Could NV centres in diamond be used to measure donor spins in silicon?

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I, David Wise, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.
ABSTRACT

This thesis primarily studies two spin species bound to defects in solid state semiconductors: the electron spin bound to donors in silicon, and the nitrogen vacancy (NV) centre in diamond. Both of these spins have properties that have made them candidates for qubits in a quantum processor. Donor electron spins have exceptionally long coherence times, in excess of seconds under ideal circumstances. In addition, the industrial expertise for fabrication of silicon devices are unrivalled. Efficient measurement of single donor spins has, however, proved challenging. The NV centre in diamond also shows excellent quantum properties with measurable quantum coherence even at room temperature. Furthermore, its spin state can be efficiently measured via optically detected magnetic resonance with relative ease and it makes for a highly sensitive, nanoscale magnetic field sensor. Fabrication technologies in diamond however, lag behind the silicon industry. If these two qubit types could be combined in a hybrid device, it may well allow for the best of both worlds.

This work performs an initial study into the potential for such a device, focussing on the question of whether a single NV centre could measure a single donor electron spin. I will examine the potential impact of laser illumination on the quantum properties of donor electron spins, the behaviour of near surface NV centres at the cryogenic temperatures needed for donor electron spins to gain their most attractive qualities, and study single NV centre atomic force microscope probes designed for single spin detection.

As well as the experimental results presented, I also show the results of a machine learning technique designed to efficiently extract the qubit noise spectrum. The qubit noise spectrum is useful both from the point of view of extending qubit coherence via bespoke pulse sequences and also for providing insight into the qubit surroundings. This technique performs well when compared with alternative techniques, offering accuracy that is similar to state of the art approaches but with significantly fewer experimental resources.
IMPACT STATEMENT

The development of technologies that harness and control the fragile states of quantum objects are anticipated to revolutionise many aspects of the modern world. Quantum computers can solve certain problems that are intractable for even the most advanced supercomputers, quantum sensors can provide exquisite sensitivity to electric fields, magnetic fields, gravity, and all manner of physical phenomena. The work presented here has potential long term applications to quantum computing but in the near and more realistic term develops a point like magnetic field sensor that has nanoscale resolution. These diamond NV sensors have the potential to function as fantastically accurate diagnostic tools in engineering settings and have also been touted for their potential to work with biological samples, due in large part to the inertness of diamond.

In addition, this work develops a machine learning technique for the efficient extraction of the qubit noise environment. Understanding the noise experienced by a qubit can allow for coherence extension via bespoke control sequences or for a more detailed insight into the physical surroundings being probed. Traditional techniques tend to be relatively inaccurate or are experimentally demanding. The machine learning approach developed here is both accurate and experimentally undemanding, allowing it to be employed with minimal effort across a variety of quantum technologies.
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1 INTRODUCTION

Why do I get the feeling that someday, I’ll be describing this to a psychiatrist

— Lisa Simpson

Quantum computers and the broader field of quantum technologies have long been predicted to revolutionise the modern technological landscape, ever since it was first hypothesised by Richard Feynman [1, 2]. Whilst quantum effects have been part of progress in the field of computing since the development of the transistor, it is only recently that we have begun to attempt to control the states of quantum objects. Computers that are based on quantum bits (qubits) have been shown to perform certain tasks exponentially faster than is possible with computers based on a binary architecture [3]. With the ever-growing signs that we are approaching a plateau of classical computing power gains, and with the recent demonstration of the first quantum supremacy experiment, interest in what the field can achieve is only strengthening [4, 5].

The qubit is the basic unit of a quantum computer and is the quantum analogy for the classical bit. The classical bit can be represented by a 0 or a 1, which corresponds to a switch preventing or allowing the flow of current. Connecting together many of these switches, in the form of transistors, allows a computer to perform logic. The logic on which modern computers are based is capable of solving any problem, but the efficiency with which that problem can be solved is not guaranteed [2, 6]. Typically, the hardness of a problem is judged by its complexity class, which determines how the time and memory required to solve a problem scales with the size of the problem. The time to find the solution of a $\mathcal{P}$ type problem scales polynomially with problem size: imagine for example finding the smallest number in a list, as the list gets longer the time to find that smallest number gets longer but it does so at the same rate. The time to find the solution of an
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$NP$ type problem scales exponentially with the size of the problem. In this case imagine finding all the prime factors of a number, a problem that can take a trivially short time for a computer factoring a small number but which can take many years if that number gets large.

If you can build a computer that is based on qubits rather than bits then some of these problems that quickly become intractable for classical computers can remain solvable for quantum computers. A qubit state can be represented as follows:

$$|\psi\rangle = \cos \frac{\theta}{2} |0\rangle + e^{i\phi} \sin \frac{\theta}{2} |1\rangle$$

(1.1)

where $\theta$ and $\phi$ are angles that allow the state to be represented as a point on a sphere, usually called the Bloch sphere, shown in figure 1.1. It’s clear from this representation that the qubit can take an infinite possible number of values, quite different from the binary bit. This is not the source of a quantum computer’s excess capability however. Analogue computers have the same feature but this does not allow them to do what a quantum computer can. The truly unique feature of the qubit is phase, the relationship between the $|0\rangle$ and $|1\rangle$ states given by equation 1.1. The phase of a qubit allows it to exist in a state known as superposition, where it can be thought of as being in both $|0\rangle$ and $|1\rangle$ states simultaneously. A computer made up of a large number of qubits can, in principle, be in a superposition of all the possible states of those qubits at once.

In effect, the computer can thus represent a huge number of potential questions at once and have them all tested simultaneously as potentially correct answers. This highly parallel nature is part of what makes a quantum computer powerful — but statements to the effect of ‘a quantum computer works because it can try all possible solutions at once’ frequently garner ire [7]. The problem is that although the computer’s qubits can be in all these states at once, when the system is measured only one of these states is observed. This phenomenon is known as wavefunction collapse — a single qubit is only ever observed in either $|0\rangle$ or $|1\rangle$ state, never in its superposition state [2]. As a result, the highly parallel nature of quantum computers is useless unless we can guarantee that the answer we get when we measure at the end of a computation is the correct one\(^1\). Phase allows this, by

\(^1\)Even if we would get all the answers out at once, we’d be left with a gigantic pile of incorrect ones. The correct answer would be left as a needle in a colossal haystack.
Figure 1.1: The Bloch sphere representation of a single qubit state.

letting different states of the system interfere with one another. This interference can be constructive or destructive, and quantum algorithms work by getting correct answers to interfere constructively, whilst incorrect answers interfere destructively.

Sadly, quantum states are fragile and the creation of qubits that can be controlled and measured with sufficient precision to perform quantum algorithms is a huge task. There are many candidate systems and none is without its faults. Superconducting qubits have been the basis of the most successful quantum processors developed up until now, but even the most advanced still have fewer than 100 qubits [5], whilst a fully realised quantum computer, capable of correcting the inevitable errors that arise during computation would likely require many millions [8, 9]. Due to their current size, there are significant concerns that a superconducting qubit based processor could not be scaled to such numbers [10]. Quantum dots in silicon are another qubit species under investigation for use in a quantum processor and whilst they currently lag behind superconducting qubits, their small size and ability to leverage the traditional semiconductor industry suggest that they may have a bright future [11, 12].
1 Introduction

The species that this work is primarily concerned with is the spin defect qubit in the solid state. These employ the spin of an electron or nucleus to store quantum states, due to its natural two level system structure the electron spin is in many ways the prototypical qubit [13]. There are many spin defects under investigation as potential qubits and this work looks at two in detail: the electron spin of donors in silicon, and the Nitrogen Vacancy centre in diamond [14, 15, 16].

1.1 Spin defects as qubits

The spins of donors in silicon have been a long time candidate for the qubits in a quantum computer, not least because of the ability to leverage the huge expertise developed in the semiconductor industry in the last century [13]. One of the most influential proposals in this area was made by Kane [14] and envisioned using the nuclear spin of phosphorus donors in silicon to store qubit states. These nuclear spins possess extraordinary quantum properties, with coherence times — the length of time a qubit remains in a quantum state and one of the key metrics for judging the suitability of a qubit — in excess of seconds. Figure 1.2(a) shows a schematic of the proposal. The challenge with this approach is that it required the contact interaction between the nuclear spins to mediate two qubit gates and so necessitated extremely close (sub nanometre), deterministic positioning of these donors. Furthermore, as understanding of quantum computing has developed focus has shifted to being able to implement error correcting schemes such as the surface code [17, 18]. These necessitate that two groups of qubits are produced: data and measurement qubits. The data qubits must be isolated from one another to prevent errors on a single qubit propagating to others — the measurement qubits mediate the interaction instead. In addition, work with donors in silicon has tended to shift towards working with the electron spin over the nuclear spin, as coherence times are excellent at longer than 1s (although shorter than the nuclear spin) and control operations via microwaves are significantly faster and easier to implement [19, 20, 21].

A work by O’Gorman et al presents a vision of an updated silicon quantum processor based around the surface code [15]. The data qubits in this case are the electron spins of donors in silicon, implanted in the silicon lattice but unlike the Kane architecture these
1.1 Spin defects as qubits

Figure 1.2: Potential silicon quantum computing architectures. (a) is reproduced from [14] and shows the 'Kane' architecture. This was an architecture based on using the nuclear spins of phosphorus donors in silicon as the qubits in a quantum computing architecture. As the microwave control fields are hard to apply locally, a global field is applied instead and electrical gates ('A' gates in the figure) shift qubits on and off resonance with that field using the stark shift, coupling between qubits is mediated by the electrons bound to the different nuclei and 'J' gates are used to control this. (b) is reproduced from [15] and shows a modern understanding of a silicon quantum computing architecture. In this setup, the silicon qubits are the electrons bound to a donor species in silicon and they are controlled by a separate spin species in a movable measurement grid above. This architecture is designed to facilitate a surface code error correcting scheme, where data qubits are constantly measured in groups of four by measurement qubits. This scheme proposes using the magnetic dipole interaction between two spin species to perform this measurement.
can be separated by 100s of nanometres, thereby requiring significantly lower precision during implantation. The work also introduces the concept of a moveable layer of measurement qubits — also spin defects — each of which is designed to measure the parity of groups of four qubits\(^2\). The interaction between the measurement qubits and the data qubits is based on the magnetic dipole interaction, requiring a separation between the two layers of approximately 40 nm. One crucial component of the scheme is that the spin species have different energy levels in a static magnetic field, if they have the same energy level then they can undergo spin flip-flop interactions and exchange states. Nitrogen Vacancy (NV) centres in diamond are suggested as the measurement spin species due to their large zero field splitting of 2.87 GHz. The NV centre in diamond also makes great sense as they are perhaps the easiest spin defect on which to perform state readout [22, 23]. Whilst readout of single spins bound to donors in silicon has been performed, it is a highly challenging operation [24].

Challenges abound when seeking to implement such a technique, some of which this work seeks to explore. The electron spin of the NV centre in diamond has excellent quantum properties, remarkably showing coherence times in excess of 0.5 ms at room temperature — for reference, an electron spin bound to a phosphorus donor in silicon would need to be below 10 K to exhibit similar coherence. It is well studied as a sensitive and precise magnetic field sensor at room temperature, but this room temperature excellence has meant that the cold behaviour of the defect is relatively unexplored — particularly for the near surface defects required for field sensing. To ensure that the electron spin in silicon has sufficient coherence, the scheme described above would need to operate well below 10 K, and likely closer to 1 K. Moreover, the NV centre is controlled partly via green laser illumination and light is known to have an impact on the electron spin bound to donors in silicon. This effect is likely particularly strong for light with photon energies above the silicon band gap — equivalent to wavelengths of less than 1058 nm. Works by Feher and Gere have studied the impact of laser illumination on donors in silicon, but have focussed on the impact on relaxation, a classical effect, whilst the chief determiner of quantum properties is the coherence. The coherence is ultimately limited by the relaxation, but effects above and beyond that are possible.

\(^2\)Parity — 0011, 1111 have even parity; 0111, 1000 have odd parity.
1.2 The NV centre in diamond

Figure 1.3: NV magnetometry: (a) the change in CW-ODMR fluorescence of an NV centre with magnetic field, (b) cartoon of a scanning probe magnetometer and fluorescence image of a hard disk. (a) shows fluorescence as a function of microwave driving frequency, at 0 field, a dip in fluorescence is observed at the zero field splitting of 2.87 GHz, as magnetic field increases and the \( m_s = \pm 1 \) spin states split in energy the frequency of this dip changes, allowing for accurate inference of the magnetic field. (b) a cartoon of an NV centre in a scanning probe, which is then scanned over a sample and its fluorescence recorded — showing the magnetic structure of the computer hard disk sample. Both figures reproduced from [27]

1.2 The NV centre in diamond

Proposed as one part of a quantum processor above, the NV centre has become one of the most widely used qubit types over the last two decades across a range of quantum technologies [16, 23]. One of the few qubit types that exhibit quantum properties at room temperature, along with trapped ion qubits [25], their spin and point like nature have made them an ideal magnetic field sensor [26]. The basis of their utility is a spin triplet ground state that couples to a spin-preserving optical transition. When this optical transition is excited with laser light, the NV centre fluoresces. The level of the fluorescence changes based on the initial spin state, with an \( m_s = 0 \) state fluorescing more than \( m_s = \pm 1 \) state. By applying a constant microwave field and changing its frequency, a dip in fluorescence is observed at the point the microwave energy equals the spin state energy splitting.
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In a magnetic field, the spin $m_s = \pm 1$ states split in energy, which changes the position of this fluorescence dip — one dip moves down in frequency and the other up in frequency, as shown in figure 1.3. This allows for highly accurate DC magnetic field sensing, with sensitivity proportional to the linewidth of the ODMR dip and the contrast of the NV centre — the difference in fluorescence between the two spin states. In optimal conditions, including use of ultra-pure diamond, this allows the NV centre to have a field sensitivity as low as 40 nT Hz$^{-1/2}$.

If the field being sensed is AC rather than DC, then the sensitivity of the NV centre is significantly better, as it is limited by its homogeneously broadened linewidth rather than inhomogeneously broadened linewidth. With AC field detection, sensitivities as low as 10 nT Hz$^{-1/2}$ can be achieved [28].

The key features that determine NV sensitivity are its overall fluorescence (number of photons emitted per second), its fluorescence contrast (difference in photons emitted between bright and dim states), and its coherence time. Whilst fluorescence and contrast are somewhat fixed features of an NV centre (although they can be improved during fabrication and implantation), coherence time can be improved via the use of control sequences. The key factor affecting coherence time of an NV centre is its local magnetic environment and particularly local magnetic noise [29]. The noise experienced by an NV, or any qubit, is typically described via a noise spectrum, $S(\omega)$, which gives the power of the noise and how it changes with frequency. Standard pulse sequences are designed to mitigate noise but are not specific to the noise spectrum of a given qubit. If the noise spectrum of an individual NV centre can be determined then bespoke control sequences can be used to increase its coherence time [30]. The noise spectrum cannot be measured directly experimentally and instead mathematical approximations are required to derive it from measurements of coherence. However, these tend to be either inaccurate or experimentally very taxing.

More than its pure sensitivity, what makes the NV centre attractive as a magnetic field sensor is its point like nature. This means that a near surface NV centre, mounted in a probe, can sense magnetic fields to extraordinary resolution — below 1 nm in ideal conditions. Schemes to make use of this use single NV centres in the tips of diamond probes mounted to atomic force microscope (AFM) hardware. The AFM can be used to
1.3 Developing a hybrid silicon-spin, NV centre architecture

Figure 1.4: Figure reproduced from [31], showing (a) a schematic of a scanning magnetometer setup using AFM and optical readout of a near surface NV centre in a diamond probe. (b) shows a close up SEM image of the diamond probe.

bring the tip into very close contact with the sample and keep it there. Constant readout of the NV fluorescence can then be used to map the change in magnetic field.

Figure 1.4 shows an example of such a probe, used by Maletinsky et al [31]. This setup has been shown to be capable of single spin detection and confirms the capability of a similar setup to perform initial research into the feasibility of a hybrid silicon donor spin/NV centre quantum computing architecture.

1.3 DEVELOPING A HYBRID SILICON-SPIN, NV CENTRE ARCHITECTURE

The central inspiration of this work is the paper by O’Gorman et al, mentioned briefly above, on the potential for a hybrid quantum computing architecture based on donor electron spins in silicon as data qubits and using optically addressed qubits as the measurement qubits [15]. Taking NV centres as the optically addressed qubit in this case I now outline the procedure in more detail and highlight the key technical challenges that will provide the framework for the research performed here.

The intuition behind the technique is relatively easily developed. As discussed above, the crucial first step for a surface code architecture is the ability to perform a parity measurement on groups of 4 data qubits with a single measurement qubit. This clearly requires an interaction between data and measurement qubits. In the case of donor spins
in silicon and NV centres, this interaction is the magnetic dipole interaction between the two spins. An NV centre in the presence of a magnetic field will precess about the perpendicular component of that magnetic field. In the proposed architecture, an NV centre is brought very close to an electron spin bound to a donor in silicon. An external magnetic field along the NV centre axis defines the $z$-axis for both qubits. The donor electron spin will produce a small magnetic field along the $z$-axis of the NV centre — causing it to precess about this field when the NV centre qubit is projected into the $x - y$ plane of the Bloch sphere. Ignoring the precession caused by the static field (a typical approach in spin qubits, known as the rotating frame approximation [32]), the NV centre qubit will precess about the Bloch sphere depending on the strength of its interaction with the magnetic field of the donor spin. As the state of the NV centre changes due to the magnetic field, this field can then be measured — a principle that forms the basis of AC magnetic field detection with NV centres [31]. The phase acquired depends not just on the strength of the magnetic field but also its direction: this means that if the spin state of the donor electron is flipped from $|0\rangle \rightarrow |1\rangle$ then the direction of precession will be reversed.

If the NV centre in question could be moved, such that it could interact with 4 different donor spins in turn, this interaction can be used to perform a parity measurement. Imagining that the NV centre is prepared in a $|+\rangle$ state then if the time of interaction at each donor spin is tuned such that the NV centre will acquire a $\pi/2$ phase shift at each site, a parity measurement can be performed. Even parity states of the donor electron spins (e.g. $|0000\rangle$ or $|0011\rangle$) will result in the NV centre finishing its interactions in the $|+\rangle$ state, whilst odd parity (e.g. $|0001\rangle$ or $|0111\rangle$) will leave the NV in a $|−\rangle$ state. The NV centre state can then be measured to determine the outcome of the parity measurement. O’Gorman’s work scales this idea by imagining two layers, one of silicon and one of diamond, each implanted with a grid of donor spins and NV centres respectively. These grids are brought close together and moved relative to one another (several protocols are suggested and their feasibility analysed) to allow simultaneous parity measurements of many data qubits by many measurement qubits.
1.3 Developing a hybrid silicon-spin, NV centre architecture

1.3.1 Experimental Milestones

Whilst the intuition for the technique outlined above is relatively simple, there is no doubt that the technical and scientific challenges introduced by such an architecture are considerable. I now briefly outline milestones required to achieve such an target, before identifying those that this work will seek to explore.

Significant progress must be made with the individual qubit platforms before they can be successfully integrated. Both donor electron spins and NV centres have shown excellent properties individually, with long coherence times relative to gate times in both systems [28, 33, 34, 35]. In almost all cases, however, these exceptional coherence times are achieved in the bulk, whereas the protocol outlined above requires near-surface (<10 nm) defects to facilitate fast qubit interaction times. Surface states typically have significant effects on qubit coherence time and thus a good deal of study needs to be undertaken to understand how to mitigate these effects. This can be approached from several angles, including studying surface treatments to minimise coherence reduction [36, 37], or by exploring dynamical decoupling techniques to extend coherence in the presence of such effects [38]. In reality, a combination of both will likely be required to successfully mitigate surface effects.

In addition to mitigating surface effects, significant progress will be required in the deterministic implantation of defects in silicon and diamond. Defects must be implanted in a grid with sufficient precision to enable to protocols performed here, and this must be done with a minimum of ‘dead pixels’: locations where either no defects are present or multiple defects are [39, 40].

Selective control of both defect species is a key requirement - both laser and microwave control are inherently global, and will naturally effect large regions of a sample, whereas the requirement here is to address single defects in turn. The most promising approach for both species is to use strain or electrical based shifts in their energy levels to allow individual control despite global fields [41, 42].

A further milestone will be identifying the impact of laser illumination on donor spins in silicon, which is known to significantly reduce qubit relaxation times [43, 44]. NV centres are measured with laser light at approximately 520 nm – 640 nm, meaning that photon energies are significantly above the silicon band gap. This is anticipated to cause
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significantly greater effects than below band gap energies [44]. If this problem proves to
be insurmountable then alternative optical defects may need to be developed, such as the
di-vacancy centre in silicon carbide [45].

This is a short summary of the scientific roadmap for this potential architecture and
is necessarily not an exhaustive recipe but provides context for the work undertaken in
this thesis. I will now discuss in detail the research documented by this thesis, which in
most cases relates directly to the milestones outlined above.

1.4 Research goals

The central goal of this work is assessing the potential for a hybrid architecture involving
electron spins bound to donors in silicon, and the NV centre in diamond. This is mainly
in the form of working towards the detection of a single donor spin using a scanning NV
magnetometer. The research presented here falls into three main parts:

1. An initial investigation into the effect of near band-gap laser illumination on co-
herence times of electron spins bound to phosphorus donors in silicon, found in
chapter 4.

2. Research determining the behaviour of single near-surface NV centres in diamond
nano-pillars at low temperatures. First this was undertaken on a sample with many
nanopillars, each of which was implanted with a small number of NV centres (ide-
ally one). Secondly experiments were carried out on single NV centres in scanning
probes, including magnetometry of some test samples but with the unforeseen ob-
ervation of a significant lack of NV robustness at cryogenic temperatures. This
research forms chapters 5 and 6.

3. An investigation into using machine learning to extract the spectrum of noise ex-
perience by a qubit using minimal experimental resources, with the view to in-
creasing the efficiency of quantum sensing of magnetic fields and yielding poten-
tially longer qubit coherence via optimised dynamical decoupling. This research
is found in chapter 7.
1.4 Research goals

Due to the typical optical control wavelengths of NV centres being at wavelengths of approximately 520 nm, this light is expected to have significant impact on the behaviour of donor electron spins in silicon. Proposals to avoid this in a similar scheme have usually centred around use of a different species of optically addressable qubit that can be readout at longer wavelengths — crucially at photon energies below the silicon band gap of 1058 nm. The defect in mind during these investigations was the divacancy in silicon carbide, which whilst not as well developed as the NV centre exhibits many attractive quantum properties, including excellent coherence times, good ODMR contrast, and high initialisation and readout fidelities \cite{46, 47}. Crucially, they can be addressed at above 1100 nm. Initially, the goal was to replicate the scanning magnetometre setup previously described with NV centres with the divacancy in silicon carbide and that goal formed the context for these initial investigations. As the work progressed, it became clear that whilst the divacancy made sense in the long term, in order to make some research contributions in the medium term the NV centre was a more appropriate initial defect to work with. This study focusses on the impacts of wavelengths close to the silicon bandgap on the relaxation and coherence times of the electron spin bound to phosphorus donors in silicon, the potential mechanisms that cause the observed effects, and whether they can be mitigated.

To study the behaviour of near-surface NV centres in diamond at low temperatures (and to validate the capabilities of a newly constructed confocal microscope) we carry out a low temperature study, from 100 K to 15 K, of the key characteristics of the NV centre and how they vary. This study was performed on a diamond sample implanted with near-surface NV centres and then patterned into pillars. These NV centres are thus in a similar environment to those in a scanning probe, and we hope that these studies will be representative of the behaviour of these probes. The key characteristics monitored are those important for the magnetic field sensitivity of the NV centre: its overall fluorescence, its fluorescence contrast, its coherence time, and its charge state. We identify a group of NV centres and monitor all these characteristics for each of them as they are cooled.

With the work on the diamond pillar sample complete, we move on to work with commercially produced scanning diamond tips implanted with near-surface single NV cen-
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tres. These tips are cooled with the intention of first performing verification experiments on a simple sample fabricated with DC wiring, with the intention of performing magnetic field maps of that sample. Results were hampered however by the short lifetime of these NV centres once cooled to low temperatures, with the key NV characteristic of fluorescence contrast absent after no more than two weeks. Whilst we managed some initial verification of these probes, no single spin sensing was achieved.

The final research presented here is a computational study into the use of machine learning techniques to extract the qubit noise spectrum efficiently. As was mentioned above, the noise spectrum experienced by a qubit is one of the key determiners of its coherence time and accurate knowledge of the noise spectrum can be used to extend coherence. In the context of data qubits in a quantum computer, such as donor spins in silicon, this potentially adds to the time in which coherent quantum operations can be applied to them. For an NV centre used as a magnetic field sensor, extension of coherence can lead directly to greater magnetic field sensitivity. Current approaches to noise spectrum extraction are either inaccurate or experimentally taxing. We develop a neural network-based approach to the problem, aiming to provide highly accurate noise spectrum inference whilst adding minimal experimental complexity. We compare this approach with a simple but inaccurate mathematical approximation and also an accurate but demanding state of the art technique. In addition, we examine how to best process noisy experimental data for such a task and attempt to highlight how the nascent techniques shown could be improved in the future.

Having now introduced the context of the research presented in this work, I now move on to the theoretical and experimental underpinnings of spin defects and how they are used for quantum information processing and quantum sensing.
2 Spin Defects

When you come to a fork in the road, take it.
— Yogi Berra

2.1 Electron Spin Resonance

2.1.1 Spin States

Paramagnetic defects in crystals are one of the major experimental areas under investigation as potential qubit platforms. This thesis focuses on the paramagnetic defects found in two semiconductor crystals: silicon and diamond. In silicon, neutrally charged group V donors offer a system analogous to a Hydrogen atom: a single unpaired electron bound to a nucleus with a net positive charge. Both electron and nucleus in this system have the property of intrinsic angular momentum or spin, $S$, a vector property of the system with components $S_x, S_y, S_z$. The projection of the particle's spin along any given axis is one of a series of discrete values dependent on the total spin of the system and spaced by integer values of $\hbar$. Typically and from here $\hbar$ is treated as being equal to $1$ for ease of calculations. The electron is a spin-$\frac{1}{2}$ particle and can take only the values (or eigenstates) $-\frac{1}{2}, \frac{1}{2}$. A nucleus, however, may have a variety of different spin values. Phosphorus donors in silicon have a spin-$\frac{1}{2}$ nucleus whilst Bismuth donors have a spin-$\frac{9}{2}$ nucleus. As the $S_{x,y,z}$ operators are non-commuting, the spin can have a defined value in only one cartesian dimension, usually defined as $S_z$. For a free electron, not in the presence of a magnetic field, space is isotropic, meaning any axis can be specified as $S_z$ and the two eigenstates $\pm \frac{1}{2}$ are degenerate in energy.
2 Spin Defects

Associated with the spin of a particle is a magnetic dipole moment, \( \mu \), that determines the degree of interaction between the particle and a magnetic field, known as the Zeeman interaction \([48]\). For an electron, this moment, \( \mu_e \), is equal to \(-g \mu_b S\) where \( \mu_b = \frac{e\hbar}{2m_e} \). The energy of this dipole interacting with a magnetic field, \( B \), is then equal to \(-g \mu_b S \cdot B\). In practice the \( S_z \)-axis of the spin is defined as being aligned with the magnetic field giving two spin eigenstates. The Hamiltonian governing the electron spin can then be written:

\[
H = -g \mu_b B_0 S_z
\]  

(2.1)

Where \( B_0 \) is the magnitude of the magnetic field |\( B \)|. This Hamiltonian then gives two spin eigenstates, designated as \(|0\rangle\) and \(|1\rangle\) or \(|\uparrow\rangle\) and \(|\downarrow\rangle\), corresponding to the spin being aligned and anti-aligned with the magnetic field. The energy difference between these states is:

\[
\Delta E = g_e \mu_b B,
\]  

(2.2)

This results in an energy splitting as seen in figure 2.1 a. Typically, the energy level splittings are referred to by their frequency, according to the equation \( E = h\nu \), as this gives the frequency of a microwave pulse resonant with the transition.

In practice, electrons bound to defects in semiconductors are not free, and cannot be described fully by the simple Hamiltonian shown in 2.1. The chief reason for this is that the electron is bound to a nucleus with its own spin state, \( I \). To account for the nucleus, the Hamiltonian requires the addition of two further terms: one to account for the hyperfine interaction and one to account for the nuclear spin's interaction with the magnetic field. The hyperfine interaction refers to the effect of the magnetic fields from electron and nucleus interacting with each other. This interaction leads to two possible energy states, where electron and nuclear spin are aligned (higher energy) and where they are anti-aligned (lower energy). Due to the small nuclear magneton, \( \mu_N \) of the nucleus, the hyperfine interaction is typically a significantly greater energy effect than that of the nuclear Zeeman term, except at very high magnetic fields (>1 T). The full Hamiltonian of the electron-nuclear spin system can be written as follows \([49]\):

---

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2.1 Electron Spin Resonance

![Graph showing energy level splitting](image)

Figure 2.1: (a) The energy level splitting of a free electron in a magnetic field, showing how separation in energy increases with magnetic field. (b) the energy level splitting of the spin states of a phosphorus spin system in a magnetic field. $|\uparrow\rangle$ refers to the electron spin state and $|\uparrow\uparrow\rangle$ to the nuclear spin state. Note the lower energy state of the anti-aligned nuclear spin state for a given electron spin state, due to the dominance of the hyperfine coupling term over the nuclear Zeeman term in equation 2.3.

\[
\hat{H} = -g_\mu_B \mathbf{B} \cdot \mathbf{S} + g_\mu_N \mathbf{B} \cdot \mathbf{I} + \hat{A} \mathbf{S} \cdot \mathbf{I}
\]  

(2.3)

The energy level structure of a phosphorus donor in silicon is described by this Hamiltonian. The phosphorus nucleus, like the electron, is a spin-$\frac{1}{2}$ system ($I = 1/2$), meaning that the joint system has a four level structure shown in figure 2.1b. At low magnetic fields, this has a singlet ($m_s = 0$) — triplet ($m_s = 1$) structure, due to the dominance of the hyperfine splitting term over the Zeeman terms. At these low fields the spin projection in the $B_0$ direction ($S_z$) of the electron and nucleus does not represent a good quantum number — meaning that the projection does not remain constant under time evolution, instead it is their total spin that best represents the system state. At high magnetic fields, where the Zeeman term dominates, the degeneracy of the triplet state is lifted and four well defined energy levels emerge. At these high fields the spin states of electron and nucleus are isolated, meaning their $z$-projection is a good quantum number. Most experiments with phosphorus donors in silicon are performed at these high fields.
2 Spin Defects

In addition to causing this level splitting, the magnetic field causes the electron spin to precess about the magnetic field at the Larmor frequency, given by:

$$\omega_0 = \frac{g\mu_B}{\hbar} B_0$$  \hspace{1cm} (2.4)

2.1.2 The Bloch Sphere

The eigenstates of the electron spin in a magnetic field allow the spin to be described as a two level system and represented on the Bloch Sphere [50, 51]. The Bloch sphere provides a convenient method for representing and visualising quantum states. The two spin states form a basis and are represented by the kets $|0\rangle$ and $|1\rangle$ corresponding to up and down spin or low and high energy levels. These form the North and South poles of the Bloch sphere respectively. As well as these two spin eigenstates, any linear superposition of them is also a valid state of the system [2]:

$$|\psi\rangle = \alpha |0\rangle + \beta |1\rangle$$  \hspace{1cm} (2.5)

If the condition that $\sqrt{\alpha^2 + \beta^2}$ is met than this state is said to be ‘pure’. All of these pure states of the system are represented by points on the surface of the Bloch sphere. Mixed states, where some classical uncertainty is taken into account in the state’s representation, fall inside the sphere.

