Quantum information with NV− centers in diamond

Dissertation zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften (Dr.rer.nat)

vorgelegt von Shkolnykov, Vladyslav

an der Universität Konstanz

Mathematisch-Naturwissenschaftliche Sektion
Fachbereich Physik

Konstanz, 2019
Tag der mündlichen Prüfung: 19.12.2019
1. Referent: Prof. Dr. Guido Burkard
2. Referent: Prof. Dr. Wolfgang Belzig
Abstract

The development of quantum information in the last decades has opened new horizons in science and technology. It turns out that quantum physics, apart from playing a fundamental role in the structure of matter, also opens new opportunities for computation and communication, if one can harness the quantum superposition and entanglement. This started a new scientific challenge to find the platform that can offer two well isolated discrete levels (a qubit), that are a standard building block for many quantum devices, like bits are those for a classical computer. In this thesis we focus on one such platform, the negatively charged nitrogen-vacancy (NV$^{-}$) center in diamond. It uses the triplet states of two fermionic spin-$1/2$ particles (holes) to encode the information.

In order to build a working device, be it a quantum computer or a communication hardware, one needs to have a very good control over the quantum system. Usually, the NV$^{-}$ centers are controlled with the microwave magnetic field of an antenna, that is placed in the vicinity of the NV$^{-}$. One of the issues we address in this thesis is whether we can replace the magnetic field with electric field or strain to control the system. We derive the corresponding coupling Hamiltonian and discuss the schemes to measure its parameters. Another approach we are investigating to simplify the control of an NV$^{-}$ based device is replacing the antenna magnetic field with spin-waves, that couple to the NV$^{-}$ centers. We show that for a magnetic material with low damping, the spin waves can propagate over very long distances with no dissipation and can provide the control of NV$^{-}$ centers even if the microwave antenna is far away and can not reach the center. We develop the theoretical formalism that allows to calculate the coupling enhancement, offered with this approach with respect to a pure antenna driving.

Another essential ingredient of a quantum device is the ability to generate state superpositions and entanglement between different qubits. This is done by means of quantum gates, that must be performed with extremely high fidelity in order for the system to work. We investigate the possibility to perform geometric quantum gates, that are tolerant to certain types of errors, on the spin of NV$^{-}$ centers in diamond. We are interested in both adiabatic and non-adiabatic geometric quantum computation. Inspired by a recent observation of Berry phase with NV$^{-}$ centers, we develop an effective Hamiltonian description of adiabatic geometric gates, alternative to conventional Berry connection approach. For non-adiabatic geometric gates, we analyze the fidelities and error channels, when the gates are performed optically through the orbital excited state of the NV$^{-}$ centers. We also develop a scheme to apply all-microwave universal non-adiabatic geometric gates on small registers of coupled NV$^{-}$ and nuclear spins. Finally, we develop an entanglement protocol, that generates a universal two-qubit gate on two NV$^{-}$ centers, coupled to a common mode of a high Q cavity. We show that it is possible to implement this gate fast and at a fidelity, that is high enough to apply error-correction protocols.
Zusammenfassung

Die Entwicklung der Quanteninformation in den letzten Jahrzehnten hat Wissenschaft und Technologie neue Horizonte eröffnet. Es zeigt sich, dass die Quantenphysik nicht nur eine grundlegende Rolle für die Struktur der Materie spielt, sondern auch neue Möglichkeiten für Informationsverarbeitung und Kommunikation eröffnet, wenn es gelingt die Quantensuperposition und Quantenverschränkung zu nutzen. Damit ergab sich die neue wissenschaftliche Herausforderung, eine Plattform zu finden, die zwei gut isolierte diskrete Zustände (ein Qubit) bietet, welche wie Bits für einen klassischen Computer ein Standardbaustein für viele Quantengeräte sind. In dieser Arbeit konzentrieren wir uns auf eine solche Plattform, das negativ geladene Stickstoff-Fehlstellen-Zentrum (NV\textsuperscript{−}) in Diamant. Dabei nutzt man die Triplettzustände von zwei fermionischen Spin-1/2-Partikeln (Löchern), um die Informationen zu kodieren.

