ELECTRICAL MANIPULATION OF DONOR SPIN QUBITS IN SILICON AND GERMANIUM

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Abstract

Many proposals for quantum information devices rely on electronic or nuclear spins in semiconductors because of their long coherence times and compatibility with industrial fabrication processes. One of the most notable qubits is the electron spin bound to phosphorus donors in silicon, which offers coherence times exceeding seconds at low temperatures. These donors are naturally isolated from their environments to the extent that silicon has been coined a “semiconductor vacuum”. While this makes for ultra-coherent qubits, it is difficult to couple two remote donors so quantum information proposals rely on high density arrays of qubits. Here, single qubit addressability becomes an issue. Ideally one would address individual qubits using electric fields — which can be easily confined. Typically these schemes rely on tuning a donor spin qubit onto and off of resonance with a magnetic driving field. In this thesis, we measure the electrical tunability of phosphorus donors in silicon and use the extracted parameters to estimate the effects of electric-field noise on qubit coherence times. Our measurements show that donor ionization may set in before electron spins can be sufficiently tuned. We therefore explore two alternative options for qubit addressability.

First, we demonstrate that nuclear spin qubits can be directly driven using electric fields instead of magnetic fields and show that this approach offers several advantages over magnetically driven spin resonance. In particular, spin transitions can occur at half the spin resonance frequency and double quantum transitions (magnetic-dipole forbidden) can occur.

In a second approach to realizing tunable qubits in semiconductors, we explore the option of replacing silicon with germanium. We first measure the coherence and relaxation times for shallow donor spin qubits in natural and isotopically enriched germanium. We find that in isotopically enriched material, coherence times can exceed 1 ms and is limited by a single-phonon $T_1$ process. At lower frequencies or lower temperatures the qubit coherence times should substantially increase.
Finally, we measure the electric field tunability of donors in germanium and find a four order-of-magnitude enhancement in the spin-orbit Stark shift and confirm that the donors should be tunable by at least 4 times the electron spin ensemble linewidth (in isotopically enriched material). Germanium should therefore also be more sensitive to electrically driven nuclear magnetic resonance. Based on these results germanium is a promising alternative to silicon for spin qubits.
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Portions of this thesis have previously been published in one or more of the following papers:


Chapter 1

Introduction

1.1 The quantum bit

Ever since Feynman’s seminal paper envisioning quantum computation [35], physicists have dreamt of the ability to simulate complex quantum systems. Over the past decade, the field of quantum information has grown tremendously and this experimental thesis aims to advance one of the more promising implementations of quantum computing, that is the field of semiconductor spin qubits.

The fundamental building block of any classical computer is the bit. The bit is essentially a quanta of information, which is physically represented by a voltage. A voltage above some threshold corresponds to a logical 1 whereas a voltage below that threshold corresponds to a logical 0. By allowing these bits to interact through gates, one can perform simple arithmetic. When one combines many logical gates together in specific ways, rather complicated problems can be solved ranging from routing a car in real time through traffic to downloading and displaying this thesis.

Likewise, the basis of any quantum computer is the quantum bit (qubit). Whereas the classical bit was implemented as a voltage on a wire, the qubit is physically made up of a quantum mechanical system with two discreet energy levels. Since quantum
information processing as a field is still in its infancy, there are many competing qubit implementations. Some examples include motional and spin states of trapped ions [17, 133, 76, 43]; charge, flux, or phases in microwave superconducting circuits [61, 24, 23]; polarizations of light [60, 64]; and the focus of this thesis: electronic and nuclear spins in semiconductors [55]. No matter the implementation, there are some basic quantum mechanical principles that enable quantum computation.

First, qubits can take either one of two states, $|0\rangle$ or $|1\rangle$, or superpositions (linear combinations) of those states, $\alpha|0\rangle + \beta|1\rangle$. In this Dirac formalism, the kets ($|0\rangle$ or $|1\rangle$) are the quantum systems’s wavefunction in the 0 or 1 states, respectively. $\alpha$ and $\beta$ are complex wavefunction amplitudes that satisfy a normalization condition $|\alpha|^2 + |\beta|^2 = 1$ and the probability of measuring the system in $|0\rangle$ or $|1\rangle$ is $|\alpha|^2$ or $|\beta|^2$, respectively. Before measurement, the qubit can exist in a superposition of states such that if the qubit were in $(|0\rangle + |1\rangle)/\sqrt{2}$, it exists simultaneously in both the $|0\rangle$ and $|1\rangle$ states. However, measurements in quantum mechanics are said to be projective. This means that once the state of a quantum system is measured, the system is entirely in that state. If we were to measure the system in the state ($(|0\rangle + |1\rangle)/\sqrt{2}$) and observe a $|0\rangle$, the system would immediately take on the $|0\rangle$ state and $\beta$ would become 0. The very act of measurement therefore influences the quantum system. While this behavior seems strange, it is very clearly demonstrated in some beautiful experiments including double slit and quantum erasure experiments [57, 85, 104, 47].

Things get more interesting when we add a second qubit to the system. In this case we can take advantage of an effect known as entanglement. Entanglement implies that the states of two qubits are correlated, and to demonstrate this we can consider the case of a system ($\psi$) prepared into a maximally entangled state (Bell state). That is, $|\psi\rangle = \alpha_{00}|00\rangle + \alpha_{11}|11\rangle$. Now consider what happens when one of the qubits are measured. If the first qubit is measured and found to be $|1\rangle$, we know that the state of the system must be $|11\rangle$ and qubit 2 is therefore $|1\rangle$. This holds regardless of the
separation of the qubits. By observing qubit 1, we can influence qubit 2, regardless of their separation. If one were to pull the two qubits very far apart and make simultaneous measurements on them (such that any lag in measurement is short relative to the qubit separation divided by the speed of light) one would always find that the two qubits states were correlated. In a famous paper\cite{31}, Einstein, Podolsky, and Rosen brought up this very point suggesting that the quantum mechanical description of these qubits must be non-physical. Years later, a clever experiment was envisioned by Bell \cite{7} which tested the entanglement of remote particles. Bell’s experiment was later conducted and the results showed that the behavior described by Einstein as a proof for the absurdity of quantum mechanics is indeed physical \cite{4, 3, 105, 46}.

It is because of these strange and non-intuitive effects that researchers such as myself are drawn to quantum mechanics. By taking advantage of these non-classical effects, quantum computing algorithms have been developed that are suspected to outperform their best known classical alternatives \cite{42, 108}. While universal quantum computers have still not been developed, quantum mechanical effects are crucial to the operation of much of our technology ranging from transistors to lasers to medical imaging devices. Quantum effects are also already implemented in security technologies including random number generation and quantum key distribution.

### 1.2 Properties of a good qubit

Since this thesis seeks to advance the physical implementations of qubits, it is natural to first address the question, “What makes a good qubit?” These were answered by David DiVincenzo \cite{25} in what have now been coined “The DiVincenzo Criteria”. They are:

1. *A scalable physical system with well characterised qubits.*
This criteria has two parts to it. First, since qubits are quantum mechanical systems having two states, it would be important that the qubits have controllable, well-defined states. It is not so hard to find a two level system that makes a good individual qubit, but it is difficult to find a good two level system that is scalable.

To solve classically intractable problems using quantum computers, algorithms will require an incredible number of qubits so scalability is an important issue. If one tries to factor a number containing 2000 bits using surface codes, the algorithm is estimated to require $10^9$ qubits (assuming error rates at 10% of the error threshold) \[36\]. When one begins to consider computers consisting of billions of qubits, clearly it is important that the qubits also be able to share resources (i.e. the experimental setup should not grow substantially with the number of qubits). If each qubit requires its own microwave source or its own laser, the system is not scalable.

2. \textit{The ability to initialise the state of the qubits to a simple fiducial state}

The function of any computer, quantum or classical is to take information in, manipulate it (perform a calculation), then output the results. If one can not control the input of a computer, then it is of no practical use. We therefore require that one can initialize the qubit into a particular state.

3. \textit{Long relevant decoherence times}

Decoherence is effectively loss of quantum information. It typically occurs when qubits interact with either other qubits or their environment in an unknown and uncontrollable way. The decoherence time is therefore related to the amount of time that one can store quantum information. It is important that decoherence times be long relative to the time it takes to perform an operation, otherwise the output of any quantum computer will be pseudo-random.

4. \textit{A universal set of quantum gates}

In classical computing, “NAND” or “NOR” gates are considered universal logic gates because any other logic gate can be constructed from them given enough of the
gates wired in the proper configuration. Likewise, to ensure there are no limitations in programming a quantum computer, it is desirable to have a set of universal quantum gates. We require that the universal set of quantum gates allow both single- and two-qubit operations. One example of a universal set of gates would be the Hadamard gate, the phase rotation gate, and the controlled-not gate \[\text{[83]}\].

5. A qubit-specific measurement capability

Finally, in order for any computer – quantum or classical – to be useful, one must be able to read the results of the calculation. Some quantum error correction schemes, such as the surface code architecture, require the ability to also individually read the state of each qubit in the system.

6. The ability to interconvert stationary and flying qubits

These last two criteria are not directly aimed at realizing quantum computers, rather they are requirements for allowing quantum communication. If one envisions future quantum networks, one will need quantum interconnects. For many quantum implementations it is not realistic to physically transmit qubits from one location to another so one must be able to write states of stationary processing qubits onto moveable “flying” qubits such as photons.

7. The ability to faithfully transmit flying qubits between specified locations

It is important to not only be able to write qubit states to “flying qubits”, but it is important that those qubits maintain the information encoded in them until they reach their destination and are read out.

These criteria have become the checklist researchers consider when evaluating their particular qubit implementations. With these criteria in mind, we turn to the qubit that is the focus of this thesis, the donor spin qubit.
1.3 The donor spin qubit

Spin qubits come in many varieties, each with their own strengths and weaknesses. These include quantum dots which are easy to manipulate but often have short coherence times, defects in diamond (nitrogen-vacancy color centers, silicon-vacancy color centers) which have long coherence times and are optically addressable but are difficult to reliably fabricate, and donor spin qubits which are the subject of this thesis.

The donor spin qubit consists of a single substitutional donor atom in a semiconductor lattice. The most common donor spin qubit is the $^{31}$P atom in silicon. In this system the $^{31}$P atom replaces a single silicon atom. However, phosphorus has five electrons in its outer shell, four of which form covalent bonds with silicon atoms — since silicon has a diamond cubic lattice. The extra electron sits in the conduction band and the donor is ionized at room temperature. The ionized donor has a positive charge so at low temperatures, the electron is weakly bound to it. There are two different two-level systems that can be used as qubits in a neutral donor: The nuclear spin and the electronic spin. The energy levels of the spins can be tuned by applying a static magnetic field with the two states being spin down with the spin oriented parallel to an externally applied magnetic field, or spin up, with the spin oriented antiparallel to the magnetic field.

The advantages of donor spin qubits in silicon are numerous, but one of their most striking qualities is their exceptionally long coherence times. Donor electron spins in silicon have been shown to have coherence times exceeding seconds when the host material is isotopically enriched to contain no magnetic nuclei [122] and this is extended to minutes for ionized donor nuclear spins [117]. Moreover, semiconductor qubits have the advantage of being uniform — one can easily implant $10^9$ donor qubits into a piece of silicon and be confident that they are all have the same frequency to within some small inhomogeneous linewidth [33]. Finally, semiconductor-based qubits
can take advantage of the many technological advances made by the semiconductor industry over the last several decades.

The main downside to donor spins in silicon is the difficulty in controllably mediating two-qubit interactions and individually controlling and reading out spins. The first promising approach to quantum computing in silicon which offered solutions to these problems is known as the Kane quantum computer and it is still being pursued by many research groups [55, 26].

1.3.1 The Kane quantum computer

The Kane quantum computer is based on high density (∼20 nm pitch) arrays of $^{31}$P donor spin qubits implanted very near the surface of a silicon substrate. At the interface there are arrays of electrostatic gates referred to as “A-gates” and “J-gates”. These mediate the one and two qubit interactions, respectively. An artist’s rendition of this quantum computing scheme is shown in Fig. 1.1.

A-gate control of individual spins

One of the downsides of donor-spin based quantum computing is that magnetic fields are used drive spin transitions and manipulate individual qubits. While it is relatively simple to produce resonant magnetic fields, it is difficult to confine magnetic fields to individual donor qubits in high-density devices. Stray magnetic fields can unintentionally drive neighboring qubits unless they are physically separated by large distances. This will pose a problem for implementing two-qubit gates and will limit the scalability of these systems.

The approach suggested in the Kane proposal is to apply non-resonant microwave magnetic fields over the entire device, and rely on tuning individual qubits into and out of resonance with that field. When the field is suitably off-resonance it can not drive spin transitions. However, when the spin is tuned on resonance, spin transitions
will be driven at some frequency determined by the magnitude of the field. The power of this approach is that electric, and not magnetic, fields can be used to tune the spins through what is known as the Stark effect. Electric fields are much easier to confine at the nanoscale making this approach much more scalable. This method of control was recently demonstrated for nuclear spin qubits [136] but it remains an open question whether the same form of control will work for electronic spins. We discuss the prospects of Stark tunability for electron spins in Ch. 4.

**J-gate mediated two-qubit interactions**

It is not particularly difficult to get two spins to interact, but it can be difficult to get them to interact in a controllable way such that two qubit gates can be turned on and off at will. The approach suggested by Kane is to make use of an electronic “exchange interaction”. This interaction occurs when two neighboring electronic wavefunctions overlap. To control the interaction, J-gate electrodes are placed between neighboring donors. By applying a positive bias, the potential well produced by the nucleus can be distorted and pulled towards the gate as shown in Fig. [1.1]. The electronic wavefunctions are likewise distorted and pulled towards the J-gate so that they overlap. The electronic wavefunctions which interact with the nuclei through hyperfine interactions can then mediate an interaction between remote nuclear spins.

**Challenges to implementing a Kane quantum computer**

One of the biggest challenges to implementing a Kane quantum computer is the stringent fabrication requirements. Due to intervalley interference effects, the exchange interaction between neighboring donors varies rapidly with donor separation and is predicted to oscillate with a period that is comparable to the atomic spacing [62, 63, 129]. One therefore needs to be able to place individual dopant atoms in a lattice with single lattice site precision. The current state-of-the-art in nanolithog-
Figure 1.1: Cartoon rendition of a Kane style quantum computer taken from [114]. The donor nuclei are shown in orange with their electronic wavefunctions shown in black. When no voltages are applied (left most case) the electronic wavefunction is symmetric about the nucleus. When a voltage is applied to an “A-gate” (central case) the electronic wavefunction is shifted and the qubit frequency changes. If both the “A-gate” and “J-gate” is biased the electronic wavefunctions overlap and the exchange interaction is turned on.

raphy has almost solved this problem by achieving a one-lattice-site uncertainty [40]. This is made possible by using scanning tunneling microscopes to pattern hydrogen resist as described in [40].

1.3.2 Hybrid approaches to quantum computing

It addition to the Kane quantum computer, there are other promising quantum computing schemes involving donor spins based on “hybrid architectures.” The field of hybrid quantum computing combines multiple implementations of qubits into a system that hopefully performs better than either system could on their own.

Some of the most promising examples of hybrid quantum systems include the combination of superconducting qubits with spin qubits [66, 65, 87] and the coupling
of donor spins to quantum dots [88, 102]. Both superconducting qubits and quantum
dots offer the ability to perform two-qubit gates while donor spin qubits offer long
coherence times. Additionally, superconducting qubits offer the ability to transfer
quantum states to remote qubits since quantum information can be mapped onto
microwave photons. In these architectures, electron spins are typically treated as
quantum memories [66, 65].

1.4 Outline

This thesis begins with an overview of electron spin resonance and the electron spin
resonance spectrometer in Ch. 2. We then discuss superconducting circuits for low
temperature pulsed electron spin resonance spectroscopy in Ch. 3. Chapter 4 then
discusses electric field tunability of donor spins in silicon. In chapter 5 we discuss how
the Stark effect can lead to AC electric field manipulation of nuclear spins and show
the first demonstration of electrically driven nuclear magnetic resonance in silicon.
With electric field manipulation in mind, we shift our focus to another promising host
for donor spins — germanium. We show that donor spins in germanium, like silicon,
offer long coherence times (Ch. 6) in conjunction with a four order-of-magnitude
enhancement in the Stark effect (Ch. 7).
Chapter 2

Electron Spin Resonance and Experimental Techniques

2.1 The spin Hamiltonian

The donor electronic and nuclear spin system can be described by a spin Hamiltonian which is written as

$$H = H_{EZ} + H_{HF} + H_{NZ} + H_Q$$  \hspace{1cm} (2.1)

where the four individual terms correspond to the electron Zeeman, hyperfine, nuclear Zeeman, and quadrupolar terms, respectively \[103\]. We describe these interactions in detail in the following sections.

2.1.1 The electronic Zeeman interaction

The electronic Zeeman interaction arises from the electronic spin’s magnetic moment experiencing a torque when an external magnetic field is applied. This interaction takes the form
\[ H_{EZ} = \mu_B \cdot \hat{g} \cdot \vec{B}_0 \cdot \vec{S} \]  

(2.2)

where \( \hat{g} \) is the Lande \( g \)-tensor, \( \vec{B}_0 \) is the externally applied magnetic field, and \( \vec{S} \) is the electronic spin. In the unperturbed ground state, the \( g \)-tensor is isotropic for donors in silicon and germanium and is typically reported as a scalar value \( g_0 \) (\( \hat{g} = g_0 \cdot I \) where \( I \) is the identity matrix). The free electron \( g_0 \) is 2.0023 and any deviation from this value is typically due to a spin-orbit interaction. \( g_0 \) therefore varies depending on the material and can be used to identify trace impurities in spectroscopy applications. \( g \)-values for the donors discussed in this thesis are outlined in Table 2.1.

### 2.1.2 The hyperfine interaction

In addition to the electronic Zeeman interaction, there is a large contact hyperfine interaction between the donor bound electron and the nuclear spin. This interaction is isotropic and given by

\[ H_{HF} = A_{iso} \cdot \vec{S} \cdot \vec{I} \]  

(2.3)

where \( A_{iso} \) is the isotropic hyperfine coupling constant and is listed in Table 2.1.

This interaction is proportional to the electronic wavefunction overlap at the nucleus and therefore varies depending on orbital state of the electron, the shape and depth of the nuclear potential well, and the electrostatic environment of the nucleus. As such, measuring this interaction can give valuable information regarding the donor species, local strains or electric fields affecting the donor (as will be discussed later in this thesis), or the symmetry of the ground state wavefunction \[33, 131\].

### 2.1.3 The nuclear Zeeman interaction

The nuclear Zeeman interaction is analogous to the electronic Zeeman interaction except that it involves the nuclear magnetic moment instead of the electronic mag-
netic moment. At magnetic fields typically used in ESR experiments (∼0.3 T), the nuclear Zeeman interaction is small compared to the electronic Zeeman and hyperfine interactions, so its effect is often negligible. Nonetheless, it will be important when we discuss electron-nuclear double resonance experiments in Chapter 5 so we list it here. The nuclear Zeeman interaction is given by

\[ H_{NZ} = \mu_n g_n \vec{B}_0 \cdot \vec{I} \]  

(2.4)

where \( \mu_n \) is the nuclear magneton and \( g_n \) is the nuclear gyromagnetic ratio, which is listed in Table 2.1.

### 2.1.4 The nuclear quadrupole interaction

Nuclei with a spin greater than 1/2 can have a non-spherical nuclear charge distribution, which interacts with electric field gradients at the nucleus. In crystals with cubic symmetry (silicon and germanium), electric field gradients due to bonding electrons as well as the donor bound electron cancel at the donor site so this interaction is typically neglected. As we will see in this thesis, if the donor electron is perturbed, it can produce electric field gradients at the donor nucleus, which leads to measurable effects. In its simplest form, we write the quadrupolar interaction as

\[ H_{NQ} = \vec{I} \cdot \hat{Q} \cdot \vec{I} \]  

(2.5)

where \( \hat{Q} \) is the nuclear quadrupole tensor. This tensor is traceless and depends on the quadrupole moment of the nuclei, the charge distribution of the nuclei, and the nuclear spin. This can be calculated as described in [103, 92].
2.1.5 Summary of donor ESR and NMR parameters

The experimentally measured donor ESR and NMR constants are summarized in the following table.

<table>
<thead>
<tr>
<th>Host Material</th>
<th>Donor</th>
<th>Nuclear Spin</th>
<th>$g_e$</th>
<th>$A_{iso}$</th>
<th>$g_n$ (free atom)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>$^{31}$P</td>
<td>1/2</td>
<td>1.99875</td>
<td>117.53 MHz</td>
<td>2.2632</td>
<td>[33]</td>
</tr>
<tr>
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<td>3/2</td>
<td>1.99837</td>
<td>198.35 MHz</td>
<td>0.95965</td>
<td>[33]</td>
</tr>
<tr>
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<td>$^{121}$Sb</td>
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<td>1.99858</td>
<td>186.80 MHz</td>
<td>1.3454</td>
<td>[33]</td>
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<tr>
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<td>101.52 MHz</td>
<td>0.72861</td>
<td>[33]</td>
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<tr>
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<td>$^{209}$Bi</td>
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<td>229 MHz</td>
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2.2 The Bloch sphere and spin transitions

To simplify the following discussion, we will consider a spin-1/2 electron and neglect all but the electronic Zeeman term, which is dominant at moderate magnetic fields.

To visualize the state of the spin, we make use of the “Bloch sphere” as shown in Fig. 2.1. The Bloch sphere is a spherical representation of the spin state, which rotates at the spin precession frequency. The north pole corresponding to the ground state ($|0\rangle$) and the south pole corresponding to the excited state($|1\rangle$). The $X$ and $Y$ axes correspond to the $(|1\rangle + |0\rangle)/\sqrt{2}$ and $(|1\rangle + i|0\rangle)/\sqrt{2}$ states, respectively.