2.1.3 Driving Spin Transitions

A sufficiently strong static magnetic field, $B_0$, splits the electron energy states and gives the spin eigenstates $|0\rangle$ and $|1\rangle$ but gives no way of driving transitions to other states on the Bloch sphere. To achieve this, a second magnetic field, $B_1$, is typically applied perpendicular to the static field. The spin precesses around this second magnetic field at the Larmor frequency determined by its field strength [51]. A static $B_1$ field can be used as long as the Larmor frequency of this field is significantly faster than that of the $B_0$ field, meaning that precession around $B_0$ can be disregarded whilst the $B_1$ field is applied. In reality, it is not practical to apply such a strong field, so instead a field is applied via an
oscillating magnetic field. This means that the $B_1$ field rotates in the $x - y$ plane of the Bloch sphere at $\omega$, the Hamiltonian of this process can then be written:

$$H = g\mu_B B_0 S_z + g\mu_B B_1 \cos(\omega t) S_x$$  \hspace{1cm} (2.6)

For convenience of calculation and understanding, it is typical to perform a transformation on this Hamiltonian into the rotating frame by applying the following transformation:

$$U = \begin{pmatrix} e^{i\omega t} & 0 \\ 0 & e^{-i\omega t} \end{pmatrix}$$  \hspace{1cm} (2.7)

This results in the Hamiltonian in the rotating frame being:

$$\tilde{H} = \begin{pmatrix} \frac{1}{2}(\omega - \omega_0) & \omega_1 \cos(\omega t)e^{-i\omega t} \\ \omega_1 \cos(\omega t)e^{i\omega t} & \frac{1}{2}(\omega - \omega_0) \end{pmatrix}$$  \hspace{1cm} (2.8)

Where $\omega_0$ is the Larmor precession frequency of the $B_0$ field, $\omega_1$ is the precession frequency of the $B_1$ field and $\omega$ is the frequency of oscillation of the $B_1$ field. The counter-rotating terms in the off-diagonal elements of the Hamiltonian can be ignored, as they
2 Spin Defects

oscillate quickly relative to the spin (effectively, far off resonance) and so provide only a minor perturbation to its evolution. As such, the final Hamiltonian in the rotating frame can be written:

$$\hat{H} = \begin{pmatrix} \frac{1}{2}(\omega - \omega_0) & \frac{\omega}{2} \\ \frac{\omega}{2} & \frac{1}{2}(\omega - \omega_0) \end{pmatrix}$$

(2.9)

The diagonal elements of this Hamiltonian depend on the detuning between the Larmor precession frequency of the applied $B_0$ field and the frequency of the $B_1$ field and go to 0 when these are on resonance. So the Hamiltonian at resonance is effectively:

$$\hat{H} = \frac{\omega_1}{2} \sigma_x$$

(2.10)

This allows the precession of the qubit in the static magnetic field to be disregarded, along with the precession of the oscillating $B_1$ field. The application of an on-resonance $B_1$ field causes a $|0\rangle$ state to precess about the $x$-axis at the Larmor frequency of that field. Off-resonance dynamics are more complex, causing precession about an axis in the Bloch sphere determined by the detuning of the $B_1$ field. As detuning increases, the angle of rotation varies quickly relative to the spin vector, meaning that at large detunings the rotational effect averages out and can be ignored — except in cases where the $B_1$ field is comparable to $B_0$ in magnitude. In most experiments the $|B_1| \ll |B_0|$ requirement holds and the effect of a strongly detuned $B_1$ field can be disregarded. Figure 2.3 shows the behaviour of the spin state on the Bloch sphere in the case of both on and off-resonance excitation. The frequency at which the spin rotates in the $B_1$ field when on-resonance is usually termed the rabi-frequency and is often designated by $\Omega$. By varying the time the $B_1$ field is applied for, the spin can be rotated to any point on the $z - y$ plane of the Bloch sphere. To perform arbitrary rotations on the Bloch sphere, the phase of the applied $B_1$ field can be varied. This causes the spin to precess about an axis in the $x - y$ plane, whose angle from the $x$-axis is determined by the phase of the $B_1$ field. By varying this phase and the time the field is applied for it can be used to rotate the qubit to any point on the Bloch sphere.
2.1 Electron Spin Resonance

Figure 2.3: Qubit evolution under application of an oscillating magnetic field $B_1$, transformed into the rotating frame. In the on resonance case, where the frequency of the $B_1$ field is equal to the Larmor precession frequency of the $B_0$ field, (a) and (b) show the evolution of the expectation values of the Pauli matrices ($\sigma_x$, $\sigma_y$ and $\sigma_z$) and the state dynamics on the Bloch sphere respectively. (c) and (d) show the same figures for the case of off-resonance excitation, where the $B_1$ frequency is 0.5% lower than the Larmor precession frequency.
2 Spin Defects

2.1.4 Pulsed Electron Spin Resonance

The processes described above show how a spin can be controlled via the application of magnetic fields, one, $B_0$, splits the electron spin states in energy whilst a second $B_1$ can be used to control the electron spin state. In practice, the process of controlling and measuring the spin states of electron is known as Electron Spin Resonance (ESR) or equivalently Electron Paramagnetic Resonance (EPR). There are two broad categories of ESR, continuous wave ESR (CW-ESR) and pulsed ESR. Typically, ESR is performed on large ensembles of electron spins, meaning that the behaviour of these spins is somewhat classical in nature as their individual magnetic moments $\mu$ sum to produce an overall magnetic field vector $\bf{M}$.

CW-ESR refers to the process of detecting spin-transitions through the application of a constant oscillating magnetic field to a sample of interest. This field is applied via a resonator and the reflection of this field from the resonator is measured. An external magnetic field is varied and the reflection is monitored. Whilst holding the static $B_0$ field constant and varying the $B_1$ field frequency is equivalent in theory, the resonators used for the oscillating fields have narrow ranges of operation meaning that varying the $B_0$ field is much more practical. As the static magnetic field is varied, electron spin transitions may come on resonance with the applied oscillating field, causing less of it to be reflected. This can be detected and the spin transition characterised by its g-factor [44, 52]. This form of ESR is not used extensively in this work.

Pulsed ESR does not apply constant $B_1$ fields but instead uses pulses to control spin orientation. As described above, pulse duration (or power) and phase can be varied to rotate the spin vector $\bf{M}$ to any point on the Bloch sphere. These pulses are usually referred to by their phase the angle of rotation they produce in the spin. So a pulse of duration $\Omega t = \pi$ is termed a $\pi$-pulse and serves to rotate a $|0\rangle$ state to a $ket1$ state. A $\frac{\pi}{2}$-pulse would rotate a $|0\rangle$ state to a point on the $x-y$ plane of the Bloch sphere.

These pulses provide a means to control the spin states but to be useful for experiments the spin state must be detectable as well. This is done by making use of the precession of the spins in the static magnetic field $B_0$. As these spins precess in the magnetic field they produce a small amount of electromagnetic radiation, with an oscillation frequency equal
to their Larmor precession frequency. This radiation can be detected via the resonator that applies the pulses. The amplitude of this radiation is determined by the projection of the precessing spin vector in the $x - y$ plane, so a $|0\rangle$ or $|1\rangle$ produces no signal, whilst a state on the edge of the Bloch sphere in the $x - y$ plane produces a maximum signal.

In a perfect system, all spins measured in this manner would precess at the same rate and produce a constant signal based on their projection in the $x - y$ plane. However, due to sample imperfections and spacial inhomogeneity in the applied $B_0$ field, each measured spin precesses at slightly different rates. The upshot of this is that the spin signal, made up of multiple signals from many spins, will rapidly lose phase-coherence and the overall signal will go to 0 due to destructive interference between spins rotating with different relative phases. This process is aptly named dephasing.

To counteract this, it is possible to use a sequence of pulses to reverse this loss of phase coherence. Whilst many pulse sequences exist the simplest is the spin-echo or Hahn-echo sequence [51, 53]. This pulse sequence starts with the spin state at $|0\rangle$, where no dephasing occurs, a $\frac{\pi}{2}$ pulse is used to rotate the spin vector to the $x - y$ plane, at which point dephasing begins immediately causing the spin signal to decay. This decaying spin signal is known as Free Induction Decay and can be measured to determine the spin state. It is typically not as the sensitive detection equipment used to measure the low-power spin signal can be damaged by high power control pulses, which can remain in the resonator for a short time after the pulse application. Instead the spin ensemble is allowed to dephase in the $x - y$ plane for an amount of time $\tau$ after which a $\pi$ pulse is applied, causing the spin ensemble to invert. The spins now experience the $B_0$ field in reverse and the dephasing they experienced is also reversed. Provided the inhomogeneities that cause the dephasing are constant in time, the spins will rephase after an additional time $\tau$ has elapsed, causing a brief spike in their signal known as a spin echo. A schematic of this is shown in figure 2.4. A Hahn echo sequence represents the simplest of a broader class of pulse sequences known as Dynamical Decoupling or DD sequences, which can be used to protect a spin ensemble or qubit against a variety of different sources of noise.
2 Spin Defects

Figure 2.4: The Hahn Echo sequence and its impact on an ensemble of spins on the Bloch sphere. The pulse sequence is shown above, starting with a $\frac{\pi}{2}$ pulse to take the $|0\rangle$ state into the $x - y$ plane. This then begins to dephase resulting in the rapid loss of signal — observed as the Free Induction Decay or FID. Next a $\pi$ pulse inverts the dephased spins after time $\tau$, causing them to experience a reversed magnetic field and to begin to rephase. After they rephase for another period of $\tau$ their signals interfere constructively once more and the characteristic echo is observed in the signal.
2.1.5 Relaxation and Decoherence

The process of dephasing, described above, introduces the concept of spin ensembles and their loss of phase coherence. This process of dephasing is part of a set of processes by which the ESR signal of an ensemble of spins might be lost or changed over time without control input. Broadly, these processes fall into the categories of relaxation or decoherence [51]. Relaxation refers to the processes by which an ensemble of spins disturbed from thermal equilibrium returns to that equilibrium, its timescale is usually referred to as $T_1$. Decoherence refers to the irreversible loss of phase coherence and its timescale is referred to as $T_2$. Dephasing, the reversible loss of phase coherence is characterised by $T_2^*$. Although these processes are understood typically from the point of view of spin ensembles, they have analogous processes when single spins are addressed as well. Relaxation is the process of a qubit returning to its ground state after a certain amount of time. Decoherence is the process of a qubit losing internal phase coherence: the rate at which a superposition state decays into a maximally mixed state with no quantum nature [2].

Spin Lattice Relaxation

The spin relaxation process is most easily understood as the phenomenon that a spin prepared in some state on the Bloch sphere will eventually ‘relax’ back to the $|0\rangle$ ground state. Spin lattice relaxation is the dominant relaxation process for electron spins in silicon and is caused by the absorption or emission of phonons from the spin into the silicon lattice. From a more intuitive perspective, vibrations in the lattice cause fluctuating magnetic fields that mediate the energy transfer between the spins and the lattice.

As a phonon-mediated process, the dominant determiner of the spin lattice relaxation rate is the temperature of the lattice. There are three main spin-lattice interactions that can cause spin relaxation: direct, Raman and Orbach [51, 54, 55].

The direct spin lattice relaxation process is simply the case where the spin absorbs a phonon with frequency equal to the energy of the spin transition. The efficiency of this process is dependent on the phonon and vibrational mode density at the spin transition frequency and temperature, so scales with both. The exact dependence is material specific but at the high magnetic field limit can be approximated by:
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\[
T_1 \propto B_0^{-4} T^{-1}
\]  

(2.11)

The direct process is not typically the dominant relaxation process for spins in solids at typical temperatures (>4 K) as maximum phonon density is typically at significantly higher frequencies than the spin transition frequencies. This means that less efficient processes dominates as more phonons are available to mediate the transition.

The first of these is the two-phonon Raman process, whereby the spin first interacts with a phonon of significantly greater energy, \( \omega_p \), than the spin transition frequency \( \omega_0 \). This excites the spin to a virtual excited energy state, before the spin decays back to its ground state by emitting a phonon of energy \( \omega_p + \omega_0 \). The virtual nature of the energy level allows all phonon energies to mediate this process. The dependence is:

\[
T_1 \propto T^{-9}
\]  

(2.12)

This process is dominant for donors in silicon between 4 K and 10 K.

The final significant process for donor relaxation is the Orbach two-phonon process. This is similar to the Raman process but involves the spin being excited to a real energy level rather than a virtual one by a resonant phonon. This process is dependent on the available excited states for the spin, which is donor dependent, and has an exponential dependence:

\[
T_1 \propto e^{-\Delta E/k_BT}
\]  

(2.13)

This Orbach process is dominant in silicon donors at temperatures > 10 K. A schematic showing the three spin lattice relaxation processes is shown in figure 2.5.

The measurement of the relaxation time of a qubit is typically performed via an inversion recovery experiment. This involves the use of a \( \pi \)-pulse followed by a Hahn echo sequence. This produces an inverted spin echo, by increasing the time between the initial \( \pi \) pulse and the Hahn echo sequence, the spin is allowed to partially relax before being projected into the \( x - y \) plane. As this time is increased the echo amplitude is measured, once the time is significantly greater than the \( T_1 \) time of the spin, the spin fully relaxes before the Hahn echo sequence giving a fully positive echo once again. By fitting an ex-
Figure 2.5: Simple schematic of the three spin-lattice relaxation processes: direct, Raman and Orbach. The direct process is dominant below 4 K and involves resonant absorption or emission of a single phonon, the Raman process dominates between 4 K and 10 K and involves non-resonant excitation by a phonon to a virtual energy level before emission of a phonon during relaxation from that energy level. Finally the Orbach process is a resonant two-phonon process requiring excitation to a real energy level before relaxation via phonon emission.
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ponential to the measured echo amplitude vs pulse spacing the $T_1$ time can be extracted as the time constant of the exponential echo recovery.

2.1.6 Decoherence

Decoherence as a process is conceptually similar to dephasing, with it constituting the loss of phase coherence in a spin ensemble such that this phase coherence cannot be regained by spin inversion as in a Hahn echo sequence. The process in a single spin or qubit is less intuitive but results in the decay of a qubit placed in superposition to a mixed state. The coherence time of a spin ensemble or qubit ($T_2$) is ultimately limited by its relaxation time $T_1$, but in the vast majority of qubit platforms $T_2$ is further limited by other environmental factors. Understanding and mitigating coherence remains one of the most significant challenges for the development of quantum technologies. In the case of spin ensembles and spin qubits, decoherence is most significantly contributed to by magnetic field noise \[25, 56\]. Magnetic fields that change over time alter the relative phase of spins in a way that is not reversible, although more complex dynamical decoupling sequences can be employed to mitigate loss of coherence to a significantly greater degree than is possible with a Hahn echo \[57, 58, 59, 60\]. Here, I detail the primary categories of decoherence for spins in solids.

Spectral Diffusion

Spectral diffusion is the decoherence process caused by spins of a separate species to the spin of interest. It is primarily a result of spins that are not addressed as part of the control pulses acting on the target spin. These unaddressed spins can be of the same species, remaining unaddressed due to the distribution of transition frequencies being greater than the bandwidth of the control pulses used. Alternatively these can be completely different species of spins that have a different g-factor. These unaddressed spins can undergo a flip-flop interaction, whereby two spins of opposite spin state can exchange their spin state via a $S_xS_x + S_yS_y$ interaction. If these spins are of the same species then this interaction results in a minimal overall energy change, however the resulting change in the
local magnetic environment can cause irreversible phase acquisition by the target spins, resulting in a loss of overall phase coherence [61].

In natural silicon, spectral diffusion is the dominant decoherence process once temperature is low enough that \( T_1 \) is no longer limiting. This is due to the natural abundance of the \(^{29}\text{Si} \) nucleus, which has spin-\( \frac{1}{2} \). This typically limits the coherence of \( T_2 \) measured via Hahn echo pulse sequences to 100-300 \( \mu \)s [56].

### Instantaneous Diffusion

Instantaneous diffusion is a decoherence process caused by interaction between subsets of addressed spins, rather than unaddressed spins affecting the central spins as in the case of spectral diffusion. It is primarily caused by the magnetic dipole-dipole coupling between the spins. Depending on the distribution of spins in a sample, there is an inhomogeneous broadening of their transition frequencies as different spin experience different coupling strengths. As all addressed spins are inverted during a standard \( \pi \)-pulse, there is no refocusing of this effect as a \( S_z S_z \) coupling will become a \((-S_z)(-S_z) = S_z S_z \). As it is caused by the dipolar coupling between addressed spins, it is strongly dependent on the spin concentration in the sample of interest, with \( T_2^{\text{ID}} \) scaling as:

\[
\frac{1}{T_2^{\text{ID}}} = C(2\pi\gamma_e)^2 \frac{\pi}{9\sqrt{3}}\mu_0 \hbar
\]

(2.14)

Here \( C \) is the spin concentration and \( \gamma_e = g\mu_b \). As spin density is reduced this coherence increases, giving coherence times in excess of 10 ms in purified silicon [19, 62].

As a fundamentally ensemble based effect, instantaneous diffusion should be significantly reduced or absent for isolated qubits. This has been measured in ensemble samples by adjusting pulse lengths so that rotation angles are significantly less than \( \pi \). This has the effect of probing fewer spins, reducing signal and also the impact of instantaneous diffusion [19, 62]. This allowed the extension of \( T_2 \) beyond 1 s and extraction of three further decoherence mechanisms, present once instantaneous diffusion is no longer dominant.

The first of these is Indirect \( T_1 \), this mechanism is observed to limit qubit coherence in the intermediate temperature regime, where \( T_1 > T_2 \) but some reduction in \( T_2 \) is observed beyond the low temperature limit. This is caused by the coupling between neigh-
bouring spins and the central addressed spins. The increased relaxation rate of neighbouring spins can cause a fluctuating magnetic field environment for the central spin via the $S_zS_z$ coupling, resulting in a reduced $T_2$. The decoherence rate as a function of this process can be described by a stretched exponential of the form $\exp\left(-\left(\frac{2\pi}{\sqrt{T_1}}\right)^2\right)$ [19].

The second is the indirect flip-flop mechanism — this is discussed above in the spectral diffusion section, where unaddressed spins of the same species as the addressed spin exchange state and impact the addressed spin via the $S_zS_z$ coupling.

The third is the direct flip-flop mechanism — in this case rather than disruption to the magnetic field environment via flip-flops of unaddressed spins, the central spin itself undergoes a flip-flop interaction with an unaddressed spin. This process limits coherence but is notably similar to relaxation as its mechanism is a spin flip, rather than a shift in the spin frequency due to its local magnetic field.

2.1.7 Dynamical Decoupling, Coherence and Noise Spectra

With the mechanisms of decoherence now presented, I move on to a short discussion of how coherence can be best preserved. The Hahn echo sequence is the simplest method to preserve qubit coherence, but is only effective at reversing dephasing, the result of static magnetic field inhomogeneities. As the magnetic field inhomogeneities that limit coherence are time dependent, an alternative approach is required to mitigate them. Dynamical decoupling sequences do this at a simple level by adding more $\pi$ pulses to the spin refocussing sequence. The result is that the precession direction of the spin or spins is reversed multiple times before the system is measured. This means that for a given time between state initialisation and measurement, the cumulative effect of changing fields can be reduced. This can be easily understood from figure 2.6, which shows how two different pulse sequences, a Hahn echo and 4-pulse sequence, change the amount of phase that is acquired before echo readout.

The simplest type of dynamical decoupling sequence is the Carr-Purcell-Meiboom-Gibbs (CPMG) sequence, which uses a sequence of equally spaced $\pi$-pulses. The first of these occurs at time $\frac{T}{2}$ after the initial $\pi$ pulse, with subsequent $\pi$-pulses occurring at time $+\tau$ after that. After the final $\pi$ pulse, an echo forms after $\frac{T}{2}$. Typically, $T_2$ increases as a function of number of pulses according to $N^k$, where $N$ is the number of pulses and
2.1 Electron Spin Resonance

Figure 2.6: Schematic showing the effect of dynamical decoupling on phase acquisition for a changing magnetic field. Shown are a simple Hahn echo sequence and a 4 \( \pi \)-pulse CPMG sequence, with different dephasing directions marked by + and − both on the magnetic field graph and the sequence schematics. In the Hahn echo case, the extra cumulative dephasing effect is clear, as the average magnetic field experienced during the + dephasing is 0.25 mT, whilst it is 0.75 mT in the − case. The CPMG sequence [59, 60] mitigates this effect by reversing the dephasing direction more frequently, reducing the difference in acquired phase over time between the + and − directions.

\( k \) depends on bath dynamics but is always less than 1. As number of pulses increases, the impact of potential pulse errors becomes more significant, yielding diminished signal strength. To counteract this, it is possible to use a modification of the standard CPMG sequence, the XY sequence. This sequence is based on identical principles, using equally spaced \( \pi \)-pulses, but alternates the phase of each pulse by \( \pi/2 \). This means that if the first \( \pi \) pulse is a rotation about the \( x \)-axis, the second is about the \( y \)-axis. This has the effect of making the sequence insensitive to pulse errors, to first order.

Figure 2.6 shows a very simple time varying magnetic field, but in all physical cases the magnetic noise experienced by a spin is complex. The most common way to represent this noise is in terms of its power spectral density, \( S(\omega) \). This shows the amplitude of the magnetic field noise and how it varies with frequency. A pulse sequence can be viewed as interacting with this noise spectrum via the filter function of that sequence \( F(\omega, t) \). This filter function determines the amount exposure of the spin to magnetic field noise at a given frequency. The filter function, \( F(\omega, t) \) is dependent on the pulse sequence used and can be calculated from the pulse duration \( \tau_\pi \) and the pulse timings \( t_k \) by using the following equation:
Figure 2.7: The filter function for two different CPMG sequences, one 4-pulse and the other 8, but with the same $\tau$ value ($\pi$-pulse spacing) of 2 $\mu$s. Of note is the dominant feature that occurs at $\frac{\pi}{\tau\omega}$, with higher frequency harmonics also clear.
2.1 Electron Spin Resonance

\[ F(\omega, t) = \left| 1 + (-1)^{n+1}e^{i\omega n\tau} + 2 \sum_{k=0}^{n} (-1)^{k} e^{i\omega t_k} \cos \left( \frac{\omega T_\pi}{2} \right) \right|^2 \]  \hspace{1cm} (2.15)

where \( n \) is the total number of \( \pi \) pulses and \( k \) indexes the pulses for summation. Two example filter functions are shown in figure 2.7, of note is the presence of a dominant peak, centred at the frequency \( \frac{\pi}{\tau} \), which shows the frequency that the spin or qubit is most sensitive to for this sequence. This dominant frequency is dependent on the pulse spacing in the sequence and not its overall length. Also clear in the figure are the higher frequency harmonics at lower magnitudes for both cases. As pulse number increases, the peaks in the filter function become increasingly narrow, exposing the qubit to a narrow range of noise. As well as increasing coherence, this also has the effect that the spin is more sensitive to any noise sources with localised frequencies such as different spin species precessing in the magnetic field. This effect can be used to increase the sensitivity of a spin being used as a quantum sensor [63].

The relationship between the coherence value of the qubit, the noise spectrum it experiences, and the filter function of the pulse sequence used to control it can be described by the following equation [64, 65]:

\[ \chi(t) = -\ln C(t) = \int_0^\infty \frac{d\omega}{2\pi} S(\omega) \frac{F(\omega t)}{\omega^2} \]  \hspace{1cm} (2.16)

Here, \( \chi(t) \) is known as the decoherence functional and \( C(t) \) is the value of coherence as a function of evolution time. These two equations can be used in combination to derive a spin’s coherence decay with respect to time, providing that the noise spectrum \( S(\omega) \) can be regarded as stationary, Gaussian and as coupling only along the spin’s \( z \)-axis. Typically, the noise spectrum that affects a spin or qubit is not known a priori, so equation 2.16 is of most interest for deriving the underlying noise spectrum from a known pulse sequence filter function and a measured coherence decay. This noise spectrum may be of interest for several reasons, either so that pulse sequences can be designed to best decouple the qubit from its environment [66, 67] or to reveal information about that environment in the quantum sensing context [68]. The equation (an instance of the group of integral equations known as Fredholm equations [69]), however, is not generally solvable for \( S(\omega) \) when the qubit coherence decay \( C(t) \), and filter function are known. As a result a simple
2 Spin Defects

![Graphs showing coherence decay curves and noise spectrum.](image)

Figure 2.8: (a) the coherence decay curves, $C(t)$, for a simulated noise spectrum, calculated using equation 2.16 from a single pulse Hahn echo sequence and a 4 pulse CPMG sequence. In addition in (b) the actual noise spectrum is shown, along with the inferred noise spectra from each coherence decay curve, calculated using equation 2.17. Of significance is the relative inaccuracy with which the approximation is able to infer the noise spectrum, as in unsurprising when comparing the filter functions shown in figure 2.7 with a $\delta$-function.

The approximation is often used to extract a noise spectrum $S(\omega)$ from a measured coherence decay, which requires the treating of the filter function as a delta function centred at the frequency $\frac{\pi}{\tau}$. With this approximation, a simple relationship between coherence decay and noise spectrum can be derived [30]:

$$S(\omega_0) = -\frac{\pi}{t} \ln C(t)$$  \hspace{1cm} (2.17)

Figure 2.8(a) shows the coherence decay curves, $C(t)$, calculated from a simulated noise spectrum. The $\delta$-approximation is used to infer the underlying noise spectra which are shown in (b) and contrasted with the actual underlying spectrum. The approximation does relatively poorly at reconstructing this noise spectrum, as is unsurprising when the filter functions shown in figure 2.7 are compared with the equivalent $\delta$-function centred at their main peak. The $\delta$-function quite clearly fails to capture the impact of the peak width as well as the impact of the higher frequency harmonics on the coherence decay.

Alternative approaches to deriving the underlying noise spectrum from a coherence decay measurement aim to increase the accuracy of the inference in one of two main ways: either by using more accurate but more complex mathematical approximations to extract the underlying noise spectra [67] or by using more complex pulse sequences.
when measuring the qubit coherence decay to produce a filter function that is closer in shape to a $\delta$-function \cite{70, 71}. Both these approaches introduce significant extra experimental complexity to the measurement of coherence decay and a significant focus of this work will be the use of machine learning to perform a more accurate extraction of the underlying noise spectrum whilst minimising experimental complexity.

\section*{2.2 Nitrogen Vacancy Centres in Diamond}

\subsection*{2.2.1 Diamond and Nitrogen Vacancy Structure}

The second spin defect that will be studied in this work is the Nitrogen-Vacancy (NV) centre in diamond. This defect has become one of the most studied of all qubit platforms due to its many attractive characteristics. Unlike the electron spins bound to donors in silicon, the NV centre can have coherence ($T_2$) times at room temperature in the millisecond regime. In addition, the possibility for the NV centre spin state to be determined via optical readout means that controlling and measuring these defects as single spins rather than ensembles is relatively straightforward, particularly when compared with the challenges presented by the electron spin in silicon \cite{23, 24}.

Diamond is a crystalline form of Carbon, which in its ground state has six electrons bound to it in a $1s^22s^22p^2$ configuration. When forming diamond under high temperature and pressure, the electrons are in excited states and the carbon orbitals undergo hybridization, maximising the number of potential bonds, whilst minimising the energy of the individual bonds. In diamond, the $s$ and $p$ orbitals mix and form four hybridized $sp^3$ orbitals, arranged tetrahedrally and forming a face-centred-cubic lattice. The outstanding properties of diamond can be attributed in large part to this lattice structure, with the strong covalent bonds between the carbon atoms contributing to its extreme hardness — it is the hardest known bulk material, with Mohs hardness of 10 and also one of the most effective thermal conductors \cite{72}.

The NV centre in diamond is a substitutional point defect in the carbon lattice, arranged along the diamond crystal’s [111] direction, a simple schematic is shown in figure 2.9(b). An NV centre is made up of a carbon atom replaced by a nitrogen atom, with one of the four bonded carbon atoms missing leaving a vacancy in the lattice — this gives
Figure 2.9: (a) the diamond unit cell with only carbon atoms present, the carbon atoms for a tetrahedral structure due to the hybridization of the $s$ and $p$ orbitals. All carbon atoms in this structure with mutual angle of 109.5° are bound equally strongly to one another. The red atoms highlight the tetrahedral arrangement for one central carbon and the four carbon atoms to which it is bound. (b) shows the same unit cell with an NV centre present. In this case one of the carbon atoms is replaced by a nitrogen atom, whilst another is replaced by a vacancy — a gap in the carbon lattice.
2.2 Nitrogen Vacancy Centres in Diamond

the NV centre a $C_{3v}$ triagonal symmetry [73]. The tetrahedral structure of the diamond lattice leads to four possible orientations of the defect: [111], [111], [111], [111]. These correspond to a central Nitrogen, with the vacancy displacing one of the four bonded carbon atoms. The orientations of NV centres found in diamond are roughly evenly distributed between these four possibilities [74], which determine the preferred spin quantisation axis. This is notably unlike the case of electrons bound to donors in silicon, where the spin has no preferred orientation in the high magnetic field limit.

