

MAGNETIC NOISE DUE TO INTERACTIONS BETWEEN BULK IMPURITIES AND
ELECTRONS IN NITROGEN VACANCY CENTER DIAMONDS

by

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A THESIS

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DEDICATION

I dedicate this thesis to my parents Heberto and Martha Barrios, my sisters Brenda and Donna Barrios, my brother Derek Barrios, friends and family, for their love and support throughout my educational endeavors.

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Magnetic Noise due to Interactions Between Bulk Impurities and Electrons in Nitrogen Vacancy Center Diamonds

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ABSTRACT

Nitrogen vacancy centers (NV) diamonds present great interest as robust atomic-scale magnetic field sensors. One of the serious problems of NV-center diamond devices is electric and magnetic field noise. The noise can be verified by the optically detected magnetic resonance (ODMR) line-broadening; the noise reduce sensitivity of the devices. In this work we theoretically study the magnetic field noise caused by the magnetic dipole-dipole interactions between the bulk impurities of ^{13}C , ^{14}N and the electron in the NV-center. We use the cluster correlation expansion method to calculate the magnetic field fluctuations, and then, obtain the noise spectrum. The noise spectra is greater at lower frequencies but decrease at higher frequencies.

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List of Abbreviation

ODMR	optically detected magnetic resonance
NV-center	nitrogen vacancy center
^{12}C	carbon 12 atom
^{13}C	carbon 13 atom
^{14}N	nitrogen 14 atom
N^+	nitrogen ion
Fig.	figure
H_0	Unperturbed Hamiltonian
H_Z	Zeeman Hamiltonian
H_{hf}	Hyperfine Hamiltonian
H_{SI}	Dipole-dipole interaction NV-center and bulk impurities Hamiltonian
H_{II}	Dipole-dipole interaction bulk impurities Hamiltonian
EPR	electron paramagnetic resonance
HPHT	high pressure high temperature
CVD	chemical vapor deposition
DND	Detonation nanodiamonds
ZPL	zero phonon line
ZFS	zero field splitting
MNR	nuclear magnetic resonance
N^0	nitrogen vacancy center neutral
N^+	nitrogen vacancy center positive
N^-	nitrogen vacancy center negative

CHAPTER I: INTRODUCTION

Nitrogen Vacancy Centers (NV-centers) in diamonds present a great interest in contemporary times due to its possible applications as biomarkers, atomic-scale magnetic field sensors, quantum computing and more [1] [2] [3] [4]. Although NV-centers are stable at room temperature, one serious drawback of devices manufacturing is electric and magnetic field noise. The noise causes optically detected magnetic field resonance (ODMR) line-broadening, which reduces sensitivity of the devices. In this work we theoretically study the magnetic field noise caused by the magnetic dipole-dipole interactions between the impurities of naturally occurring 1% carbon-13 (^{13}C) atoms, nitrogen-14 (^{14}N) atoms interacting with the electron spin in the NV-center.

CHAPTER II: BACKGROUND

2.1 History

In 1772, Antoine Lavoisier provided evidence that diamonds and charcoal were chemically alike [2] and since then the synthesis of diamonds and diamond defects have been the focus of many studies [5] [6]. For decades the study of diamonds was primarily for their commercial value. But since the advent of synthetic diamond fabrications in the mid to late 1950's diamonds gained high interest due to their possible applications. Diamonds have high sensitivity to electric and magnetic fields [7], with proposed applications such as biomarkers, nanomagnetometry, quantum computing and metrology [2] [8]. Although diamonds should be perfectly transparent, they display a variety of colors [9], these variations in colors are attributed to defects in the crystal structures of the diamond. Diamond crystal structures are categorized in three main categories; A, B and C centers (Fig1). These categories can be viewed in more detail from various reference materials, such as Optical Engineering of Diamonds [2] and further discussion of C-centers to follow. In general center defects can consist of one or more impurity atoms or vacancies in the lattice structure of the diamond [2]. These defects cause the various colorations in diamonds. For the purpose of device manufacturing it is important that the NV-center is at near surface ($\sim 2\text{-}5\text{ nm}$).

2.2 Manufacturing and Structure

There are several methods for the synthesis of diamond center defects (point defects); High-Pressure, High-Temperature (HPHT) Synthesis, Chemical Vapor Deposition (CVD), Detonation Synthesis Nanodiamond (DND), and Ion implantation [2] [9]. HPHT and CVD produce plate size coalitions of center defects in the 10 mm range; at this point it is important

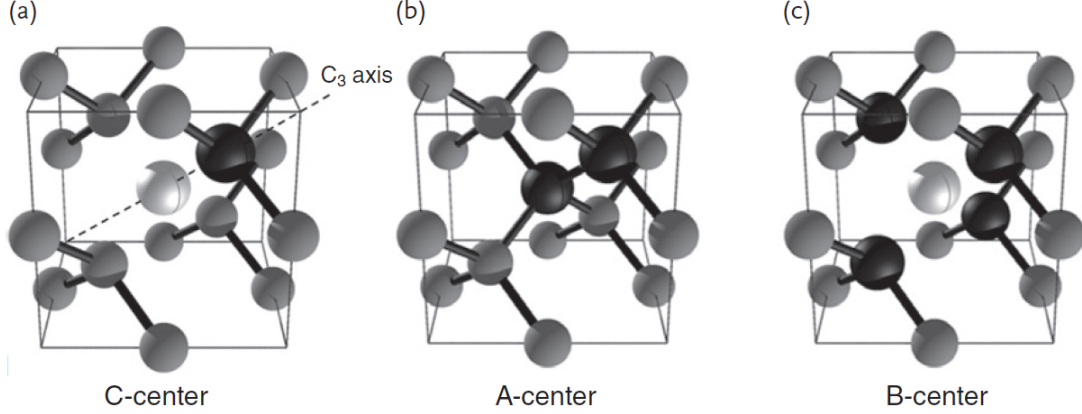


Figure 1: Structures of nitrogen vacancy center defect categories. (a) C-center, single substitution of carbon atom and one vacancy (b) A-center have a near pair neighbors of carbon atoms are substituted by two nitrogen atoms. (c) B-center defects there are four nitrogen atoms substitution of carbon atoms surrounding a center vacancy. The nitrogen atoms are shown in black, carbon atoms are in gray, and the vacancies in white with no bonds [9].

to note that not all crystal structure will be formed into center defects. DND roughly form plate structure in the 4 to 5 nm range [2] [9]. Yet ion implantation is the most effective method of producing center defects.

Although there are many methods to synthesize point defects, with each method having variations in properties, our study will use the properties of the ion implantation NV-centers as they are the most reliable method to produce NV-centers. The purpose of ion implantation is that it provides us with a method that is a more accurate way of introducing dopants into the crystal lattice of a substrate at near surface and in a method that is independent of thermal dynamic factors [9] [10] [11]. Ion implantation (doping) is a method by which a surface layer of a solid substrate is irradiated by accelerated ions; ions in the keV [12] to the MeV range [10] [13] (Fig 2).

To manufacture diamond substrate for ion implantation it is crucial that the environment is free of all possible impurities; such as nitrogen. This allows for a more controlled

quantity of NV-center to be added at shallow depths. From this method there can be up to a 10 % conversion of center defects, which correspond to tens of parts per million (10ppm), at shallow surface depths of around 2-5 nm [2]. Having NV-centers at near surface allows is crucial for device manufacturing. Doping semiconductors, in our case diamonds, allows us to add impurities which change the valance bands by adding new energy states this then allows electrons to easily flow into the conduction band (depending on dopant n or p type).

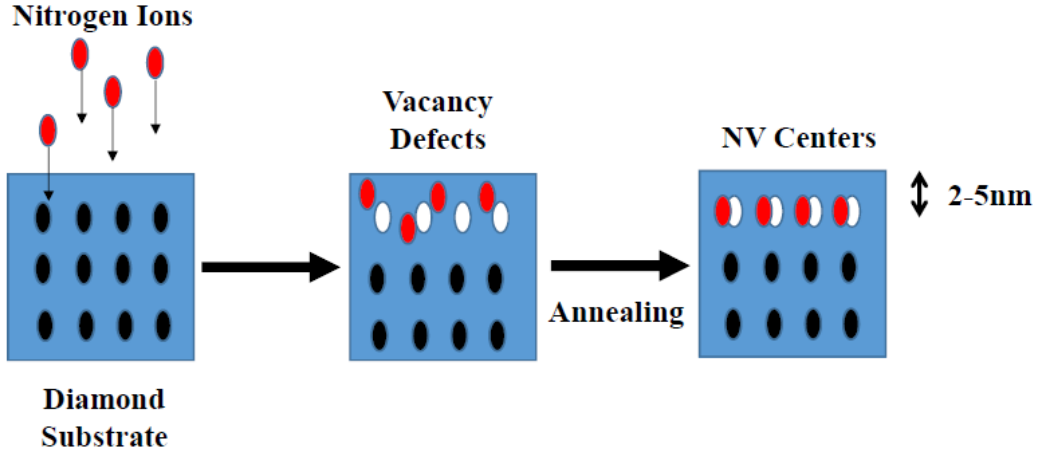


Figure 2: Figure 2: Surface ion implantation (doping) of defects in diamond substrate with N^+ atoms. The left side most panel shows a diamond substrate is irradiated with N^+ ions. In panel 2, carbon atoms are displaced and nitrogen atoms interact with the remaining impurities. In panel 3, after annealing NV-centers are formed. Nitrogen ions (N^+) in red, carbon impurities (^{12}C and ^{13}C) in black and vacancy centers in white.

In our previous paragraphs we kept the discussion of point defects general. There three types of NV-centers NV^0 , NV^+ and NV^- (Fig. 3 (a), (b) & (c)). Although we do have three different vacancy centers, for both NV^0 and NV^+ vacancy, neither are magneto-optically active and most experiments are carried out on the NV^- centers [2]. For the purposes of our study we will limit our focus on the NV^- (NV's, NV-centers) as they magneto-optically active and most suited for device manufacturing. In the case of NV-centers, Nitrogen (N^+) ion's are collided with a diamond substrate with naturally occuring 99% ^{12}C and 1 % ^{13}C . In

this case the irradiated surface molecules lose carbon atoms and get doped with N^+ . After the samples have been irradiated they are annealed at $\sim 800 - 850$ °C [14] to mobilize the vacancies while keeping the nitrogen atoms fixed [9]; annealing at these temperatures will not cause the nitrogen ions to diffuse due to the low activation energy [14]. The ^{14}N has five valence electrons which form covalent bonds with the neighboring carbon atoms leaving two unpaired electrons from the ^{14}N [11].

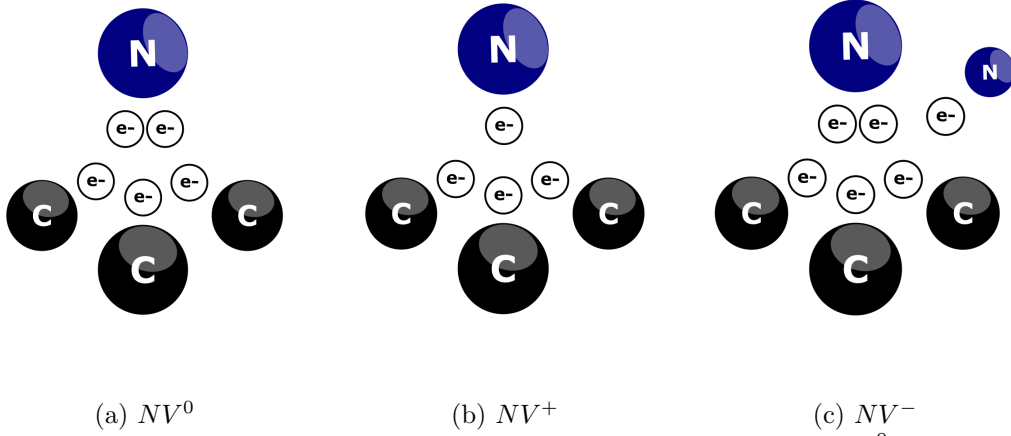


Figure 3: During formation, nitrogen vacancy centers can be either neutral (N^0 (a)), positive (N^+ (b)) or negative (N^- (c)). Both nitrogen vacancy centers positive (N^+) and neutral (N^0) are magneto-optically active; therefore the focus of this and many other studies are on the nitrogen vacancy negative (N^- , (c)) molecule.