Um ein funktionierendes Gerät zu bauen, sei es ein Quantencomputer oder Kommunikationshardware, muss man eine sehr gute Kontrolle über das Quantensystem haben. Normalerweise werden die NV\textsuperscript{−}-Zentren mit dem Mikrowellenmagnetfeld einer Antenne gesteuert, die sich in der Nähe der NV\textsuperscript{−} befindet. Eine der Fragen, die wir in dieser Dissertation behandeln, ist, ob das Magnetfeld durch ein elektrisches Feld oder eine mechanische Belastung ersetzt werden kann, um das System zu kontrollieren. Wir leiten den entsprechenden Kopplungs-Hamilton-Operator ab und diskutieren die Methoden zur Messung seiner Parameter. Ein anderer Ansatz, den wir untersuchen, um die Steuerung eines NV-basierten Geräts zu vereinfachen, besteht darin, das Antennenmagnetfeld durch Spinwellen zu ersetzen, die mit den NV-Zentren gekoppelt sind. Wir zeigen, dass sich die Spinwellen in magnetischem Material mit geringer Dämpfung ohne Verlust über sehr lange Strecken ausbreiten können und die Steuerung von NV\textsuperscript{−}-Zentren ermöglicht werden kann, selbst wenn die Mikrowellenantenne weit entfernt ist und das Zentrum nicht erreichen kann. Wir entwickeln den theoretischen Formalismus, mit dem die Kopplungsverbesserung berechnet werden kann, die mit diesem Ansatz bezüglich einer reinen Antennenansteuerung erreicht wird.

Zwei-Qubit-Gatter für zwei NV$^-$-Zentren erzeugt, die an dieselbe Mode eines Resonators mit hoher Güteklasse (Q) koppeln. Wir zeigen, dass es möglich ist, dieses Gatter schnell und mit einer ausreichend hohen Genauigkeit zu implementieren, um Fehlerkorrekturprotokolle anzuwenden.
Acknowledgments

First of all, I would like to thank my supervisor Prof. Dr. Guido Burkard for his ongoing support and for all the work we have done and published together. I really enjoyed our discussions and learned a lot from them. I want to thank my collaborators, Brian Zhou, Paul Jerger, Joseph Paul Heremans, David Awschalom, Péter Udvarhelyi, Adam Gali, András Pályi and Clara Mühlherr, with who we completed interesting projects together. Especially I would like to thank Brian Zhou and Paul Jerger for an interesting theory-experiment collaboration.

I want to thank all my current and former colleagues, Alessandro David, Jonas Mielke, Matthew Brooks, Maximilian Russ, Monica Benito Gonzáles, Florian Ginzel, Philipp Mutter, Benjamin D’Anjou, Thiago Lucena de Macedo Guedes, Matthias Kizmann, Amin Hoseinkhani, Csaba Péterfalvi, Marco Rančic, Andrey Moskalenko, and Andor Kormányos for helpful discussions and your support during my PhD. You made these four years very pleasant for me, thank you. Especially, I want to thank Jonas Mielke for his help during the preparation of this thesis.

I want to thank my school teacher, Dolgih Inna Afanasievna. It was her who first introduced me to Physics and showed me the interesting problems it studies. Last but not least I want to thank my family for always supporting me in everything I do. Especially, I want to thank my wife, Anna Prozhyzhko, for her care and patience during the preparation of this thesis.
## Abbreviations

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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Qubit</td>
<td>quantum bit</td>
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<tr>
<td>NV</td>
<td>nitrogen-vacancy</td>
</tr>
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<td>NV−</td>
<td>negatively charged nitrogen-vacancy</td>
</tr>
<tr>
<td>ZPL</td>
<td>zero-phonon line</td>
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<tr>
<td>ODMR</td>
<td>optically detected magnetic resonance</td>
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<tr>
<td>EPR</td>
<td>electronic paramagnetic resonance</td>
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<tr>
<td>I</td>
<td>identity</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
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<td>QI</td>
<td>quantum information</td>
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<tr>
<td>ES</td>
<td>excited state</td>
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<tr>
<td>GS</td>
<td>ground state</td>
</tr>
<tr>
<td>$H$-gate</td>
<td>Hadamard-gate</td>
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<tr>
<td>$\Phi$-gate</td>
<td>phase-gate</td>
</tr>
<tr>
<td>CNOT-gate</td>
<td>controlled-NOT gate</td>
</tr>
<tr>
<td>CPHASE-gate</td>
<td>controlled-PHASE gate</td>
</tr>
<tr>
<td>YIG</td>
<td>yttrium iron garnet</td>
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<tr>
<td>PDMS</td>
<td>polydimethylsiloxane</td>
</tr>
<tr>
<td>GGG</td>
<td>gadolinium gallium garnet</td>
</tr>
<tr>
<td>MSL</td>
<td>microstripline</td>
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<tr>
<td>SW</td>
<td>Schrieffer-Wolff</td>
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Chapter 1

