluorescence counts than NV⁻ centers in the $m_s = 0$ state.







Figure 4.14: Goniometer and Microwave Board

necessary to probe the NV⁻ $m_s=0 \leftrightarrow m_s = \pm 1$ transitions at a large range of magnetic fields. The microwave boards used in this setup are identical to those used in the NV-1 setup.

4.2.3 Magnetic Field Control

Unlike the NV-1 setup, the NV-2 uses a permanent magnet for magnetic field control. The experiments done on the NV-2 setup usually required the use of large fields on the order of $\sim 1,000$ Gauss. The goniometer has a 7.5" inner diameter, and 8.5" middle diameter and a 10.5" outer diameter, see figure 4.14. The goniometer was measured to have a field precision of ± 1 Gauss.

4.2.4 Timing Controls

All timing control was done using a 75 MHz PulseBlaster-DDS-I-300 (Spin Core inc.). The pulse blaster has 24 digital output channels with a minimum pulse time of 14 ns. Only channels 1-4 are used in this setup. Channels 1, 2, 3 and 4 are dedicated to controlling

pulse sequence initialization, AOM switching, microwave switching and detection triggering respectively.

The experiments run on the NV-2 setup were all of a 'pseudo-CW' nature, where the laser and microwave pulse lengths were significantly longer than any component switching delays. As a result, incorporating time-compensation was not particularly critical. Most often the laser was switched on for the full duration of an experiment and the microwaves were switched on for data collection and off for background collection. If desired, time compensation can be implemented in a similar way as described in section 4.1.4.

4.2.5 Detection

NV⁻ fluorescence was detected using an APD. The APD voltage was then sent to a DAQ card (Compuscope Gage Octopus) with a 25 MS/s sampling rate and an onboard memory of 128 MS. The DAQ card begins to collect data as soon as channel 4 is turned on. The DAQ card continues to collect data for a time specified by the sampling rate (25 MS/s) and number of points 'per segment'. These segments are stored on the DAQ card 'on board memory' and are downloaded to the CPU memory at a 200 MB/s transfer rate.

4.2.6 Software and Signal Processing

Labview visual programming language was also used for the NV-2 setup. Because only continuous-wave experiments are run on the NV-2 setup, the software used on this setup is considerably simpler than for the NV-1. The frequency synthesizer is controlled using GPIB and the pulse blaster and DAQ cards are all controlled using the same kind of software as mentioned in the NV-1 section. Signal processing involved a subtraction of the background signal (NV⁻ fluorescence with microwaves off) from the data signal (NV⁻ fluorescence with microwaves on) followed by normalization.

4.3 NV-1 Microfluidics Overview

The NV-1 setup was modified for microfluidic magnetometry experiments. All of the optical components are identical to what is shown in figure 4.1. Here we attempted to detect nuclear spin magnetization of protons in water in a microfluidic chip using an ensemble of nitrogen-vacancy centers, see figures 4.15 and 4.16. We inverted the nuclear spin magnetization using RF coils, created a fluctuating magnetic field and attempted to detect this fluctuation using an NV⁻ ensemble.

Here we present the microfluidic flow system, the chip designs and experimental methods used for detection of spin magnetization. Results obtained using this setup are discussed in Chapter 10 of this thesis.



Figure 4.15: NV-1 Microfluidics Setup



Figure 4.16: Adiabatic inversion of nuclear spin magnetization experiment. The magnetic field is aligned along one of the NV⁻ axes of a [110] diamond. Since the NV⁻ center is most sensitive to magnetic fields that fluctuate along its axis, the nuclear spin magnetization is inverted using a B_1 oscillating field that is perpendicular to the NV⁻ axis. This has the effect of modulating the nuclear spin magnetization along the NV⁻ axis.

4.3.1 Flow System

A syringe pump (Harvard Apparatus pHD Ultra) was used for flowing ultra-pure water through 0.030" (760 μ m) i.d. 1/16" (1588 μ m) o.d. tubing to a 2 T magnet. The tubing was wound multiple times around a delrin casing within the magnet to ensure a pre-polarization time greater than the T₁ of water. At the exit of the magnet a MicroTight adapter was used to connect the 1/16" o.d. tubing to PEEK 360 μ m x 150 μ m tubing. This PEEK tubing was then connected directly into a microfluidic chip using PEEK Nanoports. Nanoports were placed on the microfluidic chip inlet and outlet and held in place using epoxy. A thin 20 μ m thick diamond containing a large concentration of NV⁻ centers was embedded in the chip at a distance of < 20 μ m from the microfluidic chip and discarded into a glass flask. Figure 4.15 shows the full configuration of the NV-1 Microfluidics setup.

4.3.2 Microfluidic Chip

A few different chips were used for these experiments. Polydimethylsiloxane (PDMS) chips were used for the first set of experiments due to the ease with which they could be fabricated. Chips were fabricated using photolithography methods. A silicon wafer was coated with a negative photoresist (SU-8), illuminated with UV after being covered with a mask, and then rinsed with an SU-8 developer to remove the portions of the photoresist that were not irradiated with UV. The remaining photoresist forms a mold that a PDMS solution can then be poured into. The PDMS is then peeled away from the silicon wafer to reveal a small recess that forms the microfluidic channel. Another layer of PDMS is then bonded on top of this PDMS layer using O₂ plasma bonding. The inlet and outlet is formed by punching holes into the PDMS using a blunt needle or micro diameter aluminum tube. These PDMS chips contained two channels, as seen in figure 4.18. The two channels were 300 μ m apart, 100 μ m deep and 100 μ m wide and were to be used as part of a gradiometer configuration in which the proton magnetization in channel 1 was to be 180 degrees out of phase with the proton magnetization in channel 2. It turned out that these chips were not sufficiently rigid for our experiments and so these were later replaced with glass chips.

The fabrication for glass chips is considerably more extensive and so it will not be mentioned here. The procedure can be found in Appendix B. The glass chips had a single microfluidic channel 300 μ m wide, 35 μ m deep, and 5cm long. The large width to depth ratio in the chip design maintains the form of the flow within the Taylor-Aris Dispersion regime [127, 128], that is, within a regime where convective flow is minimized and plug type flow is favored. One side of the chip contained the channel and the other side of the chip contained a recess <20 μ m from the channel in which a diamond was placed.

4.3.3 RF Control

Two configurations of RF irradiation were used. In one set of experiments, the RF coils were wound directly around the PEEK tubing prior to entering the microfluidic chip, as seen



Figure 4.17: The microfluidic chip made from PDMS was secured in place using a teflon and delrin casing. Ports were threaded into the casing to allow for the connection of microfluidic tubing. This stage shows a gradiometer configuration where the water from the syringe pump is split into two micro channels. Below the chip is a microwave board used to supply the microwaves for ODMR measurements. The main stage is made out of aluminum and the screws securing the delrin casing to the stage are made of brass.



Figure 4.18: PDMS microfluidic chip with two channels. The chip is configured with nanoports and the diamond is fixed onto a microwave board and pressed against the PDMS chip. The blue piece in the center is a Ametes MFS 3A sensor for measuring the homogeneity of the magnetic field from the 3-axis helmholtz coil.



Figure 4.19: The inlets, outlets and RF coils are shown. The large aluminum piece above the delrin manifold was used in an attempt to shield the NV^- center from residual fields produced by the RF pulses.

in figure 4.19. However, this configuration did not account for the effects of turbulent flow at the transition from the peek tubing to the microfluidic chip. It was surmised that the spin magnetization 'packets' shown in figure 4.16 were mixed, and the resulting modulation in the magnetization was destroyed. In another set of experiments, planar coils were placed above and below the microfluidic chip to create a localized homogenous RF field 4.21 at the channel before the water passed over the diamond. In this way, the flow remains laminar throughout the RF irradiation and detection at the NV center. An arbitrary waveform generator (AWG 520) was used to apply RF pulses. Since the magnetic field at the RF coils was not known exactly nor the precise field homogeneity of the RF field, the inversion of the spin magnetization was done using adiabatic fast passage (AFP) [129]. AFP inversion is much less sensitive to field inhomogeneity due the main static magnetic field or the RF magnetic field. The AWG programs used for microfluidics experiments are found in the AWG 520 Programming manual under frequency sweep programs. The results of these experiments are discussed at the end of Chapter 10.



Figure 4.20: Planar coils were used to apply a B_1 field to the nuclear spins in a subsequent iteration of the microfluidic experiment (as compared to figure 4.19). This figure shows a trace of one of the planar coils used.



Figure 4.21: Only a single channel was used in the 2nd Iteration microfludic glass chip design. Input and outport ports are labeled as well as the RF coils that are upstream of the NV^- magnetometer.

4.3.4 Detection and Signal Processing

For signal processing and analysis, the APD output voltage is sent to a pre-amplifier (SR560). The pre-amplifier is used as a bandpass filter to isolate fluorescence modulations related to inversions of the nuclear spin magnetization. The output of the pre-amplifier is then sent to the Gage data acquisition card for additional processing. The detection program for this experiment continuously runs a pulse blaster sequence that maintains both the AOM and the microwave switch on throughout the detection sequence while periodically sending a trigger signal to the gage acquisition card. Since we are attempting to detect low frequency signals, on the order of Hz, the Gage acquisition settings were modified to achieve a low sampling rate and long integration time. In addition, the limitations on data storage on the Gage acquisition card nucleas multiple data acquisition and CPU download sequences. Hence, the output from the pre-amplifier was collected for a fixed integration time, the data downloaded and the detection sequence was reinitiated at a fixed interval that was synced with the AWG pulse sequence. The signal from each interval is then summed and averaged. The pulse blaster sequence ensures that the averaged signals are in phase. The incoming signal was then Fourier transformed to give the signals shown in Figure 10.3.

4.4 Diamond Materials Prep

Type I-b and II-a diamonds were used for experiments described in this thesis. Type I-b diamonds have nitrogen impurities as the main defect in the diamond, usually in the range of 100-500 ppm. All type I-b diamonds were grown using HPHT methods and were purchased from Element-6. II-a diamonds usually have much lower nitrogen concentration <1 ppm. II-a diamonds were grown using CVD methods and were also purchased from Element-6. In addition, some electronic grade diamond samples with <5 ppb diamond were used for shallow implantation relaxation measurements that are not discussed here.

Type I-b diamonds typically have a large concentration of paramagnetic nitrogen defects (N_S) in the diamond lattice (~ 100 ppm). These diamonds were used for NV⁻ ensemble magnetometry experiments as well as for studies of the coherence properties of NV⁻ ensembles in an electron-rich spin-bath. The type I-b diamonds were irradiated with electrons at energies ranging from 1 MeV-5 MeV, with a fluence of 1×10^{18} /cm². The 5 MeV irradiation was used for samples that were thicker than 1 mm. The type I-b diamonds used in the microfluidics experiments were irradiated with protons at 2.8 MeV with a fluence of 1×10^{16} . These fluence parameters were chosen based on information from reference [44]. The type I-b diamonds used in each of the experiments described in this thesis are included in the chapter discussions.



Figure 4.22: Continuous Wave Experiments

4.5 Continuous Wave Experiments

Continuous wave (CW) measurements were done in either a 'pseudo-CW' or a CW fashion. For the case of 'pseudo-CW' experiments, the laser and microwave sequence is shown in figure 4.22. This sequence was repeated for a range of microwave frequencies in order to obtain an ODMR spectrum. The reference signal was then subtracted from the absolute signal and then normalized to give the final spectrum. Most 'pseudo-CW' experiments were done to investigate interesting features in the NV⁻ ODMR spectrum at a range of magnetic fields.

For the case of CW experiments, the laser and microwaves were turned on continuously and the fluorescence signal was collected continuously as well. Often these CW experiments involved the use of a lock-in amplifier for signal processing, see section 4.1.5. As a reminder, a lock-in amplifier works by multiplying an incoming oscillating signal by a reference signal set to a specific frequency. It then outputs a DC voltage that has a magnitude proportional to the the amplitude of the signal components with frequency overlap between the reference signal and the oscillating signal. This serves to remove most fluctuations in fluorescence intensity that are not fluctuating at a specified reference frequency.

Figure 4.8, shows an ODMR derivative spectrum in the case where a static magnetic field is aligned along one NV⁻ orientation. To produce this spectrum, the fluorescence was modulated by applying a low frequency microwave frequency modulation on top of the center microwave frequency during the collection of the ODMR spectrum, see figure 4.23 for clarity. As mentioned in chapter 3, the $m_s = \pm 1$ spin states of the nitrogen-vacancy center are sensitive to magnetic fields. If the NV⁻ center experiences an oscillating magnetic field, the frequency position of the $m_s = 0 \leftrightarrow m_s = \pm 1$ transitions will modulate at the frequency of the oscillating field, with a modulation amplitude of $|\gamma_e B_z m_s|$, where z is defined to be along the NV⁻ axis and B_z is the amplitude of the oscillating field along the NV⁻ axis. The derivative maximum, shown in figure 4.8, occurs at the microwave frequency where the NV⁻ fluorescence is most sensitive to a fluctuating magnetic field.



Figure 4.23: Continuous wave magnetometry measurement. The frequency of the microwaves is modulated as the center microwave frequency is swept during continuous optical illumination of the NV⁻ center. The resulting modulation in the fluorescence amplitude gives the strength of the modulated microwave field.



Figure 4.24: NV⁻ Fluorescence Modulation, due to a 24Hz, 5.8μ T magnetic field

All NV⁻ ensemble continuous wave magnetometry experiments were done by applying a continuous microwave field at a frequency corresponding to the derivative maximum for a given NV⁻ orientation. Modulations in the fluorescence intensity were then observed when a low frequency magnetic field was applied, see figure 4.23 and figure 4.24.

4.6 Pulsed Experiments

In this section, we discuss a few of the multi-pulse sequences we used on NV⁻ centers, their effects on the NV⁻ centers, and the kind of information that can be obtained from them. It is important to note that any phase cycling incorporated into the pulse sequences here is done for the purpose of pulse error compensation. In addition, the laser polarization and probe scheme shown in figure 4.25 is identical for all of the pulse sequences, only the number of microwave pulses, their lengths and phases are changed from one experiment to the next. The length of the laser polarization pulse is partly dependent on the laser intensity incident on the diamond, and also dependent on the NV⁻ singlet state lifetime. For the laser intensities and thus, also polarization rates that we worked with here, we typically used a laser polarization pulse length of several microseconds. The probe pulse length was optimized to limit the effects of NV⁻ re-polarization on the collected fluorescence signal. The form of the pulse sequences used is shown in Figure 4.26.



Figure 4.25: Spin-Echo Sequence

As previously mentioned, the NV⁻ spin ensemble can be optically pumped into the $m_s = 0$ spin state using 532 nm laser light. In order to isolate only one NV⁻ orientation, a static magnetic field is typically applied along one of the 4 principal axes of the NV⁻ ensemble. This gives the ODMR spectrum seen in figure 3.10. The static magnetic field also serves the purpose of spectrally separating the $m_s = 0 \leftrightarrow m_s = +1$ and $m_s = 0 \leftrightarrow m_s = -1$ transition frequencies. The NV⁻ ground state spin can then be addressed using microwaves resonant with either the $m_s = 0 \leftrightarrow m_s = -1$ transition or $m_s = 0 \leftrightarrow m_s = +1$ transition. In the case where $B_z \gg B_x$ we can treat either one of these manifolds as a two-level system.

In a typical Ramsey pulsed ODMR experiment, a $\pi/2$ microwave pulse resonant with the NV⁻ m_s = 0 \leftrightarrow m_s = -1 transition is first applied. This forms a coherence between the two Zeeman levels: m_s = 0 and m_s = -1⁷. The NV⁻ ensemble spin system will then begin to evolve under the system-bath Hamiltonian. In the case where we only consider the perturbative effects of a small DC magnetic field b, the Zeeman levels acquire some relative phase, $\phi \propto (g\mu_B/\hbar)b\tau$, where g is the g-factor of the NV⁻, g ≈ 2 , μ_B is the Bohr magneton, \hbar is the reduced Planck constant and τ is the evolution time [31]. After the evolution time, another $\pi/2$ pulse is applied to transform the relative phase accumulation into a population. Unlike in conventional nuclear magnetic resonance experiments, the readout in an NV ODMR experiment occurs when the spin magnetization is in the form of populations, not single quantum coherences. The NV⁻ center spin populations are then read out optically, to give a single point measurement. The Zeeman shift can be inferred from the relative change in the fluorescence intensity before and after the pulse sequence is applied. [31].

4.6.1 Rabi Nutation

The Rabi nutation frequency characterizes the strength of the coupling between an electromagnetic field and a two-level quantum system. In order to determine the coupling strength (and therefore the length of a π pulse) between the applied microwaves and the

⁷The same can be done for the $m_s = 0 \leftrightarrow m_s = +1$ transition.



Figure 4.26: Microwave pulse sequences for relaxation measurements and decoupling experiments.

 $NV^- m_s = 0 \leftrightarrow m_s = -1$ transition we perform a Rabi nutation experiment. The form of this experiment is shown in figure 4.26. The NV^- ensemble is first spin polarized into the $m_s =$ 0 state, then the laser is turned off. Microwaves are then applied for a time τ before being turned off. A probe pulse then reads out the NV^- spin state. The time τ is varied and the NV^- spin state is read out for each value of τ . The Rabi nutation curve for three different microwave powers is shown in figure 4.27. The fluorescence signal is at its lowest intensity when most of the NV^- population is in the $m_s = -1$ state, the microwave pulse length at which this occurs defines the π pulse length, or a multiple of the π pulse length.

The signal was processed as described in the section 4.1.6. The NV⁻ fluorescence absolute signal is first collected followed by a reference measurement in which the microwaves are turned off. These are then subtracted from one another and normalized to give the resulting graph shown in figure 4.27.

4.6.2 Hahn Echo

The results of a Hahn echo give us information about the coherence lifetime and decoherence rate of the $m_s = 0 \leftrightarrow m_s = -1$ (or +1) coherence. The decoherence rate, and how it changes with different perturbations applied to the system (RF pulses, large magnetic fields, etc.) gives us valuable information about the sources of decoherence. As described in Ref. [53], we can fit the coherence decay curve to determine whether the primary NV⁻ decoherence mechanism is related to electron spin-bath coupling or nuclear spin-bath coupling.

NV⁻ centers in an ensemble can often find themselves in different environments and as a result, these NV⁻ centers can experience different local magnetic fields with respect to other



Figure 4.27: Rabi Nutation Curves at Different Microwave Powers

 NV^- centers in the ensemble. When this occurs, the phase accumulation that occurs once the NV^- center is placed in a coherent state can vary from center to center. As some $NV^$ spins accumulate phase more quickly, and some accumulate phase more slowly, a dephasing effect is observed. This results in a rapid coherence decay. The Hahn echo sequence works by removing coherence decay due to these kinds of dephasing effects. In a Hahn echo sequence, after the $\pi/2$ pulse, the NV^- coherence will evolve according to a particular Hamiltonian, and will accumulate some amount of phase for some time τ . The coherences can be brought back into phase by inverting the NV^- ensemble spin magnetization using a π pulse. When this is done, the NV^- coherences will come back into phase after an evolution time τ . It is important to note that the Hahn echo sequence perfectly decouples **static** non-uniform couplings to the NV^- spin, not dynamic ones (i.e. magnetic field fluctuations due to spinflip-flops in the neighboring spin bath).

In a Hahn echo, see figure 4.26, a coherence between the $m_s = 0$ and $m_s = -1$ (or +1) is formed using a $\pi/2$ pulse. We wait a fixed time τ_1 and then apply a π pulse and wait a time τ_2 before applying another $\pi/2$ pulse and optically reading out the NV⁻ spin state. We then vary the time τ_2 to obtain the graph shown in figure 4.28, where we used a τ_1 value of 200ns.

The fluorescence signal was processed as described in the section 4.1.6. The NV^- fluorescence absolute signal is first collected followed by a reference measurement in which the microwaves are turned off. These are then subtracted from one another and normalized to give the resulting graph shown in the figure.

4.6.3 Relaxation Measurements: T_1 , T_2

Much like the Hahn Echo measurement, measurements of the spin-lattice and spin-spin relaxation constants of the NV⁻ center give us information about the local spin environment surrounding the NV⁻ center. We can measure T₁ relaxation by first inverting the NV⁻ electron spin magnetization using a π pulse⁸. We can then monitor the change in the spin populations after some time τ .

The T₂ measurement is identical to the Hahn Echo measurement, except in this case $\tau_1 = \tau_2 = \tau$. τ is then varied, and the NV⁻ fluorescence is probed at the end of the sequence for each value of τ . This sequence is also labeled as the electron spin envelope echo modulation (ESEEM) experiment, and is of particular importance in chapter 6.

The T_2 signal processing was done in the same way as the previous cases. In the case of T_1 measurements, rather than collect a background measurement with no microwave pulses on, we collected a background measurement after applying a 2π pulse to the NV⁻ ensemble. This was done to reduce any pulse errors in the first π pulse. This background measurement was then subtracted from the absolute measurement.

⁸We will remind the reader that for all of these microwave pulse sequences, the laser pulse sequence in figure 4.25 is used. The NV^- ensemble is always optically pumped before any of these sequences are run.



Figure 4.28: Hahn Echo for the case of $\tau_1 = 200$ ns.



Figure 4.29: T₁ relaxation of NV⁻ centers formed in HPHT I-b diamond, with T₁ $\sim 390 \mu s$.



Figure 4.30: $\rm T_2$ relaxation of NV^- centers formed in HPHT I-b diamond, with $\rm T_2 \sim 500$ ns.

4.6.4 Decoupling Sequences: CPMG, XY-N, UDD

Extending the coherence time of spin systems is often desired because it allows us to have longer interrogation periods in which we can collect information about a spin coupling to selected parts of the environment. The coherence of a spin can be dynamically protected by refocusing certain spin \leftrightarrow bath interactions via application of decoupling sequences. The effectiveness of this refocusing is largely due to the nature of spin-bath interactions that are present and also the kind of decoupling sequence used. The spin-bath interaction can come in the form of a pure dephasing interaction, where only the S_z operator is involved, or it can come in the form of a pure spin-flip interaction where the operators S_x and S_y are present. In addition, the spin-bath interaction can be of a general interaction form where S_x , S_y and S_z operators are all involved. [52]

The Carr-Purcell-Meiboom-Gill sequence (CPMG) is a sequence that involves a train of spin echoes, and has the effect of decoupling bath interactions that operate on two components of the spin angular momentum (S_x , S_y , S_z). Unlike the Hahn echo case, where only static inhomogenous couplings are decoupled, the CPMG sequence also decouples **dynamic** interactions between the spin system and the neighboring spin-bath, in other words, in addition to decoupling constant frequency offsets of the $m_s=0\leftrightarrow m_s = -1$ (or +1) transition, CPMG also corrects for frequency offsets that vary over time. The sequence is shown in figure 4.26 [130, 131]. The π inversion pulses in the CPMG sequence shown in figure 4.26 invert the spin magnetization along one axis, y. In order to decouple a spin-bath interaction that is of a general form, we would have to invert the spin magnetization along another axis as well. The XY-N sequence is a small modification on the CPMG sequence that does this. It decouples general spin-bath interactions by alternating the phase of the inversion pulse between x and y phase. Because of this phase inversion, it is also better designed to compensate for pulse imperfections [132].

The Uhrig Dynamic Decouping (UDD) sequence is quite similar to the CPMG sequence as well, except that the timing in between pulses is a bit different. The design of the UDD sequence is based on considering the relationship between the number of π pulses applied and the order of the time varying frequency offset that is removed. For example, a Hahn echo with one π pulse removes static offsets, while an echo train of two π pulses remove any offsets that change linearly with time. So then, in principle, one could design a pulse sequence with N pulses that removes frequency offsets that change as an (n-1) polynomial with time [133], [134]. In this case one would have a train of pulses separated by a time $\tau_{N+1}, \tau_N, ...\tau_2, \tau_1$, where $\tau_i = t_i - t_{i-1}$ and t_i is the total time that has passed after pulse number 'i'. An expression that calculates t_i is,

$$t_i = t_{N+1} \sin^2 \left(\frac{\pi i}{2(N+1)} \right),$$
(4.2)

where N is the total number of pulses, i is the ith pulse, and t_i is the total time that has passed up until the ith pulse. A derivation of this expression can be found in [134]. It is important to note that the main difference between CPMG and UDD sequences is related to the equivalent



Figure 4.31: NV⁻ Ensemble in HPHT type I-b diamond. The $m_s = 0 \leftrightarrow m_s = -1$ coherence lifetime of the NV⁻ center is extended using a CPMG decoupling sequence. The coherence lifetimes are shown for the case of 8, 16 and 64 CPMG π pulses.
spacing of the pulses. CPMG has equivalent spacing of the π pulses while UDD does not. Studies have shown that the CPMG works best for decoupling high frequency spin-bath interactions, while the UDD works best for low frequency spin-bath interactions [52]. All the pulse sequences are shown in figure 4.26. Phase cycling was done in each of these cases to remove any pulse errors. The first step of signal processing for each of these experiments is similar to the processing mentioned earlier.

In the ensuing chapter we discuss methods for decoupling the NV⁻ center from an electron spin dominated spin bath and demonstrate a new method that reduces the effective noise amplitude that the NV⁻ experiences by a factor of ~ 8 , and as a result, extends the coherence lifetime by a factor of 2.

Chapter 5

Suppression of Decoherence using Perpendicular Magnetic Field

In this section, we explore the coherence lifetime of NV⁻ centers in an electron dominated spin bath. This chapter was previously published in Ref. [54] and is republished here, with minor changes, with permission.

5.1 Abstract

We demonstrate that the spin decoherence of negatively charged nitrogen vacancy (NV⁻) centers in diamond can be suppressed by a transverse magnetic field if the electron spin bath is the primary decoherence source. The NV⁻ spin coherence, created in a decoherence-free subspace, is protected by the transverse component of the zero-field splitting, increasing the spin-coherence time about twofold. The decoherence due to the electron spin bath is also suppressed at magnetic fields stronger than ~ 25 G when applied parallel to the NV⁻ symmetry axis. Our method can be used to extend the spin-coherence time of similar spin systems for applications in quantum computing, field sensing, and other metrologies.

5.2 Introduction

In coupled spin systems, coherent superposition of spin states evolving in the presence of magnetic noise lose their spin coherence due to locally fluctuating magnetic fields [135–137]. Long coherence times are desirable because they permit the system to be interrogated for a longer time, yielding improved sensitivity or precision in the estimation of frequencies. Achieving a long spin-coherence time is therefore a central problem in a variety of applications, such as magnetic resonance spectroscopy, magnetometry, and spintronics. [31,138–142] Recently, the negatively charged NV⁻ center in diamond has attracted significant attention due to its unique optical and spin properties [32, 37, 38, 87, 143, 144].



Figure 5.1: (a)Energy level structure of the NV⁻ center showing spin triplet ground (${}^{3}A_{2}$) and excited (${}^{3}E$) states with single states (green arrows for optical excitation at 532 nm, red arrow for fluorescence decay, gray arrows for nonradiative decay via singlet states, and blue arrow for microwave excitation). (b) Schematic of an NV center spin, coupled to bath spins dominated by substitutional nitrogen (N_S) spins (blue balls with arrow for N_S spins).

Once again, we remind the reader that the NV⁻ center consists of a substitutional nitrogen atom at a carbon lattice site and a vacancy that is adjacent to the nitrogen atom. The ground state of the negatively charged NV⁻ center has electron spin S = 1, with $m_s = 0$ and $m_s = \pm 1$ sublevels that are separated by a zero-field splitting of D = 2.87 GHz, as shown in Fig. 5.1a. The quantization axis of the NV⁻ center is along the C_{3v} symmetry axis of the defect. [94, 96]. The electron spin of the NV⁻ center can be highly polarized to the $m_s =$ 0 state via optical pumping, [85] and its spin-state-dependent fluorescence intensity allows convenient optical readout of the spin state of the electron spin with high fidelity at room temperature [86].

Several approaches have been developed to extend the NV⁻-electron spin-coherence time, including the engineering of a spin system devoid of magnetic couplings through the use of magnetically pure (^{12}C) diamond, dynamical decoupling of the probed spin from the noisy environment through multiple-pulse sequences, such as Carr-Purcell-Meiboom-Gill (CPMG) or Uhrig dynamical decoupling (UDD), [145, 146] or the active detuning of bath spin fluctuations with a large external magnetic field [84]. All of these methods are effective in protecting spin coherence of the NV^- center from noisy environments and, in doing so, they enhance the coherence times. For example, an electron-spin-coherence time of several milliseconds at room temperature [87] and about half a second at 77 K (Ref. [55]) was achieved for NV⁻ centers in isotopically pure ¹²C diamond. As a result, the NV⁻ center has been proposed as an ideal platform for the development of quantum-information processors and ultrasensitive magnetometers. It has been previously reported that, when the NV^- center is coupled to a mesoscopic quantum bath consisting of randomly distributed ¹³C nuclei in diamond, [87, 147, 148] a spin coherence between $m_s = +1$ and $m_s = -1$ states (rather than between $m_s = 0$ and $m_s = \pm 1$) has an anomalously long lifetime. [149, 150] This differential relaxation can be exploited by multiple pulse dynamical decoupling sequences.

Here we report a complementary approach that corresponds instead to the creation of a long-lived state or decoherence-free subspace: the energy eigenstates of the NV⁻ spins are prepared such that the effective magnetic noise which causes fluctuation of the spin states is renormalized by the transverse external magnetic field in combination with the transverse component of the zero-field splitting parameter E of the NV⁻ center. The coherent superposition of the energy eigenstates thus becomes robust with respect to the magnetic noise. We theoretically and experimentally show that this method can be realized for an ensemble of NV⁻ centers in diamond. Specifically, experimental results showed that the coherence time was enhanced by a factor of ~ 2 at ~ 25 G. In principle, based on our theoretical model, the coherence time of the electron spin of the NV⁻ center can be enhanced by a factor of ~ 60 , however, other effects, such as decoherence due to the strongly coupled neighboring ¹³C nuclei or due to the electric field noise, limit the attainable enhancement [147, 151].

In extremely pure diamond with a low substitutional paramagnetic nitrogen concentration of the order of a part per billion (ppb) (type II-a diamond), the coherent dynamics of the NV⁻ center depends strongly on the anisotropic hyperfine interaction with nearby ¹³C nuclei, randomly distributed in the diamond lattice at natural abundance (~1.1%) [143]. In spin-echo spectroscopy, the coherence of the NV⁻ center decays as the strongly coupled ¹³C

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nuclear spins in the bath evolve in the presence of an effective field that depends on the electron spin state of the NV⁻ center. With the external magnetic field applied along the NV⁻ quantization axis, all ¹³C nuclei have the same Larmor frequency when the electron is in the $m_s = 0$ state. The phase accumulation associated with couplings between the electron and ¹³C nuclear spins is refocused by the spin echo if the two equal periods of the free evolution are a multiple of the Larmor period. [143, 147] When the external magnetic field is misaligned from the NV⁻ quantization axis, however, transverse components of the magnetic field mix the electron spin states, and the effective g tensor of a ¹³C nuclear spin (the Knight shift [143, 144, 147, 152]) is enhanced in a way that depends on the position of each nucleus, relative to the NV⁻ center. The ensemble ¹³C nuclei in the bath are thus not uniformly coupled to electrons in the $m_s = 0$ state, which leads to fast decay of the electron spin coherence and strong angular dependence of the coherence time of the NV⁻ axis and the external static magnetic field). This angular dependence has been extensively studied [143, 147, 153, 154].