For the most part, at this point the NV-center has two electrons from the nitrogen doping and three from the surrounding carbon atoms (Fig. 3, (a)); two of these carbon atom electrons form quasi-covalent bonds. These quasi-covalent bonds interchange positions between the ^{13}C atoms providing the center electrons [11]. At this time the point defects can be either NV^- , or NV^0 (Fig. 3 (c), (a) respectively); the surrounding impurities in the lattice will dictate the negativity or neutrality of the defect. These impurities can either be donors (p-doped) or acceptors (n-doped) of electrons. In the case of NV^- the NV^0 atom with 5 electrons obtains an additional electron from a donor atom in the lattice. The donor atom can come from a carbon-13 (^{13}C) or nitrogen-14 (^{14}N), depending on the relative position of

the center and the atom. But typically the additional electron comes from a nitrogen donor [2]. The reliability of NV^- on the donor atom in the lattice implies that both NV^- and NV^0 can exist in the same diamond structure. As mentioned before the NV^0 or the NV^+ are magneto-optically inactive and the focus of most and our study of NV's are on the NV^- (Fig. 3 (c)).

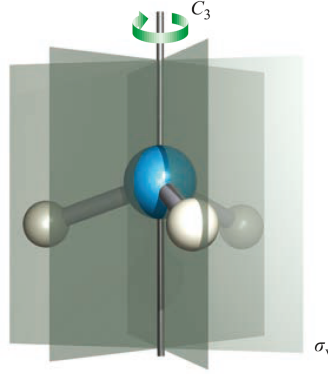


Figure 4: NV-centers (C-center) have c_{3v} rotational symmetry along the crystallographic axis [15]. Nitrogen (^{14}N) atom in blue, carbon (^{13}C) atoms in white; the angle between carbon atoms is 120° . Grey planes show reflectional symmetry of NV-centers.

Diamond defects are classified as either intrinsic or extrinsic, according to the nature and origin of the center defect [9]. NV^- are extrinsic diamond defects as they are formed by the substitution of the carbon atom with a nitrogen ion (Fig 6). As stated before point defects are classified as A, B or C-centers (Fig.1(a)), NV^- are C center diamonds defects. C-centers are vacancies categorized as a single substitution of a carbon atom with a nitrogen atom and a vacancy left from a missing ^{13}C atom. This ^{13}C substitution and vacancy will form nitrogen vacancy center neutral (NV^0) and nitrogen vacancy center negative (NV^-). C-center diamonds defects will have a yellow/ brownish color variation [16]. NV-centers have tetrahedral symmetry, belonging to the C_{3v} group [17] [18] (Fig.4). The rotational symmetry of the NV-center is 120° about the C_3 principal crystallographic direction axis [111], as well there are four possible orientations for the nitrogen (^{14}N) atom (Fig 7) [2] [11]. NV 's much

like other semiconductors (silicon and germanium) also possesses a face center cubic space lattice (Fig. 5) [15] [19] [20].

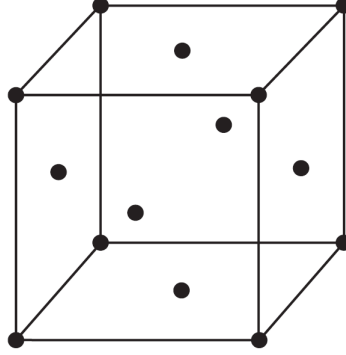


Figure 5: Like other semiconductors NV-center has face center cubic unit cell [19] [20] [15]. A face center cubic unit cell is characterized by a simple cubic symmetry by where four atoms are located at the center of each face of the cube [21].

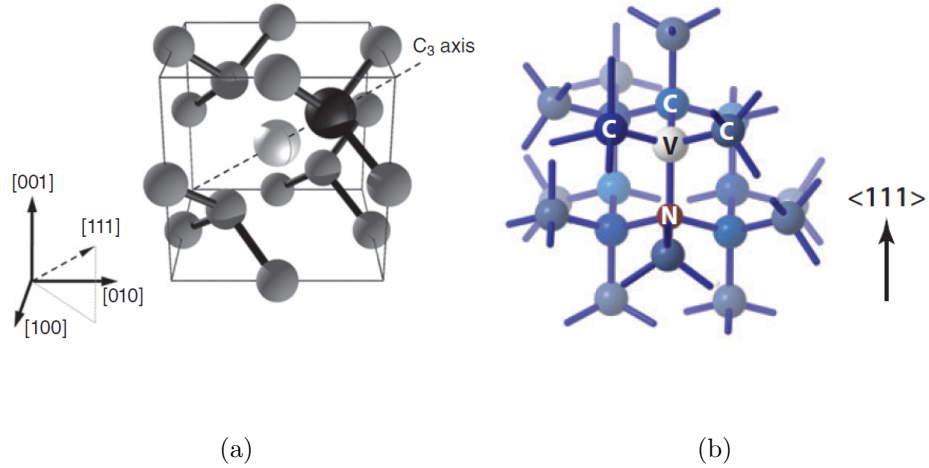


Figure 6: Two representations of nitrogen vacancy center with crystallographic axis. a) The nitrogen atom is shown in black, the carbon atoms are shown in gray and the vacancy in white [9]. b) Nitrogen atom is shown in red, the carbon atoms in blue and the vacancy is shown in white [2].

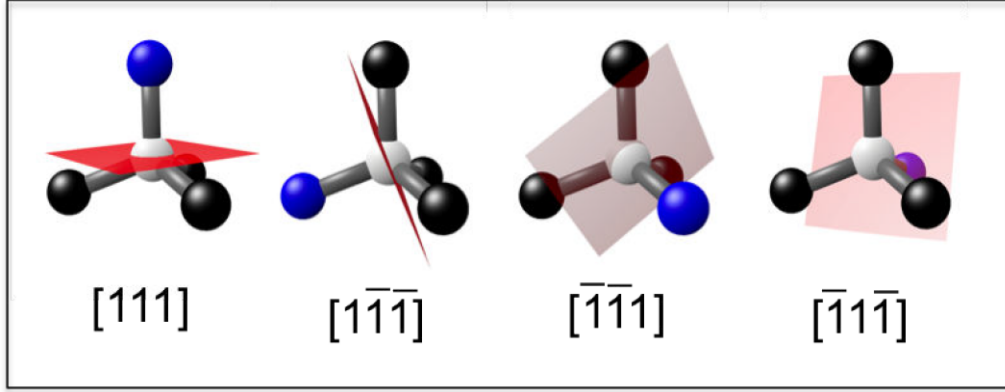


Figure 7: Schematic representation of the four possible orientations of NV defects in a (111)-oriented diamond sample with the plane orthogonal to the NV axis containing the two orthogonal absorption dipoles [22]

2.3 Physical and Optical Properties

Up to this point we have mentioned some of the possible application for NV-centers, synthesis and structure but not the optical and physical properties that make NV-centers desirable. The two most interesting properties of NV-centers are optical and spin properties [23]. At room temperature NV-centers are single photon emitters in the visible range, they are photo-stable, immune to photo-bleaching, they have long spin coherent times and can undergo spin-sensitive optical transitions [9]. As stated before nitrogen vacancy center diamonds are a semiconductor with a wide band-gap of 5.5 eV [24], which can be seen in figure 8 [25], which corresponds to a wavelength of 225 nm (Ultraviolet) [9].

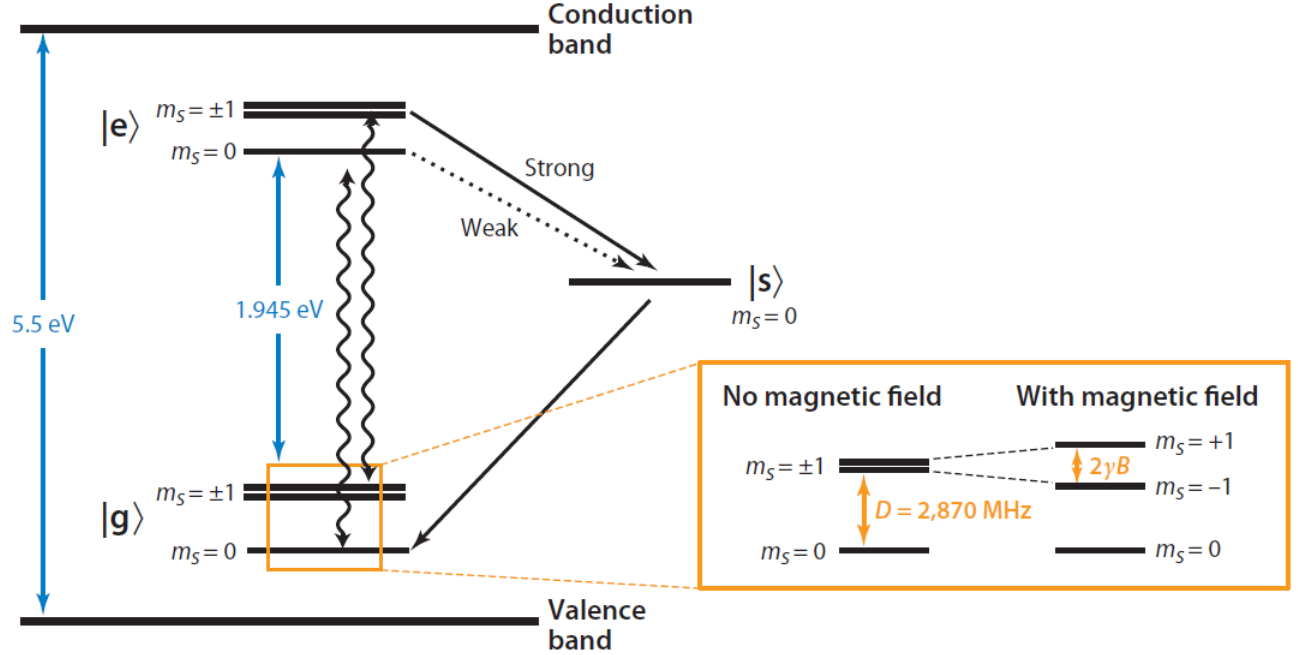


Figure 8: Nitrogen vacancy center energy level diagram, with zero field splitting, Zeeman degeneracy breaking and band gap. The energy levels are labeled as g for the ground state, e for the excited state and s for the meta stable state. The transitions between the $m_s = 0$ ground and excited states are excited and decay directly; the $m_s = \pm 1$ state have a greater probability to decay through the meta stable state. NV-center have a wide band gap of 5.5 eV [2]

At the ground state nitrogen vacancy centers are paramagnetic. They are a spin one state system ($S = 1$), with a triplet ground state [9] [22] [26]. The degeneracy of the ground state is broken by the coupling of the electrons of the NV-center. This degeneracy breaking will split the triplet state into an $m_s = 0$ ground state and a degenerate $m_s = \pm 1$ ground state. As well the excited state of the NV-center will also have an $m_s = 0$ excited state and an $m_s = \pm 1$ degenerate state. The zero field splitting (ZFS) between the $m_s = 0$ and the degenerate $m_s = \pm 1$ ground state is approximately 2.87 GHz. The ZFS splitting between the $m_s = 0$ excited state and the $m_s = \pm 1$ degenerate excited state is approximately 1.40 GHz. The zero phonon line (ZPL) splitting between the ground and excited state is at a wave length of 637nm (1.945eV) (Fig 8) [27] [28].