Introduction

1.1 Overview and thesis structure

The nitrogen-vacancy (NV) color center in diamond is a point defect in the diamond crystal structure, where one carbon atom is replaced by nitrogen and the adjacent carbon is missing (see Fig. 1.1). The center can occur in negative (NV\(^-\)) or zero (NV\(^0\)) charge states, but the most frequently it is NV\(^-\), where one extra electron hopes into the defect site. NV\(^-\) center shows a broad fluorescence with zero-phonon line (ZPL) at 637 nm \([1, 2]\) lying in the optical domain, while its ground state is a spin triplet (\(S = 1\)) even at room temperature \([3-6]\). Below we will show that using the technique of optically detected magnetic resonance (ODMR), the electron spin of an NV\(^-\) center can be efficiently initialized and read out at the single defect level \([7]\). The ground state spin of NV\(^-\) center can be coherently manipulated using microwave field \([8]\). The spin state is robust against
decoherence effects even at room temperature as the electron spin coherence time $T_2$ can reach hundreds of microseconds in naturally abundant diamond \[9\] and milliseconds in isotopically enriched diamond \[10\]. This is why NV$^-$ centers are a good platform for the experimental realization of many quantum information protocols \[11\]. Entanglement between distant NV$^-$ center based nodes has successfully been generated \[12\]-\[15\], which is a crucial point for successful quantum communication. The application of NV centers in quantum sensing has now reached industrial level and involves a lot of work in many scientific groups \[10\]-\[25\]. Universal quantum computation with NVs is the most challenging issue, as it is not easy to scale the system up. One of the strategies to overcome this problem is to use an NV$^-$ center to control $^{13}$C isotopes, that are always present in natural diamond (1.1% of all carbon atoms) and are hyperfine coupled to the NV$^-$ center. The sizes of these registers can thus be quite big and universal quantum computing can readily be performed with these registers. Work done with such registers can be qualitatively separated in two categories. The first one deals with those nuclear spins that are relatively close to the NV$^-$ center \[23\]-\[31\], while the second one aims to control the nuclear spins that are quite far from the NV$^-$ center and thus couple very weakly to the electron spin of an NV$^-$ center \[32\]-\[35\]. The nuclear spins have extremely long coherence times and such a hybrid approach to quantum computation allows to use them as a quantum memory, while storage and read out are done through the electron spin of an NV$^-$ center.

In this thesis we develop and analyze the schemes that tackle the challenges in using the NV$^-$ centers for quantum information purposes. The basic issues we are interested in are control of individual NV$^-$ centers, universal quantum computation with NV$^-$ centers, the perspective to perform geometric gates with the NV$^-$ center based registers. The rest of this chapter will be devoted to introducing the basic concepts of quantum information and geometric quantum computation and giving a short introduction to the physics of NV$^-$ centers. In a separate section we consider the technique of optically detected magnetic resonance, which merges quantum information and NV$^-$ centers together.

The chapter 2 is a revised version of \[36\] and deals with spin-strain interaction in NV$^-$ centers. Its aim is to fill the gap that has long existed in the literature on this topic, constructing all the spin-strain coupling Hamiltonians from first principles and designing the experiments that should allow to measure all the unknown coupling parameters. This paves the way towards efficient control of NV$^-$ centers using strain, as well as increases its potential to be used as strain sensors.

The chapter 3 is a revised version of \[37\] and deals with yet another problem, efficient addressability of NV$^-$ centers. By now the control of the spin of NV$^-$ centers is performed through application of microwave pulses using microwave antennas. The further away form the antenna the NV$^-$ is, the less efficient is the coupling. Motivated by the recent experiment \[38\], we theoretically develop a model describing the coupling of spin waves in YIG to the NV$^-$ centers. Low damping of spin waves in YIG allows long range coupling of an antenna to a NV$^-$.

The chapter 4 is a revised version of \[39\]. Here we consider the perspective to scale the NV$^-$ center based quantum platform up by putting the NVs in a cavity. We develop the protocol to perform adiabatic optical two-qubit gate with this system, that together with the single-qubit operations forms a universal set of two-qubit gates. This potentially allows to use NV$^-$ centers for universal quantum computation.

The chapter 5 is a revised version of \[40\]. In this section we develop a new method to calculate the adiabatic geometric phase, alternative to non-Abelian Berry connection. We apply our method to generalized Lambda-systems and present the cases when our method works more efficiently.