The NV centre has two charge states that it is readily found in: NV$^0$ and NV$^−$ [23, 75]. The neutrally charged NV centre is made up of 5 electrons, from the dangling bonds of the nitrogen and carbon atoms surrounding the vacancy, giving a system with overall electron spin $S = \frac{1}{2}$ [76]. The negatively charged NV centre therefore has six electrons giving an overall spin of $S = 1$. The centre of most interest in almost all quantum technologies research is this negatively charged centre, due mainly to its strong magneto-optical properties. In all cases in this manuscript where an NV centre is referred to generically, the NV$^−$ is implied and where the neutrally charged NV$^0$ is referred to it will be specified.

**The Electronic Structure of the NV Centre**

The exact nature of the electronic structure of the NV centre has been under long investigation, and there are still some uncertainties surrounding it. Nevertheless, its basic form is now well understood and shown in figure 2.10. The ground state of the NV centre is a triplet spin state with $^3A_2$ symmetry, the excited state is a triplet state with $^3E$ symmetry. In addition, there is a pair of meta-stable singlet states with symmetries $^1A_1$ and $^1E$ symmetries [23, 77]. There is a zero-field splitting between the triplet states with $m_s = \pm 1$ and $m_s = 0$ due to spin-spin interactions. This allows for microwave control of the electron spin-state even at zero magnetic field.

The spin states of the NV centre allow for qubit manipulation in the same vein as has been described earlier with electrons bound to donors in silicon, however what differentiates the NV centre and has made it so popular in quantum technologies research is its optical properties. The transition between the ground state and excited state triplet can be initiated by off-resonance illumination by laser light, typically at wavelengths in
2 Spin Defects

Figure 2.10: The electronic structure of the negatively charged nitrogen vacancy (NV) centre. The system is made up of a ground state spin triplet with $^3A_2$ symmetry and an excited state spin triplet with $^3E$ symmetry. The NV centre can be excited to this state via optical illumination, and will fluoresce into its zero-phonon line of 637 nm upon decay to the ground state. As well as the ground and excited triplet states, there is a meta-stable singlet state that offers a potential decay path for the NV centre, via which it decays via radiation in the infrared (1042 nm). The spin $\pm 1$ states of the NV centre couple more strongly to this alternative decay path, which in turn is more likely to decay into the $m_s = 0$ ground state. This allows for optical discrimination between the spin states as well as optical initialisation into the $m_s = 0$ state. There is a zero-field splitting between $m_s = \pm 1$ and $m_s = 0$ states of 2.87 GHz, allowing microwave control of the spin state even in zero magnetic field.
the green part of the visible spectrum and at 520 nm in this work. This transition is spin preserving and can be followed by a similar spin preserving decay from excited to ground state, with the excited state having a lifetime of approximately 10 – 20 ns \([78]\). This transition has a zero-phonon-line (ZPL) of 637 nm, but NV centres will typically only emit about 4\% of their fluorescence at this wavelength, with the rest being emitted into phonon sidebands \([79]\). A second possible decay path is via the meta-stable singlet states, in this case the transition is not spin preserving and fluorences at a ZPL of 1042 nm when decaying radiatively but may also decay non-radiatively. The meta-stable singlet states have a lifetime of approximately 300 ns \([78]\).

The path that the NV centre decays by is strongly dependent on its initial spin state, the \(m_s = 0\) state is very unlikely to decay via the meta-stable singlet states, meaning that in almost all cases it will decay via emitting a photon into the ZPL or its phonon sidebands. The \(m_s = \pm 1\) state, however, has a 50\% chance to decay via the singlet states instead of via spin-preserving radiative decay. Decay from the meta-stable states back to the ground state preferentially results in the \(m_s = 0\) state. This allows for optical initialisation of the NV centre spin state, with several microseconds of illumination resulting in the repeated excitation and decay of the spin. This results in initialisation into the \(m_s = 0\) state with high fidelity of typically > 90\% \([33, 80]\).

The properties that allow polarisation of the NV centre spin state also allow readout of its spin state via optical means. The \(m_s = 0\) spin state decays almost exclusively via radiative emission, but the propensity of the \(m_s = \pm 1\) state to decay via the non-radiative singlet states means that it will appear to be significantly less fluorescent than the \(m_s = 0\) state. Approximately 30\% fewer photons will be emitted by the NV when it is in the \(m_s = \pm 1\) state, allowing for a clear way to discriminate between NV spin states via optical readout. The difference between the fluorescence of the two spin states is known as the contrast and the amount will vary between NV centres depending on their position in the diamond lattice. The counting of the photon emission must occur within the first 300 ns of the laser pulse (the lifetime of the singlet states) as after this the NV centre will be initialised back into the \(m_s = 0\) state, destroying the spin information.
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The NV centre Hamiltonian

Similarly to the electron spin in silicon, the NV centre’s behaviour in its triplet ground state can be described by its Hamiltonian. In this case, the \( S_z \) axis is chosen to align with the NV centre axis — determined by the nitrogen and vacancy orientation in the diamond lattice. The Hamiltonian consists of three major parts: the zero-field splitting, \( H_{ZFS} \); the Zeeman interaction, \( H_Z \), and the spin-spin hyperfine interaction, \( H_{HF} \), with the Hamiltonian being the sum of these terms:

\[
H = H_{ZFS} + H_Z + H_{HF}
\]

In full, it can be written:

\[
H = D(S_z^2 - \frac{2}{3}) + k_\perp E_x(S_x^2 - S_y^2) + k_\perp E_y(S_z S_y + S_y S_z) + g_e \mu_B B_z S_z + S_A I + Q I_z^2 \tag{2.18}
\]

here as above \( \hbar \) is taken to be one, giving energy results in units of frequency. \( D \) is the zero-field splitting parameter, \( k_\perp \) is the electric field susceptibility, \( E_{x,y} \) are the components of the electric field in the transverse plane (i.e. not along the NV centre axis), \( S_{x,y,z} \) are the spin operators of the NV centre, for the spin 1 NV\(^-\) these are \( 3 \times 3 \) matrices. As in the case of electrons bound to donors in silicon, \( g_e, \mu_B \) are the electron g-factor and Bohr magneton respectively. \( B_z \) is the magnetic field in the NV axis. \( A \) is the hyperfine coupling term, \( Q I_z^2 \) is the nuclear quadrupole term.

The zero-field parameter \( D \) acts along the NV axis and is 2.870 GHz at room temperature, but has a dependence on temperature of \(-74.2 \) kHz/K \cite{81}. The transverse terms \( k_\perp \) and \( E_{x,y} \) describe the impact of both electric field and strain on the ground state energy levels.

The Zeeman interaction term functions very similarly to that of the electron in silicon but in this case acts only to lift the degeneracy between the \( m_s = \pm 1 \) states, having no effect on the \( m_s = 0 \) state. The result is that the energy of the \( m_s = -1 \) state is reduced whilst the \( m_s = +1 \) energy is increased. Along with the impact of the electric field components in the transverse plane, the transition frequencies for the spin state can be derived from:
\[ v_{\pm 1}(B_z) = D \pm \sqrt{(g_e\mu_B B_z)^2 + (E_{\perp})^2} \]  

(2.19)

For cases where the strain and electric field are small, therefore, the transition frequency can be approximated to be equal to \( D \pm g_e\mu_B B_z \), where \( g_e\mu_B \approx 28 \text{ GHz T}^{-1} \). In cases where strain is present, it interacts with the NV centre via the electrical susceptibility terms in the Hamiltonian. Whilst typically unavoidable for single NVs near the diamond surface, any level mixing effects of strain can be mitigated by applying a static magnetic field at a significantly greater magnitude than the strain contribution.

With this Hamiltonian, it can be seen that the spin of the NV centre can be manipulated in much the same way as that of a single electron bound to a donor in silicon. Typically, the \( m_s = 0 \) state is used as a the \( |0\rangle \) ground state, whilst either \( m_s = -1 \) or \( m_s = +1 \) is used as the \( |1\rangle \) state, with the unused spin state ignored. For this to be valid the \( B_z \) field must be sufficiently strong that the unused transition is negligibly driven by a microwave field that is on-resonance with the used transition.

### 2.2.2 NV Centre Magnetometry

The shift in the resonant frequency of the NV centre spin transitions with magnetic field and the potential for high efficiency readout and initialisation make the NV centre an ideal candidate for magnetic field sensing [27]. To define the sensitivity of a magnetic field sensor, the first thought is how changes in the sensor are being detected and how those changes relate to magnetic field. For an NV sensor, spin detection is performed by measurement of the defect’s fluorescence, which changes based on the transition frequencies of the spin states. Assuming an initial fluorescence intensity of \( I_0 \), the change in measured fluorescence for an infinitesimal shit in \( B \) is given by:

\[ \frac{\partial I_0}{\partial B} \times \partial B \Delta t \]  

(2.20)

here \( \Delta t \) is the measurement duration, with greater measurement times yielding greater changes in overall measured fluorescence. The noise in the readout of the spin state is dominated in NV experiments by the photon shot noise, which is given by \( \sqrt{I_0 \Delta t} \) as
 photon detection is a Poissonian process. By taking this along with equation 2.20, the NV sensitivity to dc magnetic fields can be written as [27]:

\[
\eta = \Delta B \sqrt{\Delta \nu} = \frac{\sqrt{T_0}}{(\partial I_0 / \partial B)} \approx \frac{\hbar}{g \mu_B} C \sqrt{T_0} \Delta \nu
\]  

(2.21)

where \(\Delta \nu\) is the linewidth of the spin transition and \(C\) is the contrast of the transition both of which are shown in figure 2.11. Typical contrasts for single NV centres are between 10% and 30%, but this characteristic is heavily dependent on the individual NV. NV centres deep in the diamond lattice ('bulk' NVs) tend to have significantly higher contrasts than NV centres close to the surface of the diamond lattice. The key to DC magnetic field sensitivity is thus narrow linewidths and large contrasts. The linewidth is fundamentally limited by the dephasing time, \(T_2^*\), of the NV centre but tends to be larger as both the impact of the laser and the driving microwave field serve to broaden
the spin transition frequency. To reduce the impact of power broadening and reach the intrinsic inhomogeneous linewidth of the spin transition it is necessary to separate spin manipulation, magnetic field induced phase accumulation and spin state readout. This can be achieved by performing pulsed Ramsey sequences, which have a $\frac{\pi}{2} - \tau - \frac{\pi}{2}$ structure. Taking the spin $|m_s = 0\rangle$ state as $|0\rangle$ and the $|m_s = 1\rangle$ state as $|1\rangle$, the dynamics of this pulse sequence can be described as follows. The spin is initialised in a superposition $|+\rangle$ state, allowed to acquire phase due to the magnetic field and then projected into the $|1\rangle$ state. During the free-precession period the spin acquires a phase $\phi = \tau g\mu_B B/\hbar$, leaving it in an overall state of $|\psi\rangle = \frac{1}{\sqrt{2}}(|0\rangle + e^{i\phi}|1\rangle)$. The final $\frac{\pi}{2}$ pulse then projects this state onto the NV $z$-axis, which encodes the phase in the populations of the $|0\rangle$ and $|1\rangle$ states. Zero phase acquisition would result in a final state of $|1\rangle$ and a measured fluorescence associated with that state of $I_0(1 - C)$, whilst any phase between 0 and $\pi$ yields increasing counts up to $I_0$. The longer the spin is allowed to precess for the more phase it is able to acquire so the more sensitive the measurement is to magnetic field. However, as the NV centre precesses it also loses phase coherence meaning that its effective contrast is reduced according to the dephasing time $T_2^*$. Dreau et al have shown in [82] that the optimal phase acquisition time to balance these two effects is $\tau \approx T_2^*$. This means that the best case field sensitivity can be written:

$$
\eta_{dc} \approx \frac{\hbar}{g\mu_B C \sqrt{I_0 I_L}} \times \frac{1}{\sqrt{T_2^*}}
$$

(2.22)

AC Magnetometry

The procedures described above allow for the sensing of dc magnetic fields, and in this case overall sensitivity is limited by the $T_2^*$ time of the NV centre. If the magnetic field that is to be sensed is ac instead of dc then it possible to significantly enhance the sensitivity of the NV centre. This is done by exploiting the features of dynamical decoupling sequences and the way they interact with magnetic noise at different frequencies.

The sensitivity of NV centres to dc fields is limited by $T_2^*$, as dynamical decoupling sequences that refocus the dephasing of the centre also refocus any phase acquired due to the magnetic field that is to be sensed. Time varying fields, or ac fields, do not suffer
2 Spin Defects

from this limitation. As such the sensitivity of the NV centre to magnetic fields is limited by \( T_2 \), rather than \( T^*_2 \), which in most cases can be orders of magnitude larger and be extended further with dynamical decoupling sequences such as CPMG. The sensitivity can then be written \([63, 83, 84]\):

\[
\eta_{ac} = \eta_{dc} \sqrt{\frac{T^*_2}{T_2}}
\]  

(2.23)

This equation can be rewritten from scratch to take into account the added errors introduced by experimental technique, most importantly the need for finite initialisation and readout periods of the qubit \([83]\):

\[
\eta_{ac} = \frac{\pi \hbar}{2 g \mu_B} \sqrt{\frac{T_2 + t_I + t_R}{(T_2)^2}} \frac{\sigma_R}{\sigma_R}
\]  

(2.24)

where \( t_I \) is the initialisation time of the NV centre, \( t_R \) is the readout time of the NV centre and \( \sigma_R \) is the spin readout noise and is related to the signal-to-noise ratio of the NV centre (SNR) by:

\[
\sigma_R = \sqrt{1 + \frac{2}{\text{SNR}^2}}
\]  

(2.25)

SNR can be derived in multiple ways but is easily derived from the photon emission rate from the \( |m_s = 0\rangle \) state, \( I_0 \) and the contrast: \( \text{SNR} = \sqrt{I_0 \frac{C}{C_{\text{SNR}}}} \). When multiple repeats of an experiment are carried out, \( N \), the averaged SNR is: \(< \text{SNR} >= \sqrt{N} \times \text{SNR} \).

Importantly, these conditions only hold when the frequency of the ac magnetic field is matched by the frequency of the dynamical decoupling sequence used to probe it. This is shown in figure 2.12. An ac magnetic field oscillating very quickly or slowly imparts limited phase to the NV centre, due to its impact being averaged out during a CPMG sequence. An ac magnetic field oscillating at the same rate as the spin is flipped, however, imparts a maximum phase to the spin, as the spin is reversed whenever the field is so the phase acquisition between \( \pi \) pulses is summed rather than subtracted.
2.2 Nitrogen Vacancy Centres in Diamond

![Diagram of magnetic fields](image)

Figure 2.12: Schematic depicting the interaction between two different ac magnetic fields and a 4 pulse CPMG sequence. In the above case the field oscillates fast with respect to the NV centre spin flips, meaning that the impact of the changing magnetic field is averaged out, resulting in limited phase acquisition and spin projection into the $|m_S = 0\rangle$ state so fluorescence $= I_0$. In the lower case, the spin flips at the same frequency as the magnetic field, maximising phase acquisition and resulting in projection into a superposition state and reduced fluorescence.

**Spin Sensing with NV Sensors**

One of the key questions this work seeks to address is the potential for single NV centres to detect the magnetic field of a spin bound to a phosphorus donor in silicon. To answer this, we must have some idea of the magnetic field due to an electron spin and the conditions that need to be met in order for an NV centre to have sufficient sensitivity to detect it. Considering a single electron spin, the relevant magnetic field from it can be extracted from its magnetic dipole field, given by:

$$B = \frac{\mu_0}{4\pi} \left( \frac{3r (\mathbf{m} \cdot \mathbf{r})}{r^5} - \frac{\mathbf{m}}{r^3} \right)$$  \hspace{1cm} (2.26)$$

where $\mu_0$ is the permeability of free space, and $\mathbf{r}$ is the displacement vector from the spin, $\mathbf{m}$ is the magnetisation of the spin which for a single electron is just the Bohr magneton, $\mu_B$, with an orientation given by the spin's axis of orientation. For an electron bound to a phosphorus donor in silicon and assuming an experimental setup that used a magnetic field oriented along the sensing NV centre's axis of orientation, this spin would have the same orientation as the NV centre. This information can be used to plot 3D contours of constant magnetic field. The relevant field strength at any point is the field
2 Spin Defects

Figure 2.13: (a) how magnetic field sensitivity for an NV centre varies with contrast. This is calculated using equation 2.24, assuming typical experimental values of $t_L$ and $t_R$ of 3 μs and 400 ns respectively, $T_2$ of 50 μs. As contrast increases the NV centre’s sensitivity is observed to increase (the minimum field it can detect decreases). (b) shows the magnetic iso surfaces for an electron spin at the maximum and minimum sensitivity values in (a). The iso surfaces show the maximum distance from the electron spin that the NV centre with the described parameters could be and still detect its magnetic field.

projected along the axis of the NV centre as to first order, the NV centre is insensitive to low magnitude transverse magnetic fields. Figure 2.13 shows how the sensitivity of a typical near-surface NV centre varies with its contrast and also the magnetic iso-surfaces showing the maximum distance the NV centre could be from an electron spin at the maximum and minimum calculated sensitivities. This figure highlights the requirement for extremely close proximity between NV centre and spin in order for efficient sensing of the magnetic field. In addition, it highlights the importance of the NV centre parameters in determining its sensing ability. An NV centre with contrast of 30% can sense an electron spin at a distance of approximately 30 nm, whilst an NV centre with contrast 5% would need to be within 15 nm.

2.2.3 Summary

We have seen here the theoretical background describing electron spins bound to donors in silicon and how they can be controlled and measured in the paradigm of electron
2.2 Nitrogen Vacancy Centres in Diamond

spin resonance. Their capacity to act as a model two-level quantum system, a qubit, has been discussed. The concepts of relaxation and decoherence have been introduced and the factors contributing to them presented. I have introduced dynamical decoupling sequences and their capacity to extend qubit coherence as well as the concept of a filter function and how it interacts with the qubit noise spectrum. Finally I have discussed a second spin defect, the NV centre in diamond and how it too can form a qubit and a quantum sensor via optically detected magnetic resonance.

In chapter 3 I introduce the equipment and techniques used to study both electron spins in silicon and NV centres in diamond. The focus for electron spins in silicon is traditional spin resonance experiments, examining how they are affected by illumination. For NV centres in diamond I show experimental apparatus designed to allow the creation of a mobile quantum probe.
3 EXPERIMENTAL APPARATUS AND TECHNIQUES

That is one fine looking barbecue pit...why doesn’t mine look like that?! — Homer Simpson

3.1 PULSED ESR SPECTROMETER

3.1.1 BRUKER SPECTROMETER SETUP

The studies on electrons bound to donors in silicon in this work are carried out in a commercial E500 Bruker ESR spectrometer. The basic schematic of a Bruker spectrometer is shown in figure 3.1. The silicon sample of interest is placed in a Bruker resonator at the centre of a sapphire ring cavity, this resonator is held in an oxford instruments helium flow cryostat. The cryostat uses a combination of helium flow and a PID controlled heater close to the sample to control the sample temperature based on a user-defined setpoint. This cryostat is able to operate at temperatures down to 4.2 K, and can remain stable at temperatures up to 70 K. The frequency of the microwave source is determined by the sapphire ring resonant frequency, which is measured via application and measurement of unamplified CW microwaves, the frequency of which is swept and the response measured to find the resonator ‘dip’, which for these experiments is at approximately 9.7 GHz. Once identified, a pulse generator is used to modulate the output of the source to produce square pulses, which are then amplified via either a travelling wave tube (TWT) amplifier or a solid state amplifier. These pulses are then fed via a circulator to the sap-

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3 Experimental Apparatus and Techniques

Phire ring resonator and the sample. The resonator is designed so that when microwave pulses are coupled into it, it produces an oscillating magnetic field at its centre, where the sample is placed. This provides the $B_1$ field discussed in the introduction to ESR above. The $B_0$ field is provided by an electromagnet which can be set to ensure that the electron spin transition is on resonance with the driving microwave field.

When the spins are allowed to precess in the static magnetic field they produce electromagnetic radiation at their precession frequency \[51\]. This radiation couples back into the resonator and returns up the same microwave lines as the pulses are delivered through. The circulator redirects the signal to an IQ mixer where it is compared with a reference signal from the microwave source, usually termed the ‘local oscillator’. The IQ mixer produces two outputs — I and Q — which describe the in-phase and out-of-phase components of the signal relative to the reference from the source. These outputs have two frequency components at $f_{\text{sig}} + f_{\text{LO}}$ and $f_{\text{sig}} - f_{\text{LO}}$, meaning that when the frequencies are the same, the low frequency component is dc. The outputs are directed through a low pass filter, to remove the high frequency component, before being passed to a digitiser and then to a computer for analysis. The I and Q components allow both the phase and the magnitude of the spin signal to be analysed, with their relative magnitude determining the phase of the spin ensemble in the $x - y$ plane of the Bloch sphere. Typically, the phase of the local oscillator is adjusted so that an expected $|+\rangle$ state gives a maximum signal in the I channel, meaning that a $|+i\rangle$ state returns a maximum signal in the Q channel.

Two final considerations when performing a pulsed-ESR experiment are the pulse power and resonator quality factor. Together they determine the strength of the $B_1$ field that is experienced by the spin ensemble. The most important factor as a result of this is the length of the pulse required to invert the spin ensemble — the $\pi$-pulse time. The length of the pulse determines its bandwidth, with a relationship of $BW \approx 1/t$, the bandwidth is vital as the spin ensemble with have a distribution of frequencies — typical linewidths in natural silicon are on the order of MHz — and a long pulse has insufficient bandwidth to drive all of them. The Q factor of the resonator also determines its bandwidth — with high Q factors resulting in narrow bandwidths, as such pulse power and Q
3.1 Pulsed ESR Spectrometer

Figure 3.1: A simple schematic of the microwave setup of a Bruker ESR spectrometer. A microwave source generates microwaves in the X-band range which are fed to a pulse generator for conversion to square pulses. These pulses are amplified by either a travelling wave tube or solid state amplifier before entering a microwave circulator which is oriented to allow these pulses to enter a resonator in an Oxford instruments helium flow cryostat. The pulses are coupled into a sapphire ring resonator via an antenna, which is designed to focus the $B_1$ field of the microwaves at its centre where the sample of interest is placed. Signal from the sample is measured via the same microwave line as the excitation, with the circulator coupling the signal into an IQ mixer where it is compared with a reference signal from a microwave source. The output I and Q information from the IQ mixer is then fed into a lock in amplifier and finally a computer where it can be analysed.
factor must be adjusted so that the pulse is sufficiently short to drive the whole spin line (if desired) and the resonator bandwidth is broad enough to accept it.

3.1.2 ESR Pulse Sequences

With the working principles of the Bruker ESR spectrometer established, I now describe the principal experiments that are carried out and the pulse sequences associated with them. Figure 3.2 shows three pulse sequences and example measurement outcomes: Rabi, inversion recovery and decoherence measurements. In most cases, measurement results are recorded by integrating under the echo to measure its intensity and then monitoring how this changes with some aspect of the pulse sequence.

The Rabi sequence is used to find the ideal $\pi$-pulse time: a Hahn echo sequence has an extra pulse added before it and the length of this pulse is swept, resulting in an oscillating signal from the echo. The frequency of this oscillation gives the Rabi frequency, which gives the ideal $\pi$-pulse time. Alternatively a two pulse sequence can be used, sweeping the length of the pulse that would be the $\pi/2$ pulse here, but the 3-pulse sequence has been found to be more effective experimentally.

The inversion recovery sequence is used to measure the relaxation time of the spin ensemble. The ensemble is first inverted using a $\pi$-pulse and its component in the $z$-axis of the Bloch sphere is then measured using a Hahn echo sequence, with the time between initial $\pi$-pulse and echo sequence increasing over the measurement. Initially this results in an inverted echo, but as the time from $\pi$-pulse to echo sequence increases the ensemble undergoes relaxation. When the gap is sufficiently long, the ensemble relaxes completely before the Hahn echo sequence, resulting in a fully positive echo.

3.2 Attocube Atomic Force Microscope and Cryostat

The second major piece of experimental apparatus used in this work is an Attocube combined atomic force microscope (AFM) and confocal microscope (CFM), capable of operating at temperatures down to $< 1.8\,\text{K}$ using an Attocube Attodry 2100 closed cycle cryostat. I discuss the principles of operation of the AFM and cryostat first before dis-
3.2 Attocube Atomic Force Microscope and Cryostat

Figure 3.2: Three ESR pulse sequences for measuring the spin ensemble Rabi frequency, relaxation time ($T_1$) and decoherence time ($T_2$) and example measurements taken with these sequences. Each point on the graph is the echo intensity. (a) shows the pulse sequence for measuring the Rabi frequency of a given spin ensemble. This sequence depicts the typical experimental approach, where three pulses are used: a Hahn echo sequence is set up, using anticipated $\pi$ and $\pi/2$ pulse times, and a third pulse is added before the sequence. The resulting sinusoidal shape can be used to identify the ideal $\pi$-pulse length. The graph is observed to decay over time as a result of the ensemble dephasing. (b) shows the sequence for an inversion recovery to measure $T_1$, a $\pi$-pulse is added before the Hahn echo sequence, inverting the spin ensemble and giving a negative echo. The time between $\pi$-pulse and Hahn echo sequence is increased, allowing the ensemble to relax in between. Once the time is sufficiently long, the initial pulse has no effect on the final spin state, meaning a fully positive echo is recovered. (c) shows a decoherence measurement, where the $\tau$ value of the Hahn echo sequence is increased and the echo response measured to give a $T_2$ measurement. As the ensemble loses phase coherence irrecoverably, the echo intensity decreases to 0.
3 Experimental Apparatus and Techniques

cussing in detail the confocal microscopy and ODMR setup designed for study of NV centres.

3.2.1 Atomic Force Microscope

The fundamental principles of atomic force microscopy are fairly simple. Belonging to the larger class of scanning probe microscopes, they were developed primarily to map the surfaces of materials at the nanoscale. Unlike scanning tunnelling microscopes, AFMs do not require that the surface they are studying is conductive [85]. This extra flexibility has led to their widespread use and they have been adapted to perform tasks well beyond the simple topographical mapping that they were first used for [86, 87, 88]. An AFM works on a similar principle to a record player, where a fine tip responds to a bumpy surface and relays information about that surface. Whilst a tip on a record player is usually about 50 µm in radius, the tip in an AFM is considerably smaller, usually on the order of 10s of nanometres or less.

AFM Operational Principle

Whilst the fundamental principle of a fine tip responding to the topography of a surface remains the same across different AFMs, how the topography of the surface is measured can differ. Typically, either the tip or the sample is moved via piezoelectrics in 3 dimensions, with the sample approximately flat in the $x - y$ plane. Originally, a laser was focused on the back of the tip and its reflection detected by a photodiode, as the tip was deflected by the sample topography this could be measured by the movement of the laser reflection on the photodiode, with the long beam path meaning that the system is very sensitive to small deflections in the tip.

In modern AFM systems, there is typically a feedback loop that aims to keep the tip at constant distance from the sample by measuring some proxy for this and using a PID loop to keep it constant via movement of the $z$ axis piezo. There are a number of different techniques for performing this kind of AFM scanning, with many different modes of operation for the probe, which fall broadly into categories of contact and dynamic. In contact modes, the tip is in contact with the sample and the deflection of the tip cantilever
3.2 Attocube Atomic Force Microscope and Cryostat

changes the position of a laser spot, with a feedback loop aiming to keep the spot position constant via changes in $z$ position.

In this work all AFM scanning is via a dynamic mode, which involves no sample contact between tip and sample. This is achieved via a probe that can be resonantly excited to vibrate at a particular amplitude, frequency and phase. The change in one of these can be used as the error signal in a PID feedback loop. In all cases in this work, the amplitude is used as the error signal. In the case of the probes used in this work, they are shaped like a tuning fork and made from quartz with electrical contacts. A ‘dither’ piezo shakes the tuning fork and the piezoelectric response of the quartz can be measured to deduce the amplitude of oscillation of the tuning fork. Once the resonant frequency of the tuning fork is found and the dither piezo set to this frequency, the amplitude of oscillation can be used as a setpoint and error signal for the $z$-piezo position. As the tip of the probe approaches the sample short-range Van der Waals forces interact with the tip and alter the shape of its resonance. As the resonance alters so does the amplitude of oscillation of the probe. This change is used to alter the $z$-position to keep the amplitude of oscillation constant. The changes in the $z$-position can then be used to map the sample topography.

Attocube AFM Setup

Whilst it is common for AFMs to have freedom of movement for either the sample or the probe, in the case of the Attocube AFM/CFM, both can be moved and scanning can be performed with either tip or sample. To accomplish this, the AFM mechanism consists of two stacks: one for the sample and one for the tip with both made up of multiple stages. Both stacks have two different types of stage for $x-y-z$ movement, with one set known as scanners and the other as positioners. The scanners are responsible for the short range movement of sample or tip when AFM images are being acquired. The $x-y$ scanners have a limited range of approximately 40 $\mu$m at room temperature, which is reduced to 20 $\mu$m at 1.8K. The $z$ scanner has a much smaller range of approximately 2 $\mu$m. The short range of the scanners means that they are unsuitable for long range movement of sample or tip so for this task the positioners are used. The positioners function via a slip-stick mechanism, which enables a piezo with an expansion range of only $1 - 2 \mu$m to translate a stage over several millimetres. This is accomplished by having the piezo expand slowly,
3 Experimental Apparatus and Techniques

![Figure 3.3: Two modes of operation of AFM probes. (a) shows a traditional cantilever design which measures the deflection of the cantilever using a laser reflected off its rear surface. (b) shows the style of probe used in this work, which uses a cantilever attached to a driven tuning fork. The tuning fork is driven at its resonant frequency and the piezoelectric effect of the quartz recorded. Van der Waals forces from the sample shift the resonant frequency and the amplitude of oscillation which is used to feedback to the probe $z$-position to keep the amplitude of oscillation constant. The resultant shifts in the $z$-piezo are measured and used to record the sample position.](image)

pushing a guiding rod that is loosely coupled to the sample or tip stage. When expanding slowly the piezo does not overcome the static friction between rod and stage. The voltage applied to the piezo is then turned off and a spring causes the guiding rod position to be reset. The speed at which this happens overcomes the static friction between guiding rod and stage and so does not move it. Repeating this motion multiple times allows for long range translation of the sample and tip stages.