As the NV-center is optically excited (with green laser light 532nm [29] [30]) the transitions between states will tend to favor direct transitions ($\Delta m_s = 0$). For example the $m_s = 0$ ground state will favor a transition to the $m_s = 0$ excited state. Similar for the $m_s = \pm 1$ ground state to the $m_s = \pm 1$ excited states. Although the transition between the excited and ground are straight forward the decays on the other hand are different. The $m_s = 0$ excited state will have the greatest probability of decaying to the $m_s = 0$ ground state through spontaneous emission. But the $m_s = \pm 1$ excited state will have a greater probability of decaying through a metastable state and onto the $m_s = 0$ ground state (Fig: 8) [2] [9]. These decays ($m_s = 0$ excited to ground state) repump the ground state $m_s = 0$ (Fig. 12), which cause a 30% reduction in fluorescence; which can be seen in figure 9 [14]. Therefore if we look at the fluorescence of the NV-center the primary source of it will be from the $m_s = 0$ transitions.

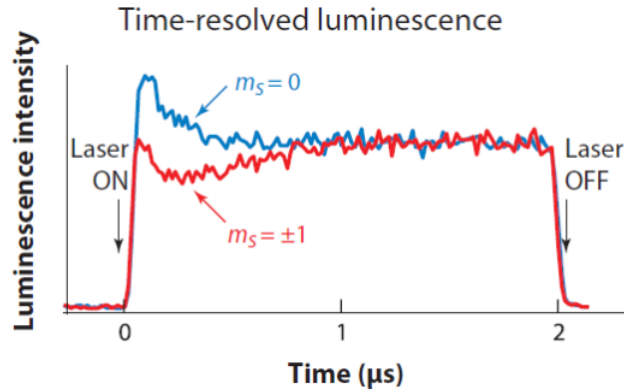


Figure 9: Histogram of photon emission during a $2\mu s$ laser pulse that shows the initial peak due to rapid radiative transitions followed by a slow recovery due to singlet decay; the $m_s = \pm 1$ state intensity is limited by its metastable decay rate which pumps the $m_s = 0$ state [2].

From figure 8 we see that the resonance frequency between the ground and excited states is approximately 1.945 eV this corresponds to a resonant wavelength of roughly 638nm, at

zero phonon line (ZPL) splitting [2]. When looking at a single ensembles of nitrogen vacancy center transitioning between the excited and ground state very little photons will be emitted from this transition and can be seen in figure 10. The primary photons emitted from this transition will be from the vibrational side bands, between 620 to 800 nm [2].

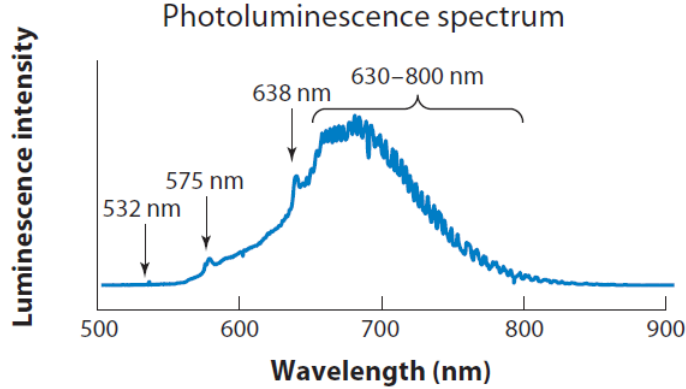


Figure 10: Photo-luminescence spectrum of an ensemble of NV centers, showing excitation laser (532nm), the NV^0 zero phonon line (575nm), the NV^- zero phonon line (638nm), as well the NV^- vibrational side bands (630 – 800nm) [2].

Since the NV-centers have unpaired electron we can perform electron paramagnetic resonance (EPR) spectroscopy to study the state transitions. The experiments are carried out by exciting the nitrogen vacancy center with green light, while at the same time sweeping through an applied microwave frequency. Which can be seen from figure 11, as the applied microwave frequency reaches the resonant frequency between the ground state $m_s = 0$ and the degenerate $m_s = \pm 1$ ground state (~ 2.87 GHz [14] [31]), there will be an absorption line. This absorption line comes from the electrons in the $m_s = 0$ ground state being excited to the degenerate $m_s = \pm 1$ state (Fig. 11) [32]. In the same way the EPR spectrum with an applied field can be observed; given by figure 12 [2] [14].

From figure 12 we can see the degeneracy breaking between the $m_s = \pm 1$ ground states

when there is an applied magnetic field. The absorption splitting seen in figure 12 is proportional to the projection of the applied magnetic field on to the NV-center crystal axis. It is important to note that these experiments (ODMR, etc.) are carried out at room temperature [33]. Unlike most atoms the NV-center is immune to photo bleaching [9], which implies that the NV-center always produces the same number of photons and can last indefinitely. The optically detected magnetic resonance (ODMR) signal of the NV-center is peculiar to it and has only been observed in a handful of other molecules or crystal structure defects [2].

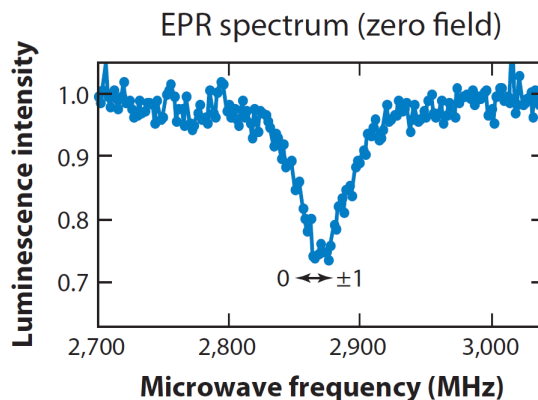


Figure 11: The Electron Paramagnetic Resonance (EPR) signal for a single NV-center without an applied magnetic field. The NV-center is optically excited with green laser light while an applied microwave frequency is swept in and out of the ground state resonance frequency [2].

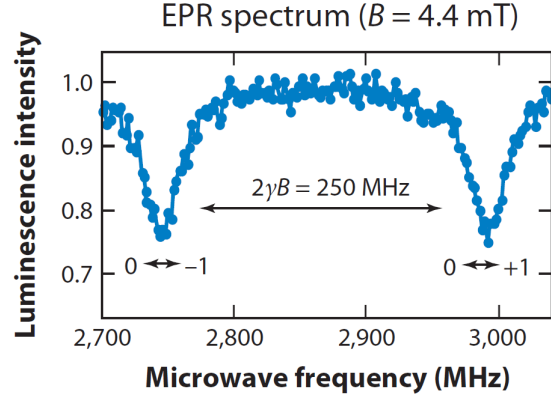


Figure 12: The Electron Paramagnetic Resonance (EPR) signal for a single NV-center with an applied magnetic field. The NV-center is optically excited with green laser, an applied magnetic field is use the microwave frequency is swept in and out of the ground state resonance frequency. We can see the two peak transitions between $m_s = 0$ state to the $m_s = \pm 1$ states do to the degeneracy breaking of the magnetic field [2].

CHAPTER III: PROJECT GOALS

3.1 Problem

In our previous section the general properties and description of nitrogen vacancy center were given, we now take that a step further. As stated before nitrogen vacancy centers are center defects in crystal structures of a diamond; with desirable properties suitable for device manufacturing, yet the draw back in any type of device manufacturing is its sensitivity (noise). In the case of nitrogen vacancy centers its sensitivity is limited by noise created by electric and magnetic fields. There have been studies that suggest that the magnitude of both the electric and magnetic field noise can be comparable; which leads to the purpose of our groups study of NV-centers.

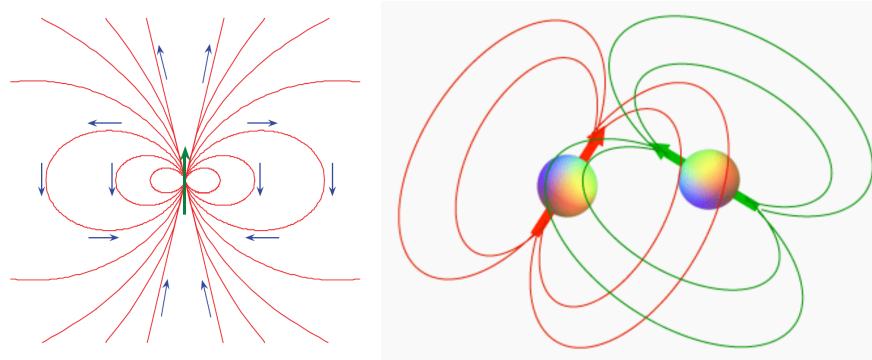
A previous member of our group took on the task of finding the cause for electric field noise; the study found that the cause of electric field noise is surface charge fluctuations [7]. In this study we seek to complete our groups study of noise in nitrogen vacancy centers by analyzing the cause of magnetic field noise. In our work we will be focusing on electron spins in the NV-center interacting with the nuclear spins of the bulk impurities in the system (^{13}C , ^{14}N); in the case of magnetic field noise the magnetic dipole-dipole interaction between the NV-center and the bulk impurities, as will be explained in our next section.

3.2 Magnetic noise

Magnetic noise at its most simplest form is a result of magnetic dipole-dipole interaction between two atoms. Atoms have two forms of magnetic dipole moments; orbital magnetic moment and spin moment [34] [35]. If we look at a classical interpretation of a single atom we find that the spin-orbit moment is caused by the electron motion around the nucleus.

In a similar way, although much more complicated the nuclear spin moment is caused by the nuclear polarization of the protons and the neutrons revolving around each other (Fig. 13 (a)). We should note that in bound electrons the magnetic moments of the nuclear spin are permanent, the orbital magnetic moments are not; the orbital magnetic moment of the electron is proportional to the magnetic field applied [35]. Therefore the orbital magnetic moment of the electrons is and induce magnetic moment [35].

The classical interpretation of magnetic moments is by far a very simplified case of what is really happening, but for the purposes of our study these are sufficient. Magnetic dipole moments should not be confused with electric dipole-moments; whereby electric dipole moments are only caused by the presence of another oppositely charged particle. If we take a simplified version of our problem, by taking two independent atoms and placing them a distance apart (Fig. 13). Each atom will feel a magnetic field (induced field) created by the other (Fig. 13 (b)). This induced field will cause a disturbance in the other magnetic moment, which can manifest as a flip-flop of pole(s) or precession of alignment to reduce the energy in the system. This disturbance in the magnetic moments of the atom by the other causes the magnetic noise in the system.



(a) Free atom

(b) Two atom interaction

Figure 13: a) Magnetic dipole moment of a single atom; caused by orbital angular momentum and the nuclear spin [36]. b) The magnetic Dipole-Dipole interaction between two atoms; in the case of our study we are looking at the nuclear spin interaction between the NV-center and the bulk impurities [37].

It is important to note that dipole-dipole interaction not only take place between nuclear interaction, they can also take place with unpaired electrons as is the case of NV-centers. In our initial description of magnetic moment interaction we neglected to mention that not all atoms will create significant disturbance (magnetic field), only atoms that are magnetic will create the disturbance. The magnetic properties of the atom is dictated by the internal structure of the nucleus and its balance or lack of balance, between the number of protons and neutrons in the atom; atoms with equal number of protons and neutrons will be magnetic neutral [38].