The Bloch sphere is also often used to represent the classical magnetization vector of a spin $\vec{M}$ either aligned (pointing along $+Z$) or antialigned (pointing along $-Z$) with the magnetic field $\vec{B}_0$. In this case the $X$ and $Y$ axes represent out-of-phase ($Q$) and in-phase ($I$) precession, respectively.
2.2.1 Static and off resonance spin perturbations

In the lab frame, with some magnetic field $\vec{B}_0$ applied to an ensemble of spins, the spins will experience a torque that causes them to precess about $\vec{B}_0$ at a frequency ($\omega_Z$) determined by the Zeeman splitting ($g\mu_B\vec{B}_0$). Now consider what happens when an additional static field $\vec{B}_{1s}$ is applied orthogonal to $\vec{B}_0$. This additional field will cause the spins to undergo an additional precession about $\vec{B}_{1s}$ at a frequency $\omega_{R'}$. The spins, however, are rotating at $\omega_Z$ meaning that from their reference frame, $\vec{B}_{1s}$ is rotating at a frequency $\omega_Z$, and $\omega_{R'}$ changes sign at that same frequency $\omega_Z$. Therefore if $\omega_{R'}$ is slow compared to $\omega_Z$ the effect of $\vec{B}_{1s}$ averages out in what is known as the rotating wave approximation.

If the applied magnetic field was rotating at a frequency that is different from $\omega_Z$, the spins would experience a field rotating about $B_0$ at a frequency equal to the detuning, $\omega_\delta = \omega_Z - \omega_{R'}$. If the applied field is highly detuned ($\omega_\delta > \omega_{R'}$), the rotating wave approximation still applies and the effect of the off-resonance field is negligible.
2.2.2 Resonant driving of spins

Now we consider what happens if a magnetic field co-rotating with the spin ($\vec{B}_1$) is applied. This field is static from the spin’s reference frame so the spin will undergo precession about both $\vec{B}_1$ and $\vec{B}_0$. The precession about the $\vec{B}_1$ axis will cause the spin to oscillate between the ground and excited states at some frequency known as the Rabi frequency ($\Omega_R$) as shown in Fig. 2.2. By controlling the phase and duration of the $\vec{B}_1$ field applied, one can rotate the spin to be in any arbitrary state on the Bloch sphere.

This discussion begs the question: how are rotating fields applied? Physically rotating a coil or the sample at typical resonance frequencies ($\sim$10 GHz) is impractical, so we make use of microwave cavities. With a microwave cavity, it is relatively straightforward to set up a microwave standing wave with a magnetic field antinode in the sample region. This gives a linearly polarized microwave field can be decomposed into two components, one that is left-circularly polarized, and another that is right-circularly polarized. If the microwave cavity is on resonance with the spins, one of the circularly polarized components can be made to co-rotate with the spin, while the other is detuned by $2\omega_Z$. By the rotating wave approximation this detuned component averages out. For certain experiments (determining the sign of a gyromagnetic ratio, for example) it is important to suppress this counter-rotating magnetic field and this can be done through the use of some clever microwave cavity designs, but at the cost of increased experimental complexity [139, 32, 16, 54].
Figure 2.2: Cartoon showing resonant driving of spins in the Bloch sphere. The spin starts in the ground state (a) and begins precessing about the $X$ axis at a rate of $\Omega_R$ upon application of $\vec{B}_1$ (b). After $\vec{B}_1$ is turned off the spin becomes stationary in the Bloch sphere as shown in (c). By timing the duration and phase of $\vec{B}_1$ the spin can be placed anywhere on the Bloch sphere.

2.3 Basic ESR experiments

2.3.1 CW spectroscopy

Continuous wave (CW) ESR is a technique that relies on resonant absorption of microwave photons. In the simplest picture, a spin can absorb a microwave photon only if the photon’s energy is equal to the spin transition energy, otherwise the photon is not absorbed. One can therefore probe the spin transition energies by shining microwaves of known frequency into a spin ensemble, and measuring the absorption as a function of applied magnetic field — since the spin transition frequency depends on field. Continuous wave ESR spectroscopy does exactly this.

In CW ESR, microwaves are pumped into a resonant cavity (to enhance sensitivity) and the absorption is determined by measuring the reflected microwave power. For technical reasons related to sensitivity (discussed in the following section on spectrometers), CW ESR typically measures the derivative of the ESR spectra as shown in a representative spectra of $^{75}$As donors in Ge displayed in Fig. 2.3.
Figure 2.3: Example CW ESR spectra for $^{75}$As donor electron spins in germanium. There are four derivative lines visible, which correspond to the four possible nuclear spin states. This splitting gives a measure of the hyperfine interaction. The center of mass of the spectra corresponds to the electronic $g$-factor. This spectra was taken at 2K with a microwave frequency of 9.6 GHz.

### 2.3.2 Free induction decay

The simplest pulsed ESR experiment one can perform is the single-pulse free induction decay. In this experiment the spin ensemble is prepared in the ground state — this can be done by simply waiting the spin-lattice relaxation time ($T_1$) or by shining above-gap light on the sample [34]. Upon application of a microwave $\pi/2$-pulse, the spins are tilted $\pi/2$ radians such that they lie within the X-Y plane of the Bloch sphere. It is important to recall that the ensemble consists of many spins (often $> 10^9$ spins), which are coherent and spontaneously emitting. Since the spins are coherent, their emission constructively interferes and can stimulate further emission in what is known as “brightened spontaneous emission” [103]. This induces a microwave current in the cavity. It is important to note that spin ensembles are never perfectly uniform and local magnetic and strain inhomogeneities lead to the ensemble having a finite linewidth. Each spin in the ensemble therefore precesses at a slightly different frequency. After the $\pi/2$ pulse, each spin will accumulate a different phase and over time the ensemble will become incoherent. The decay in the coherence and subsequent loss of emission is known as the free induction decay and the characteristic time over
which the free induction decay occurs is known as $T_2^*$. This quantity is directly related to the ESR linewidth ($\Delta \nu$) (in frequency units) by $\Delta \nu = 1/(\pi T_2^*)$ A typical pulse sequence and free induction decay is shown in the following figure.

Figure 2.4: Evolution of the spin ensemble during a free induction decay experiment. The state of the spins is shown on the Bloch sphere at times indicated in the lower graphs by the blue arrows. (a) The spin ensemble starts out in the ground state and undergoes a $\pi/2$ rotation (b). After the $\pi/2$ pulse, the magnetization lies along the $Y$—axis but the spins accumulate a phase depending on their local inhomogeneous environments. The net magnetization therefore decreases and the induced microwave signal decays exponentially (as shown in the pulse sequence).

### 2.3.3 Hahn echo

Many of the inhomogeneities associated with the free induction decay are static over the course of the experiment and this allows us to separate static and dynamic inhomogeneities in what is known as a Hahn echo pulse sequence. This experiment begins with a simple free induction decay, but after some time, $\tau$, a microwave $\pi$-pulse is applied which flips all of the spins. Upon completion of this pulse, the spins precess in the opposite direction but assuming the inhomogeneities remain the same, the spins that were precessing faster continue to precess faster. If one wait an additional time $\tau$, all of the spins will refocus and once they are in phase will emit into the cavity in a Hahn echo. An Bloch sphere representation of the evolution of several spins during a Hahn echo pulse sequence is shown in Fig. 2.5.
Figure 2.5: Evolution of the magnetization vector for a packet of spins during a two-pulse Hahn echo experiment. Each frame corresponds to a snapshot whose time corresponds to the labels on the pulse sequence shown at the bottom of the figure.

Our discussion of the Hahn echo pulse sequence made the important assumption that none of the inhomogeneities change throughout the pulse sequence. If we allow these inhomogeneities to vary with time, not all of the spins will refocus. In the limit of very long delay times, $\tau$, one would expect no spins to refocus and no echo would be observed. This irreversible loss of phase information is known as decoherence and its characteristic timescale is $T_2$. By measuring the Hahn echo as a function of delay time $\tau$ we can extract the coherence time of a spin ensemble. The shape of the $T_2$ decay also gives information about the processes involved in the decoherence.
2.4 The ESR spectrometer

There are two main categories of ESR spectrometers that are designed for two different types of ESR experiments. These are continuous wave (CW) and pulsed spectrometers. They differ in the excitation and read out electronics, but both rely on resonant cavities to confine the microwave fields and enhance the sensitivity. A thorough discussion of microwave cavities is included in Chapter 3 of this thesis. Here we discuss the difference in CW and pulsed microwave bridges and discuss our home-built spectrometer.

2.4.1 CW ESR spectrometer

In general, the amount of power used in a CW ESR experiment is large compared to the amount of power absorbed by the spins. We are then left with the challenge of measuring a small signal on a very large background. To overcome this, we make use of a technique for measuring the derivative of the reflected power instead of the absolute reflected power. This is done by incorporating modulation coils which are small Helmholtz coils placed around the ESR resonator. They are used to modulate the applied magnetic field ($\vec{B}_0$) at frequencies that are typically 10s of kHz. The reflected microwave signal is then measured using a diode and demodulated using a lock-in amplifier which is locked to the modulation frequency. A simplified schematic of a CW microwave bridge is shown below in Fig. 2.6

Properly tuning a CW spectrometer can be difficult owing to the large parameter space available. The parameters that can typically be tuned are the modulation frequency, modulation amplitude, microwave power, resonator quality factor, and integration time. There are whole textbooks devoted to CW ESR spectroscopy techniques and it would be difficult to condense them here. I therefore refer the reader to [94].
2.4.2 Pulsed ESR spectrometer

Pulsed ESR is a powerful technique that allows one to not only conduct spectroscopy, but also study dynamics. The bulk of this thesis is concerned with pulsed electron spin resonance which relies on measuring the time domain signal coming from an ensemble of spins. There are two basic parts to a pulsed ESR spectrometer: the pulse forming unit and the microwave bridge. The pulse forming unit provides the microwave pulses that drive spin rotations whereas the bridge is responsible for mixing down the microwave spin echo signal to DC signals that can be more easily measured. The experiments discussed in this thesis were conducted using a home-built ESR spectrometer with the schematic shown below in Fig. 2.7. A parts list is included in Appendix A.
Figure 2.7: Schematic of the home-built pulsed spectrometer. In this configuration, the spectrometer is equipped with two microwave sources so that double resonance techniques can be easily implemented. The colored boxed denote the pulse forming unit (red), bridge (green), and cryostat insert (blue). Not shown is a personal computer equipped with a pulse generator to trigger and program the displayed components.

The pulse forming unit

The bridge displayed is equipped with two microwave sources: a digitally synthesized vector microwave source (Agilent E8267D) and an analog scalar source (Agilent 8257D). The digital source is also equipped with two internal AWGs and an internal IQ mixer so that complex pulse shapes can be formed (including the adiabatic pulses discussed in Ch. 3). An additional option added to this source is a “high-coherence carrier loop” which gives us access to the internal local oscillator of the source. Access to the local oscillator allows us to perform homodyne microwave measurements which are insensitive to slow microwave phase drifts in the experimental setup. The maximum output of this microwave source is 17 dBm and can be increased by an additional 16 dB if the M Square TWT is used. The analog source is used almost exclusively as an RF source to drive nuclear spins in electron-nuclear double resonance
experiments. To suppress harmonics generated in this source at RF frequencies, a set of seventh-order Butterworth filters are used at the output.

**The microwave bridge**

The microwave bridge takes the microwave spin echo signal and mixes it down to DC frequencies which can be readily measured using a data acquisition card or oscilloscope. It is important that the bridge have high sensitivity, but one of the challenges in building a bridge arises from the difference in power between the echo signal and the microwave pulses used to drive spin rotations. For our typical samples, echo signals have powers below 100 pW, whereas the microwave pulses are of order Watts. The bridge therefore must be protected during any microwave pulses, but because we are interested in studying spin dynamics on microsecond timescales, it is important to be able to measure rapidly after applying a pulse. Our bridge uses two microwave switches to blank the pulses which switch over 100ns timescales, so our spectrometer “deadtime” is determined primarily by the ringdown of the microwave cavity.

The bridge itself was built using simple off the shelf components. The workhorse of the bridge is the microwave IQ mixer which converts the microwave signal into low frequency in-phase (I) and quadrature (Q) signals. There are many other components added to the bridge which serve to condition the microwave signals so that the best signal-to-noise ratio can be achieved. There is a reference arm of the spectrometer which takes the local oscillator signal from the microwave source, then changes the phase and amplitude of the signal so that it is optimized for the low noise amplifier. The signal arm takes in the microwave echo signal and amplifies it before putting in into the IQ-mixer. The signal arm is also equipped with a PIN protection diode which offers up to 50dB of protection from the microwave pulses. After the signal is demodulated in the IQ-mixer, the DC I and Q components are fed into variable-gain,
low-noise video amplifiers. The amplified signal is then sent to the data acquisition card on the PC.

The signal to noise ratio of the spectrometer is comparable to the signal to noise of our state-of-the-art Bruker spectrometer (Elexsys E580), but with an enhanced bandwidth. The spectrometer performs well over the 3.2-10 GHz frequency range. Above 10 GHz, a frequency doubler must be added to the reference arm, but we have successfully operated the spectrometer at frequencies as high as 12 GHz.

2.5 The ESR resonator

The resonator is one of the most important components of the ESR spectrometer. It determines the spin sensitivity of the spectrometer and imposes many experimental constraints including microwave power necessary for ESR, frequency of microwave excitation, microwave pulse bandwidth, microwave microwave field homogeneity, and spectrometer deadtime.

There are two types of resonators used in this thesis, commercially available dielectric resonators (Bruker MD-5) and self-fabricated superconducting coplanar waveguide resonators. The main difference in the resonators comes from their dimensionality. Superconducting coplanar waveguide (CPW) resonators are of order a microwave wavelength in only one dimension (and much smaller in the other dimensions) whereas dielectric resonators are large and of a wavelength in all three dimensions. This has major implications on the power required and spin number sensitivity as will be discussed in the following chapter.

The Bruker MD5 dielectric resonator has been engineered to produce high homogeneity microwave magnetic fields ($\vec{B}_1$) over the sample volume. They can be operated at room temperature and are equipped with built-in modulation coils so that they can be used in both pulsed and CW ESR experiments. Their coupling can
be tuned *in situ* via a movable antenna and the internal quality factor can be as high as 100,000 at 2 K, though they are typically operated with loaded quality factors of 1,000-10,000.
Chapter 3

Coplanar Waveguide Resonators

Superconducting coplanar waveguide (CPW) resonators are a good alternative to conventional volume resonators for many applications because of their high sensitivity, low power requirements, and small size [75, 65, 49, 110]. They are particularly sensitive to near surface spins, allowing one to discriminate between bulk and surface effects, which is difficult to do with volume resonators. Their low power requirements allow for ESR operation at dilution refrigerator temperatures, and the ability to tailor devices for specific applications, greatly increases the experimental reach of electron spin resonance.

Superconducting resonators are also of interest in the construction of hybrid quantum systems utilizing the long coherence times of spin-based qubits and the strong coupling of superconducting qubits [66, 127, 137, 123]. These systems are limited by dephasing of the spin ensemble ($T_2^*$), which is often hundreds of nanoseconds in solids. This can be improved by employing (Hahn echo) refocusing techniques as discussed in Ch. 2. This enables spin memories to be effective over the full coherence time of the electron spin ($T_2$), which can be 10 s in Si [122, 135]. However, refocusing pulses are difficult to implement because the microwave magnetic field ($\vec{B}_1$) is inhomogeneous in a CPW. Furthermore, it has been suggested that driving ensemble rotations
with microwave pulses is too slow for quantum computing and can lead to excessive microwave heating of the system \[26\].

We are therefore not only motivated to advance to state-of-the-art in spin resonance for spectroscopy application, but also interested in addressing these spin-ensemble-based memory issues. In this chapter we report CPW resonators capable of performing π-rotations on a spin ensemble in 40 ns while using microwave powers compatible with dilution refrigerators (40 µW peak). We also present data showing the use of adiabatic microwave pulses to overcome $\vec{B}_1$ inhomogeneity, enabling accurate spin manipulations over a randomly distributed ensemble. We begin, however, with an overview of coplanar waveguide devices.

### 3.1 Overview of coplanar waveguides

Coplanar waveguides are a simple type of transmission line consisting of a conducting strip line sandwiched between two coplanar ground planes. The impedance ($Z_0$) of the waveguide depends on the ratio of the center conductor width ($S$) with the gap width ($W$) and can be easily defined lithographically. Coplanar waveguides can be made into resonators by defining boundary conditions along the transmission line. These boundaries can take the form of DC shorts, AC shorts, or impedance steps. A CPW cross section is shown in Fig. 3.1 and its impedance can be calculated as described in Appendix B.

For RF or microwave currents running through a length of CPW, the magnetic and electric field distributions can be calculated using conformal mapping techniques \[130\] or finite element electromagnetic solvers. The field distributions used in this thesis were calculated using conformal mapping and are shown in Fig. 3.2 (a-b). The field magnitude depends on the microwave currents running through the CPW, which varies depending on applied microwave power, resonator quality factor, and position.
along the length of resonator. These field distributions can be calibrated experimentally, but here we simply plot the normalized field distributions. The microwave magnetic field ($\vec{B}_1$) distribution is shown in Fig. 3.2(a) and the electric field ($\vec{E}_1$) is shown in Fig. 3.2(b). The electromagnetic mode is TEM (transverse electric and magnetic) in the lossless limit, and thus $\vec{E}$ and $\vec{B}$ are perpendicular everywhere.

There are three CPW geometries that will be used throughout this thesis: quarter wavelength hangers, quarter wavelength capacitively terminated hangers, and coplanar photonic bandgap resonators. They each offer different advantages depending on the experiment. We will briefly present the geometry of each device and discuss their advantages and disadvantages.

### 3.1.1 Quarter-wavelength hangers

Quarter-wavelength (1/4λ) hanger resonators are the simplest geometry considered in this thesis. They consist of a section of superconducting CPW transmission line that is shorted on one end and left open on the other. They can be capacitively coupled to a transmission line as shown in Fig. 3.3. The boundary condition at the short is a voltage node whereas the open is a voltage antinode. The length $L$ of the device therefore determines the resonance frequency $\nu_N$ and its $(N - 1)$th harmonics, which
Figure 3.2: Plot of normalized magnetic (a) and electric (b) fields in a coplanar waveguide structure. The coplanar waveguide conductors are represented by the cartoon rectangles at the bottom of each plot.

are given by

\[ \nu_N = \frac{(2N - 1)c}{4L\sqrt{\epsilon_{eff}}} \]  

(3.1)

where \( c \) is the speed of light, and \( \epsilon_{eff} \) is the effective dielectric constant (see appendix B). These resonators are capacitively coupled to a transmission line and many resonators can be frequency multiplexed on a single device as shown in Fig. 3.3. These devices require only a single layer of lithography and if they are patterned on low loss substrates (high resistivity silicon or sapphire) they can have very high quality factors (~20,000 at 4 K).
Figure 3.3: (a) Cartoon representation of a 1/4 λ resonator capacitively coupled to a microwave transmission line. The ends of the resonant cavity are defined by a short circuit and open circuit as labeled on the figure. (b) Optical micrograph of a representative device. This device has 6 resonators coupled to a common transmission line. To avoid crosstalk, each resonator has a different resonant frequency.

3.1.2 Quarter-wavelength capacitively terminated resonators

For some experiments, we will need the ability to apply a DC voltage bias to the CPW resonator center pin. This poses a problem for standard 1/4 λ resonators, which use a DC short to define one wall of the microwave cavity. Any applied voltage is shunted to ground. We were therefore motivated to make a resonator that replaces the DC short with an AC short in the form of a large area parallel plate capacitor. The coplanar waveguide extends beyond the capacitively shorted region so that wire bonds can directly contact the cavity center pin to apply low frequency DC voltages.

An example device having a frequency of 7.1 GHz is shown in Fig. 3.4(b). This device was patterned from 35 nm thick Nb films deposited on silicon. This capacitive short consists of a 2.9 nF parallel plate capacitor having a plate area of 0.5 mm² and
separation of 17 nm. The capacitor is filled with an atomic layer deposition grown \( \text{Al}_2\text{O}_3 \) dielectric (recipe available in appendix [E]) and satisfies the design rule for a good capacitive short [113]:

\[
\frac{1}{2\pi f C} \leq \frac{Z_0}{50}
\]

where \( f \) is the resonator frequency, \( C \) is capacitance, and \( Z_0 \) is the characteristic impedance of the CPW (50 Ω).

Figure 3.4: (a) Cartoon schematic of a capacitively terminated quarter wavelength resonator. The microwave feedline comes in from the left and the DC feedline comes from the right. The cavity is defined by a length of coplanar waveguide with a coupling capacitor (microwave open) on the left and a parallel plate capacitor (microwave short) on the right. (b) Optical micrograph of an actual device.

### 3.1.3 Coplanar photonic bandgap resonators

Coplanar photonic bandgap (PBG) resonators are perhaps the most complicated of the designs discussed in this thesis, but they also offer the most flexibility and are
easy to fabricate. They only require one layer of lithography but can have DC voltage or current biases applied to the CPW center conductor and they allow for broadband transmission at lower frequencies.

The photonic bangap resonator is based on one dimensional photonic bandgap devices, which can be thought of as microwave stopband filters. They are constructed by periodically varying the impedance of a microwave transmission line, which is analogous to a Bragg reflector. By defining two microwave Bragg reflectors on either side of a half-wavelength strip of coplanar waveguide, one defines a half-wavelength cavity.

The Bragg mirrors in a photonic bandgap device have a finite size and the mode extends beyond the cavity region into the Bragg reflectors. To have well defined mode distribution over our sample, we therefore pattern the PBG resonators onto sapphire and attach samples directly to the surface using a phosphor bronze clip. Alternatively, we can selectively implant devices to only have donors in the cavity region.

3.2 High-speed, low-power manipulation of spins

We now turn to the challenges associated with implementing coplanar waveguides in hybrid quantum devices. One major challenge to performing rotations on a spin ensemble at low temperature is microwave heating. A typical X-band pulsed spectrometer performing 40 ns $\pi$-rotations can require an input power of tens of watts for a high quality factor (Q) volume resonator or up to a kilowatt of power for the lower-Q resonators used in studying systems with short coherence times. Most of that energy is reflected from the resonator, but heating can be significant. However, coplanar waveguide resonators have a substantially smaller mode volume, so less power is required to drive ensemble rotations. The small mode volume is possible because CPW
resonators require only one dimension to be on the order of the resonant frequency wavelength. The other two dimensions can be made arbitrarily small.