**Interferometric Positioning System**

Typically, AFM systems record position in $x - y - z$ via the relationship between the voltage applied to the scanners and the expansion coefficient of the piezoelectric crystals. Whilst this gives relatively accurate results the response of piezos to voltage is almost always non-linear, giving scans that are distorted. In addition, there is no way of determining long range position when movements are instigated by the positioners rather than the scanners, meaning that it is easy to become 'lost' on large samples without many recognisable features. The AFM system used in this work has two systems that allow for
Figure 3.4: Picture and schematic of the AFM stacks, (a) and (c), along with closeup view of the AFM probe head with standard AFM tip, (c) and (d).
3 Experimental Apparatus and Techniques

accurate global position and for scanning with additional feedback to ensure accurate $x - y$ distances are recorded.

The first is a resistance based system, which uses metal brushes attached to the positioning scanners that touch a resistive material. As the positioners move, the brush moves along this resistive material and a circuit measures the overall resistance of the system, that resistance can then be translated to the brush position and so to the position and movement of the sample or tip in $x - y - z$. This system is accurate to approximately 1 µm, so is not useful for improving scanning response but provides excellent information about absolute position of sample and tip.

The second system is based upon interferometry: two mirrors are placed on the tip and sample holders with one normal to $x$ and one to $y$. A laser is directed at this mirror via a fibre-optic which also captures the mirrors reflection. This reflection interferes with the original laser light and the interference pattern is used to detect movement [89]. This has precision on a nanometre scale and can be used to feedback the position of the scanners during sample probing, allowing for highly accurate $x - y$ measurements and little to no distortion in acquired images. It is also capable of long range positioning — allowing for global awareness of tip and sample position. It does not operate in the $z$ direction, so the resistive system must be relied upon for global positioning in this axis, and the scanner voltages for $z$ axis measurements.

AFM Probes

There are two types of probes used in this work, one a standard tuning-fork type AFM probe with a silicon tip from Akiyama [90], used primarily for testing and validation of the AFM system. The second style is similar, based upon the tuning-fork style, but with a diamond instead of silicon tip. These diamond tips are designed to have a single NV centre at their apex, which can be addressed via ODMR in this system. The primary concern when using these tips is the information gained from studying the NV centre, and not the AFM feedback itself. The AFM here is used for tip positioning for confocal measurements and for positioning relative to the sample. The probes are discussed in detail later in this work but are provided by two companies: Qzabre and Qnami.
3.2.2 **Attodyr Closed Cycle Cryostat**

One of the key features of the AFM/CFM used in this work is the ability to work between room temperature and 1.8 K, this is achieved via a closed cycle cryostat, an Attodyr 2100. The Attodyr 2100 works via a combination of a pulse tube cooler and a Joule-Thomson cooling loop \([91, 92]\). The cryostat is designed specifically to minimise vibrations, which are unsurprisingly disastrous for accurate atomic force microscopy.

The basic working principles of the cryostat are simple: a vacuum chamber contains the head of a pulse tube cooler which is thermally coupled to a helium condenser, reducing its temperature to below 4 K. An isolated loop is fed helium from a room temperature storage vessel, which circulates in this loop via a scroll pump. Room temperature helium from the storage vessel liquifies in the condenser and then flows out of this condenser via a Joule-Thomson valve. The action of the pump reduces the helium vapour pressure, causing it to evaporate. The helium flows through a low and constricted metal pipe — which thermally isolates the VTI and sample chamber from the condenser — and into a VTI, which it cools via the Joule-Thomson effect to below 1.8 K. The evaporated helium then returns round the loop and recondenses in the condenser. The VTI and sample space are isolated from one another and just thermally coupled, allowing samples to be exchanged without air contaminating the main Joule-Thomson cooling loop. The sample chamber itself is filled with helium during sample exchange, which acts as an exchange gas to cool the AFM stacks and the sample and tip.

PID controlled heaters in the VTI and sample holder can be used to accurately control the sample temperature, allowing operation of the AFM anywhere between its base temperature and room temperature. The thermal and physical isolation of the VTI and sample space from the remainder of the cryostat allows for sample exchanges to be performed while the majority of the cryostat is kept cold with only VTI and sample space heated to room temperature. Sample exchanges can thus be performed without the warming of most of the cryostat, allowing exchanges to be done within hours rather than days.

In addition to its cooling capabilities, the cryostat contains a 111 superconducting vector magnet. This allows the application of a magnetic field of any orientation to the sample space, at a magnitude of up to 1 T. This component allows for the alignment of
Figure 3.5: The Attodry 2100 cryostat and the functioning of its gas handling system. (a) shows the cryostat without vacuum cladding, with the VTI (variable temperature insert) obvious in the middle, the large tin foil covered lump below the second stage is the cryostat’s vector magnet. (b) shows the cryostat in its external housing. (c) shows a schematic of the gas handling system in the cryostat. Pure helium is stored at room temperature in the Helium Storage Vessel (referred to as ‘Dump’), the cryostat internals including the condenser are cooled by a pulse tube cooler to below 4 K, at which point helium is fed into the system in short pulses via the dump out valve and the scroll pump. The helium condenses to a liquid and flows out the bottom of the condenser via a Joule-Thomson valve, the reduced pressure as a result of the scroll pump evaporates the helium causing a cooling effect. This helium is sucked through the VTI and back round the loop to the condenser, where it liquifies again. The cooling effect of the helium evaporation reduces the VTI temperature to below 1.8 K at its coldest. The sample space is separate from the VTI and only coupled thermally, allowing sample exchanges without the loop being contaminated by air. The sample space itself is cooled by the addition of pure helium during cooldown.
the field to the axis of an NV centre — which removes the necessity to align the sample itself.

3.3 Confocal Microscopy Setup

The major advantage of the Attocube AFM/CFM system is the ability to perform simultaneous atomic force and confocal microscopy. This allows the study of NV centres via optically detected magnetic resonance and crucially the study of NV centres in the tips of AFM probes whilst those probes interact with a surface or sample of interest. Having detailed the functionality of the AFM part of the system, I now discuss the home-built confocal microscopy setup that was constructed to perform the bulk of the experiments reported on in this work.

3.3.1 Principles of Confocal Microscopy

Confocal microscopy is a subset of fluorescence microscopy, developed originally for imaging of biological samples [93]. The main advancement over more traditional techniques is the ability to collect fluorescence information that is restricted both in the $x - y$ plane and in the $z$-axis. This allows for the imaging of 'slices' of samples, whereas traditional techniques would collect from cylinders of the sample, with no way to determine $z$-position [94, 95]. In the case of NV centres this is a vital ability for imaging of single defects. For imaging of single NVs in bulk samples, restriction of fluorescence collection in the $z$-axis of the sample ensures that no fluorescence contribution is obtained from fluorescing centres above or below the defect of interest in the sample. In the case of single NVs in tips, it ensures that no fluorescence collection comes from colour centres in a studied sample.

Figure 3.6(c) shows a simple schematic of the working principle of a confocal microscope. Crucially, the microscope must be able to:

1. Focus laser light into a spot on the sample — achieved using an objective
2. Collect fluorescence from the sample — achieved again using an objective
3 Experimental Apparatus and Techniques

![Diagram of confocal microscopy](image)

Figure 3.6: The basic concepts of confocal microscopy. (a) shows a cartoon of an objective focusing laser light on a diamond sample embedded with NV centres. (b) shows the results of a confocal scan on a diamond sample with a grid of single NV centres embedded. (c) shows a simple schematic of confocal microscopy. 520 nm laser light is reflected off a dichroic mirror that reflects wavelengths below 650 nm and transmits wavelengths above it. The laser light is then focussed on the diamond sample via an objective, which then collects the fluorescence from NV centres as well as the reflected light from the laser. The objective is characterised by its numerical aperture (NA) which determines the angle from which it is able to collect light. The collected light is transmitted back to the dichroic mirror, which transmits the NV fluorescence at >650 nm, whilst reflecting the green laser light allowing for the two to be distinguished. The transmitted fluorescence then passes through a lens that focuses the light through a pinhole. Only light collected from the objective’s working distance follow parallel paths, light from other z positions in the sample is divergent and is not focused through the pinhole. Finally the light passes into a single photon detector where it is measured.
3.3 Confocal Microscopy Setup

3. Distinguish reflected laser light from fluorescence — achieved using a dichroic mirror that reflects light at the laser wavelength but transmits light at the fluorescence wavelength.

4. Reject fluorescence from $z$-positions above and below the area of interest — achieved by focussing the fluorescence through a pinhole. Fluorescence from $z$-positions outside the focal distance of the objective diverges and so is not focused sufficiently to pass through the pinhole.

5. Detect the fluorescence — usually achieved using a single photon detector but a less sensitive photon amplifier may be used if fluorescence is very strong.

The final key ingredient is the ability to change the position of the laser spot relative to the sample of interest. Unlike typical fluorescence microscopy, the fluorescence in confocal microscopy is collected ‘pixel-by-pixel’ from the laser spot location, so the laser spot or sample must move in order to build up an image. The most common way to do this is to use a pair of mirrors whose rotation can be controlled by a galvanometre. This changes the beam angle of the laser, which changes the spot position on the sample [96]. The alternative, that is used in this work, is to use piezoelectrics to move the sample relative to the laser spot. Whilst the galvanometre approach has significant advantages in terms of speed of acquisition it adds significant extra optical complexity. As the galvanometre approach is not of use in the context of using an NV centre in a diamond to study a sample — as the laser spot must remain fixed — confocal scans in this work are all taken with a fixed laser spot and movement of the sample via the piezoelectrics of the AFM stages.

3.3.2 Spatial Resolution in Confocal Microscopy

The most important determinant of the performance of a confocal microscope is the objective used to focus the laser light on the sample and to collect fluorescence. The numerical aperture (NA) of an objective largely determines its behaviour as it determines the maximum angle of light emitted from a point at its focal length that it accepts, according to the equation:
3 Experimental Apparatus and Techniques

\[ NA = n \sin \theta \]  
(3.1)

where \( n \) is the refractive index of the medium the objective is in (\( \approx 1 \) in this work) and \( \theta \) is the angle of acceptance for light from a point source at its focal length. An NV centre illuminated by light typically emits fluorescence in a sphere, meaning that the larger the NA of the objective, the greater the fraction of the emitted light it collects. The objective used in this work is a 0.81 NA apochromatic objective, meaning that it is corrected to have the same focal length across a range of wavelengths (in this case 565 – 770 nm).

The spatial resolution of the confocal microscope in the \( x - y \) plane is determined primarily by the size of the laser spot that the objective produces at its focal length is. This is determined by the wavelength of light used and the NA of the objective according to the equation:

\[ \phi_r = \frac{k \lambda}{NA} \]  
(3.2)

where \( \lambda \) is the laser wavelength and \( k \) is a modifying number close to 1, which can be used to describe either a theoretical or practically achieved resolution. The Airy unit diameter defines the diffraction limited spot size of a uniform beam as 1 A.U. \( = 1.22\lambda/NA \), so in this work with a 520 nm laser and 0.81 NA objective, the Airy diameter is 780 nm. This means that the minimum distance between two NV centres that can be reasonably distinguished is 390 nm. In practice this distance may be larger due to imperfections in the optical beam path.

The resolution in the \( z \)-axis of the confocal microscope is given by the optical depth of field. The first requirement is the distance from the first intensity peak of the laser spot to the first diffraction minimum, given by [93, 94]:

\[ z_{min} = \frac{2n\lambda}{NA^2} \]  
(3.3)

the optical depth of field is then:

\[ \phi_z = \frac{1}{2} z_{min} \]  
(3.4)
this distance is defined as 1 R.U. — one Rayleigh unit. Whilst this defines the optical depth of field, light from \( z \)-planes outside the one at the objective focal length cause a strong contribution to the detected fluorescence, the pinhole in the detection beam path is essential to avoid this and allows a practical confocal microscope to reach this \( \phi_2 \) limit.

### 3.3.3 Confocal Setup Detail

The homebuilt confocal setup used in this work consists of two main parts: a laser fibre coupling section on a standard optical table, and an excitation and collection section which is built on a sliding optical plate on top of the Attocube cryostat. A detailed schematic of the optical setup is found in figure 3.7. In addition to the components found in the simple setup described above, this setup contains a beam expander which expands the excitation beam so that its diameter is equal to the back aperture of the objective. When the diameter of the excitation beam is smaller than the objective back aperture the size of the focal spot is increased, which reduces the spatial resolution of the microscope. After the 650 nm dichroic mirror there is an additional 650 nm long pass filter to ensure complete extinction of reflected laser light. Finally there is also a 90/10 beamsplitter, which redirects 90% of collected light to a camera, allowing for wide field imaging of the sample through the objective. This is essential for locating an AFM tip at the focal point of the objective, as pixel by pixel scans would be exceptionally slow in a 3D search space.

### 3.4 Optically Detected Magnetic Resonance

In addition to the requirements for fluorescence measurement using a confocal setup, effective control of NV centres requires the ability to perform magnetic resonance experiments. This requires the ability to deliver controlling microwaves to the NV centres of interest and to read out their state using based on their fluorescence.
3 Experimental Apparatus and Techniques

Figure 3.7: Details of the confocal setup: (a) a detailed schematic of the confocal setup used in this work. The setup consists first of a section for coupling the excitation laser beam into a fibre-optic cable, the core size of which acts as the required pinhole in the excitation path. The fibre carries the beam to the excitation and collection setup which is on an optical plate on top of the Attocube cryostat. The excitation beam is reflected off a dichroic mirror and passes through a beam expander — this beam expander means the laser spot size fills the back aperture of the objective, which reduces the focussed spot size on the sample [94]. Mirrors reflect the beam down into the top window of the cryostat where it the passes into the objective and is focussed onto the sample. Fluorescence and reflected light pass are collected by the objective and focussed back along the collection path. The dichroic mirror transmits wavelengths > 650 nm and reflects wavelengths < 650 nm, meaning that the laser light is filtered out leaving fluorescence with an additional 650 nm longpass filter further improving the extinction of the laser. The fluorescence is focussed into a collection fibre, whose core acts as the pinhole of the collection path, and is then transmitted to a single photon counter. In addition, there is a 90/10 beam splitter in excitation and collection paths that can be used for widefield imaging of the sample. (b) shows the laser coupling setup and (c) shows the excitation and collection optics on top of the Attocube cryostat.
3.4 Optically Detected Magnetic Resonance

3.4.1 Equipment for ODMR

The Attocube probe insert that contains the AFM stacks and control lines also has two high frequency cables for delivering microwaves. To perform ODMR, we use 5 key pieces of equipment:

1. An arbitrary waveform generator (AWG) that can produce pulses to control other equipment — this is a Swabian Instruments PulseStreamer 8/2

2. A vector source generator (VSG) that can produce microwaves at frequencies up to 6 GHz — a Rohde and Schwarz SGS100A

3. A laser whose output can be pulsed — a 520 nm Swabian Instruments diode laser

4. A single photon detector that can record incident photons and emit a voltage pulse when one is detected

5. A timetagger that can record ‘clicks’ from the SPD along with their time of measurement — a Swabian Instruments TimeTagger 20

The arbitrary waveform generator acts as the master instrument, with the other pieces of equipment acting as workers. This allows all pieces of equipment to work on a single clock, meaning that their operation can be synchronised in time by commands from the AWG. The AWG has 2 analogue outputs that are used as the I and Q input to the VSG, meaning that both amplitude and phase of the applied pulses can be controlled. The VSG output is then amplified by a minicircuits 46dB gain amplifier. An SMA cable delivers the microwaves to the Attocube probe head and a rigid cable goes from there to the sample chamber. A PCB is fixed to the top of the sample stack and is connected to the rigid SMA cables via flexible cables that allow the sample holder to move. The return line is via a second rigid SMA cable which ends in a 50 ohm terminator.

Microwaves are delivered to the sample of interest in two major ways in this work, the first is via a 20 μm diameter copper wire, soldered between the RF lines on the PCB so that it is tight against the sample. The microwave pulses travelling through this wire produce an oscillating magnetic field in concentric circles around it, allowing for NV centre spin control. The second is via a sample patterned with microwave striplines in
3 Experimental Apparatus and Techniques

Figure 3.8: The ODMR setup: (a) a simple schematic of the ODMR setup used in this work. (b) an example of one of the PCBs used for delivering microwave pulses to a sample of interest. (c) A schematic of an advanced PCB design allowing for application of dc voltages to the sample.

gold and niobium, with the goal of studying simultaneous AFM and NV fluorescence imaging. A schematic and picture of this patterned sample is shown in figure 3.9.

The collected fluorescence enters an avalanche photodiode (APD) single photon detector. This produces square TTL (transistor-transistor-logic) pulses whenever it detects a photon, these pulses are transmitted to the timetagger, which counts them and attaches a measurement time to each. This information allows for almost all necessary ODMR experiments, as photons can be selectively counted based on their arrival time.

3.4.2 ODMR Pulse Sequences

ODMR pulse sequences are broadly similar to those described in section 3.1.2, but with the additional requirement of laser pulse control. The 520 nm laser light acts both to initialise and readout the NV centre spin state, as described in detail above. So the majority of pulse sequences begin with a laser initialisation pulse and end with a readout pulse. As the laser readout pulse also acts to initialise the spin into the $|m_s = 0\rangle$ state, the time when relevant photons can be collected is limited — if they are collected for too long then the spin is re-initialised and information about its spin state lost. The read time (which is defined by looking at photon clicks in a given time window on the timetagger) must
3.4 Optically Detected Magnetic Resonance

Figure 3.9: Sample used for microwave delivery and testing of simultaneous AFM and confocal imaging of NV fluorescence. (a) shows the schematic of the patterned sample with 4 separate devices, 2 patterned in gold and 2 in niobium. Each device is made up of an MW stripline, 3 dc lines for static magnetic field imaging, and a grid for AFM alignment and testing. (b) shows an image through the confocal objective of the sample, with the dc lines and AFM grids visible. The bright triangle in the top half of the image is an Akiyama tip raised above the objective focal plane.

be carefully calibrated to ensure that strong contrast between $|m_s = 0\rangle$ and $|m_s = \pm 1\rangle$ states is achieved, whilst still maintaining a good signal to noise ratio. In addition to read time optimisation, the delay between laser pulse and starting the readout window must be calibrated, to take account of the time of flight between laser, sample, and detector.

Figure 3.10 shows the results of experiments to calibrate these figures, with delay duration of 200 ns and readout window duration of 300 ns found to be optimal. Single NV centres have typical count rates of approximately 100,000 counts per second (cps), meaning that these read times typically result in a photon being counted once every 30 runs, meaning that a large number of averages are required for a reasonable SNR, which in this case is dominated by photon shot noise. For the count rate to be mapped to the NV centre spin state, an accurate count of the photons expected when the NV centre is prepared in the $|m_s = 0\rangle$ state is required. As drifts in this may occur overtime, whenever a microwave pulse sequence is run it is immediately followed by an initialisation and readout sequence with no microwaves applied — giving a figure for expected photon counts from the ground spin state.
3 Experimental Apparatus and Techniques

![Graph](image)

Figure 3.10: Calibration of (a) delay between start of readout laser pulse and readout window and (b) duration of readout window for a balance of contrast and SNR. Whilst reducing readout window duration improves contrast it also reduces photon counts, reducing SNR. A balance between the two based on this information was found at a readout window of 300 ns.

Unlike the case of ESR measurements of ensembles in silicon, the NV centre spin must be read out in the eigenbasis of the $S_z$ operator, meaning that the state must always be projected onto the $z$-axis of the Bloch sphere. The microwave sequences used are thus similar to those used for ensemble measurements, but when the component of the state in the $x-y$ plane is required (as in a coherence decay measurement), the measurement finishes with a $\pi/2$ pulse before the laser readout.

A final measurement performed in this work is an autocorrelation or g2 measurement, used to determine if measured fluorescence is sourced from a single quantum emitter. The fluorescence collected is passed through a beam splitter onto two separate paths, each of which are connected to a different single photon detector. The timetagger is used to count photons from both and the time differences between arriving photons on the two channels are recorded and binned. A quantum emitter should only emit a single photon at any one time, meaning that fluorescence sourced from a single NV centre is unable to cause photons to arrive at the same time at both detectors. As a result a histogram of time differences should show no events with 0 time difference — a $g^{(2)}$ dip. In reality, background fluorescence and noise make a dip reaching zero highly unlikely, and a dip
3.4 Optically Detected Magnetic Resonance

below 0.5 on a fluorescence normalised graph is usually taken as indicative of a single emitter.
4 ILLUMINATION INDUCED DECOHERENCE OF PHOSPHORUS DONORS IN SILICON

Lights flicker from the opposite loft
In this room the heat pipes just cough
— Bob Dylan, Visions of Johanna

Successful integration of qubit platforms based on optically addressable spin qubits such as NV centres in diamond and divacancy centres in silicon carbide requires an understanding of how optical readout techniques impact the coherence times of donors in silicon. Studies in the past have focussed on the impact of illumination on relaxation, but have not shown detailed results on the impact on coherence, which is typically the limiting factor for quantum operations. This chapter examines this impact from light at different wavelengths and powers close to the silicon band gap energy. The sample used for all experiments in this chapter is a 1.5 × 1.5 × 10 mm natural silicon sample with 5% abundance of $^{29}$Si nuclei, doped with phosphorus to a concentration of $6 \times 10^{15}$ cm$^{-3}$. In all cases measurements are performed on the electron spin of the phosphorus donor. Illumination is applied via a Toptica DL Pro laser, tuneable between 1058 nm and 1080 nm.

4.1 Initial Measurements

Measurements on the impact of illumination in this chapter were performed at two temperatures, 8 K and 7 K, with $T_1$ at these temperatures found to be 2.8 ms and 32 ms
Illumination induced decoherence of phosphorus donors in silicon

Figure 4.1: Measurements of (a) $T_1$ via inversion recovery and (b) $T_2$ via Hahn echo. $T_1$ measurement shows a characteristic simple exponential recovery of echo signal, giving a $T_1$ time of 2.8 ms at 8 K. $T_2$ measurement shows a stretched exponential decay, which is characteristic of natural silicon and is caused by spectral diffusion caused by the $^{29}$Si bath. $T_2$ is found to be 240 μs.

respectively. $T_2$ at both temperatures was found to be 240 μs, indicating that 8 K is a sufficiently low temperature for $T_1$ to have no limiting effect on $T_2$. Figure 4.1 shows example measurements of $T_1$ and $T_2$ at 8 K, with a characteristic single exponential decay/recovery seen in the inversion recovery measurement of $T_1$ and a stretched exponential observed in the $T_2$ measurement. This stretched exponential shape indicates spectral diffusion and is a sign that the coherence of the electron spin is limited by coupling to the $^{29}$Si spin bath.

Measurements of $T_1$ and $T_2$ under laser illumination were taken at three different wavelengths: 1058 nm, 1070 nm and 1080 nm. The first observation made when taking these measurements is the impact on the shape of the inversion recovery when recording $T_1$. Whilst a simple exponential decay is sufficient to fit the signal recovery when tested in the dark, when under illumination the recovery exhibits a strongly biexponential shape, as shown in figure 4.2(a).

Of the two time constants, one is observed to be significantly longer than the other and figure 4.2(b) shows how the two change with power at illumination of 1070 nm.
4.1 Initial Measurements

Figure 4.2: Figure (a) highlighting the biexponential nature of inversion recovery for the spin ensemble when under illumination. The measurement here was recorded whilst the sample was at 8 K and under illumination from laser light at 79 mW and 1070 nm. (b) shows how the two time constants of the biexponential fit applied to $T_1$ measurements at 1070 nm vary with power. The shorter of the two follows a fixed power-law relationship of $T_1 \propto 1.1^{0.66}$. The slower of the two time constants is observed to vary with power but much less significantly and saturation behaviour is observed at lower powers.

The shorter of the two time constants follows a constant power-law relationship with laser power, whilst the longer is significantly less affected and saturates at powers below 10 mW. The cause of this biexponential decay is thought to be caused by the large size of the sample relative to the laser spot. The laser spot itself is approximately $1.5 \times 1.5$ mm, meaning that it only impacts on a part of the sample. The area of the sample that is not directly illuminated by the laser is expected, therefore, to be affected differently to the region of the sample that is directly illuminated. The nature of bulk ESR measurements mean that both regions contribute to the final signal and lead to the observation of two distinct relaxation rates. To best infer the action of the laser on the spins, I focus on the shorter of the two relaxation times as this is anticipated to best describe the effect of direct illumination.
4 Illumination induced decoherence of phosphorus donors in silicon

![Graph showing the relationship between T^-1 and power for different wavelengths.](image)

Figure 4.3: How power and wavelength affect the measured electron $T_1$. Wavelengths of 1058 nm have photon energies approximately equal to the silicon band gap energy and are thus expected to have a greater impact on $T_1$ than longer wavelengths, as is shown in this graph. The fits on this graph are according to $\frac{A}{\tau^{\alpha}}$, with $\alpha = 0.73, 0.68$ and 0.68 in order of increasing wavelength.

4.2 High Power Wavelength Effects

4.2.1 Relaxation Effects

Measurements comparing the effect of laser power on $T_1$, $T_2$ from a Hahn echo sequence, and $T_2$ from a 4 pulse dynamical decoupling sequence were taken at wavelengths of 1058 nm, 1070 nm and 1080 nm. At 1058 nm, the photon energy is approximately equal to the silicon band gap energy, meaning that absorption is expected to be higher and the impact on the electron spin properties greater. The generation of free-carriers in the silicon conduction band is thought to be the dominant effect on the relaxation times [44], so the longer wavelengths are expected to have a reduced impact as photon energies are below the silicon band gap.

Figure 4.3 shows the measured $T_1$ for these wavelengths at powers between 10 mW and 130 mW. These also show a line fit according to $\frac{A}{\tau^{\alpha}}$, with the rationale behind this
4.2 High Power Wavelength Effects

relationship being that $T_1$ is inversely proportional to the photon flux, which in this setup power is a proxy for. The value of $\alpha$ for each wavelength is 0.73, 0.68 and 0.68 for 1058 nm, 1070 nm and 1080 nm respectively. This does demonstrate a marked difference in the impact on $T_1$ for above and below band-gap photon energies. $T_1$ is however still significantly reduced even in the case of below band-gap illumination, with an apparently stronger dependence on power than on wavelength. The lack of a stronger difference between the above and below band gap illumination may well be a function of silicon’s indirect band gap — for an electron to be excited at this photon energy would require that the transition is phonon assisted as a significant gain in momentum is required in addition to the energy change. As photon energy increases the effect would be expected to become more significant as the direct band gap energy of silicon is crossed. Furthermore, the presence of band tail states that are capable of absorbing photons at longer wavelengths can lead to greater effects at below band gap photon energies than might be expected otherwise.

4.2.2 Decoherence Effects

Although the impact of illumination on donor relaxation rates is relatively well studied [44], the effects on decoherence rates are not well known. The mechanisms of decoherence were discussed in detail above and most significant for spin decoherence is the presence of magnetic field noise. As illumination creates free carriers in the electron conduction band it is possible that they would contribute a source of extra noise that would reduce $T_2$ beyond the limitations of the reduced $T_1$.

Figure 4.4 shows measurements of $T_1$ and $T_2$ vs power for 1058 nm and 1070 nm. There is a clear drop in $T_2$ at high powers, and it appears that $T_1$ becomes strictly limiting at powers above 30 mW. More interestingly, $T_2$ is observed to decline even at lower powers when $T_1$ is still above the dark $T_2$ value of 240 $\mu$s. It’s also clear from this graph that $T_2$ is beginning to saturate towards its dark value as laser power is reduced. To better understand this a second set of measurements were carried out at low laser power, with results shown in figure 4.5. This figure shows the reduction in $T_2$ begins at powers of approximately 1 mW, when $T_1$ is still measured at approximately 1 ms, $4 \times$ the dark $T_2$ value. This behaviour is also observed in the $T_2$ measured with a 4-pulse CPMG
sequence, though an increase in $T_2$ for this sequence over the Hahn echo sequence is observed until both sequences are strictly $T_1$ limited.

The cause of this reduction could potentially come from two sources, the first is an additional effect on decoherence over relaxation caused by the impact of laser illumination. Whilst this is possible, there is a lack of a marked difference between the impacts of 1058 nm illumination and 1080 nm illumination, with the difference in recorded $T_2$ very small, and within the margin of error of the laser power values and coherence decay fits. This lack of differentiation suggests that the effect is not being caused by a mechanism that differs strongly between the two wavelengths. As we expect a reduction in the number of free carriers as wavelength increases, this suggests that this mechanism may not be responsible. The second explanation for this effect is the action of reduced $T_1$ via the indirect $T_1$ of neighbouring donors, as described in section 2.1.6 above.

To further explore the effects of illumination on relaxation, I now examine results on relaxation times under illumination at 7 K.
4.3 Temperature and Relaxation

For better understanding of the mechanisms behind the results seen so far, the experiments above were performed at 7 K. The first expected result is that the observed saturation of $T_1$ will occur at lower laser powers, as there is the higher dark $T_1$ value of 32 ms. What is of particular interest is how the $T_1$ behaves in cases that the laser power is having a strong effect — where there is a significant reduction in $T_1$ at both temperatures.