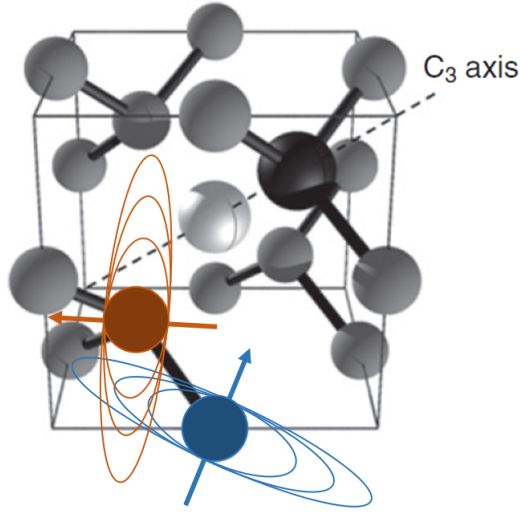


Figure 14: Simple representation of our nuclear spin interactions. Nitrogen vacancy center in the lightest shade of grey (white) interacts with the nuclear spins of nitrogen (^{14}N) in black and carbons (^{13}C) in grey [9]. The nuclear spins in the bulk impurities are randomly orientated and viewed from the crystal axis.

The dipolar coupling mentioned thus far have been quite simple and classical, but in solid state systems the interactions are more complicated. In some simpler systems where there are only two magnetic atoms the aforementioned interaction resembles the system quite nicely; but in the NV-center system where there are several atoms in a molecule with magnetic properties the classical interpretation becomes more complicated yet relevant. If we take a single unit lattice of an NV-center, such as in figure (Fig. 14) and we superimpose magnetic field lines onto the carbon (^{13}C) atoms (in this case we only choose two ^{13}C atoms) we can see the complications that can arise for many atoms interaction. The magnetic dipole-dipole coupling between atoms in our system come from the unpaired electrons in the NV-center and the bulk impurities (^{13}C , ^{14}N atoms). The magnitude and orientation of the magnetic field between atoms is dictated by the direction of the magnetic moment creating the field and the spatial orientation of the atom [20].

In solid state systems such as NV-centers the spacial orientation of the atoms will not change (in contrast to soft matter) [39], therefore magnitude and orientation of the field is dictated by the orientation of the magnetic moment. In the case of NV-centers, as the system is perturbed the spin bath system will flip-flop as they relax back to equilibrium. This flip-flop process creates the magnetic noise in the system. Please note that the NV-center electron spins will not flip flop due to the Pauli exclusionary principal. Certain Thermal and magnetic field perturbations are utilized to limit the flip-flop process in the system [13].

CHAPTER IV: METHODS & RESULTS

4.1 Our Model

As stated before our study is focused on the magnetic field noise between the bulk impurities (nuclear spins of ^{13}C & ^{14}N atoms) and the electrons in nitrogen vacancy center diamonds (Fig 6, 15). In our previous discussions the naturally occurring 1 % ^{13}C atoms are naturally occurring in all diamonds and the ^{14}N impurities come from the formation of the NV-center during ion implantation, of N^+ ions. If we look at figure 15 we see the ^{13}C in black, the ^{14}N in blue interacting with the NV-center electrons in white. From our work of previous groups or other reference materials we know that on average there are $\sim 10^{19}\text{cm}^{-3}$ naturally occurring ^{13}C atoms and roughly $\sim 10^{18}\text{cm}^{-3}$ ^{14}N atoms [40]. As we will see in the upcoming section the number density of the atom plays an important role in the noise spectra of the NV-center.

The magnetic noise spectra of our system is dictated by the magnetic dipole-dipole interaction of the NV-center electron spin and the nuclear spin of the bulk impurities. As the interaction between the NV-center and the bulk impurities take place there will be a loss of information [8]. This loss of information comes in the form of loss of coherence between the electrons in the NV-center, as well certain elements in the system (such as energy states) will no longer be able to interact with each other [8] [41]. The loss of information causes the sensitivity of NV-centers to be compromised. Therefore understanding the interactions between NV-centers and bulk impurity spins is crucial to understand the loss of information, which in turn is vital to the development of the devices. We must clarify that the concentration of nitrogen can vary depending on the accuracy of the ion implantation.

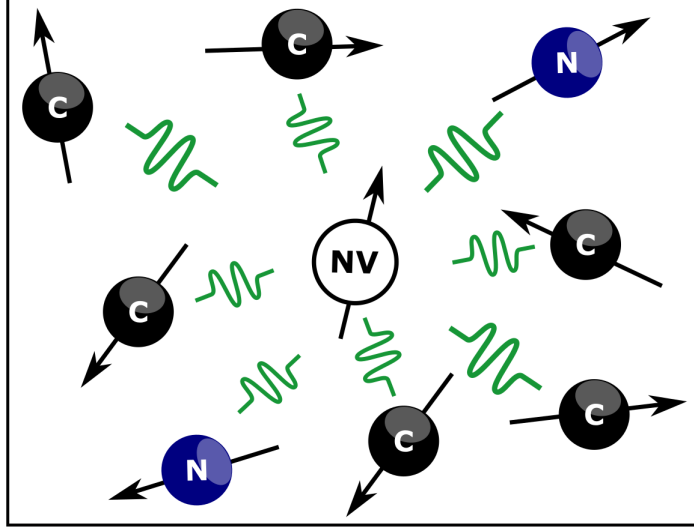


Figure 15: Interaction between the NV-center electron spin and the nuclear spin impurities carbon (^{13}C) in black and (^{14}N) in blue. The density of naturally occurring 1% carbon atoms is roughly one order of magnitude larger than that of nitrogen ($^{13}\text{C} \sim 10^{19}\text{cm}^{-3}$, $^{14}\text{N} \sim 10^{18}\text{cm}^{-3}$). Coupling strength decrease as $\sim \frac{1}{r^3}$.

4.2 Hamiltonian

Since the NV-center is a microscopic system of interacting particles, it lies in the realm of many body physics. Therefore in order to describe the system we must describe it through a quantum mechanical perspective [8], looking at the Hamiltonian for the system, we then will find the noise spectra and conclude by taking a numerical evaluation of the spectrum. The total Hamiltonian of our system is given by equation 4.2.1 below. Note that we did not add other corrections terms such as the Stark or fine structure to this Hamiltonian as they are not pertinent to our study.

$$H = H_0 + H_Z + H_{hf} + H_{II} + H_{SI} \quad (4.2.1)$$

The Hamiltonian of equation 4.2.1 is defined by the following summations of Hamiltonian's

H_0 for the unperturbed Hamiltonian, H_Z is the Hamiltonian due to the Zeeman effect, H_{hf} is the Hamiltonian due to the hyperfine interaction, H_{II} is the Hamiltonian due to the nuclear spin interaction between the bulk impurities (self coupling, self dipolar coupling) and H_{SI} is the NV-center electron spin interaction with the nuclear spin of the bulk impurities (dipolar coupling) namely ^{13}C , ^{14}N atoms. We have used the more conventional operator notation of I for the nuclear spin of the impurities and S for electron spin of the NV-center. At this point we make a simplification for our study. Since the zero-field splitting is roughly three orders of magnitude larger than any other coupling we ignore the lateral components of the center's spin $\vec{S}$ (i.e $\vec{S}_x$ and $\vec{S}_y$) [8]. We can now move forward and look at the Hamiltonian's that are of most interested in our study; the Zeeman correction for the system is given by H_Z and its definition can be found in equation 4.2.2 [8].

There are three regions of consideration when considering applied magnetic fields. The weak field is characterized by a magnetic field of up to 0.01 Gauss [8] [42] [43]. The mid field ranges from 0.01 Gauss up to 300 Gauss [8] [42] [43]. The high field is any field above the 300 Gauss field [8] [42] [43]. Although the magnitudes of the applied magnetic field can vary slightly in definition; we will label zero to low magnetic fields, for fields less than 1 Gauss. And we will call high magnetic field anything above 300 Gauss.

$$H_Z = \sum_i \vec{I}_i \cdot \vec{\omega}_i \quad (4.2.2)$$

where ω is given by the Larmor precessions; $\omega_i = \gamma_I B_0$ (the Larmor equation). The nuclear gyromagnetic ratio is given by γ_I which is roughly 67.2828×10^6 (Coulomb / kg) for carbon (^{13}C) atoms and 19.331×10^6 (Coulomb / kg). The applied magnetic given by B_0 can be either high or low in accordance to the aforementioned conditions. For the Zeeman effect in equation 4.2.2 we take the i^{th} component of the nuclear spin (of the bulk impurities)

interacting with the applied magnetic field.

We move on to the Hamiltonian for the spin path interactions given by H_{II} (equation 4.2.3 [8]). To insure clarity the H_{II} is the Hamiltonian for the nuclear spin interaction between the bulk impurities, excluding the NV-center.

$$H_{II} = \sum_{j < i} \frac{b}{r_{ij}^3} \left[\vec{I}_i \cdot \vec{I}_j - 3 \frac{(\vec{I}_i \cdot \vec{r}_{ij})(\vec{r}_{ij} \cdot \vec{I}_j)}{r_{ij}^2} \right] \quad (4.2.3)$$

where i and j are the ith nuclear spin interacting with the jth nuclear spin component of the spin bath system. The separation distance or vector for the self coupling is given by r_{ij} , $\vec{r}_{ij}$ (Fig. 16). The separation distance and vector $(r_{ij}, \vec{r}_{ij})$ can have an angle dependence; what will dictate this angle dependence will be its relative position to the crystallographic axis. This will be presented in more detail in the upcoming section. The constant b is given by:

$$b = \frac{\mu_0 \mu_I^2}{4\pi \hbar} \quad (4.2.4)$$

μ_0 is the permeability of free space given as 1.257×10^{-6} (Newton/ Amp^2), μ_I is the nuclear magnetic moment of the bulk impurities given by 5.051×10^{-27} (Joule/Tesla) and $\hbar$ is Planck's reduce constant given by 1.05457×10^{-34} Joule sec.

The Hamiltonian for the interaction between the nitrogen vacancy center electron spins and the bulk impurities of carbon and nitrogens (^{13}C , ^{14}N) is given by H_{SI} [8], we have defined H_{SI} in equation 4.2.5.

$$H_{SI} = \sum_i \frac{a}{R_i^3} \left[(\vec{S} \cdot \vec{I}_i - 3 \frac{(\vec{S} \cdot \vec{R}_i)(\vec{R}_i \cdot \vec{I}_i)}{R_i^2} \right] \quad (4.2.5)$$

R_i is the separation distance between the i^{th} nuclear spin cluster component and the NV-center (Fig. 16). $\vec{R}_i$ is the vector between the i^{th} nuclear spin cluster component and the NV-center (Fig. 16). Although it is not apparent at the moment clustering is at the heart of our solution to the many body problem and will be described in detail in the upcoming sections. The constant a is given by the following equation:

$$a = \frac{\mu_0 \mu_e \mu_I}{4\pi \hbar} \quad (4.2.6)$$

Once again we have that μ_0 is the permeability of free space given above, μ_I is the nuclear magnetic moment of the bulk impurities given above and $\hbar$ is Planck's reduced constant given above. μ_e is the magnetic moment of the electron and is given by -9.285×10^{-24} (Joule/Tesla). It is important to note the Hamiltonian H_{SI} is incomplete in our definition : there should be one additional term, called the Fermi contact term. The Fermi contact term is a term where the radial distance from the center of a nuclear moment to a point r' ; where r' is at the boundary of the atom. We omit the term since we are looking at distances (r') larger then the radius of the atom; therefore the term is not relevant to our discussion.