Another challenge to manipulating an ensemble of randomly distributed spins is $\vec{B}_1$ inhomogeneity, which is intrinsic to CPW designs. Field inhomogeneity leads to non-uniform control over a macroscopic ensemble, because the tipping angle of a given spin is proportional to the driving field strength. Spins in regions of large $\vec{B}_1$ will be rotated more than spins in regions of small $\vec{B}_1$. There are essentially two approaches to overcoming these inhomogeneities. The first is to tailor the device geometry such
that spins are located in regions of homogeneous $\vec{B}_1$. This is accomplished by either changing the resonator structure \cite{8} or by confining the ensemble to a small region where $\vec{B}_1$ is uniform. These methods typically require that the volume of the spin ensemble be smaller than the mode volume of the resonator, leading to weaker coupling. The second approach is to construct microwave pulses that compensate for $\vec{B}_1$ inhomogeneities. This allows for uniform control over an ensemble filling nearly the entire mode volume of the resonator. We have chosen the latter method and utilize adiabatic microwave pulses, which produce $\vec{B}_1$-insensitive spin rotations. Such adiabatic pulses are known in the nuclear magnetic resonance community, and we have tested several varieties\cite{20, 41, 67}. The best results were obtained by combining a WURST-20 (Wideband, Uniform Rate, Smooth Truncation 20) envelope shape\cite{67} with a BIR-4 ($\vec{B}_1$ Insensitive Rotation 4) phase compensation\cite{41}. The WURST-20 envelope shapes the pulse as $\sin^2(\pi t/t_p)$ where $t$ is time and $t_p$ is the pulse length. The BIR-4 technique breaks the WURST-20 pulse in half and combines four of these waveforms in a time-reversed order. The BIR-4 technique is robust against off-resonance effects, and specifically compensates for geometrical phase errors. Individually, BIR-4 and WURST-20 have been discussed in the literature\cite{20, 41, 67}.

The spin ensemble consisted of a 25 $\mu$m epitaxial layer of $^{28}$Si grown on high resistivity p-type Si. The epi-layer was doped to a concentration of $8 \times 10^{14}$ $^{31}$P donors/cm$^3$. This layer had 50 nm of Al$_2$O$_3$ grown on the surface to protect against a SF$_6$ plasma used in the device fabrication. Six CPW resonators were patterned in 50 nm thick Nb films directly on the Al$_2$O$_3$ surface and they are shown in Fig. 3.3(b). The fabrication techniques have been described previously \cite{75}. The CPW center conductor width was 30 $\mu$m, with a gap width of 17.4 $\mu$m defining an impedance of 50 $\Omega$. Each resonator had a unique frequency, spanning a range from 7 GHz - 8 GHz, and all were nearly critically coupled to a common transmission line. Most of the results reported in this chapter were obtained using one resonator with a 7.17
GHz center frequency, $Q$ of $\sim$2000, and coupling coefficient of 1.15. Resonators were wire bonded to copper printed circuit boards equipped with microwave connectors and cooled to 1.7 K. The output of the resonator transmission line was attached to a low-noise cryogenic preamplifier (Caltech LNA 1-12). We applied a direct current (DC) magnetic field to the sample, taking care that the plane of the Nb film remained parallel to the field. Careful alignment prevented the trapping of magnetic flux vortices in the superconducting film, which are lossy and serve as a decoherence mechanism\cite{75}.

Two-pulse Hahn echo experiments were conducted with a delay time ($\tau$) of 15 $\mu$s and the results are shown in Fig. 3.6(b). Because the relaxation time ($T_1$) of $^{31}$P donors at 1.7 K is on the order of minutes, the back side of the sample was illuminated with a 1050 nm light emitting diode for 50 ms prior to each two-pulse experiment. The light relaxes the spins allowing fast repetition rates. For 400 ns rectangular $\pi$-pulses, the optimal microwave power was $-34$ dBm (400 nW). The experiment was repeated using BIR-4-WURST-20 adiabatic pulses. For our devices, the optimal adiabatic pulse chirped from 2 MHz below to 2 MHz above the resonant frequency in 11 $\mu$s. This chirp bandwidth was chosen to be wider than the ESR linewidth of 0.3 MHz in order to excite the entire spin ensemble. The corresponding peak microwave power was $-30$ dBm (1 $\mu$W). The integrated signal-to-noise (S/N) ratio for the single shot (no signal averaging) rectangular and adiabatic pulse experiments are 84 and 146, respectively. Thus, by using adiabatic pulses the signal increased by a factor of 1.74.

To demonstrate that microwave manipulation of spin ensembles can occur on timescales compatible with quantum computing, shorter rectangular pulses were tested on a second device. That device had a $Q$ of 3200, center frequency of 7.14 GHz, and coupling coefficient of 1.15. The optimal power for 400 ns and 40 ns rectangular $\pi$-pulses was $-33$ dBm and $-13$ dBm, respectively (400 nW and 40 $\mu$W
Figure 3.6: Single shot spin echoes acquired using adiabatic (top black) and rectangular (bottom red) pulses. The adiabatic pulse echo has been shifted by 0.8 for clarity. Data were taken at 1.7 K in a DC magnetic field of 0.26 T.

peak powers). We expect the 40 ns $\pi$-pulse to be distorted by the high-Q resonator. However, a 20 dB increase in power still led to order-of-magnitude shorter excitation pulses.

Two-pulse experiments (nominally $\pi/2(+x) - \tau - \theta(+y) - \tau -$ echo) were also performed where the tipping angle of the second pulse was varied. For rectangular pulses, a microwave power of $-27$ dBm was used with the first pulse being 200 ns. The second pulse was varied from 0 ns to 1400 ns. The echo intensity as a function of pulse length is plotted in Fig. 3.7(a). This is compared to a similar experiment conducted using adiabatic pulses, shown in Fig. 3.7(b). When using adiabatic pulses, tipping angles were well defined such that the first pulse performed a $\pi/2$ rotation and the second pulse tipping angle varied from 0 to $4\pi$. An optimal peak microwave power of $-30$ dBm was used for these experiments. It is clear from the data that the
\( \vec{B}_1 \) inhomogeneity greatly affects the rectangular pulse experiment, which shows no Rabi oscillations, while the adiabatic pulses produce Rabi oscillations as expected.

To understand these experiments, a model was developed to simulate the results. The normalized \( \vec{B}_1 \) distribution in the CPW resonator was computed using a conformal mapping technique \[130\], and the echo intensity was determined by summing over the contribution of each individual spin, as previously described\[75\]. The contribution of a single spin to the echo \( (E) \) is given by

\[
E(\vec{r}) = g_s(\vec{r}) \sin(\theta_1(\vec{r})) \sin^2(\theta_2(\vec{r})/2) \tag{3.3}
\]

where \( g_s(\vec{r}) \) is the coupling of a spin at position \( \vec{r} \) to the resonator, \( \theta_1(\vec{r}) \) is the tipping angle of the first pulse (the first pulse is nominally \( \pi/2 \), but the actual tipping angle varies with spin position), and \( \theta_2(\vec{r}) \) is the tipping angle of the second pulse. For rectangular pulses, the tipping angle is \( g \mu_B B_1(\vec{r}) t_p/\hbar \), where \( g \) is the electron g-factor, \( \mu_B \) is the Bohr magneton, and \( \hbar \) is the reduced Planck constant. The spin-resonator coupling is linearly proportional to \( B_1(\vec{r}) \), the microwave magnetic field. We can write \( B_1(\vec{r}) = C B_{1n}(\vec{r}) \) where \( B_{1n} \) is the normalized \( B_1 \), and \( C \) depends on the microwave power, cavity coupling, and \( Q \). Thus, by writing \( g_s(\vec{r}) = AB_{1n}(\vec{r}) \), the total signal becomes

\[
E = \int d\vec{r} A C B_{1n}(\vec{r}) \sin \left( \frac{g \mu_C B_{1n}(\vec{r}) t_1}{\hbar} \right) \sin^2 \left( \frac{g \mu_C B_{1n}(\vec{r}) t_2}{2\hbar} \right) \tag{3.4}
\]

where \( t_1 \) is the first pulse duration and \( t_2 \) is the second pulse duration. The constant, \( A \), simply normalizes the vertical scale whereas \( C \) determines the shape of the curve shown in Fig. 3.7(a). By varying \( C \) for a given microwave power, we obtain a good fit to the data. From \( C \), we compute \( B_1(\vec{r}) \), which includes resonator \( Q \), losses, and coupling.
Figure 3.7: Echo intensity as a function of tipping angle for (a) rectangular pulses and (b) adiabatic pulses. Experimental data is represented by solid squares. The curve in (a) is the best fit curve from the model (Eq. 3.4) and the curve in (b) assumes ideal spin rotations. Data were taken at 1.7 K in a DC magnetic field of 0.26 T.
To evaluate the performance of adiabatic pulses quantitatively, we performed echo experiments with a high-homogeneity commercial dielectric resonator (Bruker MD5). We used a bulk doped $^{28}\text{Si}$ crystal with $3.3 \times 10^{15}$ P donors/cm$^3$. The sample volume was $1\ \text{mm} \times 2\ \text{mm} \times 4\ \text{mm}$, and $B_1$ homogeneity varied by no more than 5% over the sample volume. In these experiments, adiabatic pulse tipping angles were defined as $\pi/2$ and $\pi$, while the microwave power and thus $B_1$ was varied. The integrated echo intensity as a function of $B_1$ is shown in Fig. 3.8. As a comparison, the experiment was repeated using rectangular pulses with a $\pi$-pulse width of 400 ns ($B_1 \sim 10$ times the ESR linewidth), and these data are also shown. At least half of the maximum echo intensity is observed for $B_1$ in the range of 6 $\mu$T to 83 $\mu$T for adiabatic pulses, while the range is 24 $\mu$T to 61 $\mu$T for rectangular pulses. This comparison shows that adiabatic pulses correct $\vec{B}_1$ inhomogeneity for over an order of magnitude variation (two orders of magnitude in microwave power).

Combining the simulated $\vec{B}_1$ distribution with our measurements of echo intensity as a function of $\vec{B}_1$ (Fig. 3.8), we identified the regions of the sample contributing most to the echo signal. Fig. 3.9(a) is a cross section of the CPW resonator at an antinode in the magnetic field (near the shorted end of the resonator). The CPW is depicted at the top of the plot, and the magnitude of $\vec{B}_1$ in the sample is shown with contours (the 8 $\mu$T contour is labeled, and $\vec{B}_1$ for each subsequent contour increases by a factor of two). The hatched regions in the figure denote where 2/3 of the signal originates for the rectangular and adiabatic pulses. The Si sample used for these experiments had a 25 $\mu$m thick P-doped $^{28}\text{Si}$ epi-layer, and thus the ensemble volume only extends down to the green cross-hatched region. Using the $\vec{B}_1$ distribution, the contribution of all spins, at each value of $\vec{B}_1$, to the echo was computed and is plotted in Fig. 3.9(b) for both adiabatic and rectangular pulses. By integrating over these curves we obtained the total signal intensity and found that adiabatic pulses produce a signal that is 1.73 times larger than the signal produced by rectangular pulses.
Figure 3.8: Plot of echo amplitude as a function of $B_1$ for a sample in a high-homogeneity resonator with adiabatic pulses (black) and rectangular pulses (red). Data were taken at 4.6 K in a DC magnetic field of 0.34 T. The solid line is a spline fit to the data and is used later in a simulation.

This is in excellent agreement with the value of 1.74 observed in experiment. Note that because adiabatic pulses are sensitive to a volume larger than the epi-layer, the adiabatic pulse signal would increase when using a bulk doped sample. We also note that rectangular pulses are sensitive to a thin region of spins, which could allow for high resolution tomography experiments.

From these simulations, we estimate the sample volume coupled to our resonators to be $3.9 \times 10^{-6}$ cm$^3$. The doping density of the sample is $8 \times 10^{14}$ donors/cm$^3$, so there are $1.6 \times 10^9$ spins coupled to the resonator per hyperfine line. We measured these spins in a single shot (using no signal averaging and utilizing a single two-pulse sequence) and found a S/N of 84 using rectangular pulses and 146 with adiabatic pulses. Scaling to S/N = 1, we have sensitivity to $2 \times 10^7$ spins when using rectangular pulses and $1 \times 10^7$ spins using adiabatic pulses. ESR sensitivity is often
Figure 3.9: (a) Cross section of resonator at an antinode in $B_1$ with contour lines indicating $\vec{B}_1$ magnitude for a 400 nW input power. The hatched regions denote the location of spins contributing to 2/3 of the echo intensity for rectangular (red) pulses and adiabatic (blue) pulses (violet where they overlap). The green-hatched region below 25 $\mu$m denotes the undoped portion of the sample. (b) Plot of the echo intensity contribution of all spins at particular values of $B_1$. 
reported in units of spins/√Hz. These units are appropriate for continuous wave experiments. However, in pulsed electron spin resonance, this sensitivity is limited by the shot repetition rate. Our typical shot repetition rate is 100 Hz (determined by optical spin relaxation) giving a sensitivity of 10^6 spins/√Hz. By employing refocusing pulses in a CPMG (Carr-Purcell-Meiboom-Gill) sequence, much faster repetition rates have been achieved\cite{11}. Our projected sensitivity when using rectangular pulses in a CPMG sequence is 3 \times 10^4 spins/√Hz. This represents an order of magnitude improvement over recently reported values for spin resonance detected by a superconducting qubit\cite{65} and is on par with sensitivities reported using surface loop-gap microresonators\cite{11}. By going to lower temperatures where spins are fully polarized, and by incorporating quantum limited parametric amplifiers, the state-of-the-art has recently become 10^3 \text{–} 10^4 \text{ spins/shot} \cite{10, 30}.

In summary, we have demonstrated the use of superconducting CPW resonators to perform pulsed electron spin resonance using an ultra low power of -34 dBm (400 nW) with a π-pulse length of 400 ns. We also verify that 40 ns π-rotations can be achieved using peak powers of about 50 µW, making CPW resonators compatible with dilution refrigerators. We report a single-shot sensitivity to 10^7 spins or 3 \times 10^4 spins/√Hz. Finally, we have shown that BIR-4-WURST-20 pulses can be used to compensate for \vec{B}_1 inhomogeneities spanning an order of magnitude. These adiabatic pulses improved our S/N by a factor of 1.74 and substantially improve the uniformity of microwave manipulations of a randomly distributed spin ensemble.
Chapter 4

Anisotropic Stark Effect for Donor Spin Qubits in Silicon

4.1 Introduction to the Stark effect in Si

Many donor-based quantum computing architectures rely on the tuning of a donor in and out of resonance with a global microwave magnetic field to perform spin rotations as discussed in Ch. 1. This is achieved through modulation of either the donor hyperfine coupling or the donor electron $g$-tensor in what is known as the Hyperfine and spin-orbit Stark shift, respectively. The Stark effect was first measured for $^{121}$Sb donors in silicon using an interdigitated capacitor arrangement, and both spin-orbit and hyperfine Stark parameters were reported [12]. However, it was later discovered that the spin-orbit component of the Stark shift was an artifact of the analysis assuming the system was in the high-field limit [112]. In a more recent work, the hyperfine Stark parameters for $^{75}$As, $^{31}$P, $^{121}$Sb, and $^{208}$Bi were measured [90], but could not resolve the spin-orbit component of the Stark shift. Similarly, strong electroelastic tuning of the hyperfine interaction for P donors in Si has been demonstrated using an electrically detected magnetic resonance scheme [27]. In this
present work, we measure the Stark shift of phosphorus donors in Si using ESR with capacitively terminated, coplanar waveguide (CPW) resonators. These high-sensitivity resonators allow us to measure small ensembles of spins subjected to locally homogeneous electric fields. Using them, we resolve both the hyperfine and spin-orbit Stark shifts and confirm a previously predicted anisotropy in the spin-orbit Stark shift due to valley repopulation [96].

It is expected that electric-field noise can contribute substantially to decoherence in the presence of strain [28, 55]. Large strains and/or electric fields are present in gated single-donor devices [82]. By measuring the linear Stark effect, we estimate the effective electric field due to strain in our devices and the resulting sensitivity of the donors to electric-field noise. The effect of electric-field noise on the donor spin coherence depends on the field and strain orientation and thus the detailed device configuration. From our results we find magnetic fields and crystal orientations where the spin-orbit and hyperfine components of the Stark shift cancel, such that spins are protected from electric-field noise. These “noise-suppression points” may be important for near-surface donors and quantum devices incorporating electrostatic gates.

4.2 Device details

These experiments were performed using 1/4-wavelength superconducting CPW resonators. The devices have a frequency of 7.1 GHz and an example is shown in Fig. 3.4. Resonators were patterned from 35 nm thick Nb films deposited on 2 μm, P doped, $^{28}$Si epilayers. One end of a resonator is capacitively coupled to a single port transmission line used for exciting the resonator and measuring the spin signal. The other end is capacitively shorted to ground. This capacitive short consists of a 2.9 nF parallel plate capacitor having a plate area of 0.5 mm$^2$ and separation of 17 nm. The
capacitor is filled with an atomic layer deposition grown Al₂O₃ dielectric and provides a good AC short at 7 GHz.

The CPW capacitive short allows the center conductor to be voltage biased, providing a DC electric field between the center pin and the ground plane of the resonator as shown in Fig 4.1. The electric field \( E \) is inhomogeneous except for a region near the plane of the CPW and in the gap between the center pin and the ground plane. To confine spins to these homogeneous regions, we employ a thin 2 \( \mu \)m \( ^{31} \)P doped \( ^{28} \)Si epitaxial layer as our spin ensemble. However, because only the microwave magnetic field \( \vec{B}_1 \) perpendicular to the DC magnetic field \( \vec{B}_0 \) contributes to spin rotations in ESR, the regions producing the spin echo vary depending on the sample orientation. Taking into account the inhomogeneous \( \vec{B}_1 \), as well as the spin-to-resonator coupling, we extract the regions of spins contributing to at least half of the echo signal and shade them red in Fig. 4.1(a) and Fig. 4.1(b) for \( E \perp B_0 \) and \( E \parallel B_0 \), respectively. The weighted electric-field distribution over these subensembles is shown in Fig. 4.1(c). The standard deviation of the distribution in the x-component magnitude (the dominant component that is directed from the ground plane to the center pin) is \( \sim 8\% \) for both orientations.

When fabricating the resonators, the center pin was oriented perpendicular to either the [010] or the [-110] crystal axes. These orientations ensure that the electric field applied to the spins producing the signal is oriented along either the [100] or [110] axes. These resonators were wire bonded to copper printed circuit boards equipped with a low-noise, cryogenic preamplifier and placed in a DC magnetic field. With the field oriented in the plane of the Nb to avoid trapping magnetic flux vortices, devices were cooled to 1.7 K to conduct pulsed ESR experiments.
Figure 4.1: Electric potential lines are shown at an antinode in $\vec{B}_1$ for $\vec{E} \perp \vec{B}_0$ (a) and $\vec{E} \parallel \vec{B}_0$ (b). The CPW cross section is depicted by a cartoon at the top of the plot. The 0.9 V line is labeled (given a 1 V bias) and each subsequent line represents a 100 mV decrease in potential. Red regions denote where 50% of the ESR signal originates. Microwave power was optimized to enhance sensitivity to spins at the center of the CPW gap where $\vec{E}$ is most uniform. (c) $\vec{E}$ distribution in the CPW (for a 4 V bias) weighted by the signal contribution.

4.3 Experimental techniques

A pulsed ESR technique sensitive to small resonance shifts [12, 77] was used to measure the quadratic Stark shift. This technique uses a two-pulse Hahn echo sequence ($\pi/2(x) - \tau - \pi(y) - \tau - \text{echo}$), with an electric-field pulse applied to the spins during the first dephasing period, $\tau$. The electric field detunes the spins relative to the driving microwaves such that they accumulate an additional phase, $d\phi$, in the Hahn echo, which is measured using a quadrature detector. This experiment utilized bipolar electric-field pulses (pulse sequence IV in [12]) consisting of a positive pulse immediately followed by a negative pulse of the same amplitude and duration. These pulses refocus linear Stark effects (arising from random strain as discussed below) thus allowing the measurement of the quadratic Stark effect. The phase shift is given
by
\[ d\phi = \tau_E df = [\eta_g g \mu_e B_0 + \eta_h a M_I] \vec{E}^2 \tau_E / \hbar \] (4.1)

where \( df \) is the frequency shift of the spins, \( \eta_g \) and \( \eta_h \) are the spin-orbit and hyperfine Stark fitting parameters, respectively, \( g \) is the electron g-factor, \( \mu_e \) is the Bohr magneton, \( a \) is the hyperfine coupling constant, \( M_I \) is the nuclear spin projection, \( \tau_E \) is the duration of the electric-field pulse, and \( \hbar \) is the reduced Planck constant [12]. A model was developed to simulate the Stark effect in our device including the inhomogeneity in both \( \vec{B}_1 \) and \( \vec{E} \). Both fields were computed using a conformal mapping technique [130], and each spin’s contribution to the echo was calculated as described in [110]. This model also took into account \( \vec{B}_1 \) inhomogeneity present along the length of the CPW. The total echo phase shift of the spin ensemble, \( \Delta \phi \), was determined by taking a weighted average of the Stark shift of each spin:

\[ Ae^{i \Delta \phi} = \frac{\sum_i e^{-id\phi_i} g_i \sin^3 (g\beta B_{1i} \tau_p / \hbar)}{\sum_i g_i \sin^3 (g\beta B_{1i} \tau_p / \hbar)} \] (4.2)

where the sum is taken over all \( i \) spins, \( A \) is an amplitude coefficient, \( d\phi_i \) is the phase shift of the \( i \)th spin, \( g_i \) is the coupling of the \( i \)th spin to the resonator, \( B_{1i} \) is the microwave magnetic field seen by the \( i \)th spin, and \( \tau_p \) is the duration of the first microwave pulse in the Hahn echo sequence. In this expression, the \( \sin^3 \) term takes into account signal attenuation due to pulse errors arising from \( \vec{B}_1 \) inhomogeneity [75]. We note that the phase shift of a single spin, \( d\phi_i \), is not affected by these errors [103].