In diamond with a high concentration (~ 100 ppm) of paramagnetic nitrogen that can be categorized as type I-b diamond, the electrons form a strong spin bath, as schematically shown in Fig. 5.1b. In type I-b diamond the N_S center is the primary defect, and is the source of the dominating electron spin bath fluctuations. The spin coherence of the NV^- center decays in the baths fluctuating dipole field, which has a mean strength of ~ 1 MHz [53,84]. Each N_S center has strong hyperfine coupling (~100 MHz) between the electron spin and the ¹⁴N nuclear spin. At zero field, the energy eigenstates are doubly degenerate entangled states between the electron and nuclear spins of the N_S center and the dipolar interaction between N_S centers induces rapid random reorientation of the N_S spins. As the external magnetic field is increased, this spin reorientation becomes improbable, due to the large energy difference between eigenstates as compared to the strength of the dipolar interaction. This slows down fluctuations of the bath spins, resulting in suppression of decoherence of the NV^- center. For example, in a strong external magnetic field of 740 G applied along the NV⁻ axis, the coherence time of a single NV⁻ center was an order of magnitude longer than at zero magnetic field. [84] Here we instead study the coherence time of ensemble NV⁻ centers in type I-b diamond in a weak external magnetic field ($B_0 \leq 75$ G).

We report sharp angular dependence of the coherence time with a maximum at $\theta = 90^{\circ}$, in contrast to the case where ¹³C nuclei dominate the bath dynamics. In what follows, the hyperfine interaction between electron spins and ¹⁴N nuclear spins of the NV⁻ center can be safely neglected, since spin-spin relaxation, induced by the hyperfine interaction, is largely suppressed due to the energy mismatch.

5.3 Theory

The ground state Hamiltonian of the NV^- center can be written as [80, 94],

$$\mathcal{H} = D[S_z^2 - S(S+1)/3] + \gamma_e [\mathbf{B} + \mathbf{b}(\mathbf{t})] \cdot \mathbf{S} + E(S_x^2 - S_y^2), \tag{5.1}$$

where D and E are the parallel and transverse zero-field splitting parameters of the NV⁻ center, respectively. Note that the coupling constant D characterizes spin-spin interactions, while E is due to the crystal field induced by the nonaxial components of the strain that lower the symmetry [104]. $\gamma_e/2\pi \approx 2.8$ MHz/G is the gyromagnetic ratio, **S** is the vector operator for the electron spin, **B** is the external static magnetic field, and **b**(**t**) is the fluctuating dipole field experienced by the NV⁻ center due to the bath. In a weak magnetic field, i.e., $D \gg |\gamma_e \mathbf{B}|, |\gamma_e(\mathbf{b}(\mathbf{t}))|$, terms in the Hamiltonian that couple states separated by the large zero-field splitting can be treated as perturbations. We write an effective Hamiltonian that includes elements only within the space spanned by the nearly degenerate states, i.e., $m_s = \pm 1$ states. The effective Hamiltonian can be approximated as a series, [155, 156] with eigenstates defined as $|0\rangle, |+\rangle$, and $|-\rangle$; the latter two states arise from mixing between $m_s = \pm 1$ states caused by the transverse component of the magnetic field.

From second-order perturbation theory, the transition energies are approximated as,

$$E_{|0\rangle\leftrightarrow|\pm\rangle} = D + \frac{3\delta E}{2} \pm [\gamma^2 (B_z + b_z)^2 + |\widetilde{E}|^2]^{1/2},$$
(5.2)

where δE and \tilde{E} are defined as,

$$\delta E = \frac{\gamma^2 [(B_x + b_x)^2 + (B_y + b_y)^2]}{D},$$
(5.3)

and,

$$\widetilde{E} = E + \frac{\gamma^2 [(B_x + b_x) \pm i(B_y + b_y)]^2}{2D}.$$
(5.4)

A comparison of exact energies with energies calculated using second-order perturbation theory shows that for typical values of the parameters appearing in Eqs. 5.2-5.4, secondorder perturbation theory is valid for describing frequency shifts in a perpendicular magnetic field of up to ~150 G. When $E/2\pi$ is on the order of several MHz and $|\gamma \mathbf{b}(\mathbf{t})|/2\pi \sim 1$ MHz, the radical in Eq.5.3 can be expanded as a series in b_z , and we find that the transition frequencies are,

$$E_{|0\rangle\leftrightarrow|\pm\rangle} \approx = D \pm (\gamma^2 B_z^2 + |\widetilde{E}|^2)^{1/2} + \gamma \widetilde{b}(t), \qquad (5.5)$$

where the renormalized noise $\gamma \tilde{b}(t)$ is defined as,

$$\gamma \widetilde{b}(t) \equiv +\frac{3\delta E}{2} \pm \frac{\gamma^2 B_z b_z}{(\gamma^2 B_z^2 + |\widetilde{E}|^2)^{1/2}} \pm \frac{|\widetilde{E}|^2 \gamma^2 b_z^2}{2(\gamma^2 B_z^2 + |\widetilde{E}|^2)^{3/2} + O(b_z^3)}.$$
(5.6)

In the case where B_z is nonzero but $B_x = B_y = 0$, the renormalized noise can be approximated as,

$$\gamma \widetilde{b}(t) \approx \pm \frac{\gamma^2 B_z b_z}{(\gamma^2 B_z^2 + |\widetilde{E}|^2)^{1/2}} \pm \frac{|\widetilde{E}|^2 \gamma^2 b_z^2}{2(\gamma^2 B_z^2 + |\widetilde{E}^2)^{3/2}} + O(b_z^3), \tag{5.7}$$

and the largest contribution of the noise to the frequency shift between the energy eigenstates is from the first term in Eq. 5.7, i.e.,

$$\gamma \widetilde{b}(t) \approx \frac{\gamma^2 B_z b_z}{(\gamma^2 B_z^2 + |\widetilde{E}|^2)^{1/2}}.$$
(5.8)

On the other hand, in the case where B_x is nonzero but $B_y = B_z = 0$, the linear noise term $B_z b_z$ in Eq. 5.6 becomes zero, and the renormalized noise can be approximated as,

$$\gamma \widetilde{b}(t) \approx \frac{2\gamma^2 B_x b_x}{D} \pm \frac{\gamma^2 b_z^2}{2|\widetilde{E}|}.$$
(5.9)

The frequency shift given by Eq. 5.7 includes a term quadratic in b_z as well as a term linear in b_x that is scaled by the zero-field splitting D. Equations 5.8 and 5.9 show that when $|\gamma \mathbf{b}(\mathbf{t})| \ll |\gamma \mathbf{B}| \ll D$, the transverse magnetic field reduces the effective noise amplitude $\tilde{b}(t)$ experienced by the electron spin of the NV⁻ center, suppressing the mechanism of decoherence. For example, numerical calculation using parameters $D/2\pi = 2870$ MHz, $E/2\pi = 4.85$ MHz, and $\gamma b_x/2\pi = \gamma b_y/2\pi = \gamma b_z/2\pi \sim 0.7$ MHz (estimated from the free induction decay of our sample with an estimated NV⁻ concentration of ~5 ppm and a nitrogen concentration of ~100 ppm) shows that the frequency shifts associated with magnetic noise are smaller by about a factor of ~8 when a magnetic field of 25 G is applied perpendicular to the NV⁻ quantization axis, as compared to the case where the magnetic field is applied parallel to the NV⁻ axis.

5.4 Results and Discussion

We experimentally measured the coherence decay of the NV⁻ center using a Hahn echo pulse sequence with optically detected electron spin resonance (ODESR) techniques at a static magnetic field of 25 G, applied parallel or perpendicular to the NV⁻ axis. The detailed experimental procedure for ODESR is described elsewhere [157]. As shown in Fig. 5.2, the spin-echo signal of the NV⁻ center decays about twofold more slowly when the field is perpendicular to the NV⁻ axis. We note that Dolde et al. showed that the coherence time of a single NV⁻ center in the presence of inhomogeneous broadening is greatly increased when the longitudinal magnetic field becomes zero, [151] which could be explained by the renormalization of the linear noise term shown in Eqs. 5.8 and 5.9.

Next, the coherence time of the NV⁻ center at various polar angles θ was measured, and a striking angular dependence of the coherence time on the external magnetic field was observed. Specifically, the electron spin-coherence time of the NV⁻ center is relatively insensitive to the angle (θ) between the NV⁻ quantization axis and the external magnetic field when θ is varied between 0° and ~80°, but T₂ increases sharply as the angle is increased from 85° to 90°, with a maximum at $\theta=90^{\circ}$, as shown in Fig. 5.3.

This angular dependence of the spin-coherence time is due to renormalization of the noise, and the mechanism is completely different than in the case where 13 C nuclear spins dominate



Figure 5.2: Coherence decay of ensemble NV⁻ electron spins with an external magnetic field of ~25 G applied parallel or perpendicular to the NV⁻ quantization axis (solid lines are fits to a single exponential decay). The measured coherence time was $1.17\pm0.01\mu$ s for $\theta = 0^{\circ}$ (crosses) and $2.01\pm0.01\mu$ s for $\theta = 90^{\circ}$ (circles).

the bath. In a weak magnetic field, the spin-coherence time of the NV⁻ center in a bath dominated by the ¹³C nuclear spins is very sensitive to the magnetic field alignment and is at a minimum with the external magnetic field perpendicular to the NV⁻ axis. This is due to a position-dependent modification of the effective g tensor of nearby ¹³C nuclear spins when the transverse component of the external field enhances the mixing of electronic and nuclear states [143, 147, 153]. In contrast, the coherence time of the electron spin is lengthened by a transverse field when the NV⁻ center interacts with a bath of N_S centers, since the first-order frequency shift associated with the fluctuating field component b_z is eliminated. In general, fluctuating magnetic field components along x, y, and z can cause decoherence of the NV⁻ electron spins by inducing inhomogeneous frequency shifts. However, direct spin-flip relaxation due to the perpendicular components of the fluctuating magnetic fields is negligible, since the spectral density of the fluctuating dipole fields that couple the electron spin states (separated by ~7 MHz at the transverse field of ~25 G) is at least three orders of magnitude smaller than the secular broadening. The coherence time is limited by secular broadening, and it can be written as [80, 136],

$$\frac{1}{T_2} = \gamma^2 \tilde{b}^2 \tau_0, \tag{5.10}$$

where τ_0 is the characteristic correlation time of the fluctuating field in the bath. On the basis of Eq. 5.10, we expect that the coherence time (T_2) will increase greatly due to the



Figure 5.3: Coherence decay rate $(1/T_2)$ as a function of magnetic field orientation (θ) with respect to the NV⁻ axis at ~25 G. The solid line is a fit of experimental data $(1/T_2)$ to Eq. (10) using τ_0 as a free parameter, together with an offset that accounts for the residual noise contributions. The value $\gamma b_z/2\pi \sim 0.69 \pm 0.01$ MHz was estimated from the free induction decay, while $E/2\pi \sim 4.85$ MHz was estimated from the ODMR spectrum at ambient field. The outliers at 55° and 65°, which might be affected by NV⁻ centers in other orientations, were not included in the fitting.

aforementioned noise scaling. For instance, a decrease in magnetic noise by a factor of ~8 corresponds to an increase in the coherence time by a factor of ~60 at 25 G field applied perpendicular to the NV⁻ axis. Though the theoretical model predicts a large enhancement in the coherence time, our experimental results might be limited by residual linear noise of the form given by Eq. 5.8, due to the imperfect zeroing of B_z . For example, with residual $B_z \sim 0.5$ G, comparable to the Earth's magnetic field (the ambient field in our experiment), the linear noise term with $B_z b_z$ in the numerator dominates the renormalized noise in Eq. 5.6. It is also possible that the experimental results might be limited by other sources of decoherence not included in the model, such as electric field noise, strain noise, and/or the strongly coupled ¹³C nuclei [147, 151, 154]. A larger enhancement of spin-coherence time is therefore expected for NV⁻ centers in isotopically enriched ¹²C diamond, where decoherence, in the absence of ¹³C nuclei, is primarily due to the residual N_S centers [53, 87].

Under the assumption that the term proportional to $B_z b_z$ in Eq. 5.6 is dominant, experimental measurements of $(1/T_2)$ as a function of polar angle were fitted to Eq. 5.10 using τ_0 as a free parameter with $\gamma b_x/2\pi = \gamma b_z/2\pi \sim 0.7$ MHz. We also include an offset term that accounts for the residual noise contributions from other terms in Eq. 5.6. Excellent agreement between experimental data and the theoretical model was obtained, as shown in Fig. 5.3. At $\theta = 55^{\circ}$ or 65° , transition frequencies of the NV⁻ centers in other orientations are close to the transition frequencies of the centers we intended to observe. Therefore, outliers in red at 55° and 65° are not included in the fitting, since the coherence decay was likely affected by efficient cross relaxation between the NV⁻ centers in different orientations or by off-resonant contributions of those NV⁻ centers. This would result in faster decay due to imperfections in the π pulse for the off-resonant components.

We further measured the coherence time of the NV⁻ center as a function of the magnitude of the external magnetic field, oriented either parallel to the NV⁻ axis or perpendicular to the NV^{-} axis, as shown in Fig. 5.4. As the external magnetic field parallel or perpendicular to the NV⁻ axis increased to ~ 20 G, the coherence time of the NV⁻ center increased rapidly. At zero field, there are degenerate states in a N_S center, allowing for fast transitions driven by the dipole fields. However, the degeneracy is removed as the field is increased to ~ 25 G, where the electron Zeeman interaction is comparable to the hyperfine interaction of the N_S center. This freezes out most of the dynamics of the bath, which is gradually suppressed more fully as the field increases further [84]. When a larger magnetic field (≥ 25 G) was applied parallel to the NV⁻ axis, the NV⁻ coherence time slowly increased. On the other hand, the NV^{-} coherence time increased faster when the magnetic field was applied perpendicular to the NV⁻ axis, which could be due to the renormalization of the noise through the E term in Eqs. 5.4 and 5.9. We note that in principle further suppression of decoherence can be achieved by applying transverse electric and/or strain fields that can increase E through the electric dipole interaction. [151] We found that the dependence of coherence time (T_2) on the perpendicular magnetic field levels off at larger magnetic fields of ~ 50 G. This is possibly due to the non-negligible contribution of the linear noise term in Eq. 5.9.

Just as in the spin-echo experiments, the coherence times under the CPMG pulse were also enhanced by a transverse field, i.e., to 9.8 μs from ~5.8 μs with a longitudinal field, as



Figure 5.4: Spin-coherence time as a function of the amplitude of a magnetic field applied parallel to the NV⁻ axis ($\theta = 0^{\circ}$), or perpendicular to the NV⁻ axis ($\theta = 90^{\circ}$). (Solid lines serve to guide the eye.)

shown in Fig. 5.5. Spin-coherence time under dynamical decoupling pulse has been reported to observe a power-law relation $T_2 \sim N^r$, where N is the number of π pulse, and the index r is related to characteristics of the bath [53, 158, 159]. The spin-coherence time of the ensemble of NV⁻ centers in our sample fits well to the power-law relation with $r \sim 0.47\pm0.04$ for longitudinal fields and $r \sim 0.42\pm0.01$ for transverse.

In conclusion, we demonstrated that a transverse magnetic field enhanced the spincoherence times by approximately a factor of 2 from that with a longitudinal magnetic field. Experiments qualitatively agreed with our noise renormalization model that shows effective dipole fields experienced by the NV⁻ electron spins can be renormalized by the external magnetic field and the zero-field splitting parameters of the NV⁻ center, resulting in suppression of the decoherence of the NV⁻ electron spin at a given external magnetic field. Our measurements also showed that the spin-coherence time of the NV⁻ center in type I-b diamond is associated with fast spin reorientation of the N_S center, which are greatly suppressed in magnetic fields larger than ~25 G. Further enhancement of spin-coherence time with transverse magnetic field is expected for NV⁻ centers in isotopically enriched ¹²C diamond, where ¹³C nuclei are greatly depleted. Our method can be used to enhance the coherence time of NV⁻ centers and similar spin systems for various applications in metrology and quantum-information technology.



Figure 5.5: Spin-coherence time of ensemble NV⁻ centers as a function of the number of π pulses (N) in the CPMG pulse sequence at ~75 G applied parallel or perpendicular to the NV⁻ quantization axis. Solid lines are fits to $T_2 \sim N^r$ with $r = 0.47 \pm 0.04$ for $\theta = 0^{\circ}$ and 0.42 ± 0.01 for $\theta = 90^{\circ}$

Chapter 6

Optically Detected Nuclear Quadrupole Resonance

This chapter was previously published in Ref. [160] and is republished here, with minor changes, with permission.

6.1 Abstract

We report sensitive detection of the nuclear quadrupolar interaction of the ¹⁴N nuclear spin of the negatively charged nitrogen-vacancy (NV^-) center using the electron spin-echo envelope modulation technique. We applied a weak transverse magnetic field to the spin system so that certain forbidden transitions became weakly allowed due to second-order effects involving the nonsecular terms of the hyperfine interaction. The weak transitions cause modulation frequency is primarily determined by the nuclear quadrupolar frequency; numerical simulations confirm the analytical results and show excellent quantitative agreement with experiments. This is an experimentally simple method of detecting quadrupolar interactions, and it can be used to study spin systems with an energy structure similar to that of the NV^- center.

6.2 Introduction

Recently, the negatively charged nitrogen-vacancy (NV⁻) centers in diamond have drawn much attention for applications ranging from physics to biology because of their favorable optical and spin properties. High spin polarization to the $m_s = 0$ state at room temperature via optical pumping [85], convenient optical readout of the spin states via spin-state-dependent fluorescence detection, and long electron spin coherence time of milliseconds [87] at room temperature offer opportunities for using NV⁻ centers as sensitive detectors or in spin-based quantum information technologies [31, 32, 37, 38, 139–141, 157]. Here, we report the optical detection of the nuclear quadrupolar interaction of the $^{14}\mathrm{N}$ nuclear spin associated with NV⁻ centers.

The interaction of nuclei with the local electric field gradient can provide information about orbital electron states, so the nuclear quadrupole coupling constant is often used to study bond hybridization, degree of covalency, and orbital population in molecules that contain a nucleus of angular momentum $I \ge 1$ [80,161]. It can also be used as a fingerprint of target molecules in narcotics and explosives [162,163] due to the strong dependence of the quadrupole coupling constant on the electronic environment [161,164–166].

Several techniques are used to measure nuclear quadrupolar interactions. For instance, nuclear magnetic resonance (NMR) spectroscopy is used to measure the quadrupolar coupling when it is a small perturbation to the much larger Zeeman interaction [80]. For atoms with a large atomic number, however, the quadrupolar coupling can be comparable to or larger than the nuclear Zeeman interaction inside a high-field NMR spectrometer. In this case, nuclear quadrupole resonance (NQR) in a low magnetic field or near-zero magnetic field [167–169] can be used to measure pure quadrupole resonance. In NQR, a radiofrequency excitation pulse is applied at a frequency resonant with a transition of the quadrupolar Hamiltonian, resulting in a linearly oscillating signal similar to a free induction decay. However, at near-zero magnetic fields, the thermal polarization at room temperature is very low because \mathcal{H}_Q/kT is small. NQR measurements therefore often require ultrasensitive detectors, such as superconducting quantum interference devices [170] or vapor cell magnetometers [171].

Alternatively, electron spin-echo envelope modulation (ESEEM) [11] has been used on photo-excited triplet states of certain molecular crystals to measure nuclear quadrupole coupling constants and/or hyperfine coupling constants [168, 172, 173]. In a magnetic field applied parallel to the electron spin quantization axis, the anisotropic terms of the hyperfine interaction, such as $S_z A_{zx} I_x$, give different nuclear spin eigenstates for different states of the electron spin. In other words, changes in the electron spin state project the nuclear spin onto a different set of eigenstates. As a result, the envelope of the electron spin echo is then modulated at frequencies determined by the hyperfine interaction, the nuclear quadrupolar interaction, and the nuclear Zeeman interaction [174].

The ¹⁴N nuclear spin associated with NV⁻ center, however, does not induce any modulation in the electron spin-echo envelope when a magnetic field is applied parallel to the NV⁻ quantization axis. This is because the quantization axis of the ¹⁴N nuclear spin is parallel to the NV⁻ quantization axis and the nuclear spin eigenstates are independent of the electron spin state. Thus, any effect of the frequency shifts due to interactions involving the nuclear spin is completely removed by the spin echo. Other more elaborate techniques, such as optically detected Raman heterodyne NMR or optically detected Raman heterodyne electron nuclear double resonance (ENDOR), have therefore been employed to extract the nuclear quadrupole coupling constant from the dependence of the spectral peaks on magnetic field strength (~1000 G) and orientation [28, 175].

For the experiments reported here, we applied a small transverse magnetic field perpendicular to the NV^- quantization axis and observed modulations in the echo envelope of the NV^- electron spin, as shown in figure 6.1. The theoretical model described below shows that



Figure 6.1: Solid lines represent experimental results (circle or square markers are used only for the purpose of figure legends), and dashed lines represent simulation results. An external magnetic field of 75 G was applied along the NV⁻ axis ($\theta = 0^{\circ}$) or perpendicular to the NV⁻ axis ($\theta = 90^{\circ}$). Modulation of the exponential decay for $\theta = 90^{\circ}$ is due to the ¹⁴N nuclear quadrupolar coupling of the NV⁻ center. The inset shows the experimental result for the CPMG pulse sequence with 10π pulses when the magnetic field is oriented at $\theta = 90^{\circ}$

the transverse magnetic field mixes electron spin states, which in turn leads to mixing between product states of the electron and nuclear spin due to the hyperfine interaction terms $S_+ I_-$ and $S_- I_+$. This mixing of product states, which is a second-order effect involving two nonsecular terms in the Hamiltonian, causes certain forbidden transitions to become weakly allowed. In general, forbidden transitions lead to modulation of the electron spin-echo envelope [11]. The simulations described below confirm that under our experimental conditions, the nuclear quadrupolar Hamiltonian determines the modulation frequencies.

6.3 Optically detected ESR with the NV^- center

Optically detected electron spin resonance (ODESR)¹ was employed to measure the coherence decay of the NV⁻ center using the Hahn echo (HE) pulse sequence [10, 11] or the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [130, 131] in the presence of a static magnetic field of ~75 G, applied perpendicular to the NV⁻ axis. A diamond sample with an estimated NV⁻ concentration of ~ 5 ppm and a nitrogen concentration of less than ~ 100 ppm was mounted on a printed circuit board, and a microwave (MW) field was applied using a small loop (~1.5 mm in diameter) fabricated on a printed circuit board. The MW frequency was matched to the transition frequency between two electron states (denoted by $|\psi_z\rangle$ and $|\psi_y\rangle$). The NV⁻ center was optically excited by a 532-nm laser, and the fluorescence signal was detected by an avalanche photo diode. The detailed experimental procedure for ODESR is described in the experimental section of this thesis.

As a reminder, the NV⁻ center in diamond consists of a substitutional nitrogen atom at a carbon lattice site and a vacancy adjacent to the nitrogen atom, as shown in Fig. 6.2. The negatively charged NV⁻ center has electron spin S = 1 in the ground state with $m_s = 0$ and $m_s = \pm 1$ sublevels that are separated by a zero-field splitting of 2.87 GHz that characterizes the spin-spin interactions [94, 96, 104].

ESEEM has previously been studied for NV⁻ centers in diamond with natural-abundance $(\sim 1.1\%)^{13}$ C nuclei and low (on the order of parts per billion) ¹⁴N impurities. Under these conditions, the envelope modulation of electron spin-echo signals is frequently dominated by the strongly coupled ¹³C nuclear spins that are randomly distributed in the diamond lattice [26, 143]. Due to the anisotropic hyperfine interaction between NV⁻ centers and neighboring ¹³C nuclear spins, the electron spin-echo signal shows modulation even in a magnetic field applied along the NV⁻ quantization axis. The modulation becomes more complicated when the magnetic field is no longer aligned along the axis of the NV⁻ center. A misaligned magnetic field enhances the electron-nuclear spin state mixing, and the g-factor of the¹³C nuclei becomes position dependent, often this is discussed in the literature as an 'enhanced g-factor' effect. Ultimately this leads to neighboring ¹³C nuclei precessing at different frequencies depending on their position relative to the NV⁻ center, this significantly changes the shape of the electron spin modulation in an ESEEM experiment. [143, 147, 154].

In contrast to the hyperfine interaction with ¹³C, the hyperfine interaction with the ¹⁴N

¹The terms ODMR and ODESR are used interchangeably in this thesis.



Figure 6.2: The blue sphere with a blue arrow represents the ¹⁴N nuclear spin, and the light gray sphere with a gray arrow at the vacancy represents the NV⁻ electron spin. The green arrow represents the z component of the electric field gradient at the ¹⁴N nuclear site. Dark gray spheres represent carbon atoms in the diamond lattice. The red arrow represents the external magnetic field along the x axis

nuclear spin of the NV⁻ center is almost isotropic and has principal axes parallel to the NV⁻ axes [176]. Nuclear spin mixing within manifolds defined by a given eigenstate of the electron spin is generally suppressed due to the large quadrupolar interaction (~ 5 MHz) that is also parallel to the NV⁻ quantization axis [84]. Therefore, modulation associated with the ¹⁴N nuclear spin of the NV⁻ center has not been observed in the spin-echo envelope.

However, a weak transverse magnetic field (~ 75 G) can induce mixing in the NV⁻ electron spin states, and we show below that as a result, nonsecular terms of the hyperfine interaction enable forbidden transitions that cause modulation of the spin-echo envelope at the ¹⁴N quadrupolar frequency. Although the Zeeman interaction with a weak transverse field is still a small perturbation to the large zero-field-splitting Hamiltonian (~ 1000 G) of the NV⁻ center, the mixing of electron spin states induced by the Zeeman interaction is accompanied by mixing of product states induced by the hyperfine interaction. The forbidden transitions that prevent complete refocusing by a MW π pulse in a spin echo are due to this mixing of product states, a second-order effect involving the transverse field, as well as the nonsecular terms of the hyperfine interaction.

6.4 Theory

The spin Hamiltonian of the ground state NV^- center is [94, 176]

$$\mathcal{H} = \mathcal{H}_{ZFS} + \mathcal{H}_B + \mathcal{H}_Q + \mathcal{H}_{HF}, \tag{6.1}$$

where,

$$\mathcal{H}_{ZFS} = D[S_z^2 - \mathbf{S}(\mathbf{S}+1)/3] + E(S_x^2 - S_y^2),$$

$$\mathcal{H}_B = \gamma_e \mathbf{B} \cdot \mathbf{S} - \gamma_{^{14}N} \mathbf{B} \cdot \mathbf{I},$$

$$\mathcal{H}_Q = Q[I_z^2 - \mathbf{I}(\mathbf{I}+1)/3],$$

$$\mathcal{H}_{HF} = \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} = \mathcal{H}_{HF\parallel} + \mathcal{H}_{HF\perp},$$

$$= A_{\parallel}S_z I_z + A_{\perp}(S_+I_- + S_-I_+)/2.$$
(6.2)

Where $D/2\pi = 2870$ MHz and $E/2\pi = \sim 2.75$ MHz (sample dependent) are zero-field splitting parameters of the NV⁻ center, $Q/2\pi = -5.04$ MHz is the nuclear quadrupole coupling [176], γ_e is gyromagnetic ratio of the NV⁻ electron spin, γ_{14N} is the gyromagnetic ratio of the ¹⁴N nuclear spin, and **A** is the hyperfine tensor, with $A||/2\pi = 2.3$ MHz and $A\perp/2\pi$ = 2.1 MHz. The energy-level diagram for the NV⁻ center in the presence of a transverse magnetic field of 75 G along the x axis is shown in Fig. 6.3. S and I are the electron and nuclear spins, respectively and z is defined to be along the NV⁻ quantization axis.

For qualitative analysis, let us first consider a spin Hamiltonian where the hyperfine interaction $\mathcal{H}_H F$ has been turned off in equation 6.2. In the presence of a weak transverse external magnetic field B_x along the x axis, $m_s = -1$ and $m_s = +1$ states are no longer good quantum numbers, so we must use perturbation theory to determine the new basis states



Figure 6.3: The Hamiltonian \mathcal{H}_{ZFS} is responsible the zero-field splitting of the NV⁻ center, \mathcal{H}_B governs the Zeeman interaction, \mathcal{H}_Q governs the quadrupolar interaction, and \mathcal{H}_{HF} governs the hyperfine interaction. Approximate energy eigenstates are indicated next to the corresponding energy levels, where $|\psi_x\rangle$, $|\psi_y\rangle$, and $|\psi_z\rangle$ are electron spin states and $|\phi_x\rangle$, $|\phi_y\rangle$, and $|\phi_z\rangle$ are nuclear spin states. On the right side of the figure, the product state making the dominant contribution to each energy eigenstate is shown. Allowed (solid arrows) and forbidden (dashed arrows) spin transitions are also shown

expressed in terms of the old basis. The energy eigenstates are approximately,

$$\begin{aligned} |\psi_z^{(0)}\rangle &= |m_s = 0\rangle, \\ |\psi_x^{(0)}\rangle &= \frac{1}{\sqrt{2}}(-|m_s = +1\rangle + |m_s = -1\rangle), \\ |\psi_y^{(0)}\rangle &= \frac{i}{\sqrt{2}}(|m_s = +1\rangle + |m_s = -1\rangle), \end{aligned}$$
(6.3)

and the nuclear eigenstates are approximately,

$$\begin{aligned} |\phi_{z}^{(0)}\rangle &= |m_{n} = 0\rangle, \\ |\phi_{x}^{(0)}\rangle &= \frac{1}{\sqrt{2}}(-|m_{n} = +1\rangle + |m_{n} = -1\rangle), \\ |\phi_{y}^{(0)}\rangle &= \frac{i}{\sqrt{2}}(|m_{n} = +1\rangle + |m_{n} = -1\rangle). \end{aligned}$$
(6.4)

(States with subscript x, y, or z are eigenstates of the corresponding Cartesian spin operators.) The superscript (0) indicates that these states are zero-order approximations that do not include mixing of electron spin states separated by the zero-field splitting D or nuclear spin states separated by the quadrupole coupling Q.

The mixing due to the Zeeman interaction, neglected in these zero-order approximations, is represented by coefficients $\gamma_e B_x/D$ for electron spins and $\gamma_N B_x/Q$ for the nuclear spin. A transverse magnetic field of ~75 G, together with the E splitting, separates the energies of the electron spin eigenstates $|\psi_y^{(0)}\rangle$ and $|\psi_x^{(0)}\rangle$ by ~20 MHz. We studied only the transitions associated with states $|\psi_z^{(0)}\rangle$ and $|\psi_y^{(0)}\rangle$ due to a resonant MW $\pi/2$ pulse of 50 ns; for simplicity, our analysis neglects possible off-resonant effects involving the state $|\psi_x^{(0)}\rangle$.