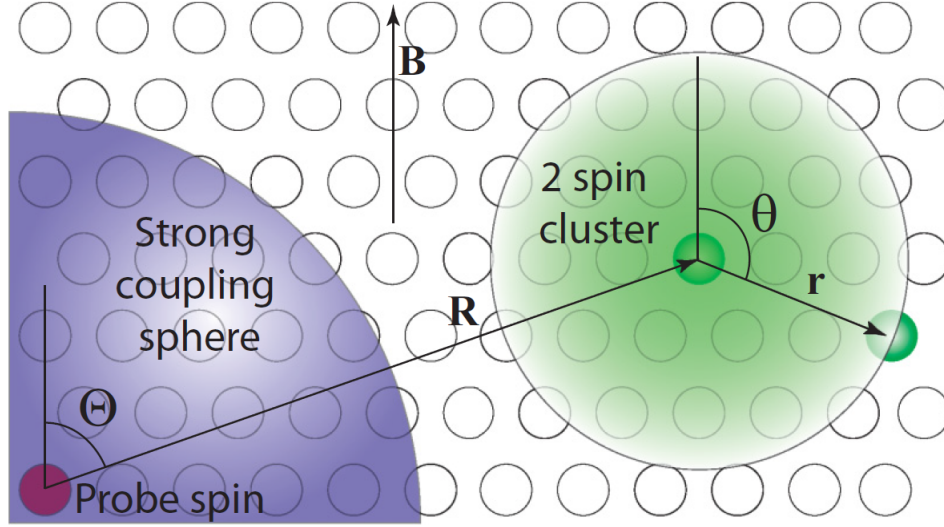


Figure 16: Cluster representation of the system. Blue region is strong coupling sphere which includes the hyperfine and near neighbor clusters interaction of the NV electrons and the donor impurities. The distance from the NV center to the cluster is labeled as R . The cluster sphere region is given in green with a radius r . The crystallographic axis direction and an applied magnetic field is given by upward facing arrow [8].

You may have noticed that above in the total Hamiltonian (4.2.1), we made no mention or reference as to the ordering of magnitude for each Hamiltonian. The magnitude ordering of the Hamiltonians in equation 4.2.1 will give rise to regions by where certain interactions will be stronger than others, but this will be more clear shortly. From equation 4.2.1 we can extract the Hamiltonians that we are most interested in studying; H_Z , H_{SI} and H_{II} . If we only take into account the Zeeman effect (H_Z), the interaction between NV-center and bulk impurities (H_{SI}), and the interaction between the bulk impurities themselves (H_{II}), we see that there are six permutations in the ordering of magnitude for the Hamiltonians. The magnitude ordering of Hamiltonians are conducted in certain regions (distance from NV-center to cluster) figure 17.

In order to find such regions we will employ a simple but effective method. But first, for brevity and clarity of work we will adopt a short hand notation for Hamiltonians. For the

spin dipole-dipole coupling between the NV-center defect and the bulk impurities (^{13}C , ^{14}N) we will relabel H_{SI} as S. The dipole-dipole coupling between the bulk impurities them selves will be relabeled from H_{II} to E. The Zeeman interaction will be relabeled from H_Z to Z. Now that we have relabeled our Hamiltonians we can now employ our method of finding the regions of operation. If we order the six permutation by the mean of their squares (given by equation 4.2.7) we find the regional conditions for the clusters, which can be seen in figure 17.

$$\langle H_Z^2 \rangle \gg \langle H_{SI}^2 \rangle \gg \langle H_{EE}^2 \rangle \quad (4.2.7)$$

The regions that are given equation 4.2.7 above and which is shown in figure 17, will be given the following names ultra strong coupling for the region which result from the hyperfine interaction between the electrons in the NV-center and the donor atoms (^{13}C , ^{14}N), the strong coupling region will have couplings between the NV-centers and the nuclear spin cluster of the impurities, the larger regions will be the same as the strong coupling region but the interaction strength between them and the NV-center will be much weaker. This may be clear to understand if we refer back to equation 4.2.3 and 4.2.5; in both equations we see that the magnitude of the Hamiltonians decay as $\frac{1}{r^3}$, implying that even if the distance varies by a small amount there will be significant reduction to the Hamiltonian magnitude. In our illustration (Fig. 17) we see the interaction indicators (the oscillating line connection in black) are oscillating faster for some and not others, as well the atoms are closer or further away from each other these notation are use to show the coupling strength between atoms. Atoms that are strongly coupled will be depicted by and indicator lines with more oscillations as well the atoms will be closer to each other.

Now that we have taken the time to understand the regions of activity for the Hamiltonians and have adopted a short hand notation we can proceed in evaluating these regions. The short hand notation above can be clarified by the following example; if we are looking at the region where the Zeeman effect is larger then both the NV-center interaction with the bulk impurities spin (dipolar coupling) and the self interactions between the bulk impurities (self coupling); while at the same time NV-center interaction with the bulk impurities (dipolar coupling) is larger then that of the self coupling (i.e. $H_Z > H_{SI} > H_{II}$), would be label as ZSE (Fig. 17) [8]. As for the regional condition we have expressed it in equation 4.2.8. For the purposes of our study we are most interested in the $H_Z > H_{SI} > H_{EE}$ (eq.4.2.8), $H_{SI} > H_Z > H_{EE}$ (eq.4.2.9) and $H_{SI} > H_E > H_Z$ (eqt.4.2.10) regions (ω is the Larmor frequency).

$$\left(\frac{a}{\omega}\right)^{1/3} \leq R \leq r \left(\frac{a}{b}\right)^{1/3}, \quad R \left(\frac{b}{a}\right)^{1/3} \leq r \leq \infty \quad (4.2.8)$$

$$0 \leq R \leq \left(\frac{a}{\omega}\right)^{1/3}, \quad \left(\frac{b}{\omega}\right)^{1/3} \leq r < \infty \quad (4.2.9)$$

$$0 \leq R \leq r \left(\frac{a}{b}\right)^{1/3}, \quad R \left(\frac{b}{a}\right)^{1/3} \leq r \leq \left(\frac{b}{\omega}\right)^{1/3} \quad (4.2.10)$$

From equations 4.2.8 and 4.2.9 we can see that for the six permutations in Hamiltonian strengths there are certain constraints to the interaction distances. For the ZSE, the nuclear spin interaction between the self coupling and the NV-center-impurity coupling are far from each other and the center, that the Zeeman effect dominates over both. In the SZE ordering

the NV-impurity coupling are closer to each other which is different from the impurity self coupling, yet the Zeeman interaction is greater than the impurity self coupling. Similar for equation 4.2.10 for the $\langle H_{SI}^2 \rangle \gg \langle H_{II}^2 \rangle \gg \langle H_Z^2 \rangle$ ordering. The additional permutations ZES, EZS, ESZ can have constraint such as 4.2.8 through 4.2.10 but are limited by other factor such as crystal lattice atom occupations distance; these can be seen in further details in reference [8] but are not important to our study. From the permutation above we can clearly see that we will have two major variation in correction ordering. Either the Zeeman effect will be the dominant term or it will not be; we will refer to these as secular and non-secular approximation respectively. Although there is a particular convention for the use of secular and non-secular approximations, in our study we will refer to the secular approximation as the Zeeman effect being larger than both the NV-impurity spin coupling ($S \cdot I_i$) and the spin bath self coupling ($I_i \cdot I_j$). If both the NV-impurity spin and the self coupling of the spin bath are larger than the Zeeman effect, we will refer to this as the non-secular approximation. This convention although unorthodox is used primarily in the field of MNR.

4.3 Correlated Cluster Expansion Method

As stated above the nitrogen vacancy center (NV-center) is part of the many body problem in physics; since we are dealing with a large number of microscopic interacting particles we must treat the system as such. In the past few decades there has been a various number of approaches taken to solve these problem. One such method was the semiclassical approach; in the semiclassical approach the spin bath system was treated as a magnetic field that mimic the flip-flop rate dynamics on the nitrogen vacancy center. Yet the semiclassical classical approach fell short as it did not described the interaction between the NV-center electron spins and the nuclear spin of the bulk impurities (^{13}C , ^{14}N) [8]. In the case when the nuclear spin-spin interaction (self coupling) between the bulk impurities is stronger than

the NV-center electron spin the semiclassical approach falls short[8].

As the semiclassical approach fell short other methods to study the many body problems were used. Some of the more popular approaches were the cluster correlated expansion [44], quantum cluster expansion, disjoint clusters approach, linked-cluster expansion, the pair-correlation approximation, disjoint clusters approach [8][43]. Yet a more modern theoretical approach to solving the problem was to model the system as a classical Ornstein-Uhlenbeck noise source [8]; by where the interaction motions where described as a Brownian particle with friction [45] [46]. An although the NV-center dynamics is a stochastic one, the approach fell short as it ignored the interaction of the nitrogen vacancy center and the environment.

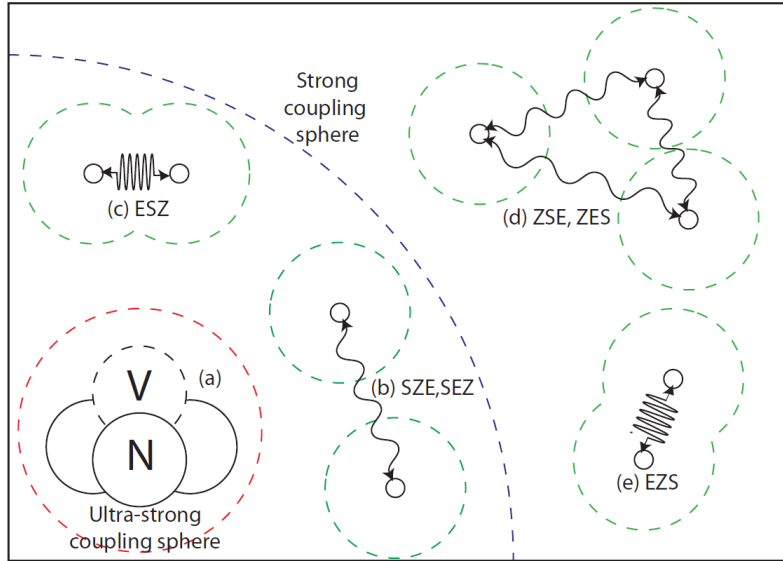


Figure 17: Correlated cluster regions. The ultra strong coupling region defined by the red dotted circle; this region includes the hyperfine interaction. The strong coupling region includes the ultra strong region and the near neighbors clusters. Note that the curve line represent interactions (coupling); the denser the curve lines the stronger the coupling. The magnitude of couplings are given by Z, the Zeeman interaction, E the self coupling by the impurities, S includes the NV-center coupling to the bulk impurities. Therefore ZSE implies the order of magnitude to be $Z > S > E$ [8].

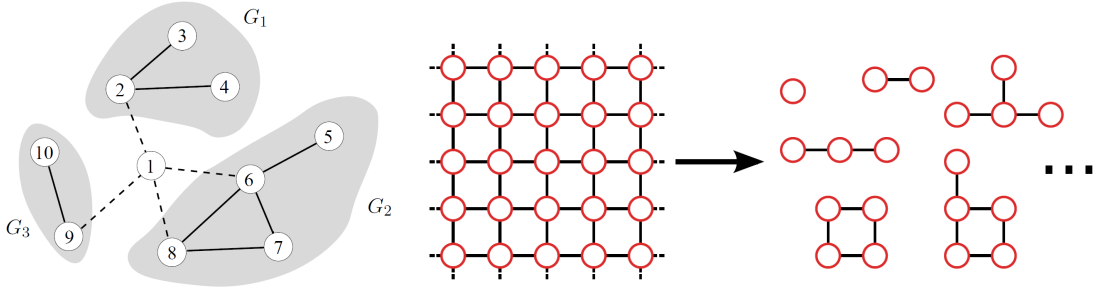
The two most recent approaches that best describe the interaction of the NV-center with the spin bath impurities, are the cluster expansion and correlated cluster expansion methods [8]. The cluster expansion methods takes the random distribution of spins and forms them into strongly interacting clusters; this method is most suited for scattered spins [8]. But in the case where the impurities are more densely populated or in a region where the decoherence of the center is equal to or longer than the autocorrelation time of the environment the cluster correlation function converges better [8]. In this study we will be using the correlated cluster expansion method as it is more suited for the density of the nitrogen vacancy center. The correlated cluster expansion method can be applied to quantum models of many interacting particles, discrete systems, spin models and lattice particle models [47].