Figure 4.6 shows the effect of laser power on relaxation time for 1058 nm illumination and at 8 K and 7 K. Immediately obvious is the clear difference in the $T_1$ time even in cases where the laser has a strongly limiting effect. At 30 mW in the graph, the $T_1$ is reduced by more than an order of magnitude for both temperatures but there is a difference in the value of $T_1$ of approximately 30%. If the mechanism of relaxation was temperature independent we might expect the $T_1$s to be the same in this high power regime. That they are not suggests that temperature may have an impact.
Figure 4.6: How relaxation rate is affected by laser power at 1058 nm for two different temperatures: 8 K and 7 K. Of note is the clear distinction in relaxation rate for the two temperatures, even where the laser is having a strong effect and the $T_1$ is reduced below 100 μs.
4.3 Temperature and Relaxation

4.3.1 Heating induced relaxation

Heating of silicon at cryogenic temperatures by light of below band gap photon energies has typically been regarded as a minor effect [97]. Judging how much heating may be caused by the laser in this case is challenging, as any change in temperature would be small and not recognised by the cryostat thermometer. However, from the Debye model we can infer that at this low temperature the heat capacity of silicon will be significantly reduced and as a result large temperature shifts can occur as the result of very small changes in the heat energy of the silicon sample. The poor photo-emitting characteristics mean that electrons absorbing photons tend to relax via phonon emission into the lattice, causing heating. The absorption characteristics of silicon at low temperatures are not well studied, with assumptions being that it is virtually transparent to below bandgap wavelengths as there are few phonons to assist in free carrier creation. One of the few studies into this focussed on the potential use of low temperature silicon as part of a gravitational wave detector — making use of this anticipated transparency [97]. Instead it was discovered that for bulk silicon at 6 K, it had an absorption coefficient of 0.030 cm\(^{-1}\) for light at 1550 nm. Whilst not identical to the system explored here, it allows for an estimate of approximately 0.5% of incident laser light being absorbed by the sample. Whilst the sample in the referenced study was found to increase in temperature as long as it was illuminated by laser light, the conditions were somewhat different, with a weak thermal coupling to its cool apparatus. It is likely that in this case of a helium flow cryostat a steady state of the system will be reached. To estimate the total heat retained in the sample, we can compare the measured \(T_1\) values with the temperature that would be expected to produce those measurements. Doing this gives a figure of approximately 1% of the laser energy being retained in the sample whilst the laser is on, which tallies well with the figures referenced.

The heat capacity of silicon and its dependence on temperature is relatively well understood, so these figures can be used to produce estimates of \(T_1\) and \(T_2\) whilst assuming the presence of this heating mechanism [98, 99] and using the equations described in section 2.1.6. In addition to the heating contribution to \(T_1\) we take into account the effect of donor ionisation on relaxation. Direct donor ionisation appears as a relaxation process in the measurements taken here — an electron is ionised to the conduction band, with its
ESR signal therefore lost, before relaxing back to the thermal equilibrium of the system. The cross section of direct donor ionisation is small — it peaks at $17 \times 10^{-15}$ cm$^{-2}$ but at the wavelengths used here is closer to $1.5 \times 10^{-16}$ cm$^{-2}$ [100, 101].

Figure 4.7(a) shows the simulated $T_1$ and $T_2$ values for laser power based on heating and donor ionisation, based on the assumptions above. The simulations here do not provide a perfect description of the results observed, with the results matching experiment relatively well in the low and intermediate power regime, but predicting significantly higher rates of relaxation at powers above 30 mW. The results do suggest that the $T_1$ reduction is sufficient to account for the observed increase in decoherence rate at the intermediate power region. The significant increase in relaxation rate relative to experiment times at higher powers may suggest that as heating increases, the cryostat begins to compensate via a reduction in its own heater power.

### 4.4 Summary and Future Work

The results obtained here provide some insight into the anticipated impact of laser illumination on relaxation and coherence times of donors in silicon. A biexponential inversion recovery is observed when the sample is under illumination, suggesting that the
4.4 Summary and Future Work

impact of illumination is restricted to the area of the sample that is directly addressed by the laser. The effect of illumination is shown to be reduced once the laser wavelength is increased to give photon energies that are below the silicon bandgap, as observed in the relaxation times for 1058 nm illumination and 1070 and 1080 nm illumination. The difference observed is less sharp than may be expected which is potentially a result of the indirect silicon bandgap — with the low temperature meaning that phonon assisted transitions are less common.

At low powers the reduction in $T_1$ and $T_2$ is observed to saturate to the values in the dark as expected. The $T_2$ reduction at high powers is limited by $T_1$ but at intermediate powers the $T_2$ begins to reduce even whilst $T_1$ is still significantly higher than the dark $T_2$ value of 240 μs. This additional effect appears to be well explained by the effect of reduced $T_1$ of neighbouring donors — as explained in section 2.1.6, but may indicate an additional source of decoherence caused by the laser illumination.

Reducing temperature from 8 K to 7 K causes an increase in $T_1$ at a given laser power, suggesting that a heating mechanism may be a component of the observed $T_1$ reduction. Simulations were carried out based on information about the absorbance characteristics of silicon and its expected specific heat capacity at low temperature to estimate the $T_1$ and $T_2$ impact of increasing temperature. These simulations were found to agree moderately well with observed behaviour but showed an increased effect at higher powers than was observed.

Two avenues of investigation present themselves to further this work: the first is to better understand the mechanisms that cause the observed effects, the second is to expand the wavelength region investigated to better understand the impacts at the typical wavelength range of NV centre experiments.

To investigate the mechanisms of these observations better, two experiments present themselves. To investigate the heating mechanism, a simple investigation could be carried out by performing experiments at a fixed temperature but with a varying amount of cryostat cooling power. This can be achieved by increasing the flow of helium to the cryostat, requiring greater power to the PID controlled sample heater. Sample temperature can be monitored and kept constant via measurements of $T_1$ in the dark. Were increased cooling power at the sample to lead to increased $T_1$ under laser illumination,
Illumination induced decoherence of phosphorus donors in silicon

even at equivalent dark $T_1$ values, then that would strongly imply heating as a relevant mechanism. Conversely, measurements of carrier density, potentially using sample conductivity as a proxy, could reveal whether free-carrier creation is a significant effect and give insight into how that changes with wavelength and power.

Investigations into the impact of laser power at significantly higher photon energies, such as those found in would be of great interest. As the effects are likely to be much stronger, a key question is how quickly the effects dissipate. Standard readout techniques of the NV centre require laser pulse lengths of 5 μs, and are likely to have a significantly different impact than the CW illumination used in experiments here. A shorter pulse time will likely mitigate the impacts of the shorter wavelengths but to what extent requires further investigation.
5 Temperature Dependent characteristics of single NV centres in nanopillars

Early one morning the sun was shining
I was laying in bed
Wondering if she’d changed at all
If her hair was still red
— Bob Dylan, Tangled Up In Blue

5.1 Sample Study and Characterisation

5.1.1 Diamond Pillar Sample

The sample used primarily in this chapter is a diamond sample, provided by the group of Professor Ania Jayich (UC Santa Barbara). The sample is a 26 µm thick grown piece of diamond implanted with $^{14}$N at a dose of $5 \times 10^{10}$ cm$^{-2}$ and with a 15 keV implantation energy. This was expected to give an average NV centre depth of 20 nm with a spread of 6 – 7 nm. After implantation and annealing, the sample was etched to give grids of nanopillars with a tip diameter of approximately 400 nm and prominence of approximately 800 nm. Figure 5.1 shows SEM and light microscope images of the sample. The SEM close up image shows the pillar dimensions whilst the widefield light microscope gives an impression of pillars grids and alignment markers, the dark rectangles below the pillar fields.
5 Temperature Dependent characteristics of single NV centres in nanopillars

(a) (b)

Figure 5.1: The diamond pillar sample: (a) SEM image of the pillars in the sample with markers of diameter and height, provided by UCSB. (b) shows an image taken using a room temperature spherically corrected objective, with two pillar arrays visible along with alignment markers.

The purpose of this sample was initially for calibrating the confocal microscope setup and confirming its ability to detect single NV centres and to control their spin state. The reason for using near-surface NVs embedded in diamond pillars was to provide a system that was analogous to the scanning diamond probes that would be used in the AFM tip setup. The large number of available probes would allow for a representative study of NV characteristics to be performed and for the system to be adapted as needed.

For this study, the sample was attached to a pcb with microwave capabilities and a copper wire was soldered across the sample close to the pillar arrays as described in section 3.4.1. This was attached to the top of the Attocube sample stack and inserted into the cryostat with the tip stack not included for operational simplicity.

5.1.2 NV CENTRE IDENTIFICATION

The first challenge for studying a collection of NV centres was to identify a region of the sample that had a good number of centres within the scanning range of the AFM sample stack. This would allow for automated measurements to be performed sequentially on a
series of selected NVs as the interferometric positioning system of the AFM would allow for each to be returned to deterministically. Whilst several regions of the sample showed only background fluorescence, a suitable section was identified with a large number of pillars showing the likely presence of NV centres.

Figure 5.2(a) shows a confocal fluorescence scan of a promising area of the sample. To verify the presence of NV centres, CW ODMR was performed at the NV centre zero-field-splitting frequency of 2.87 GHz, shown in figure 5.2(b). The reduction in fluorescence at this frequency is a clear indicator of the presence of an NV centre. Figure 5.2(c) shows an autocorrelation (g2) measurement to assess how many emitters are causing the fluorescence. The characteristic dip in the centre (anti-bunching) indicates the presence of a small number of emitters — thought the dip to 0.6 suggests that there is more than one [102, 103, 104]. The peaks at either side of the dip, which become more prominent at higher powers, are indicative of photon bunching. Under strong laser illumination, where the NV centre has a high chance of being excited again very shortly after decaying to the ground state, there is a higher probability of sequentially detected photons being separated by the lifetime of the excited state. At lower powers the NV centre is less likely to be excited and so this effect is less prominent.

With the presence of NV centres verified, the next step was to perform magnetic field alignment. This is performed by applying a small magnetic field, 5 mT in this case, with the vector magnet and performing a CW ODMR measurement once again. The central ODMR dip is then split into two, caused by the splitting of the $|m_s = \pm 1\rangle$ states. The splitting between the peaks only matches the frequency expected from a given magnetic field (given by $\nu = 28 \cdot 10^9 \cdot B$) when that field is aligned with the NV centre axis. An off axis magnetic field also causes a reduction in the contrast between the $|m_s = 0\rangle$ and the $|m_s = \pm 1\rangle$ states due to state mixing, meaning that the spin number no longer represents a good quantum number and thus are no longer eigenstates of the field. Due to the crystal structure, once the magnetic field has been aligned to one NV centre subsequent alignments become significantly easier as they can be in only one of the four orientations described earlier. In addition, the magnetic field measurements provide a further check on the number of defects contributing to illumination, as there is only a $1/4$ chance that two NV centres being examined are aligned. With the ODMR dip splitting and contrast
5 Temperature Dependent characteristics of single NV centres in nanopillars

Figure 5.2: Verifying NV centre presence: (a) a confocal fluorescence map of a grid of diamond nanopillars with suspected NV centres. (b) shows CW ODMR performed on the indicated NV centre with a characteristic dip in fluorescence at 2.87 GHz, indicating that the emitter is an NV centre. (c) shows a second order autocorrelation measurement on the emitter (usually termed a ‘g2’ measurement) to verify whether or not it is a single emitter, performed at two laser powers. The central dip in the centre is caused by anti-bunching and is indicative of a small number of emitters, whilst the peaks either side are caused by bunching and are determined by the excited state lifetime of the NV centre.
optimised for a given field magnitude the magnet could then be further calibrated against this splitting to give the expected frequency difference of 14 MHz between zero-field dip and 5 mT field dip.

Figure 5.3(b) shows the results for CW ODMR at an aligned magnetic field of 5 mT. Most obviously, the high field dip is shown to have significantly lower contrast than the low field dip. This is due to the transmission characteristics of the microwave apparatus, which shows significantly reduced transmission above 2.98 GHz. For this reason, experiments were conducted at the low field transition — $|m_s = 0\rangle \rightarrow |m_s = -1\rangle$, which act as the $|0\rangle$ and $|1\rangle$ states respectively.

Figure 5.3: Standard measurements of NV characteristics. (a) ODMR at zero-field and high and low field lines at 5 mT aligned to the NV axis. (b) Rabi oscillations driven between $|m_s = 0\rangle$ and $|m_s = -1\rangle$ states, with fit showing fluorescence contrast and $\pi$ pulse length. (c) a coherence decay measurement, with interaction between central NV and $^{13}$C bath clear in loss and recovery of coherence. (d) the Fourier transform of the coherence decay, showing the frequency of oscillation of the $^{13}$C bath [105].
Figure 5.3(b) shows the results for performing a measurement of Rabi frequency on the NV centre, showing the oscillation between the two states as pulse length is increased. The data is then fit with an exponentially decaying sinusoid to calculate the contrast, which here is 12.5% and $\pi$-pulse length of 73.0 ns. The decay in oscillation amplitude is due to the dephasing of the spin equivalent to the $T_2^\ast$.

Figure 5.3(c) shows a Hahn echo coherence decay measurement, performed by initialising the state and then projecting it into the $x-y$ plane and allowing it to decohere before inverting with a $\pi$ pulse after time $\tau$ and finally projecting onto the $z$-axis with a final $\pi/2$ pulse. The decay is shown from 1 to 0.5 as the sequence is performed by first projecting the state onto the $|0\rangle$ state with a positive $\pi/2$ pulse before the sequence is repeated but finishing with a negative $\pi/2$ pulse to project the state onto the $|1\rangle$ state. This allows the final graph to be plotted as the decay of the state vector from an initial $|\text{plus}\rangle$ state to a maximally mixed state. Whilst the state remains coherent, it can be projected using a pulse sequence back into the $|0\rangle$ or $|1\rangle$ state deterministically. After it has decohered, it is found in one state or the other with $p = 0.5$, meaning that average fluorescence of the mean of the fluorescence from each state.

The graph in figure 5.3(c) does not decay in a simple exponential, but instead decays rapidly initially before recovering, decaying again and recovering again. This is due to the interaction of the NV centre with the $^{13}$C bath of the diamond. The $^{13}$C nucleus has a spin $\frac{1}{2}$ and a gyromagnetic ratio of approximately 10 MHz/T. This nucleus precesses in the applied magnetic field at its Larmor frequency, creating magnetic noise at that frequency. When the $\tau$ value of the Hahn echo sequence is equal to half the time period of the $^{13}$C noise then the spin flip caused by the sequence maximises the impact of the noise rather than mitigating it. The result is that at these frequencies the NV spin rapidly decoheres — as is indicated by the sharp dips to 0.5 on the graph. At a magnetic field of 5 mT, the $^{13}$C bath is expected to precess at 50 kHz, giving a maximum interaction at a $\tau$ value of 10 $\mu$s, or a $2\tau$ value of 20 $\mu$s, which is shown on the graph. This can be further confirmed by performing a fast-Fourier-transform (FFT) on the coherence decay, which is shown in figure 5.3(d).
5.2 NV Selection

To measure the spin coherence time, the troughs in the coherence decay are neglected and a stretched exponential decay is fit to the peaks of the graph, as is shown in figure 5.3. Doing this returns a decay constant ($T_2$) of 67.2 $\mu$s.

With the presence of NV centres verified and the key ODMR sequences tested and working, the next step in this experiment was to select a group of NVs whose characteristics could be tested at a variety of temperatures.

5.2 NV Selection

Due to their excellent quantum properties at room temperature, with long $T_1$ and $T_2$ times relative to other qubits, with between 60 $\mu$s and 350 $\mu$s achievable at room temperature [34, 106], NV centre properties at low temperatures remain relatively unstudied. This is particularly true for near-surface NV centres in unusual structures such as the pillar sample used in this chapter and the diamond AFM probes used in the next chapter. To better understand this regime, we conduct an analysis of the properties of several NV centres from 100 K down to 5 K focusing on NV centre count rate, contrast and $T_2$ times.

5.2.1 Field Choice

The NV centre selection process involved first identifying a field of NV centres that were within the range of the AFM sample stage scanners from the 100 K high temperature measurement to the 15 K low temperature measurement, where range is reduced to 20 $\mu$m. Additionally, a large number of candidate NVs was required due to experience with several nanopillars having multiple NV centres present, and with count rate not being a reliable metric for NV number. Figure 5.4 shows the chosen field, along with a closeup image of a single nanopillar. The fluorescence profile of the nanopillar is also shown, the gaussian shape is a function of the shape of the laser spot rather than the fluorescence source itself (which in the case of the NV centre is point-like). When fit with a Gaussian this profile has a standard deviation of 640 nm, indicating a beam size very close to the diffraction limited spot size as described in section 3.3.2.
5 Temperature Dependent characteristics of single NV centres in nanopillars

A cut off count rate was selected at 40 kC/s, so as to maintain a reasonable balance between experiment time and SNR. In the field of pillars shown in figure 5.4, 35 pillars had this property. The positions of these were recorded and the AFM set up to move between them in sequence, performing a $g^{(2)}$ measurement at each.

5.2.2 $g^{(2)}(0)$ Measurements

Figure 5.5 shows the results of the $g^{(2)}$ measurements on each of these NVs, with (a) showing the distribution of $g^{(2)}(0)$ values — the minimum value of the $g^{(2)}$ dip. To be reasonably confident that NVs selected were in fact single, NVs with $g^{(2)}(0) > 0.45$ were not included in further measurements. Figure 5.5 compares the count rate of each NV centre measured to its $g^{(2)}(0)$ value, with the selected NVs shown in dark blue. Of interest is the seeming lack of relationship between the two characteristics in the case of the centres with $g^{(2)}(0) > 0.5$ whilst there is a clear reduction in $g^{(2)}(0)$ as counts increase in the case of NV centres with initial $g^{(2)}(0)$ values below 0.5. This is in line with the expectation that there is a relatively consistent amount of background counts contributing to the autocorrelation measurement, meaning that a reduced $g^{(2)}(0)$ value is obtained as base counts increase.

After selecting ten NVs based on these values, the magnetic field alignment of each was required for pulsed ODMR experiments. This was performed as described above. During alignment three further NVs were discarded, leaving a total of 7, due to extremely poor contrast in two cases and the splitting of the ODMR dip in the final case — suggesting that the NV was not in fact single. The relatively high $g^{(2)}(0)$ value of 0.44 indicated that this was likely.

5.3 Temperature dependence of NV characteristics

5.3.1 100 K Measurements

100 K was chosen as the starting measurement temperature and I detail here the three experiments carried out at each temperature and their associated characteristics that are monitored, shown in Figure 5.6. First is a CW-ODMR sequence, shown in Figure 5.6(a),
5.3 Temperature dependence of NV characteristics

Figure 5.4: A confocal image of the field of nanopillars used for temperature dependence measurements of NV properties. (a) shows a wide-field scan of the region, which contains 35 nanopillars exhibiting greater than 40 kC/s. (b) shows a close up of one of the nanopillars and (c) shows the fluorescence profile of the pillar — giving the beam shape of the laser spot. The width of this profile of approximately 800 nm shows a beam size close to the diffraction limit.
5 Temperature Dependent characteristics of single NV centres in nanopillars

Figure 5.5: $g^{(2)}(0)$ distributions: (a) the $g^{(2)}(0)$ distribution of the 35 selected pillar fluorescences and (b) the relationship between counts and $g^{(2)}(0)$, NVs with $g^{(2)}(0) < 0.45$ were selected for study and these are marked in dark blue on (b). The orange line provides a guide for the eye as to the relationship between count rates and $g^{(2)}(0)$ value. As might be expected as count rate increases, $g^{(2)}(0)$ decreases commensurately, as the classical contribution of background counts has a smaller effect on the $g^{(2)}(0)$ value.

This is performed at each temperature and at each NV centre to verify that the correct pulse frequency is being used, which varied slightly between different NVs and varies with temperature. In addition, the measurement provides a reference for expected results for contrast when measured with Rabi oscillations. Were a significant reduction to be observed in the Rabi experiment, then this would be an indication of potential issues with the experiment.

Secondly and as shown in Figure 5.6(b), Rabi oscillation frequencies for each NV were measured giving values for both the expected $\pi$-pulse length for each NV centre as well as the fluorescence contrast for each NV. From the data, it is clear to see that there are two distinct Rabi frequencies for the NV centres. Two of the NV centres have a $\pi$-pulse length of between 95 ns and 100 ns, whilst the remaining five have $\pi$-pulse lengths distributed between 160 ns and 190 ns. This is readily explained by the alignment of the NV centres relative to the driving microwave field. The fast NVs both are oriented in the $[\bar{1}1\bar{1}]$ orientation whilst the other NVs belonged to the $[\bar{1}1\bar{1}]$ orientation. Whilst the $B_z$ field due to the copper wire is not exactly uniform, it may be assumed to be approximately in-plane at the distance of the NVs from the wire of 200 $\mu$m. The angle of the field to the NV centre axes would lead to approximately a doubling of the field's projection.
in the transverse axis of the NV centre. As the \( \pi \)-pulse length is directly proportional to the NV’s Larmor precession frequency about this field, this tallies well with the observed differences. The variations in \( \pi \) pulse length can be attributed to the driving field inhomogeneity and also to the potential for the distinctive structure of the sample to lead to local variations in the spin orientation.

Figure 5.6(c) shows the measurements of \( T_2 \) for each of the NV centres via Hahn echo decay. A high resolution measurement of coherence decay, where both coherence troughs and revivals are visible as in figure 5.2(c), is extremely time consuming so measurements are taken so that the time-vector coincides with the revivals of the NV centre from interaction with the \(^{13}\text{C} \) bath, as these are the points to which a stretched exponential is fit to give the expected \( T_2 \). This serves to keep experiment times reasonable, which would otherwise stretch to many days at each temperature. The measured \( T_2 \)s for all of these NV centres is relatively long for near-surface defects, varying between 230 \( \mu \)s and 420 \( \mu \)s and suggests that their distance from the surface may in fact be greater than the \( \approx 20 \) nm previously assumed. A study by Wang et al used etching to precisely control the depth of an NV centre, showing that an initial \( T_2 \) of 234 \( \mu \)s at 55 nm depth declined to 80 \( \mu \)s at a depth of 9 nm \[107\]. The \( T_2 \) was observed to saturate towards its bulk value below 30 nm depth, the approximately 20 nm implantation depth was anticipated to have a 7 nm spread for this sample, so NV centres at the edge of that range might well be expected to have \( T_2 \) values close to those measured here.

### 5.3.2 Temperature Variation of NV Characteristics

Measurements of each of the features described above were taken at: 100 K, 70 K, 55 K, 40 K, 25 K and 15 K.

#### \( \pi \)-Pulse Variation with Temperature

Figure 5.7 shows the measured \( \pi \)-pulses for each of the measured NV centres and how they varied with temperature. Due to the two groups of pulse lengths, one approximately twice as long as the other, expanded views of both are shown for added clarity. Additionally, the mean values at each temperature are shown in orange. Clear from both groups is
5 Temperature Dependent characteristics of single NV centres in nanopillars

![Graphs](image)

Figure 5.6: Figures showing the three measurements used for comparing NV characteristics between 100 K and 15 K, with each colour representing a different NV centre. (a) shows CW-ODMR, (b) shows Rabi oscillations for contrast and $\pi$-pulse measurements, (c) shows a coherence-decay measurement, and (d) shows the count rates for each NV centre. (a) was used mainly as a fine-tuning of the ODMR frequency at which to perform experiments to account for potential variations from NV to NV. Rabi oscillations were used to calculate both $\pi$-pulse length and contrast of the NV, from the graph it is clear that there are two distinct rabi frequencies — accounted for by the NV crystal alignment. (c) shows the measurement of $T_2$ via a Hahn echo, with time vector chosen to coincide with the peaks of the $^{13}$C recoveries, thereby reducing experiment time.
5.3 Temperature dependence of NV characteristics

a reduction in $\pi$-pulse length by approximately 10% between 100 K and 40 K and saturation thereafter. The likely explanation of this is the reduction in resistance for the copper wire delivering the microwaves to the spins, whilst microwave power was kept constant. This would lead to an increase in the current flow in the wire and a commensurate increase in the magnetic field experienced by the spin. The effect appears to saturate at approximately 40 K, with no further reduction in $\pi$-pulse length observed. This appears to be in line with the expected behaviour of the copper resistivity at these temperatures. The copper wire used has a residual resistivity ratio (RRR) of approximately 40, which from results in [108] would suggest that resistivity would indeed stop declining with temperature between 35 K and 45 K.

$T_2$ variation with temperature

Figure 5.8 shows the variation in $T_2$ time for each NV centre with temperature. The error bars for the stretched exponential fitting are relatively large due to the reduced signal to noise ratio for this experiment. Nevertheless, it is clear from the graph that there is no obvious pattern for $T_2$ variation with temperature in this regime. The mean values show some inconsistent variation with temperature but this is within expected error for the small number of NV centres measured. In itself this is good news — $T_2$ time is one of the key metrics for magnetic field sensitivity of NV centres and a significant reduction in it with temperature would be a serious issue for the prospect of detecting and interfacing with spins in silicon that require temperatures below 15 K for non-limiting $T_1$ times. the $T_2$ results are also interesting in the context of the impact of temperature on both the NV’s contrast and count rate, which I address now.

Contrast and count variation with temperature

Figure 5.9 shows the variation in contrast (a) and counts (b) for each NV centre with temperature, including the mean value for each displayed in orange. Unlike the case of $T_2$, which showed little temperature dependence, both contrast and count rate show a reduction in their values between 100 K and 40 K. Contrast is reduced by approximately 70% on average at 40 K, whilst count rate is reduced by 25% at the same temperature.
5 Temperature Dependent characteristics of single NV centres in nanopillars

Figure 5.7: How \( \pi \)-pulse length varies with temperature based on Rabi oscillation frequency. For clarity, expanded views are shown of the two different length regimes, fast and slow. The mean values at each temperature are shown in orange. When viewing a zoomed in view and when the average behaviour is examined, it is clear that there is a small reduction in \( \pi \)-pulse length between 100 K and 40 K, with an approximately 10% decrease in pulse length observed. The likely explanation for this is that as the copper wire delivering the microwaves is cooled, its resistance decreases, leading to higher currents for a given microwave power and therefore a higher \( B_1 \) field experienced by the spins.
5.3 Temperature dependence of NV characteristics

![Graph showing temperature dependence of NV characteristics](image)

**Figure 5.8:** Figure shows how the $T_2$ values of each NV centre change with temperature. There is no clear pattern that occurs across all NV centres and the relatively large error bars suggest that observed variations are plausibly explained by noise.

Somewhat surprisingly, both values then recover partially by 15 K, with contrast recovering to 80% of its original value and count rate to 88%.

The first potential explanation of the effect observed here is a shift in the alignment of the magnetic field, with off axis alignment having the effect of both count and contrast reduction. This could be caused by shifts in the alignment of the sample chamber and VTI as the temperature changes, with some reversal of changes occurring once the temperature is below 40 K. To verify this, we can make a comparison between the CW-ODMR measurements at 100 K and at 40 K, the two temperatures that show the greatest variation in NV characteristics. Were the magnetic field now off axis, this should be observed as a shift in the resonance dip in the ODMR spectrum, as the magnetic field projection in the NV centre axis would be reduced. Figure 5.10 shows the results for CW-ODMR performed at 40 K. The loss in SNR is clear, due to both contrast and count rate degradation, however there is no apparent shift in the resonant frequency of the spins. Fitting Lorentzians to the dips to get an estimate for central frequency shows an average frequency shift ranging between 0.5 and 3 MHz, a figure that is within the margin
5 Temperature Dependent characteristics of single NV centres in nanopillars

of fitting error in any case. Even taking the extreme of this range, this would equate to a maximum transverse $B_0$ field of approximately 0.5 mT. Tietjens et al show in [109] that a threefold reduction in contrast is not observed before transverse fields in excess of 10 mT are present. This is explained by the perpendicular Zeeman term in the Hamiltonian being significantly smaller than the parallel term and the zero-field-splitting term. As a result, the NV spin projection in $z$ remains a good quantum number and the spin has eigenstates in that basis. A transverse magnetic field large enough to cause significant reduction in counts and coherence — on the order of twice the magnitude of the experimentally applied magnetic field — would therefore have to be perfectly transverse to avoid producing a visible shift in the ODMR frequencies of the NV spins. Moreover, the studied spins have different alignments to the diamond lattice, making this mechanism extremely unlikely.

The lack of variation in $T_2$ is instructive — off axis magnetic fields are typically associated with strong reductions in $T_2$ due to the same mixing of spin levels mechanism that causes contrast and count reductions [110, 111, 112]. The work of Shin et al in [113], however, shows that in the case where the spin decoherence is dominated by coupling to the electron spin bath of substitutional nitrogen (P1) centres, rather than the $^{13}$C nuclear spin bath, then a transverse field acts to increase the $T_2$ time rather than decreasing it. The main decoherence mechanism of these near surface spins is electron effects at the surface, meaning that it is possible that transverse fields may have a limited effect on $T_2$. Nevertheless, the evidence I have presented above suggests that a transverse field is highly unlikely.

Given that the effect is observed to impact count rate and contrast but not coherence, the most likely explanation for the observations is changes in the NV charge state. As stated above in section 2.2.1, the NV$^0$ state of the NV centre has no observable magnetic resonance. In addition, the NV$^0$ defect emits fluorescence with a different spectral line shape than the NV$^-$ defect, with a ZPL at 575 nm, rather than 637 nm. The confocal setup used here is optimised for collection of NV$^-$ fluorescence and therefore includes a dichroic mirror that reflects wavelengths below 650 nm as well as a long pass filter that transmits above 650 nm. The NV$^0$, which emits a greater proportion of its fluorescence at shorter wavelengths, therefore causes a reduction in counts relative to the NV$^-$. In
5.3 Temperature dependence of NV characteristics

Figure 5.9: Contrast and countrate temperature dependence: (a), contrast variation for each NV centre with temperature and (b) overall count rate variation with temperature, in both cases the mean is shown in orange. In both these graphs there is an obvious pattern of reduction in count rate and contrast at approximately 70 K. Of particular interest is the subsequent recovery in both these values between 40 K and 15 K in the case of contrast and between 30 K and 15 K in the case of count rate. This is also clear in the mean values which show contrast reduced by approximately 70% of its value at 100 K when at 40 K, before it recovers to 80% of its 100 K value. Count rate shows a drop by approximately 25% of its 100 K value at 40 K before recovering to 88% of the 100 K value.
Temperature Dependent characteristics of single NV centres in nanopillars

Figure 5.10: CW-ODMR of the single pillar NVs at 40 K, for comparison with results shown in figure 5.6. Whilst the signal to noise in this case is significantly reduced, as a result of loss of counts and contrast at this temperature, there is no obvious change in the spin resonant frequency. This suggests that shifts in the static magnetic field are not a cause of the NV contrast and count loss observed.

addition, as these counts are from a spin exhibiting no ODMR contrast, this causes a reduction in the visible contrast of the measured fluorescence.