In addition to causing shifts in the energy, the transverse field induces small but non-negligible mixing of the electron states $|\psi_z^{(0)}\rangle$ and $|\psi_y^{(0)}\rangle$ such that the electron spin eigenstates can be approximated as,

$$|\psi_z\rangle \approx |\psi_z^{(0)}\rangle + \Delta |\psi_y^{(0)}\rangle, \tag{6.5}$$

and,

$$|\psi_y\rangle \approx \Delta' |\psi_z^{(0)}\rangle + |\psi_y^{(0)}\rangle, \tag{6.6}$$

where mixing coefficients $|\Delta| \approx |\Delta'| \approx \gamma_e B_x/D \sim 0.07$. The electron spin state $|\psi_x\rangle$ can be identified with $|\psi_x^{(0)}\rangle$, which is an eigenstate of the Hamiltonian representing the Zeeman interaction with the transverse field, B_x . In the notation for states $|\psi_y\rangle$ and $|\psi_z\rangle$, we retain the subscripts used for the corresponding zero-order states, even though these mixed electron states are not eigenstates of Cartesian spin operators. At the same level of approximation, the nuclear spin eigenstates are,

$$|\phi_z\rangle \approx |\phi_z^{(0)}\rangle,\tag{6.7}$$

and,

$$|\phi_{x,y}\rangle \approx |\phi_{x,y}^{(0)}\rangle. \tag{6.8}$$

Here it is seen that we neglect the mixing term since $\gamma_{^{14}N}B_x/Q$ is an order of magnitude smaller than $\gamma_e B_x/D$.

We will now move into a product basis description of the electron and nuclear states, represented as : $|\psi_j\rangle|\phi_k\rangle$. Until now we have defined our eigenstates for the case where we have a transverse magnetic field B_x , but no ¹⁴N hyperfine interaction. We will now explore how these states change when we turn on the axial part of the hyperfine interaction. The term proportional to $S_z I_z$ in the hyperfine interaction causes mixing between the product states $|\psi_y\rangle|\phi_x\rangle$ and $|\psi_x\rangle|\phi_y\rangle$, as well as between $|\psi_y\rangle|\phi_y\rangle$ and $|\psi_x\rangle|\phi_x\rangle$. In particular, the states $|\psi_y\rangle|\phi_x\rangle$ and $|\psi_y\rangle|\phi_y\rangle$ that participate in resonant transitions are replaced by $|\psi_y\rangle|\phi_x\rangle + \eta|\psi_x\rangle|\phi_y\rangle$ and $|\psi_y\rangle|\phi_y\rangle + \eta'|\psi_x\rangle|\phi_x\rangle$, respectively, where the coefficients η and η' represent mixing due to the hyperfine interaction.

We see that the forbidden transitions enabled by this mixing cause modulation of the spin-echo envelope. For example, the transition $|\psi_z\rangle|\phi_y\rangle \leftrightarrow |\psi_y\rangle|\phi_x\rangle$ is forbidden by the selection rules for the MW field because of the change in the nuclear spin state, but the transition $|\psi_z\rangle|\phi_y\rangle \leftrightarrow (|\psi_y\rangle|\phi_x\rangle + \eta|\psi_x\rangle|\phi_y\rangle)$ is weakly allowed. The transition $|\psi_z\rangle|\phi_y\rangle \leftrightarrow (|\psi_y\rangle|\phi_x\rangle + \eta|\psi_x\rangle|\phi_y\rangle$ is also allowed, so a MW $\pi/2$ pulse creates a coherence between $|\psi_z\rangle|\phi_y\rangle$ and a linear combination of the states $|\psi_y\rangle|\phi_x\rangle + \eta|\psi_x\rangle|\phi_y\rangle$ and $|\psi_y\rangle|\phi_y\rangle + \eta'|\psi_x\rangle|\phi_x\rangle$. The evolution of this linear combination causes modulation in the spin-echo envelope. Since the nuclear spin states $|\phi_x\rangle$ and $|\phi_y\rangle$ have the same energy under the quadrupolar Hamiltonian, the energy difference between states $|\psi_y\rangle|\phi_x\rangle + \eta|\psi_x\rangle|\phi_y\rangle$ and $|\psi_y\rangle|\phi_y\rangle + \eta'|\psi_x\rangle|\phi_x\rangle$ is small, and the envelope modulation occurs at very low frequencies.

Now let us consider how the eigenstates change when $\mathcal{H}_{HF\perp} = A_{\perp}(S_{\perp}I_{\perp} + S_{\perp}I_{\perp})$ is also included in the spin Hamiltonian. In the basis of product states $|\psi_i\rangle |\phi_k\rangle$, the largest matrix elements of $\mathcal{H}_{HF\perp}$ have magnitude ~ A_{\perp} . These matrix elements cause mixing between pairs of product states for which the electron is in distinct spin states, e.g., $|\psi_{y}\rangle|\phi_{z}\rangle$ and $|\psi_{z}\rangle|\phi_{y}\rangle$. The operator $\mathcal{H}_{HF\perp}$ also has smaller matrix elements of magnitude $\sim \gamma_e B_x A_\perp / D$ that mix $|\psi_y\rangle|\phi_y\rangle$ and $|\psi_y\rangle|\phi_z\rangle$, as well as $|\psi_z\rangle|\phi_y\rangle$ and $|\psi_z\rangle|\phi_z\rangle$, because $|\psi_z\rangle$ and $|\psi_y\rangle$ are each a mixture of $|\psi_z^{(0)}\rangle$ and $|\psi_y^{(0)}\rangle$. The larger matrix elements of $\mathcal{H}_{HF\perp}$ involve states separated by the large zero-field splitting (2870 MHz) and thus introduce negligible mixing $\sim A_{\perp}/D$, but mixing due to the smaller matrix elements cannot be neglected, since the states are separated only by the nuclear quadrupolar frequency (~ 5 MHz). In particular, the mixing of states separated by the quadrupolar frequency is $\sim \gamma_e B_x A_\perp/(DQ)$, while the mixing of states separated by the zero-field splitting is smaller by a factor of ~ 40 . The significant mixing of states is a second-order effect that depends on two nonsecular terms in the Hamiltonian. A resonant MW field induces allowed transitions (marked as solid arrows in Fig. 6.3) but also causes additional forbidden transitions (marked as dashed arrows in Fig. 6.3) due to this second-order effect. The spin coherences that develop as a result of the forbidden transitions involve linear combinations of energy eigenstates that have the nuclear spin in different eigenstates of the quadrupolar Hamiltonian, and the spin-echo envelope is modulated at the quadrupolar frequency because of the evolution of these linear combinations. The coherences are not fully refocused by the MW π pulse unless the period of free evolution that precedes the π pulse allows for an integral number of oscillations at the quadrupolar frequency.

6.5 **Results and Discussions**

For quantitative analysis, numerical simulations were carried out using the density matrix formalism. The spin Hamiltonian shown in Eq. 6.1 was first numerically diagonalized. Simulations were performed in an interaction frame where the large energy differences were removed from the diagonalized Hamiltonian. The time-dependent Hamiltonian $\gamma_e B_1 \cdot S_x \cos(\omega t)$, which represents a resonant MW field with frequency ω and amplitude B_1 directed along the x axis, was first represented in the energy eigenbasis and then transformed into this interaction frame for simulation of the pulses. The population of the electron spins after optical polarization was assumed to be in state $|m_s = 0\rangle$. After the MW $\pi/2$ pulse, spin coherences freely evolve under the interaction-frame Hamiltonian during $t = 2\tau$, with a π pulse applied at $t = \tau$. At $t = 2\tau$, another $\pi/2$ pulse is applied to convert coherences to populations, and the ESEEM signal for each τ is obtained from the resulting population in state $|m_s = 0\rangle$.

For numerical simulations, we used parameters corresponding to the experimental conditions: $E/2\pi = 2.75$ MHz, $B_x = 75$ G, and $\gamma_e B_1/2\pi = 5.00$ MHz. Coherence decay due to the various spin-spin relaxation processes was phenomenologically included in the simulation. As shown in Fig. 6.1, the simulations showed excellent agreement with experimental results. When the magnetic field was applied along the x axis, perpendicular to the NV⁻ axis, observable modulation appeared in the ESEEM signal. No modulation was observed when the magnetic field was applied along the z axis, parallel to the NV⁻ quantization axis. The simulated modulation depth (~ 4%) of the ESEEM signal also showed excellent agreement with experimental data. When a CPMG pulse sequence with 10π pulses was employed in the experiments, this modulation was amplified, as shown in the inset of Fig. 6.2.

The frequency spectra shown in Fig. 6.4 were obtained by taking the Fourier transform of the experimental and simulation data after exponential decay was subtracted from the data. (The result of subtracting the exponential decay is shown in the inset of Fig. 6.4.) The experimental spectrum acquired with the Hahn spin-echo sequence showed excellent quantitative agreement with the simulated spectrum at ~5 MHz. Simulation and experimental data also showed a spectral peak at ~10 MHz, consistent with the fact that ESEEM gives envelope modulation at frequencies $\omega_0, \omega_+, \omega_0 - \omega_+$, and $\omega_0 + \omega_+$, where ω_0 and ω_+ stand for the transition frequencies of the nuclear spin associated with the electron spin states $|\psi_z\rangle$ and $|\psi_y\rangle$, respectively [174].

It was confirmed in the simulation that $\mathcal{H}_{HF\perp}$ is responsible for the electron-nuclear mixing, since the modulation disappeared when A_{\perp} was set to zero. It was also confirmed that the frequencies of modulation changed linearly with the quadrupole coupling frequency. Under our experimental conditions, the modulation frequencies of the spin-echo envelope are primarily determined by the quadrupolar interaction of the ¹⁴N nuclear spin. The energy eigenstates responsible for the modulation can be approximated as product states in which the nuclear spin is in an eigenstate of the quadrupolar Hamiltonian \mathcal{H}_Q , and \mathcal{H}_Q makes the dominant contribution to the energy differences that determine the modulation frequencies; in particular, the contribution from the hyperfine interaction and the Zeeman interaction is



Figure 6.4: Solid lines with circles or squares represent experimental data obtained using the HE pulse sequence or the CPMG pulse sequence, respectively. The dotted line with triangles represents a simulation that used the HE pulse sequence. The inset shows the ESEEM signal after the exponential decay was subtracted.

less than 1% of the contribution of that of the quadrupolar interaction.

Other frequency components in the experimental data could originate from the hyperfine interactions with neighboring ¹³C nuclei in the diamond lattice. The modulation frequencies due to the hyperfine interaction with ¹³C nuclei could be greatly modified from the secular term A_{zz} of the hyperfine interaction, since the net contribution of the hyperfine interaction to transition frequencies is a function of magnetic field strength and orientation when a static magnetic field is misaligned from the NV⁻ quantization axis. This has been well studied in the literature and is not a focus of our discussion [143, 147, 174]. In our method, the frequency shift of the ESEEM signal due to the Zeeman Hamiltonian is less than $\sim 1\%$, so the measurement of the quadrupole interaction does not require a highly accurate measurement of the applied field. The accuracy of our measurement method is currently limited by the NV^{-} spin coherence time, since the oscillation due to the quadrupole interaction is indirectly measured by observation of the electron spin coherence. Therefore, with a highpurity diamond sample that has a lower concentration of NV⁻ centers and ¹⁴N impurities, the measurement accuracy can be improved. Finally, the spin coherence time was enhanced by a factor of ~ 2 when the magnetic field was oriented perpendicular to the NV⁻ quantization axis, as shown in Fig. 6.1. This was attributed to the fact that the effective noise amplitude can be renormalized by the combined effect of the transverse magnetic field and the zero-field splitting parameters, as discussed in our recent paper [54].

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6.6 Conclusion

We reported optical detection of the ¹⁴N nuclear quadrupole coupling in the NV⁻ center by employing ESEEM techniques in the presence of a transverse magnetic field. Numerical simulations and a theoretical model showed excellent agreement with experimental results. By applying a small magnetic field of 75 G perpendicular to the NV⁻ quantization axis, we modified the symmetry of the spin system. The ¹⁴N nuclear quadrupole coupling, which is normally undetectable in spin-echo experiments with the NV⁻ center, modulated the spinecho envelope as a result of forbidden transitions associated with second-order mixing involving two nonsecular terms in the Hamiltonian. Although other techniques such as optically detected Raman heterodyne ENDOR and optically detected Raman heterodyne NMR have been employed to detect the quadrupolar interaction, our technique is experimentally much simpler. In principle, this technique can be used to map out the hyperfine tensor and/or the nuclear quadrupole coupling tensor of a spin system with a similar energy structure [172].

Chapter 7

Optically Detected Cross-Relaxation

This chapter was previously published in Ref. [42] and is republished here, with minor changes, with permission.

7.1 Abstract

The application of magnetic resonance spectroscopy at progressively smaller length scales may eventually permit chemical imaging of spins at the surfaces of materials and biological complexes. In particular, the negatively charged nitrogen-vacancy (NV⁻) center in diamond has been exploited as an optical transducer for nanoscale nuclear magnetic resonance. However, the spectra of detected spins are generally broadened by their interaction with proximate paramagnetic NV⁻ centers through coherent and incoherent mechanisms. Here we demonstrate a detection technique that can resolve the spectra of electron spins coupled to NV⁻ centers, in this case, substitutional nitrogen and neutral nitrogen-vacancy centers in diamond, through optically detected cross-relaxation. The hyperfine spectra of these spins are a unique chemical identifier, suggesting the possibility, in combination with recent results in diamonds harboring shallow NV⁻ implants, that the spectra of spins external to the diamond can be similarly detected.

7.2 Introduction

Recent experiments have employed single NV⁻ centers to detect distant nuclear spins in diamond [140,141,147,177,178] and external, nanoscale nuclear spin ensembles [37,38], laying the foundations for routine magnetic resonance imaging with nanometre resolution [36,179]. Electron spins, in the form of either paramagnetic centers in the diamond lattice or radicals intimately associated with the diamond surface, have also been optically detected through their coupling to the NV⁻ center [180–182]. The characteristic spectra of the detected spins, however, are often broadened by these same interactions [180–182]. The spectroscopic details are, in general, not sufficiently resolved to provide critical chemical information.



Figure 7.1: (a) Transition frequency of each electron spin system in diamond as a function of the magnetic field. The magnetic field is aligned along one of the NV⁻ axes (solid and open black squares: the NV⁻ center parallel to and ~109° relative to B_z , respectively; solid blue triangles: the N_S center; solid and open purple circles: the NV⁰ center parallel to and ~ 109° relative to B_z , respectively). The conditions where cross-relaxation occurs are labelled by green circles at $B_z = 0$, 51.4, 59.5 and 102.5 mT. (**b** – **d**) The structures of the NV⁻ (**b**), N_S (**c**) and NV⁰ (**d**) centers. Orange outlines indicate sites at which ¹³C atoms could experience strong hyperfine coupling (> 10 MHz) with the corresponding electron spin in the ground states of the NV⁻ and N_S centers, or in the ⁴A₂ excited state of the NV⁰ center. (**e**) Illustration of the NV⁻ center (grey spin symbol) in cross-relaxation with the nearest N_S center (blue spin symbol, ~ 3 nm away) or NV⁰ center (purple spin symbol) in diamond.

One demonstration of optically detected spectroscopy of the electron spin using the NV⁻ center was performed by sweeping the magnetic field through the cross-relaxation condition between the NV⁻ and the substitutional nitrogen defect (N_S) near ~ 51.4 mT, where the two electron spin species have commensurate transition frequencies [83] (Fig. 7.1a). However, this method requires frequency matching between allowed transitions in the two spin systems at a specific magnetic field, such that spin flip-flop zero-quantum processes (with $\Delta m = 0$, where $\Delta m = 0$ is the change of total angular momentum) induced by the dipolar interaction are nearly energy conserving and become allowed; this prevents it from serving as a generic method for optical detection of dark electron or nuclear spins. Frequency matching is only one of many possible conditions that can lead to cross-relaxation [14] (Fig. 7.1a). For instance, cross-relaxation can occur via multiple quantum (for instance, $\Delta m = \pm 2$) spin flip-flop processes that involve the exchange of angular momentum with the lattice, or via multiple spin flips in one system combined with one spin flop in another [14]. Cross-relaxation becomes more obvious at weak magnetic fields, where the difference in the Zeeman energy between spin species is reduced. This is indeed the case for NV⁻ centers in diamond (Fig. (7.1b), as previously suggested by observed dips in the NV⁻ spin-lattice relaxation time (T_1) and by sudden reduction in the optical hole depth (hole bleaching) in the zero-phonon adsorption, in weak magnetic fields (<5 mT) [108, 120, 121, 183].

Here, using a method based on cross-relaxation phenomena in a weak magnetic field, we demonstrate optically detected spectroscopy of electron spins, namely, the N_S and neutral nitrogen vacancy (NV⁰) centers in diamond (Fig. 7.1c, and d, respectively), by identifying their respective spectral characteristics in the NV⁻ cross-relaxation ODMR spectrum. This technique is the only demonstrated ODMR method that can provide detailed spectra of the detected electron spins. Such information is essential for the use of the NV⁻ center for the detection and identification of radicals or relaxation centers, and for the transduction of chemically informative NMR spectra by optical means.

7.3 Results

In the following, we present optically detected hyperfine spectra of dark electron spins. We demonstrate this technique on an ensemble of NV⁻ centers in a single-crystal diamond, host to several types of paramagnetic defects that may be identified from the ODMR spectra as shown in Fig. 7.2 (see Methods section). The measured spectra have chemically informative fine features that differ vastly from ODMR spectra based on the allowed electron spin transitions of the NV⁻ center alone [44,58]. The majority of the fine features can be assigned to the N_S center [120], [121], [108], [119], from which almost all calculated transitions (blue lines on top of each spectrum) are present in the observed spectra. For instance, the three calculated transition frequencies of the N_S center at $B_z \approx 0$ mT (that is, ambient field), namely, 18.4, 130.2 and 148.6 MHz (Figure 7.3), are matched with peaks in the ODMR spectrum (Fig. 7.2a).

The intensity of the peaks agrees well with the 1:3 population ratio of N_S centers oriented either parallel to the B_z (for example, the peak at 240 MHz in Fig. 7.2d) or $\approx 109^{\circ}$ relative to



Figure 7.2: The spectra are acquired at (a) $B_z \approx 0$ mT (ambient field), (b) $B_z = 1.44$ mT, (c) $B_z = 2.29$ mT and (d) $B_z = 3.89$ mT. The fine features of the observed spectra are assigned to the N_S and NV^0 centers, which are colored in blue and purple, respectively. Such assignment is based on the calculated transition frequencies of the N_S (blue lines on the top of each spectrum) and NV^0 (purple lines on the top of each spectrum) centers. All transitions from the NS center and the relevant transitions of the NV^0 center oriented parallel to B_z are shown. The short and long blue lines correspond to the N_S centers oriented parallel to B_z and $\sim 109^\circ$ relative to B_z , respectively, which should have a 1:3 ratio in population. The red asterisks (*) represent the difference in transition frequencies between the magnetically inequivalent NV^- centers.

 B_z (the peak at 223 MHz in Fig 7.2d). The observed fine features are also plotted against the calculated hyperfine structure of the N_S center as a function of magnetic field in Fig. 7.4a. Most of the observed fine features can be assigned to the unique hyperfine structure of the N_S center at various magnetic fields (< 5mT). Although the N_S center is a dark spin whose hyperfine parameters were determined by electron paramagnetic resonance (EPR) [119], our observations show that the characteristic spectra of the N_S centers can also be resolved by ODMR.

With the majority of the fine spectral features assigned, there remain some fine features that cannot be matched with the hyperfine structure of the N_S center, as shown in green squares in Fig. 7.3a. This indicates that we may have observed other defect centers in diamond. The unassigned fine features can be used to identify these additional centers by comparing with the unique hyperfine structures of known defect centers that are commonly found in diamond [94].

We find that the remaining fine features are most consistent with transitions of the NV⁰ center in the spin-3/2 ${}^{4}A_{2}$ excited state [122–124]. The purple lines on top of each spectrum in Fig. 7.2 are representative of the transitions of the NV⁰ center. The eigenstates of the NV⁰ center as a function of field can be seen in Fig. 7.5.¹ For instance, there is an excellent agreement between calculations and the observed transitions at 60, 70, 84 and 92 MHz at 1.44 mT (figures 7.2b and 7.3b). These demonstrate that the NV⁰ center is optically detected with part of its characteristic spectrum resolved. As the magnetic field increases above 2 mT, most transitions of the NV⁰ center overlap with those of the N_S center, suggesting that a very weak magnetic field is required to separately resolve the two species. The NV⁰ center is a dark state of the NV⁻ center because it requires shorter excitation and detection wavelength than those optimized for NV⁻ center, and unlike the NV⁻ center it has not been detected previously using ODMR [124, 125, 184]. EPR spectra of the NV⁰ center have been observed only recently for its ${}^{4}A_{2}$ exited state under laser illumination [122].

We demonstrate here that the ${}^{4}A_{2}$ excited state of the NV⁰ center can also be detected by ODMR via its coupling to the NV⁻ center. Our observation of the NV⁰ center agrees with the previous characterization of this particular diamond crystal, in which a considerable amount of NV⁰ centers have been created along with NV⁻ centers [44]. The ratio of zerophonon line intensity of NV⁻ and NV⁰ was measured to be 39 depending on the depth from the diamond surface, after proton irradiation and annealing at 500°C, and this ratio was shown to remain on the same order of magnitude for subsequent annealing processes [44]. Felton et al. [122] have shown in an EPR experiment that the NV⁰ center is selectively polarized to the S⁰_z =±1/2 sublevel of its spin-3/2 ⁴A₂ excited state under laser illumination. An optical excitation energy higher than ~2.2 eV (wavelength <563 nm) is required for such polarization [122], suggesting that the 532nm laser used in our experiment can also polarize the ⁴A₂ exited state of the NV⁰ center. This polarization process of the NV⁰ center starts with the optical excitation from the ²E ground state to the ²A₂ excited state [185], followed

¹We would encourage the reader to review the Diamond Spin Bath section in Chapter 3, where the form of the N_S and NV^0 Hamiltonians is described. The eigenvalues in figures 7.3 and 7.5 were calculated using the hamiltonians described in Chapter 3.



Figure 7.3: (a) The majority of fine features (open squares) can be assigned to the hyperfine structure of the N_S center (blue solid lines: the N_S center parallel to B_z ; blue dashed lines: the N_S center ~109° relative to B_z). Several fine features that cannot be assigned to the N_S center are highlighted by green boxes. All possible transitions between the hyperfine structure of the N_S center are shown. (b) The remaining fine features (within green boxes) agree well with the hyperfine structure of the NV⁰ center (purple solid lines: the NV⁰ center parallel to B_z ; purple dashed lines: the NV⁰ center ~109° relative to B_z). For simplicity, only the relevant hyperfine transitions are shown for the NV⁰ center.



Figure 7.4: The energy levels of the N_S center as a function of magnetic field are shown. Energy levels were calculated using the N_S Hamiltonian, Eq. 3.8 in Chapter 3 of this thesis. m_{s^1} denotes the N_S center electron spin state, while m_{I^1} denotes the ¹⁴N nuclear spin. Figure (a) shows the energy levels at weak fields, and Figure (b) shows the energy levels for a magnetic field range of 0-200 mT. Solid lines are N_S centers oriented along the applied magnetic field B_z and the dashed lines are the N_S centers that are oriented ~ 109° with respect to B_z.

by the intersystem crossing from ${}^{2}A_{2}$ to ${}^{4}A_{2}$ excited state with the details of its mechanism requiring further investigation [185]. The long lifetime of the ${}^{4}A_{2}$ excited state allows for detection by EPR measurement [122]. Our observations of the ${}^{4}A_{2}$ excited state of the NV⁰ center are consistent with these previous experimental and theoretical studies on the NV⁰ center. The origin of NV⁰-related peaks can potentially be further examined by using orange (wavelength ~593 nm) rather than green light (wavelength ~532 nm) for optical excitation [125]. The former wavelength can maximize ionization (from NV⁻ to NV⁰) and minimize recombination (from NV⁰ to NV⁻) such that the majority (~80%) of the NV⁻ centers are in the NV⁰ charged state [125]. This can be combined with EPR techniques to improve the precision of the hyperfine structure of the NV⁰ center [122]. However, our instrument is currently not set up to perform either wavelength-dependent excitation or conventional low temperature EPR experiments, and so further investigation is warranted.

7.3.1 Cross-relaxation as the optical sensing mechanism

The favorable optical and magnetic properties that allow ODMR observation of the NV⁻ center are known to be absent in the N_S and NV⁰ centers: the N_S center is a dark spin, while the NV⁰ center is a dark state of the nitrogen-vacancy center and its fluorescence intensity does not depend on the spin state [83], [124, 125, 184]. The radiofrequency (RF)-driven transitions of the N_S and NV⁰ centers must therefore be sensed by the neighboring NV⁻ centers to be observed in the ODMR spectra. That is to say, the magnetic resonance of the N_S and NV⁰ centers are converted into an optical signal by the NV⁻ center. Such indirectly detected transitions should therefore be a second-order effect compared with the allowed transitions of the NV⁻ center. This is consistent with the much smaller (~1/60) optical contrast of the observed hyperfine features compared with that of the allowed NV⁻ transitions.

On the other hand, the fine features of the N_S and NV⁰ centers are observed at the frequencies of their own hyperfine structure, far below the allowed transition frequencies of the NV⁻ center. This suggests that the N_S and NV⁰ centers are instead perturbing seemingly forbidden transitions, for instance, the transition between the $|+1\rangle$ and $|-1\rangle$ sublevels of the NV⁻ center. Such perturbation is possible because there is indeed an energy match between the hyperfine levels of the N_S (or NV⁰) and the $|+1\rangle \leftrightarrow |-1\rangle$ sublevels of the NV⁻ center [120]. Although the $|+1\rangle \leftrightarrow |-1\rangle$ transition cannot be directly induced by application of microwaves (MWs) due to the selection rule ($\Delta m_S \pm 1$), cross-relaxation between the NV⁻ and N_S centers via the $|+1\rangle$ and $|-1\rangle$ sublevels at weak magnetic field is an established process that has been thoroughly studied, both experimentally and theoretically [120, 121], [186–189].

Cross-relaxation can occur among almost any two spin systems as long as there is an energy matching condition, such as between two sub-ensembles of NV^- centers at zero field, between the NV^- and N_S centers at weak magnetic field, and between magnetically inequivalent or equivalent NV^- centers at certain values of the strength and angle of the applied magnetic field [120, 121], [186–189]. Cross-relaxation between two spin systems occurs when



Figure 7.5: The energy levels of the NV⁰ center as a function of magnetic field are shown. Energy levels were calculated using the NV⁰ Hamiltonian, Eq. 3.9 in Chapter 3 of this thesis. m_{s^0} denotes the NV⁰ center electron spin state, while m_{I^0} denotes the spin state of the ¹⁴N nuclear spin of the NV⁰. Figure (a) shows the energy levels at weak fields. The additional splitting of the NV⁰ levels is due to the ¹⁴N hyperfine interaction. Figure (b) shows the energy levels for a magnetic field range of 0-200 mT. Because the ¹⁴N hyperfine interaction becomes small relative to the electron Zeeman energy at larger fields, we have neglected to include the additional splitting as in the top graph.

energy exchange between two systems provides additional spin-lattice relaxation pathways for both systems. The signature of cross-relaxation can be verified by perturbing the relaxation process of one spin system while monitoring the relaxation response (that is, the change in T_1) of the other system.

The fact that we observe the characteristic hyperfine spectra of N_S and NV^0 centers within the ODMR continuous-wave (CW) spectra of NV^- centers is thus a signature of cross-relaxation. First, the applied RF drives the hyperfine transitions of N_S and NV^0 centers only (as it is off-resonance for NV^- allowed transitions). Second, the ODMR signal comes solely from the NV^- centers because both N_S and NV^0 are dark under the experimental conditions [83], [124], [125], and the optical signal (steady-state fluorescence intensity) is directly related to the T_1 of the NV^- centers [83]. We therefore altered the relaxation response of NV^- centers by perturbing the relaxation process of N_S or NV^0 centers. More specifically, the energy matching condition required by cross-relaxation is satisfied between the $|+1\rangle$ and $|-1\rangle$ sublevels of the NV^- centers and the hyperfine levels of the N_S or NV^0 centers. The spin flip-flop processes between NV^- and N_S (or NV^0) centers can thus be induced by the dipolar interaction between them, which couples the two spin systems via efficient energy exchange and leads to cross-relaxation. Here we must point out that cross-relaxation via the $|+1\rangle$ and $|-1\rangle$ sublevels of the NV^- centers will result in a decrease in the steady-state fluorescence intensity.

Since the $|0\rangle$ sublevel of the NV⁻ center is the brighter state, a relative population change between $|+1\rangle$ and $|-1\rangle$ sublevels will not directly lead to a change in fluorescence intensity. However, while the ODMR CW spectra are acquired, the processes of optical pumping towards the $|0\rangle$ sublevel and relaxation back to the $|\pm 1\rangle$ sublevels reach equilibrium. When cross-relaxation occurs via the $|+1\rangle$ and $|-1\rangle$ sublevels, a different equilibrium condition will be established, resulting in lower population on the $|0\rangle$ sublevel and thus a decrease in fluorescence intensity.² This occurs because the continuous optical pumping process couples together the populations of all three sublevels of the NV⁻ center, and enhanced relaxation between the $|+1\rangle$ and $|-1\rangle$ sublevels will affect the population on the $|0\rangle$ sublevel as well. Such a phenomenon has been observed in experiment, and the cross- relaxation mechanism has been suggested as well [120]. This is different from the pulsed ODMR experiment, in which the polarization is optically initialized first, and then MW irradiation is used to manipulate the populations of different sublevels; the steady-state condition in the CW experiment ceases to exist when the optical pumping cycle is turned off. Furthermore, when the spin transition between two hyperfine levels of the N_S or NV^0 spin system is driven by resonant RF, the spin-lattice relaxation of the NV⁻ spin will be further enhanced (that is, T_1 is shortened) by cross-relaxation. As a result, the fluorescence intensity of the NV⁻ center decreases [83, 121, 125], leading to the observed ODMR peaks as shown in Fig. 7.2, serving as the basis for cross-relaxation spectroscopy. Here, the resonant RF only affects the N_S or NV⁰ spins, while the laser irradiation and optical detection occur through the NV⁻ centers (Fig. 7.6). The cross-relaxation provides an effective energy exchange between the

²The steady state fluorescence can be modeled by considering the optical pumping rate and RF pumping rate, see Eq. 7.1-7.4, in Theory section for a more explicit explanation.

spin systems and serves as a generic mechanism to convert the magnetic resonance of N_S and NV^0 spins into changes in optical signal of the NV^- center.

7.3.2 Cross-relaxation among NV⁻ centers

In addition to the fine features in the ODMR spectra, relatively broad peaks with fullwidth at half-maximum (FWHM) of ~ 20 MHz are also observed. The central frequency of each broad peak agrees well with the calculated energy difference between magnetically inequivalent NV⁻ centers (different orientations either parallel to B_z or ~109° relative to B_z) or between neighboring magnetically equivalent NV centers (both parallel to B_z). The calculated energy difference is labelled by asterisks in Fig. 7.2 and the NV⁻ energy levels as a function of magnetic field are indicated in Fig. 7.7. We see that in Fig. 7.2b, the middle broad peak at ~54 MHz matches the energy difference between the $|+1\rangle$ sublevel of NV⁻ parallel to B_z and the $|-1\rangle$ sublevel of NV⁻ ~109° relative to B_z (or vice versa), suggesting that cross-relaxation occurs between magnetically inequivalent NV⁻ centers.