In a system with many interacting particles such as the NV-center, one analyze the interaction between individual atoms and then sum over all the interactions in the system. But as you can imagine the task of doing so is daunting when dealing with large number of atoms, as is the case with bulk impurities. The method of correlated cluster expansion allows us to simplify the many body problem by separating linked particles into smaller clusters. We then study the interactions between the clusters and the NV-center. By doing so we can take the sum over all the interacting clusters and obtain the same results as if we would have calculated each individual interaction [48]. Figure 18 below has two description; figure 18 (a) can be seen as the NV-center at position 1, surrounded the bulk impurities. These bulk impurities are separated into clusters of strongly interacting atoms. Note that the cluster are not of the same size (number of atoms) or that the radial dimensions are different.

The power of the correlated cluster expansion method is that the clusters need not be of the same size (number of atoms or dimension). Figure 18 (b) can be seen as a symmetric crystal structure that is clustered in to smaller interacting particles; which again do not need

to be symmetric. The key point in using the correlated cluster expansion method is that the interacting cluster need to be strongly coupled (strongly interacting). One clarification we should make is that although the physical symmetry does not effect the cluster use, the distance between atoms in a cluster may; as stated before they should be strongly interacting. In the case of nitrogen vacancy centers there is a symmetry to the crystal structure (i.e. c_{3v}) but we are more interested at strongly interacting atoms in a region of space. Looking at figures 16 and 17 we see how these regions can be created.

For simplicity we have chosen to use a symmetric spherical region in space as it will neatly encapsulate the interacting atoms; this can be see clearly in figure 16 where we see the radius of a cluster (r) at a distance (R) away from the NV-center. In a similar form in figure 17 we see that the strongly interacting atoms have green doted radial spheres that overlap each other will weakly interacting atoms do not. In the upcoming section we will create the cluster expansion to find the noise spectra of our system, but the reader must remember that we are stating that the atoms in the cluster are strongly interacting.



(a) Random location Linked clusters

(b) Ideal location Linked clusters

Figure 18: a) Correlated cluster expansion is a useful tool to solve the many body problem. Linked cluster can be of any size as depicted by (a) and (b). a) Linked clusters in gray region surrounding a central point. Cluster regions need not be symmetric. [47]. b) With linked cluster expansion we separates clusters and sums up all the effect on the cluster on the point of interest [48].

4.3.1 Single Impurity

Understanding the Hamiltonian, the magnitude ordering possibilities and regions of interest, we can now focus on the magnetic interaction between the nitrogen vacancy center electron spins and the nuclear spins of the bulk impurities. As stated before our method of studying the magnetic field noise is the cluster correlation expansion method. So we will begin by using the simplest system possible and building from there. If we can imagine for a moment, that in the single unit cell of a diamond the only interaction taking place is between the NV-center and one nuclear spin. Using this simplified version of the problem we will find the magnetic field felt by the NV-center. Starting from Maxwell equation, we know that $\nabla \cdot \vec{B} = 0$ which implies that the magnetic field can be written as a vector potential, $\vec{B} = \nabla \times \vec{A}$. Where for a magnetic dipole centered at the origin $\vec{A}$ is given by:

$$\vec{A} = \frac{\mu_0}{4\pi} \frac{\vec{m} \times \vec{r}'}{r'^3} \quad (4.3.1)$$

where μ_0 is the permeability given above, r'^3 and $\vec{r}'$ are the distance between the center of the magnetic moment to some distance located external to the atom and the position vector of the aforementioned distance, respectively. For brevity we have made a change in notation at least for the time being; the magnetic moment of the proton $\mu_p = m$, as well r' in equation 4.3.1 is not the same as the separation distance between cluster spins. From 4.3.1, we can write the magnetic field as:

$$\begin{aligned} \vec{B} &= \frac{\mu_0}{4\pi} \nabla \times \vec{A} \\ &= \frac{\mu_0}{4\pi} \nabla \times \frac{\vec{m} \times \vec{r}'}{r'^3} \end{aligned} \quad (4.3.2)$$

For the derivation of effective magnetic field produced by a nuclear dipole moment we will be using the Levi-Civita notation [49], as well some steps will be omitted for brevity. Equation 4.3.2 can be written in the following notation:

$$\begin{aligned} B_i &= \frac{\mu_0}{4\pi} \varepsilon^{ijk} \partial_i \frac{\vec{m} \times \vec{r}}{r^3} \\ &= \frac{\mu_0}{4\pi} \varepsilon^{ijk} \partial_i \epsilon^{kab} \frac{m_a r_b}{r^3} \end{aligned} \quad (4.3.3)$$

since the differentiation operator ∂_i does not effect ϵ^{kab} we can freely switch their places, giving:

$$B_i = \frac{\mu_0}{4\pi} \varepsilon^{ijk} \epsilon^{kab} \partial_i \frac{m_a r_b}{r^3} \quad (4.3.4)$$

we can use the Einstein summation notation [50] for repeated indices, and we know that $\varepsilon^{kij} \epsilon^{kab} = \delta_{ia} \delta_{jb} - \delta_{ib} \delta_{ja}$ [51]. For now we will ignore the constants in front at write equation 4.3.4 as:

$$\left(\delta_{ia} \delta_{jb} - \delta_{ib} \delta_{ja} \right) \partial_i \frac{m_a r_b}{r^3} = \left(\delta_{ia} \delta_{jb} - \delta_{ib} \delta_{ja} \right) m_a \frac{\partial_i r_b}{r^3} = \left(\delta_{ia} \delta_{jb} - \delta_{ib} \delta_{ja} \right) m_a T_{jb} \quad (4.3.5)$$

where:

$$\frac{\partial_i r_b}{r^3} = \frac{\delta_i r_b}{r^3} - 3 \frac{r_b r_j}{r^5} = \frac{\delta_{jb} - 3 \hat{r}_a \hat{r}_b}{r^3} = T_{jb} \quad (4.3.6)$$

therefore:

$$\begin{aligned}
B_i &= \frac{\mu_0}{4\pi} \left(\delta_{ia} \delta_{jb} - \delta_{ib} \delta_{ja} \right) m_a T_{jb} \\
&= \frac{\mu_0}{4\pi} \left(m T_r(T) - T_{ij} m_j \right)
\end{aligned} \tag{4.3.7}$$

and solving for the trace $T_r(T)$, will yield $m T_r(T) = 0$. Which will in turn give the magnetic field felt by the NV-center due to one nuclear spin impurity:

$$B_i = -\frac{\mu_0}{4\pi} T_{ij} m_j = T_{ij} I_j \tag{4.3.8}$$

where T_{ij} is a symmetric tensor and I_j is the nuclear spin operator. It is important to note that this is the magnetic field that is produced by one nuclear impurity spin which can be either ^{13}C or ^{14}N atom. If we define our system in the cartesian coordinate we can write i, j as x, y, z components. From our previous discussion above the crystallographic direction of the molecule is given by $[111]$ ($\hat{z}$) and which can be seen in figure 6. For our studies we will focus our efforts around the crystal axis, therefore all magnetic fields (applied or not) will be seen from this perspective which implies that we can re-write equation 4.3.8 as:

$$B_z = T_{zj} I_j \quad ; \quad j = x, y, z \tag{4.3.9}$$

4.3.2 Single Cluster with N_k Nuclear Spins

Now that we have found the magnetic field (equation 4.3.9) for the most simplified version, we can extrapolate from it to define the magnetic field felt by the NV-center due to one cluster:

$$B = \sum_{n=1}^{N_k} (T_{zx}^n I_x^n + T_{zy}^n I_y^n + T_{zz}^n I_z^n) \quad (4.3.10)$$

where N_k is the total number of nuclear spins in the k^{th} cluster. Although equation 4.3.10 can be expanded for N_k number of nuclear spins, we will simplify by using two spin per cluster. Recall that this is allowed by the cluster correlation expansion method, as all the cluster will be added together. When we expand equation 4.3.10 for two nuclear spins, we will arrive at the following equation:

$$B = T_{zx}^1 I_x^1 + T_{zy}^1 I_y^1 + T_{zz}^1 I_z^1 + T_{zx}^2 I_x^2 + T_{zy}^2 I_y^2 + T_{zz}^2 I_z^2 \quad (4.3.11)$$

4.4 One Cluster Case

Now that we have obtained the expression for the magnetic field felt by the NV-center due to a two nuclear spin cluster (given by equation 4.3.11) we can find the correlation function. Up to know we have only discussed the magnetic field in the form of strength, now we will label the correlation function in terms of approximations taken. In the field of nuclear magnetic resonance (MNR) the convention to call a strong applied magnetic field as secular approximation is common [52]. Non-secular approximation will indicate that zero to low magnetic fields has been applied. Although this is in contrast to the definition in physics for the purpose of our study we will adopted the MNR convention. Therefore the autocorrelation function of the system which we have derived from equation 4.3.11 for both the secular and non-secular approximation is given by equations 4.4.1 and 4.4.2 receptively.

$$\begin{aligned} \langle B(t)B(0) \rangle_S = & T_{z,1}^2 + T_{z,2}^2 + (T_{x,1}^2 + T_{x,2}^2 + T_{y,1}^2 + T_{y,2}^2) \cos(\omega t) - \left([T_{z,1} - T_{z,2}]^2 \right. \\ & \left. + [T_{x,1} - T_{x,2}]^2 + [T_{y,1} - T_{y,2}]^2 \right) \cos(\omega t) \sin^2 \left(\frac{B_{12}t}{2} \right) \end{aligned} \quad (4.4.1)$$

$$\begin{aligned} \langle B(t)B(0) \rangle_{NS} = & \left(T_{z,1}^2 + T_{z,2}^2 \right) \left[1 - \frac{4}{3} \sin^2 \left(\frac{3B_{12}t}{4} \right) \right] - \frac{2}{3} \left[T_{z,1}^2 - \right. \\ & \left. T_{z,2}^2 \right] \sin^2 \left(\frac{B_{12}t}{4} \right) + \frac{1}{2} \sin^2 \left(\frac{B_{12}t}{2} \right) - \sin^2 \left(\frac{3B_{12}t}{4} \right) \end{aligned} \quad (4.4.2)$$

where the axial flipping rate is given by $B_{12} = \frac{b}{r_{12}^3}(1 - 3\cos^2(\theta_{12}))$; b is a constant given by equation 4.2.4, ω is the Larmor frequency given by the Larmor equation $\omega = \gamma_I B_0$, B_0 is the applied magnetic field), r_{12} is the distance between nuclear spins in the cluster and θ_{12} is the angle between the vector $\vec{r}_{12}$ and the z axis. Since we are looking along the crystal axis we can ignore the first z sub indicator for the crystal axis and use the simpler notation $T_{z,(z,x,y)}^j \equiv T_{(z,x,y),j}$. Considering only the z axis we can simplify equations 4.4.1 and 4.4.2 which result in the following

$$\langle B(t)B(0) \rangle_S = T_{z,1}^2 + T_{z,2}^2 - [T_{z,1} - T_{z,2}]^2 \sin^2 \left(\frac{B_{12}t}{2} \right) \quad (4.4.3)$$

$$\langle B(t)B(0) \rangle_{NS} = (T_{z,1}^2 + T_{z,2}^2)^2 \left[1 - \frac{4}{3} \sin^2 \left(\frac{3B_{12}t}{4} \right) \right] \quad (4.4.4)$$