4.4 Results and discussion

Data for \( \vec{E} \) applied along the [100] and [110] axes with bias voltages up to 8 V are shown in Fig. 4.2. These data were taken with an electric-field pulse length
Figure 4.2: Measured ESR frequency shift as a function of CPW center pin voltage for \( \mathbf{B}_0 \) oriented along the [100] (a) and [110] (b) crystal axes. Data are plotted for \( \mathbf{E} \) either parallel (red diamond) or perpendicular (black square) to \( \mathbf{B}_0 \). Smooth curves are fits to the data using Eq. 4.2. Note that the hyperfine Stark shift is symmetric whereas the spin-orbit Stark shift is asymmetric with respect to zero as a function of \( M_I \). The error bars for the data are smaller than the points used in the plot. Data were taken at 1.7 K with a \( B_0 \) of 0.26 T.

of 38 \( \mu s \) and microwave \( \pi \)-pulses of 400 ns. Eq. 4.2 was fitted to the data and the fitting parameters are given in Table 4.1. While the hyperfine Stark parameter remains nearly constant, the spin-orbit Stark parameter changes sign and magnitude depending on the \( \mathbf{E} \) orientation relative to \( \mathbf{B}_0 \) and the crystal axis.

This anisotropic Stark shift was predicted by Rahman et al. [96] and is explained using a valley repopulation model [132]. Silicon has six conduction band valleys and the ground state electron wavefunction has an amplitude in all six valleys. The \( g \)-factor of an electron in a single valley is related to its effective mass in the direction of \( \mathbf{B}_0 \) so the non-spherical valleys produce a non-uniform \( g \)-factor. In the unperturbed
Table 4.1: Si:P Stark Shift Fitting Parameters

| $\vec{E}$-direction | $||$ / $\perp$ $\vec{B}_0$ | $\eta_a$ (µm²/V²) | $\eta_g$ (µm²/V²) | $\eta_g$ theory† (µm²/V²) |
|---------------------|-----------------|----------------|----------------|----------------|
| [100]               | $\vec{E} \parallel \vec{B}_0$ | $-2.6 \pm 0.1 \times 10^{-3}$ | $-8 \pm 2 \times 10^{-6}$ | $-12 \times 10^{-6}$ |
| [100]               | $\vec{E} \perp \vec{B}_0$ | $-2.8 \pm 0.1 \times 10^{-3}$ | $6 \pm 1.5 \times 10^{-6}$ | $14 \times 10^{-6}$ |
| [110]               | $\vec{E} \parallel \vec{B}_0$ | $-2.7 \pm 0.1 \times 10^{-3}$ | $-3.5 \pm 1.5 \times 10^{-6}$ | - |
| [110]               | $\vec{E} \perp \vec{B}_0$ | $-2.7 \pm 0.1 \times 10^{-3}$ | $-2.8 \pm 1.5 \times 10^{-6}$ | - |

Theoretical values are taken from tight binding calculations reported in [96].

ground state with a symmetric valley combination, the $g$-factor is equally averaged over all valleys, and no $g$-factor anisotropy can be resolved. However, when an electric field is oriented along a valley axis ($\{100\}$ for Si), the valley degeneracy is partially lifted, and electrons preferentially fill valleys oriented along the electric field. This changes the effective $g$-factor and induces an anisotropy in the Stark parameter $\eta_g$. The anisotropy is most pronounced when the electric field is oriented along a valley axis. Moreover, application of an electric field in the $\{111\}$ axes would result in no valley repopulation, since it makes the same angle with all valleys. This orientation is not accessible in our device geometry, but we were able to apply a $[110]$ oriented electric field, and, as expected, the spin-orbit anisotropy became small as shown in Table 1.

It is through the Stark shift that $\vec{E}$ noise can decohere spins and we note the existence of ESR transitions insensitive to this noise. From Eq.(1), we infer that decoherence from $\vec{E}$ noise can differ substantially for the two donor nuclear spin projections, $M_I$. Moreover, $\vec{B}_0$ can be tuned such that the first two terms cancel, leading to a transition insensitive to $\vec{E}$ [12]. Due to the dependence of $\eta_g$ on the orientation of $\vec{E}$, these noise-suppression points vary with the direction of $\vec{E}$, and no single $\vec{B}_0$ can cancel all randomly oriented electric-field noise. For this reason, noise suppression points are most effective in situations where the primary source of noise (and thus the direction of $\vec{E}$) is known, such as in gated donor architectures.

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In the simplest picture, electric-field noise (which is presumably small) should not contribute to decoherence, since the Stark effect is quadratic. However, this changes dramatically when a large DC electric field (present in gate-addressed architectures) or strain is applied. In this work we consider this field coming from strain [13], inducing a shift in the ESR frequency by modulating the hyperfine interaction [27] and causing valley repopulation [132]. The Stark shift in the presence of strain is given as

\[ df = \left[ \eta g g \beta B_0 + \eta a a M_1 \right] (\vec{E}^2 + 2 \vec{E} \cdot \vec{E}_{\text{strain}}) / \hbar, \]  

(4.3)

where \( \vec{E}_{\text{strain}} \) is the effective electric field due to strain. When electric-field noise, \( \vec{E}_{\text{noise}} \), is small, the \( \vec{E}^2_{\text{noise}} \) term is negligible whereas the \( \vec{E}_{\text{noise}} \cdot \vec{E}_{\text{strain}} \) term can be large. Using data in [132], we calculate that a strain of \( 10^{-3} \) is equivalent to an effective electric field of \( 10 V/\mu m \). We hereafter refer to strain in units of \( V/\mu m \), which corresponds to the strength of \( \vec{E}_{\text{strain}} \).

To investigate strain we use unipolar (positive bias) pulses, instead of the bipolar pulses used to gather the data for Fig. 4.2. Bipolar pulses cancel the linear term of Eq.(3) whereas unipolar pulses lead to a broadening of the ESR line and loss of signal when internal strains are inhomogeneous across the spin ensemble. This is due to a distribution in the Stark shifts over the spin ensemble. Recovery of the echo signal when applying bipolar electric-field pulses indicate that the distribution is due to linear Stark effects. The unipolar pulse data taken with bias amplitudes up to \( 4 V \) are displayed in Fig. 4.3. These data are fit using Eq.(4.3) assuming a Gaussian distribution of strain with a 0.8 V/\( \mu m \) standard deviation. We compare this to a similar sample (10 \( \mu m \) P doped epitaxial layer of \( ^{28}\text{Si} \)) reported [121] with an electron nuclear double resonance (ENDOR) linewidth of 100 kHz. Assuming that broadening of the ENDOR line is due primarily to strain, this linewidth corresponds to an \( \vec{E}_{\text{strain}} \) distribution spanning \( 0.75 V/\mu m \), comparable to our results.
Figure 4.3: Plot of the normalized ESR signal intensity as unipolar pulse voltage is varied. The decrease in the signal indicates a distribution in the linear Stark effect, which leads to additional dephasing in the spin ensemble. The data is fitted using Eq.(4.2) and (4.3) from the main text. Assuming a Gaussian distribution of strain, the strain has a standard deviation of 0.8 V/µm.

For these strains, the spins’ sensitivity to electric-field noise, $df/dE$, can be large. The $\vec{E}_{\text{noise}}$ limited coherence time ($T_2$) is inversely proportional to $(df/dE)^2$ [21] so electric-field sources of decoherence can be substantial. While the $\vec{E}_{\text{noise}}$ contribution to the coherence time will vary from system to system, we calculate (using [21]) that for 10 µV of noise on our CPW center pin, $T_2$ would be limited to 70 ms in the devices used in these experiments. Devices with gates more strongly coupled to the donors would have their $T_2$ affected more severely. These $T_2$ effects are not directly observed in our devices since the coherence time is already limited by instantaneous diffusion to $\sim$2 ms. Recent experiments on single-donor devices have reported a Hahn echo $T_2$ of $\sim$ 1 ms where it was determined that the dominant noise is not electrical in this device configuration [82]. As other noise sources are eliminated and coherence is pushed to longer timescales, electric-field noise may become dominant.

Internal strains can also lead to errors in measuring $\eta_g$, even when using bipolar pulses. This is because $\eta_g$ depends on the direction of the total electric field, which
includes $\vec{E}_{\text{strain}}$. Since $\vec{E}_{\text{strain}}$ is random, there is uncertainty in the actual direction of the total electric field relative to $\vec{B}_0$. Care was taken to minimize strain when mounting the devices, but not all strain can be avoided and in our devices we found that $\vec{E}_{\text{strain}}$ was larger than the applied electric fields. The errors arising from strain should become small as $\vec{E}$ becomes large, so data taken at higher bias voltages were weighted more heavily when fitting the model. For our samples we estimate that the magnitude of $\eta_g$ can be underestimated by up to a factor of 2.5 for the [100] data.

Taking into account strain, we quantitatively compute the sensitivity of spins to electric-field noise ($df/dE$). For the simple case, where the strain is uniform and oriented in the same direction as the $\vec{E}_{\text{noise}}$, we plot $|df/dE|$ in Fig. 4.4(a) (assuming $\vec{E}_{\text{strain}}$ is 1V/µm). $\vec{E}$ noise suppression points appear as minima in $|df/dE|$. This case applies to bulk $^{28}\text{Si}$ crystals where the strain distribution can be small ($<10^{-3}$ V/µm) and single-donor systems.

We recognize that in devices containing ensembles of spins, randomly oriented strain leads to a distribution in $\eta_g$ over the ensemble, washing out noise suppression effects. Assuming random strain of order 1 V/µm, comparable to the strain in our samples, $df/dE$ should on average decrease by a factor of 5 for one hyperfine line compared to the other. This corresponds to an increase in $T_2$ by a factor of 25 (because $1/T_2 \propto (df/dE)^2$ in the Bloch-Wangness-Redfield limit [21]). This implies that, even with the simple approach of choosing the optimal field and hyperfine line, one can substantially suppress $\vec{E}$ noise.

We propose applying a large uniform external strain or DC electric field as a remedy to random strain effects. This external field adds to $\vec{E}_{\text{strain}}$ such that the total field becomes nearly uniform. The overall $\vec{E}$ vector is pinned along the external-field axis and is insensitive to any small variations in $\vec{E}_{\text{strain}}$. External strain fields of up to 10 V/µm have been studied [132] and for our samples we calculate that applying a strain of this magnitude would decrease $df/dE$ by a factor of $\sim 25$ (increases $T_2$ by
two orders of magnitude). However, one must take care when orientating the external strain. If it is large and oriented in the same direction as the electric-field noise, a slight deviation from perfect alignment can lead to substantial decoherence due to the linear term in Eq.(4.3). Applying strain perpendicular to the $\vec{E}$ noise will suppress the linear term and protect the donor spin from electric-field induced decoherence. Fig. 4.4(b) shows the effect of external strain on the magnitude of $|df/dE|$.

While electric-field noise suppression points seemingly undermine the electrostatic addressability of donors, only one of the two hyperfine lines for phosphorus is protected. Global RF pulses can be used to flip the nuclear spins, toggling between electric field protected and sensitive states. Furthermore, applying an external strain or electric field enhances the Stark effect for spins in the sensitive state.

Nonetheless, it is uncertain whether $^{31}$P donor electron spins can be electrically addressed in silicon. Given donor ionization is expected to set in at 1.5 V/$\mu$m [90]. Our data suggests that the maximum Stark shift in an unstrained crystal is therefore 550 kHz at typical qubit frequencies, which is of order the narrowest linewidth observed for near-surface spins. Nuclear spin addressability was demonstrated [136], but only for bulk donors in highly enriched $^{28}$Si (40 ppm $^{29}$Si). There has also been a report of Stark tuning a single electron spin on and off resonance with an electric field [69], but that is insufficient for multi-donor quantum computing schemes where one must tune by an ensemble linewidth. Appropriate strain engineering (to enhance the linear Stark effect) may still offer a way to implement a Kane quantum computer, but it remains an open question whether the applied strains can be uniform enough to enhance tunability without severely broadening the ESR line.

In conclusion, we have measured the quadratic Stark shift for phosphorus donors in silicon using a novel, capacitively-terminated CPW resonator. We resolved both a hyperfine and a highly anisotropic spin-orbit Stark shift. We measured $\vec{E}_{\text{strain}}$ in our samples to be on the order of 1 V/$\mu$m and showed that this leads to a large linear
Figure 4.4: (a) Plot of the electric-field sensitivity of P donors in Si for various orientations of $\vec{E}$ and $\vec{B}_0$ as a function of $B_0$. This plot assumes an internal strain of 1 V/$\mu$m directed along $\vec{E}$. Dashed lines indicate $M_I = -1/2$ whereas solid lines indicate $M_I = +1/2$. $\vec{E}$ noise is suppressed at 19.12 GHz, 27.41 GHz, and 45.32 GHz. Another minima for the [110] oriented $\vec{E} \perp \vec{B}_0$ occurs at 56.65 GHz but is not shown. (b) Plot of the maximum (worst case) $\vec{E}$ sensitivity of spins subject to random strain (with magnitude 1 V/$\mu$m) as a function of externally applied strain. This plot assumes the external strain is oriented perpendicular to the $\vec{E}$ noise.
Stark shift for even small applied electric fields, making spins sensitive to electric-field noise. Using our data, we predict DC magnetic fields where electric-field noise can be suppressed. In the presence of randomly distributed internal strains, the noise suppression is weakened, but by choosing the correct ESR transition, we calculate that one can enhance $T_2$ by a factor of 25. We have proposed the use of large external strains to overcome this limitation such that $T_2$ can then be extended by two orders of magnitude. Based on our measured Stark shift parameters, similar strains will need to be applied to enhance donor tunability if one hopes to implement a Kane quantum computer and tune donors by more than an ensemble linewidth. While the noise suppression techniques described in this paper use phosphorus donors in Si as an example, they should extend to other donor qubits as well.
Chapter 5

Electrically Driven Nuclear Magnetic Resonance

5.1 Introduction

Based on our data in Ch. 4, it will be technically challenging and likely impractical to electrically tune a donor electron spin in silicon beyond an ensemble linewidth before ionization sets in. We are therefore interested in finding alternative methods for controlling donor spins. In this chapter we discuss and demonstrate the use of electric fields to directly drive nuclear spin transitions. If one can electrically drive spins, the drive fields can be confined and we no longer need the ability to tune individual spins by more than an ensemble linewidth.

In this chapter, by using coplanar photonic bandgap resonators, we electrically drive Rabi oscillations on nuclear spins by employing the donor-bound electron as a quantum transducer, much in the spirit of recent work with single-molecule magnets [119]. Electric control has major advantages over magnetic control stemming from the ability to spatially confine electric fields. Electric field confinement leads to lower power requirements, higher qubit densities, and faster gate times. We also show that
electric field control allows for driving spin qubits at either their resonant frequency or
the first subharmonic of that frequency, thus reducing device bandwidth requirements.
Finally, we demonstrate that double quantum transitions can be driven, which opens
up a richer computational manifold and makes it feasible to implement nuclear spin
based qudits (4-state systems) using $^{75}$As donors [5].

In recent years, schemes for all-electrical control of donor spin qubits have been
proposed [19, 120] but no experimental demonstrations have been reported. Some
success has been shown in fundamentally different spin systems including defects in
SiC [59], quantum dots [91, 68, 87], and single molecule magnets [119], but this work
represents the first demonstration of electrically driven nuclear magnetic resonance
(EDNMR) for donor spins in silicon. This material system is particularly attractive
since it already boasts record coherence times [81, 100, 86], and atomically precise
lithography techniques that can truly benefit from electrical control are becoming
mature [40, 101].

We find that there are two distinct mechanisms that lead to EDNMR depending
on the donor species. $^{31}$P donor nuclei are driven through modulation of the orbital
electronic states through the spin-orbit Stark shift [12, 112, 111]. This tilts the
direction of the quantization axis of the electronic spins and induces an effective
anisotropy in the hyperfine interaction. $^{75}$As is subject to the same form of control but
we find that the $^{75}$As Rabi frequencies are too large for this effect to be responsible.
Electric field modulation of the quadrupolar coupling is likely responsible for the
EDNMR in $^{75}$As.

5.2 Experimental Methods

In this work, we make use of the hyperfine interaction to read out the nuclear spin state
($M_I$) using the Davies electron-nuclear double resonance (ENDOR) technique [18]
In this measurement, one probes the electron spin resonance (ESR) transitions while simultaneously performing nuclear magnetic resonance. The ESR transition intensity depends on the nuclear spin state, so by performing conventional ESR on the donor electron spin, one also obtains $M_I$. This technique therefore requires both microwave magnetic ($\vec{B}_1$) and radio frequency magnetic ($\vec{B}_2$) fields. In this study, to electrically probe nuclei, we also require RF electric fields ($\vec{E}_2$) fields. To maintain a suitable signal-to-noise ratio (SNR), a high quality factor microwave resonator is used.

Commercial ENDOR resonators exist, but they require large powers (making them incompatible with ultra-low temperature measurements) and are designed to provide RF magnetic, and not electric fields. This led us to develop superconducting coplanar photonic bandgap (PBG) resonators, which allow broadband RF and microwave transmission above and below a lithographically defined photonic bandgap [141, 73, 138, 14]. These were discussed in Ch. 3 and design considerations are outlined in Appendix B. A schematic of the device is shown in Fig. 5.1(a). The bandgap is constructed by periodically alternating the impedance of a superconducting CPW transmission line to form a one-dimensional microwave Bragg grating. By incorporating a 1/2 wavelength defect in the photonic bandgap, the device supports a resonant mode, which can be used for ESR. Equivalently this structure can be thought of as two discrete Bragg mirrors defining the boundaries of a half wavelength cavity [50]. The sample is located above the cavity region of the device. This resonator design has a continuous center conductor, which is isolated from the ground plane and allows for easy application of DC voltage or current biases. These devices require only one layer of lithography and will be convenient for other areas of quantum information processing and ESR.

These resonators have a built-in feature that allows us to easily select whether electric or magnetic RF fields are present in the sample. The RF frequencies used
Figure 5.1: (a) Cartoon schematic of a photonic bandgap resonator. The left port of the device is used for microwave excitation and readout and the right port can be terminated to select whether RF electric or magnetic fields are present in the device. An optical micrograph of an actual device is shown in (b) with a silicon sample (bright rectangular feature) mounted using a phosphor bronze clip. The serpentine structures above and below the sample are the Bragg mirrors. The inset shows a zoomed in view of an impedance step. The microwave transmission through this structure is shown in (c) for the device in a magnetic field of 250 mT at a temperature of 1.9 K. The photonic bandgap spans the frequency range between 4.5 GHz and 9 GHz with nearly lossless transmission below 4 GHz. The resonance appears at 7.3 GHz with a Q factor of 20000. The loss outside of the bandgap is due to the coaxial test cables, which were not calibrated out.

in this work have a wavelength that is large compared to the scale of the device and are unperturbed by the photonic bandgap (since they lie well below the gap). We can therefore set up RF standing waves by terminating the transmission line at the output port of the device (labeled “variable termination” in Fig. 5.1(a)). A high impedance (open) termination is used to reduce $\vec{B}_2$ and enhance $\vec{E}_2$ whereas a low impedance (shorted) termination enhances $\vec{B}_2$ and reduces $\vec{E}_2$ in the sample. Due to
the finite size of the device, one can never fully suppress the \( \vec{E}_2 \) and \( \vec{B}_2 \) fields but we estimate that the residual undesired field amplitudes are reduced by at least a factor of 50 in the sample. The microwave magnetic field, \( \vec{B}_1 \), has a wavelength that is set by the \( \lambda/2 \) section of the device and is well confined by the two Bragg mirrors. It is unperturbed by the termination off-chip so that we can select between \( \vec{E}_2 \) and \( \vec{B}_2 \) in the device without changing \( \vec{B}_1 \) or the ensemble of spins probed by the ESR.

The resonators used in this work were patterned in a 50 nm thick Nb film e-beam evaporated on the surface of a C-plane sapphire wafer. The structures were defined using optical lithography and SF\(_6\) plasma etching as previously described [110, 75]. These resonators can be patterned directly on the silicon sample to offer enhanced sensitivity, but to ensure that the spin signal only comes from the 1/2 wavelength defect region of the resonator (and not spins within the Bragg mirrors), the sample was clipped to the surface of the resonator using a phosphor bronze spring as shown in Fig. 5.1(b). This particular device has five periods of Bragg mirror on either side of the half wavelength defect. Each period consists of both a high impedance (95 \( \Omega \), 4 mm long) and a low impedance (30 \( \Omega \), 4 mm long) strip of waveguide. The cavity is 6 mm long with a 10 \( \mu \text{m} \) wide center pin and gap. The RF termination is defined by either leaving the output port floating, or by shorting it to ground using aluminum wirebonds.

The device was cooled to 1.9 K in a pumped helium cryostat equipped with a rotatable sample holder. This allows for in-situ alignment of the device with an externally applied magnetic field \( \vec{B}_0 \) [75]. With \( B_0 = 250 \text{ mT} \) applied in the plane of the Nb, the microwave transmission spectrum was measured and is plotted in Fig. 5.1(c). The photonic bandgap gives about 80 dB of attenuation from 4.5 - 9 GHz and the microwave resonance appears at 7.3 GHz. The resonator is slightly undercoupled and has a temperature-limited quality factor of approximately 20000. The spin sensitivity of this resonator was determined to be \( 5 \times 10^6 \) spins per shot at
2 K using phosphorus doped $^{28}\text{Si}$ (800 ppm $^{29}\text{Si}$). This is on par with other planar resonators [110, 75] and could be further improved by incorporating quantum-limited parametric amplifiers [10, 30].