This can be further verified, as will be shown later, owing to the different resonance frequencies for the magnetically inequivalent NV⁻centers. The FWHM here (~ 20 MHz) is approximately twice the FWHM of the peaks associated with allowed transitions in ODMR spectra (~ 10 MHz, see Fig. 7.8), providing additional evidence that the applied RF matches the energy difference between two NV^- centers. Here, the RF enhances cross-relaxation by providing the energy difference between two NV⁻ centers, which otherwise need to exchange energy via phonons [118]. This effect is different from the cross- relaxation between NV⁻ and N_S (or NV⁰) centers, in which RF provides the energy cost for N_S (or NV⁰) transitions, and the energy cost for $NV^- \leftrightarrow N_S$ or $NV^- \leftrightarrow NV^0$ spin flip-flop processes is taken from the lattice. In both cases, the RF is applied to provide the energy required for efficient cross-relaxation process. An additional broad peak at ~ 28 (or ~ 81) MHz in Fig. 7.2b matches the energy difference between the $|+1\rangle$ sublevel of one NV⁻ and the $|-1\rangle$ level of another NV⁻ in close proximity, both of which are $\sim 109^{\circ}$ relative to B_z (or both parallel to B_z). It is likely that cross-relaxation between magnetically equivalent NV⁻ centers is the dominant mechanism for these peaks. This, however, cannot be further verified because the magnetically equivalent NV⁻ centers have identical resonance frequencies, and neighboring centers thus cannot be separately addressed. There could also be contributions from the small mixing between $|0\rangle$ and $|\pm 1\rangle$ sublevels that makes the $|-1\rangle \leftrightarrow |+1\rangle$ transition weakly allowed and causes a small optical contrast. Nevertheless, the three broad features have near equal intervals because the energy levels of neighboring NV⁻ centers, either magnetically inequivalent or equivalent, are nearly evenly spaced (Fig. 7.7a). The hyperfine interaction with ${}^{13}C$ is not considered here because only about 3.3% of the NV⁻ centers experience strong hyperfine interaction (~ 130 MHz, Figure 3.12) with a first-shell ¹³C. For the majority of the NV⁻ centers in the ensemble, hyperfine interaction with ¹³C causes line broadening with little effect on the central frequency³.

³The strength of ¹³C-NV⁻ hyperfine coping at different lattice sites is listed in table 3.6.



Figure 7.6: Cross-relaxation occurs between the NV⁻ and N_S centers, between the NV⁻ and NV⁰ centers and between magnetically inequivalent NV⁻ centers. When one of the N_S or NV⁰ transitions is saturated by RF radiations, the fluorescence intensity of the NV⁻ centers decreases, resulting in the observed ODMR spectra


Figure 7.7: The energy levels of the NV⁻ center as a function of magnetic field are shown. Energy levels were calculated using the NV⁻ Hamiltonian, Eq. 3.3 in Chapter 3 of this thesis. $|0\rangle$, $|-1\rangle$, and $|+1\rangle$ are the NV⁻ electron spin states. Figure (a) shows the energy levels at weak fields. Figure (b) shows the energy levels for a magnetic field range of 0-200 mT.



Figure 7.8: Cross-saturation between NV⁻ centers with different orientations, either parallel to B_z or ~ 109° relative to B_z at $B_z = 1.16$ mT. The black line shows the ODMR spectrum (left and bottom axes) acquired near ~2.87 GHz, where the allowed transitions of the NV⁻ centers at different orientations can be resolved. The effective longitudinal relaxation time T_1^* (scatter data with error bars representing the s.d., right and top axes) is measured at 2.8375 GHz (blue arrow), the frequency of the $|0\rangle \leftrightarrow |-1\rangle$ transition of the NV⁻ centers oriented parallel to B_z , while saturating another MW frequency. The change in T_1^* is well correlated with the ODMR spectrum; T_1^* is significantly reduced (red arrows) when the saturating frequency is resonant with the transitions of the NV- centers oriented ~109° relative to B_z , or with the $|0\rangle \leftrightarrow |+1\rangle$ transition of the NV⁻ centers oriented parallel to B_z .



Figure 7.9: The ODMR spectrum is acquired at $B_z = 101.4 \text{ mT}$. The most intense peak, centered at ~2.857 GHz and colored orange, is an artifact whose second harmonic matches the frequency of the $|0\rangle \longleftrightarrow |+1\rangle$ ground state transition of the NV⁻ center parallel to B_z . Each resolved side peak is fitted into a Gaussian function and assigned to either the N_S center (blue curves) or the NV⁰ center (purple curve). The assignment is based on the calculated transition frequencies of each center and its respective Hamiltonian, as shown by the vertical bars at the bottom. All allowed transitions of the N_S center in the ground state are clearly resolved at the predicted transition frequencies (blue bars). The rest of the observed side peaks are consistent with the $|m_{S^0}\rangle = |-1/2\rangle \longleftrightarrow |+1/2\rangle$ transitions of the NV⁰ center in the 4A_2 excited state with discrepancies from the predicted transition frequencies (purple bars) probably due to the accuracy of the available spin Hamiltonian parameters

Cross-relaxation between magnetically inequivalent NV⁻ centers can be directly observed by measuring the spin-lattice relaxation time of the NV⁻ center parallel to B_z, while saturating either the transition of the NV⁻ center ~109° relative to B_z, or the other allowed transitions of the NV⁻ center parallel to B_z (see Methods). Figure 7.9 shows the apparent spin-lattice relaxation time (T₁*), measured at the $|0\rangle \leftrightarrow |-1\rangle$ transition frequency of the NV⁻ centers oriented parallel to B_z, as a function of the saturation MW frequency. The apparent relaxation time becomes much shorter when the saturation frequency is on resonance with either the allowed transitions of the NV⁻ centers ~109° relative to B_z, or with the $|0\rangle \leftrightarrow |+1\rangle$ transition of the NV⁻ centers parallel to B_z. These observations provide direct evidence that there is cross-relaxation among the NV⁻ centers. Since cross-relaxation is reciprocal, the apparent relaxation time measured at the frequency of any one of the four peaks in CW spectra will become shorter when the saturation frequency is tuned to the frequency of another peak. Note that saturation of dark electron spin transitions does not cause an observable change in the T₁* of the NV⁻ centers because of the relatively low polarization of the N_s and NV⁰ centers.

7.3.3 Cross-relaxation at the ground state-level anti-crossing

Additional evidence to support the claim that cross-relaxation is the conversion mechanism from magnetic resonance to optical signal is supplied by an investigation of spectra at other known conditions at which cross-relaxation occurs. It is known that cross-relaxation occurs near the ground state-level anti-crossing (GSLAC) at ~102.5 mT [120], where the $|0\rangle$ and $|-1\rangle$ sublevels of the NV⁻ center approach degeneracy and the $|0\rangle \leftrightarrow |+1\rangle$ transition frequency of the NV⁻ center is almost twice the transition frequencies of the N_S and NV⁰ centers (Fig. 7.1a).

Cross-relaxation at the GSLAC can occur through a NV⁻ flip paired with the flops of two electron spins, with the balance of the angular momentum transferred to the rigid lattice [14]. The applied resonant MW radiation induces transitions between energy levels of the N_S and NV⁰ centers, which indirectly affects the NV⁻ center via cross-relaxation. The cross-relaxation process itself is governed by the mutual interaction between spins, and thus is not directly affected by the applied MW. The characteristic peaks of the N_S and NV⁰ centers are clearly resolved and identified in the ODMR spectrum within the 2.7-3.0GHz range (Fig. 7.9). Four possible orientations of the N_S centers lead to two triplets (blue bars on the bottom of the spectrum in Fig. 7.9) with overlapping central peaks when the external field is aligned with one of the N_S (or NV⁻) symmetry axes [83], [182], [190].

The remaining peaks agree well with the calculated $|m_{S^0} = -1/2\rangle \leftrightarrow 1/2\rangle$ transition frequencies of NV⁰ centers oriented parallel to B_z; discrepancies and unassigned peaks may be due to the accuracy of the available quadrupolar interaction parameters [124], and the zero-field splitting and hyperfine interaction parameters that were determined for the ¹5NV⁰ system at the spin-3/2 ⁴A₂ excited state [122]. Although the S⁰_z = ±1/2 sublevels of the NV⁰ ⁴A₂ excited state are selectively polarized, the direct transition between them has not been observed by EPR, probably because it is obscured by other paramagnetic centers in diamond [122]. Near the GSLAC, the nearly complete electron spin polarization of the NV⁻ centers can be transferred to the neighboring electron spins via their mutual interactions, resulting in greater polarization [190] and thus greater signals from the N_S and NV⁰ electron spins, similar to observations at the cross-relaxation condition near ~51.4 mT [83]. Thus far, the hyperfine features of the N_S and NV⁰ centers in ODMR spectra are observed at two separate cross-relaxation conditions (that is, weak magnetic field and GSLAC). This confirms that the cross-relaxation serves as the sensing mechanism by converting magnetic resonance of the N_S and NV⁰ centers to an optical signal produced by the NV⁻ center.

7.4 Discussion

Our cross-relaxation spectroscopy technique generically detects the spectra of electron spins using the NV⁻ center (Fig. 4). The steady-state fluorescence intensity of the NV⁻ center is directly observed without requiring the creation or manipulation of NV⁻ spin coherences as in other methods. This effectively moves the detection of electron spins from the indirect to the direct frequency dimension, thereby improving both frequency resolution and detection sensitivity. Detection is no longer limited by the coherence time of the NV⁻ center, and as a result much longer detection times can be used to improve the signal-to-noise ratio. The fine frequency resolution and high sensitivity of this technique may also allow the identification of additional unknown paramagnetic centers that have been obscured by the N_S center in EPR [122] measurements, in a similar manner to our detection of the NV⁰ center. These results provide an optically detected analogue of nuclear magnetic cross-relaxation spectroscopy in solid and dilute spin systems [191, 192].

It may also be possible to use cross-relaxation spectroscopy for detection of electron spins external to the diamond sample. The potential detection distance through crossrelaxation should be at least ~8 nm, as estimated by the average separation of neighboring NV⁻ centers in our diamond sample, between which cross-relaxation is clearly detected in our measurements [193] . Such a detection distance would allow for observation and identification of dark electron spins deposited on the diamond surface [181], if using shallowimplanted NV⁻ centers in ultrapure diamond [87,194]. For that purpose, ultrapure diamond with much lower N_S center concentrations must be used to remove the background hyperfine features from the N_S impurities in diamond. The optically detected spectra of radicals via NV⁻ centers can be used to determine chemical identity by comparing with a database of characteristic hyperfine structures of known radicals, a process similar to existing EPR methods for determining hyperfine constants of a radical.

In Fig. 7.11 and section 7.6.3, we consider as an example the free radical diphenyl picryl hydrazyl, which has hyperfine structures vastly different from the detected centers in diamond [195, 196]. Furthermore, radicals on the diamond surface could be used as a detection intermediate for external nuclear spins located at even further distances [197]; an ensemble of radicals of a single type could significantly increase the detected magnetic flux [198], while spatially engineered arrays of radicals of different species could provide spatial resolution for detection of distant nuclear spins or simply act as a gradiometer [105, 182].

7.5 Methods

7.5.1 Materials and experiments

The diamond sample used in our experiments was fabricated commercially by Element-6 using high-pressure high-temperature synthesis. It was then irradiated, annealed and characterized as previously reported [44, 105], where it was labelled as sample S9. The diamond sample has been shown to contain NV⁻ centers (up to ~ 2 p.p.m. in the most dense location), N_S centers (~50 p.p.m.) and NV⁰ centers (NV⁻ : NV⁰ = 3 to 9, depending on the depth from the diamond surface) [44]. The average distance between nearest NV⁻ centers is ~ 8 nm and that between an NV⁻ center and the nearest N_S center is ~ 3 nm, as estimated by the Poisson distribution for the typical distance between neighboring particles [199]. The ODMR apparatus was described in detail elsewhere [58] and we only briefly describe it here. A continuous beam from a 532-nm laser with optical power of 2 mW is focused on the diamond by an objective lens with a numerical aperture of 0.7 to achieve optical power density of $\sim 5 \text{ mW} \ \mu m^{-2}$. The fluorescence signal from the NV⁻ is collected by an avalanche photo detector after passing a dichroic mirror and a long-pass filter [105]. The external magnetic field is applied using a permanent magnet aligned to one of the NV^{-} symmetry axes, with the field strength adjusted by the magnets distance to the diamond and determined using the NV^{-} centers as a magnetometer [44,58]. The RF radiation is swept from 1 to 300 MHz using a single copper wire loop to produce an oscillating magnetic field of ~ 0.1 mT in amplitude. The ODMR CW spectra record the steady-state fluorescence intensity under conditions of continuous RF excitation, compared with that with RF turned off for reference. The spectra are averaged over 2,000 scans. In the double resonance experiments, pulsed MW excitation is delivered using the same copper wire loop, while continuous MW radiation is applied with an additional copper wire to saturate additional transitions. A standard inversion recovery sequence is used to measure the change in T_1^* at the $|0\rangle \leftrightarrow |-1\rangle$ transition frequency of the NV⁻ centers oriented parallel to B_z , while saturating transitions of the NV⁻ centers oriented $\sim 109^{\circ}$ relative to B_z at a different MW frequency.

7.6 Cross Relaxation as the Optical Sensing Mechanism

7.6.1 Cross relaxation via the $|-1\rangle$ and $|+1\rangle$ sublevels of the NV⁻ centers reduces the steady state fluorescence intensity.

Cross relaxation via the $|-1\rangle$ and $|+1\rangle$ sub levels of the NV⁰ centers will cause a decrease in the steady-state fluorescence intensity. The fluorescence intensity is directly related to the polarization of NV⁻ spins because of the spin-dependent intersystem crossing, resulting in stronger emission intensity from the $|0\rangle$ sub level. During the acquisition of continuouswave ODMR spectra, a steady-state condition is established between optical pumping (which



Figure 7.10: The energy levels on the left are the triplet ground state of the NV⁻ center, and the energy level on the right are two relevant hyperfine energy levels of another spin $(N_S, NV^0, \text{ or } NV^- \text{ center})$. The grey arrow on the left indicates the optical pumping process including the optical excitation and the spin-dependent intersystem crossing (details not shown for simplicity).

increases polarization) and the spin-lattice relaxation (which decreases polarization) (Figure 7.10); the applied RF/microwave irradiation does not affect the NV^- polarization directly because they are off-resonance. The populations of all three NV^- sub levels, considering the cross-relaxation effect, are given by the following rate equations,

$$n_0 + n_{-1} + n_{+1} = N,$$

$$\frac{dn_0}{dt} = -w_-(n_0 - n_{-1}) - w_+(n_0 - n_{+1}) + p(n_{-1} + n_{+1}) = 0,$$
 (7.1)

$$\frac{dn_{-1}}{dt} = w_-(n_0 - n_{-1}) - w_\pm(n_{-1} - n_{+1}) - pn_{-1} - w_x(n_{-1}n_{S^+} - n_{+1}n_{S^-}) = 0,$$

where n_0 , n_{-1} and n_{+1} are the populations of three NV⁻ sub levels, respectively, w_- , w_+ , w_{\pm} are the relaxation rates among the NV⁻ sublevels, respectively, p is the overall rate of optical pumping through the intersystem crossing, n_{S^-} and n_{S^+} are the populations of two relevant energy levels of another electron spin system (N_S, NV⁰, or NV⁻), w_x is the cross relaxation rate ($w_x = 0$ if there is no cross relaxation), and N and N_S are the total number of NV⁻ centers and the other spin system, respectively. The steady-state population of each NV⁻ sub level can be calculated by setting dn/dt = 0 for each state. If there is no cross relaxation ($w_x = 0$), then the solution is,

$$\frac{n_0^{w_x=0}}{N} = \frac{p^2 + p(w_- + w_+ + 2w_\pm) + w_+ w_\pm + w_-(w_+ + w_\pm)}{p^2 + 2p(w_- + w_+ + w_\pm) + 3(w_+ w_\pm + w_-(w_+ + w_\pm))},$$

$$\frac{n_{-1}^{w_x=0}}{N} = \frac{pw_- + w_+ w_\pm + w_-(w_+ + w_\pm)}{p^2 + 2p(w_- + w_+ + w_\pm) + 3(w_+ w_\pm + w_-(w_+ + w_\pm))},$$

$$\frac{n_{+1}^{w_x=0}}{N} = \frac{pw_+ + w_+ w_\pm + w_-(w_+ + w_\pm)}{p^2 + 2p(w_- + w_+ + w_\pm) + 3(w_+ w_\pm + w_-(w_+ + w_\pm))}.$$
(7.2)

Adding the cross relaxation effect $(w \neq 0)$, the solution becomes,

$$\frac{n_0^{w_x \neq 0}}{N} = \frac{[p^2 + p(w_- + w_+ + 2w_\pm) + w_+ w_\pm + w_-(w_+ + w_\pm)] + w_x [pN_S + w_+ n_{S-} + w_- n_{S+}]}{[p^2 + 2p(w_- + w_+ + w_\pm) + 3(w_+ w_\pm + w_-(w_+ + w_\pm)] + w_x [(p+w_+ + w_-)N_S + w_+ n_{S-} + w_- n_{S+}]]},$$

$$\frac{n_{-1}^{w_x \neq 0}}{N} = \frac{pw_- + w_+ w_\pm + w_-(w_+ + w_\pm) + w_x n_{S+}(w_+ + w_-)}{[p^2 + 2p(w_- + w_+ + w_\pm) + 3(w_+ w_\pm + w_-(w_+ + w_\pm)] + w_x [(p+w_+ + w_-)N_S + w_+ n_{S-} + w_- n_{S+}]]},$$
(7.3)
$$\frac{n_{+1}^{w_x \neq 0}}{N} = \frac{[pw_- + w_+ w_\pm + w_-(w_+ + w_\pm)] + w_x n_{S-}(w_+ + w_-)}{[p^2 + 2p(w_- + w_+ + w_\pm) + 3(w_+ w_\pm + w_-(w_+ + w_\pm)] + w_x n_{S-}(w_+ + w_-)]}.$$

. Comparing these two solutions, we see that the cross relaxation term w_x provides additional relaxation pathways from the $|0\rangle$ sub level $(n_0 \longrightarrow^{w_x:|\pm 1\rangle} n_{S\pm})$ even though the cross relaxation occurs only via the $|-1\rangle$ and $|+1\rangle$ sub levels of the NV⁻ center. It is a well-known feature of cross relaxation phenomena that any additional relaxation pathways accelerate the relaxation process and shorten the T₁ of both spin systems. The increased relaxation rate, compared to the unchanged pumping rate, will lead to decreased population on $|0\rangle$ and therefore lower emission intensity under the steady-state condition (i.e., $n_0^{w_x=0} > n_0^{w_x\neq 0}$).

We can also compare $n_0^{w_x=0}$ and $n_0^{w_x\neq0}$ quantitatively by assuming for example $w_- \approx w_+ \approx w_{\pm}$ and $p \sim 10w_-$ for the NV⁻ center (i.e. the NV⁻ polarization is close to unity), and $n_{S^-} \approx n_{S^+} \approx N_S/2$ (corresponding to low polarization for the impurity spin, or for the saturation condition driven by microwave irradiation). We then have,

$$\frac{n_0^{w_x=0}}{N} \approx \frac{143}{169} > \frac{w_x[pN_S + w_+n_S - + w_-n_{S+}]}{w_x[(p+w_+ + w_-)N_S + w_+n_{S-} + w_-n_{S+}]} = \frac{121}{169},$$
(7.4)

which can be used to prove $n_0^{w_x=0} > n_0^{w_x\neq 0}$ by simple arithmetic (A/B>A'/B' \Rightarrow A/B > (A+x· A')/(B+x· B'), for positive numbers).

This also proves that cross relaxation via $|-1\rangle$ and $|+1\rangle$ sub levels of the NV⁻ center will reduce the emission intensity. Although changing the relative population between $|-1\rangle$ and $|+1\rangle$ sub levels does not change the emission intensity of the NV⁻ center directly, the newly established steady-state condition with cross relaxation will lead to a less populated $|0\rangle$ sub level and a decreased emission intensity. This is different from the pulsed experiment, in which the NV⁻ polarization is optically initialized first, and then microwave radiation is used to manipulate the population among different sub levels. The steady-state condition cannot be re-established after the laser is turned off.

In the language of spin temperature, the cross relaxation establishes a "thermal contact" between NV⁻ and N_S (or NV⁰ centers. The latter spin system has a spin temperature equal to room temperature when RF/microwave is turned off for ODMR signal reference, and a spin temperature above room temperature or even approaching infinite temperature when resonant RF/microwave is turned on. The spin temperature of the NV⁻ system will increase due to cross relaxation, leading to decreased emission signal (the reference signal). The spin temperature will further increase if a resonant RF/MW drives the spin temperature of N_S (or NV⁰) even higher (approaching infinite spin temperature upon saturation), leading to the observed ODMR signal in this study. The key here is that cross relaxation via the $|-1\rangle$ and $|+\rangle$ sub levels of the NV⁻ center establishes a "thermal contact" between NV⁻ and N_S (or NV⁰) centers: a spin temperature change in the N_S (or NV⁰) spin system can be sensed by the NV⁻ fluorescence intensity under the steady-state condition. This provides the mechanism of optical transduction that converts the magnetic resonance of electron spins to optical signal of the NV⁻ centers via cross-relaxation.

7.6.2 Average distance between neighboring centers

The typical concentration of the relevant paramagnetic centers (NV⁻, N_S, and NV⁰) in diamond are on the order of magnitude of ppm. In such dilute spin systems, the average distance between one NV⁻ center and its neighboring centers (NV⁻, N_S, and NV⁰) can be estimated by setting the probability of finding no neighboring center within a distance r of the NV⁻ center to 1/2 [193],

$$exp[-(4\pi\rho r^3/3)] = 1/2, \tag{7.5}$$

where ρ is the concentration of the relevant defect species. The average distance R is then simply given by $R = 0.55\rho^{-1/3}$, with $\rho(NV^-) \approx 2$ ppm and $\rho(N_S) \approx 50$ ppm as previously determined [44, 105]. The average distance between two neighboring NV⁻ centers is thus $R(NV^-) \approx 8$ nm and that between one NV⁻ center and its neighboring N_S center is $R(N_S)$ ≈ 3 nm. Such an average separation is a good estimation of effective detection distance based on the agreement between observed and calculated transition frequencies; the few anomalous NV⁻ centers with closer neighbors will experience significantly shifted transitions that are not evident in the measurements.

7.6.3 Simulated energy levels of a free radical

To further demonstrate the characteristic hyperfine structure of radicals (something which we believe might be measured using the methods we have developed here, see chapter 11 of this thesis) we calculate the energy levels of Diphenyl Picryl Hydrazyl (DPPH, a free radical) [195, 196]. The hyperfine structure of DPPH arises from one unpaired electron and two hydrazyl nitrogen atoms. The Hamiltonian of the system is given by [195, 196],

$$\mathcal{H}_{DPPH} = \gamma_e \mathbf{B} \cdot \mathbf{S}^{\mathbf{r}} + \mathbf{S}^{\mathbf{r}} \cdot \mathbf{A}^{\alpha} \cdot \mathbf{I}^{\alpha} + \mathbf{S}^{\mathbf{r}} \cdot \mathbf{A}^{\beta} \cdot \mathbf{I}^{\beta}, \tag{7.6}$$

where $\mathbf{S}^{\mathbf{r}}$ is the unpaired electron spin of DPPH ($\mathbf{S}^{r} = 1/2$), \mathbf{I}^{α} and \mathbf{I}^{β} are the α and β nitrogen spins (¹4N, $\mathbf{I}^{\alpha} = \mathbf{I}^{\beta} = 1$), respectively, and \mathbf{A}^{α} ($A_{z}^{\alpha} = 0$ MHz, $A_{x}^{\alpha} = A_{y}^{\alpha} = 52.4$ MHz) and \mathbf{A}^{β} ($A_{z}^{\beta} = 16.2$ MHz, $A_{x}^{\beta} = A_{y}^{\beta} = 77.0$ MHz) are the hyperfine tensors of the α and β nitrogen spins. The angle between the two symmetry axes (\mathbf{A}_{z}^{α} and A_{z}^{β}) is ~13° [195, 196]. The calculated energy levels of DPPH of different orientations are shown in figure 7.11.



Figure 7.11: The hyperfine energy levels of DPPH at weak magnetic fields (a) and between 0-200 mT (b), as calculated based on the Hamiltonian given in Supplementary Eq. 4. The solid and dashed lines represent the orientations with the magnetic field parallel to the A_z^β axis and perpendicular to the A_z^β axis of DPPH, respectively.

Chapter 8

Sensitive Magnetic Control of Ensemble Nuclear Spin Hyperpolarization in Diamond

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8.1 Abstract

Dynamic nuclear polarization, which transfers the spin polarization of electrons to nuclei, is routinely applied to enhance the sensitivity of nuclear magnetic resonance. This method is particularly useful when spin hyperpolarization can be produced and controlled optically or electrically. Here we show complete polarization of nuclei located near optically polarized nitrogen-vacancy centres in diamond. Close to the ground-state level anti-crossing condition of the nitrogen-vacancy electron spins, ¹³C nuclei in the first shell are polarized in a pattern that depends sensitively upon the magnetic field. Based on the anisotropy of the hyperfine coupling and of the optical polarization mechanism, we predict and observe a reversal of the nuclear spin polarization with only a few millitesla change in the magnetic field. This method of magnetic control of high nuclear polarization at room temperature can be applied in sensitivity enhanced nuclear magnetic resonance of bulk nuclei, nuclear-based spintronics, and quantum computation in diamond.

8.2 Introduction

Several techniques based on spin polarization transfer have been developed to enhance the magnetization of nuclei. They are applied widely in NMR-based probes of the chemistry and structure of proteins, materials and organisms [200–203], in devices that exploit spin-dependent electron transport in solids (spintronics) [204, 205], in neutron scattering for



Figure 8.1: (a) Atomic representation of NV⁻ center in diamond lattice with one of the firstshell carbon sites (C_a occupied by ¹³C (red). (b) The energy diagram of the ground-state triplet (³A, solid lines) and the excited-state triplet (³E, dashed lines) versus the magnetic field. The level anti-crossing occurs at ~ 51 mT in the excited state (ESLAC, dashed circle) and at ~ 102.5 mT in the ground state (GSLAC, solid circle).

structural characterization [206, 207] and in quantum information experiments for preparation of pure initial states [82, 208]. Dynamic nuclear polarization (DNP), in particular, comprises a family of techniques that transfer the greater spin polarization of electrons to nearby nuclei through hyperfine-mediated processes [80, 81]. In a typical DNP experiment at high magnetic fields, stable paramagnetic centers (usually organic radicals) are introduced into an otherwise diamagnetic sample as a polarization source. The equilibrium polarization of electrons is sufficient to act as a polarization source for nuclei, because the gyromagnetic ratio of electrons is at least three orders of magnitude higher than that of nuclear spins [57, 209, 210]. In addition to the high magnetic field, the experiment requires cryogenic temperatures to attenuate competing spin-lattice relaxation processes, and it relies upon strong microwave irradiation near the electron precession frequency to accomplish polarization transfer. In alternative incarnations of this experiment that have been less generally applied, the initial electron polarization is produced by an optical pumping cycle involving the spin-orbit coupling [211] in a suitable substrate; the subsequent nuclear polarization can be controlled by electrical current in certain semiconductors and at cryogenic temperatures [212–214].

The negatively charged nitrogen-vacancy (NV^-) centre in diamond has been exploited in many applications, including solid-state magnetometry [31, 32, 44], bioimaging and in single-photon sources [215]. Among its unique properties, the NV⁻ centre (Fig. 8.1a) can be prepared in a near-perfect state of electron spin polarization by optical illumination. Unlike in semiconductors that exhibit optical nuclear polarization, the high magnetic purity of the lattice in which the NV⁻ defect is situated, and the correspondingly long spin-lattice relaxation times, means that this can be accomplished even at room temperature. This feature makes diamond a particularly attractive substrate for spintronic devices or as a general source of polarization for NMR experiments, in which spin order can be transferred from a hyperpolarized diamond lattice to external spins of interest [35,117]. The utility of the NV⁻ centre in either application would be enhanced by the precise and non-inductive control over the lattice nuclear polarization, as is possible electrically in certain [216] semiconductors but not for insulating solids. Further, strongly coupled and polarized nuclear spins may serve both as quantum bits in information processing experiments and as auxiliary quantum registers that enhance the fidelity of certain quantum algorithms [86, 144, 217].

The initial electron polarization of the NV⁻ results from optical pumping: the laser preferentially pumps the electron spin to the $|0\rangle$ sublevel of the spin triplet (³A) ground state and creates electron spin polarization on the order of unity. This occurs because the electron spin goes through a spin-dependent intersystem crossing from the excited triplet state $({}^{3}E)$, leading to enhanced spin polarization of the $|0\rangle$ sublevel in the ground state [103,218]. The laser can be gated to switch the electron polarization on and off, but the polarization does not depend linearly on the laser intensity. In general, the electronic polarization of the NV^{-} centre is not accompanied by nuclear polarization because of the mismatch in the electron and nuclear resonance frequencies. However, the electrons and nuclei can exchange polarization if the hyperfine interactions have a non-negligible role in the dynamics of the system [35]. Such a condition can be established near the level anti- crossing in the excited state (ESLAC at ~ 51 mT, Fig. 8.1b); near 100% polarization has been observed for nuclei such as ¹⁴N or ¹⁵N adjacent to the vacancy (that is, the nuclei of the nitrogen component of the NV⁻ centre), as well as proximal ¹³C. In these experiments, the broad dependence of ¹⁴N or ¹⁵N polarization on magnetic field suggests the involvement of the isotropic component of the hyperfine interaction (the hyperfine interaction with ¹⁵N or ¹⁴N is isotropic in the excited state [77, 176]). The ¹³C hyperfine couplings, on the other hand, are generally anisotropic in the ground state, and they vary with the lattice site [96,114]. As we will demonstrate below, the anisotropic hyperfine interaction can lead to a sharp dependence of electron- nuclear mixing, and hence nuclear spin polarization, on the magnetic field. This has been obscured in previous studies by the short lifetime of the excited state, and by the minimal electronnuclear mixing in the ground state near the ESLAC condition due to the different zero-field splitting in the ground and excited states [35, 117]. A level anti-crossing condition can also be reached in the ground state (GSLAC, or LAC for short, at ~ 102.5 mT, Fig. 8.1b) [83], whose long lifetime allows the electron-nuclear mixing to be probed in detail. Here, we demonstrate a near total nuclear polarization of an ensemble of the first-shell ${}^{13}C$ (${}^{13}C_a$, Fig. 8.1a) coupled to NV⁻ near LAC. It is convenient to study ${}^{13}C_a$, because the strong hyperfine interaction allows the transitions associated with the NV⁻⁻¹³C_a pair to be clearly resolved from those of NV⁻ centres without ${}^{13}C_a$. We further investigated, experimentally and theoretically, the dependence of such nuclear polarization on the magnetic field. Probed by RF excitation in continuous-wave optically detected magnetic resonance (ODMR) spectra, the frequency distribution and the relative intensities of observed transitions reveal only one level anti-crossing condition for the $NV^{-13}C_a$ pair, at a magnetic field slightly higher than that for NV⁻ without ${}^{13}C_a$. Near such level anti-crossing condition, the nuclear polarization



Figure 8.2: The spectra are acquired at (a) $B_z = 90.8$ mT with four peaks associated with NV⁻⁻¹³C_a pairs clearly resolved, and (b) $B_z=96.4$ mT, above which the $|\alpha\rangle \leftrightarrow |\delta\rangle$ transitions disappear. The spectra are averaged over 2,000 scans. All peaks are fit to Gaussian lineshapes. The intense primary peak associated with NV⁻ centres without ¹³C_a is used to determine the magnetic field as shown in light blue solid lines. The weaker peaks associated with NV⁻¹³C_a pairs are color-coded and labelled according to the related transitions determined in Fig. 8.10. The peak labelled by a red * is an artifact whose second harmonic matches the frequency of the main peak.

depends sensitively on the magnetic field: at the most sensitive region near 105 mT, the nuclear polarization changes from spin-up to spin-down and back to spin-up, within a few mT. The ${}^{13}C_a$ spin polarization serves as an illustrative example for ${}^{13}C$ at other lattice sites with different hyperfine parameters. Indeed, the polarization and control mechanism should apply to all hyperfine-coupled ${}^{13}C$, although each set of hyperfine parameters will give rise to a different nuclear polarization at the same magnetic field.