4.5 N Clusters

It is important to note that equations 4.4.3 and 4.4.4, are the secular and non-secular approximations (receptively) for one cluster of two nuclear spins. In order to obtain the complete system correlation function we must use the statistical probability function:

$$P(r) = \left(4\pi nr^2\right) \exp\left(-\frac{4\pi nr^3}{3}\right) \quad (4.5.1)$$

which tells us the probability of encountering a nuclear spin at r [8]; n is the number density for ether ^{13}C or ^{14}N impurities. If we multiply the two spin cluster correlation (equation 4.4.3 & 4.4.4) and sum over all the cluster in the environment (4.5.2) we will find the autocorrelation function for both secular (4.5.3) and non-secular (4.5.4) approximation of the system [8].

$$C(t) = \sum \langle B(t)B(0) \rangle_{S,NS} P(r) \quad (4.5.2)$$

$$C(t)_S = \frac{8}{5} \left(\frac{4}{3}\pi an\right)^2 \left[1 - \frac{1}{3}M(t)\right] \quad (4.5.3)$$

$$C(t)_{NS} = \left(\frac{8}{3}\pi an\right)^2 [1 - N(t)] \quad (4.5.4)$$

$M(t)$ and $N(t)$ are the cluster magnetization functions of the system and are given in equation 4.5.5 and 4.5.6.

$$M(t) = \frac{4\pi\sqrt[3]{6}}{\Gamma(\frac{8}{3})}(\pi bnt)^{5/3} - \frac{8\pi}{\sqrt{3}\Gamma(\frac{4}{3})}(\pi bnt)^2 \quad (4.5.5)$$

$$N(t) = \left(\frac{4}{9}\pi^2 bnt\right) \quad (4.5.6)$$

where $\Gamma(\frac{8}{3})$ and $\Gamma(\frac{4}{3})$ are gamma functions and b is constant defined above. It must be noted that equations 4.5.5 and 4.5.6 are not directly the magnetization rate of the system, both have been derived from it as given in equations 4.4.3 and 4.4.4.

4.6 Noise Spectra

Now that we have found the correlation function of the system we can generate the noise spectrum. From the Wiener–Khinchine theorem (4.6.1 and 4.6.2) we know that for a stochastic process the noise spectrum and the correlation function of the system are cosine Fourier transforms of each other and contain the same information [53].

$$S(\omega) = \int_0^\infty C(t)\cos(\omega t) \quad dt \quad (4.6.1)$$

$$C(t) = \int_0^\infty S(\omega)\cos(\omega t) \quad d\omega \quad (4.6.2)$$

Before we use the Wiener–Khinchine theorem there is a quick note that we would like to add. As can be seen from equations 4.6.1 and 4.6.2 the bounds of the equation ($0 \rightarrow \infty$) work for most but not all noise spectra or correlation functions. For stochastic systems as

is the case with NV-centers we must use a truncated time interval, the new truncated noise spectra for the secular and non-secular are given by equations 4.6.3 and 4.6.4.

$$\begin{aligned}
S(\omega)_S &= \int_0^t C(t)_S \cos(\omega t) \, dt \\
&= \frac{8}{3} \left(\frac{4}{3} \pi a n \right)^2 \int_0^t \left[1 - \frac{1}{3} M(t) \right] \cos(\omega t) \, dt
\end{aligned} \tag{4.6.3}$$

$$\begin{aligned}
S(\omega)_{NS} &= \int_0^t C(t)_{NS} \cos(\omega t) \, dt \\
&= \left(\frac{8}{3} \pi a n \right)^2 \int_0^t [1 - N(t)] \cos(\omega t) \, dt
\end{aligned} \tag{4.6.4}$$

the truncated time interval in the cosine Fourier transform can be seen as a result of the time scale the event takes place. Most stochastic process operate over certain time intervals and extending that time interval can result in inclusions of information that is nonphysical.

In the case of our system we solved for the zeros of the cluster magnetization function and found $t \approx 10^{-6}$ s. This time interval can imply that the spin flip flops take place on an interval of microsecond or at least that the system reaches some form of equilibrium in that time. Therefore our truncated stochastic noise spectra from equations 4.6.3 and 4.6.4 can express in there complete form (4.6.5 and 4.6.6). Where $M(t)$ would be the function that scales for the applied magnetic fields.

$$S(\omega)_S = \frac{8}{3} \left(\frac{4}{3} \pi a n \right)^2 \int_0^{1.9999 \times 10^{-6}} \left[1 - \frac{1}{3} M(t) \right] \cos(\omega t) \, dt \tag{4.6.5}$$

$$S(\omega)_{NS} = \left(\frac{8}{3}\pi an\right)^2 \int_0^{1.999 \times 10^{-6}} [1 - N(t)] \cos(\omega t) dt \quad (4.6.6)$$

after the integrals have been taken, the functions will be plotted over a frequency range that is experimentally susceptible.

CHAPTER V: NUMERICAL EVALUATION & DISCUSSION

Now that we have obtained the noise spectrum from the autocorrelation functions given by equations 4.6.5 and 4.6.6 we can proceed to numerically evaluate. In order to numerically evaluate the noise spectra above, we created a simulation via Mathematica which was then transported to Matlab for graphical representation. There are several figures that we will present in this section. But before we dive into it is important to recall the definition of the secular and non-secular approximation. Secular approximation refer to an approximation that is made when there are high magnetic fields applied to the system. For low to zero magnetic fields we referred to this as non-secular approximation. For our purposes we consider a high applied magnetic field to be above 300 Gauss and low applied fields to be under 1 Gauss.

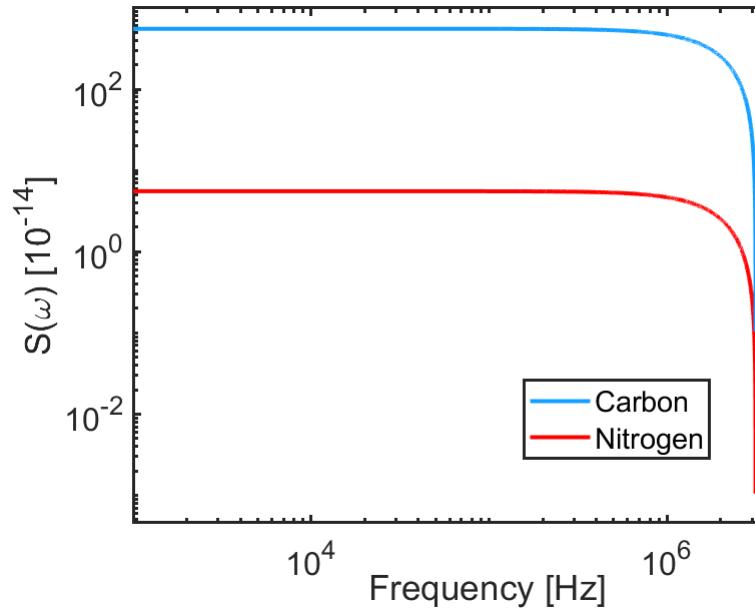


Figure 19: Magnetic noise spectrum versus frequency considering large magnetic field (secular) approximation, for bulk impurities (carbon and nitrogen). When comparing the magnetic field noise of the naturally occurring 1 % carbon (^{13}C) impurities and the nitrogen (^{14}N) impurities, we find that ^{13}C has roughly two orders of magnitude larger magnetic field noise than nitrogen which is attributed to number density difference between (^{14}N) versus (^{13}C).

In figure 19 we have chosen to compare the bulk impurities (^{13}C and ^{14}N) interacting with the nitrogen vacancy center for applied magnetic fields that are strong (high). From the graph we can see that for the secular approximation the ^{13}C atoms interaction with the NV-center are roughly two orders of magnitude greater than that of the ^{14}N atoms interacting with the NV-center. We attribute this to the number density of the impurities. The order of magnitude for the bulk impurities is 10^{18} cm^{-3} for the ^{14}N atoms and 10^{19} cm^{-3} for the ^{13}C atoms. There are two factors that can be associated to the number density; first, the mean distance to the NV center and second, the number of flip flop taking place.

We attribute the noise in crease that there are more carbon atoms in the system the distance between the carbon atoms and the NV-center will be slightly closer than that of the nitrogen atoms. Which will make the interaction between the ^{13}C and the nitrogen vacancy centers will be greater, when compared to the ^{14}N NV-center interaction. As well since there is a greater population of ^{13}C atoms to ^{14}N there will be more nuclear spin flip flops that take place of the ^{13}C ; therefore the correlation time is minimized much faster. Now that we found the carbon-13 atoms where the primary source of noise for the secular approximation, we wanted to see if this translated to the non-secular approximation.

Figure 20 is the interaction between the nitrogen vacancy center electrons spin and the nuclear spin of the bulk impurities at low applied magnetic fields. What we see in Figure 20 is that there is still two orders of magnitude difference between the magnetic field noise of the carbon-13 atoms and the nitrogen-14. Since the number density of the carbons and nitrogen do not change for either approximation we can conclude that the density is a key factor in the magnitude difference in noise. In the above paragraph we gave two possible reasons separation in magnitude between the carbon and nitrogen atoms. But there may be one other factor that can be part of the process. The hyperfine interaction between the

electrons of the nitrogen vacancy centers and the donor atoms.

If we refer back to figures 17 and 16 we see that there are region of ultra strong coupling. These regions of ultra strong coupling are dictated by the hyperfine interaction. The ultra strong coupling region was not in the scope of this work, therefore it was not scrutinized here. But it maybe an avenue of approach for further corrections in future works. Although at the moment it is difficult to see, if we refer back to figures 19 and 20 you can see a slight difference in the magnitudes between the secular and non secular approximation. This difference will become more apparent in the upcoming graphs.

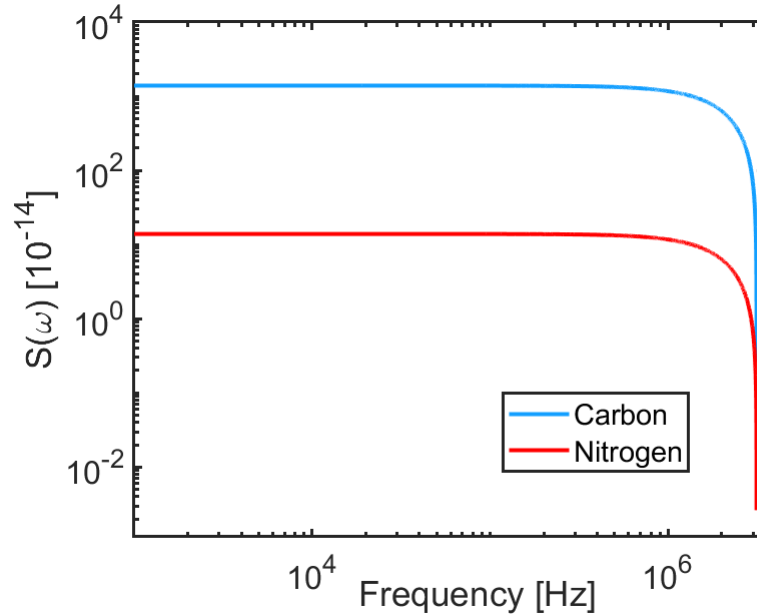


Figure 20: Magnetic noise spectrum versus frequency considering zero to low magnetic field (Non-secular) approximation, for bulk impurities (carbon and nitrogen). When comparing the magnetic field noise of the naturally occurring 1 % carbon (^{13}C) impurities and the nitrogen (^{14}N) impurities at low to zero field, we find that ^{13}C has roughly two orders of magnitude larger magnetic field noise than nitrogen which is attributed to number density difference between (^{14}N) versus (^{13}C).