The phenomenon whereby the NV centre changes charge state, causing repeated changes in its fluorescence levels is known as 'blinking' [114, 115, 116]. Figure 5.11 shows a histogram of count rates for a single NV centre, measured at the same temperatures as in the rest of the study and also at 2 K with time bins of 1 ms. The figures show the reduction in counts as temperature is reduced from 100 K to 40 K and then a clear splitting into two modes of fluorescence — a bright and dim state. It is highly likely that this is a result of charge state switching of the NV centre. It is a feature particularly common in near-surface NV centres, due to the potential for the diamond surface to cause changes in the local electrical environment, making ionisation and subsequent trapping of the extra NV electron significantly more likely. Imperfections in the surface can lead to dangling bonds, which act as electron traps, as well as surface band bending caused by the surface termination.

How the diamond surface is terminated — the atoms that attach to the carbon dangling bonds at the surface — is an ongoing area of research and particularly relevant for near-surface NV centres, which many of the sensing based applications of NV centres rely on. Hydrogen terminated diamond surfaces result in upward band-bending and a
5.4 Summary

We have shown in this chapter a detailed study of the temperature dependence of the count rate, Rabi frequency, ODMR contrast, and $T_2$ of seven different single NV centres.
5 Temperature Dependent characteristics of single NV centres in nanopillars

![Histogram of NV centre count rates at different temperatures](image)

Figure 5.11: A histogram of NV centre count rates at temperatures between 100 K and 2 K. The reduction in count rate from 100 K to 40 K is obvious and shown clearly by figure 5.9. However, below 40 K the presence of two distinct modes of NV fluorescence is seen — one brighter and one darker. This 'blinking' is a feature of near-surface NVs and indicates transitions between the NV$^-$ and NV$^0$ charge states.

These NV centres are implanted in a sample that is highly analogous to the scanning probes that will be used for sensitive magnetometry and for potential spin-spin interaction. Although the contrast and count rate are shown to be reduced at 40 K, their recovery at 15 K bodes well for low temperature performance of the system.
Figure 5.12: Field sensitivity of NV centres (a) the maximum sensitivity of the pillar NVs measured in this study (b) the maximum distance at which they could be expected to detect a single electron spin given these parameters.

To get some idea of what NVs in probes with these properties would mean for detection of individual spins, figure 5.12(a) shows the calculated field sensitivity for each NV centre at 15 K. Figure 5.12(b) shows the expected maximum distance in \( z \) that an NV centre with the properties listed would be able to detect a single electron spin. For NVs 0, 1 and 6 this distance is over 30 nm, lending credence to the idea that this single spin detection is possible. The main cause of the sensitivity of these NV centres is their relatively long coherence times for surface NVs, this was discussed earlier and it is possible that they are as close as 20 – 30 nm from the surface, in which case they would be capable of sensing spins in silicon at a depth of up to 10 nm. With the potential to significantly extend coherence time using dynamical decoupling techniques, the field sensitivity and thus sensing distance and depth could be increased. Furthermore, these sensitivities are based off 1s of total measurement time. By increasing total measurement time \( t \) minimum field sensing improves by a factor of \( \sqrt{t} \) whilst maintaining the same SNR, allowing measurements at greater depths.

Further work studying samples such as this could enable a significantly better understanding of the processes at play and the behaviour of NV centres at low temperatures. Given that the hypothesised cause of the measured loss in both contrast and count rates is charge state switching of the NV centre, a more detailed study of blinking on several NVs, as shown in figure 5.11, would enable a more robust conclusion as to the significance of
5 Temperature Dependent characteristics of single NV centres in nanopillars

the effect. Better timing resolution might reveal state switching in the intermediate temperature regime of 40 K where reduction in count rate and contrast is observed but no bimodal distribution.

To better understand the surface chemistry effects that may be causing the charge state dynamics, the same experiments could be repeated with different surface treatments. The possibility of added stability of surface NV− due to fluorine termination has been discussed but there are further options, including nitrogen termination [37].
6 DIAMOND SCANNING PROBES

It's like déjà vu all over again.

— Yogi Berra

With the detailed study of the behaviour of near-surface NV centres in a pillar configuration complete, we now turn to examining the behaviour of NV centres in commercial diamond AFM probes, designed for simultaneous magnetometry and atomic force microscopy, with the view to studying single electrons bound to donors in silicon. Probes studied in this chapter are purchased primarily from one commercial source — Qzabre — with the studies on three of these probes forming the bulk of the work here.

The experiments were hampered by a very short lifetime of each probe once it had been cooled to cryogenic temperatures in the Attocube cryostat, with a loss of all ODMR signal observed over the course of the experiments, which I will address later. One of the central aims of future work in this area will be to determine how the effects observed can be mitigated and these diamond probes can be made stable enough for sustained measurements at low temperature.

6.1 QZABRE PROBES 1 AND 2 CHARACTERISATION

The first two probes examined were from Qzabre and were expected to show photon count rates in excess of 100 kC/s and CW-ODMR contrast in excess of 15%. These two probes were measured sequentially, with both ultimately experiencing very high count rates from the NV centre (>600 kC/s) and significantly diminished ODMR contrast.
6 Diamond Scanning Probes

6.1.1 AFM Performance

Whilst AFM performance is a secondary consideration when compared with the optical performance of the diamond probes, for scanning magnetometry to be implemented effectively the performance of the AFM must be sufficient to keep the probe in contact with the sample in order to maintain maximum magnetic field sensitivity. To examine the diamond probe AFM performance, we compare its scans of a silicon test sample that has been etched with ridge and checkerboard patterns with scans undertaken with a standard Akiyama AFM probe. Figure 6.1 shows a comparison of scans made by (a) the Akiyama probe and (b) the diamond probe.

![Image](image_url)

Figure 6.1: Measurement of an AFM silicon test sample marked with ridges and checkerboard patterns. (a) shows the results of measuring a checkboard region of the test sample with an Akiyama probe, whilst (b) shows the results of a measurement of a ridged section of the sample. Scans were carried out inside the Attocube cryostat at room temperature.

These scans can be analysed to give estimates for the effective mean noise of the tip. By selecting a smooth region in both scans we find that the scan performed with the Akiyama probe shows an average roughness (RMS deviation from the mean) of 660 pm whilst the Qzabre probe shows average roughness of 850 pm. This performance is well within the specifications of the instrument for both probes and is expected to approximately double at low temperatures where the cryostat vibration influences the performance. These test sample scans also allow for the estimation of the tip profile using the...
6.1 Qzabre probes 1 and 2 characterisation

![Figure 6.2: Predicted diamond tip shape and features, derived using blind estimation in the Gwyddion software package and using scans of a test sample [121].](image)

Gwyddion software package and the blind estimation algorithm developed by Jóźwiak et al [120, 121]. The results of doing this with the tip are seen in figure 6.2.

6.1.2 Probes 1 and 2: Fluorescence characteristics

Probes 1 Fluorescence

The fluorescence characteristics of the diamond probe were examined in a similar manner to the single NV centres in diamond nanopillars above, although in this case via tip scanning rather than sample scanning. Figure 6.3 shows measurements of the NV centre fluorescence along with the fluorescent images of the probe ‘petal’, which is the small piece of diamond on which the tip is fabricated. The chief difference in expected fluorescence in this system when compared with the diamond nanopillars examined above is the orientation of the tip — here the tips are illuminated from behind the sample with the tip facing away from the objective, the reverse of the pillar orientation. In this setup, the efficiency of NV fluorescence is expected to increase (i.e. lower laser power yielding the same fluorescence) as the pillar acts as a waveguide for the excitation laser. In addition, the NV centre fluorescence is expected to increase due to the pillar acting as a cavity to which the NV emission couples [122, 123, 124, 125]. Whilst typical NV collection efficiency is on the order of 3%, due to the emission of light in all directions and the high refractive index of diamond making internal reflection of photons more likely,
collection efficiency of NVs in diamond nanopillars is expected to be increased to up to 40%. Photon counts of 30 kC/s are expected for NVs in the diamond bulk, meaning that count rates in excess of 200 kC/s can be expected for NVs in nanopillars.

Figure 6.3(b) shows a confocal measurement of the tip fluorescence with the tip very clear in the centre of the image. Faint fluorescence around the outside is from the petal on which the tip is fabricated. The tip count rate is seen to be in excess of 620 kC/s, which is significantly higher than expected from the manufacturer specifications and from the reasonable expectation of a single NV, even one with enhanced emission due to a nanopillar. Figure 6.3 confirms the suspicions that the source of fluorescence is not an NV\textsuperscript{−} defect, with no ODMR signal visible. The tip was returned to Qzabre for measurement, with a contrast of approximately 2% identified, suggesting that an NV centre was still present. The cause of the significant increase in counts was unexplained however — the observed contrast of 2% would be well explained by a single NV emitting at 100 kC/s with a contrast of 15%, with some highly fluorescent background contributing to the excess 500 kC/s. Were this background to be dirt or similar contamination, it would be expected to bleach (reduce in counts) after long term exposure to laser light, however no such bleaching was observed. As no obvious explanation was available, we decided to move on to test the performance of the second available probe.

**Probe 2 Fluorescence**

The second Qzabre probe used was specified to have a contrast in excess of 15% and was mounted and measured via the fabricated sample as before. Figure 6.4(a) shows a confocal scan of this probe taken at room temperature, with an inset showing a close up of the pillar fluorescence. In this case the measured fluorescence is 110 kC/s, in line with specification and much closer to the expected fluorescence for a single NV centre. Figure 6.4(b) — (d) show NV saturation, \( g^{(2)} \) and CW-ODMR measurements respectively. The saturation curve is a measurement of the change in rate of NV fluorescence as laser power is increased — this is expected to saturate due to the finite lifetime of the NV excited state limiting its overall emission rate [126]. The \( g^{(2)} \) measurement suggests that this is not in fact a single NV centre, with a \( g^{(2)}(0) \) value of 0.6, higher than the typical cut-off of 0.5. The manufacturer suggested that this was not cause for immediate
6.1 Qzabre probes 1 and 2 characterisation

Figure 6.3: Figure shows (a) AFM scan of the fabricated silicon device used for application of microwave pulses and for magnetometry testing in this work, the wire imaged is intended for DC electric currents to be applied for magnetic field imaging. (b) shows the confocal fluorescence image of the diamond probe tip, with the NV centre emission and pillar obvious in the centre. The faint fluorescence seen towards the edges of the is from the edge of the diamond petal that the tip is fabricated from. The tip fluorescence in excess of 600 kC/s is high, even in the context of a pillar NV. (c) shows an ODMR measurement of the tip fluorescence, with no dip observed confirming the suspicions raised by the confocal image that the light source is not an NV centre.

concern as the pillar itself can lead to an increase in background counts, increasing the minimum $g^{(2)}(0)$ value. Finally the ODMR measurement shows a contrast of 16% with a spin linewidth of 12.3 MHz. This linewidth is a result of power-broadening of the NV spin transition and is typically attributed to the spin spending longer in the excited state during constant laser excitation [126].

Following these encouraging results, the sample and probe were cooled to 2 K in the cryostat to examine their behaviour at low temperature, allowing for use of the vector magnet and the superconducting microwave lines on the sample (at room temperature, gold lines were used instead). After cooling, however, the tip fluorescence exhibited similar behaviour to what had been observed from the start in the first probe. The fluorescence increased significantly — as shown in figure 6.5 — and the ODMR contrast was reduced to below 1.5%. In an attempt to revive the NV’s previous characteristics, several steps were undertaken. First, the sample chamber was warmed to 100 K and measured
Figure 6.4: Confocal image and fluorescence characteristics of the second Qzabre probe. (a) shows a confocal image of the probe petal, with inset showing a close up image of the pillar fluorescence, which shows a much more reasonable maximum of 110 kC/s. (b) shows the NV saturation curve, measuring NV fluorescence rate against vs laser power. NV fluorescence is expected to saturate as laser power increases, due to the finite maximum emission rate of the centre as a result of the lifetime of the excited state. (c) shows a $g^{(2)}$ autocorrelation measurement used to check for a single defect — the dip only reaching 0.6 indicates that this may not be a single defect, although pillar fluorescence characteristics may add significant extra background fluorescence. (d) shows a measurement of ODMR, with a contrast of $\approx 16\%$ and linewidth of 12 MHz observed.
there to verify that the loss in contrast was still present, which it was. This was repeated at room temperature with no further improvement. At room temperature the sample chamber was pumped to a high vacuum \((P < 1 \times 10^{-5} \text{ mBar})\) and repeatedly flushed with helium to remove any potential contaminants.

Contamination seemed the most likely source of the excess counts, however the lack of any increase in counts from the diamond petal — average petal counts were 20 kC/s at room temperature and 16 kC/s at 2 K after the significant extra tip fluorescence had developed — means that this would have to have been localised to the tip. No AFM scanning had been performed with this probe so this as a source of contamination could be ruled out. One potential source is that laser light can have an ‘optical tweezer’ effect, whereby matter can be trapped in its beam due to the interaction of the strong electric field at the beam waist with dielectric materials \([127, 128]\). This was tested for by apply the laser for an extended period to another part of the petal, but no increase in fluorescence was observed. Finally and as before no bleaching of the tip fluorescence was observed, suggesting that this was not simple dirt or similar which would exhibit a rapid reduction in count rate during continuous laser exposure.

Explaining the observed behaviour is challenging due to the small sample size, but may well be explained by either changes in the NV centre charge state or by the presence of other defects within the pillar. If the NV centre were simply changing charge state from NV\(^{-}\) to NV\(^{0}\), the result would be a loss of contrast and a reduction in the counts recorded as described during the analysis of the pillar NV centres above. The increase in counts, with a corresponding loss of contrast, suggests that the measured fluorescence is coming from other sources within the pillar, potentially activated by the change in chemistry as a result of cooling.

### 6.2 Probe 3: Dynamical Decoupling and Magnetometry

The third Qzabre probe measured was active for close to three weeks before suffering the same fate as its predecessors.
Figure 6.5: NV fluorescence (a) and ODMR signal (b) approximately 2 weeks after initial measurements. The fluorescence map (a), has a non-linear mapping applied to enable both the diamond petal fluorescence and the NV fluorescence to be visible, the average petal fluorescence is 14 kC/s, whilst the NV itself shows a fluorescence of approximately 600 kC/s, an increase in NV fluorescence of 6×. The ratio of NV fluorescence has increased 8×. (b) shows that the increase in fluorescence has been accompanied by a commensurate drop in ODMR contrast, from 16% observed previously to < 1.5%.

6.2.1 Probe 3 Characteristics

The third Qzabre probe used in this work showed initially excellent characteristics, measurements were performed at 5 K using the fabricated sample to deliver microwaves. Count rates were in excess of 200 kC/s at 5 K, showing only an 15% drop from the room temperature value. Figure 6.6 shows measurements of ODMR, \( g^{(2)} \) and Rabi oscillations. CW-ODMR contrast is measured to be 13%, with a Rabi contrast of 19.1%. \( g^{(2)}(0) \) values were the lowest recorded for one of these tip NVs, with \( g^{(2)}(0) \) of 0.28 with 50 μW of power and 0.31 with 150 μW of power. The bunching observed at the higher laser power measurement — the increase in \( g^{(2)} \) above 1 — is a feature of the NV\(^-\) centre, and is caused by the non-radiative decay path via the metastable singlet state. If the system is a simple two level oscillator then the rate equations for the level populations can be written as:

\[ \begin{align*}
    \frac{dP_1}{dt} &= -A_1 P_1 + A_2 P_2 + \alpha_1 P_1 - \gamma_1 P_1 \\
    \frac{dP_2}{dt} &= A_1 P_1 - A_2 P_2 + \alpha_2 P_2 - \gamma_2 P_2
\end{align*} \]
6.2 Probe 3: Dynamical Decoupling and Magnetometry

Figure 6.6: The characteristics of the NV in the tip of the third Qzabre probe, measured at 5 K. (a) shows CW-ODMR measurements at zero field and at 2 mT, (b) shows measurements of $g^{(2)}$ at 50 and 150 µW, (c) shows measurements of Rabi oscillations at -10 dBm and -6 dBm in microwave power.

$$
\begin{pmatrix}
\dot{p}_1 \\
\dot{p}_2
\end{pmatrix}
= 
\begin{pmatrix}
-k_{12} & k_{21} \\
 k_{12} & -k_{21}
\end{pmatrix}
\begin{pmatrix}
p_1 \\
p_2
\end{pmatrix}
$$

(6.1)

where $p_i$ is the population of the level, $\dot{p}_i$ is the rate of change of that population, and $k_{ij}$ is the rate of state transfer between these two levels ($k_{12}$ equivalent to excitation rate, $k_{21}$ equivalent to spontaneous emission). These coupled rate equations can be solved to give the second order autocorrelation function [129, 130].

$$
g^{(2)}(\tau) = \frac{p_2(\tau)}{p_2(\infty)} = 1 - e^{-(k_{21} + k_{12})\tau}
$$

(6.2)

where $p_2(\tau)$ is the population of level 2, the excited state, at time $\tau$ and $p_2(\infty)$ is its population in the limit of long time. It’s clear from this equation that in this case the value of $g^{(2)}(\tau)$ is always less than 1, which fails to account for the observed bunching behaviour for higher laser powers. To explain this behaviour requires a third ‘shelving’ level that captures the electron and prevents emission, with the time that the electron is captured for leading to a characteristic bunching. In this case the coupled rate equations are [131]:

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6 Diamond Scanning Probes

\[
\begin{align*}
\dot{p}_1 &= -k_{12}p_1 + k_{21}p_2 + k_{31}p_3 \\
\dot{p}_2 &= k_{12}p_1 - (k_{21} + k_{23})p_2 \\
\dot{p}_3 &= k_{23}p_2 - k_{31}p_3 \\
1 &= p_1 + p_2 + p_3
\end{align*}
\]

(6.3)

by assuming that \( k_{21} \) and \( k_{12} \) are much greater than \( k_{23} \) and \( k_{31} \), we can then write that:

\[
g^{(2)}(\tau) = 1 - \beta e^{-\gamma_1 \tau} + (\beta - 1)e^{-\gamma_2 \tau}
\]

(6.4)

where:

\[
\gamma_1 \simeq k_{12} + k_{21}
\]

(6.5)

\[
\gamma_2 \simeq k_{31} + \frac{k_{12}k_{23}}{k_{12} + k_{21}}
\]

(6.6)

\[
\beta \simeq 1 + \frac{k_{12}k_{23}}{k_{31}(k_{12} + k_{21})}
\]

(6.7)

Equation 6.4 can then be used to directly fit the measurements of \( g^{(2)}(\tau) \) to obtain values for \( \gamma_1, \gamma_2 \) and \( \beta \), which can then be used to derive values for the \( k_{ij} \) for the NV centre levels. As there are four unknown values and currently a set of three equations, a final relationship is required, for which we use:

\[
R = \xi k_{21}p_2(+\infty)
\]

(6.8)

where \( R \) is the fluorescence rate and \( \xi \) is the collection efficiency of the optical setup. This can be combined with the equations above and (with some length rearranging) yield the cubic equation:

\[
k_{12}^3 - \gamma_1 k_{12}^2 + \frac{R}{\xi} \left( \gamma_1 + \frac{X}{k_{31}} \right) k_{12} + \frac{RX}{\xi} = 0
\]

(6.9)

where \( X = (\beta - 1)\gamma_1\gamma_2/\beta \). Whilst this in theory allows the calculation of all the rates we need, it requires knowledge of \( \xi \), the collection efficiency of the optical setup, which is
6.2 Probe 3: Dynamical Decoupling and Magnetometry

Figure 6.7: (a) relationship between laser power and $g^{(2)}$ measurement, with fits applied according to equation 6.4. (b) $\gamma_1$ and $\gamma_2$ parameters from fits and their relationship with power.

It is hard to calculate even with detailed knowledge of the optics in question. Instead, we can obtain an estimate of $k_{21}$ by plotting the variation of $\gamma_1$ with power, and observing the relationship given by equation 6.5. As power approaches 0, the rate of excitation from ground state to excited state $k_{12}$ also goes to 0, meaning that at 0 laser power $\gamma_1 = k_{21}$. So applying a linear regression to the relationship and taking the y-intercept gives a value for $k_{21}(0)$, as seen in figure 6.4. We may also make the assumption that $k_{21}$, the spontaneous emission rate, does not change with laser power [131], which allows us to use the first three equations to calculate the coupling rates, without having to rely on knowing the collection efficiency of the optical setup. Fitting the values of $\gamma_1$ in figure 6.4(b) we get a value of $0.046\pm0.005$ ns$^{-1}$ for $k_{21}$, which equates to an excited state lifetime of $21.6\pm0.9$ ns, in excellent agreement with previously reported results [130, 132, 133].

With estimates for the coupling rates $k_{ij}$ now possible, we can provide an estimate for the collection efficiency of the system by solving equation 6.9 for a series of efficiency values and comparing the resultant $k_{12}s$ with those expected from the experimental measurements to find a match. We can then estimate our collection efficiency to be between $1.5 \times 10^{-3}$ and $3.0 \times 10^{-3}$, with the relatively wide range due to the inaccuracy in fitting only four autocorrelation measurements. This again compares well with reported
collection efficiencies for other optical groups, allowing us to take confidence that measurements on this system are representative.

6.2.2 NV Dynamical Decoupling

The next set of measurements performed on this NV centre were to ascertain the expected $T_2$ times of the spin and to what extent this could be mitigated via dynamical decoupling sequences, as increased $T_2$ is one of the chief factors in improving magnetic field sensitivity. To increase $T_2$ time relative to what is achieved with a simple Hahn echo sequence, dynamical decoupling sequences are used. The simplest of these is the CPMG sequence, which adds $\pi$-pulses in between the spin initialisation and readout, with the expectation that as more pulses are added the spin coherence increases. In this case instead of standard CPMG, we use XY8 which reverses the phase of each $\pi$-pulse sequentially in an $x-y-x-y-x-y-x$ pattern, to yield higher robustness to pulse errors [134, 135]. This is shown in figure 6.8, with (a) showing the results of measurements of coherence with XY8 sequences of 8, 16 and 24 pulses (higher pulse numbers are just concatenated XY8 sequences). The measured $T_2$ is shown in (b), extracted by fitting a stretched exponential to the coherence decay.

![Graph](image)

Figure 6.8: Comparison between CPMG sequences: (a) coherence decay curves for a single NV centre measured with Hahn echo and XY8 sequences of 8, 16, and 24 pulses. (b) shows the measured $T_2$ extracted from each.

In figure 6.8, the coherence decay curves are plotted as a function of the number of pulses multiplied by $\tau$ the interpulse spacing. This is useful for deriving qubit coherence
6.2 Probe 3: Dynamical Decoupling and Magnetometry

times but makes the interaction of the NV centre with its magnetic noise environment less obvious, as that interaction is dependent on pulse spacing $\tau$ rather than total sequence length. The qubit’s coherence is most sensitive to noise with a period of $2\tau$. The clear dips in coherence visible in figure 6.8 become much more obvious when the same data is plotted against $\tau$ rather than $n\tau$, which is shown in figure 6.9. From this, it’s clear to see that these dips in coherence occur repeatably for the XY8, XY16, and XY24 pulse sequences and at the same $\tau$ values, indicating consistent magnetic field noise at the corresponding frequencies. This observation indicates the promise of the NV centre as a sensor of its local environment with strong coherence reactions to environmental magnetic noise.

With this sensitivity established, we next sought to test whether we could detect an artificially generated AC magnetic field, applied through the wires fabricated on the MW delivery sample.

6.2.3 Magnetometry of AC Fields

To test whether the spin could detect an alternating magnetic field applied artificially the sample was first moved so that the diamond tip and NV centre were positioned above the 1 $\mu$m Niobium wire on the fabricated sample. The tip was not brought into contact via the AFM due to concerns over this being a potential cause of the loss of NV centre characteristics that had been observed previously. Instead, the tip was positioned at an approximate distance of 2 $\mu$m from the wire. A signal generator was then used to apply 250 kHz AC voltage across these wires with peak-to-peak voltages between 50 mV and 10 mV. To verify whether this was detected by the NV centre, coherence measurements were repeated for each of the 8, 16 and 24 pulse sequences and the results examined to look for changes. At higher peak-to-peak voltages, the resulting sequences showed quite rapid decoherence without clear features as a result of the applied AC field. At 10 mV however, a clear dip was visible centred at a $\tau$ value of 2 $\mu$s, corresponding to the applied frequency of 250 kHz. The results of the XY8 measurement for the cases of field on and field off are shown in figure 6.10.

These results can be used to estimate the magnetic field experienced by the NV centre [136]. When the NV centre is flipped by $\pi$-pulses at approximately the same rate as a
Figure 6.9: The variation in coherence for four dynamical decoupling sequences, plotting against $\tau$ rather than $n\tau$ and thereby equalising the effective frequency response for each sequence. In this form, the repeatable dips in coherence are visible across the three XY sequences, indicating interaction with magnetic field noise at the frequencies labelled on the graph.

Local magnetic field varies, the flipping no longer serves to average out the magnetic field but to enhance the qubits interaction with it. The extra phase acquired by the NV centre during a time of $\tau$ interacting with the field is added to during the next $\tau$ as the field also reverses polarity. The phase acquisition of the NV centre spin is, however, dependent on the phase difference between the spin and the magnetic field, even in the case that that field has the same frequency as the decoupling sequence.

Considering that the field can be expressed in the form:

$$B_{ac}(t) = b_{ac} \cos(2\pi f_{ac} t + \alpha)$$

where here we take $\alpha$ to be the phase difference between the pulse sequence and the magnetic field. When $\alpha$ is 0, indicating that a half period of oscillation of the field is perfectly contained in a time $\tau$ between two $\pi$-pulses, then the phase acquisition of the spin
Figure 6.10: A comparison in NV coherence decay for an 8-pulse XY sequence, with no AC field applied shown in dark blue and with a 250 kHz field applied shown in light blue. The clear agreement between the two cases is obvious except for the dip centred at 2 µs in the latter case, indicating a magnetic field at approximately 250 kHz affecting the NV coherence.
is maximised. When $\alpha = \pi/2$ however, the magnetic field switches polarity perfectly at the centre of a gap between two pulses, meaning that it cancels itself out and total phase acquisition by the qubit is 0. We can calculate the qubit phase acquisition, $\phi$ as a function of the phase difference $\alpha$ from [136, 137]:

$$ \phi = \int_0^{t_s} 2\pi\gamma_e h(t)B_{ac}(t)dt = 4\gamma_e b_{ac} t_s \cos(\alpha) $$

(6.11)

where $t_s$ is the total sequence time, $\gamma_e$ is the electron gyromagnetic ratio in Hz, and $h(t)$ is a function that accounts for the switching of phase acquisition direction with each $\pi$-pulse. The total phase acquisition of the qubit can then be translated into the expected readout state of the spin. In the case that the spin acquires a perfect $\pi$ phase for example, then it would be projected into the $|m_s = 0\rangle$ state at the end of the sequence, rather than the $|m_s = -1\rangle$ state, which is detected in our measurements as an inversion of the fluorescence signal (i.e. from 1.0 to 0.0). Whilst this equation is useful in the case of constant $\alpha$, this is a situation that is unlikely to practically arise as careful clock synchronisation between signal and pulse sequence would be required. As measurements are averages over many repeats, the phase is likely to randomised and experienced as the average of the phases at each measurement. The probability of projecting into the $|m_s = 0\rangle$ state at the end of the sequence in the case of random phases can be calculated with:

$$ p_0(t) = \frac{1}{2} \left[ 1 - \frac{1}{2\pi} \int_0^{2\pi} \cos(\phi(\alpha))d\alpha \right] $$

(6.12)

$$ = \frac{1}{2} \left[ 1 - J_0(2\pi\gamma_e b_{ac} N_\tau W_{N,t}(f_{ac})) \right] $$

where $J_0$ is the Bessel function of the first kind at $n = 0$, and $W_{N,t}(f_{ac})$ is the filter function of the pulse sequence at the frequency corresponding to the $\tau$ value in question.

With this information we are able to apply a fit of equation 6.12 to the coherence decays measured with the AC field applied. We first fit a stretched exponential to the coherence decays to normalise the measurements to 0, and then apply a fit of the equation above to the region of interest, with both $b_{ac}$ and $f_{ac}$ left as variables for the algorithm to obtain.
Figure 6.11: The coherence decay curves for 8, 16, and 24 pulse sequences measured during application of an AC magnetic field at 10 mV pp and 250 kHz. Only the region around the $\tau$ value matching the frequency of interest is shown and the traces are spaced vertically for clarity. Fits have been applied to each using equation 6.12 to extract field and frequency parameters.
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<table>
<thead>
<tr>
<th></th>
<th>Field (µT)</th>
<th>Frequency (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 Pulse</td>
<td>1.39 ± 0.08</td>
<td>259 ± 1.6</td>
</tr>
<tr>
<td>16 Pulse</td>
<td>1.08 ± 0.15</td>
<td>271 ± 2.4</td>
</tr>
<tr>
<td>24 Pulse</td>
<td>1.04 ± 0.16</td>
<td>264 ± 3.1</td>
</tr>
</tbody>
</table>

Table 6.1: Table showing results of fits in figure 6.11 to obtain values of field and frequency.

Figure 6.12: A 2D scan of the sample, with a measurement of coherence taken at each point for a value of $\tau = 2\mu m$. The scan is taken at approximately 3 µm above the surface of the sample, the blue region at the top corresponds to the 1 µm wide wire, whilst the bottom of the sample shows the beginning of the effect of the 2 µm wire which is at a distance of 10 µm.