8.3 Results

At a given magnetic field, the degree of electron- nuclear spin state mixing is determined by the energy separation between the electron and nuclear eigenstates and the relative con-

tribution of the hyperfine interaction to the total Hamiltonian (that is, the matrix elements connecting these states). This also determines the energy levels and the resulting transition frequencies between the two mixed states that are eigenstates of the perturbed Hamiltonian. In turn, the intensities of the various transitions depend on the populations of the mixed states, and both the frequencies and the relative intensities of allowed transitions can be measured in ODMR spectra [35]. Figure 8.2 shows representative ODMR spectra of the NV^{-} ensemble near LAC. (see Figs 8.3 and 8.4 for additional spectra at ambient magnetic field and near LAC, respectively). The smaller peaks that are resolved from the intense primary peak are assigned to NV⁻ centres coupled to ${}^{13}C_a$ [77,114,219]. As there are only three equivalent C_a sites for each NV⁻, and because of the low natural abundance of ¹³C (1.1%), the peak intensities (that is, integrated area of the peak) associated with $NV^{-13}C_a$ pairs are much smaller than the primary peaks originating from the greater fraction of NV⁻ centres without ${}^{13}C_a$. The spectra taken near LAC may have one, two, three or four peaks, and are thus different from the spectra taken at ambient or low (<10 mT) magnetic field, see figure 8.3, where the two peaks associated with NV⁻¹³C_a pairs are separated by \sim 130MHz and asymmetrically located on either side of the primary peaks [219]. The number of observed resonances near LAC suggests that the electron-nuclear spins are in mixed states. Were this not the case, the selection rules permit only two electron spin transitions to be observed optically, each of which is associated with one nuclear spin state [86].

8.3.1 Theoretical calculations of energy levels and eigenstates.

The relevant NV⁻ spin Hamiltonian, including its hyperfine interaction with ${}^{13}C_a$, is given by [109, 147, 220],

$$\mathcal{H} = D \cdot S_z^2 + E(S_x^2 - S_y^2) + \gamma_e \mathbf{B} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} - \gamma_{^{13}C} \mathbf{B} \cdot \mathbf{I},$$
(8.1)

where the axial (D = 2,870 MHz) and transverse (E = 3.5 MHz) zero-field splitting parameters are determined from the spectra at ambient magnetic field, S is the electron spin of NV⁻ with the electron gyromagnetic ratio of γ_e , z is defined along the NV⁻ symmetry axis, B is the external magnetic field, I is the ¹³C_a nuclear spin with the gyromagnetic ratio γ_{13C} , and A is the hyperfine-interaction tensor between NV⁻ and ¹³C_a, given by A \perp =123 MHz and A|| = 205 MHz, with its principal axis ~74° relative to the symmetry axis of the NV⁻ as characterized by ESR [94].

This hyperfine tensor can also be quantized along the NV^- symmetry axis through a rotation [11,80],

$$\mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} = 129MHz \times S_z I_z + 80.4MHz \times (S_+ I_- + S_- I_+) -21.5MHz \times (S_z I_x + S_x I_z) + 18.9MHz \times (S_+ I_+ + S_- I_-),$$
(8.2)

where the **x** axis lies within the NV⁻¹³C_a plane, and **y** is perpendicular to the NV⁻- C_a plane, forming orthogonal coordinates (See Fig. 8.5), and the ladder operators are $S_{\pm} = S_x \pm i \cdot S_y$ and $I \pm = I_x \pm i \cdot I_y$. The Hamiltonian can then be diagonalized near LAC to obtain the



Figure 8.3: The observed transitions associated with $NV^{-13}C_a$ pairs (relatively weak peaks at 2814 and 2941 MHz on either side of the main peaks) are in excellent agreement with the transition frequencies (2813 MHz and 2941 MHz) calculated from the theory presented in the main text. The spectrum is averaged over 400 scans. Remaining uncertainties in these estimates arise from uncertainties in the source hyperfine parameters and inaccuracies in the measurement of the angle relative to the NV^- axis.



Figure 8.4: The spectra are acquired at $B_z = 104.2 \text{ mT}$ (a), $B_z = 105.2 \text{ mT}$ (b), and $B_z = 107.1 \text{ mT}$ (c). The spectra are averaged over 2000 scans. All peaks are fit to Gaussian lineshapes. The intense primary peak associated with NV⁻ centers without ${}^{13}C_a$ is used to determine the magnetic field as shown in light blue solid lines. The weak peaks associated with NV⁻- ${}^{13}C_a$ pairs are color- coded and labelled according to the related transitions specified in Fig. 8.10. The peak labelled by a red * is an artifact whose second harmonic matches the frequency of the main peak.



Figure 8.5: The symmetry axis of the NV⁻⁻¹³C_a hyperfine interaction is along the axis connecting the vacancy and ${}^{13}C_a$.

energy levels (Fig. 8.6) and eigenstates (Fig. 8.7 and figures 8.8, 8.9). The mixed states, namely $|\alpha\rangle$, $|\beta\rangle$, $|\chi\rangle$ and $|\delta\rangle$, are defined as in Fig. 8.6. Near the LAC, the energy of the $|0\rangle$ and $|-1\rangle$ sublevels converge, and all terms in Equation 8.2 contribute to the dynamics and cannot be truncated [11,80]. The off-diagonal hyperfine elements may give rise to additional level anti-crossing conditions and provide a polarization transfer mechanism via simultaneous electron-nuclear flip-flops. For instance, the crossings of the eigenstate projections in Fig. 8.7 correspond to level anti-crossing conditions [219,220], among which is the near-crossing between $|\alpha\rangle$ and $|\chi\rangle$ at ~100 mT (LAC–) and the crossing between $|\beta\rangle$ and $|\chi\rangle$ at ~105mT (LAC+). They are caused by the $S_{-}I_{+}$ and $S_{-}I_{-}$ hyperfine elements, respectively, near LAC at ~102.5 mT.

8.3.2 The observed level anti-crossing condition.

The NV⁻ electron spin is polarized to the $|0\rangle_z$ state under laser irradiation [85, 221]. However, it is unclear how the spin population is distributed among the four electron-nuclear mixed states when the two electronic states are split by the large hyperfine interaction near LAC. Resolved ODMR spectra might provide such detailed information, if each observed peak can be assigned to a pair of eigenstates connected by the transition. Figure 8.10 shows a comparison of the observed transition frequencies with those calculated from the energy levels as shown in Fig. 8.6. The excellent agreement confirms that the low-intensity peaks originate from the NV⁻¹³C_a pairs and enables each observed transition to be unambiguously assigned to a pair of eigenstates. Based on the distribution of the observed transitions over an ~30 mT range near LAC, only one level anti-crossing condition is observed for NV⁻¹³C_a pairs, at LAC+ , even though each off-diagonal hyperfine element, in principle, introduces an additional level anti-crossing condition. The first signature of this condition is the discontinuous disappearance of the $|\alpha\rangle \leftrightarrow |\beta\rangle$ transition and the appearance of the $|\alpha\rangle \leftrightarrow |\chi\rangle$ and $|\alpha \leftrightarrow |\delta\rangle$ transitions as B_z crosses LAC+ (Fig. 8.10). Absent the hyperfine



Figure 8.6: Energies of the four eigenstates near LAC. The LAC-, LAC and LAC+ are labelled by vertical dashed lines. The spin symbols illustrate how the polarization evolves at different magnetic field strengths, given the dominant nuclear projection of each state



Figure 8.7: Eigenstates are expressed by their projections onto the $|m_s = 0, m_I = \uparrow / \downarrow \rangle_z$ states of the NV⁻⁻¹³C_a pair, where m_s and m_I are electron and nuclear quantum numbers, respectively. The LAC-, LAC, and LAC+ are labelled by circles



Figure 8.8: Eigenstates are expressed by their projections onto the $|m_s = -1, m_I = \uparrow / \downarrow \rangle_z$ states of the NV⁻¹³C_a pairs. The LAC-, LAC, and LAC+



Figure 8.9: Each mixed state is expressed by its respective projections onto the $|m_s = 0/-1, m_I = \uparrow / \downarrow \rangle_z$ states of the NV⁻⁻¹³C_a pairs. This figure contains the same information as shown in Fig. 8.7 and Fig. 8.8.



Figure 8.10: Assignment of the observed transitions (solid symbols) based on frequency in comparison with theoretical calculation (solid lines). Some allowed transitions related to the $NV^{-13}C_a$ pair may be obscured by the main peak from NV^{-} without ${}^{13}C_a$ (grey area with its width determined by the intense primary peak). The region where certain transitions near LAC+ disappear is shown by an open black square.

interaction, the transition frequency changes continuously as the energy of the polarized state $|0\rangle$ becomes greater than that of the $|-1\rangle$ state, when B_z crosses the LAC (Fig. 8.1b). This was previously identified by the inverted phase of the ESR signal when sweeping the magnetic field across LAC [176]. Further, due to the anisotropic hyperfine interaction we anticipate a frequency change when the polarized state goes from the lower to higher energy levels at the level anti-crossing condition, which is exactly what we observed at LAC+(Fig. 8.10). The second signature is the disappearance of the $|\alpha\rangle \leftrightarrow |\beta\rangle$ transition between 104 mT and 105 mT (within the open black square in Fig. 8.10), because the population in the $|\beta\rangle$ state becomes small, which was also shown by ESR [176]. Similar phenomena are not observed at LAC-. These observations suggest that the mixed state with the greatest polarization or population changes from $|\beta\rangle$ to $|\chi\rangle$ at LAC+, but not from $|\alpha\rangle$ to $|\chi\rangle$ at LAC-, see 8.11. These phenomena follow from the form of the anisotropic hyperfine Hamiltonian responsible for electron-nuclear polarization transfer. The NV⁻ electron spins are optically pumped to the $|0\rangle_z$ sublevel, but as the $|0\rangle_z$ and $|-1\rangle_z$ sublevels approach degeneracy near LAC, the only available electronic transitions for the transfer of polarization are the $S_{-}I_{+}$ or $S_{-}I_{-}$ hyperfine elements. As the $S_{-}I_{+}$ hyperfine element has much larger magnitude than that of the S_I_- in equation 8.2, the former effectively pumps the nuclear spin to the $|\uparrow\rangle_z$ state over a wide range of magnetic fields (with an exception discussed in the following section). The combined effect of continuous laser irradiation and polarization transfer therefore tends to populate the $|0,\uparrow\rangle_z$ state. This explains why only LAC+ is observed, occurring at the magnetic field where the two mixed states with the largest $|0,\uparrow\rangle_z$ component, namely $|\beta\rangle$ and $|\chi\rangle$, meet the level anti-crossing condition (Fig. 8.7).

8.3.3 The polarization of the electron-nuclear mixed states.

With each transition assigned to the mixed states and the effective level anti-crossing conditions identified, the relative peak intensities within the same spectrum reveal the spin polarization below and above LAC+. The spin polarization among the four mixed states is illustrated in Fig. 8.6 and can be explained as follows: from ~88 to ~105 mT, $I_{|\alpha\rangle\leftrightarrow|\delta\rangle}$ (the integrated area of the $|\alpha\rangle \leftrightarrow |\delta\rangle$ peak) decreases until it completely disappears above ~96 mT, while $I_{|\beta\rangle\leftrightarrow|\delta\rangle}$ continues to increase up to ~105 mT (Fig. 8.2). This suggests that the spin population of $|\alpha\rangle$ is gradually pumped into $|\beta\rangle$, with nearly complete polarization in the $|\beta\rangle$ state above ~96 mT (Fig. 8.2b and Fig. 8.4a). This occurs as the combined effect of optical pumping and the $S_{-}I_{+}$ hyperfine element near LAC- tends to pump the spins to $|0,\uparrow\rangle_z$, which is the primary component of the $|\beta\rangle$ state below ~105 mT (Fig. 8.7). The same effect also suggests that $|\chi\rangle$ is the most polarized state above ~106 mT, where $|\chi\rangle$ has the largest projection onto $|0,\uparrow\rangle_z$. This is indeed observed, as demonstrated by the larger intensity of $I_{|\alpha\rangle\leftrightarrow|\chi\rangle}$ and $I_{|\beta\rangle\leftrightarrow|\chi\rangle}$ compared with that of $I_{|\alpha\rangle\leftrightarrow|\delta\rangle}$ (Fig. 8.4c). The level anti-crossing at LAC+ thus changes the most polarized state from $|\beta\rangle$ to $|\chi\rangle$. However, within a narrow range of 105-106 mT near LAC+, $I_{|\alpha\rangle\leftrightarrow|\chi\rangle}$ is observed to be smaller than $I_{|\alpha\rangle\leftrightarrow|\delta\rangle}$ (Fig. 8.4b), suggesting that the spin population in $|\delta\rangle$ is slightly larger than that in $|\chi\rangle$. This occurs as $|0\rangle_z$ has its largest projection onto $|\delta\rangle$ within this field range, so the optical



Figure 8.11: Nuclear polarization measured via different electronic sublevels of the NV⁻. $P_{|0\rangle\leftrightarrow|-1\rangle}$ is shown in red up triangles, $P_{|0\rangle\leftrightarrow|+1\rangle}$ (with artifacts from the solid effect removed) is shown in blue down triangles. The black line is the calculated spin flip-flop probability (r) resulting from the combined effect of the $S_{-}I_{+}$ and $S_{-}I_{-}$ hyperfine elements. The red and blue dashed lines are fitting curves based on two Lorentzian functions for $P_{|0\rangle\leftrightarrow|-1\rangle}$ and $P_{|0\rangle\leftrightarrow|+1\rangle}$, respectively, that resemble the features of ρ . The error bars are propagated from the s.d. of the parameters used for Gaussian fittings of peaks in the ODMR spectra, and the subsequent area integration of each individual peak.

pumping mechanism tends to preferentially populate $|\delta\rangle$ (Fig. 8.7). As the major projection component of the $|\delta\rangle$ state at LAC+ is $|0,\downarrow\rangle_z$ (Fig. 8.7), the $S_{-}I_{-}$ hyperfine element, instead of $S_{-}I_{+}$, must dominate the polarization transfer processes. The competing effect between $S_{-}I_{+}$ and $S_{-}I_{-}$ hyperfine elements will be further discussed in the following section.

Our tabulation of observed transition frequencies demonstrates how spin polarization is affected by the anisotropic hyperfine interaction near the level anti-crossing. The detailed observation of spin polarization and its dependence on the magnetic field provide insights into the mechanism of electron and nuclear spin polarization using the NV⁻ centre [85].

Nuclear polarization and its dependence on magnetic field.

Both the polarization of the electron-nuclear mixed states and their projections onto each nuclear spin state depend on the magnetic field, suggesting that the nuclear polarization should as well. In addition to the eigenstates we have calculated (Fig. 8.7 and Figs 8.8, 8.9), we must know the spin population of each electron-nuclear mixed state in order to determine the nuclear polarization. In principle, the spin population can be calculated from the peak intensities of all transitions between any two mixed states (out of six transitions in total). However, not all transitions associated with $NV^{-13}C_a$ pairs can be individually resolved; several transitions are obscured by the large peak arising from NV⁻ centres that are not coupled to ${}^{13}C_a$ (the grey area in Fig. 8.10). In order to estimate the nuclear polarization, we assume that the ratio of the intensities of two individual peaks, such as $|\alpha\rangle \leftrightarrow |\delta\rangle$ and $|\beta\rangle \leftrightarrow |\delta\rangle$, approximates the ratio of spin populations in the $|\alpha\rangle$ and $|\beta\rangle$ states, respectively, (see Methods for the estimation of nuclear polarization). We further assume that the electron spin polarization is near unity. The estimated nuclear polarization measured via the $|0\rangle \leftrightarrow |-1\rangle$ transition $(P_{|0\rangle\leftrightarrow|-1\rangle}$, red up triangles) is shown in Fig. 8.11 as a function of the magnetic field. The nuclear polarization increases as B_z increases until ~96 mT, because the normalized spin population in $|\beta\rangle(p_{\beta})$ is much greater than that of $|\alpha\rangle(p_{\alpha})$, leading to almost complete nuclear polarization. Such polarization decreases to zero and changes sign near LAC+. Above LAC+, the spin distribution among $|\chi\rangle$ and $|\delta\rangle$ causes the polarization to increase up to 60% before decreasing to 30% at ~ 115 mT.

In order to obtain a complete picture of the spin dynamics and an independent estimate of the nuclear polarization, we also measured the ODMR spectra via the $|0\rangle \leftrightarrow |+1\rangle$ transition. The frequencies and assignments of observed transitions are shown in Fig. 8.12. These results largely agree with those accomplished by measurement via the $|0\rangle \leftrightarrow |-1\rangle$ transitions. For example, the signatures of level anti-crossing conditions are also observed at LAC+. The polarization of the electron-nuclear mixed states agrees with the measurement via the $|0\rangle \leftrightarrow |-1\rangle$ transitions (Fig. 8.6): from ~94 to ~103 mT, all observed transitions are associated with the $|\beta\rangle$ state; within a narrow range near LAC+, $|\delta\rangle$ is the most polarized mixed state; and all transitions are associated with either $|\chi\rangle$ or $|\delta\rangle$ above LAC +. Our observations of the $|\beta\rangle \approx |0,\uparrow\rangle \leftrightarrow |+1,\downarrow\rangle$ transition (Fig. 8.12), however, indicate that there is an additional nuclear polarization mechanism induced by the applied microwave field. Specifically, the $|0,\uparrow\rangle \leftrightarrow |+1,\downarrow\rangle$ transition is usually forbidden under the selection



Figure 8.12: The assignment of the observed transitions associated with the NV⁻⁻¹³C_a pairs (open symbols) or with NV⁻ without ¹³C_a (black solid squares), based on the measured frequency in comparison with theoretical calculation (solid lines for the NV⁻⁻¹³C_a pairs, and dashed line for the NV⁻ without ¹³C_a). The disappearance of $|\beta\rangle \leftrightarrow |+1,\uparrow\rangle$ or $|\chi\rangle \leftrightarrow |+1,\uparrow\rangle$ transitions near LAC+ is shown by an open light blue square, as one of the signatures of the level anti-crossing condition. The observed $|\beta\rangle \leftrightarrow |+1,\downarrow\rangle$ transition corresponds to the solid effect, a nuclear spin polarization mechanism in the basis of mixed electron-nuclear eigenstates. The observed frequencies agree completely with the solid effect theory.

rules. In the presence of hyperfine interaction, the eigenstates in the $|0,\rangle, |-1\rangle$ manifold are no longer pure states near LAC (for instance, $|\langle 0, \downarrow |\beta \rangle|^2 \neq 0$, in Fig. 8.7). A resonant microwave field can excite transitions from this manifold of eigenstates that are mixed basis states to the $|+1\rangle$ sublevels. These transitions are forbidden in the basis of pure states (that is, simultaneous flip-flop of the electron and nuclear spins). This mechanism of dynamic nuclear polarization is the well-known solid effect, documented in the literature [80, 81, 222] and routinely employed for sensitivity enhancement in paramagnetically doped solids. Under our experimental conditions, we estimate that the nuclear polarization at 94.9 mT is only $\sim 43\%$ when the solid effect is considered, as compared with $\sim 100\%$ without the solid effect (Fig. 8.13). As the solid effect operates only at a narrow resonance condition (a given microwave frequency at a given magnetic field), only the seemingly forbidden transition $(|\beta\rangle \leftrightarrow |+1,\downarrow\rangle)$, is affected. The rest of the observed peaks (all other transitions except $|\beta\rangle \leftrightarrow |+1,\downarrow\rangle$ in Fig. 8.12) are associated with allowed transitions that can be used to estimate the nuclear polarization with artifacts from the solid effect removed $(P_{|0\rangle\leftrightarrow|+1\rangle}$, blue down triangles in Fig. 8.11, see Methods). We thus use only these in our calculations. Under the condition such that the hyperfine interaction causes strong electron-nuclear spin mixing between the $|0\rangle$ and $|-1\rangle$ sublevels near LAC, the dynamics within this manifold are explained largely by allowed, rather than forbidden, transitions; thus the solid effect does not contribute to the polarization measured via the $|0\rangle \leftrightarrow |-1\rangle$ transition.

The observed nuclear polarization can be explained by the probability of the electronnuclear spin flip-flop induced by the $S_{-}I_{+}(\rho_{\uparrow})$ and $S_{-}I_{-}(\rho_{\downarrow})$ hyperfine elements [35]. The transition probabilities corresponding to each hyperfine element can be calculated from the degree of mixing between relevant eigenstates [35] (see Methods and Fig. 8.14). It is clear that ρ_{\uparrow} is relatively larger over the entire range of magnetic field in this study (88-118 mT) except the region of 104-106 mT where ρ_{\downarrow} is larger. The combined effect (ρ , black line in Fig. 8.11) explains the pattern of nuclear polarization as a function of magnetic field. Both experimentally measured estimates for the nuclear polarization, $P_{|0\rangle\leftrightarrow|-1\rangle}$ and $P_{|0\rangle\leftrightarrow|+1\rangle}$, agree with the predicted ρ to a good approximation. The $P_{|0\rangle\leftrightarrow|+1\rangle}$ seems to be more accurate than $P_{|0\rangle\leftrightarrow|-1\rangle}$, because the former estimate is based on transitions from a mixed state to a nearly pure state and all transitions are resolved, whereas the latter is based on transitions between two mixed states and not all transitions can be resolved. For instance, $P_{|0\rangle\leftrightarrow|-1\rangle}$ tends to overestimate the nuclear polarization within the magnetic field of 102-112 mT. Nevertheless, both measurements show a nearly complete nuclear polarization near LAC- and inverted polarization to nuclear spin down at LAC+, confirming the sensitive dependence on the magnetic field and the assumptions of our theory.

8.4 Discussion

As we have demonstrated elsewhere [223], shaped optical irradiation can be used to produce a time- and space-varying pattern of polarization up to the diffraction limit; here we demonstrate that the magnetic field can act as a complementary control parameter. The anisotropic hyperfine interaction of NV^- centres with the surrounding lattice carbons in di-



Figure 8.13: The $|\beta\rangle$ state is shown in its leading projection onto $|0,\uparrow\rangle$ and small (η) mixing with $|0,\downarrow\rangle$. The transition $|\beta\rangle \leftrightarrow |+1,\downarrow\rangle$ can be excited by the resonant microwave field (~5.47 GHz), indicated by a blue Gaussian curve fit to a representative ODMR spectrum. The transition at ~5.6 GHz is an allowed transition and not affected by the solid effect, such that the polarization is solely due to the level anti-crossing condition within $|0\rangle \leftrightarrow |-1\rangle$ transitions. The change of nuclear polarization due to the solid effect can be estimated by comparing the peak intensity of $|\beta\rangle \leftrightarrow |+1,\downarrow\rangle$, $I_{|\beta\rangle\leftrightarrow|+1,\downarrow\rangle}$, and that of $|\beta\rangle \leftrightarrow |+1,\uparrow\rangle$, $I_{|\beta\rangle\leftrightarrow|+1,\uparrow\rangle}$, in the ODMR spectrum acquired at 94.9 mT via $(P - P_{solid}/P = I_{|\beta\rangle\leftrightarrow|+1,\downarrow\rangle}/I_{|\beta\rangle\leftrightarrow|+1,\uparrow\rangle}$, suggesting ~57% of nuclear polarization to its spin down state by the solid effect



Figure 8.14: Nuclear polarization results from two competing hyperfine elements, $S_{-}I_{+}(\rho_{\uparrow},$ red line) resulting in nuclear spin up (positive sign), and $S_{-}I_{-}(\rho_{\downarrow},$ blue line) resulting in nuclear spin down (negative sign). The combined effect of these hyperfine elements ($\rho = \rho_{\uparrow} - \rho_{\downarrow}$, black line) leads to the net nuclear polarization near LAC.

amond allows the magnetic field to be used as an active and sensitive control of the nuclear polarization near 105 mT (LAC+). The effect of the hyperfine interaction is pronounced only at the near-degeneracy condition of electronic states, which is at the level anti-crossing for the NV⁻ centres in diamond. A similar nuclear polarization mechanism has also been used in GaAs semiconductors at the fractional quantum Hall regime with a filling factor of $\mathbf{v} = 2/3$ [224–226]. When the cyclotron energies of the first two Landau levels match the electron spin Zeeman energy at the filling factor of $\mathbf{v} = 2/3$, the electronic states become nearly degenerate and the nuclear spin can be polarized by electrical current and measured by resistivity [226]. Unfortunately, cryogenic temperatures (<4.2 K) and high magnetic field (a few tesla) are generally required for such nuclear polarization in semiconductors. The advantages of the NV⁻ centre in diamond, by contrast, are that similar control over polarization can be achieved at room temperature and low magnetic field (~ 0.1 T). The combination of optical pumping and initialization, precise magnetic control and optically detected polarization as demonstrated here are a complete set of non-inductive techniques that are potentially useful for nuclear-based spintronics in insulating or semiconducting diamonds [215, 216]. Our experiments, demonstrating complete polarization of the ¹³C nuclei at ~ 0.1 T and room temperature, together with the results of King et al. [34] demonstrating transport of polarization to bulk nuclei via spin diffusion at ~ 9.4 T, suggest that the bulk polarization of ¹³C nuclei in our diamond sample approaches several percent [59]. Thus, our method may be applied wherever hyperpolarized bulk ¹³C nuclei are required [34], including in DNP-enhanced NMR experiments, in spintronic devices and for NV⁻-based devices including magnetometers and gyroscopes [227].

8.5 Methods

8.5.1 Materials and experiments

The diamond used in our experiments (labelled S9 in previous studies [44, 105]) contains ~ 2 p.p.m. of negatively charged NV⁻. A continuous beam from a 532-nm laser with optical power of 2 mW is focused on the diamond by an objective with a numerical aperture of 0.7 to achieve optical power density of $\sim 5 \text{ mW}/\mu m^{-2}$. The fluorescence signal from NV⁻ is detected by an avalanche photo detector after passing a dichroic mirror and a long-pass filter [105]. The external magnetic field is applied with a permanent magnet aligned to one of the NV⁻ symmetry axes with a precision better than $\sim 1^{\circ}$, otherwise the large transverse magnetic field may obscure the effect of the off-diagonal hyperfine elements. The strength of the magnetic field is adjusted by the distance of the magnet from the laser focus point on the diamond. The magnetic field is determined precisely using the NV⁻ without proximal $^{13}C_a$ nuclei acting as a magnetometer; the central frequencies of the intense primary peaks in the ODMR spectra are directly related to the magnetic field [44]. A single copper wire loop arranged about the laser focus produces an oscillating RF magnetic field with Rabi frequency \sim 350 kHz. The ODMR spectra are measured by recording the fluorescence intensity while the excitation frequency is scanned from 1 to 500 MHz for the $|0\rangle \leftrightarrow |+1\rangle$ transition (or from 5.4 to 6.1 GHz for the $|0\rangle \leftrightarrow |+1\rangle$ transition) and are normalized to the fluorescence intensity obtained without RF excitation.

8.5.2 Estimation of nuclear polarization

Assuming that the electron polarization is near 100%, almost all spin population resides either at $|\alpha\rangle$ or at $|\beta\rangle$ below LAC+, and either at $|\chi\rangle$ or at $|\delta\rangle$ above LAC+, that is, the normalized spin population $(p_{|\psi\rangle})$ is approximately given by $p_{\alpha} + p_{\beta} = 1$ and $p_{\chi} = p_{\delta} = 0$ below LAC+. In addition, the ODMR peak intensity is also affected by the optical contrast between $|0\rangle$ and $|-1\rangle$. Below LAC+, the spin population can be related to the observed peak intensities of $I_{|\beta\rangle\leftrightarrow|\delta\rangle}$ and $I_{|\alpha\rangle\leftrightarrow|\delta\rangle}$ by considering the fluorescence contrast of the two states,

$$\frac{I_{|\beta\rangle\leftrightarrow|\delta\rangle}}{I\alpha\rangle\leftrightarrow|\delta\rangle} = \frac{p_{\beta}\times(|\langle 0|\beta\rangle|^2 - |\langle 0|\delta\rangle|^2)}{p_{\alpha}\times(|\langle 0|\alpha\rangle|^2 - |\langle 0|\delta\rangle|^2)}.$$
(8.3)

The nuclear polarization measured via the $|0\rangle \leftrightarrow |-1\rangle$ transition, $P_{|0\rangle\leftrightarrow|-1\rangle}$, can be estimated based on the polarization among the mixed states and their projections onto each nuclear spin state,

$$P_{|0\rangle\leftrightarrow|-1\rangle} = p_{\beta} \times (|\langle\uparrow|\beta\rangle|^2 - |\langle\downarrow|\beta\rangle|^2) + p_{\alpha} \times (|\langle\uparrow|\alpha\rangle|^2 - |\langle\downarrow|\alpha\rangle|^2)$$
(8.4)

The transitions associated with $|\chi\rangle$ are obscured by the main peak (the grey area in Fig. 8.10), and we may disregard these transitions under the assumption that $p_{\chi} = p_{\delta} = 0$. A similar method is used to calculate $P_{|0\rangle\leftrightarrow|-1\rangle}$ above LAC+ by comparing $I_{|\beta\rangle\leftrightarrow|\chi\rangle}$ with $I_{|\alpha\rangle\leftrightarrow|\delta\rangle}$, and by assuming that $p_{\alpha} = p_{\beta} = 0$ and $p_{\chi} + p_{\delta} = 1$. Here, $I_{|\beta\rangle\leftrightarrow|\chi\rangle}$ is used instead of $I_{|\alpha\rangle\leftrightarrow|\chi\rangle}$, because the $|\alpha\rangle \leftrightarrow |\chi\rangle$ and $|\alpha\rangle \leftrightarrow |\delta\rangle$ transitions approach the same frequency (the two peaks merge) as the magnetic field increases above ~118 mT. The comparison between $I_{|\beta\rangle\leftrightarrow|\chi\rangle}$ and $I_{|\alpha\rangle\leftrightarrow|\delta\rangle}$ therefore more accurately represents the nuclear polarization above LAC+.