From figure 19 and figure 20 we saw that the interaction between the nitrogen vacancy center electrons spins and the naturally occurring 1 % carbon nuclear spins are the primary source of noise for low and high magnetic fields applied. This two order of magnitude splitting between the nitrogen-13 atoms and the carbon-13 atoms led us to plot figure 21. In figure 21 we are comparing the the interaction between the nitrogen vacancy center and the nuclear spins of the carbon atom for both the secular and non-secular corrections. We see from the graph that there is a slight variation in the magnitude the secular and no secular corrections. The non-secular plot given by the blue line is greater then that of the secular approximation given by the red line. Although the magnitude splitting between the secular and non-secular approximations is not as drastic or extreme as the splitting between carbon and nitrogen, there is a difference .

Since the number density does not change we must look deeper at the optical properties(Fig. 8). As an external magnetic field is applied to the NV-center we will get a degeneracy breaking in the excited and ground $m_s = \pm 1$ states; as can be seen in Figure 8. The degeneracy breaking by the applied magnetic field will limit the state available for transition by the nitrogen vacancy centers electron spins. The lack of transitions will shield the nitrogen vacancy center to flip flops of the bulk impurities.

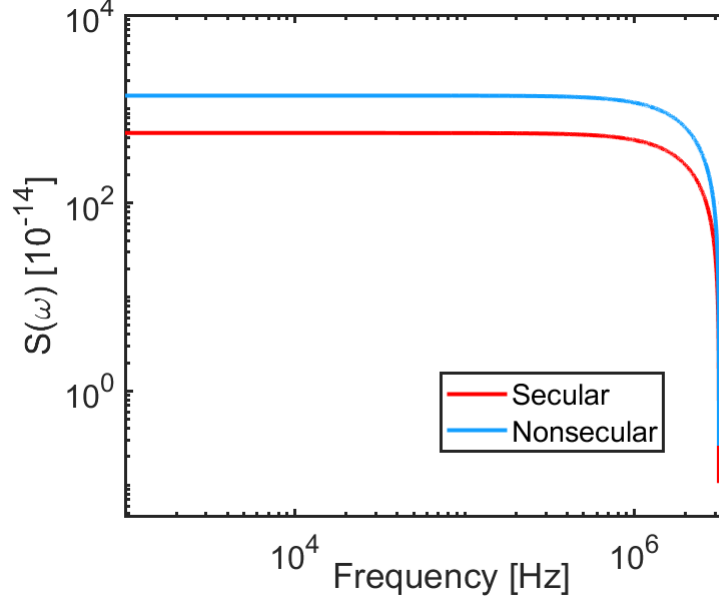


Figure 21: Magnetic noise spectrum versus frequency considering zero to low magnetic field (Non-secular) and large magnetic field approximation, for carbon impurities. Magnetic field noise is larger in zero to low magnetic fields when compared to larger fields. This is caused by shielding of the NV-center from the bulk impurity carbon atoms¹ by the applied field.

From the above graphs we see that the non-secular approximation can be used for zero to low magnetic field and for high magnetic field. But if high magnetic field have been used the secular approximation is valid. For completeness we have decided to add figure 22; figure 22 is the secular and non-secular approximations for the nitrogen-14 impurities interacting with the electron spins of the nitrogen vacancy center. We can see that similar to the carbon-13 comparison in figure 21 the magnitude of the non-secular approximation is larger then that of the secular approximation. Indicating that the secular approximation is valid for high applied magnetic fields.

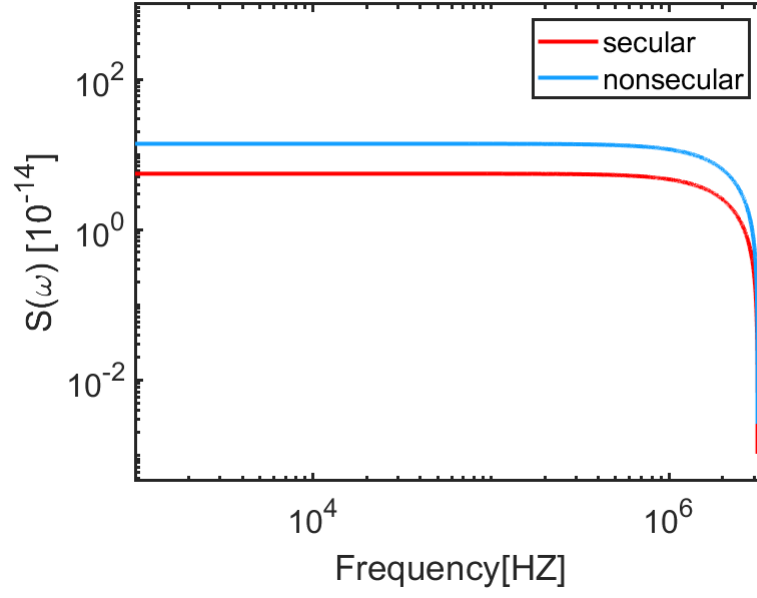


Figure 22: Magnetic noise spectrum versus frequency considering zero to low magnetic field (Non-secular) and large magnetic field approximation, for nitrogen impurities. Magnetic field noise is larger in zero to low magnetic fields when compared to higher fields. This is caused by shielding of the NV-center from the bulk impurity nitrogen atoms by the applied field.

CHAPTER VI: CONCLUSION

Nitrogen Vacancy Centers in diamonds are of high interest due to their possible applications as biomarkers, atomic-scale magnetic field sensors, quantum computing and more [1] [2] [3] [4]. The effectiveness of device manufacturing is the limit to sensitivity (noise). For nitrogen vacancy centers the noise is caused by electric and magnetic fields; the noise causes optically detected magnetic field resonance (ODMR) line-broadening [54]. This line-broadening reduces sensitivity of the devices. The electric field noise was found to be caused by surface charge fluctuations.

In this work we theoretically investigated the magnetic field, noise cause by the electron spins of the NV-center and the bulk impurities (^{13}C , ^{14}N). The bulk impurities of the system consist of the naturally occurring 1 % ^{13}C atoms in a diamond and the ^{14}N atoms that are implanted or remaining from the doping. Magnetic noise is cause by an induced magnetic field from one atom on the other. The dipole dipole interaction can also be caused by unpaired electron and external atoms; as is the case of NV-centers. As the dipole dipole interaction take place in the NV-center with the impurities the system will begin to flip flop. It is important to note that by the Pauli exclusionary principal the free electrons in the NV-center will not flip, therefore the spin bath (bulk impurities) will be the only spins that will flip flop. It is this flip flop process that produces the magnetic field noise in the system. The reader must recall that magnetic dipoles are permanent and cause by orbital angular momentum (which is proportional to the magnetic field applied) and the nuclear spin. While on the other hand electric dipoles are not permanent and cause by a near by charge.

The many body problem in physics is the term given to a microscopic system that densely populated with interacting particle [55]; as is the case of nitrogen vacancy centers. Since the

system is microscopy we must describe the system quantum mechanically. Looking at the system through the quantum mechanical representation given by the Hamiltonian (4.2.1) we can gain a deeper insight into the regions where the cause of noise may be greater or smaller. For our study we are primarily interested in three Hamiltonian corrections. The Zeeman interaction, the interaction between the NV-center electron spins and nuclear spins of the bulk impurities, and the self interaction between the bulk impurities. Looking at the three Hamiltonian corrections we saw that there were six possible permutations of magnitude ordering.

For brevity we relabeled the corrections by Z for the Zeeman effect, S for the interaction between the NV-center electron spins and nuclear spins of the bulk impurities and E for the self interaction between the bulk impurities. Having the shorthand notation in place we ordered the interaction strength by the mean square of the Hamiltonian's. Through some simple algebra manipulation we were then able to obtain the region of interactions strength: which can be seen in mathematical form in equations 4.1.8 to 4.1.10 above or by the physical interpretation seen in figure 17. In an attempt to solve the many body problem there have been many methods proposed. While some give somewhat accurate results they are incomplete; the incompleteness of these methods arises from their treatment or lack of inclusion of the nitrogen vacancy center interaction with the bulk impurities.

The two most recent methods of solving the many body problem (NV-center interactions) are the cluster expansion method and the correlated cluster expansion methods. Since the nitrogen vacancy centers are densely populated the correlated cluster expansion will give a better result. The concept of the correlated cluster expansion is simple; instead of looking at individual atoms interacting with the NV-center and summing over all the interactions, we can form clusters of interacting particles and see their effect on the NV-center and sum over

all the cluster to get the total effect without loss of generality. The power of the correlated cluster expansion method is that we are not constricted by the number of spins in the clusters or the shape chosen to include spins into a cluster.

We began the correlated cluster method by looking at the most simplified version of a cluster we could create. In our case the simplest cluster that can be created is a cluster of one nuclear spin (from the bulk impurities) interacting with the electron spins of the nitrogen vacancy center. From here we were able to find an expression for magnetic field that was felt by the NV-center due to the nuclear spin. After obtaining this magnetic field we were able to extrapolate an equation that would accommodate N_k number of spin in a cluster. Once we had the magnetic field as felt by the NV-center due to the dipole-dipole interaction with the bulk impurities, we expanded for a two nuclear spin cluster.

From the two nuclear spin clusters we found the correlation function of the cluster; please note that this was not the correlation functions of the system. Needing to account for large magnetic fields and low to zero magnetic fields led to the evolution of the correlation function to two equations. In order to find the correlation functions for all clusters in the system we used the statistical probability function. The probability function gives us the probability of finding n number of nuclear spins in a region r . By multiplying the correlation functions by the probability function and summing over all the cluster in the system we were able to find the correlation function of the system; as given by equations 4.5.5 and 4.5.6 above.

After finding the correlation functions of the system we used the Wiener-Khinchin theorem to find equation of the noise spectra. The Wiener-Khinchin theorem tells us that the correlation function and the noise spectra are cosine Fourier transforms of each other and contain the same information. We first numerically evaluated the interaction between

the nitrogen vacancy center electron spins and the nuclear spin for both the ^{13}C atoms and the ^{14}N atoms at low magnetic fields. From the graph we saw that the ^{13}C noise was roughly two orders of magnitude larger than that of ^{14}N noise. We attributed the noise splitting between the ^{13}C noise and the ^{14}N noise to the number density. There is roughly one order of magnitude more carbon atoms than nitrogen atoms in the molecule. This increase in number density can result in closer interactions between the carbon atoms and the NV-center or a larger amount of flip flops taking place; which in turn reduces the correlations between the electrons in the NV-center.

Knowing that for low magnetic fields the primary source of noise was the ^{13}C atoms, we wanted to see if the trend would continue for large magnetic fields. Therefore, we plotted the interaction between the NV-center and the bulk impurities at large magnetic fields. After obtaining the numerical evaluation for low magnetic fields, we found that like before there is a two order of magnitude difference in the noise splitting. Which was expected if the number density was the cause of the noise splitting. Having found these results we noticed that the magnitudes between the large and low applied fields had a slight variation in magnitude.

We took our numerical evaluation a step forward and plotted the interaction between the NV-center and the 1 % naturally occurring ^{13}C atoms for large and low fields. We confirmed that there was a variation in magnitude between the two graphs. Since the number density did not change, the noise splitting for the carbon atom comparison is caused by something else. Looking at the optical properties of the NV-center [28], as we apply a large magnetic field we will have degeneracy breaking in the $m_s = \pm 1$ ground and excited state. By breaking the degeneracy of the system we limit the energy states available for transition. This limitation of the transition in effects shields the nitrogen vacancy center from flip flop transition of the

bulk impurities.

We confirmed our result by numerically evaluating the nitrogen atoms for both large and low magnetic field and found a difference in noise magnitude. In nuclear magnetic resonance there is a convention of using the terms of secular and non-secular for large applied magnetic field and for low applied magnetic fields respectively. We will adopt this convention to conclude our study. Our study has found that non-secular approximation is valid for all fields applied to the nitrogen vacancy center dipole-dipole interaction with the bulk impurities. But for large applied magnetic fields the secular approximation can be used.

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