The chapter 6 is a revised version of \[41, 42\]. In this work we first show how optical geometric gates can be implemented on NV$^-$ centers. We analyze the main decoherence
sources and calculate the corresponding gate fidelities. We then develop a scheme to perform all-microwave fast geometric universal quantum computing using registers of coupled NV centers and nuclear spins.

1.2 NV$^{-}$ structure and symmetry, group theoretical perspective

1.2.1 Groups and representations

In this section we review the physics of NV$^{-}$ center, necessary to understand the rest of the thesis. The NV$^{-}$ center is a highly symmetric object, this manifests itself in the invariance of the defect structure with respect to certain euclidean operations. For example, rotations by 120° around the axis, connecting the nitrogen and vacancy, will transform the defect into itself (Fig. 1.1). The description of such objects, in particular identification of their energy levels and interactions with external field becomes simpler if one uses the formalism of group theory [43]. We will first review the basic concepts of this powerful mathematical apparatus and then apply them to the NV$^{-}$ center in diamond.

Definition 1. Consider a set of elements $S = \{A, B, C, \ldots\}$, such that an operation ($\cdot$) on the set is defined, which associates a third element to any ordered pair of elements. This set is called the group, if

1. The product of any two elements is in the set (for any $A, B \in S$, $A \cdot B \in S$) (the set is closed under group operation)
2. The associative law holds, i.e. for any $A, B, C \in S$, $A \cdot (B \cdot C) = (A \cdot B) \cdot C$
3. There is a unit element $I$, such that $I \cdot A = A \cdot I = A$
4. Each element $A$ in the group has an inverse $A^{-1}$, such that $A \cdot A^{-1} = A^{-1} \cdot A = I$

We will restrict our attention to finite groups, for which the number of group elements $N$ is a finite number. In the following we will skip writing $\cdot$ and just write $AB$ instead of $A \cdot B$. The simplest groups can be constructed with usual numbers. For example $\{-1,1\}$ form a finite group under the operation of number multiplication. Here each element is its own inverse. Another example of a finite group would be the numbers $\{0,1,2,\ldots,k-1\}$ under the operation of addition modulo $k$. Both these groups are the so called Abelian groups, meaning $AB = BA$. This must not generally be true, as will be clear in our next example.

We will now consider a very important example of the $C_{3v}$ point group. Let us start with the figure 1.2 (a) and ask the question, what is the set of operations (rotations, inversion, reflections), that leaves this structure invariant (meaning that after the transformation the structure will transform into itself). Obviously, rotation by 0 degrees will not change the structure (the identity transformation), as well as rotations by $\pm120^\circ$ around the z-axis in Fig. 1.2 (b), shown with cyan arrows. Obviously, these are not all such operations, as we may also reflect the structure in planes $\sigma_1$, $\sigma_2$, $\sigma_3$ (Fig. 1.2 (b)), which will yield the same structure as well. From simple geometrical considerations it is obvious that no other transformation, other than these 6 exists, that would leave the structure invariant. Now let us introduce the product of two transformations $A$ and $B$, as a transformation $C = B \cdot A$ that occurs when two transformations are performed in series, first $A$ and then $B$. Let us now return to the six transformations we have identified. If we perform any two of them in series, the result will obviously not change the structure in Fig. 1.2 (a) because it is the product of two operations that do not change it. But that means this product must by itself coincide with one of the six transformation, as there
Figure 1.2: (a) A structure that is invariant under the operations of the point group $C_{3v}$. (b) This figure depicts the operations of the point group $C_{3v}$. Rotations by 120 degrees in both directions around the z-axis, as well as reflections in planes $\sigma_1$, $\sigma_2$, $\sigma_3$ leave the structure in figure (a) invariant. Together with identity transformation the six elements form a group. The operation in the group, that gives a result to any ordered pair of elements, now corresponds to performing transformations one after the other with result being the resulting transformation.

are no other euclidean transformations that leave Fig. 1.2 (a) invariant. We can thus conclude, that the six operations we have identified (identity $I$, rotations by $120^\circ$, that we name $(R_\pm)$ and three reflections named $\sigma_1$, $\sigma_2$, $\sigma_3$) form a group under the operation of product on group elements, described above. Indeed, all four properties in the group definition above are fulfilled, the set is closed under group operation, there is a unit element (identity) and every element has an inverse. Associativity follows from the properties of euclidean transformations, only their order matters, but the brackets can be put arbitrarily.