The nuclear polarization measured via the $|0\rangle \leftrightarrow |+1\rangle$ transition with artifacts from the solid effect removed, $P_{|0\rangle\leftrightarrow|+1\rangle}$, is estimated by first comparing the intensities of the transitions to $|+1,\uparrow\rangle(I_{|+1,\uparrow\rangle})$ and to $|+1,\downarrow\rangle(I_{|+1,\downarrow\rangle})$ in the ODMR spectra other than the forbidden transition due to the solid effect $(|\beta\rangle \approx |0,\uparrow\rangle \leftrightarrow |+1,\downarrow\rangle)$, for instance via,

$$\frac{I_{|+1,\uparrow\rangle}}{I_{|+1,\downarrow\rangle}} = \frac{p_{\chi} \times |\langle 0|\chi\rangle|^2}{p_{\delta} \times |\langle 0|\delta\rangle|^2}.$$
(8.5)

The projections onto each nuclear spin state is then included via,

$$P_{|0\rangle\leftrightarrow|+1\rangle} = p_{\chi} \times (|\langle \downarrow |\chi \rangle|^2 - |\langle \downarrow |\chi \rangle|^2) + p_{\delta} \times (|\langle \uparrow |\delta \rangle|^2 - |\langle \downarrow |\delta \rangle|^2).$$
(8.6)

A similar method is used to calculate $P_{|0\rangle\leftrightarrow|+1\rangle}$ below LAC+ by using $I_{|\beta\rangle\leftrightarrow|+1,\uparrow\rangle}$ and also $I_{|\delta\rangle\leftrightarrow|+1\rangle,\downarrow\rangle}$ for the magnetic field within 102-105 mT.

8.5.3 Probability of electron-nuclear spin flip-flop.

The probability of electron-nuclear spin transitions induced by the $S_{-}I_{+}(\rho_{\uparrow})$ and $S_{-}I_{-}(\rho_{\downarrow})$ hyperfine elements are calculated by the degree of mixing between relevant eigenstates shown in Fig. 8.7 [35],

$$\rho_{\uparrow} = 4 \cdot |\langle 0, \downarrow | \alpha \rangle|^{2} \cdot [|\langle 0, \downarrow | \chi \rangle|^{2} + |\langle 0, \downarrow | \delta \rangle|^{2}]$$

$$\rho_{\downarrow} = 4 \cdot |\langle 0, \uparrow | \beta \rangle|^{2} \cdot |\langle 0, \uparrow | \chi \rangle|^{2}$$
(8.7)

where both $|\rangle 0, \downarrow |\chi\rangle|^2$ and $|\langle 0, \downarrow |\delta\rangle|^2$ for ρ_{\uparrow} are considered because of the mixing effect due to $S_z I_x$. The calculated probabilities and their combined effect ($\rho = \rho_{\uparrow} - \rho_{\downarrow}$) are shown in Fig. 8.14.

Chapter 9

Room-temperature operation of a radiofrequency diamond magnetometer near the shot-noise limit

This chapter includes content from the previously published work [105], and is republished here with minor changes, with permission.

9.1 Abstract

We operate a nitrogen-vacancy (NV⁻) diamond magnetometer at ambient temperatures and study the dependence of its bandwidth on experimental parameters including optical and microwave excitation powers. A model based on the Bloch equations is used to analyze the NV⁻ centers response time, τ , during continuous optical and microwave irradiation, and τ^{-1} is shown to be a weighted average of \mathbf{T}_1^{-1} and \mathbf{T}_2^{-1} , where \mathbf{T}_1 and \mathbf{T}_2 are the longitudinal and transverse relaxation times of the electron spin during optical irradiation. We measured a maximum detection bandwidth of ~ 1.6 MHz with optical excitation intensity of $\sim 2.3 \text{ MW/cm}^2$, limited by the available optical power. The sensitivity of the NV⁻ ensemble for continuous-wave magnetometry in the presence of photon shot noise is analyzed. Two detection schemes are compared, one involving modulation of the fluorescence by an oscillating magnetic field while the microwave frequency is held constant, and the other involving double modulation of the fluorescence when the microwave frequency is modulated during the detection. For the first of these methods, we measure a sensitivity of 4.6 ± 0.3 nT/ \sqrt{Hz} , unprecedented in a detector with this active volume of $\sim 10 \ \mu m^3$ and close to the photonshot-noise limit of our experiment. The measured bandwidth and sensitivity of our device should allow detection of micro-scale NMR signals with microfluidic devices.

9.2 Introduction

The negatively charged nitrogen vacancy center (NV⁻), a substitutional point defect in diamond, exhibits favorable optical and magnetic properties that have recently been exploited in several applications. For example, their brightness, optical stability, and biological inertness make NV^- defect-harboring nanodiamonds ideal probes in bioimaging [228] and fluorescence resonance energy transfer [229] experiments. More importantly, the NV⁻ defect forms a magneto-optical system whose spin state can be initialized and read out optically. Because the NV⁻ spin-coherence lifetimes can be as long as milliseconds in an isotopically pure diamond lattice, [87] the system is an ideal platform for experimental quantum information science. Among such devices are precision magnetometers that have applications as industrial sensors, probes of magnetic materials, and as detectors of magnetic resonance. Practical magnetic-field sensors for electron spin resonance (ESR), nuclear magnetic resonance (NMR), and other similar applications must sensitively detect weak, oscillating magnetic fields whose frequency and bandwidth cannot be arbitrarily controlled. Thus, the transient response of an ensemble of NV⁻ centers, characterized by its sensitivity to magnetic fields oscillating over a wide bandwidth, is a critical metric for applications in NMR and magnetic resonance imaging.

Using a single NV⁻ center in isotopically pure diamond, a magnetic sensitivity of ~4 nT/\sqrt{Hz} has recently been reported [87] and an extrapolated (but not measured) sensitivity of ~20 nT/\sqrt{Hz} using an ensemble of NV⁻ centers was also reported, [230] both at ambient temperatures. Infrared absorption detection, using an NV⁻ ensemble, achieved a sensitivity of ~7 nT/\sqrt{Hz} at 45 K [107]. In that work, a theoretical bandwidth of a few MHz was suggested, but experimental operation was limited to a few hundred Hz. With a single NV⁻ center, a detection bandwidth of a several hundred kHz has been reported. [231] In combination with pulsed decoupling schemes, probes incorporating single NV⁻ centers in isotopically pure (i.e., ¹²C) diamond matrices are ideal for scanning probe magnetometry applications. By contrast, continuous wave NV⁻ magnetometry at a larger scale and with an ensemble of NV⁻ centers in more readily available diamond matrices (HPHT) is more adapted to industrial applications such as microscale NMR within microfluidic devices. In these applications, the detector volume is matched to the microfluidic channel; thus, detector sensitivity and bandwidth are much more important variables than spatial resolution.

In general, detector bandwidth is limited by the characteristic time constants of the NV⁻ center. We overcome this limit by using optical excitation powers at which the effective T_1 and T_2 of the NV⁻ center are shortened by the optical pumping cycle. With an optical excitation intensity of ~2.3 MW/cm² (optical excitation intensity refers to the average intensity throughout the paper), limited by the available optical power, we measured bandwidths as large as ~1.6 MHz. With optimized operational parameters, we also measured a sensitivity of ~4.6\pm0.3 nT/ \sqrt{Hz} . These measurements used fluorescence detection techniques at room temperature with an active volume of only ~10 μ m³, matched to the size of microfluidic channels and much smaller than is practical with inductive NMR detection techniques. Section 9.3 describes the bandwidth and sensitivity measurements, in which we record the

fluorescence signal from the NV⁻ centers under frequency modulation of the microwave field and/or an oscillating magnetic field. The latter simulates an NMR signal of interest, as shown in Fig. 9.1. In Sec. 9.4, we study the transient response of an NV⁻ center under continuous microwave and optical irradiation, in order to understand the dynamics that limit the bandwidth of the magnetometer. The NV⁻ spin system can be modeled as a set of three two-level systems, whose resonant frequencies are separated by ~2.1 MHz due to the hyperfine coupling between the electron spin and the ¹⁴N nuclear spin. Since the two-level systems can be considered essentially isolated from each other, [232] Bloch equations are used to model the response of each system individually, with the optically induced spin-relaxation included in the model only through T_1 and T_2 , the effective longitudinal and transverse relaxation times under continuous optical excitation, respectively. The Bloch-equation model is used to analyze the NV⁻ centers response time, τ , and τ^{-1} is shown to be a weighted average of T_1^{-1} and T_2^{-1} : The theory is validated by comparison with experiment.

Section 9.5 analyzes the sensitivity limit imposed by photon shot noise of the fluorescence signal from the NV^- centers. When the microwave field is tuned to a frequency where the slope of the optically detected magnetic-resonance (ODMR) spectrum is maximal, an oscillating magnetic field can be measured by detecting the corresponding oscillations in the fluorescence from the NV⁻-center ensemble, as schematically shown in Fig. 9.1(b). An alternative measurement method is to modulate the microwave frequency about the center of the ODMR spectrum during the detection of the magnetic field. The oscillations in fluorescence have the functional form $\cos(\omega_m t + \phi_m) \cos(\omega_c t)$, where ω_c is the frequency of the carrier wave that modulates the microwave frequency, ω_m is the frequency of the oscillating magnetic field, and ϕ_m depends on the relative phase of the carrier wave and the magnetic field. Demodulation using a lock-in amplifier and a spectrum analyzer in sequence yields an estimate of the magnetic field. We will refer to these two measurement techniques as singlemodulation and double-modulation methods, respectively, due to the modulation they induce in the fluorescence. Consistent with the analysis, experimental tests show that the singlemodulation method is preferred if the effects of low-frequency fluctuations in laser power are eliminated, for example, by the use of a gradiometer configuration. For measurements performed using the single-modulation method, the sensitivity of the diamond magnetometer was near the shot-noise limit.

9.3 Device Operation

The diamond sample in our experiments is S9 (NV⁻ concentration of ~2 ppm) described in [44], and the geometry of our experiment is illustrated in Fig. 9.1(c). The NV⁻ center ground state is a spin triplet (S = 1) with zero field splitting of 2.87 GHz between sublevels $m_s = 0$ and $m_s = \pm 1$. For ODMR experiments, a static magnetic field of ~20 G was applied along the [111] crystal orientation to break the orientational degeneracy of the NV⁻ center. The static field also shifts the transition between $m_s = 0$ and $m_s = +1$ out of resonance with the applied microwave field that is matched to the transition between $m_s = 0$ and $m_s = -1$. The experiments generally probed a single manifold of resolved hyperfine lines.


Figure 9.1: (a) Fluorescence image of the diamond and a representation of the thin wire (80 μ m diameter), which is used to produce small oscillating magnetic fields. A similar wire was used to produce the microwave field. A three-axis set of Helmholtz coos was used to produce the static field B₀, while B_{MW} was generated using a high frequency microwave source. The oscillating field B_{AC} from the 80 μ m OD wire was produced using a function generator. (b) Schematic of modulated fluorescence detection technique, where frequency-modulated MW is applied. (c) Schematic of experimental setup. MO refers to the 20x microscope objective with N.A. of 0.4, and LF and DM are a long-pass filter (cut-off at 650 nm) and a dichroic mirror, respectively, and APD stands for avalanche photodetector. The two excitation spots (shown in inset) were separated by ~ 300 μ m. The green refers to the 532 nm excitation, and red to the fluorescence signal.



Figure 9.2: (a) Derivative spectra at optical excitation intensity of 2.3 MW/cm² with various Rabi frequencies ($\omega_1/2\pi$), indicated in MHz in the figure. Center frequency shift due to heating effects was compensated for in the plot. All derivative spectra were measured with a microwave modulation amplitude of 250 kHz at a microwave modulation rate of 25 kHz. (b) A closeup of the curve for Rabi frequency of 0.06 MHz with an additional fit. Black circles indicate the experimental data, and the solid line shows a fit to the derivative of three summed Lorentzian line shape functions. Estimated T₂^{*} from the ODMR spectrum was 130± 5 ns.

[230] Microwaves were applied to the NV⁻ spins using a wire loop of inner diameter 1.5 mm, placed close to the diamond surface (described fully in the figure captions). Derivative spectra were obtained by applying a frequency modulated microwave signal at various microwave powers, as shown in Fig. 9.2(a), and T_2* was estimated to be 130 ± 5 ns, as seen in Fig. 9.2(b).

9.3.1 Bandwidth measurement

The frequency response of the NV⁻ ensemble at a given optical and microwave power was obtained by applying frequency-modulated microwaves at the peak of the derivative spectrum, i.e.,

$$f_{mw}(t) = f_{peak} + \Delta f \cos(2\pi f_m t + \phi), \qquad (9.1)$$

where f_{mw} is the instantaneous microwave frequency, centered at f_{peak} , and f_m is the modulation rate, which was varied from 1 kHz to 2 MHz with a constant modulation amplitude $\Delta f = 1$ MHz. The modulated signal, normalized to the peak amplitude was plotted as a function of modulation rate, as seen in Figs. 9.3 and 9.4. In order to qualitatively understand how the dynamics of the ensemble NV⁻ centers under continuous optical and microwave excitation depends on experimental parameters, we first measured the T_1 of 462.6 μs and T_2 of 2.0 μs in the absence of optical excitation. Measurements of T_1 and T_2 were repeated under continuous optical excitation at various powers, and the ensemble T_1 and T_2 were found to decrease significantly as optical power increased, due to faster repolarization. For example, at an optical excitation intensity of $\sim 0.3 \text{ MW/cm}^2$, estimated from the measured power before the microscope objective and the diffraction limited spot size, the ensemble T_1 is ~11.0 μ s and T_2 is ~ 1.0 μ s, decreasing to 2.2 μ s and 140 ns, respectively, at ~2.0 MW/cm^2 . This dramatic change in the measured time constants, T_1 and T_2 suggests that the Gaussian profile of the beam introduces significant spatial inhomogeneity in T_1 and T_2 . As the microwave power is increased, we can expect that the full ensemble of NV⁻ centers, inhomogeneously illuminated by the laser, will contribute to the dynamics, with each NV⁻ center having a different transient response and fluorescence intensity. In order to account for the spatial inhomogeneity of the laser intensity in simulations, we include two sets of T_1 and T_2 values, which is later referred to as the two NV⁻ center simulation in Sec. 9.4, to serve as a simple model of multiple classes of NV⁻ centers.

In Fig. 9.5, we illustrate similar experiments repeated at various optical and microwave excitation powers, along with estimated bandwidths, defined as the modulation rate at which the amplitude decreases by 3 dB. At an optical excitation intensity of ~2.3 MW/cm², the measured bandwidth increased to ~1.6 MHz as $\omega_1/2\pi$, the Rabi frequency associated with the resonant component of the microwave field, was increased to 4.10 MHz. At a lower optical excitation intensity of 0.02 MW/cm², the bandwidth increased only to ~39 kHz when $\omega_1/2\pi$ was increased over the same range.



Figure 9.3: Comparison of simulation and experiment for a bandwidth measurement at laser intensity of 1.95 M/cm² and microwave field strengths, corresponding to $\omega_1/2\pi = 0.010$ MHz and 4.10 MHz, respectively. For $\omega_1/2\pi = 0.15$ MHz, the central microwave frequency was set to a resolved hyperfine peak at the edge of the derivative spectrum, which offset the microwave frequency by 0.6 MHz from the nearest resonance of the ODMR spectrum. The magnetometer response at a given rate ω_m was characterized using frequency modulation of the microwave field with amplitude 1.0 MHz and modulation rate ω_m . The experimentally measured time constants used for the two NV-center ensemble simulation, described in Sec. 9.4, were $T_1 = 7.0 \ \mu$ s and $T_1 = 1.1 \ \mu$ s (obtained from a biexponential fit to a repolarization curve), and $T_2 = 150$ ns. For $\omega_1/2\pi = 4.10$ MHz, the hyperfine splittings were not resolved, and the offset from resonance was 3.0 MHz. The modulation amplitude used for the measurement, as well as the time constants T_1 , T_2 used for the simulation, were the same as for the $\omega_1/2\pi = 0.15$ MHz case. (Numbers in the figure correspond to the Rabi frequencies, and Exp and Sim refer to the experimental data and simulation data, respectively.)



Figure 9.4: Representative experimental data together with simulation data at an optical excitation intensity of 1.95 MW/cm². Unlike Fig. 9.3, this simulation with a 2 NV-center ensemble, uses two sets of T_1 and T_2 , i.e., $T_1 = 15 \ \mu s$, $T_2 = 1.5 \ \mu s$ and $T_1 = 1.5 \ \mu s$, $T_2 = 0.1 \ \mu s$, which are NOT based on the measured values but adjusted to fit the data. (Numbers in the figure correspond to the Rabi frequencies, and Exp and Sim refer to the experimental data and simulation data, respectively)



Figure 9.5: Experimentally estimated bandwidth in MHz is plotted as a function of the optical excitation intensity and the microwave Rabi frequency. The system shows saturation behavior at ~ 0.6 MW/cm² of optical excitation intensity, for $\omega_1/2\pi > 2.0$ MHz.

9.3.2 Sensitivity Measurement

In sensitivity measurements using the single-modulation technique, microwave excitation was applied at the frequency where the slope of the ODMR spectrum is maximal, a small magnetic field at 2 kHz was applied to the ensemble of NV⁻ centers within the excitation spot, and the modulated fluorescence signal was integrated for 1 sec using a spectrum analyzer (Stanford Research 770) with a uniform window function. In the gradiometer configuration, two 532 nm beams were used to excite NV⁻ centers in two distinct spots, separated by ~300 μ m in the diamond sample. In principle, the gradiometer setup can efficiently cancel common mode noise from sources such as laser intensity or ambient magnetic-field fluctuations. In single modulation experiments with optical excitation intensity of ~2.02 MW/cm², we measured a magnetic field sensitivity of ~4.6±0.3 nT/ \sqrt{Hz} using the gradiometer and ~6.7±0.4 nT/ \sqrt{Hz} using the single input channel, as shown in Fig. 9.6.

We performed a double-modulated experiment in which we applied, at the zero crossing of the derivative spectrum, a frequency-modulated microwave excitation with amplitude of 4.5 MHz at various modulation rates from 10 to 100 kHz. An additional oscillating magnetic field of calibrated amplitude at low modulation frequencies from 10 to 200 Hz was applied, in order to simulate an NMR signal. [233] The signal was first demodulated by the lock-in amplifier, and the output of the lock-in amplifier was integrated for 1 sec by the spectrum analyzer. In double modulation experiments, we obtained a magnetic field sensitivity of $\sim 11.9 \pm 0.9 \text{ nT}/\sqrt{Hz}$ with gradiometer implementation of this technique.

	10.0 Hz	20.0 Hz	$50.0~\mathrm{Hz}$	100.0Hz	$150.0~\mathrm{Hz}$	200.0 Hz
10.0 kHz	24.0	29.4	22.1	22.2	23.2	29.7
20.0 kHz	20.0	25.4	22.7	20.9	18.5	26.1
$50.0 \mathrm{~kHz}$	17.9	20.0	17.6	11.9	16.8	18.4
$100.0~\mathrm{kHz}$	19.1	15.9	15.5	14.3	17.4	17.8

Table 9.1: Magnetic field sensitivity (nT/\sqrt{Hz}) of double modulation technique as a function of low modulation frequency (Hz) at various carrier frequencies (kHz). The optical excitation intensity was 2.3 MW/cm², and the microwave-excitation strength corresponded to $\omega_1/2\pi$ = 1.56 MHz.

Table 9.1 shows the results of performing double-modulation experiments at various frequencies. The sensitivity in double-modulation experiments generally improved as the first modulation rate, i.e., the high frequency modulation rate, increased; this is attributed to the 1/f noise of the laser and is the principal advantage of the approach, particularly where low-quality lasers are employed.



Figure 9.6: Magnetic field sensitivity measurements in single modulation mode, using single fluorescence channels, labeled as APD1 and APD2 and a gradiometer with optical excitation intensity of 2.02 MW/cm² and microwave Rabi frequency of $\omega_1/2\pi = 1.6$ MHz, with one-second signal integration time. The inset shows the sensitivity as a function of optical excitation intensity using a single channel. Circles indicate measured data and the solid line is a fit to Eq. 9.25.

9.4 Transient response of the NV⁻ Center under CW

9.4.1 Bloch-equation model

Since the static magnetic field shifts the transition between $m_s = 0$ and $m_s = +1$ out of resonance with the microwave field, applied to the transition between $m_s = 0$ and $m_s = -1$, the response of an individual NV⁻ center to the microwave irradiation can be determined by modeling the center as a set of three two-level systems, with the frequencies of the three systems separated by the hyperfine interaction that couples the electron spin and the ¹⁴N nuclear spin. Cross relaxation between the three systems, corresponding to flips of the ¹⁴N nucleus, is expected to occur slowly on the time scale of the longitudinal and transverse relaxation of the electron spin toward its steady-state value under laser irradiation. The three two-level systems can thus be considered essentially isolated from each other. We use the Bloch equations, which are valid in the case where the coupling between spins is sufficiently weak that individual spins relax independently, [234] to describe the evolution of each of the two- level systems associated with an NV⁻ center, and the response of the NV⁻ center is found by summing the responses of the two-level systems.

An adaption of the Bloch equations can be used to take account of the fact that thermal relaxation and laser-induced repolarization have opposing effects on longitudinal relaxation. In the reference frame rotating with the resonant component of the microwave field, the evolution equations can be written as,

$$\frac{d}{dt}\mathbf{M} = \gamma \mathbf{M} \times \mathbf{B}_{\text{eff}} - \frac{1}{T_{1t}}M_z \mathbf{k} - \frac{1}{T_{1\rho}}(M_z - M_p)\mathbf{k}, - \frac{1}{T_2}(M_x \mathbf{i} - M_y \mathbf{j}),$$
(9.2)

$$= \gamma \mathbf{M} \times \mathbf{B}_{\text{eff}} - \frac{1}{T_1} (M_z - M_0) \mathbf{k} - \frac{1}{T_2} (M_x \mathbf{i} - M_y \mathbf{j}).$$
(9.3)

In Eq. 9.2, M is the magnetization, γ is the gyromagnetic ratio of the electron, B_{eff} is the effective field in the rotating frame, T_{1t} is the time constant for thermal relaxation toward $M_z = 0$, and T_{1p} is the time constant for repolarization toward $M_z = M_p$, where M_p is the maximum obtainable polarization under optical pumping, and $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are the unit vectors in the directions x, y, z, respectively. In Eq. 9.3,

$$T_1 \equiv \left(\frac{1}{T_{1t}} + \frac{1}{T_{1p}}\right)^{-1},\tag{9.4}$$

and

$$M_0 \equiv \frac{T_{1t}}{T_{1p} + T_{1t}} M_p, \tag{9.5}$$

are effective values of the time constant T_1 for longitudinal relaxation and the steady-statemagnetization M_0 . Note that Eq. (2) is a standard way of expressing the Bloch equations. The resonance frequency ω_0 and the relaxation time constants T_1 , T_2 depend on the microscopic environment, which can include modifications of the Hamiltonian induced by strain and temperature, as well as couplings to randomly distributed ¹³C, paramagnetic nitrogen, and NV⁻ centers with other orientations. The values of the parameters ω_0 , T_1 , T_2 are thus expected to vary across the region probed by the laser. An additional source of inhomogeneity in T_1 and T_2 is variation of beam intensity in this region, due to the Gaussian profile of the beam. While these effects could be modeled and included in an ensemble simulation, our intent here is to present a simple model of the physics that governs the magnetometers response to a changing field during continuous microwave irradiation, rather than to give a detailed description of the inhomogeneities in the probed region of the diamond.

In order to visualize the way in which magnetometer bandwidth depends on T_1 and T_2 , we performed simulations using two-center ensembles. Bloch-equation simulations were compared to experimental curves showing the magnetometers response as a function of frequency. Two sets of simulations were performed. For the first set, measured values were used for all parameters, aside from a normalization constant that set the amplitude of the low-frequency response to 1. The two centers in a given ensemble had distinct values of T_1 but identical values for all other parameters. The reason that two values of T_1 were used for these simulations is that biexponential curves were needed to yield good fits to experimental T1 curves. For these biexponential fits, the initial amplitudes of the two decaying exponentials were equal, to within a few percent, and so the ensemble simulations gave equal weighting to the two NV⁻ centers. The resonance frequencies of the simulated two-level systems were chosen to coincide with the measured hyperfine peaks of the ODMR spectrum.

At optical excitation intensity of 0.05 MW/cm2, the simulated bandwidth measurements matched the experimental data over the full range of microwave powers for which measurements were performed (0.1 MHz $\leq \omega_1/2\pi \leq 4MHz$). At higher optical intensities (from 0.30 MW/cm² to 1.95 MW/ cm²), the simulated curves matched experimental data only for the lowest microwave powers. Figure 9.3 compares simulation and experiment for measurements performed with different microwave powers at optical excitation intensity of 1.95 MW/cm².

A natural rationalization of these observations is that increasing the laser excitation intensity above 0.05 MW/cm² introduces a strong inhomogeneity in the relaxation rates of the NV⁻ centers, due to variation in laser intensity across the beam profile, and this inhomogeneity has a significant effect on the magnetometer response when the microwave field is sufficiently strong to excite a substantial fraction of the ensemble. Consistent with this rationalization is the fact that T_1 decreases sharply as the laser excitation intensity is increased from 0.05 MW/cm² to 0.30 MW/cm². (The best fits of single exponential curves to the experimental T_1 data at these two powers suggest that T_1 decreases by roughly a factor of 5 over this range.) For a rough characterization of the way in which inhomogeneities in T_1 and T_2 affect the bandwidth, a second set of simulations was performed, using time constants chosen to reproduce the experimental data obtained at the highest laser power and microwave power (shown in Fig. 9.4). These time constants used in the simulation fall within the range of values that can reasonably be expected for the inhomogeneous distribution at high optical power. These time constants were not selected in a methodical way; rather, they were guesses motivated by inspection of Fig. 9.3, which shows that the measured values of T_1 and T_2 give a simulated curve that is too flat in the low-frequency region but drops too steeply in the high-frequency region. Increasing the values of T_1 and T_2 for one center and decreasing these values for the other produced a closer fit to the experimental data, as shown in Fig. 9.4. (The relative population of these two NV⁻ centers was chosen so that the simulation matched the experimental data at 1 kHz and 300 kHz.) This simple choice of a two-center ensemble is helpful in visualizing the way in which bandwidth at higher laser power is affected by inhomogeneities in T_1 and T_2 .

9.4.2 Time constant of the transient response

The Bloch-equation model can be used to find the time constant τ that governs the NV⁻ response during a continuous-wave (CW) experiment. In the reference frame rotating with the resonant component of the transverse microwave field, the spins evolve under an effective field \mathbf{B}_{eff} that includes a longitudinal component due to the offset Δ from resonance,

$$-\gamma \mathbf{B}_{\mathbf{eff}} = (\omega_1, 0, \delta). \tag{9.6}$$

A weak longitudinal magnetic field oscillating at frequency ω_m in the laboratory frame causes the resonance frequency of the NV⁻ center to vary, which in turn causes movement of \mathbf{B}_{eff} . As the effective field moves, the corresponding steady-state solution to the Bloch equations changes as well, both in orientation and magnitude. Throughout the modulation cycle, the magnetization $\mathbf{M}(\mathbf{t})$ relaxes toward the instantaneous steady-state solution $\mathbf{M}_{s}(\mathbf{t})$. In the limit where the effective field changes slowly, $\mathbf{M}(\mathbf{t}) = \mathbf{M}_{\mathbf{s}}(\mathbf{t})$. For higher oscillation frequencies ω_m , where the effective field moves too quickly for $\mathbf{M}(\mathbf{t})$ to relax fully to steady-state, a drop in the magnetometer response is observed. We show in the appendix that the relaxation of $\mathbf{M}(\mathbf{t})$ in the rotating frame includes a contribution from a transient $\mathbf{M}'_{\mathbf{t}}(\mathbf{t})$ that relaxes without precessing about the effective field, as well as contributions from two linearly independent transients $\mathbf{M}'_{2}(\mathbf{t}), \mathbf{M}'_{3}(\mathbf{t})$ that precess. If the Rabi frequency $\sqrt{\omega_{1}^{2} + \Delta^{2}}$ is large compared to ω_m , the precessing transients will not contribute directly to the detected response at frequency ω_m . An additional simplification associated with a large Rabi frequency is that we can approximate $M'_1(t)$ as evolving independently of the two precessing transients, since interconversion of $M'_1(t)$ and $M'_2(t)$, $M'_3(t)$ is averaged to zero by the fast oscillation of $M'_{2}(t)$ and $M'_{3}(t)$. A roughly similar mechanism makes adiabatic fast passage [235] possible in NMR: magnetization initially aligned with an effective field will follow the field if it tips slowly, rather than being converted into precessing components perpendicular to the field.

A qualitative understanding of the NV⁻-magnetometers bandwidth can be obtained from the simplified model in which a single transient $\mathbf{M}'_1(\mathbf{t})$ is continually relaxing in the rotating frame without precessing about the instantaneous effective field. As discussed in the appendix, simulations have validated this model of the magnetometers response, and physical arguments can be used to obtain an analytic expression for the time constant τ that governs the relaxation of $\mathbf{M}'_{\mathbf{1}}(\mathbf{t})$. When $|\omega_1| \gg T_1^{-1}, T_2^{-1}$, we have,

$$\frac{1}{\tau} = \frac{\omega_1^2 / T_2 + \Delta^2 / T_1}{\omega_1^2 + \Delta^2},\tag{9.7}$$

i.e., τ^{-1} is a weighted average of T_1^{-1} and T_2^{-1} , with the weightings determined by the components of the effective field. More generally,

$$\frac{1}{\tau} = \frac{(\omega_1 \cos \phi)^2 / T_2 + \Delta^2 / T_1}{(\omega_1 \cos \phi)^2 + \Delta^2},$$
(9.8)

where $\omega_1 \cos \phi$ is the transverse component of $-\gamma \mathbf{B}_{\text{eff}}$ in the vertical plane of the transient. The angle ϕ can equivalently be defined by the equation,

$$\tan \phi = \frac{\delta(1/T_2 - 1/T_1)}{(\omega_1 \cos \phi)^2 + \Delta^2}.$$
(9.9)

When the time scale of the electron-spin relaxation is comparable to the time scale for precession about the resonant transverse component of the microwave field, the term $\cos^2 \phi$ / in Eq. (4) shifts the weighted average toward T_1^{-1} increasing the time constant τ . In the experiments performed at low microwave power and high laser power, for example, $\cos^2 \phi \sim 1/4$. The inverse time constant τ^{-1} gives a rough estimate of the bandwidth, since a distinct drop in the response of a two- level system is expected as the modulation frequency ω_m is increased from a value near zero to $\sim \tau^{-1}$. Numerical tests using the parameters measured at optical excitation intensity of 1.95 MW/cm² found that the response of a two-level system drops by $\sim 1/3$ in this range. Although τ^{-1} does not specify the frequency at which the magnetometer response drops by an exact numerical factor, Eqs. 9.7 and 9.8 give qualitative insight into the dependence of the magnetometer bandwidth on the time constants for electron-spin relaxation.