The sample used throughout this work consists of a 2 $\mu$m isotopically enriched $^{28}\text{Si}$ epitaxial layer grown on a high resistivity p-type substrate. The epi-layer was grown to have $5 \times 10^{15}$ $^{31}\text{P}/\text{cm}^3$ and the sample was ion implanted with $^{209}\text{Bi}$ and $^{75}\text{As}$. After implantation, the donors were activated by annealing the sample in a $\text{N}_2$ atmosphere at $800^\circ \text{C}$ for 20 minutes [128]. The simulated implantation profiles are shown in Fig. 5.2(a) [142]. Two-pulse Hahn echo measurements were performed at 1.9 K and an echo-detected field swept spectrum is shown in Fig. 5.2(b), revealing the $^{31}\text{P}$ and $^{75}\text{As}$ hyperfine lines. Using pulsed spin counting techniques, we estimate the $^{209}\text{Bi}$ activation to be about 50% whereas the $^{75}\text{As}$ donors are fully activated. Because the $^{209}\text{Bi}$ signal is very weak (due to low donor activation and a large nuclear spin, 9/2), the ENDOR experiments were only performed on the $^{31}\text{P}$ and $^{75}\text{As}$ donors.

Figure 5.2: The sample consists of a $^{31}\text{P}$ doped $^{28}\text{Si}$ epitaxial layer, which has been implanted with $^{209}\text{Bi}$ and $^{75}\text{As}$ as shown in (a). An echo detected field sweep spectrum is shown in (b) resolving the two $^{31}\text{P}$ and the four $^{75}\text{As}$ hyperfine lines. The hyperfine lines are labeled by their nuclear spin projections with colors matching the data in Fig. 5.3. These data were taken at 1.9 K with a resonator frequency of 7.3 GHz.
In the presence of $\vec{B}_1$ inhomogeneity, one can measure entirely different subensembles of spins subject to different RF electric or magnetic fields by varying the microwave power\cite{110}. It was therefore important to calibrate $\vec{B}_1$ before every ENDOR experiment by performing two-pulse Hahn echo experiments as a function of microwave power. The electric and magnetic field distributions are well known\cite{75,112} and are plotted in Ch. 3. It has been shown that inhomogeneity in $\vec{B}_1$ can be overcome by using adiabatic (BIR-WURST) pulses \cite{110}. In the supplementary information we demonstrate that they also overcome $\vec{E}_2$ inhomogeneity. These pulse shaping techniques make PBG resonators useful for complex ENDOR experiments requiring high fidelity manipulations. We measure Rabi frequencies in the following experiments, which were thus conducted using rectangular pulses.

Prior to every experiment, the spins were prepared in thermal equilibrium using a combination of RF and optical pulses as described in \cite{121} since nuclear spin relaxation times are long at these temperatures.

5.3 Results

Davies ENDOR experiments were first performed using only RF magnetic fields (shorted device termination). The ENDOR spectra for all four of the $^{75}$As donor hyperfine lines are plotted in Fig. 5.3(b) but the experiments were also performed on the $^{31}$P donors as shown in the appendix C. Only the magnetic dipole allowed transitions could be resolved in this configuration. Those are $\Delta M_s = 0, \Delta M_I = \pm 1$, with $M_s$ and $M_I$ being the electronic and nuclear spin projections, respectively.

The device was reconfigured to have $\vec{E}_2$ fields in the sample (open termination) and the measurements were repeated with the results displayed in Fig. 5.3(c) ($^{31}$P data available in the supplementary information). In addition to the allowed ENDOR transitions, several additional transitions appeared in the $^{75}$As spectra and are
Figure 5.3: (a) Energy level diagram illustrating the electronic Zeeman ($m_S$) and nuclear hyperfine ($m_I$) splittings for $^{75}$As donors in Si. The single (SQT) and double (DQT) quantum transitions are labeled using the green numbers and pink numerals, respectively. These labels are also used in (b-d). The Davies ENDOR spectra measured using magnetic (b) and electrical (c-d) RF pulses are plotted. The magnetically driven ENDOR spectra shows the six SQTs whereas the electrically driven spectra (c) reveals both the SQTs and DQTs. Electrically driven ENDOR also resolves transitions at subharmonics of the SQTs as shown in (d). The SQTs in (b) are power broadened.
denoted by the arrows. These very narrow transitions occur at exactly half the frequency of forbidden double quantum transitions ($\Delta M_s = 0, \Delta M_I = 2$). The single quantum transitions are power broadened in this plot, since power was optimized for the double quantum transitions. Transitions were also observed at subharmonics of the allowed transition frequencies and are shown in Fig. 5.3(d).

The double quantum transitions do not exist for $^{31}$P donors since they have nuclear spin-1/2. EDNMR was observed at the fundamental and subharmonic transitions frequencies for $^{31}$P, but it was noticed that $^{31}$P donors require more RF power than $^{75}$As donors. To quantify the difference, two dimensional EDNMR measurements of the Rabi nutation were conducted on both donors. These experiments used the standard Davies ENDOR pulse sequence but varied the RF pulse length and power. The data for the subharmonic transitions are plotted in Fig. 5.4 (a-b) and the Rabi data for the fundamental transitions are shown in appendix C. From the data, it is clear that the arsenic donors respond over an order of magnitude more strongly to the electric fields (shorter RF pulses are necessary); indicating that different mechanisms may be responsible for the EDNMR in these two donors.

To verify that residual RF magnetic fields (due to the finite length of the device) can not be responsible for the EDNMR, $\vec{B}_2$ was calibrated in the device using a Rabi-nutation experiment and the results were compared against the EDNMR data for both $^{31}$P and $^{75}$As. We found one would need 300 times more power for the residual $\vec{B}_2$ fields to account for the EDNMR.

To ensure that the subharmonic transitions were not artifacts driven by second harmonics generated in the RF source, the output of the RF source was fed directly into a spectrum analyzer. We observed that in the worst case configuration, a second harmonic was present and attenuated by 35 dB compared to the fundamental harmonic. To further suppress this second harmonic, a set of seventh order Butterworth low pass filters (Crystek CLPFL) were used in every experiment, adding 35-50 dB of
Figure 5.4: Rabi oscillations are recorded as a function of RF voltage amplitude for $^{31}\text{P}$ (a) and $^{75}\text{As}$ (b) subharmonic transitions. The $^{75}\text{As}$ transition is at 46.5 MHz and the $^{31}\text{P}$ transition is at 54 MHz. The simulated plots (c-d) show similar dependences to the data, but larger RF amplitudes must be assumed indicating that our models underestimate the transition frequencies by a factor of 3-4. The phosphorus simulation takes into account g-tensor modulation leading to an anisotropic hyperfine coupling whereas the arsenic simulation also takes into account quadrupolar modulation. All data were taken at 1.9 K in a magnetic field of 250 mT.

5.4 Discussion

This is the first demonstration of electrically driven NMR for donors in silicon. We have identified two mechanisms that likely lead to the observed EDNMR, but more theoretical and experimental work will be needed to confirm our explanation.

To understand the EDNMR, we turn to the spin Hamiltonian common to group V donors in silicon. This is given by

$$H/h = \beta \vec{B}_0 \cdot \hat{g}_e \cdot \vec{S} + \vec{S} \cdot \vec{A} \cdot \vec{I} - \beta_n g_n \vec{B}_0 \cdot \vec{I} + \vec{I} \cdot \hat{Q} \cdot \vec{I}$$

(5.1)

attenuation. Given the more than 70 dB power difference between the first and second harmonics, we are confident that the observed subharmonic ENDOR transitions are not due to harmonics generated from the RF source.
where $\beta$ is the Bohr magneton, $\hat{g}_e$ is the electron gyromagnetic tensor, $\vec{S}$ is the electronic spin, $\hat{A}$ is the hyperfine tensor, $\vec{I}$ is the nuclear spin, $g_n$ is the nuclear g-factor, $\beta_n$ is the nuclear magneton, and $\hat{Q}$ is the nuclear quadrupole coupling tensor. The terms in the spin Hamiltonian that are sensitive to electric fields are the electronic Zeeman ($\hat{g}_e$), hyperfine ($\hat{A}$), and quadrupolar ($\hat{Q}$) tensors. Because EDNMR is observed for both $^{75}\text{As}$ and $^{31}\text{P}$ (which has no quadrupole moment), we first neglect quadrupolar effects.

Both $\hat{A}$ and $\hat{g}_e$ can be modulated through the hyperfine and spin-orbit Stark effects, respectively. These effects are quadratic to first order due to inversion symmetry at the donor site, but linear terms can arise from strain\[132, 90\]. We therefore expect to drive transitions at both the electric field frequency, $f$, and $f/2$ (since $\sin^2(f) \propto \cos(2f)$). Similar subharmonic transitions have been observed for electrically driven spin resonance in quantum dots\[68, 98\]. Since the fundamental transition (at $f$) is strain dependent, we will restrict our discussion to the subharmonic transition, which should be more robust against sample-specific strains.

Spin transitions cannot be driven solely by modulation of an isotropic hyperfine interaction due to the disparity in the electronic and nuclear precession frequencies. Any transition matrix elements involving $A_{XX}$ and $A_{YY}$ terms average out in the rotating wave approximation and $A_{ZZ}$ terms can not drive spin rotations. We therefore require an anisotropic hyperfine interaction with $A_{ZX}$ terms to drive nuclear spins.

To find the source of the anisotropy, we turn to the spin-orbit Stark shift. We can compute the electric field modulation of $\hat{g}$ using the multivalley effective mass theory of \[132\] and the experimental Stark shift values from \[112\] and \[90\] as outlined in appendix C. We find that the spin-orbit Stark shift directly modulates the quantization axis of the electron spin such that electron and nuclear spins are quantized along different axes. RF electric fields then lead to RF modulation in the hyperfine field, as seen by the nuclear spin, which can lead to nuclear spin rotations.
To test this mechanism against the experiment, we developed a model that simulates the Rabi-nutation experiments in our device. This model accounts for rotation angle errors in both the ESR and NMR pulses, spin-resonator coupling, inhomogeneity in the RF and microwave fields, and the implant profile of the donors. This simulation takes into account valley repopulation for electric fields in the (100) crystallographic directions (the dominant effect) but neglects the “single valley” effect described in [132]. We find reasonable agreement with the experimental data for the phosphorus donors as shown in Fig. 5.4(c). Note that the simulation is plotted on a different voltage scale indicating a $4\times$ discrepancy between the simulation and data, which is reasonable given our necessarily rough estimates of the parameters. However, the equivalent $^{75}$As simulation (shown in supplementary information) would require a $40\times$ larger voltage which implies that another mechanism must dominate.

The only significantly different term in the $^{75}$As and $^{31}$P Hamiltonians is the quadrupolar coupling, so this is a possible source for the discrepancy in the EDNMR Rabi frequencies. It is difficult to determine transition frequencies for quadrupolar modulation, due to uncertainties in screening potentials from inner shell electrons and no studies have reported electric field induced modulation of the quadrupolar interaction. There have, however, been several recent reports of quadrupolar shifts for $^{75}$As [38, 39] and $^{209}$Bi [92] donors in silicon subject to strain. By comparing the strain-induced hyperfine splitting measured in [39] to the hyperfine Stark data of [90], we can approximately scale the experimentally measured quadrupolar shifts in [39] to correspond to the electric fields we apply in our experiments. By repeating the Rabi-nutation experiment simulations while including the modulation of the quadrupolar interaction, the Rabi frequencies are enhanced by more than a factor of 10 as shown in Fig. 5.4(d). We find reasonable agreement to our data, again given the uncertainties in the parameters. We therefore conclude that the quadrupolar interaction is most
likely responsible for the spin transitions in $^{75}$As, however more theoretical work is warranted.

For the largest RF electric fields applied in this work, the average Rabi frequency is approximately 70 kHz for the fundamental transition and 60 kHz for its subharmonic. These applied fields are a factor of 10 below the donor ionization threshold [74], indicating that MHz frequency EDNMR manipulations should be possible in unstrained Si. The fundamental transition Rabi frequencies depend on strain, suggesting that strain engineering should allow one to achieve even higher Rabi frequencies and the ultimate limit is unknown.

5.5 Conclusion

In summary, we have demonstrated the use of coplanar photonic bandgap microresonators to perform low temperature, high sensitivity ESR and ENDOR on $^{28}$Si:P and $^{28}$Si:As. We demonstrate for the first time all-electric-field control of donor nuclear spins in silicon for $^{75}$As and $^{31}$P donors using these structures. The EDNMR appears to arise from two distinct physical mechanisms. First, electric fields modulate the $g$-tensor to induce an effective anisotropic hyperfine interaction which appears to drive the $^{31}$P nuclear spin transitions. Secondly, for $^{75}$As, the quadrupolar interaction can be modulated to rotate nuclear spins. These experiments probe new physical mechanisms that manipulate nuclear spins which appear to depend on not only the electronic orbital structure, but also the interaction of the inner shell electrons with the donor-bound electron. As such, this should lead to new physical insights in the donor electron system.

Our technique for controlling nuclear spins has several advantages over magnetic control. It relaxes power requirements since voltages rather than currents are used, and allows for high density, individually addressable arrays of donor nuclear spins.
since electric fields are more easily confined than magnetic fields. Since we are able to drive spins at subharmonics of their resonance frequencies and at subharmonics of double quantum $\Delta m_I = 2$ transitions, our electric field control method substantially reduces the bandwidth requirements for quantum devices while simultaneously expanding the computational Hilbert space. From these results, one can envision new quantum computing architectures based on donor nuclear spins in silicon. These techniques should extend to other material systems with long coherence times such as donors in germanium[109] which offer a four-order-of-magnitude enhancement in the spin-orbit Stark shift [111, 89]. The larger Stark effect should translate into significantly faster EDNMR gates.
Chapter 6

Coherence of Spins in Germanium

Germanium was the original material for transistors, and is now being developed for the latest semiconductor electronics [70]. Recently, it has become a key material for spintronics [71, 29, 107] and quantum computing [126, 96, 134] devices. Compared to silicon, donor electrons in Ge have higher mobility (~ 3 times) [70], larger wavefunctions (6.5 nm compared to 2.5 nm), [131, 33], stronger spin-orbit coupling [72], and highly anisotropic conduction band valleys [96]. These indicate that it should offer many orders of magnitude stronger electric field tunability than donors in silicon [111, 96]. Given its likely advantage in tunability, if germanium can support long coherence times it should be an ideal alternative to silicon for quantum information applications.

Much of silicon’s success in the quantum computing community has hinged on the attainability of long coherence times ($T_2$) exceeding seconds when Si is isotopically enriched to have no magnetic nuclei [80, 122, 135, 53]. Germanium also has non-magnetic isotopes so it has been expected to support long coherence times. In this chapter, we report the first electron spin coherence measurements for donor electron spins in Ge. We find that spectral diffusion due to $^{73}$Ge limits $T_2$ in natural Ge samples whereas the spin-lattice relaxation time, $T_1$, limits $T_2$ in isotopically enriched
Ge. The longest $T_2$ we measured is $T_2 = 2T_1 = 1.2$ ms at 350 mK in a magnetic field ($B_0$) of 0.44 T. The low-temperature $T_1$ fits the temperature dependence theorized by Roth [99] and Hasegawa [45], which also predicts $T_1 \propto B_0^{-4}$. This suggests that considerably longer coherence times are possible at lower fields.

While $T_2$ for donors in Ge is shorter than the times demonstrated for Si, Ge-based qubits have some important advantages. For example the larger electron wavefunctions relax the lithographic requirements for exchange coupling two donors, which is important for most donor-based quantum computing schemes [55]. This is advantageous considering Ge is compatible with most of the same nanofabrication techniques as silicon and single-donor devices are achievable [101]. Another useful feature of Ge is the large spin-orbit coupling and shallow donor depth, which leads to a very large spin-orbit Stark shift in Ge (nearly 5 orders of magnitude larger than in silicon) [96] meaning that Ge based qubits are extremely tuneable. This will be important for gated quantum devices [55].

Despite these features, the spin coherence of donor electrons in Ge has remained mostly unstudied. The first experiments were conducted over fifty years ago by Feher, Wilson, and Gere [34, 131], but their measurements were limited to continuous wave (CW) ESR spectroscopy. They estimated $T_1$ for $^{75}$As and $^{31}$P donors based on power saturation measurements, but experimental errors were large. These experiments were difficult because wavefunction overlap occurs for densities as low as $10^{15}$ donors/cm$^3$ such that only lightly doped samples with correspondingly weak signals are useful for isolated donor experiments. Some limited experiments on Sb [93] and $^{31}$P [79] donors in highly strained Ge were also reported. More recently, pulsed nuclear magnetic resonance studies were conducted on $^{73}$Ge nuclear spins [125, 124, 84], which found that the $^{73}$Ge nuclear spin coherence in germanium can be $> 100$ ms.

The samples discussed in this chapter include commercially available, natural Ge doped either $10^{15}$ As/cm$^3$ or $10^{12}$ P/cm$^3$. $^{73}$Ge is the only naturally occurring isotope
of Ge (7.75% abundance) with a nuclear spin and is thus expected to be a limiting factor in the donor spin coherence at low temperatures. Three isotopically enriched samples were prepared at Lawrence Berkeley National Laboratory. The first is a piece of neutron transmutation doped \( ^{74}\)Ge described in Ref.\[52, 51\]. This sample is uniformly doped with \( ^{75}\)As to a density of \( 3 \times 10^{15} \) donors/cm\(^3\) and contains a residual 3.8% \( ^{73}\)Ge. The other two samples are 96% \( ^{70}\)Ge crystal (0.1% \( ^{73}\)Ge) and a 99.99% \( ^{70}\)Ge crystal (0.01% \( ^{73}\)Ge). They have \( ^{31}\)P concentrations of \( \sim 10^{12} \) donors/cm\(^3\) and \( \sim 10^{11} \) donors/cm\(^3\), respectively and are described in \[52, 2\]. The crystallographic orientation of the samples was determined using X-ray diffraction. The sample details are summarized in Table 6.1.

The experiments down to 1.65 K were performed in a pumped He cryostat (H.S. Martin), and lower temperature data were obtained in a \( ^{3}\)He cryostat (Janis Research). All data were taken at X-band (9.65 GHz) in a Bruker dielectric resonator (MD5). The ESR spectra were measured via echo-detected field sweeps using a standard Hahn-echo pulse sequence (\( \pi/2 - \tau - \pi - \tau - \text{echo} \)). Typical spectra are shown in Fig. D.1(a) for phosphorus donors in the 0.1% \( ^{73}\)Ge:P sample and in Fig. 6.1(b) for arsenic donors in the 3.8% \( ^{73}\)Ge:As sample. From these plots we extract a hyperfine coupling constant of 3.55 mT for \( ^{75}\)As and 2.04 mT for \( ^{31}\)P.

The ESR linewidth depends strongly on the sample orientation and the abundance of \( ^{73}\)Ge present in the sample, as noted by Wilson \[131\]. With \( B_0 \) oriented along one of the \( \langle 001 \rangle \) directions, the linewidth is narrowest and is limited primarily by hyperfine interactions with \( ^{73}\)Ge. At this orientation the line broadening from spin-orbit strain effects is suppressed by valley symmetry about the \( \langle 001 \rangle \) as explained in Refs.\[131, 99, 45\]). To give a sense of the strain-induced line broadening for \( B_0 \) away from [001] equivalent directions, Fig. 6.1(c) shows the angular dependence of the linewidth for select samples rotated in the \( \langle 1 \overline{1} 0 \rangle \) plane relative to the [001] axis. There is also an isotopic dependence of the linewidth away from the \( \langle 001 \rangle \) direction.
Table 6.1: Sample Details

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>(^{70}\text{Ge})</th>
<th>(^{72}\text{Ge})</th>
<th>(^{73}\text{Ge})</th>
<th>(^{74}\text{Ge})</th>
<th>(^{76}\text{Ge})</th>
<th>Doping (cm(^{-3}))</th>
<th>([001]) Linewidth (mT)</th>
<th>(T_2^*) (ns)</th>
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<td>(^{\text{n}\text{at}}\text{Ge}:\text{As})^*</td>
<td>20.57%</td>
<td>27.45%</td>
<td>7.75%</td>
<td>36.50%</td>
<td>7.73%</td>
<td>(1 \times 10^{15}) As</td>
<td>1.2</td>
<td>11</td>
</tr>
<tr>
<td>(^{\text{n}\text{at}}\text{Ge}:\text{P})^*</td>
<td>20.57%</td>
<td>27.45%</td>
<td>7.75%</td>
<td>36.50%</td>
<td>7.73%</td>
<td>(\sim 10^{12}) P</td>
<td>1.1</td>
<td>13</td>
</tr>
<tr>
<td>3.8% (^{73}\text{Ge}:\text{As})</td>
<td>0.1%</td>
<td>0.9%</td>
<td>3.8%</td>
<td>92.6%</td>
<td>2.6%</td>
<td>(3 \times 10^{15}) P</td>
<td>0.8</td>
<td>17</td>
</tr>
<tr>
<td>0.1% (^{73}\text{Ge}:\text{P})</td>
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<td>2.1%</td>
<td>0.1%</td>
<td>1.2%</td>
<td>0.3%</td>
<td>(\sim 10^{12}) P</td>
<td>0.069</td>
<td>211</td>
</tr>
<tr>
<td>0.01% (^{73}\text{Ge}:\text{P})</td>
<td>99.99%</td>
<td>-</td>
<td>0.01%</td>
<td>-</td>
<td>-</td>
<td>(\sim 10^{11}) P</td>
<td>0.051</td>
<td>284</td>
</tr>
<tr>
<td>Nuclear Spin</td>
<td>0</td>
<td>0</td>
<td>9/2</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Percent abundances for the natural germanium samples were taken from Ref. \[9\]
and we presume this is due to isotopic strain [118]. The strong dependence of the linewidth on field orientation conveniently allows for accurate *in situ* orientation of the crystals. Unless otherwise noted, all data presented in this manuscript assumes $B_0$ is oriented along a $\langle 001 \rangle$ axis.

One can predict the effect of $^{73}$Ge on the ESR linewidth through the hyperfine interaction using a second moment calculation [58], which gives $\Delta B \propto f^{1/2}$, where $\Delta B$ is the linewidth, and $f$ is the percent abundance of $^{73}$Ge. The measured ESR linewidths for samples of various isotopic enrichment with $B_0\parallel\langle 001 \rangle$ is shown in Fig. 6.1(d). The point at $f = 0.8\%$ was taken from Wilson [131]. The solid curve in Fig. 6.1(d) gives the expected $f^{1/2}$ dependence for broadening of the line due to $^{73}$Ge hyperfine interactions for $^{75}$As. The solid curve fits the data well, implying that $^{73}$Ge is indeed the dominant mechanism for line broadening in this orientation. The linewidth can be interpreted as an ensemble dephasing time, $T_2^*$, which is also shown in Table 6.1.