The results of these fits can be seen in figure 6.11, with the fitting parameters of field and frequency shown in table 6.1.

With the ability to take coherence decay measurements and detect AC fields, this technique was then adapted to perform a 2D sample scan whilst taking a measurement of coherence at each point. Instead of taking a full coherence decay measurement, only the value of coherence at $\tau = 2\mu s$ was measured giving maximum sensitivity to the applied 250 kHz magnetic field. Figure 6.12 shows the results of this measurement, which was taken over the 1 µm wire on the sample. The reduction in coherence over this wire is clear in the top of the figure, with the width of the effect approximately 2 µm, a result of the tip to sample separation of approximately 3 µm.

These results were encouraging, clearly demonstrating the capacity of this experimental setup to make measurements of AC magnetic fields at high sensitivities and with 2D
scanning. These measurements were followed by a degradation in NV characteristics, with CW-ODMR contrast going from the 16% initially measured to less than 2%. Unlike the previous two tips, this was not accompanied by a large increase in the fluorescence of the NV. The need, however, to better understand the processes at play was clear, as tip robustness is essential for long term experiments to be carried out.

6.3 Summary and Future

As the three tips initially tested had been provided by the same manufacturer, Qzabre, we decided to perform a set of tests on a tip from a second manufacturer, Qnami, to test whether potential differences in the fabrication process may have yielded more robust NV centres. Testing of this final probe proceeded very similarly to the previous three and initial results were excellent and performance highly comparable in ODMR contrast, Rabi contrast, fluorescence and $T_2$. As before characteristics degraded over the course of approximately 2 – 3 weeks, though like the final Qzabre probe measured only contrast was lost with no significant change in fluorescence. Figure 6.13 shows confocal scans as well as ODMR measurements taken at first cooling down of the probe, and again two weeks later accompanied by a drop in contrast from 16% to less than 4%.

The initial performance of the probes was excellent and well within the parameters that would be required for single spin detection. With its initial characteristics of 200 kC/s, 19.1% contrast and up to 40 μs $T_2$ with dynamical decoupling the NV centre in the third Qzabre probe would have a sensitivity of approximately 50 nT/√Hz, capable of sensing a single spin at a distance of 27 nm with a total measurement time of 1 second. Taking this in the context of a scanning measurement, we can work out a minimum detectable field for a given total measurement time and scan range. We imagine a scanning region of 200 × 200 nm, and a total pixel number of 400 (10 nm per pixel) and a reasonable total measurement time of 20 hours. With these specifications, measurement time per pixel is 180 seconds, giving a minimum detectable field of approximately 4 nT — corresponding to a maximum sensing distance of up to 65 nm. Whilst this shows that this system has the clear potential for single spin sensing, the short lived nature of these NV centres must be addressed.
Figure 6.13: Confocal scan (a) and ODMR plots (b) and (c) for the tested Qnami probe. (a) Shows the whole tip petal, with a close up scan of the pillar fluorescence inset, with maximum pillar fluorescence similar to that from the Qzabre probes. (b) Shows initial measurements of ODMR contrast, with approximately 16% observed initially. (c) Shows the degradation in contrast after approximately two weeks of low temperature measurements to below 4% contrast.
6.3 Summary and Future

The repeated low temperature failure of these probes has necessitated a change in approach to this investigation. As probe failures typically occur with 2 – 3 weeks of cooling to below 10 K, we have been unable to develop the setup capabilities to the point where single the detection of electron spins in silicon via an NV centre in a diamond tip would be achievable. Testing of each tip is a slow process — with 1 – 2 weeks required to characterise it and reach the stage where relevant magnetometry experiments can be performed. With this in mind, it seems unlikely that repeated testing of individual tips will yield one that can be used for the intended purpose of sensing of single electron spins bound to donors in silicon. As such, we are currently planning to perform a similar set of experiments as were undertaken in chapter 5 with the diamond nanopillars. Our experience with the diamond tips does not correspond well with the results with diamond nanopillars. There low temperature changes to NV characteristics were observed but long term stability was seemingly unaffected by temperature change. As such, we are currently planning to perform similar experiments on a sample fabricated in the same manner as the diamond tips in this research but with fields of nanopillars allowing for efficient study of multiple NV centres, and with different regions with different NV implantation depths and pillar diameters.

To do this we need to try and understand the cause of the loss of NV characteristics. It is noted that in the four tips mentioned here, two failed by losing contrast and showing massive fluorescence increases, whilst the other two simply lost contrast. The key question is whether the observed effects are due to a combination of laser illumination and cooling, or a result of cooling alone. To study this, key NV characteristics of a region of single NV centres will be tracked from 100 K to 2 K (having been first characterised at room temperature). In addition to this main region, new regions will be examined at each temperature, to ensure that a ‘fresh’ set of NV centres are examined each time. At the base temperature of the cryostat at 2 K we will perform long term illumination studies. One region will be exposed to laser illumination at a relatively high intensity, whilst another will be exposed to a relatively low laser intensity — all whilst ODMR contrast is tracked over the period of approximately a month, as this was the period over which degradation has been observed in the tip NV centres. In addition, fresh regions
6 Diamond Scanning Probes

will be examined periodically to verify the behaviour over the long term in areas with no illumination.

This procedure, combined with the ability to examine different regions with different fabrication characteristics, will hopefully yield enough information to make some clear predictions about the required fabrication characteristics for near surface NV centres that will survive at low temperatures. With this information, we hope to be able to proceed to relevant studies using diamond tips with long lived low temperature NV centres.
7 MACHINE LEARNING FOR PROBBING
THE QUBIT ENVIRONMENT

That’s one thing he hated! The NOISE! NOISE!
NOISE! NOISE!
— Dr Seuss, How The Grinch Stole Christmas

Much of the work presented above has focussed on the ability for a single spin qubit, particularly an NV centre, to successfully probe and infer its magnetic noise environment. The noise a qubit experiences directly influences its behaviour, and particularly its coherence time. In the case of magnetic field sensing, the length of that coherence time is one of the key components determining its ultimate magnetic field sensitivity, along with its overall fluorescence counts and fluorescence contrast. Furthermore, the noise that the qubit experiences often reveals information about the nature of its environment. In the last chapter, we saw that the AC magnetic noise from a wire could be used to detect that wire whilst the noise generated by specific spin species in a magnetic field can be used to identify those spins.

The noise experienced by a qubit can be most accurately understood via its noise spectrum, which describes the noise power at a given frequency, and the filter function of any control pulse sequence. The filter function convolved with the noise spectrum gives the qubit’s coherence decay. Experimentally, we have access to the filter function of the pulse sequence and the coherence decay we measure with that pulse sequence. The noise spectrum itself is hidden, yet could reveal a great deal if it could be mitigated. In the case where extended qubit coherence is desired, accurate knowledge of the noise spectrum could allow for the creation of bespoke decoupling sequences to maximally mitigate it. In the case where the noise spectrum contains relevant information about the qubit en-
7 Machine learning for probing the qubit environment

...environment, such as in the case of quantum sensing, then knowing it would yield insight into that environment.

In this chapter, I cover our application of machine learning and specifically deep learning techniques to the field of qubit noise spectrum extraction. We focus on use of simple experimental techniques to gain the maximum possible insight into the noise spectrum via deep learning and investigate how these approaches perform relative to simple traditional noise spectrum extraction techniques and state-of-the-art but experimentally taxing approaches.

7.1 Introduction to machine learning and the noise spectrum

7.1.1 Machine learning and quantum mechanics

Background to neural networks

The term machine learning covers a huge range of computer science techniques, and falls under the larger umbrella of artificial intelligence. The history of artificial intelligence has contained several false dawns, leading into two significant ‘winters’, where significant optimism in the field was replaced by disappointment when anticipated breakthroughs did not materialise [138]. AI can be broadly categorised into two groups: rules based or computationalist, and emergent property based or connectionist. Computational approaches view the effective AI as taking a series of inputs, acting on them in a predefined way, and returning the correct output. Connectionism views intelligence as an emergent property of a complex system, where computations take place across a distributed and highly parallel network [139]. A further distinction made between approaches to artificial intelligence is the difference between traditional preprogrammed abstract entities and learning based approaches where an embodied system gains intelligence based on information provided to it [140].

Machine learning falls into the latter of both these two distinctions: it is connectionist, and focuses on learning rather than preprogramming. At is simplest, machine learning takes a set of inputs, applies a model to them and then compares the output of that model
to a set of desired outputs before updating the model so that the outputs are closer to the target. This process can be as simple as finding the best fit line to a set of data or as complex as producing a novel story from a prompt [141, 142]. Whilst there is a huge range of machine learning techniques, the one dealt with here is deep learning, which primarily uses models based on deep neural networks. Neural networks as a concept are surprisingly old, given that their rise to dominate the world of artificial intelligence has only occurred in the last decade. The concept of an artificial neuron (and similar concepts like perceptrons), the building block of most neural networks, was first proposed in 1943 [143]. The concept is relatively simple, a series of inputs are multiplied by individual weights, summed and then an activation function determines the output of the neuron. This action can be summed up by the following equation:

$$AN(x) = \phi \left( \sum x_i w_i + b_i \right)$$  \hspace{1cm} (7.1)

where $x$ is the vector of inputs, $w_i$ are the weights, $b_i$ is a bias and $\phi$ is an activation function. The choice of activation function is a crucial one, and for the creation of a deep neural network is the aim then the function must be non-linear. A deep neural network contains multiple artificial neurons arranged in layers, which are typically represented mathematically as matrices. The input vector is typically represented as a row vector ($\mathbf{x}$) and the weight matrix ($\mathbf{W}$) as a matrix with number of samples (size of the input data) equivalent to number of rows and the number of features (size of the output vector) as columns. So the action of a single neural network layer can be written as:

$$L(x) = \phi(xW + b)$$  \hspace{1cm} (7.2)

This is an example of a dense layer in a neural network — each output node is formed from weights, biases and activation function applied to all input nodes. The simplest kinds of deep neural network simply repeat this process in sequence. For a deep neural network to be worth it, the activation functions used must be non-linear, as if linear activation functions are used then it can be shown that no matter how deep the network, it can be replaced by a single layer network. Intuitively, if all layers are linear functions acting on the output of a previous layer, then the output of the final layer is simply a linear
7 Machine learning for probing the qubit environment

function acting on the input to the first layer, which can be performed by a single matrix. The choice of activation function varies from network to network and until quite recently the sigmoid activation function, \( S(x) = \frac{1}{1+e^{-x}} \), was the most popular. Now, the most commonly used function is the Rectified Linear Unit (ReLU), which applies the simple function:

\[
\text{ReLU}(x) = \max(x, 0)
\]

(7.3)

It is relatively clear how neural networks go from input to output, how they can be made to produce a target output is the question of training. To train a network, a loss function is used to create a metric for how close the output of a neural network is to some target data. A very simple case would be trying to recognise hand written digits. In this case the output of the network would be ten nodes, with each of those nodes representing one digit from 0 – 9. A perfect prediction would output a number close to 1 in the correct node, whilst a wrong prediction would put a number close to 0 in that node. A loss function quantifies how close the prediction is to the target, and that loss is then differentiated with respect to the parameters (the weights and biases) of the network. This gives a direction for each parameter in which to move to improve the loss, and the weights and biases are changed in this direction by a factor (the ‘learning rate’) of the gradient. Performing this operation repeatedly on a wide range of training data should allow the loss to be reduced and the network output to be close to the target data. Ideally, the performance of the network on unseen data is similar to its performance on training data.

Despite their age as a concept, neural networks have not gained widespread traction until the last decade, but now represent the dominant force in the machine learning field. The reasons that they have been late bloomers are twofold: first, they require extraordinary amounts of computing power to train, and second they require large amounts of data in order to generalise. In the last ten years, graphics cards have provided the massively parallel computing power that is well suited to neural network training and the rise of the internet has provided the huge amounts of data required for them to be effectively trained.
7.1 Introduction to machine learning and the noise spectrum

Neural Networks and Quantum Mechanics

Much of neural network research has been into their performance on tasks that humans perform well, but that computers typically do very poorly at. In the early part of the decade this was primarily in the field of image recognition with the advent of deep convolutional neural networks [144, 145]. In the latter part a lot of the developments have been in the area of language modelling, driven by the transformer architecture [142, 146]. At the same time, there has been increasing interest in using deep learning to work with structured or time series data where humans do not have a significant (if any) advantage over computers [147]. Specifically, the use of deep learning in physics and quantum technologies is becoming more prevalent as recognition of its capacity to solve efficiently problems that have hitherto been intractable or challenging. This includes areas such as Hamiltonian estimation, where machine learning techniques have been used to design input states and evolution parameters to optimally infer the parameters of a partially unknown Hamiltonian [148]. Deep learning techniques have also been applied to improve the efficiency of state evolution, for example by allowing the calculation of a series of gate operations that allow a complex algorithm to be implemented far more efficiently than is required theoretically but with minimum loss of fidelity [149].

Machine learning and neural networks have become more widely used in recent years for the processing of experimental data. They have been used for accelerated processing of ESR and NMR data showing extraction of the same signals with 10% of the time, extracting spin coupling parameters and probability distributions that were previously inaccessible, and processing of DEER data with accuracy comparable to state-of-the-art techniques [150, 151, 152]. Neural networks have also been used for quantum control, where they have been used to produce dynamical decoupling sequences that more effectively suppress the environment and dephasing, and have enhanced the fidelity and robustness of several studied quantum control operations [153, 154, 155]. Furthermore, neural networks can be combined with reinforcement learning techniques — which use a neural network to process environmental data and then produce a corresponding action on the environment to optimise a reward function — where they have been used to design more effective experiments, to improve the sensitivity of quantum sensors and to engineer Hamiltonians for quantum simulation [156, 157, 158, 159].
One of the key challenges when utilising deep learning techniques is sourcing enough data to effectively train a sufficiently powerful neural network without overfitting. Overfitting of a neural network is where it becomes trained to the extent that it becomes so good at recognising the training data, that it no longer generalises well to unseen data. This is usually monitored for by using a validation data set, which the network is not trained on (i.e. information from this set is never used to update the network weights), but which is periodically fed through the network to get a measure of loss. A network that is beginning to overfit shows an increase in the loss measured on the validation set, even whilst loss on the training set is continuing to fall. A third class of data is often used, known as a test set, whose loss is not checked periodically but only once a network has been optimised and is ‘complete’. This avoids the problem of overfitting to the validation set — where repeated optimisation of a network based on how well it performs on a single set of data can lead to poor generalisation.

Experimental data derived from qubits is often slow to gather — for example the single NV centre coherence decays shown in this work can take many hours of averaging before an acceptable signal to noise ratio is reached. To get round this problem, many researchers use synthetic data — which, whilst representative of real-world data can be much more efficiently produced. This will be a key technique in this chapter.

### 7.1.2 Decoherence and the Noise Spectrum

As was discussed in section 2.1.7, the coherence decay of a qubit is strongly dependent on the environmental noise that surrounds it and the way the pulse sequence used to control it interacts with that noise. The noise environment of a qubit can be effectively represented by its noise spectrum, \( S(\omega) \), whilst the pulse sequence can be represented by its filter function, \( F(\omega, t) \). The degree to which these two components overlap give the coherence of the qubit. This is given by the equation:

\[
\chi(t) = -\ln C(t) = \int_0^\infty \frac{d\omega}{2\pi} S(\omega) \frac{F(\omega, t)}{\omega^2}
\]  

(7.4)

The most important aspect of this equation to consider for the work here is that it is easily solvable in one direction: the coherence decay can be readily worked out from a
filter function and a noise spectrum. It is not solvable in the opposite direction — a noise spectrum cannot be easily derived from a known coherence decay and a filter function. Unhappily, the noise spectrum is the feature that is hard to access experimentally, whilst the filter function can be easily derived as long as the pulse sequence is known and the coherence decay is easily measured. Knowledge of the noise spectrum would, however, be of great use to an experimentalist. If a noise spectrum is well understood, then bespoke dynamical decoupling sequences can be designed to maximally mitigate the noise experienced by the qubit — extending its coherence. If, however, the qubit is designed to probe the environment then access to the noise spectrum would reveal information about noise frequencies and potentially reveal the structure of that environment [29, 38, 64, 65, 160]. The value of both of these is clear in the context of this work — enhanced coherence leads to greater AC magnetic field sensitivity and access to the noise spectrum would give further information about the surroundings of an NV centre. The traditional approach to noise spectrum extraction is to use a mathematical approximation — assuming the pulse sequence filter function to be a $\delta$-function at its dominant frequency. Whilst this allows for a simple extraction of noise spectrum from coherence decay via the equation:

$$S(\omega_0) = \frac{-\pi \ln C(t)}{t}$$  \hspace{1cm} (7.5)

the accuracy of this approach is limited. There exist more complex techniques, which I will address later, that do better but require significantly greater experimental resources.

We examine here whether machine learning can be used to plug the gap between these two approaches, to see whether accuracy can be significantly improved over the $\delta$-function approach without adding to experimental requirements.

### 7.1.3 Proposed methodology and training data generation

At its simplest, the approach here aims to take a coherence decay, feed it into a neural network and have it output the noise spectrum associated with that coherence decay to a high degree of accuracy. This involves the inversion of equation 7.4. Whilst not possible analytically this is a tailor-made situation for deep learning as neural networks can be
shown to be universal function approximators [161, 162]. So, with an adequate supply of training data, it should be possible to train a neural network to perform this task. Once again, the structure of the problem is helpful here — it is relatively trivial to generate large amounts of synthetic training data as long as synthetic noise spectra can be generated.

To do this, we investigate the noise spectra typically associated with various qubit species and find the following: $1/f^\alpha$ type noise is common in flux qubits and quantum dots — where $f$ is frequency and $\alpha$ is typically close to 1, gallium arsenide quantum dots experience mainly telegraph noise, NV centres in the diamond bulk experience Lorentzian noise, whilst near surface NVs experience double Lorentzian type noise mainly due to interaction with surface spins [29, 38, 61, 163]. We can then simulate these noise sources using physical parameters found in previous studies, before finding the coherence decays associated with these noise spectra by using equation 7.4. The coherence decay obviously depends on the pulse sequence used and its associated filter function, so for the majority of this work we choose to use a single pulse Hahn echo sequence to provide the simplest experimental implementation.

A second method for producing synthetic noise spectra is to first simulate synthetic coherence decays, according to a stretched exponential:

$$C(t) = e^{-(t/T_2^*)^\nu}$$

before using the $\delta$-function approximation to derive an approximate noise spectrum. We can then use equation 7.4 to find a coherence decay with an exact relationship to this noise spectrum. Noise spectra generated in this way are referred to as ‘stretched exponential’ in this work, whilst all others are described by their underlying noise form.

With a set of noise spectrum/coherence decay pairs generated, these can then be split into train/validation/test tranches for network training and evaluation. As described above, the training set is used for updating of network weights, the validation set loss is monitored during training to avoid overfitting and for network optimisation, and the test set is used once training and optimisation are complete for reporting of final network performance. All error and loss rates reported in this work are on the test set unless it is stated otherwise. A coherence decay can then be used as input into a neural network, with its corresponding noise spectrum used as the target output of that network to calculate
7.1 Introduction to machine learning and the noise spectrum

![Flowchart](image)

Figure 7.1: A flowchart describing the machine learning approach used in this work.

the network loss, and the network can then be updated to reduce this loss. A flowchart showing the proposed methodology is shown in figure 7.1

7.1.4 Choice of architecture

As has been mentioned above, there is a huge number of potential network architectures that can be used for deep learning. The simple dense network has been described above, where each node in a layer activates based on the weighted sum of all nodes in the previous layer. Whilst simple and often effective, this network structure has its downsides, chief of which are the all-to-all connections. This structure can have the effect of destroying local correlations as at each node all previous nodes are summed. Local correlations are clearly important when considering a coherence decay — intuitively, a 0.5 followed by a 0.4 is quite different to a 0.4 followed by a 0.5 — and will have an impact on the associated noise spectrum. Whilst these dense layers can learn to make these distinctions, it is usually much more efficient to bake awareness of local correlations into the proposed architectures. When dealing with time-ordered data like a coherence decay, two clear architectures present themselves: convolutional neural networks (CNNs) and recurrent neural networks (RNNs) [164, 165]. CNNs apply a series of learned filters to the data to infer local effects, whilst RNNs feed the data into a network in sequence, with the output of the network from one time step \( h_t \) fed back into the network along with the input for the next step \( x_{t+1} \). Extensive testing was carried out on which of these two architectures was most appropriate and ultimately a special case of the RNN architecture was found to be most effective: the LSTM.
Figure 7.2: Network architectures: (a) a schematic of an LSTM cell, (b) a schematic of the full network used here, and (c) training and validation loss for an example training case. In (a) \( c_t \) is the cell state vector which provides the network memory, \( x_t \) is the cell input — a point in a coherence decay in this case, and \( h_t \) is the cell output which is fed to the output dense layer and the next cell in the sequence. Red boxes are dense layers with sigmoid \( \sigma \) or tanh activation functions and blue circles are pointwise operations. (c) shows a simple sketch of the network, where the LSTM output is fed into a dense layer and is subsequently output and compared with the target coherence decay. (d) shows training and validation loss during training of the network, the state reached where validation and training losses have begun to diverge but validation loss has not started increasing is typically taken to be indicative of a well-trained network (neither under nor overfit).
7.1 Introduction to machine learning and the noise spectrum

LSTMs (standing for Long Short Term Memory) were developed as an extension of RNNs to overcome some issues with the typical architecture, the most important of which is the ability to maintain long term correlations — something which RNNs are not good at, with early parts of the sequence having little impact on the gradient of the loss function and therefore having their information ‘forgotten’ by the network. The cell state, \( c_t \), is introduced to the LSTM to provide long term storage of information — this cell state is added to or subtracted from (remembered — \( i_t \), or forgotten — \( f_t \)) based on the learned weights of the dense networks inside each LSTM cell, a schematic of which is shown in figure 7.2(a). The equations that govern the behaviour of a single LSTM cell are as follows:

\[
\begin{align*}
    f_t &= \sigma_g(W_f(x_t \oplus h_{t-1}) + b_f) \quad (7.7) \\
    i_t &= \sigma_g(W_i(x_t \oplus h_{t-1}) + b_i) \quad (7.8) \\
    o_t &= \sigma_g(W_o(x_t \oplus h_{t-1}) + b_o) \quad (7.9) \\
    \tilde{c}_t &= \tanh(W_c(x_t \oplus h_{t-1}) + b_c) \quad (7.10) \\
    c_t &= f_t \cdot c_{t-1} + i_t \cdot \tilde{c}_t \quad (7.11) \\
    h_t &= o_t \cdot \tanh(c_t) \quad (7.12)
\end{align*}
\]

where \( \sigma_g \) is a sigmoid activation function, \( W \)’s are the weight matrices that govern each LSTM operation, \( b \)’s are the bias vectors of these operations, \( x_t \) is the input vector at time \( t \) and \( h_t \) is the output vector at time \( t \). \( \oplus \) refers to a concatenation of two vectors. A full explanation of the workings and intuitions of an LSTM network is beyond the scope of this thesis and the author’s capabilities but many excellent works can be found in this area, including: [166, 167, 168]. Following the LSTM layer of the network a dense layer is used to produce output of the correct size, matching the noise spectrum length. Typically, for regression problems such as this a linear activation function is used on the final layer of the network, however in this case we use an exponential function due to the large values associated with the noise spectrum curves. Typically neural networks are initialised (the process of choosing the layer values before training begins) to produce outputs from a normal distribution with mean 0 and standard deviation 1. This means that convergence can be very slow as the network learns to output values in excess of \( 10^5 \), an exponential
activation makes this much faster although log scaling of the noise spectra would be an equally sensible approach.

All the neural networks reported on here are trained using the Keras module of the Tensorflow 2.0 library that Google maintains and distributes [169, 170]. Results are reported on a holdout test set and we use learning rate annealing, following the one cycle learning policy proposed by Smith [171]. To optimise the network the hyperparameters of LSTM nodes, dense layer nodes, initial learning rate, and batch size were altered and monitored using the Weights and Biases library [172].

7.2 Deep learning vs the δ-function approximation

7.2.1 Performance on single noise forms

The first data set on which the performance of the neural network was tested was a set of noise spectra with Lorentzian, $1/f$, and stretched exponential forms (the training set contained approximately 8000 examples of each). A single neural network was trained to recognise all of these forms, but each noise spectrum was only made up of one form (i.e. no cases of $1/f$ + Lorentzian). Training was typically performed for between 20 and 100 epochs, taking between 30 minutes and 3 hours. The use of one cycle learning rate scheduling, (where the learning rate of the network starts very low, is increased to a maximum, and then decreases to zero over the remainder of training) allowed excellent accuracy results with relatively few epochs and short training times. Typically, a 20 epoch run (20 – 30 minutes) would achieve an error rate of between 0.3 and 0.8% depending on noise model, whilst a 100 epoch run (2 – 3 hours) would achieve an error rate between 0.05% and 0.5%. This is encouraging for the practicality of the technique as it shows that excellent performance can be achieved with relatively short training times.

Figure 7.3 shows the performance of both the neural network and the δ-function approximation on the same set of data, in (a) and (b) stacked histograms show the distribution of errors, whilst (c) and (d) give example true and predicted noise spectra. Stacked histograms are used to give a picture of the overall performance of the techniques across the three noise types, with the bars for each noise form summing to 100% individually.
7.2 Deep learning vs the δ-function approximation

Figure 7.3: The performance of the δ-function approximation and the neural network based approach for reconstructing noise spectra from their associated coherence decays. In (a) and (b) the distribution of errors is shown for δ-function and neural network respectively. (c) and (d) show example noise spectra for each with solid lines showing the target spectrum and dashed lines the predicted spectrum. The example noise spectra in (c) and (d) are chosen from the 50th percentile error for each approach.

This is why the total histograms appear to sum to more than 100%. Table 7.1 gives detailed statistics for the performance of each approach.

The results here show a clear advantage for the neural network approach — with a mean error for each noise form of less than 0.5% in the neural network case compared with a mean error of greater than 10% in all δ-function cases. Importantly, this is a single network recognising the three different noise spectra successfully, meaning that it is able to differentiate between coherence decays produced by Lorentzian noise spectra and those produced by $1/f$. In this network, the time vector and frequency vector associated with the coherence decays and noise spectra respectively are implicit. The $T_2$s of the coherence decays in the data set range between 120 µs and 600 µs. It is entirely possible, however, to train a network to recognise coherence decays with significantly shorter $T_2$s.
7 Machine learning for probing the qubit environment

<table>
<thead>
<tr>
<th>Noise model</th>
<th>NN approach</th>
<th>δ-function approx.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>σ</td>
</tr>
<tr>
<td>Stretched Exp.</td>
<td>0.098</td>
<td>0.1</td>
</tr>
<tr>
<td>Lorentzian</td>
<td>0.39</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 7.1: Comparison of error statistics in % in noise spectrum extraction using the neural network approach introduced here versus the δ-function approximation for the pulse sequence filter function.

Figure 7.4: Percentage error distribution for inferring noise spectra from coherence decays with $T_2$ values ranging between 10 µs and 140 µs for (a) δ-function approximation and (b) neural network approach

Figure 7.4 shows the results of a neural network trained to recognise noise forms from coherence decays with significantly shorter $T_2$s than in the previous figure, ranging between 10 µs and 140 µs. In this case we can see that the δ-function approximation performs similarly as in the longer $T_2$ regime, whilst the neural network once again performs significantly better — with the majority of its errors being under 0.2%. This network was only trained on stretched exponential data, which leads to the lower error percentages. Nevertheless, this demonstrates the capacity of this approach to be adapted to different
7.2 Deep learning vs the $\delta$-function approximation

<table>
<thead>
<tr>
<th>Noise model</th>
<th>NN approach</th>
<th>$\delta$-function approx.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/f$</td>
<td>0.41</td>
<td>10.2</td>
</tr>
<tr>
<td>Lorentzian</td>
<td>0.42</td>
<td>28.4</td>
</tr>
<tr>
<td>Double</td>
<td>1.72</td>
<td>30.8</td>
</tr>
<tr>
<td>Lorentzian</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.2: Comparison of error statistics in % in noise spectrum extraction using the neural network approach versus the $\delta$-function approximation for a dataset including double Lorentzian noise forms.

qubits with different expected coherence times. The downside of the approach currently is the need to retrain the network due to the time vector not being an explicit part of the training, a more general approach could use both as input and be more flexible. However, given network retraining can be undertaken relatively quickly, adding the time vector must present enough of an improvement to offset the increase in complexity.

7.2.2 Multiple noise forms

The coherence decays used up until now have all been derived from noise spectra formed from a single noise form. In reality, qubits may well experience multiple sources simultaneously. To examine the performance of the neural network approach in this regime, we train a fresh network on a new dataset, comprised of $1/f$, Lorentzian and double Lorentzian noise forms — a simple linear sum of two Lorentzians with different parameters. These noise forms a characteristic of near-surface spins and particularly near surface NV centres in diamond [163].

Figure 7.5 shows the results of a network trained to recognise these noise forms against the results from the $\delta$-function approximation, with table 7.2 giving detailed statistics. Once again, the neural network approach significantly outperforms the $\delta$-function approach, although performance on the more complex double Lorentzian form is worse than for simple noise forms. This demonstrates however, that the network approach is robust enough to recognise multiple noise sources whilst also recognising multiple single noise sources.
Figure 7.5: δ-function (a) and neural network (b) performance when trained to recognise $1/f$, Lorentzian and double Lorentzian noise spectra. Once again the neural network approach performs significantly better than the δ-function approach, although the increase in complexity has had an impact on network performance. The distribution has a relatively long tail, with a maximum error of 200.1%, largely due to large portions of the noise spectrum being close to 0, where small absolute deviations in prediction can lead to relatively large percentage errors.
7.2 Deep learning vs the $\delta$-function approximation

A further question would be whether the network is capable of recognising previously unseen noise forms, as robust performance in this area is clearly important if we want to use the technique to explore new areas. Whilst in many qubit species we may have a good idea of the functional form of the underlying noise spectrum, we want to be somewhat confident that the network is able to deal with the case that the underlying spectrum is at least partially unknown. To explore this, we use the same network trained previously and examine its performance on a new dataset, comprised of noise with a Lorentzian $+ 1/f$ form. Results are shown in figure 7.6 and are somewhat encouraging: (a) shows an example noise spectrum and its underlying coherence decay (inset). The network is able to reconstruct it pretty effectively and most importantly outputs a prediction that has the same functional form, one that it was not trained to recognise. Whilst the error percentage is significantly higher than for a trained network, it still handily outperforms the $\delta$-function approach (11.9% vs 24.4% mean error). Furthermore, having recognised a new and untrained functional form this network can now be fine-tuned to better identify it. Generation of fresh data of the correct form is very fast — 10,000+ instances can be generated in a minute — and as a test we train the neural network for only 15 minutes. This gives the results shown in figure 7.6(c) and (d), with mean error now reduced to 3.5%. This further emphasises the practicality of the approach — the network can be adapted to the task at hand with minimal overhead when compared with experiment time.