9.5 Sensitivity Analysis

Photon shot noise is an intrinsic noise source that limits the magnetometers sensitivity. In analyzing magnetic sensitivity in the presence of shot noise, we assume that the ODMR spectrum is a Lorentzian curve and that a small magnetic field $B_z \cos(\omega_m t)$ is measured. The sensitivities of two detection methods are compared. For the single-modulation method, the microwave field is applied at a frequency where the slope of the Lorentzian curve is maximal, and the oscillations of the magnetic field modulate the fluorescence of the NV⁻-center ensemble. For the double-modulation method, frequency modulated microwave field at the modulation rate of ω_c is applied about the peak of the Lorentzian curve, during the detection of the slowly oscillating magnetic field at ω_m , where $\omega_c \gg \omega_m$.

9.5.1 Single-modulation method

When the microwave field is tuned to a frequency where the derivative of the Lorentzian spectrum is maximal, the photodiode current corresponding to the detected fluorescence can be expressed as

$$I(t) = I_0 + CB_z \cos(\omega_m t), \qquad (9.10)$$

where

$$C = \frac{dI}{dB} = \frac{3\gamma P_0 R}{4\Delta\omega} \frac{q}{E_p}.$$
(9.11)

In Eq. 9.11, P_0 is the absorbed power, R is the contrast, $\Delta \omega$ is the spacing between the maximum and minimum points in the derivative of the Lorentzian curve, E_p is the photon energy, and q is the integral of the photodiode current associated with the absorption of a single photon. Shot noise is present in I(t) due to the fact that the photodiode current consists of discrete pulses, where a pulse is associated with the absorption of a photon. The double-sided spectral density of the shot noise associated with the current I_0 is [236],

$$S_n = \frac{P_0}{E_p} q^2.$$
 (9.12)

In a phase-sensitive measurement, the noisy signal is multiplied by $\cos(\omega_m t)$ and integrated for a time t_m that corresponds to an integral number of cycles. This measurement procedure can be associated with a linear filter L that gives output

$$f_L(t) = \frac{2}{t_m} \int_{t-t_m}^t f(t') \cos[\omega_m(t'-t)] dt'$$
(9.13)

in response to an input function f(t). Formally, we can consider that the measurement is performed by reading the output of this filter at time t = 0; note that in the absence of noise, this would produce the value CB_z when I(t) is the input function. We let n(t) represent the shot noise and evaluate the mean-square value of the filtered noise $n_L(t)$ as

$$\langle n_L^2 \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} |H(\omega)|^2 S_n \, d\omega' = S_n \Delta \nu, \qquad (9.14)$$

where $H(\omega)$ is the transfer function of the filter and where the bandwidth is $\Delta \nu = 2/t_m$. Letting the random variable X represent the outcome of the measurement, we define the signal-to-noise ratio (SNR) as

$$\frac{\langle X \rangle}{\sigma_x} = \frac{CB_z}{\sqrt{S_n \Delta \nu}}.$$
(9.15)

Equation 9.15 holds for a measurement performed using a single detection channel; for a gradiometer configuration, the shot-noise-limited sensitivity increases by a factor of $\sqrt{2}$. The minimum field $\Delta B^{(1)}$ detectable by a gradiometer is found by setting the SNR to 1:

$$\delta B^{(1)} = \frac{4\Delta\omega}{3\gamma R} \sqrt{\frac{1}{Nt_m}}.$$
(9.16)

In Eq. 9.16, $N = P_0/E_p$ is the number of photons detected per unit time.

9.5.2 Double-Modulation Method

For the double-modulation measurement, the microwave frequency is modulated with amplitude A and frequency $\omega_c \gg \omega_m$ about the peak of the Lorentzian curve. During the measurement, the offset of the microwave field from the peak is

$$\omega_{t}(t) = \gamma B_{z} \cos(\omega_{m} t + \phi_{m}) + A \cos(\omega_{c} t), \qquad (9.17)$$

where ϕ_m is a constant that depends on the relative phase of the magnetic field and the carrier wave. When the amplitude A is small enough that the spectrum can be approximated by a second-degree polynomial over the modulation range, we write the photodiode current as

$$I(t) = I_0 + \frac{8A\gamma P_0 R}{3(\Delta\omega)^2} \frac{q}{E_p} B_z \cos(\omega_m t + \phi_m) \cos(\omega_c t) + \dots$$
(9.18)

Demodulation is performed by multiplying I(t) by $\cos(\omega_c t)$ and then using a low-pass filter to remove unwanted frequency components. Phase-sensitive detection at frequency ω_m is then used to measure the amplitude of the demodulated signal,

$$I(t) = DB_z \cos(\omega_m t + \phi_m), \qquad (9.19)$$

where

$$D = \frac{2A}{\Delta\omega} \left(\frac{2\gamma P_0 R}{3\Delta\omega} \frac{q}{E_p}\right). \tag{9.20}$$

In Eq. 9.20, the terms grouped in parentheses differ by a factor of order unity from C, as defined by Eq. 9.11, while the ratio outside of the parentheses can be interpreted as the fraction of the linewidth $\delta \omega$ swept through during the modulation by the carrier wave. Equation 9.12 gives the double-sided spectral density of the shot noise n(t) associated with I_0 . The noise in the demodulated signal is $n'(t) = n(t) \cos(\omega_c t)$. A simple argument suggests that multiplying n(t) by a sinusoidal function decreases its power spectrum by a factor of 2. Since n(t) is statistically uncorrelated with $\cos(\omega_c t)$,

$$\langle n^2(t)\cos^2(\omega_c t)\rangle = \langle n^2(t)\rangle \langle \cos^2(\omega_c t)\rangle = \frac{1}{2} \langle n^2(t)\rangle.$$
(9.21)

More formally, it can be shown that the power spectrum of n'(t) is

$$S'_{n}(\omega) = \frac{1}{4} [S_{n}(\omega + \omega_{c}) + S_{n}(\omega - \omega_{c})] = \frac{1}{2} S_{n}$$
(9.22)

where the second equality depends on the fact that S_n is flat in the spectral region of interest. With the outcome of the measurement denoted by random variable Y, arguments similar to those used in obtaining Eq. 9.15 show that

$$\frac{\langle Y \rangle}{\delta_Y} = \frac{DB_z}{\sqrt{S_n \delta\nu/2}}.$$
(9.23)

The minimum detectable field using double modulation with a gradiometer is

$$\delta B^{(2)} = \frac{\Delta\omega}{2A} \left(\frac{3\Delta\omega}{2\sqrt{2\gamma}R}\right) \sqrt{\frac{1}{Nt_m}}.$$
(9.24)

9.5.3 Discussion

Equations 9.16 and 9.24 can be used to compare the sensitivity of the two measurement methods when photon shot noise is the dominant noise source. For both methods, detection sensitivity depends on the gyromagnetic ratio, the line-width and contrast of the spectrum, and the rate at which photons are emitted by the ensemble. The SNR of the doublemodulation method also depends on the factor $2A/\delta\omega$. This dependence can be understood by first noting that after a small shift in the magnetic field, the region of the Lorentzian curve swept through during the frequency modulation is shifted as well. The resulting change in the demodulated signal depends strongly on the derivative of the curve at the end points of the frequency sweep, and a large modulation amplitude is needed in order to guarantee that the curve is steep at the end points of the sweep. In particular, an optimal doublemodulation measurement must sweep to the peaks of the derivative spectrum, which gives $2A/\Delta\omega = 1$. Note, however, that Eq. 9.18 is based on the assumption that the derivative varies linearly over the entire range of the frequency sweep. For a sweep with $2A/\Delta\omega = 1$, this model overestimates the magnitude of the derivative at the end points of the sweep by almost a factor of 2. For large modulations, we can thus expect the sensitivity of double modulation to be poorer than would be predicted by Eq. 9.24.

Although the factor $3/2\sqrt{2} \approx 1.1$ in Eq. 9.24 tends to favor the sensitivity of double modulation, since it is smaller than the corresponding factor 4/3 in Eq. 9.16, it is reasonable to conclude that the overestimate of the derivative implicit in the derivation of Eq. 9.24 is more significant than the difference between these numerical factors. For our experimental tests using a gradiometer configuration, the single-modulation method was more sensitive than the double-modulation method by a factor of 2.5, as described in Sec. 9.3.2. Since this difference is larger than would be predicted by Eqs. 9.16 and 9.24, even allowing for a correction due to the overestimate of the derivative associated with Eq. 9.24, it is likely that technical noise was present in the double-modulation experiment, perhaps due to noise at the output of the lock-in amplifier.

In the absence of technical noise, the sensitivity of a magnetometer configured as a gradiometer is frequently limited by the photon shot noise [107]. Under our experimental conditions with optical excitation intensity of 2.02 MW/cm², $\delta\omega/2\pi = 7.5$ MHz, R~0.043, and detected fluorescence power ~1.0 μ W, Eq. 9.16 yields a photon shot-noise limited sensitivity of 4.4 nT for an integration time of $t_m = 1$ sec, approximately the same as our measured sensitivity. When the sensitivity is limited by the photon shot noise, it should also depend on the optical excitation power as follows:

$$\delta B \propto \sqrt{\frac{1}{N}} \propto \sqrt{1 + \frac{P_s a t}{P}},$$
(9.25)

where N is number of photons of the detected signal per unit time, P_{sat} is a characteristic saturation power of the NV⁻ defects, and P is the applied optical excitation power [237]. The sensitivity of the NV⁻ ensemble to a 2 kHz oscillating magnetic field was measured at various optical excitation intensities from 0.1 to 2.3 MW/cm² and showed good agreement (inset in Fig. 9.6) with Eq. 9.25. Further sensitivity improvements will require reducing the shot-noise limit by increasing the signal contrast using polarization-selective NV^- excitation, [238] by improving either the detector volume or the collection efficiency, [138] or by using a diamond with more favorable properties, such as longer coherence times or a higher $NV^{--}:NV^{-0}$ ratio.

9.6 Conclusion

We have developed an ensemble NV⁻ magnetometer for NMR applications, where the magnetometer must detect weak magnetic fields at frequencies ranging from ten to a few hundred kHz. A maximum detection bandwidth of ~ 1.6 MHz was measured under continuous microwave and optical excitation, limited by the available optical power. A model based on the Bloch equations was used to analyze the response time τ of the NV⁻ center, and τ^{-1} was shown to be a weighted average of T_1^{-1} and T_2^{-1} , with the weightings determined by the effective field in the rotating frame. The bandwidth of the magnetometer is thus increased at high optical powers, where optically induced transitions reduce T_1 and T_2 . In this regime, the Gaussian profile of the laser beam can introduce significant spatial inhomogeneity in T_1 and T_2 . The optimized sensitivity of our ensemble NV⁻ magnetometer is 4.6 ± 0.3 nT/ \sqrt{Hz} , which is better by a factor ~ 5 than the best projected sensitivity for an ensemble NV⁻ magnetometer operating at room temperature and close to the sensitivity of a single NV⁻ center in isotopically pure diamond. Photon shot noise is the dominant noise source in our measurement. Our results demonstrate that magnetic sensitivity of a few nT at room temperature can be achieved with an ensemble of NV⁻ centers in low-cost high-pressure-hightemperature diamond, using a gradiometer configuration that make the measurements robust against most of the experimental noise. The results are promising for the development of affordable, integrated, and portable diamond magnetometers for a variety of magnetic field-sensing applications.

Chapter 10

Towards Detection of Nuclear Spins on a Microfluidic Chip

Previously we studied the effects of optical and microwave radiation on the bandwidth and sensitivity parameters of an ensemble of NV centers with the goal of using these centers as a magnetometer for ultra low field NMR. Here we present progress on bulk detection of nuclear spins in a microfluidic chip using the techniques described in the previous chapter. As initial tests to detect nuclear spin magnetization proved unsuccessful we have proposed some changes to the design and detection scheme in the conclusions section of this thesis.

10.1 Abstract

In this work, we fabricate microfluidic devices integrated with diamond wafers for remote detection experiments at low magnetic field. We flow water that has been polarized in a 2 T field to a microfluidic chip, where we periodically invert the nuclear spin magnetization via an adiabatic frequency sweep of RF irradiation at or near the proton Larmor frequency. We subsequently attempt to detect nuclear spin magnetization using an ensemble of NV⁻ centres at 5 mT. We measure a sensitivity of $3.44 \text{ nT}/\sqrt{Hz}$ for the NV⁻ magnetometer using a 10 μ m³ diamond volume with an approximate NV⁻ concentration of ~ 2 ppm. A sensitivity that should be sufficient to detect the pre-polarized nuclear spins 20 μ m from the microfluidic channel, where the magnetic field produced by the bulk nuclear spin magnetization should be on the order of a nanotesla. We have detected a 94 Hz, 600 pT simulated NMR signal and plan to detect proton spins in bulk water in the near future.

10.2 Introduction

Current state of the art magnetometers can reach magnetic field sensitivities on the order of attotesla/ \sqrt{Hz} (SQUID and alkali vapor magnetometers) [239] [240], and spatial resolutions on the order of nanometers (Hall probes) [241]. However, until recently, the

magnetometer properties of high sensitivity and high spatial resolution have been mutually exclusive. Magnetometers¹ based on the negatively charged nitrogen-vacancy (NV⁻) center in diamond afford high magnetic field sensitivity and high spatial resolution, as indicated in figure 1.2 and Ref. [41]. The NV⁻ center is an atomic scale magnetic sensor, that exhibits spin dependent fluorescence, such that the spin state of the NV⁻ center can be read out using optical methods. Perturbations of the spin state due to local magnetic fields can thus be detected using optically detected magnetic resonance methods. As mentioned in the introduction of this thesis, and once again repeated here, the sensitivity of the NV⁻ magnetometer depends on a few properties, [44],

$$\delta B \simeq \frac{1}{g_s \mu_B} \frac{1}{R_{\sqrt{\eta}}} \frac{1}{\sqrt{NtT_2^*}} \tag{10.1}$$

where μ_B is the Bohr magneton, g_s is the electron g-factor, R is the ODMR fluorescence measurement contrast η is the fluorescence detection efficiency, N is the number of spin centers, t is the interrogation time, and T_2^* is the coherence lifetime of the NV⁻ center. Improvements in the material fabrication of nitrogen vacancy centers in diamond along with improvements in fluorescence collection efficiencies have brought the sensitivity of nitrogen vacancy ensembles into the subp T/\sqrt{Hz} regime [41]. The NV⁻ center provides a unique opportunity to study small spin ensembles of nuclear spins at low magnetic fields, a regime often inaccessible using inductive detection methods due to small fluid volumes and geometric constraints. Here we fabricate a microfluidic device integrated with a nitrogen-vacancy magnetometer for high resolution remote detection experiments at low field. We flow prepolarized water to a microfluidic chip, encode nuclear spins and subsequently attempt detection using an ensemble of NV⁻ centers at tens of gauss. In this study we detect low frequency picotesla fields as a first step towards detecting nuclear spin magnetization in picoliter volumes of flowing water.

10.3 Measurements and Results

The negatively charged NV⁻ center forms an electron triplet state that can be optically pumped to produce high spin polarization in its ground state [85]. It exhibits millisecond coherence times at room temperature and has a theoretical magnetic field sensitivity on the order of fT/Hz [44,87]. The NV⁻ center can be optically pumped with 532 nm light and exhibits spin-selective fluorescence at 637 nm [86]. NV⁻ centers in $m_s = \pm 1$ states have a lower fluorescence probability than the $m_s = 0$ state, with fluorescence contrast demonstrated to be as high as 30% [104]. In the presence of a small axial field along the NV axis the m_s $= \pm 1$ levels split, shifting by $m_s \gamma_e B_z$. The $|0\rangle \leftrightarrow |-1\rangle$ transition can then be selectively driven by applying resonant microwaves perpendicular to the NV axis. For magnetic field detection, we continuously pump the NV centers while applying a fixed microwave source

 $^{^{1}}$ For a discussion of the properties of nitrogen vacancy centers, the reader is referred to chapter 3 of this thesis.

at $f_{MW} = f_{NV} \pm \Delta f/2$. Where Δ f is the FWHM and f_{NV} is the $|0\rangle \leftrightarrow |-1\rangle$ transition frequency. Any fluctuations in the local magnetic field will result in shifts of $\pm m_s \gamma_e B_z$ to f_{NV} , leading to an oscillation in the detected fluorescence signal, see Figures 4.23 and 4.24 in the experimental section of this thesis.

10.3.1 Sensitivity Measurements

The fluorescence from an ensemble of nitrogen-vacancy centers was measured under continuous optical and microwave irradiation at 532 nm and at $f_{NV} \pm \Delta f/2$ respectively. A small AC magnetic field was applied to the NV magnetometer in order to determine the sensitivity of the ensemble to small oscillating magnetic fields. The magnetic field from a test coil was calibrated by applying a range of DC voltages across the test coil loop and then measuring the shift in the position of the NV⁻ resonances, as discussed in chapter 9. Care was taken to ensure that no inductive effects would lead to a decrease in the magnetic field produced by the coil at frequencies up to several kHz. Sensitivity measurements were done as described in chapter 9, though in this case rather than use a gradiometer configuration, we used a single channel configuration. The signal was recorded using an avalanche photodiode and the voltage was sent to a spectrum analyzer (SR770) that output a power spectrum of the fluorescence signal. Signals were integrated for one second and the SNR was compared for a given magnetic field and frequency of the test coil. The sensitivity was calculated by dividing the amplitude of the magnetic field modulation (converted to Tesla using the calibration measurement) by the measured SNR after 1 second, giving a T/\sqrt{Hz} value. An example of the SR770 output is shown in Figure 10.1. We measured a sensitivity of 3.44 nT/ \sqrt{Hz} for a 2 kHz magnetic field, and a 7.51 nT/ \sqrt{Hz} for a 94 Hz magnetic field. All measurements were done after the diamond was placed in a microfluidic chip as shown in the experimental section of this thesis and as shown in figure 10.9. We then proceeded to see if the sensitivity scaled appropriately with respect to time averaging.

10.3.2 Detection of a 600 pT test field

For a sensitivity of 7.51 nT / \sqrt{Hz} , in order to detect a 600 pT signal with an SNR of 3 we would require only ~ 30 minutes of averaging. However in our experiments, several hours of averaging were required to produce the figure shown in 10.3, indicating that over long timescales, the sensitivity at 94 Hz is closer to ~30 nT/ \sqrt{Hz} . This indicates that there is some long term drift that affects the sensitivity. A decrease in the sensitivity occurs when there is a decrease in the ODMR contrast, a large shift in the position of f_{NV} , an increase in the noise floor around 94 Hz and/or a change in the charge state of the NV⁻ to NV⁰.

10.3.3 Pre-polarized Water in 2 T Magnetic Field

As detection of a 600 pT field was shown to be feasible, we moved forward with the magnetization measurements while we adjusted parameters on the experimental setup to



Figure 10.1: 2 kHz, 21nT magnetic field from a wire loop.



Figure 10.2: 94Hz, 21nT magnetic field from a wire loop.



Figure 10.3: 94 Hz, 600 pT magnetic field from a wire loop.

improve ODMR signal stability and sensitivity. Figure 4.15 shows the current configuration of the microfluidics experiments. We used a syringe pump to flow water through a prepolarized magnet to a microfluidic chip fitted with radio frequency coils and a diamond magnetometer. In order to verify that the water was exiting the microfluidic chip in a polarized state we inductively measured the nuclear magnetic resonance signal at 0.2999 Tesla downstream using a micro coil and a Kea Spectrometer. The results of these measurements are indicated in figure 10.4.

Here we verified that the protons maintained polarization through exiting the pre-polarizing magnet, through the microfluidic chip, past the diamond magnetometer and through the microfluidic chip outlet. However, flow rates below 200μ L did not show appreciable increases in the NMR signal due to the pre-polarization at a 2 T field. At these lower flow rates, the travel time between the magnet and the exit port of the microfluidic chip was on the order of T₁.

10.3.4 Adiabatic Inversion Experiments

In our experiments, we adiabatically inverted the nuclear spin magnetization of hydrogen nuclei in water as the water flowed by a set of planar RF coils, see figures 4.20 and 4.21. Adiabatic inversion pulses can be used to uniformly invert the spin magnetization in the presence of RF field inhomogeneities and frequency offsets [129]. In our experiments we swept the frequency of the RF pulse through the expected resonance frequency of the nuclear



Figure 10.4: Free induction decay of protons at the microfluidic chip exit port for different flow-rates. For 1100 μ L/min, NP indicates that the flow bypassed the pre-polarizing magnet.



Figure 10.5: Figure shows an adiabatic sweep with limitations on the speed of the sweep and requirements of the strength of the B₁ field, w_s is the RF frequency, w₁ is the Rabi Frequency for the nuclear spins, w_{eff} is the effective field, $d\theta/dt$ it the change in the orientation of the magnetization vector with respect to time. For maintaining an adiabatic condition in AFP the conditions required are $d\theta/dt \ll w_{eff}$

spins at 50 Gauss. The form of the sweep, as well as the adiabatic conditions are shown in Figure 10.5.

As pre-polarized water flowed through the pulse coils the magnetization was periodically inverted on the same timescale as the flow. Typical flow rates used range from 200 μ l/min to 500 μ l/min. For these flow rates the residence time in the coil region was on the order of milliseconds, thus requiring the detection of frequencies in the low kHz to tens of Hz region. The larger noise floor at these frequencies is problematic, but not insurmountable as demonstrated in figure 10.3. As the water flowed through the microfluidic chip we continuously recorded the NV fluorescence. Unlike the sensitivity measurements, here the voltage output was sent through a preamplifier (SR560) and the output of the pre-amplifier was collected using a data acquisition card. The signal acquisition and processing methods used to produce figures 10.3 and 10.2 is described in section 4.3.4.

The results of an adiabatic inversion flow experiment for inversions at 111 Hz is shown



Figure 10.6: Measurements of nuclear spin magnetization were inconclusive, the figure shown above is the case for inversion of the spin magnetization at 111 Hz, however it was clear that the signal was still present at 111 Hz whether or not water was flowing through the chip. We attribute this signal to incomplete cancelation of any DC offset field at the RF coils.

in figure 10.6. Though figure 10.6 indicates the presence of a fluctuating signal at 111 Hz we cannot contribute this to signal from the inversion of the nuclear spin magnetization signal. As indicated in figure 10.6 the signal was still present when the flow was turned off and the RF pulse program remained on. This indicates that perhaps we are picking up a small picoTesla to nanoTesla field being produced by some DC offset from the RF coils as the magnetic field is turned on and off at 111 Hz, rather than true spin magnetization.

In order to remove the effect of the RF coils, we incorporated a 'dummy pulse' system into our experiments, as indicated in figure 10.7. This had the effect of shifting the noise peak to a higher frequency while removing any of the noise at the lower frequency. Unfortunately, though this did remove the noise peak, it did not result in the appearance of an NMR signal. Further measurements indicated that the RF coils were not working properly and so we have begun work on a new design.



Figure 10.7: The NV⁻ ensemble was continuously irradiated with a 532 nm laser and microwaves at $f_{NV} \pm \Delta f/2$, τ_f indicates the wait time between adiabatic pulses, set by twice the residence time of the water inside the RF coil. This yields a plug of water with nuclear spins inverted due to the adiabatic pulse, followed by a plug of water that has not been inverted at all. τ_f gives the period of the expected spin magnetization signal.

10.4 Discussion and Conclusions

We have measured a magnetic field sensitivity of 3.44 nT/ \sqrt{Hz} at 2 kHz and 7.51 nT/ \sqrt{Hz} at 94 Hz with a diamond wafer integrated onto a microfluidic chip. We have also detected a 94 Hz, 600 pT simulated NMR signal using this system, however the sensitivity did not scale appropriately, due to drift, and changes in the noise floor over several hours. For such experiments to be feasible we would have to determine a better way to stabilize the fluorescence signal at low frequencies. Alternatively we could increase the sensitivity by an order of magnitude perhaps by using a larger spot size to illuminate a larger number of fluorescent centers and in corporation of a lens setup as in Ref. [41] to improve collection efficiencies. With further development in chip design and detection methodology, remote detection NMR experiments with nitrogen-vacancy centers should be possible. This could eventually lead to more robust and convenient methods to study mesoscale fluid dynamics with NMR.

10.5 Methods

Microfluidic glass chips were fabricated using photolithography and HF acid wet etch processing methods. Both sides of the glass chip were etched to maintain a 10-20 μ m separation between the channel and the diamond wafer. Spiral RF coils were fabricated using photolithography and a ferric chloride etching process. The preliminary chip design was based on Taylor-Aris dispersion models [127]. An HPHT diamond was polished to 20 μ m thickness and was proton irradiated to yield with a ~ 2 ppm NV⁻ concentration. The diamond was 20 um thick to remove background fluorescence from NV centers not experiencing the magnetic field from nuclear spins at the surface.

From Ref. [242] the magnetization M_p of a density of proton spins n_p due to pre polarizing magnet B_p at the thermal energy $k_B T$ is,

$$M_p = n_p \mu_p \frac{1}{2} \left(e^{\mu_p B_p / (k_B T)} - e^{-\mu_p B_p / (k_B T)} \right) \approx n_p \mu_p^2 B_p / (k_B T)$$
(10.2)

where μ_p is the proton magnetic moment, n_p is the spin density, B_p is the strength of the pre-polarizing magnet, k_B is boltzmann's constant, T is the temperature. We then multiply the magnetization M_p by the vacuum permittivity μ_0 to yield the strength of the magnetic field at the surface of the spin ensemble. For our system, with a 2 T pre-polarizing magnetic field, we found that the magnetic field at the surface of t



Figure 10.8: Pre-polarizing Magnet, shielded in $\mu\text{-metal}$ above 3-axis Helmholtz coil array for controlling magnetic field at NV center



Figure 10.9: Test Coil used for Low Frequency AC Field Measurements, 34 Gauge wire attached to end of a coaxial cable hooked up to an Agilent frequency generator.

Chapter 11 Conclusions and Outlook

In this dissertation, we've explored the physics of nitrogen vacancy ensembles in a number of different contexts. We've discussed the physics of the nitrogen-vacancy center in detail and have explored the effect that a variety of perturbations have on the optically detected magnetic resonance spectra of an ensemble of these centers. We then demonstrated a novel method for extending the coherence lifetime of a large nitrogen-vacancy spin ensemble by two fold, with a potential 60 fold improvement. In chapters 6 and 7 we demonstrated sensitive detection of nuclear and electron spins in a diamond lattice. Using a nitrogenvacancy ensemble we discovered a novel method for measuring nuclear quadrupoles coupled to an electron spin system in the solid state. We also reported sensitive chemical detection of the hyperfine structures of neighboring diamond defects using continuous wave ODMR measurements. In chapter 8 we demonstrated sensitive magnetic control of the nuclear spin polarization of ¹³C spins neighboring NV⁻ defects. We then shifted our focus to detecting magnetic fields and spins external to the diamond lattice. In chapter 9 we explored the effects of optical and microwave irradiation on the magnetic field sensitivity of nitrogen vacancy centers and improved the detection sensitivity by using a gradiometer method to cancel out laser noise fluctuations. We then discussed progress toward the detection of nuclear spins using NV^- centers embedded on a microfluidic chip. Using the techniques described in this thesis we hope to move forward with detection of electron and nuclear spin systems outside of the diamond lattice, and we will describe a few of the proposed experiments in the pages that follow.

11.1 Detection of NQR in Cuprite

The copper nucleus of cuprite (Cu₂O) is a spin 3/2 nucleus with an exceptionally large quadrupole splitting of ~ 26 MHz at room temperature. Due to the large quadrupole splitting of the copper nucleus in Cu₂O, the nuclear spin is highly polarized at low magnetic fields. The polarization of the copper nucleus is sufficiently large that the Cu₂O magnetic resonance spectrum can be measured inductively at very low magnetic fields. The crystal lattice of Cu₂O is exceptionally close to that of diamond, and like the zero field splitting of the NV⁻ center, the quadrupole splitting of the Cu₂O is preferentially aligned along one of the crystal axes. The Cu₂O crystal lattice can be described as a face-centered cubic embedded in a body-centered cubic. The interesting part about this is that a Cu₂O crystal could be aligned such that the NV⁻ axis and the Cu-O axis of the cuprite are parallel to one another. Because the NV⁻ center is most sensitive to magnetic fields that fluctuate about its axis, one could imagine applying an RF field that inverts the Cu spin magnetization to produce a fluctuating magnetic field that the NV⁻ centers could then detect. We have calculated the magnetic field from the cuprite to be on the order of 500 pT based on equation 10.2. Preliminary experiments are currently underway.

11.2 Cross-Relaxation with DPPH

In chapter 7, we obtained chemically specific information about defects neighboring the nitrogen vacancy center simply by looking at the NV⁻ ODMR signal. We observed changes in the NV⁻ fluorescence intensity when we applied RF matching the hyperfine transition frequencies of neighboring defects, and we attributed this effect to a cross relaxation mechanism between the NV⁻ center and the neighboring defect. In principle, we could also use this mechanism to obtain information about the fine structure of neighboring electron spins that are external to the diamond lattice. The average distance between the NV⁻ center and the detected electron defects was ~ 8 nm, thus if a high concentration of NV⁻ centers are brought sufficiently close to the surface, we could detect chemically specific information of radicals coated on the surface of the diamond.

Using nitrogen ion implantation we have formed a layer of shallow nitrogen vacancy centers in diamond ~ 5 nm from the diamond surface. We have coated the surface with DPPH and expect to see dips in the NV⁻ fluorescence intensity at irradiation frequencies corresponding to DPPH transition frequencies at zero-field. The full DPPH hamiltonian and calculated eigenvalues are shown at the end of chapter 8.

11.3 Microfluidics: Future Work

In chapter 10 of this thesis we discussed progress towards detection of bulk nuclear spin magnetization external to the diamond lattice. Our results proved inconclusive and we identified several aspects of the experiment that could be improved. We have redesigned the experiment in a number of ways, first we've modified the coils to minimize residual field effects at the diamond, second we've considered convective effects due to the interaction of the water with the edges of the microfluidic chip and third we've considered a new detection scheme that would use time correlated measurements to identify inversion patterns in the spin magnetization. The new chip designs are shown in figures 11.1 and 11.2.



Figure 11.1: The new design incorporates a new set of RF coils that will reduce any residual fields experienced by the NV^- center. The housing is made of delrin and the holder is made of aluminum. The coil will be threaded through micro machined holes in the delrin housing.



Figure 11.2: This shows another perspective of the design from Figure 11.1, showing the glass chip held in place by the delrin housing.

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Appendix A Rate Equations

Using the rate constants indicated in chapter 3 we can simulate how the NV^- spin population changes. We have included the optical pulse figure from chapter 3 for comparison with real experimental data. Starting at 0.5 us, figure A.1 should match the purple trace in the simulation data.