$T_1$ was measured using an inversion-recovery pulse sequence ($\pi - t - \pi/2 - \tau - \pi - \tau - \text{echo}$). The values of $T_1$ are plotted in Fig. 6.2 for $^{31}$P(a) and $^{75}$As(b) donors. The same two mechanisms limit $T_1$ for all of the samples. At higher temperatures, $T_1$ is limited by a highly temperature ($T$) dependent process. The theory of Roth and Hasegawa [99, 15] predicted a $T^{-7}$ Raman process to dominate at these temperatures but this dependence does not fit our data well. An Orbach process does fit the data as shown in Fig. 6.2. The Orbach process is of the form $T_1 \propto a \times \exp\left(\frac{E_{v.o.}}{kT}\right)$, where $a$ is a prefactor that can be calculated using Ref. [15], $E_{v.o.}$ is the valley-orbit splitting, and $k$ is the Boltzmann constant. The valley-orbit splittings extracted from the $T_1$ fits in Fig. 6.2 agree well with the values measured by Ramdas (2.8 meV for $^{31}$P and 4.2 meV for $^{75}$As [97]). Likewise, the values of $a$ extracted from our fits agree with the values calculated using Castner’s theory [15] to within a factor of 2.

At lower temperatures, a single-phonon process with a $T^{-1}$ dependence appears to dominate. This relaxation process is a result of the multivalley structure of ger-
Figure 6.1: (a) Echo-detected field sweep spectra for (a) 0.1% $^{73}$Ge:P and (b) 3.8% $^{73}$Ge:As with $B_0 || \langle 001 \rangle$. (c) Plot of ESR linewidths as a function of field orientation for $nat$Ge:As (blue), 3.8% $^{73}$Ge:As (red) and 0.01% $^{73}$Ge:P(black). The solid lines serve only as guides to the eye. (d) Linewidth for $B_0 || \langle 001 \rangle$ as a function of $^{73}$Ge isotopic abundance. The Ge:As data appear as black triangles whereas the Ge:P data appear as red circles. The solid line shows the expected $f^{1/2}$ dependence for broadening due to $^{73}$Ge hyperfine interactions. The ESR linewidth at 0.8% is taken from Ref. [131]. Data were taken at 1.8 K and 9.65 GHz.
Figure 6.2: Temperature dependence of $T_1$ (triangle) and $T_2$ (circle) for natural (open symbols) and isotopically-enriched (solid symbols) Ge with $B_0 \parallel \langle 001 \rangle$. The solid lines are fits for (a) phosphorus donors (0.1% $^{73}$Ge:P) and (b) arsenic donors (3.8% $^{73}$Ge:As), assuming two relaxation processes: a single-phonon ($T^{-1}$) process and an Orbach ($a \times \exp(E_{v.o.}/kT)$) process. For the $T_2$ fits, both $T_1$ and an additional (temperature independent) spectral diffusion mechanism due to $^{73}$Ge were taken into account. Note that for the 0.1% $^{73}$Ge:P sample, $T_2 = 2T_1$ down to the lowest temperatures.
manium. In the unperturbed ground state, there are four degenerate valleys located along the \(\langle 111\rangle\) equivalent crystallographic axes. Each valley has an axially symmetric g-tensor, \(\hat{g}_i\) but the effective g-tensor, \(\hat{g}_{\text{eff}}\), is given as a weighted average over all four valleys. In the electron ground state, each valley has equal amplitude, and, by symmetry, \(\hat{g}_{\text{eff}}\) is isotropic \([99]\). When strain is applied, valley energies shift relative to each other, leading to valley repopulation and a change in \(\hat{g}_{\text{eff}}\). The strain from phonons near the Larmor frequency modulates \(\hat{g}_{\text{eff}}\), effectively mixing the spin up and down states. This gives a \(T_1\) as calculated by Roth \([99]\) and Hasegawa \([45]\), which agrees well with our experimental data. The calculated estimates for \(T_1\) at 350 mK are within 10\% for Ge:As and 30\% for Ge:P. The theory predicts that \(T_1\) due to this single-phonon process should scale with the square of the \(\hat{g}_i\) anisotropy. The valley anisotropy of Ge was measured to be 3 orders of magnitude larger than in Si \([131]\), implying that the single-phonon process should be 6 orders of magnitude stronger in germanium. This accounts for the short \(T_1\) times observed for donors in germanium as compared with silicon.

An interesting property of the single-phonon spin-lattice relaxation mechanism is an anisotropy in \(T_1\) predicted by the Roth-Hasegawa theory\([99, 45]\). The 3.8\% \(^7\)Ge:As crystal was rotated in the (110) plane at 1.8 K, and the resulting \(T_1\) is plotted in Fig. 6.3. The theory predicts that, for rotation in this plane, the spin-lattice relaxation is given by:

\[
\frac{1}{T_1} = \alpha B_0^4 T (\cos^4(\theta) + \frac{1}{2} \sin^4(\theta))
\] (6.1)

where \(\alpha\) is a scaling factor, which can be calculated following Hasegawa\([45]\), and \(\theta\) is the field orientation relative to \(\langle 001\rangle\). Hasegawa calculated \(\alpha = 7.2 \times 10^4 K^{-1} s^{-1} T^{-4}\) for arsenic in Ge, but a fit to the data reveals \(\alpha = 4.1 \times 10^4 K^{-1} s^{-1} T^{-4}\). We observe that for \(B_0\) oriented along a \(\langle 111\rangle\) axis, \(T_1\) becomes 3 times longer than along \(\langle 001\rangle\).

We note that \(T_1\) for donors in highly enriched samples is shorter than it is for donors in the natural material as seen in Fig. 6.2(b). This effect is still under inves-
Figure 6.3: Angular dependence of $T_1$ for the 3.8\% $^{73}\text{Ge}:\text{As}$ sample rotated in the (1\overline{1}0) plane at 1.8 K. The curve is a fit using Eq. (6.1) assuming $\alpha = 4.1 \times 10^4$ K$^{-1}$s$^{-1}$T$^{-4}$.

tigation, but one possible mechanism is the presence of isotopic strain in the natural germanium \cite{118}. Wilson \cite{131} demonstrated the use of large strains to partially lift the valley degeneracy, thus disrupting the single-phonon relaxation mechanism. Modelling the effects of strain can be complex, as strain not only modulates $\alpha$, but can also modify the form of Eq. (6.1). Nevertheless, controlled strain may be beneficial for future quantum devices based on germanium.

We also measured the electron spin coherence time, $T_2$, for each of the samples using the standard Hahn-echo pulse sequence. The decay curves at 1.8 K for $B_0 \parallel \langle 001 \rangle$ are shown in Fig. 6.4(a) for Ge:P and in Fig. 6.4(b) for Ge:As. These decays are fit to an exponential decay of the form $A e^{-(2\tau/T_2)^n}$, where $A$ scales the amplitude, $\tau$ is the delay between the $\pi/2$ and $\pi$ pulses in the Hahn echo sequence, and $n$ is a fitting parameter that depends on the decoherence mechanism. The 0.1\% $^{73}\text{Ge}:\text{P}$ sample decays with $n=1$ over the measured temperature range. For this sample it was found that $T_2 = 2T_1$ (representing the absolute $T_1$ limit \cite{103}) down to 350 mK temperatures, meaning that decoherence due to $^{73}\text{Ge}$ is negligibly small with this level of isotopic enrichment at these temperatures. For samples with $f \geq 3.8\%$, we find

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that $n$ varies from 1 at high temperatures to 2.1 at low temperatures. This is a characteristic of $^{73}\text{Ge}$ spectral diffusion limiting the coherence. At 1.8 K, the $^{73}\text{Ge}:\text{As}$, $^{73}\text{Ge}:\text{P}$, and 3.8% $^{73}\text{Ge}:\text{As}$ samples decay with this form.

The temperature dependence of $T_2$ is also plotted in Fig. 6.2 and fit to $1/T_2 = m/(T_1) + 1/T_{SD}$, where $T_{SD}$ is the (temperature independent) spectral-diffusion-limited coherence time and $m$ is equal to 1/2 for the 0.1% $^{73}\text{Ge}:\text{P}$ sample and 2 for the 3.8% $^{73}\text{Ge}:\text{As}$ sample. For the natural germanium samples, $T_{SD}$ limits the coherence to 57 $\mu$s whereas the 3.8% $^{73}\text{Ge}:\text{As}$ sample is limited to 113 $\mu$s. From similar work in silicon [1, 22], one might expect an orientation dependence to $T_{SD}$. We measured the orientation dependence of $T_{SD}$ for the 3.8% $^{73}\text{Ge}:\text{As}$ sample at 1.8 K and fit the decays with a curve of the form $Ae^{-(2r/T_1)}e^{-(2r/T_{SD})}$ to separate the $T_1$ component from $T_{SD}$ [78]. No angular dependence of $T_{SD}$ could be resolved.

While coherence times of over one millisecond for isotopically enriched material open the possibility of using donor electrons in Ge for quantum computing devices, these coherence times are much shorter than those for donors in isotopically enriched silicon (seconds) [122, 135]. To extend the Ge donor coherence, one must either overcome the $T_1$ limit or use nuclear spins, which may support longer coherence times. There are several promising techniques to extend the $T_1$ limit. One approach is to take advantage of the $T_1$ anisotropy, which will allow for up to a factor of 3 increase in $T_1$ when devices are oriented with $B_0 \parallel \langle 111 \rangle$, but this $T_1$ enhancement comes at the expense of a shorter ensemble $T_2^*$. A simple alternative is to operate devices at lower temperatures, since $T_1 \propto T^{-1}$. Perhaps the most effective technique is to operate devices at lower frequencies since theory predicts $T_1 \propto B_0^{-4}$. More complicated strategies are also available. In particular, one can apply a large strain, as demonstrated by Wilson [131], which shifts the valley energy levels, thus suppressing valley repopulation and the associated relaxation mechanisms. Another recent proposal suggests patterning Ge in a periodic structure to open a phononic bandgap.
Figure 6.4: Two-pulse Hahn echo decay curves for natural (blue) and isotopically enriched (black) germanium doped with phosphorus(a) and arsenic(b) donors. Data were taken at 1.8 K and 9.65 GHz. The solid curves are fits to the data using $exp[-(2\tau)/T_2^n]$. 

at the Larmor frequency $^{[115]}$. Such a structure would suppress the single phonon process.

In summary, we have measured the ESR linewidths, coherence times, and spin-lattice relaxation times for donors in natural and isotopically enriched germanium at X-band microwave frequencies. We find that the linewidths are primarily broadened by hyperfine interactions with $^{73}$Ge spins when $B_0$ is oriented along the [001] axis and by strain in other orientations. We find that donor electron spin coherence is limited by spectral diffusion due to hyperfine interactions with $^{73}$Ge nuclei for the \textit{nat}Ge ($T_{SD} = 57\ \mu$s) and 3.8\% $^{73}$Ge:As ($T_{SD} = 113\ \mu$s) samples, thus $T_{SD}$ scales approximately as $1/f$ which, is similar to silicon$^{[22]}$. For the more highly enriched 0.1\% $^{73}$Ge:P sample, $T_2$ was limited to $2T_1$ down to 350 mK, the lowest temperature

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we have measured \((T_2 = 1.2 \text{ ms for } B_0 \parallel \langle 001 \rangle)\). We observe a large anisotropy in \(T_1\), which is explained by the theory of Roth and Hasegawa\(^{99, 45}\), with the longest \(T_1\) occuring for \(B_0 \parallel \langle 111 \rangle\). It is predicted that at lower magnetic fields \(T_1\) and thus \(T_2\) should become substantially longer.
Chapter 7

Stark Effect in Germanium

7.1 Introduction

Germanium’s most striking advantage over silicon is perhaps its electric field tunability. For donor qubits, the ability to reliably perform local, single-qubit operations in a scalable architecture—a prerequisite for universal quantum computing (Chapter 1) [25]—has remained elusive. The conventional approach was outlined in Ch. 4 and relies on using the Stark effect to tune individual spins on and off resonance with a globally applied microwave magnetic field [55]. The Stark effect was measured in silicon for $^{31}$P (Ch. 4 [112, 90]), $^{75}$As [74, 90], $^{209}$Bi [90], and $^{121,123}$Sb [12, 90] donors and is weak; it is unable to shift the resonance by more than a small fraction of the inhomogeneous linewidth. In this chapter, we measure the Stark effect for $^{31}$P and $^{75}$As donors in germanium and show that for even small electric fields (480 V/cm), donor electron spins can be tuned by at least four times the ensemble linewidth at X-band magnetic fields.

Germanium’s strong tunability arises from its large spin-orbit coupling, small valley-orbit splitting, and small binding energy [131]. The hyperfine interaction is two times weaker in germanium (Ch. 6), but the small binding energy means that
Figure 7.1:  (a) Cartoon illustrating the valley structure in germanium (half-ellipsoids) superimposed on a unit cell of the crystal. The sides of the cube are oriented along the (100) equivalent crystallographic directions. (b) Cartoon of the parallel plate capacitor scheme used for applying electric fields to the Ge samples. The electric field (red) is uniform over the sample volume and directed between the two Au electrodes. When placed in the microwave resonator, $\vec{B}_1$ (black) is directed up and down and $\vec{B}_0$ (green) can be oriented in any arbitrary direction orthogonal to $\vec{B}_1$. (c) Schematic representation of the pulse sequence used to measure Stark shifts. Microwave pulses are shown in black whereas the bipolar electric field pulse is shown in red.
the electronic wavefunction can be more strongly perturbed by electric fields. The overall tunability will depend on the Stark parameters (reported in this chapter) and the maximum electric field that can be applied before donor ionization occurs (lower bound reported in this chapter).

The physics governing the Stark effect is qualitatively similar in silicon and germanium except that the conduction band structure is different. The band structure controls the spin-orbit Stark effect, so the angular dependences discussed in Ch. 4 are different. While silicon has six conduction band valley ellipsoids, germanium has 4 valley ellipsoids (or 8 half valleys) centered at the L-points of the Brillouin zone (along the ⟨111⟩ equivalent crystallographic axes) [99, 15]. This is depicted by the cartoon in Fig. 7.1(a). Each individual valley has a highly anisotropic \( g \)-factor with values varying from 1.92 to 0.82 for \(^{75}\)As donors (or 1.93 to 0.83 for \(^{31}\)P donors) [131]. This anisotropy is three orders of magnitude larger than in silicon [131, 132], indicating that the spin-orbit Stark shift should also show strong anisotropy. The donor ground state is a weighted superposition of the four valleys, and therefore the overall \( g \)-tensor is given by a weighted sum over all of the individual valley \( g \)-tensors. This gives

\[ \hat{g}_{\text{eff}} = \sum_{i=1}^{4} \alpha_i \hat{g}_i \]  

(7.1)

where \( \hat{g}_{\text{eff}} \) is the overall \( g \)-tensor, \( \alpha_i \) is the wavefunction amplitude in the \( i \)-th valley, and \( \hat{g}_i \) is the \( g \)-tensor of an individual valley [31]. Each valley has an axially symmetric \( g \)-tensor given as

\[ \hat{g}_i = \begin{bmatrix} g_\perp & 0 & 0 \\ 0 & g_\perp & 0 \\ 0 & 0 & g_\parallel \end{bmatrix} \]  

(7.2)

in the valley basis, with \( g_\perp \) and \( g_\parallel \) equal to the \( g \)-factors perpendicular and parallel to the valley axis, respectively. In the absence of any electric fields or strain, the electron
wave function equally populates the valleys ($\alpha_i = 0.25$) leading to an isotropic $g$-factor ($\hat{g}_{\text{eff}} = g_0 I$ where $g_0 = 1.57$ for $^{75}$As, $1.5631$ for $^{31}$P, and $I$ is the identity matrix)\textsuperscript{[131]}. Similarly to silicon (Ch. 4), when an electric field is applied, the valleys with axes oriented along the electric field are lowered in energy, and their $\alpha_i$ increase relative to the other valleys. This gives rise to anisotropy in $\hat{g}_{\text{eff}}$. In addition to this valley-repopulation effect, a $g$-factor shift can result from the “single-valley” effect where an electric field mixes the ground state with higher lying conduction bands\textsuperscript{[34]}. This can be thought of as a modulation of $g_\parallel$ and $g_\perp$ as opposed to the modulation of $\alpha_i$ caused by the valley repopulation effect.

From symmetry considerations, the Stark effect for donor electron spins must be quadratic to first order \textsuperscript{[90, 96]} so that the Stark-induced frequency shift, $df$, can be described as

$$df = [\eta_g g_0 \beta B_0 + \eta_A A M_I] \vec{E}^2$$

(7.3)

where $\eta_g$ and $\eta_A$ are the spin-orbit and hyperfine Stark parameters, respectively, $g$ is the $g$-factor along $\vec{B}_0$, $\beta$ is the Bohr magneton, $\vec{B}_0$ is the magnetic field, $A$ is the hyperfine coupling constant, $M_I$ is the nuclear spin projection, and $\vec{E}$ is the applied electric field. The spin-orbit Stark parameter includes both the valley repopulation and single valley Stark shifts and thus depends on the direction of the applied electric and magnetic fields. In this work, we measure the angular dependence of the Stark parameters for $^{75}$As and $^{31}$P donors and find that in certain orientations they are four orders of magnitude larger than what was measured for donors in silicon. These large Stark parameters indicate that germanium-based spin qubits have some important advantages over their silicon analogues.
7.2 Experimental Methods

The Stark shift was measured using the same pulsed electron spin resonance (ESR) technique discussed in Ch. 4 [77, 12]. This technique uses a Hahn echo pulse sequence with an electric field pulse of length $t_E$ inserted between the microwave pulses as illustrated in Fig. 7.1(c). The applied electric field detunes the spins relative to the local oscillator of the microwave bridge such that they accumulate a phase, $d\phi$, which is readily measured using a quadrature detector. The phase shift is directly related to the Stark shift ($df$) by $df = d\phi/t_E$. To cancel linear Stark effects, which can arise from strain [12, 90, 112], bipolar electric field pulses were used as described in Ref. [12].

Five samples were measured in this work, and their details are outlined in Table 7.1. Three of the samples are commercially available natural germanium, and two other crystals are isotopically enriched [52, 51]. The isotopic enrichment is particularly important for these experiments because it allows the donor hyperfine structure of the ESR spectra to be resolved. In natural germanium, hyperfine interactions with the spin 9/2 $^{73}\text{Ge}$ nuclei (7.8% abundant) broaden the lines to the extent that the donor hyperfine structure and thus the hyperfine Stark shifts cannot be clearly resolved. The natural Ge samples were therefore only used to measure the spin-orbit Stark parameters. The isotopically enriched crystals were the 3.8% $^{73}\text{Ge}$:As and 0.1% $^{73}\text{Ge}$:P samples discussed in Ch. 6 [52, 51, 109].

Table 7.1: Sample Details

<table>
<thead>
<tr>
<th>Number</th>
<th>Material</th>
<th>Doping</th>
<th>Faces</th>
<th>$T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$^{74}\text{Ge}$:As</td>
<td>$3 \times 10^{15}$ As/cm$^3$</td>
<td>[110]</td>
<td>[001]</td>
</tr>
<tr>
<td>2</td>
<td>nat$^{74}\text{Ge}$:As</td>
<td>$1 \times 10^{15}$ As/cm$^3$</td>
<td>[111]</td>
<td>[011]</td>
</tr>
<tr>
<td>3</td>
<td>$^{70}\text{Ge}$:P</td>
<td>$\sim 10^{12}$ P/cm$^3$</td>
<td>[100]</td>
<td>[001]</td>
</tr>
<tr>
<td>4</td>
<td>nat$^{70}\text{Ge}$:P</td>
<td>$4 \times 10^{14}$ P/cm$^3$</td>
<td>[110]</td>
<td>[001]</td>
</tr>
<tr>
<td>5</td>
<td>nat$^{70}\text{Ge}$:P</td>
<td>$10^{13}$ P/cm$^3$</td>
<td>[111]</td>
<td>[1\bar{1}0]</td>
</tr>
</tbody>
</table>
All of the samples were cut to have faces along primary crystal axes (outlined in Table 7.1) and X-ray diffraction was used to verify that all faces were within approximately 1° of the intended planes. These faces were used to align the electric field to the crystal. Additionally, the magnetic field must be aligned to the crystal so the sample holder was equipped with a goniometer. The goniometer was calibrated to within ∼ 2° by measuring the ESR linewidth as a function of angle since the linewidth is minimized for $B_0$ in the (100) direction [131].

To apply uniform electric fields, samples were sandwiched between gold electrodes in a parallel plate capacitor arrangement as shown in Fig. 7.1(b). The electrodes were fashioned from double side polished sapphire wafers with 200 nm of gold deposited on the surface. It was necessary to keep the gold layers thin to avoid loading the microwave resonator. The samples were secured in the parallel plate structures by loosely wrapping them in teflon tape before inserting them into an X-band dielectric resonator (Bruker MD-5) equipped with a low noise cryogenic preamplifier. The samples were cooled to 1.8 K in a pumped helium cryostat.

We measured the Stark shift at 9.6 GHz using 200 ns and 400 ns $\pi/2$ and $\pi$ pulses and a resonator Q factor of 2000. All experiments were conducted at 1.8 K where the samples have conveniently short spin-lattice relaxation times, $T_1 \sim 1$ ms [109]. The spin echoes were typically signal averaged 1000 times per experiment and every experiment was repeated 50 times to further improve the signal to noise ratio. The dephasing time, $\tau$, was kept short relative to the coherence time, $T_2$, as given in Table 7.1 [109]. This sets a limit on the length of the electric field pulse, $t_E$. For the $nat$Ge samples $t_E$ was typically 10 $\mu$s while $t_E$ of 30-45 $\mu$s were used for the isotopically enriched samples.
Figure 7.2: Stark shifts measured for $^{75}$As (a-c) and $^{31}$P (d) (samples 1 and 3, respectively) for different configurations of the electric and magnetic fields (denoted by the cartoon insets). The red arrow indicates the direction of the electric field whereas the green arrow shows the direction of $B_0$ relative to the conduction band valleys (grey ellipsoids). In the plots, different symbols/colors denote different hyperfine lines ($M_I$). The fanning out of the Stark shifts comes from the hyperfine Stark effect whereas the center of mass shift comes from the spin-orbit Stark effect. Solid lines represent the global least squares fit to the data using Eq.(3) with fitting parameters listed in Table 2.