We have seen that the advantage of the neural network over the $\delta$-function approach is significant in this regime, where coherence decays are derived from Hahn echo pulse sequences and noise spectra are made up of simple, monotonic noise spectra of single functional forms or linear combinations of them. I move on to explore the network’s performance when compared with more complex pulse sequences and more complex noise spectra.
Figure 7.6: The performance of a network trained to recognise $1/f$, Lorentzian and double Lorentzian noise forms when inferring $1/f +$ Lorentzian forms. (a) shows an example noise spectrum and its coherence decay inset, with the untrained network’s prediction and the $\delta$-function prediction. (b) shows the performance distribution for both approaches, with mean percentage error of 11.9% for the network and 24.4% for the $\delta$-function. (c) shows the same noise spectrum now predicted by a network that has been trained for approximately 15 minutes on the new noise form, with (d) showing the results distribution, with mean network error now 3.5%.
7.3 Multiple pulse sequences

7.3.1 CPMG sequences

Whilst we have now demonstrated the superiority of the neural network approach when a Hahn echo pulse sequence is used, it remains to be seen whether this is a true advantage when applied to experimental derivation of noise spectra. The Hahn echo is a very simple pulse sequence with which to measure a coherence decay, and being able to accurately infer noise spectra using it is certainly an attractive feature of the technique. However, if the \( \delta \)-function approximation performs significantly better when the coherence decay is derived from a CPMG pulse sequence with a larger number of pulses, then the advantage of the neural network must be said to be limited. Whilst a 32-pulse CPMG sequence is more experimentally challenging than a Hahn echo sequence, the difference is realistically not significant for most modern experimental groups working with qubits. Moreover, this improvement may be expected as the filter function of the pulse sequence becomes narrower with more pulses, meaning that a \( \delta \)-function may well be more representative.

As such, figure 7.7 shows the performance of both approaches when the coherence decay is derived using a 32-pulse CPMG sequence rather than a Hahn echo. Significantly, the performance of the \( \delta \)-function approximation is not significantly improved and is in fact worse than the Hahn echo case. The inset in figure 7.7(a) shows the change in mean accuracy of the approximation as pulse number increases, with errors observed to increase with pulse number. Whilst slightly counter intuitive, it seems that the higher harmonics of the filter function begin to become more dominant at higher pulse numbers, offsetting the benefit of the narrower central peak.

7.3.2 State of the art pulse sequences

Although the CPMG sequence is not able to improve the accuracy of the approximation, there do exist significantly more complex sequences that aim to produce a tailored filter function with significantly reduced higher harmonics. The phenomenon of higher harmonics contributing significantly to the overlap between filter function and noise
Figure 7.7: The performance of (a) the δ-function approach and (b) the neural network approach when predicting noise spectra where the coherence decays are a result of a 32 pulse CPMG sequence rather than a simple Hahn echo. Of interest is that the accuracy of the δ-function approximation does not improve as the pulse number increases — inset is shown the mean error for the approximation compared with number of π-pulses in the CPMG sequence. The performance of the neural network is effectively unchanged from the Hahn echo case.
7.3 Multiple pulse sequences

spectrum is often termed spectral leakage [70, 173, 174]. Discrete prolate spheroidal sequences (DPSSs) are an example of a technique that attempts to reduce spectral leakage by confining the filter function to a narrow band of frequency [70, 175]. These function by applying constant modulation to the control pulses applied to a qubit. Another sequence type, Gaussian enveloped dynamic sensitivity control sequences (gDYSCO) can minimise spectra leakage, although it reduces overall sensitivity due to a broader central peak [71]. Another approach to accurate noise spectrum extraction was developed by Alvarez and Suter [67]. This approach uses multiple sequences, each with a defined $\tau$ value (pulse spacing). The number of $\pi$-pulses in each sequence is increased and the resulting decay in coherence measured. Fitting to this decay gives a decay rate, $R$, for each value of $\tau$ that can then be used to extract the contribution of the higher harmonics, as the decay rate is a function of the number of pulses and is thus time-independent. The relationship of $R$ with the noise spectrum is defined as follows:

$$ R = \sum_{k=1}^{\infty} A_k^2 S(k\omega_0) $$  \hspace{1cm} (7.13)

where $\omega_0 = \pi/\tau$ and the summed over $A_k$s represent the amplitudes of the filter function at its sensing frequencies — i.e. its higher harmonics. The value of $\tau$ gives the frequency that a given measurement probes and repeating for multiple values of $\tau$ can give a much more accurate prediction of the underlying noise spectrum than can be achieved otherwise. The number of measurements performed for each value of $\tau$ (i.e. range of pulse numbers the measurement is carried out over) gives the accuracy of each $S(\omega_0)$, whilst the total number of $\tau$ values used gives the frequency resolution of the derived noise spectrum. Whilst certainly a significant improvement over the CPMG sequence these approaches are experimentally challenging and can require repeated measurements, nevertheless a comparison between the neural network approach and a state of the art approach remains highly relevant, so I move now to a comparison with the Alvarez-Suter method.
7.3.3 Neural Network vs A-S for non-monotonic data

With the performance of the neural network on simple monotonic noise spectra well established, we choose here to compare the performance of the Alvarez-Suter method (A-S method) with the neural network approach when reconstructing non-monotonic noise spectra. Non-monotonic noise spectra are those where the value of the noise spectrum does not simply decrease as the frequency increases. Typically, this type of noise spectrum is associated with coupling between the qubit and an external spin oscillating at a particular frequency and leading to a Lorentzian peak centred at that frequency in the noise spectrum. To simulate this we start with a fresh dataset of $1/f$ type noise and add a random Lorentzian feature to approximately half of the data, with that feature having variable central frequency, amplitude and width. The feature is added to only half the data to make sure that the network is able to differentiate between monotonic and non-monotonic noise spectra. The coherence decay curves associated with each noise spectra are derived, once again using only a Hahn echo sequence. To simulate the A-S method, each noise spectrum is measured at multiple $\tau$ values to find a series of $R$ values and the noise spectrum is re-derived.

Figure 7.8 shows the results of both approaches applied to this dataset (once again, neural network results are on an unseen test set). Performance is comparable and impressive in both cases, with 2.5% mean error for the neural network and 4.6% mean error in the A-S case. (c) and (d) show an example coherence decay and corresponding noise spectra, demonstrating that both approaches successfully locate the non-monotonic peak, whilst the $\delta$-function approximation fails to. The comparable performance of the network to this significantly more experimentally taxing technique is encouraging and highlights that the approach is worth pursuing. Nevertheless, the applicability of the A-S method in any situation with confidence that it will be correct is a clear advantage and we must seek ways to train the network on as diverse a range of noise forms as possible to make sure that it can be applied in any relevant qubit regime.
7.3 Multiple pulse sequences

Figure 7.8: The performance of the Alvarez-Suter method compared with the neural network approach for prediction of non-monotonic noise spectra. (a) shows the performance of the A-S method, and (b) the performance of the neural network approach. It is clear from this that the network performs extremely comparably to the A-S method, with a mean error of approximately 2.5% compared to the A-S mean error of 4.6%. (c) shows an example coherence decay and (d) its associated underlying noise spectrum, as well as the predictions of the neural network, A-S method and the δ-function approximation. Of note is that the coherence decay does not have an obvious modulation frequency — meaning that this non-monotonic peak could not be extracted by a simple Fourier transform. The δ-function approximation does very poorly at re-constructing the noise spectrum, whilst both the neural network and A-S approach do well, successfully identifying the peak central frequency, width and amplitude.
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7.4 Experimental applicability and uses of the noise spectrum

7.4.1 Handling experimental data

Much of the focus when comparing the neural network technique used here has been on its ability to perform well despite using relatively sparse experimental resources. For that to hold, the network needs a way to successfully process experimentally measured coherence decay curves overlaid with experimental noise. A typical approach to removing experimental noise would be to apply a fit to the noisy data with a stretched exponential form to approximate the underlying decay. The problem with this approach is that applying such a fit makes an implicit assumption about the nature of the noise from which the coherence decay arises. Not all noise forms result in a stretched exponential decay.

To circumvent this problem we have proposed another neural network solution, which takes in noisy data and seeks to output the underlying curve to as low an error as possible. The benefit of this approach is that no assumption is made about the underlying structure of the data, meaning that network does not force a certain noise form on the coherence decay. We once again use an LSTM based network for this task, as these have been deployed with some success to time series denoising in the past including in the field of electrocardiogram analysis [176]. Simulated coherence decays have ±5% random noise applied to them and are used as the input to a network, whilst the non-noisy decays are used as the target.

Figure 7.9 shows the results comparing denoising performance of fitting a stretched exponential vs using a form agnostic neural network. The errors in the log of the coherence decay (log$C'(t)$) are used as that is what the noise spectrum depends on as shown in equation 7.4 and so gives the expected minimum error if these denoised curves are used to infer the noise spectrum. The performance of the network is significantly better than the fitting approach and crucially performs similarly across the four noise types tested. The fitting of a stretched exponential performs particularly poorly for Lorentzian and double Lorentzian noise, which is expected given those noise forms are known not to result in purely stretched exponential coherence decays. These results demonstrate the
7.4 Experimental applicability and uses of the noise spectrum

Figure 7.9: Comparison of curve fitting and neural networks for denoising of coherence decays. Errors are calculated with respect to the log of the coherence decay as that is what the noise spectrum $S(\omega)$ is proportional to. Insets show range of errors, with the lines in the boxes indicating the mean, the boxes the standard deviation and the bars the range of errors. Of note is the superior performance of the neural network and its consistency across noise forms. The particularly poor performance of curve fitting on coherence decays derived from Lorentzian noise spectra is unsurprising given that they are not expected to produce stretched exponential decays in general.
7 Machine learning for probing the qubit environment

<table>
<thead>
<tr>
<th>Noise model</th>
<th>NN approach</th>
<th>Curve fitting</th>
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<tbody>
<tr>
<td></td>
<td>Mean</td>
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</tr>
<tr>
<td>Stretched exp.</td>
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<td>4.84</td>
</tr>
<tr>
<td>$\frac{1}{T}$</td>
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<td>3.82</td>
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<tr>
<td>Lorentzian</td>
<td>6.35</td>
<td>4.42</td>
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<tr>
<td>Double Lorentzian</td>
<td>6.72</td>
<td>4.91</td>
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</table>

Table 7.3: Comparison of error statistics in % of $\log C(t)$ for neural network based and stretched exponential curve fitting approaches.

...importance of using functional form agnostic denoising when the noise spectrum is to be inferred from the coherence decay. Detailed results are shown in table 7.3.

7.4.2 Uses of the noise spectrum

Having shown that the neural network approach is highly successful at predicting a noise spectrum from an underlying coherence decay, a natural next question is what to do with that noise spectrum once it has been derived. In the past, knowledge of the noise spectrum has been used to extend coherence times via bespoke dynamical decoupling sequences and for shallow NV centres has been used to predict their depth [65, 66, 163].

Romach et al employed the $\delta$-function approximation to show that the noise spectrum experienced by near surface NV centres had a double Lorentzian form. This shape is hypothesised to be caused by the NV centre coupling to two distinct noise forms with differing correlation times. The slower of the two is thought to be caused by spin-spin coupling between spins in a surface bath and the faster is caused by surface-modified phonons. The coupling strengths between NV centre and the two noise sources $\Delta_\sigma$ and $\Delta_f$ are reduced as the NV centre depth increases. This relationship can be used to estimate the depths of these near surface NVs, meaning that the neural network based denoising technique developed here could in principle be used for efficient depth estimation of NV centres.

Figure 7.10 shows the use of standard optimisation based on knowledge of the noise spectrum to increase coherence time. Example coherence decays and corresponding noise spectra for $1/f$, Lorentzian and double Lorentzian are shown in (a) and (c). To
show the potential for coherence increases, we use a sequential least-squares program-
ing (SLSQP) minimisation technique from the python library SciPy [177] to optimise
the positions of pulses in a 32-pulse CPMG sequence at five values of total sequence
length. Doing this allows significant gains in coherence time when compared with CPMG
and even the more advanced Uhrig dynamical decoupling sequence [57]. The sequence
optimisation is constrained to ensure that pulse order remains constant.

The results show a significant improvement in coherence over both a CPMG sequence
and Uhrig decoupling sequence of the same evolution time. These results are promis-
ing and highlight the utility of the technique for extending coherence times, although
obviously experimental validations are required before we can confirm this.

7.5 SUMMARY AND OUTLOOK

7.5.1 EXPERIMENTAL VERIFICATION

The results presented here show that a neural network can be employed to extract the
noise spectrum experienced by a qubit from its underlying coherence decay, with sig-
ificantly greater accuracy than a δ-function approximation based technique. Further-
more, when compared with a state-of-the-art technique in the Alvarez-Suter method, the
neural network approach performs comparably whilst requiring significantly fewer ex-
perimental resources. In addition, we have shown that neural networks can be employed
to denoise experimental data in a functional form agnostic way, giving significantly im-
proved results when compared with a standard stretched exponential fitting approach.

Whilst the benefits of the approach are obvious, the areas for improvement are fairly
clear. First of all an experimental verification of the work is required to be truly con-
fident that the results are representative. There are several ways that this can be done.
First, by attempting to optimise coherence of a qubit based on the neural network pre-
dicted noise spectrum, the enhancement compared with a predicted enhancement would
give some ideas about the accuracy of the approach. Secondly, artificial noise of known
power spectral density could be applied to a qubit, its coherence measured and the noise
predicted and compared with the expected results. This is actually quite challenging —
deriving the time trace of artificial noise in order to achieve a given PSD is a similar prob-
Figure 7.10: Use of the noise spectrum to produce optimal pulse sequences for extension of coherence time. (a) and (b) show three example coherence decays and their corresponding noise spectra, with $1/f$, Lorentzian and double Lorentzian forms. (c) shows how coherence can be enhanced for each of these noise spectra at 5 different points in the decay. The ‘absolute enhancement’ referred to in (c) is measured by taking the coherence of the optimised sequence and subtracting from it the coherence of a standard 32-pulse CPMG sequence. i.e. if coherence measured with a CPMG sequence was 0.2, and coherence measured with an optimised sequence was 0.5, then absolute enhancement would be 0.3. Also shown is the enhancement provided by an Uhrig DD sequence over CPMG. The inset shows two example optimised pulse sequences, with their corresponding enhancements marked in (c).
lem to the one tackled here. A simple approach would be to apply noise at a particular frequency and verify that the network predicts a non-monotonic peak in the noise spectrum. Finally, the network predictions could be compared with the predictions of the Alvarez-Suter method, which is known to predict highly accurate noise spectra.

7.5.2 IMPROVEMENTS TO THE TECHNIQUE

The results shown here are promising, and suggest that neural networks may well be a useful tool but just as clear are where improvements could be made. First among these is the restrictive time dimension requirement — because this is an implicit rather than explicit in the network training, subsequent inference must be done on coherence decays with the same time vector. This is not a particularly restrictive requirement, as interpolation can be used to good effect to rescale the coherence decay to the trained time vector. Tests with this have shown small increases in errors but still well within expected experimental noise (<1%). Despite this option, the ability to have time vector as an input into the network would be beneficial. Time awareness is an area that is still under research in the deep learning community, although the transformer architecture’s encoding of word position in vector form suggests a potential avenue for exploration. Other researchers have followed a similar path with some success at producing vector representations of time [147, 178, 179].

The current solution to working with noisy experimental data is somewhat inelegant — the requirement to have two separate networks, one for denoising and one for noise spectrum extraction, adds complexity. Ideally, one network would be used for both. This also raises the question of how best to deal with experimental noise — the fact that the noise spectrum is sensitive to \( \log C'(t) \) means that any experimental error is magnified when extracting the noise spectrum. As such, minimisation of experimental noise is obviously desirable — the question is how best to spend experimental resources to achieve the best results. For example, whilst performing 100 averages for a Hahn echo may produce an acceptable signal-to-noise ratio, could the same experiment time be better spent measuring with two different pulse sequences? Measuring with a Hahn echo and a multi-pulse CPMG sequence for 50 averages each would yield worse signal to noise
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![Graph showing noise spectrum predictions](image)

Figure 7.11: Losses for predicting noise spectra from one of five functional forms using a convolutional autoencoder architecture rather than an LSTM. Results are improved from the LSTM, despite using fewer parameters and including more noise forms in training. Maximum error in this case was 10.1%, compared with 200% when using an LSTM to predict double Lorentzian noise spectra.

for each experiment, but having two different perspectives on the noise spectrum could yield better results, if a network were trained to take both sequences as input.

The above raises the question of the most effective architectures for this problem — whilst significant time was spent identifying the LSTM as a successful approach, as we have gained experience it has become clear that it is not the optimal one. One issue with LSTMs is their sequential nature, which means that there is limited opportunity for parallelisation of the training of the network — extending training time significantly over other networks. This is one of the reasons that the transformer architecture has superseded the LSTM as the choice for language modelling [142]. Recent work has shown that a convolutional autoencoder can actually outperform the LSTMs used in this work on the same task, whilst using an order of magnitude fewer network parameters and a significantly reduced training time due to their highly parallelisable nature. Figure 7.11 shows the losses for an autoencoder trained to predict noise from the five functional forms discussed in this work. In addition, exploration of the transformer architecture is clearly worthwhile — it is highly efficient and may well allow for the incorporation of other desirable characteristics such as the data time vector.
Finally, a key component of this approach is error estimation. This was touched on above in the section about deriving noise spectra of untrained forms but it remains a weakness of the approach. If the neural network makes a wildly inaccurate prediction then the user needs to be aware of this. There are some solutions, the first is that once a noise spectrum has been predicted, equation 7.4 can be used to verify that with the pulse sequence used that the predicted noise spectrum yields the measured coherence decay. This is a good sense-check but as the noise spectrum is not unique, it does not provide a guarantee that the prediction is correct. The use of measurements from more than one pulse sequence will improve things — though there is obviously a balance required to ensure experimental requirements are still kept as low as reasonably possible. Estimating the error of neural network predictions is an active field of research and work on probabilistic neural networks is yielding excellent results in accurate error predictions [180, 181, 182, 183, 184]. Typically, these networks use a distribution of weights rather than static weights meaning that a natural distribution in the prediction is produced — allowing for sensible error bars on any neural network output. Variational autoencoders are another technique that can be used for error prediction, as the latent vector of the autoencoder is forced to conform to a distribution during training that matches the distribution of the target data. This allows the network to mark the position of new input data in the distribution of trained data and thus to make predictions about its anticipated error [185, 186].
8 Conclusions

Hang on a minute lads, I’ve got a great idea.
— Charlie Croker

8.1 Summary

In this thesis I have presented research focussed on the potential integration of spins bound to donors in silicon with the spin of optically active defects and particularly the NV centre in diamond. This has included a study into the impact of near band-gap illumination on the quantum characteristics of electron spins bound to donors in phosphorus, a study into the effect of low temperatures on near-surface NVs in diamond, initial characterisation of commercial single NV centre probes at low temperature, and study into using deep learning for qubit noise spectrum extraction. Points to note include:

1. The results for the effects illumination on relaxation and decoherence on the electron spin bound to phosphorus donors in silicon have two major takeaways. The first is that there is no apparent increase in the rate of decoherence at the wavelengths studied, beyond the increased relaxation rate and its capacity to reduce coherence via its impact on $T_1$ of neighbouring donors [19, 35]. This is a positive result from the point of view of potential coupling between optically active defects and donor spins in silicon, with coherence typically being the limiting factor for such operations. If heating is shown to be the major mechanism behind the increased relaxation rate then the impact of illumination can be reduced via improved cooling, such as better thermal contact to a cold finger or immersion in
8 Conclusions

liquid helium. The second takeaway is that there is no sudden drop off in the impact of illumination once photon energies are below the silicon band gap energy, with laser power being still being the dominant effect. This highlights the requirement that defects used for this purpose must be read out with relatively low laser powers, ideally below 1 mW. Further work is required to investigate the effects of shorter wavelengths, and to discern the exact mechanisms that cause the increased relaxation rate.

2. We presented a detailed study of temperature effects across several near-surface single NV centres. We studied the impact of temperature on ODMR contrast, Rabi oscillations, fluorescence, fluorescence contrast and $T_2$. Rabi frequency was observed to reduce with temperature, in a manner consistent with reduction in resistance of the electrical components. Other than $T_2$, all other characteristics underwent the same pattern of change - they were reduced in quality below 70 K, hitting a minimum at 40 K, before recovering as they were cooled below 40 K to 15 K. Analysis of the blinking rate of one NV centre, combined with the lack of change in coherence with temperature, suggest strongly that the observed effects are charge state related. Largely, these results were positive as they suggested that these near surface NV centres could be used at temperatures conducive to electron spins in silicon, although with some reduction in characteristics.

3. The study on NV centres in diamond AFM probes was less positive. In all cases, NV centres were found to undergo a complete loss of NV contrast within the space of two to three weeks. In two cases this was accompanied by a fivefold increase in fluorescence whilst in two other cases contrast was lost without fluorescence increases. This was unlike the experience with the diamond pillar sample, which may have been caused by those NV centres being deeper into the bulk than those in the probes. Some characterisation was able to be performed, including extracting the collection efficiency of the confocal setup and measuring the AC magnetic field generated by a wire. However, the chief result of this chapter is highlighting the need to isolate the cause or causes of the degradation of the probe NV centres,
which may include the sample surface treatment, its fabrication process, and the cryostat environment.

4. Finally, we looked at the results of attempting to use deep learning techniques to enhance the accuracy and efficiency of extracting the noise spectrum of a qubit from its coherence decay. We saw that this technique was highly successful when extracting monotonic decays of three different functional forms and was significantly more accurate than a mathematical approximation with comparable experimental requirements. We also showed that the performance of the approximation was not improved by the use of more complex but not significantly more taxing pulse sequences, further cementing the utility of the deep learning technique. A comparison between the deep learning technique and a state-of-the-art experimental technique, the Alvarez-Suter method, for the extraction of complex non-monotonic noise spectra showed that the performance of the network was comparable or better, whilst using significantly reduced experimental resources. We saw how neural networks could be employed to facilitate function agnostic denoising of coherence decays, allowing more accurate results than was possible with a simple fitting technique. Finally, we looked at potential uses of the noise spectrum, including extension of coherence using pulse sequence optimisation.

8.2 Next Steps

Having summarised the major results of each chapter, I will now look at the next steps for each experiment and what we might hope to learn.

1. The studies in chapter 4 were made in the context of the potential use of optical defects that were controlled using infrared laser illumination at photon energies below the photon bandgap. With that in mind, there are two future avenues for this work that need exploring. Firstly, a study into the likely mechanisms behind the observed reductions in $T_1$ and consequently $T_2$. Heating was presented as a likely cause and the ways to investigate this are fairly simple - by keeping laser power constant, and increasing the cooling power at the sample it should be pos-
sible to partially mitigate the effect of any laser heating on sample temperature, whilst using the dark $T_1$ of the NV centres to keep sample temperatures consistent. To study the potential impact of electron scattering on $T_1$, the traditionally given explanation for the impact of laser illumination [44], measurements of sample conductivity and carrier density could be carried out via a Hall probe.

The second set of interesting experiments to carry out would be studies on the impact of lasers at the NV readout wavelength of 520 nm. This would give much greater insight into the potential for the integration of NV centres and donors in silicon in a qubit architecture. Whilst the impact is expected to be much greater at shorter wavelengths, the typical pulse times of 3 - 4 $\mu$s mean that there is likely to be some reduction in the potential effect. Low CW laser powers of 10 - 100 $\mu$W will be offset by greatly increased power density due to laser focusing by the objective. In short, whilst the work presented here gives some clues as to what we might expect, a significant further investigation will be required before we can speak confidently on this matter.

2. The work on both the diamond pillar sample and the single NV centre probes leaves some avenues to explore. The diamond pillar sample was initially studied as a guide as to what to expect when working with the more valuable single probes. Initial results suggested a degradation and then recovery in performance as the probes were cooled, but with otherwise no ill effects. The short lifetimes of those probes, despite initially good performance shed a new light on the prior work. The observed behaviour of the NVs in pillars, and particularly the apparent influence of surface chemistry of the diamond on the NV charge state, may indicate a similar mechanism, if with a slightly different result is affecting the NV centres in the AFM probes.

Detail of the planned future experiments to study these tip NVs was given in the summary of chapter 6. Utilising a sample with pillars fabricated in an identical way to those found on the diamond tips, but with a variety of different NV characteristics - including different pillar diameters and depth profiles. This sample will be used to perform a detailed experiment on the behaviour of these NV centres at
8.2 Next Steps

low temperature and over time, taking particular care to attempt to resolve the impact of sustained laser illumination on the NV characteristics. In addition to this process, there is a potential need to experiment with different diamond surface treatments, which may help with potential surface chemistry effects. The cryostat environment is also a potential cause of impurities that could interact with the near-surface NV centres via the diamond surface. Additional steps to control and purify the cryostat sample space, such as by the addition of charcoal traps, may yield improved low temperature performance.

3. The relative success of the deep learning technique has left several, potentially fruitful, areas of development open. First and most importantly will be an experimental verification of the technique. As has been state, the business of noise spectrum extraction is well suited to the use-case of sensing with NV centres and this is an obvious starting point. One simple experiment would be an attempt to extract the noise spectrum of an NV under influence from an artificial noise source, whether that is in the form of a full noise spectrum or a simple tone added to the background. As long as the artificial source is well controlled, this would allow us to benchmark the performance of the technique against reality. Further steps, such as increasing coherence via pulse sequence optimisation, would add greater credence to the technique's efficacy.

In addition, greater work into making the deep learning technique more user friendly would be prudent. This is of particular concern where the handling of experimental data is concerned. The current approach of a separate denoising network is inelegant and it is highly likely that an efficient single network could be employed to similar effect. Recent efforts to improve the network have resulted in a more efficient convolutional autoencoder, which achieves better results with significantly lower network complexity. Experiments on the impact of different approaches to data gathering should be employed - whether it is more efficient to spend time performing repeated averages with the same pulse sequence, or to accept higher experimental noise over two different pulse sequences. Finally, the addition of ways to estimate the errors in predictions is vital for the technique to be of use to scientists. Several probabilistic neural network techniques exist that could be em-
8 Conclusions

ployed, whilst the simple act of inverting the predicted noise spectrum allows for some basic error checking.

8.3 Outlook

Taken as a whole, the results presented here leave us on something of a cliff-hanger. We have good reason to believe that the impact of laser illumination on donors in silicon will get significantly greater upon moving to green laser light. However some mitigating factors exist, such as lower powers and reduced illumination time, that may mean the results are not as stark as feared. Particularly if we can show that the effect is mainly heating based then it may well be possible to reduce the impact to the point where some coherent spin detection is possible.

Whilst coherent measurement of silicon donor spins by NV centres will be challenging, we have shown that the NV centres studied here certainly have sufficient magnetic sensitivity (albeit with averaging) to detect the presence of single electron spins in silicon and at distances that are in line with expected separations between near surface defects in both samples. In its current state, the confocal setup is well suited to field sensing but not particularly to quantum operations, for which single shot readout would be required [187]. This represents a possible extension of this work, but is obviously a long term goal, to be addressed once low temperature longevity can be achieved with near surface NV centres.

Looking beyond the nitrogen vacancy centre, there are alternative optically active defects that are worth of consideration for a hybrid architecture. I have mentioned the divacancy in silicon carbide, which has been studied relatively extensively and shows good quantum properties, including $T_2$ measured at close to 1 ms and fluorescence contrast that is comparable to the NV centre. Count rates for the divacancy are somewhat lower than the NV centre at approximately 25 kC/s, but fabrication of on sample waveguides or lenses should improve this significantly, as has been observed with the NV centre [188, 189]. Most importantly the zero phonon line of the divacancy is at approximately 1100 nm, so the impact of readout laser light on donor spins in silicon should be significantly reduced relative to the NV centre. Furthermore, it is quite likely that a silicon
8.3 Outlook

carbide platform will present greater fabrication practicality and performance than can be achieved with diamond. Whilst diamond fabrication and manufacturing are improving and will continue to do so, it has been estimated that the industry is at approximately the stage that silicon fabrication was at in the 1960s and 70s [190]. The fabrication of high quality diamond must become consistent and standardised before the industry can reach the expansion rates that the silicon industry achieved in the 1980s. In addition, deterministic implantation of single NV centres (particularly near the diamond surface) must be improved, with typical yields currently at less than 10%, and more robust procedures typically leading to reduction in NV $T_2$ due to the creation of unwanted defects [191].

Recent results give cause for optimism. Experiments with doping of diamond have shown drastically improved yield rates of NV centres - up to 75% and with the anticipation that this can be improved to 100% given further optimisation [40, 192, 193]. As these techniques are also thought to improve qubit charge stability, they may well have significance for the low temperature issues shown in this work. Highly precise spatial positioning of NV centres has also been achieved by ion detection and NV centre creation validation [39], although processes are still relatively slow. Fabrication of high quality and consistent diamond samples continues to prove an issue but progress is happening slowly.

All in all, the future of integration between NV centres in diamond and donor spins in silicon is uncertain. There are good reasons to be optimistic but enormous technical and physical challenges to overcome. The huge scaling potential of silicon based qubits makes them endlessly attractive as do the largely unmatched properties of the nitrogen vacancy centre. Superconducting qubits undoubtedly have the lead for now but the chase has begun and there's plenty of time remaining.
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