Time units are in μ s

```
In[107]:= (*This program calculates the spin state distribution of
         NV^- centers for different pumping rates and pumping times. Thanks
         to A. Jarmola for initial code template*) (*Single NV case*)
ln[108]:= Clear[\alpha]; Clear[Na, Nz, Fpump, Frel, Fo, \alpha, Ntot, Ts, Nez, Nexy, Nxy, sol, eqs, F1];
       Ntot = 1;
       \alpha = .33; (*branching ratio to metastable states*)
       \Gamma s = \frac{1}{219} * 10^{3}; \; (*decay \; rate \; of \; metastable \; state \; 1A1 \; 219 \; ns, \; convert \; to \; us*)
       \Gamma o = \frac{1}{10} * 10^{3}; (*3E \text{ excited state decay rate, } 10ns, \text{ convert to } us*)
       \Gamma 1 = \frac{1}{10}; (*1/T1 in us*)
In[114]:= eqs =
         {Nz ' [t] == F1 (Nxy [t] - Nz [t]) - Fpump Nz [t] + Fo Nez [t] + Fs Na [t], (*^3A_{20}, ms=0*)
          Nxy'[t] == \Gamma 1 (Nz[t] - Nxy[t]) - \Gamma pump Nxy[t] + \Gamma o (1 - \alpha) Nexy[t],
          (*^{3}A_{2+-}), ms=+/-1*)
          Nexy'[t] == \Gammapump Nxy[t] - \Gammao Nexy[t], (*^3E, ms=+/-1*)
          Nez'[t] == \Gammapump Nz[t] - \Gammao Nez[t], (*^3E, ms=0*)
          Na'[t] == \Gamma o \alpha \operatorname{Nexy}[t] - \Gamma s \operatorname{Na}[t], (*^1A1*)
          (*Nz'[t]+Nxy'[t]+Nexy'[t]+Nez'[t]+Na'[t]==0,*)
          (*Ntot==Na[t]+Nxy[t]+Nz[t]+Nexy[t]+Nez[t],*)
          (*set initial conditions of NV- system*)
          Na[0] == 0, (*1A or 1E*)
          Nz[0] == Ntot / 3, (*ms=0, 3A*)
          Nxy[0] == 2 Ntot / 3, (*ms=±1, 3A*)
          Nez[0] = 0, (*ms=0, 3E*)
          Nexy[0] = 0\} (*ms=\pm 1, 3E*)
\text{Out[114]=} \left\{ Nz'[t] = \frac{1000 \text{ Na[t]}}{219} + 100 \text{ Nez[t]} + \frac{1}{10} (Nxy[t] - Nz[t]) - \Gamma pump Nz[t], \right\}
         Nxy'[t] = 67. Nexy[t] - \Gamma pump Nxy[t] + \frac{1}{10} (-Nxy[t] + Nz[t]),
         Nexy'[t] = -100 Nexy[t] + \Gamma pump Nxy[t], Nez'[t] = -100 Nez[t] + \Gamma pump Nz[t],
         Na'[t] = -\frac{1000 Na[t]}{219} + 33. Nexy[t], Na[0] = 0,
         Nz[0] = \frac{1}{2}, Nxy[0] = \frac{2}{2}, Nez[0] = 0, Nexy[0] = 0
```

2 | RateEquations.nb

```
Clear[Tpump];
Fpump = 20;(*pump rate, number of photons per microsecond*)
(*This gives 532 nm beam intensity. pump x photon energy
 532nm J x J to W conversion factor divided by irradiation
 spot size area for Gaussian Beam, spot with 1um diameter*)
Intensity = Tpump ph / usec * 10<sup>6</sup> usec / sec 3.74 *
  10^{-19} J/ph * \frac{W \sec}{J} * 1/((0.5 * 10^{-6}) cm)^2 * \pi / 2)
(*1.76*10^17/cm^3/ppm*)
(*saturation intensity for NV ensemble =
 excited state lifetime ph/s*photon energy J/ph/absorption cross section * J
    to W conversion* laser penetration depth into diamond* NV- density in
    diamond* NV density in our diamonds* illumination spot of 1um diameter*)
Isat = 1/10/10^{-9} ph/sec * 3.74 * 10^{-19} J/ph/(3 * 10^{-17} cm<sup>2</sup>) * GW
  \sec / 10^9 / \texttt{J} * \texttt{0.1 cm} * \texttt{1.76} * \texttt{10}^{\texttt{17}} \texttt{cm}^{\texttt{-3}} / \texttt{ppm} * \texttt{15 ppm} * (\texttt{.5} * \texttt{10}^{\texttt{-6}}) ^2 * \pi / 2 \texttt{cm}^2
(*note, that based on recent findings by Aslam 2013,
saturation intensity of NV-
 centers is not inversly proportional to cross section,
the effect of NV- to NVO conversion must be considerd, it is not
 considered here: we have not caluclated the error associated with that*)
(*Isat for single NV*)
Isats = 1 / 10 / 10^{-9} ph / sec * 3.74 *
  10^{-19} J/ph/(3 * 10^{-17} cm^2) * MW sec/10^{6}/J cm^2
(*SatIntensity=1/10/10^{-9}ph/sec*3.74*10^{-19}J/ph*)
  1.76*10^{17}cm<sup>-3</sup>ppm<sup>-1</sup>*15ppm*0.1cm*MW sec/10<sup>6</sup>/J*)
(*Finds symbolic solutions to system of differential equations*)
spump = Tpump * 10^6 ph / sec;
sol = DSolve[eqs, {Na[t], Nz[t], Nez[t], Nexy[t], Nxy[t]}, t];
(* FullSimplify tries a wide range of transformations on expr involving
 elementary and special functions and returns the simplest form it finds*)
gz = sol[[1, 5, 2]] // FullSimplify; (*Simplifies Nz[t]*)
gxy = sol[[1, 4, 2]] // FullSimplify; (*Simplifies Nxy[t]*)
shelf = sol[[1, 1, 2]] // FullSimplify; (*Simplifies Na[t]*)
ez = sol[[1, 3, 2]] // FullSimplify; (*Simplifies Nez[t]*)
exy = sol[[1, 4, 2]] // FullSimplify; (*Simplifies Nexy[t]*)
gs = gz + gxy; (*Total population in 3A_2 manifold*)
Needs["PlotLegends`"];
LogPlot {Re[gz], Re[gxy], Re[shelf], Re[ez] + Re[exy]}, {t, 0, 2},
 \texttt{PlotStyle} \rightarrow \{\texttt{Red}, \texttt{Blue}, \texttt{Green}, \texttt{Purple}\}, \texttt{Frame} \rightarrow \texttt{True}, \texttt{FrameLabel} \rightarrow \texttt{PlotStyle} \rightarrow \texttt{Red}, \texttt{Blue}, \texttt{Green}, \texttt{Purple}\}
  \left\{\text{"Time } [\mu s]\text{", "Population", "}\Gamma_{pump}=2 \times 10^7 \text{photons/s ~19} \frac{W}{cm^2}, \text{ } \text{T}_1=10 \text{us", "}\text{"}\right\},
 LabelStyle \rightarrow Directive[Large], PlotRange \rightarrow {0.01, 1},
 ImageSize \rightarrow 600 {1, 1 / GoldenRatio}
```

RateEquations.nb | 3



In[124]= (*This simulation shows how the spin state populations change over time, purple is the total excited state spin population, see Figure A1, green is the population in the singlet state, red is population in ms=0 state, blue is population in the ms= +-1 state *)



Figure A.1: Fluorescence of NV^- during Optical Pulse

Appendix B Microfluidic Chip Fabrication

Here we have included the protocol for glass Microfluidic chip fabrication, we are indebted to the Mathies lab for providing some of the helpful information on cleaning glass wafers. And also a special thanks to Anna Parker for developing a large portion of this protocol. The 4" glass wafers were ordered from Precision Glass and Optics, coated with 100nm of amorphous silicon, and were 1 mm thick. Two glass wafers were used for each set of chips. One glass wafer was etched with a channel and the divot for the diamond piece and the other glass wafer was placed on top of the channel to form a sealed microfluidic channel. The masks used for the chip fabrication are included in figures B.1 and B.2.

B.1 Etching of Glass Chip

B.1.1 Etching Box into First Wafer

- 1. After putting on appropriate PPE (smock, face shield, green gloves) clean wafers thoroughly in piranha (3 parts hydrogen peroxide, 7 parts sulfuric acid), rinse well with water, bake to dryness at 160 C°
- 2. Coat one side of wafer with photoresist (in this case, S1818) and place in spin coater with the following protocol:
 - (a) 10 s, 500 rpm, acceleration ~ 100 rpm/s
 - (b) 30 s, 2500 rpm, acceleration \sim 300 rpm/s
- 3. Bake wafer with photoresist for 90 s at 120 $^{\circ}$ C°.
- 4. Align mask with box for diamond over wafer in aligner and expose for appropriate amount of time. For a power of $\sim 40 \text{ mW/cm}^2$, 4 s of exposure was found to be the adequate dosage.
- 5. Develop in 1:1 microdev to water mixture just until pattern from mask is prominent, remove wafer and rinse thoroughly with water.

- 6. Once wafer is dry, cover blank side with kapton tape so as to protect it during etching.
- 7. Etch with oxygen and sulfur hexafluoride using RIE (reactive ion etching) instrument.
 - (a) The power of the RF supply for this instrument is 600 W. To etch, the vacuum for the instrument should always be running in the adjacent storage room. Valves for tanks of oxygen and sulfur hexafluoride should be opened for etching and closed when finished.
 - (b) Vent the chamber to be able to place the wafer inside, with the side to be etched facing up.
 - (c) Close chamber, pump down to ~20 mtorr, and allow ~100 mtorr (for a total 120 mtorr pressure in chamber) of oxygen into the chamber. Once the pressure stabilizes, turn on RF at 25% power (150 W) for 1 minute. This removes any organics that could be on the surface of the wafer. Plasma should show purple.
 - (d) Shut off flow of oxygen pressure, wait for chamber pressure to reach ~ 20 mtorr, and then allow ~ 100 mtorr of sulfur hexfluoride into the chamber. SF₆ requires higher flow rates to allow enough gas into the chamber. Once pressure has stabilized, expose to RF at 33% power (200 W) for 4 min. This will remove the silicon layer to expose the glass that is to be the divot.
 - (e) Pump chamber to ~ 10 mtorr and vent to atmosphere three times before venting and removing the wafer. Once the chamber is closed, pump down to ~ 20 mtorr, and turn off pumping. Close relevant gas valves in the adjacent storage room.
- 8. Etch with hydrofluoric acid in hood across from gas etching apparatus. After putting on appropriate safety gear (smock, face shield, green gloves), dispense enough HF into a teflon (nonceramic, nonmetal container) dish to adequately submerge the wafer. Mark the time the wafer is submerged. Etch in HF until appropriate amount of glass has been removed. HF usually etches around 6.5 microns/min. In case of doing very long etches, it would probably be useful to pump out the used HF and add fresh acid every hour or so. The depth of etching should be checked with calipers to ensure desired depth.
 - (a) For etching ~980 microns as in the case of this glass chip, it took ~5 hrs of etching. I would let it etch for about an hour, rinse it thoroughly and measure the progress of the etch, replace the HF, and let it sit until it was to what I estimated to be the desired depth
 - (b) Once etching is complete, submerge wafer into water bath for at least ten seconds, pump out used HF from glass dish, and then rinse every tool used thoroughly with water. Dry wafer.

B.1.2 Etch Channel on Reverse Side of First Wafer

- 1. Remove adhesive from the kapton tape that protected the opposite side of the wafer. Clean wafer thoroughly in piranha acid, rinse with acetone/IPA/water and bake at 160 C° to dryness. Cover divot-etched side with kapton tape.
- 2. Follow standard procedure for applying photoresist to new side, making sure to align channel directly over the center of the divot.
- 3. Etch with oxygen and sulfur hexafluoride following the same procedure, as well as HF using the appropriate etch time to achieve 100 micron depth of the channel.

B.1.3 Drilling Holes Into a 2nd Glass Wafer Before Bonding

- 1. Remove kapton tape from wafer, rinse with acetone/IPA/water to remove all remaining photoresist, and clean with piranha acid mixture.
- 2. Take a second piece of glass for sealing the channels and providing holes for the microports.
- 3. Drilling holes in glass wafers is problematic even with diamond drill bits. For drilling clean holes into glass, it is a good idea to temporarily bond two glass wafers with resin and drill through both. You can then separate them and discard the wafer that was used as backing.
 - (a) Heat one clean glass wafer on a hot plate covered in aluminum foil to $\sim 200 \text{ C}^{\circ}$.
 - (b) Cover the wafer with crushed pine resin, allowing resin to melt
 - (c) Smear the second glass piece over the first wafer until an adequate layer of resin is achieved between pieces, with minimal air bubbles.
 - (d) Remove foil and glass from heat and press down on glass wafers until the resin solidifies.
 - (e) Clean off exposed sides of wafer by scraping off resin and rinsing with acetone.
- 4. Mark holes to be drilled with diamond bits, this can be done in the BNC. Make sure to cover holes with drilling fluid. For this case, use 1 mm drill bit size, and ease carefully into the glass, pecking at it until the bit goes through both pieces. Go slowly, or else holes will not be clean on either wafer.
- 5. Once all holes are drilled, clean up area and separate wafers by melting the resin in the same fashion.
- 6. Scrape and clean off remaining resin.

B.2 Bonding

B.2.1 Cleaning the Two Glass Wafers, Drilled and Etched

- 1. Quick DI water rinse. (15-30 sec)
- 2. Brush clean with NovaClean to remove grease, particles, etc.
 - (a) Use the shallow pyrex pie dish for the NovaClean wash.
 - (b) Brush both sides of the wafer vigorously; rinse in the NovaClean solution repeatedly.
- 3. Longer DI water rinse, in large tank under running water (1-3 min).
- 4. Blow dry w/ N2 gun. (Skip this step if going straight to the acetone sonication.)
- 5. Acetone sonication, 5-10 min. Set wafers with the etched side facing down.
- 6. Rinse wafers with acetone, IPA, and DI H20. (Note: rinse the acetone off with IPA before it evaporates, and rinse the IPA off with H2O before the IPA evaporates.)
- 7. Blow dry w/ N2 gun. Inspect for particles, etc.
- 8. Strip Si off front side at this stage if necessary (for bonding, etc).
- 9. Piranha clean, 10 min.
- 10. Quick-dump rinse, 2 + cycles.
- 11. Spin-rinse dry top SRD is for 6" wafers, bottom SRD for 4".

If you are cleaning a wafer after holes have been drilled, it may be helpful to do an acetone sonication and rinse before the NovaClean scrub, then sonicate afterwards again with fresh acetone.

Notes on wafer handling (general):

- 1. Always wear gloves
- 2. Touch wafer only at the edges, use tweezers or vacuum wand if appropriate.
- 3. When transferring wafers between two cassettes, lock the cassettes together and flip to transfer. (This is cleaner than touching the wafers with gloves/tweezers/vacuum wand.)
- 4. When drying wafers with the N2 gun, first blow-dry the back side, then lay the wafer dry-side down on a technicloth to blow-dry the front side from center to edge. The idea here is to blow the water off the edge of the wafer onto the technicloth.
- 5. Do not put your hands, face etc directly over a wafer, especially when under a laminar flow hood. Also try not to talk over or breathe onto the wafer when you are working.

B.2.2 Bonding the Two Wafers

- 1. Choose two Macor disks
- 2. Tap out a small amount of graphite powder onto the bonding surface of each Macor disk. Look at the side of the disk the arrows scribed on the side (near the disk's name) point to the appropriate surface.
- 3. Using a technicloth, rub the powder over the surface so that the entire area receives a very thin, even coating. Put some IPA on the technicloth, then go over the surface again to wipe off excess graphite and to make the coating more uniform.
- 4. Carefully take the wafers out of the tray and sandwich them between the Macor disks. The side with drilled holes should face down. DO NOT let the wafers separate. If the wafers come apart, you will need to take them back to the Microlab and repeat the cleaning process.
- 5. Carefully slide the Macor-wafer sandwich into the furnace. You should be able to fit two 4" wafer/macor setup or one 6" wafer/macor setup into the atmospheric furnace for each bonding run.
- 6. Carefully place a stainless steel disk (1 kg) on top of each wafer-bonding assembly. Make sure that you use the stainless steel disk, NOT the graphite disk.
- 7. Check the furnace programs you want to use to make sure the rates, temperatures, and times are correct, then set the furnace to run your two linked programs.
- 8. Usual parameters for bonding borofloat wafers:
 - (a) 4" wafers, 2-layer chip: $668C^{\circ}$ for 6 hrs
 - (b) 4" wafers, 3-layer chip: 668C° for 8 hrs
 - (c) 6" wafers, 2-layer chip: $668C^{\circ}$ for 8 hrs

Additional tips and tricks can be found at: http://openwetware.org/wiki/Mathies: Glass_Bonding



Figure B.1: Square Mask for etching of diamond pocket in glass chip



Figure B.2: Photomask for Microfluidic Chip, 6 cm long, 300um wide channel

Appendix C

Adiabatic Fast Passage

%This program will find the ideal rate and sweep width for shorter pulses %that satisfy the adiabatic condition. The adiabatic condition is: %w_eff >> dtheta/dt

%For mathematical details, please see: Mathematical treatment of %adiabatic fast passage pulses %for the computation of nuclear spin relaxation rates in proteins %with conformational exchange, by Renate Auer

%This program checks the instantaneous value of dtheta/dt as w_eff(t) %changes in amplitude

%Everything in units of radians

%w_1 = Strength of B1 field
%w_s = pulse offset

%Initialize Pulse Parameters
P = 500*10^(-6);%length of pulse (s)
Dw=2*pi*300*10^3;%Sweep width radians
R=Dw/P;%Sweep rate radians/s

%Determine portion of pulse that will be ramped and ramp rate a=.20;%10 to 20% of total pulse length (region for ramping) Q= 2*pi/(a*P*4); %ramp rate (radians), % of pulse to be ramped a*P, this is one fourth of %total waveform, so multiply time by 4 this is the period of the waveform %needed to ramp up appropriately.

%Proton, gyromagnetic ratio and Larmor precession frequency gamma=4258;%Hz/G B1=10;%10 Gauss field generated by coil...7 is more realistic.

```
B0= 50; %Gauss (See if you can increase this further...like 75G)
w0=B0*gamma; %Larmor precession frequency rad/s
%Size of Matrices for Data Storage
s=10<sup>-7</sup>;%(s) sampling rate for simulation
n=round(P/s);
M = zeros(n, 7);
%Initialize effective field parameters
%for i=1:1:4
    %R=i*...
    for t=1:1:n %sample until end of pulse
        step = t*s; % step size
        w_s= R*(step-P/2);%pulse offset in Hz...
         if (step <= a*Dw/R)</pre>
             w_1= 2*pi*gamma*B1*(1-cos(Q*step));%^2if false, will go to next line
             T = (2*pi*gamma*B1*Q*sin(Q*step)/(R*step-P*R/2)-...
                  (2*pi*gamma*B1*R*(1-cos(Q*step))/(R*step-P*R/2)^2))/...
                  ((2*pi*gamma*B1)^2*(1-cos(Q*step))^2/(R*step-P*R/2)^2+1);
        elseif (step <= Dw/R-a*Dw/R)</pre>
             w_1= 2*pi*gamma*B1;
             T = 8*gamma*pi*B1*R/(16*(gamma*pi*B1)^2+R^2*(P-2*step)^2);
        else (step <= Dw/R);</pre>
             w_1= 2*pi*gamma*B1*(1+cos(Q*step+pi/2));
             T = (-2*pi*gamma*B1*Q*cos(Q*step)/(R*step-P*R/2)-...
                  (2*pi*gamma*B1*R*(1-sin(Q*step))/(R*step-P*R/2)^2))/...
                  ((2*pi*gamma*B1)<sup>2</sup>*(1-sin(Q*step))<sup>2</sup>/(R*step-P*R/2)<sup>2</sup>+1);
         end
        w_{eff} = (w_{s}^{2} + w_{1}^{2})^{.5};
        M(t, 1) = step;
        M(t, 2) = w_eff;
        M(t, 3) = w_1;
        M(t, 4) = w_s;
        M(t,5)=T; %This is d(theta)/dt,
        M(t,6) = atan(w_1/w_s) * 180/pi;
        M(t,7) = w_1/2.5;
    end
```

%end

```
%Convert everything back to Hz
figure(3)
plot(M(:,1).*10^6,M(:,2)./1000/(2*pi),'k'); %w_eff
```

```
hold on
plot(M(:,1).*10^6,M(:,3)./1000/(2*pi), 'b'); %w_1
%I need to compare this to dtheta/dt
plot(M(:,1).*10^6,M(:,4)./1000/(2*pi), 'r'); %w_s (Hz)
plot(M(:,1).*10^6,abs(M(:,5)./1000), 'g'); %dtheta/dt
plot(M(:,1).*10^6,(M(:,6)), 'c');
plot(M(:,1).*10^6,(M(:,7)./1000/(2*pi)), 'm');%w1/T2
%add a line that is at w_0 to show that it is sufficiently large with
%respect to w_eff (otherwise this should not work...)
xlabel('Time (us)')
ylabel('w(kHz)')
legend('w_eff','w_1','w_s','d\theta/dt','theta','w_1/T2')
```

```
hold off
```

Appendix D

Calculation of NV Eigenvalues

Starting with the NV⁻ Hamiltonian, we can calculate the effect of a magnetic field on the NV eigenvalues, in the $m_s = -1, 0, +1$ basis using the following code:

```
%This hamiltonian is for a single NV, no coupling of NV to bath
clear all;
load PM_spin1.mat;%Load Pauli Matrices (Sx,Sy,Sz), where S =1;
%Define relevant constants
g_e= 2.802495266;%MHz/G, gyromagnetic ratio electron
g_c=1.0705e-3;%MHz/G, gyromagnetic ratio carbon nucleus, spin 1/2
g_n=3.07e-4;%MHz/G, gyromagnetic ratio nitrogen-14 nucleus, Spin 1
D= 1420;%MHz
E= 3.5; %MHz
%Magnetic Field Orientation w.r.t. NV axis
theta=0;
phi=0;
%Set Magnetic Field Magnitude Range, G
Bi=0;%initial
Bf=1500;%final
Bs= 1;%step
Bp=zeros(Bs);%Size of Field vector
n= size(Bi:Bs:Bf,2);%select # of columns
%Initialize EigenMatrices, Pauli matrix size selected
s=size(Sz,2);
Evector =zeros(n,s,s);
Evalue = zeros(n,s,s);
%NV Hamiltonian
for k=1:n;
    B=Bi+Bs*(k-1);%Initiate at B=0
```

```
H = D*(Sz*Sz-(Sx*Sx+Sy*Sy+Sz*Sz)/3)...%D Zero-Field splitting
        +E*(Sx*Sx-Sy*Sy)...%Axial Zero-field splitting (E)
        +g_e*B*(sin(theta)*cos(phi)*Sx+sin(theta)*sin(phi)*Sy+cos(theta)*Sz);
    [Evector(k,:,:),Evalue(k,:,:)] = eig(H); %Find Eigvec and Eigval
    Bp(k,1)=B;
end
plot(Bp,Evalue(:,1,1),'ko',...
    Bp, Evalue(:,2,2),'bo',...
    Bp, Evalue(:,3,3),'ro',...
    Bp, Evalue(:,3,3),'ro',...
    Bp, Evalue(:,4,4),'go',...
    Bp, Evalue(:,5,5),'co',...
    Bp, Evalue(:,6,6),'mo');
```

Appendix E

Derivation of Time Constant for Transient Response

Chapter 9 considers the response of a two-level system to a modulated longitudinal field. When the Rabi frequency is large compared to the modulation frequency ω_m , a simplified model of the evolution can be used to explain the drop in the response as ω_m is increased from zero to $\sim \tau^{-1}$. In this appendix, we present a more formal description of this model and derive Eqs. 9.7 and 9.8, which express τ^{-1} as a weighted average of T_1^{-1} and T_2^{-1} , The Bloch equations can be written in the form,

$$\frac{d}{dt}\mathbf{M} = A\mathbf{M} + \mathbf{M_0},\tag{E.1}$$

where,

$$A = \begin{bmatrix} -1/T_2 & -\Delta & 0\\ \Delta & -1/T_2 & -\omega_1\\ 0 & \omega_1 & -1/T_1 \end{bmatrix},$$
 (E.2)

and $\mathbf{M}_{\mathbf{0}} = [0, 0, M_0]^T$. The general solution to Eq. E.1 is $\mathbf{M} = \mathbf{M}' + \mathbf{M}_s$; where \mathbf{M}_s is the steady-state solution, [235] and where the transient \mathbf{M}' satisfies,

$$\frac{d}{dt}\mathbf{M}' = A\mathbf{M}'.\tag{E.3}$$

The evolution of \mathbf{M}' can be visualized as involving both precession about the effective field and relaxation toward zero, since Eq. (A2) is equivalent to a set of Bloch equations with $M_0 = 0$. If precession about the effective field is fast compared to relaxation, transients that are initially perpendicular to the effective field precess while decaying, but a transient initially aligned with the effective field remains aligned with it during the decay, rather than precessing. More generally, we note that diagonalization of A must yield at least one real eigenvalue λ_1 , since the complex eigenvalues of a real matrix come in conjugate pairs. The corresponding unit eigenvector \mathbf{u}_1 gives the orientation of a transient that does not precess as it decays. Precessing transients correspond to linear combinations of two eigenvectors $\mathbf{u}_2, \mathbf{u}_3$ that have complex eigenvalues and evolve as decaying complex exponentials. Low-frequency modulation of the magnetic field can be visualized as occurring in a series of short time steps δt_i , each of which begins with a small change in the effective field. Corresponding to the new effective field is a steady-state solution $\mathbf{M}_{\mathbf{S}}$ and a set of eigenvectors \mathbf{u}_i . We write,

$$\mathbf{M} = \mathbf{M}_{\mathbf{s}} + \sum_{j=1}^{3} a_j \mathbf{u}_{\mathbf{j}},\tag{E.4}$$

and note that $a_j \mathbf{u}_j$ represents a decaying transient whose evolution during the time step is determined by the eigenvalue λ_j . In particular, the transients $\mathbf{M}'_j(\mathbf{t})$ referred to in Sec. 9.4.2 can be identified with the terms $a_j \mathbf{u}_j$ of Eq. E.4.

For each time step, a change in the effective field yields a modified set of eigenvectors, and the three eigenvectors used for time step δt_{i-1} are mixed to give the eigenvectors for step δt_i . Each transient is converted by means of this mixing into a linear combination of the three transients present at the end of step $\delta t_{i=1}$. In the regime where the precession frequency is large compared to ω_m , however, interconversion of $\mathbf{M}'_1(\mathbf{t})$ and $\mathbf{M}'_2(\mathbf{t})$, $\mathbf{M}'_3(\mathbf{t})$ is averaged to zero by the fast oscillation of $M'_2(t)$ and $M'_3(t)$. Since the precessing transients do not contribute to the signal at frequency ω_m , the detected response of the two-level system can be evaluated by replacing Eq. (A3) with

$$\mathbf{M} = \mathbf{M}_{\mathbf{s}} + a_1 \mathbf{u}_1. \tag{E.5}$$

From Eq. E.5, the response time of the system after a change in the field is

$$\tau = 1/|\lambda_1|. \tag{E.6}$$

Before deriving a formula for λ_1 , we note that simulations have validated the approximate model of the evolution given by Eq. E.5. The evolution is simulated by numerically solving a differential equation that governs the coefficient a_1 . In deriving this equation, we assume that the vectors \mathbf{M} , \mathbf{M}_s , and \mathbf{u}_1 are expressed in Cartesian coordinates, and we let \mathbf{w} denote the first row of the change-of- basis matrix that converts Cartesian coordinates into the coordinates a_i defined by Eq. E.4. It follows from Eq. E.5 that

$$a_1 = \mathbf{w}(\mathbf{M} - \mathbf{M}_{\mathbf{s}}). \tag{E.7}$$

The differential equation governing a_1 is obtained by summing the changes that occur on the right side of Eq. (A5) during a time step δt . The change in the effective field modifies $\mathbf{M}_{\mathbf{s}}$ and the eigenvectors $\mathbf{u}_{\mathbf{j}}$ without yielding a physical change in the magnetization \mathbf{M} . The corresponding contribution to da_1/dt is calculated by differentiating Eq. (A5) while holding \mathbf{M} constant. The physical evolution of \mathbf{M} can be expressed as a simple decay of a_1 toward zero with rate constant $|\lambda_1|$. The differential equation obtained by summing these changes is

$$\frac{d}{dt}a_1 = a_1(\frac{d}{dt}\mathbf{w})\mathbf{u}_1 + \mathbf{w}(a_1\mathbf{u}_1 + \mathbf{M}_s - \frac{d}{dt}\mathbf{M}_s) + \lambda_1 a_1.$$
(E.8)

In numerical tests using parameters similar to those meas- ured for the experiments performed at laser power 1.95 MW/ cm², simulations based on Eq. (A6) matched Blochequation simulations up to frequencies of a few hundred kHz, with the exact range of validity depending on the magnitude of the microwave field and the offset from resonance. To derive a formula for λ_1 , we analyze the exponential decay of the transient $a_1\mathbf{u}_1$ in a reference frame where the transient lies in the xz plane. Within this frame, the effective field is expressed as

$$-\gamma \mathbf{B}_{\mathbf{eff}} = (\omega_1 \cos \phi, \omega_1 \sin \phi, \Delta). \tag{E.9}$$

The evolution during δt can be visualized as occuring in three steps:

- 1. The x component and z component of the transient are multiplied by $(1 \delta t/T_2)$ and $(1 \delta t/T_1)$, respectively.
- 2. The transient precesses about the y-component of \mathbf{B}_{eff} .
- 3. The transient precesses about the component of B_{eff} lying in the xz plane.

Since the transient decays without precessing, the summed changes associated with these three steps must leave its orientation unchanged. Note that the transient remains in the xz plane during the first two steps; precession about a field component in the xz plane during step three will thus rotate it out of the xz plane and away from its initial orientation, unless the transient is aligned with the field component in this plane. It follows that

$$a_1 \mathbf{u_1} \propto (\omega_1 \cos \phi, 0, \Delta).$$
 (E.10)

Given this orientation for the transient, we find that the combined effects of longitudinal and transverse relaxation during δt change its magnitude by a factor $(1 - \delta t/\tau)$, where

$$\frac{1}{\tau} = \frac{(\omega_1 \cos \phi)^2 / T_2 + \Delta^2 / T_1}{(\omega_1 \cos \phi)^2 + \Delta^2}.$$
 (E.11)

Equation E.11 expresses τ^{-1} as a weighted average of T_1^{-1} and T_2^{-1} , with the weightings determined by the components of the effective field in the vertical plane of the transient. The angle ϕ appearing in Eq. E.11 is determined by the requirement that precession about the *y*-component of B_{eff} compensate for any change in the orientation of the transient due to the different relaxation rates of its longitudinal and transverse components. When $\omega_1 \gg T_1^{-1}, T_2^{-1}$, we have $\phi \approx 0$, and Eq. E.11 reduces to

$$\frac{1}{\tau} = \frac{\omega_1^2 / T_2 + \Delta^2 / T_1}{\omega_1^2 + \Delta^2}.$$
(E.12)

More generally, the longitudinal and transverse relaxation changes the orientation of the transient by an angle

$$\alpha = \frac{(\Delta\omega_1 \cos\phi)(1/T_2 - 1/T_1)}{(\omega_1 \cos\phi)^2 + \Delta^2}.$$
(E.13)

Setting $\alpha = (\omega_1 \sin \phi) \delta t$ shows that ϕ satisfies the equation

$$\tan \phi = \frac{\Delta(1/T_2 - 1/T_1)}{(\omega_1 \cos \phi)^2 + \Delta}.$$
 (E.14)

The dependence of ϕ on ω_1, Δ, T_1 , and T_2 can be visualized by solving Eq. E.14 graphically. The right side of the equation defines a curve that oscillates between minima at $\phi = N\pi$ and maxima at $\phi = N\pi/2$, and the parameters of the two-level system affect ϕ by determining the detailed form of this curve.