7.3 Results and Discussion

The Stark shift data for the $^{74}$Ge:As and $^{70}$Ge:P samples are plotted in Fig. 7.2 for various electric and magnetic field configurations. These were the only samples where we were able to clearly resolve all four $^{75}$As or two $^{31}$P donor hyperfine lines ($M_I$) and the measurements were performed on each line. The data clearly resolve both hyperfine (fanning out) and spin-orbit (center of mass shift) Stark effects. In Figs. 7.2(a-b) and (d) the electric field is oriented along a (100) crystallographic direction that makes equal angles with all four conduction band valleys (oriented
in the (111) equivalent directions). In this orientation, there should be no valley repopulation because all valleys experience the same energy shift. This means that only the single-valley effect is responsible for the observed Stark shifts. For Fig. 7.2(c), the electric field makes different angles with the valleys, and therefore both valley repopulation and single-valley Stark effects can occur. However, here the magnetic field makes an equal angle with all of the valleys. In this configuration, each valley has an equivalent $g$ factor and redistribution of the electronic wave function among the valleys cannot affect $\hat{g}_{\text{eff}}$. The data for $\vec{E} \parallel \vec{B}_0 \parallel (110)$ has been omitted from Fig. 7.2 since the signal-to-noise was too poor to resolve the hyperfine component of the Stark shift. We fit Eq. 3 to the data and report the extracted Stark parameters in Table 2. Since neither of the isotopically enriched crystals have faces cut in the (111) direction, we could not measure the Stark effect for $E \parallel (111)$ in these crystals.

Natural germanium crystals were available with faces cut in all of the primary crystals planes, but since they have broad ESR linewidths, we were not able to measure the hyperfine Stark shift and only measured the spin-orbit Stark shift. To accurately determine the spin-orbit term, the Stark shift was measured at the expected center of each hyperfine line and the results were averaged. Because the hyperfine Stark shift is proportional to $M_I$, averaging over opposite hyperfine lines cancels out the hyperfine Stark shift so that only the spin-orbit term survives.

The highly anisotropic spin-orbit Stark shift is shown in Fig. 7.3 for various electric and magnetic field orientations. When the electric field is oriented in the (100) crystallographic directions (Fig. 7.3(a)), the shift is solely due to the single-valley Stark effect and is small. When the electric field is oriented along the (110) or (111) directions (Fig. 7.3(b) and (c)), valley repopulation also contributes to the Stark shift, and we see that the shift is up to two orders of magnitude larger. We thus conclude that valley repopulation is the dominant mechanism contributing to the spin-orbit Stark shift. To emphasize the anisotropy in the Stark shift, all three panels
Figure 7.3: Spin-orbit Stark shift for $^{75}$As (red, solid symbols) and $^{31}$P (black, open symbols) donors in germanium. The sample number is listed in each panel’s legend and corresponds to the number listed in Table 1. The square symbols with solid lines denote $\vec{E} \parallel \vec{B}$ and triangular symbols with broken lines denote $\vec{E} \perp \vec{B}$. The cartoons to the right schematically show the electric field (red arrow) relative to the conduction band valleys (grey ellipsoids). In (a) the electric field makes equal angles with all of the conduction band valleys so only the “single-valley” Stark effect contributes to the shift. The inset shows that although small, the Stark effect is resolved in this orientation. In (b) the electric field is oriented between two valleys and in (c) the electric field is directed along one valley axis. When E is along the valley axis, the valley repopulation effect should be maximized. The lines plotted are least squares fits to the data with the exception of the nearly horizontal dashed gray line, which represents the strongest Stark shift measured for donors in silicon (hyperfine shift of Si:Sb, $M_I = 5/2$).
are plotted on the same scale. We note that while this makes it difficult to resolve the Stark shift in Fig. 7.3(a), the same data are plotted in Fig. 7.2. The data were least-squares fit with Eq. 3 (neglecting the $\eta_A$ term, which was averaged out), and we extract the spin-orbit Stark parameters as recorded in Table 2. The error reported in the table represents the fitting error.

Random strain can also lead to errors in measuring the hyperfine and spin-orbit Stark parameters since it is equivalent to internal electric fields ($\vec{E}_{\text{int}}$). When ($\vec{E}_{\text{int}}$) is superimposed with our externally applied electric field ($\vec{E}_{\text{ext}}$), it can lead to a large linear Stark effect since the Stark shift is then proportional to ($\vec{E}_{\text{int}} + \vec{E}_{\text{ext}}$)$^2$. This linear term was cancelled by applying bipolar electric field pulses as previously discussed [12].

To compare these shifts with what was reported for donors in silicon, we plot the largest Stark shift measured for donor electron spins in silicon (the $M_I = 5/2$ transition for $^{121}\text{Sb}$ donors) [90] in Fig. 7.3. This shift is colored gray and is so small that it appears flat. At a field of 50 V/cm, the shift for Si:Sb is only $\sim -3$ Hz, compared to over 9 kHz for Ge:As with a (111) oriented $\vec{E} \parallel \vec{B}_0$. From these data, it is clear that in terms of Stark sensitivity, germanium far outperforms silicon.

Of course, high sensitivity does not necessarily translate into large tunability. For the donors in a large ensemble to be gate addressable, one would like to be able to apply large enough electric fields to reliably tune the donor electron spin by more than the ensemble linewidth. In our recent work [109], we have found that the ensemble linewidth of donor electron spins in highly enriched germanium can be as narrow as 1.1 MHz (0.05 mT). With the electric fields applied in this work, we were able to demonstrate a Stark shift of only 7 kHz (Fig. 7.3 (c)). The largest electric field was limited by the high densities of $^{31}\text{P}$ and $^{75}\text{As}$ donors in our samples, which can undergo avalanche impact ionization at higher fields given the large separations between the parallel plates [116]. Much larger electric fields will be permitted in
nano-scale gated devices or in lightly doped macroscopic crystals. In the appendix D, we demonstrate that fields as large as 480 V/cm can be applied to a 0.5 mm thick crystal with $\sim 10^{12} \, \text{P/cm}^3$ without signs of donor ionization. The resulting Stark shift is 28 kHz and is relatively small because electric fields could only be applied along a (100) crystallographic axis. However, a similar non-ionizing electric field of 480 V/cm applied along the (111) direction, would produce a Stark shift of 4.2 MHz (For $\vec{B}_0$ parallel to $\vec{E}$), exceeding the ensemble linewidth (of 0.01% $^{73}\text{Ge}$) by a factor of four [89].

Because spins can be tuned by more than the ensemble linewidth, donors in germanium are compatible with Stark addressable spin manipulation schemes. Stark modulation was demonstrated for individual spins in silicon where the “instantaneous” spin linewidth is narrow [69]. In this work, a field of 8000 V/cm was applied to achieve a shift of 350 kHz. The large shift was made possible by a very large linear Stark effect, presumably due to strain in their nano-scale gated devices. Addressability has been achieved for ensembles of Sb nuclear spins, which have very narrow linewidths [136]. A field of 900 V/cm was used in this work to produce a shift of 8 kHz. These large electric fields are not necessary in germanium.

7.4 Conclusion

In summary, we have investigated the Stark tunability of $^{31}\text{P}$ and $^{75}\text{As}$ donor qubits in germanium—a largely unstudied quantum system that offers some major advantages over silicon. Our results show that the spin-orbit and hyperfine components of the Stark shift are four orders and one order of magnitude larger, respectively, when compared with silicon. We find a lower bound for ionizing fields in our enriched samples of 480 V/cm, which gives a lower limit on the Stark tunability of Ge donor qubits of 4.2 MHz, four times the ensemble linewidth (1.1 MHz [109]). This means
that even large ensembles of donor qubits in germanium can be reliably gated using electric fields. When these encouraging results are combined with the long coherence times we have already reported \[109\] and germanium’s compatibility with industrial semiconductor processing \[106, 140, 56, 101\], germanium appears to be the natural host material for the next generation of donor-based quantum bits.
The Stark parameters are largest for the $^{31}$P donors, which are shallower than $^{75}$As donors.

Table 7.2: Hyperfine ($\eta_a$) and spin-orbit ($\eta_g$) Stark parameters for $^{31}$P and $^{75}$As donors extracted from the data in Fig. 7.2 and Fig. 7.3. The theoretical values marked with (*) are taken from [96] and all other theoretical values are courtesy of Pica et al. [89]. These theories match nicely with the experimental results. Note that the Stark parameters are highly anisotropic, changing sign and amplitude by more than an order of magnitude depending on the electric and magnetic field orientations.
Chapter 8

Conclusion

In this experimental thesis, we used electron spin resonance techniques to study manipulation of donor electron spins in silicon and germanium. We begun the thesis by studying the ability to rapidly manipulate electron spins using low power magnetic field pulses. the electric-field manipulation of donor spins in silicon and germanium. We demonstrated for the first time electrically driven nuclear magnetic resonance for spins in silicon and discuss several mechanisms that can be responsible for this effect. We then turned to germanium as an alternative material to silicon for quantum information applications and and show that it supports long coherence times and has enhanced electric field tunability. Most of these results were enabled by advancements made in electron spin resonance technology including the design of superconducting coplanar waveguide devices tailored to our specific experimental applications. Our finding are summarized in the following sections.

8.1 Coplanar waveguide resonators

In Ch. 3 we demonstrated the use of coplanar waveguide resonators to perform low temperature, high sensitivity electron spin resonance. We then improved the devices to have a capacitive termination, allowing us to apply the DC electric fields necessary
for studying the Stark effect for donor spins in silicon (Ch. 4). We finally, developed coplanar photonic bandgap resonators that give us the flexibility to apply either DC and RF electric or magnetic fields in the region of our spin ensembles. This allowed us to not only extend the use of coplanar waveguides for ENDOR experiments, but also demonstrate electrically driven ENDOR.

8.2 Electrical manipulation or donors in silicon

In chapter 4 we measured the hyperfine and spin-orbit Stark effects for donor spins in silicon. We repeated the measurements for different orientations of applied electric and magnetic fields and were able to resolve an anisotropy in the spin-orbit contribution to the Stark shift arising from valley repopulation effects. From these data, we extract coherence times for P donors in silicon due to gate-induced electric-field noise and discuss techniques for mitigating this noise. Also based on these data, we find that addressing $^{31}$P donor spins through electric field tuning may not be viable.

We then explored a new approach to addressing spin qubits in silicon based on electrically driving nuclear spin transitions. Using Davies ENDOR, we demonstrated the ability to drive nuclear spins in $^{75}$As and $^{31}$P at both their resonance frequency, and the first subharmonic of that resonance frequency. Additionally we showed that double quantum transitions can be driven for $^{75}$As. We measured the nuclear Rabi frequencies as a function of electric field amplitude for both donors, and used these data to test different physical mechanisms that can be responsible for the electrically driven NMR. We find that the phosphorus donors are likely driven through electrical modulation of the spin-orbit Stark effect, which leads to an effective hyperfine anisotropy. This mechanism can not explain the data Rabi frequencies for $^{75}$As, which we attribute to modulation of the quadrupolar coupling.
8.3 Coherence of spins in germanium

In Ch. 6, we discussed the use of germanium as a substitute for silicon in donor-based quantum devices. We measured the coherence and spin-lattice relaxation times for donor spins in both natural and isotopically enriched germanium and found that spectral diffusion from $^{73}\text{Ge}$ limits the coherence in natural germanium. In isotopically enriched material, the spin lattice relaxation limits the coherence. The spin lattice relaxation is limited by two distinct mechanisms depending on temperature. An Orbach process sets the relaxation rate at higher temperature (above 3 K) and a single-phonon process dominates at lower temperatures. The maximum coherence time we measure is 1.2 ms at 350 mK for $^{31}\text{P}$ donors, but this is expected to be much longer at lower magnetic fields since the single-phonon relaxation rate scales as $B_0^4$.

8.4 Stark tunability of spins in germanium

Finally, in Ch. 7 we measured the Stark shift of spins in germanium. We found that compared with silicon, the spin-orbit Stark shift is the dominant effect and is four orders of magnitude larger. We measured the angular dependence of the Stark shift for both arsenic and phosphorus donors and found that at the largest fields applied, one can tune by at least four times the electron spin ensemble linewidth. This not only indicates that a Kane quantum computer could be implemented in germanium, it also suggests that the electrically driven NMR should be possible – and quite efficient – in germanium.
Appendix A

Microwave Bridge Parts List

See below for a list of parts used in the construction of the home-built Pulsed ESR spectrometer. The part numbers correspond to the schematic of Fig. A.1.

Figure A.1: Schematic of the pulsed microwave bridge discussed in Ch. 2 with labels corresponding to part numbers listed below.

Pulse Forming Unit:

P1: Microwave Source - Agilent E8267D PSG Vector Signal Generator (options: 005, 016, 1E1, 1EA, 520, 602, HEC, UNT, UNW, UNX)
P2: Auxiliary RF/Microwave Source - Agilent E8257D (options: 1E1, 1EA, 520, UNW, UNX)
P3: +16dB gain, 200W TWT Amplifier - M-Square model M303
P4: Microwave Switch - Hittite HMC347LP3
P5: Butterworth Low Pass Filter - Crystek CLPFL
P6: -20dB Directional Coupler connected to Agilent HCC loop - Narda 4016C-20
P7: Microwave Isolator

Bridge:
B1: Variable Phase Shifter - Arra 1269
B2: Variable Attenuator - Arra 6843-20
B3: DC Blocks - Mini-Circuits BLK-18+ and Fairview SD3258
B4: Low Noise Power Amplifier - Narda NES-0910N530-61
B5: SPST PIN Diode - Daico DSW16186
B6: Low Noise Amplifier - Miteq AFS3-08001200 14-ULN
B7: Mixer - Miteq IRM0812HC
B8: Variable Gain Video Amplifier (with 20 MHz low pass filter) - Femto DHPVA-200
B9: Digitizer Card - AlazarTech ATS9626

Not shown in schematic:
PC equipped with pattern generator (PulseBlaster PB24-100-32K)
Rubidium frequency standard - Stanford Research Systems FS725
Magnetic field controller - Bruker ER032M
Appendix B

CPW Design and Simulation

B.1 Effective Dielectric Constant and Impedance of a CPW on an Infinitely Thick Dielectric

To accurately determine the CPW impedance, we must know the dielectric constant experienced by the fields in the device. However, CPWs are typically fabricated on the surface of a dielectric substrate with electric fields extending both into the substrate and into free space. The dielectric constant in this case is not simply the dielectric constant of the substrate $\epsilon_r$, but some effective dielectric constant $\epsilon_{eff}$, which can be calculated using \[\text{(113)}\]. Assuming an infinitely thick dielectric substrate (a reasonable approximation in this work since the CPW features are small compared to the thickness of our typical wafers):

$$\epsilon_{eff} = \frac{\epsilon_r + 1}{2}$$  \hspace{1cm} (B.1)

where $\epsilon_r$ is the relative dielectric constant of the substrate. The impedance of the CPW ($Z_0$) is then simply:
\[ Z_0 = \frac{30\pi}{\sqrt{\varepsilon_r + 1}} K(k_0') \frac{K(k_0')}{2 K(k_0)} \] (B.2)

where \( K \) denotes an elliptic integral of the first kind and \( k_0' \) and \( k_0 \) are given by

\[ k_0 = \frac{S}{S + 2W} \] (B.3)

and

\[ k_0' = \sqrt{1 - k_0^2} \] (B.4)

where \( S \) is the center pin width and \( W \) is the gap width. Of course these expressions only hold for a CPW in air and on an infinitely thick dielectric substrate. Analytical solutions for the impedance of a CPW subject to many dielectric layers or near additional metal layers are available in [113].

**B.2 Photonic Band Gap Resonator Simulation and Design**

**B.2.1 ABCD Matrix Simulations**

The photonic bandgap (PBG) resonators are made up of a series of transmission lines having variable impedance. They can be designed using a transfer matrix (also known as ABCD matrix) technique as described by Pozar [95].

In the transfer matrix formalism, each segment of the PBG resonator’s transmission line is represented by its own 2×2 ABCD matrix. The whole device’s ABCD matrix is then constructed by taking the product of all of the individual ABCD matrices while maintaining their order. The ABCD matrix for a coplanar transmission line of length, \( L \), and characteristic impedance, \( Z_C \) is [95].
\[
\begin{pmatrix}
A & B \\
C & D
\end{pmatrix} =
\begin{pmatrix}
\cosh (\Gamma L) & Z_C \sinh (\Gamma L) \\
\sinh (\Gamma L)/Z_C & \cosh (\Gamma L)
\end{pmatrix}
\] (B.5)

where \( \Gamma \) is given by

\[
\Gamma = \alpha + ik
\] (B.6)

with \( \alpha \) being the attenuation constant and \( k \) being the microwave propagation constant.

The device used in Ch. 5 only consists of three different transmission line geometries, labeled here as \( T_A, T_B, \) and \( T_C \). Lines \( T_A \) and \( T_B \) make up the Bragg mirrors and are 4.2 mm long. The designed characteristic impedance of \( T_A \) is 92 \( \Omega \) whereas \( T_B \) is 34 \( \Omega \). Transmission line \( T_C \) is the defect. It has a designed impedance of 50 \( \Omega \) and a length of 6 mm. The overall geometry of the device follows the pattern \((T_A - T_B) \times 5 - T_C - (T_B - T_A) \times 5\). After computing the ABCD matrix for this device, we convert it into the more standard S-parameter matrix using the conversion [95]:

\[
\begin{pmatrix}
S_{11} & S_{12} \\
S_{21} & S_{22}
\end{pmatrix} =
\begin{pmatrix}
\frac{A+B/Z_C-CZ_0-D}{A+B/Z_C+CZ_C+D} & \frac{2(AD-BC)}{A+B/Z_C+CZ_C+D} \\
\frac{2}{A+B/Z_C+CZ_C+D} & \frac{-A+B/Z_C-CZ_0+D}{A+B/Z_C+CZ_C+D}
\end{pmatrix}
\] (B.7)

Comparing the simulated PBG resonator to the measured one, we find reasonable agreement as shown in Fig. [B.1]. The error in the simulation arises primarily from uncertainty in the position of the sample relative to the coplanar waveguide. The simulation assumes no gap between the sample and the waveguide, but even micron-scale gaps would serve to increase the resonance frequency of the device.
Figure B.1: Plot of transmitted microwave power through a device at 2 K in a magnetic field of 250 mT. The data (red) is compared to the simulated values (black).

B.2.2 Design Considerations

There are several geometrical parameters that can be used to tune the resonator frequency, the resonator quality factor, the band gap depth, the band gap width and the band gap frequency. Qualitatively, these are outlined in Table B.1.
Table B.1: Outline of the qualitative change in the photonic bandgap resonator characteristics (columns) given an increase in some lithographically defined quantities (rows).

<table>
<thead>
<tr>
<th>Increase in</th>
<th>Changes the</th>
<th>Resonator Frequency</th>
<th>Resonator Q factor</th>
<th>Resonator Coupling</th>
<th>Bandgap Span</th>
<th>Bandgap Center Frequency</th>
<th>Bandgap Attenuation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of Defect ($T_C$)</td>
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<tr>
<td># Periods ($T_A$ and $T_B$)</td>
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<tr>
<td>Length of $T_A$ and $T_B$</td>
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</tr>
<tr>
<td>Impedance Step ($Z_{T_A}/Z_{T_B}$)</td>
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<td>↑</td>
<td>↓</td>
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</table>
Appendix C

EDNMR Data and Simulation Details

C.1 Davies ENDOR of $^{31}$P Donors

Davies ENDOR experiments were performed on $^{31}$P donors in silicon using both magnetic and electrical RF fields. The spectra are plotted in Fig. C.1. We only plot the ENDOR spectra for the $+1/2$ hyperfine line since the results were very similar for the $-1/2$ hyperfine line. As shown in the figure, EDNMR could be performed at both the fundamental and subharmonic frequencies of the transitions. The slight variation in transition frequencies for the three experiments comes from slight variations in the ESR resonator frequency, since the experiments were conducted at slightly different magnetic fields. There is also a broadening observed for the lower frequency transition and the origin of this is currently unknown. This broadening also appears in the $-1/2$ hyperfine line. More experiments may be necessary to understand this lower frequency linewidth.
Figure C.1: Davies ENDOR spectra for the \(^{31}\)P donors. A conventional magnetically driven ENDOR spectrum is shown in (a) for the \(M_I = +1/2\) hyperfine line. The EDNMR spectrum is shown in (b) and nuclear spins can be driven at subharmonics of these transitions as shown in (c). These data were taken at 1.9 K in a field of 250 mT.

### C.2 Davies ENDOR Rabi Experiment Simulation

The Rabi-type ENDOR experiment involves both RF and microwave pulses. The ENDOR signal is measured as a decrease in the electron spin echo signal while varying the amplitude and duration of the RF pulses that are resonant with nuclear spin transitions. Because there are distributions in the electric and magnetic fields, it was necessary to develop a model to simulate and understand the results of the Rabi frequency measurements described in the main text.

The ESR signal from a single spin at position \(\vec{r}\) in a three pulse experiment \((\pi - T - \pi/2 - \tau - \pi - \tau - \text{echo})\) is given by [103, 75]

\[
signal(\vec{r}) = g_s(\vec{r}) \sin^5(\tau \gamma B_1(\vec{r})/\hbar)
\]  

(C.1)
where $g_s(\vec{r})$ is the coupling of a spin at position $\vec{r}$ to the resonator, $\tau_p$ is the duration of the second pulse (nominally a $\pi/2$ pulse) in the sequence, $\beta$ is the Bohr magneton, $B_1$ is the magnitude of the microwave magnetic field orthogonal to $\vec{B}_0$, and $\hbar$ is the reduced Planck constant. $g_s$ can be calculated, but is proportional to $B_1(\vec{r})$ so in simulations we simply assume $g_s = B_1(\vec{r})$ and normalize the signal intensity.

Assuming ideal microwave pulses, the Davies ENDOR response from a single donor is simply given by $\frac{1 - \cos(\theta_E(\vec{r}))}{2}$ with $\theta_E(\vec{r})$ being the tipping angle of the nuclear spin due to the RF pulse. This tipping angle is given by the product of the nuclear Rabi frequency ($\omega_R$) and the pulse length. The overall signal coming from the $i$th donor ($S_i$) is therefore

$$S_i = AB_1(\vec{r})\sin^5(\tau_p g \beta B_1(\vec{r})/\hbar)(1 - \cos(\theta_E(\vec{r}))) \quad (C.2)$$

where $A$ is a normalization constant that also accounts for microwave losses in the detection channel. The overall ENDOR response of the donor spin ensemble ($S_{total}$) is then simply

$$S_{total} = \sum S_i \quad (C.3)$$

where the sum is taken over the doped region of the sample taking into account the doping profile shown in Fig. 2 of the main text. The only unknown parameter in the above model is the nuclear Rabi frequency. The Rabi frequency depends on the specific mechanism responsible for the electrically or magnetically driven NMR, so our model should be able to test which physical mechanism is responsible for the observed EDNMR transitions. We therefore turn our attention to the various mechanisms that can be responsible.
C.3 Estimation of Rabi frequencies for different physical mechanisms

We identified three distinct effects that can lead to electrically driven nuclear magnetic resonance. The first arises from a modulation of the hyperfine interaction due to the hyperfine Stark effect, the second arises from the modulation of the electronic orbital states (which modulates the electron spin quantization axis), and finally, modulation of the nuclear quadrupole interaction.

As discussed in the main text, the subharmonic transitions should be more robust against strain compared to the fundamental transitions. We therefore focus the following discussion on the subharmonic transitions.

C.3.1 Hyperfine Stark Effect Modulation

The hyperfine Stark shift is a modulation of the hyperfine tensor due to an applied electric field. Two effects must be considered — modulation of isotropic and anisotropic hyperfine components. Modulation of the isotropic hyperfine interaction follows the form $\Delta A/A = \eta_A E^2$ where $\eta_A$ is the hyperfine Stark shift parameter reported in Refs. [12, 112, 90, 74]. The isotropic hyperfine interaction goes as $\hat{A} \cdot \hat{I}$ and there is at least a two order of magnitude difference between the precession frequency of $\hat{S}$ and $\hat{I}$. In the rotating frame $S_x \cdot I_x = S_y \cdot I_y = 0$ and the only nonzero term is $A_{ZZ} S_z \cdot I_z$. This remaining term can not drive nuclear spin transitions.

$\hat{A}$ is isotropic for donors in silicon, even in the presence of strain and electric fields. Measurements of highly strained silicon [48] resolve no anisotropy in the hyperfine coupling so we do not expect modulation of an anisotropic hyperfine coupling to be responsible for the spin flips.
C.3.2 Fluctuating Hyperfine Fields from $g$-Tensor Modulation of the Electronic Spin

One may be tempted to neglect modulation of the electronic spin-orbit interaction when considering electrically driven NMR since the spin-orbit interaction does not directly affect the nuclear spin. However, we show here that modulation of the electronic $g$-tensor in conjunction with an isotropic hyperfine interaction can lead to fluctuations in the hyperfine fields, which lead to nuclear spin flips.

In the absence of an externally applied electric field, the electronic $g$-tensor is isotropic and electron spins are quantized along the external magnetic field, $\vec{B}_0$ (Fig. C.2(a), top). The nuclei are likewise quantized along $\vec{B}_0$ (Fig. C.2(b), top). When the electron spin is subjected to an AC electric field, the spin-orbit Stark effect modulates the $g$-tensor, thus tilting the quantization axis of the electron spin (Fig. C.2(a), bottom) and by extension the hyperfine field of the electron (Fig. C.2(c), bottom). It is important to note that the RF modulation frequency is much slower than the electron Zeeman frequency and the electron is in the slow passage regime. The electron spin and its hyperfine field follow the change in the quantization axis direction. As the electron spin tilts, the nuclear spin sees a hyperfine field ($\vec{B}_{HF}$), which changes its direction (Fig. C.2(d), bottom) and has a component $\vec{B}_2$ perpendicular to the quantization axis of the nuclear spin. This component can excite nuclear spin transitions. Since the hyperfine interaction is large for donors in silicon, even small tilts in the electron spin can lead to a substantial $\vec{B}_2$ and rapid Rabi oscillations.

The Spin Hamiltonian

A more quantitative analysis follows from the general spin Hamiltonian of Eq. 1 in the main text.

$$H = \beta B_Z \cdot \tilde{g}(E, t) \cdot \vec{S} + \beta_n \cdot g_n \cdot B_Z \cdot I_Z + A_{iso} \cdot S_Z \cdot I_Z$$  \hspace{1cm} (C.4)
Figure C.2: Vector representation of the $g$-tensor modulation effect (a), which leads to a modulation of the hyperfine interaction (b). In the unperturbed case (top panels), the isotropic $g$-tensor ($g_{XX} = g_{YY} = g_{ZZ}$) results in the electronic spin quantizing along the direction of $\vec{B}_0$ (upwards). Likewise the nuclear spin is quantized along $\vec{B}_0$ and experiences an effective field due to the hyperfine interaction ($B_{HF}$) in that same direction. When an electric field is applied (lower panels) the $g$-tensor is made anisotropic ($g_{XX} \neq g_{YY}$) and the electronic spin is no longer quantized along $B_0$, but at some tilted angle. The hyperfine field seen by the nuclear spin is now also tilted resulting in a small effective $\vec{B}_2$ component orthogonal to $\vec{B}_0$. If the electric field modulation is done resonantly with the nuclear spin transition frequency, this can lead directly to spin flips.

After moving to a modulated $g$-tensor frame, where $g(E, t)$ is modulated by a resonant RF electric field, the Hamiltonian becomes

$$H = \nu_e S_{Z'} + \nu_n \cdot I_Z + A_{iso}(\cos(\delta(t)) \cdot S_{Z'} \cdot I_Z + \sin(\delta(t)) \cdot S_{Z'} \cdot I_X)$$

(C.5)

where $\nu_e$ and $\nu_n$ are the electronic and nuclear Zeeman frequencies, respectively, $Z'$ is the new electron quantization axis, and $\delta(t)$ is the time dependent tilting of the electron spin quantization axis. From this Hamiltonian, it is clear that if the $\delta(t)$ modulation is resonant with nuclear spin transitions, the $S_Z \cdot I_X$ term leads to nuclear Rabi oscillations. To determine the magnitude of $\delta$, we turn to the multi-valley effective mass theory of Wilson and Feher [132].
**g-tensor modulation from valley repopulation**

Silicon has six conduction band valleys oriented along the (100) crystallographic axes. Each valley is ellipsoidal with an axially symmetric g tensor given by

\[
\hat{g}_i = \begin{pmatrix} g_\perp & 0 & 0 \\ 0 & g_\perp & 0 \\ 0 & 0 & g_\| \end{pmatrix}
\]  

(C.6)

in the valley basis, with \(g_\perp\) and \(g_\|\) equal to the \(g\) factors perpendicular and parallel to the valley axis, respectively. The overall g-tensor can be obtained by summing over each individual valley g-tensor weighted by the wavefunction amplitude in that valley so that in the molecular frame

\[
\hat{g}_{\text{eff}} = \sum_{i=1}^{6} (\alpha_i)^2 R_\theta \hat{g}_i
\]  

(C.7)

where \(\hat{g}_{\text{eff}}\) is the overall g-tensor, \((\alpha_i)^2\) is the wavefunction amplitude in the \(i\)-th valley, and \(R_\theta\) is the set of rotation matrices that rotates \(g_i\) to be in the crystal frame.

In the absence of an electric field, the g-tensor is isotropic and given by

\[
g_{\text{eff}} = \begin{pmatrix} g_0 & 0 & 0 \\ 0 & g_0 & 0 \\ 0 & 0 & g_0 \end{pmatrix}
\]  

(C.8)

where \(g_0\) is 1.99875 (1.99837) for \(^{31}\text{P} \ (^{75}\text{As}) \) donors in silicon\(^{[132]}\). The quantization axis \(\vec{\Omega}\) of the electron spin is given by \(g_{\text{eff}} \cdot \vec{B}_0\) and for a (110) oriented magnetic field this becomes
\[ \vec{\Omega} = \beta \cdot \begin{pmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix} \cdot \begin{pmatrix} B_0/\sqrt{2} \\ B_0/\sqrt{2} \\ 0 \end{pmatrix} \]  \hspace{1cm} (C.9)

where \( \beta \) is the Bohr magneton. Now, if we assume an electric field perturbation in the \( \langle 001 \rangle \) direction, we can use the values for the valley populations derived by Wilson and Feher [132], which gives

\[ (\alpha_A)^2 = \frac{1}{4}[1 - (x + 2/3)(x^2 + 4/3x + 4)^{-1/2}] \]  \hspace{1cm} (C.10)

\[ (\alpha_B)^2 = \frac{1}{8}[1 + (x + 2/3)(x^2 + 4/3x + 4)^{-1/2}] \]  \hspace{1cm} (C.11)

where \((\alpha_A)^2\) and \((\alpha_B)^2\) are the wavefunction amplitudes for valleys along and orthogonal to the perturbing field, respectively and \(x\) is the dimensionless “valley-strain” parameter, which can be obtained by comparing Wilson and Feher’s stress measurements with the electric field Stark shift measurements of [112] to find that \(x = 0.203 \times E\) for \(^{31}\text{P}\) donors where E is in units of \(V/\mu m\).

Given an electric field perturbation along \(\langle 001 \rangle\), the \(g\)-tensor becomes

\[ \hat{g}_{\text{pert}} = \begin{pmatrix} g_0 + \delta & 0 & 0 \\ 0 & g_0 + \delta & 0 \\ 0 & 0 & g_0 - 2\delta \end{pmatrix} \]  \hspace{1cm} (C.12)

where \(\delta = 2.5 \times 10^{-6}\) for a field of 0.1\(V/\mu m\) and the precession axis of the electron spin becomes \(\hat{g}_{\text{pert}} \cdot \vec{B}_0\). This corresponds to a quantization axis tilt of \(1.9 \times 10^{-6}\) radians. Because the valley populations have a quadratic component, \(\delta\) oscillates at twice the RF electric field frequency.
Effect of $\delta$ on the hyperfine tensor

A non-zero $\delta(t)$ leads to an $S_Z \cdot I_X$ term in the spin Hamiltonian as seen from Eq. 8. For completeness, we show here the full change to the hyperfine tensor given by a tilt in the quantization axis;

$$H_{HF} = \begin{pmatrix} S_x & S_y & S_z \end{pmatrix} \begin{pmatrix} \cos \delta(t) & 0 & -\sin \delta(t) \\ 0 & 1 & 0 \\ \sin \delta(t) & 0 & \cos \delta(t) \end{pmatrix} \begin{pmatrix} a_{iso} & 0 & 0 \\ 0 & a_{iso} & 0 \\ 0 & 0 & a_{iso} \end{pmatrix} \begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix}$$ (C.13)

where the term that leads to EDNMR is the off-diagonal $A_{ZX}$ term. With the example field of 0.1 V/$\mu$m for $^{31}$P donors, the $A_{ZX}$ term becomes 330 Hz, which is comparable to the values measured in experiment as illustrated in Fig. 4 of the main text.

When repeating this analysis for the $^{75}$As donors, theory predicts that the two donors should have comparable Rabi frequencies since $A_{iso}$ and $\eta_g$ are similar in both $^{75}$As and $^{31}$P. This contradicts our experimental observation of a $40 \times$ enhancement in the arsenic Rabi frequencies as shown in Fig[C.3]. Given this discrepancy, we expect that a different mechanism is responsible for electrically driving the arsenic nuclei.

Additional effects

In addition to valley repopulation, there is a “single valley” Stark effect that is comparable in magnitude to the valley repopulation effect. The relative contributions of single-valley and valley repopulation effects to the $g$-tensor modulation varies depending on the direction of the RF fields in the sample, but given our geometry we expect the valley repopulation effect to be dominant. The spins probed in this experiment are subject to electric fields that are primarily oriented along a (100) equivalent direction. If the single valley effect was also taken into account, we would expect the Rabi
C.3.3 Modulation of the Quadrupolar Interaction

Phosphorus donors have $I = 1/2$ and do not have a nuclear quadrupole moment, so this mechanism only applies to the $^{75}\text{As}$ donors ($I = 3/2$). There is nearly a two order of magnitude difference in the Rabi frequencies for $^{31}\text{P}$ vs $^{75}\text{As}$ donors and the quadrupole interaction in the only term in the spin Hamiltonian affecting $^{75}\text{As}$ and not $^{31}\text{P}$. It is reasonable to expect that quadrupolar effects are enhancing the $^{75}\text{As}$ nuclear spins’ response to electric fields.

The quadrupolar coupling vanishes in the absence of strain or electric fields due to the cubic symmetry of the donor site. By applying RF electric fields, we are able to induce a field gradient at the nucleus, which leads to a nonzero quadrupole coupling. More rigorous theory including knowledge of the electronic wavefunction at the nu-
cleus will need to be developed to accurately determine how strongly electric fields can affect the quadrupole term, but we can make a crude approximation based on some recent experimental data. The experiments [37] measured the strain modulation of the quadrupole interaction on neutral $^{75}\text{As}$ doped Si. The data report a quadrupolar shift of 65 kHz with a simultaneous hyperfine modulation of 1%. Based on the Stark effect measurements of [90], we can infer from the hyperfine shift an effective electric field due to strain of $\sim 3\ V/\mu\text{m}$. From this we can estimate the quadrupolar coupling induced in our experiments.

**Driving transitions through modulation of $Q_{XX}$**

Quadrupolar coupling can lead to spin flips through direct modulation of the $Q_{XX}$ component of the quadrupolar coupling. The quadrupolar term in the spin Hamiltonian can be written

$$H_{NQI} = Q_{XX}(t) \cdot I_X \cdot I_X + Q_{ZZ}(t) \cdot I_Z \cdot I_Z$$  \hspace{1cm} (C.14)

where the $I_X \cdot I_X$ term leads to double quantum transitions and explains the data seen in Fig. 3(b) of the main text. This however does not directly lead to single-quantum transitions.

To drive single quantum transitions, it is necessary to have a nonzero $Q_{XZ}$ term. These can arise from misalignment of $\vec{E}_2$ such that there is some component of the RF electric field along the magnetic field or it can arise from additional internal strain fields.

If we plug the scaled values of $Q_{XX}$ into our two dimensional Rabi frequency simulation, we find an enhancement of the Rabi frequencies by a factor of 10 and reasonable agreement with data to within a factor of 4 as shown in the main text. Based on this estimate, it seems reasonable that we are driving the $^{75}\text{As}$ donors through modulation of the quadrupolar interaction.
C.4 Rabi experiments on the fundamental transitions

Strains perturb the donor spin system in a similar way to electric fields such that strain and electric fields can be superimposed. This has the effect of generating linear terms in the electric field response of the donor [12, 90]. For this reason, the linear response is complicated and depends on the magnitude and relative orientations of strain and electric fields in our device. We therefore focused our discussion on the subharmonic transitions that are not affected by strain to first order. However, experiments were also conducted at the fundamental frequencies for EDNMR transitions.

Two dimensional Rabi nutation experiments for both the $^{75}$As and $^{31}$P donors are shown in Fig. C.4. Stark effect measurements on the same material (prior to implanting the $^{75}$As and $^{209}$Bi donors) showed a large amount of strain, presumably due to the difference in the lattice mismatch between natural and isotopically enriched silicon [112]. From those measurements, we expect an internal electric field that is randomly distributed in direction and magnitude with the average magnitude being of order $1\text{V}/\mu\text{m}$.

For both $^{31}$P and $^{75}$As, we see a substantial improvement in the Rabi frequencies when driving the transitions at their fundamental frequencies as shown in Fig. C.4. The transitions probed in this experiment are the $|m_I, m_s\rangle = | + 1/2, +1/2 \rangle \iff | + 3/2, +1/2 \rangle$ for $^{75}$As and $| + 1/2, +1/2 \rangle \iff | - 1/2, +1/2 \rangle$ for $^{31}$P.

To fit the experiment to data, we simply assume some proportionality constant ($\gamma_E$) between the electric field applied ($E$) and the nuclear Rabi frequency($\omega_R$) so that

$$\omega_R = \gamma_E E.$$ (C.15)

We can then quantify the Rabi frequency for the fundamental transitions in our samples and find $\gamma_E = 2\pi \cdot 270 \text{ kHz} \cdot \mu\text{m/V}$ for arsenic and $2\pi \cdot 60 \text{ kHz} \cdot \mu\text{m/V}$ for
Figure C.4: Two dimensional Rabi experiment for $^{75}\text{As}$ (a) and $^{31}\text{P}$ (c) measured at fundamental frequencies. The simulated fits to the data are shown in (b) and (d). The $^{75}$ Data were taken at 1.9 K in a field of 250 mT.

phosphorus. Since these values are strain dependent, we should be able to enhance them by applying more strain.
Appendix D

Linear Stark Shift in Ge

Figure D.1: Plot of the Stark shift for $^{31}$P donors in isotopically enriched $^{70}$Ge (sample 3) at 1.8 K with the electric and magnetic fields both aligned along (100). Data were taken using unipolar electric field pulses 10 $\mu$s long as opposed to the bipolar electric field pulses used in the main text. The Stark shift still remains quadratic to 480 V/cm imposing a lower bound on the ionization field for this sample. Larger fields were not applied due to limitations in the pulse generator.
Appendix E

Cleanroom Recipes

E.1 RCA Clean

1. Solvent clean
   - Trichloroethylene
   - Acetone
   - Isopropanol
2. SC-1 (DI:NH$_4$OH:H$_2$O$_2$ in a 5:1:1 ratio)
   - heat deionized water to 80°C
   - when hot slowly mix in NH$_4$OH and H$_2$O$_2$
   - put sample in for 10 minutes then place in a DI water bath.
3. HF dip
4. SC-2 (H$_2$O:HCl:H$_2$O$_2$ in a 6:1:1 ratio)
   - at 80°C for 10 minutes
5. HF dip and N$_2$ dry.

E.2 Germanium Clean

1. Solvent clean
- Trichloroethylene
- Acetone
- Isopropanol

2. CP-4 etch (HF:HNO$_3$:acetic acid in a 3:5:3 ratio)

3. H$_2$O:H$_2$O$_2$ in a 1:1 ratio)

4. HF dip and N$_2$ dry.

### E.3 ALD Growth of Al$_2$O$_3$

#### E.3.1 Growth on Nb or Ge

In the Cambridge NanoTech Savannah 100 set both inner and outer reaction chamber heaters to 150°C and flow set to 20 SCCM.

Deposit 5 cycles of water using the following recipe

<table>
<thead>
<tr>
<th>Table E.1: Predeposit</th>
<th>Valve</th>
<th>Pulse (s)</th>
<th>Expose (s)</th>
<th>Pump</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>15</td>
</tr>
</tbody>
</table>

Followed by $N$ cycles of

<table>
<thead>
<tr>
<th>Table E.2: Oxide Growth</th>
<th>Valve</th>
<th>Pulse (s)</th>
<th>Expose (s)</th>
<th>Pump</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.1</td>
<td>0</td>
<td>15</td>
</tr>
</tbody>
</table>

where $N$ cycles of ALD grows approximately $N$ angstroms of Al$_2$O$_3$

#### E.3.2 Growth on Si

Set both inner and outer reaction chamber heaters to 250°C and flow set to 20 SCCM. Deposit 5 cycles of water using the following recipe
### Table E.3: Predeposit

<table>
<thead>
<tr>
<th>Valve</th>
<th>Pulse (s)</th>
<th>Expose (s)</th>
<th>Pump</th>
</tr>
</thead>
<tbody>
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<td>0</td>
<td>0.01</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>0</td>
<td>0.01</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>

Followed by 10 cycles of

### Table E.4: Slow Oxide Growth

<table>
<thead>
<tr>
<th>Valve</th>
<th>Pulse (s)</th>
<th>Expose (s)</th>
<th>Pump</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>1</td>
<td>7</td>
</tr>
</tbody>
</table>

Then fast growth

### Table E.5: Fast Oxide Growth

<table>
<thead>
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<th>Valve</th>
<th>Pulse (s)</th>
<th>Expose (s)</th>
<th>Pump</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.01</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>0.01</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>

### E.4 Polishing Germanium Wafers

1. Planarize germanium wafer by course lapping using 10 μm grit Al₂O₃.
2. Switch to 10 μm Cerium oxide slurry combined with Logitech SF-1 polishing fluid with 1000g of force applied to the wafer. The SF-1 breaks down the Cerium oxide leading to a finer grit slurry.
3. After removing ~15 μm of Ge, remove Cerium oxide and just use undiluted H₂O₂ mixed with SF-1 to polish.
4. Finally dip wafer in 1:1 H₂O₂:H₂O to chemically polish.

### E.5 Nb Etch

In the STS ICP plasma etcher
Table E.6: STS Etch recipe for 50 nm Nb

<table>
<thead>
<tr>
<th>Step</th>
<th>Chemistry</th>
<th>Flow Rate</th>
<th>Coil Power</th>
<th>Platen Power</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O₂</td>
<td>5 SCCM</td>
<td>700 W</td>
<td>0 W</td>
<td>10 s</td>
</tr>
<tr>
<td>2</td>
<td>SF₆:O₂ (10:1)</td>
<td>50 SCCM</td>
<td>100 W</td>
<td>50 W</td>
<td>50 s</td>
</tr>
</tbody>
</table>

The SF₆ plasma reacts with photoresist to form a film that is not removed by standard solvent cleans. We therefore etch the photoresist in an O₂ plasma generated in the Tepla M4L (standard Strip05 recipe) before removing any photoresist mask using solvents.
Bibliography