The structure of this group can be further illustrated using the multiplication table 1.1. Each entry of the table is the result of the product of element $A$ from the left column and the element $B$ from the upper row ($A \cdot B$). Here $A, B \in \{E, R_+, R_-, \sigma_1, \sigma_2, \sigma_3\}$. First the transformation $B$ is performed, and then $A$. We note that the group $C_{3v}$ is non-Abelian, meaning that $AB$ does not always coincide with $BA$.

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<th>$I$</th>
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<td>$\sigma_3$</td>
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<td>$\sigma_2$</td>
<td>$R_+$</td>
<td>$R_-$</td>
<td>$I$</td>
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Table 1.1: Multiplication table for the group $C_{3v}$. Each entry of the table is the result of the product of element $A$ from the left column and the element $B$ from the upper row ($AB$). Here $A,B \in \{I, R_+, R_-, \sigma_1, \sigma_2, \sigma_3\}$. First the transformation $B$ is performed, and then $A$.

Another important construction that is important for us are classes of objects within the group. To explain this concept we will first need to give a definition of conjugate elements.
**Definition 2.** Elements $A$ and $B$ from the group $G$ are called *conjugate* to each other, if $A = X^{-1}BX$, where $X$ is some element of the group $G$. In this case we write $A \sim B$.

**Remark 1.** If $A \sim B$ and $A \sim C$, then $B \sim C$. Indeed if $A = X^{-1}BX$ then $B = XAX^{-1}$. Now $A = Y^{-1}CY$, so we obtain $B = XY^{-1}CYX^{-1} = (YX^{-1})^{-1}C(YX^{-1})$ and thus $B \sim C$. We are now ready to define a class.

**Definition 3.** All elements of the group, mutually conjugate to each other, form a set called *class*.

Every element is always conjugate to itself, so it always belongs to a class, that contains at least one element (for example identity element $I$ can not be conjugate to any other element and always forms a separate class with only one element). From the remark 1 it follows that an element can not belong to two classes at the same time, otherwise the elements in these classes would be mutually conjugate as well and these two classes could then be merged into one bigger class (so initially these classes did not contain all mutually conjugate elements). This discussion results into an important remark.

**Remark 2.** Any finite group $G$ can be split into classes, that do not intersect.

Let us find the classes of the group $C_{3v}$. To do it we need to find all the mutually conjugate element. To simplify the calculations we will use the fact that $R_1^{-1} = R_+$, $\sigma_i^{-1} = \sigma_i$ ($i \in \{1, 2, 3\}$). First we will consider the rotation $R_+$ and calculate its conjugates using the definition 2 and multiplication table 1.1.

1. $I^{-1}R_+I = R_+$
2. $R_+^{-1}R_+R_+ = R_+$
3. $R_+^{-1}R_-R_- = R_+$
4. $\sigma_1^{-1}R_+\sigma_1 = \sigma_1(R_+\sigma_1) = \sigma_1\sigma_3 = R_-$
5. $\sigma_2^{-1}R_+\sigma_2 = \sigma_2(R_+\sigma_2) = \sigma_2\sigma_1 = R_-
6. \sigma_3^{-1}R_+\sigma_3 = \sigma_3(R_+\sigma_3) = \sigma_3\sigma_2 = R_-

We see that the only element conjugate to $R_+$ is $R_-$. So these two elements form a class $\{R_+, R_-\}$. The same procedure can be performed for the inversion, for example $\sigma_1$.

1. $I^{-1}\sigma_1I = \sigma_1$
2. $R_+^{-1}\sigma_1R_+ = R_-(\sigma_1R_+) = R_-\sigma_2 = \sigma_3$
3. $R_+^{-1}\sigma_1R_- = R_+(\sigma_1R_-) = R_+\sigma_3 = \sigma_2$
4. $\sigma_1^{-1}\sigma_1\sigma_1 = \sigma_1$
5. $\sigma_2^{-1}\sigma_1\sigma_2 = \sigma_2R_+ = \sigma_3$
6. $\sigma_3^{-1}\sigma_1\sigma_3 = \sigma_3R_- = \sigma_2$

We see that reflections turn out to be conjugate to each other and form a separate class $\{\sigma_1, \sigma_2, \sigma_3\}$. One more class is just the identity element $\{I\}$. We see that the group $C_{3v}$ has three classes. From physics point of view the classes unite the elements similar in some sort. Indeed, we have a class of rotations, a class of reflections and identity class.

**Definition 4.** Let $G$ and $\tilde{G}$ be two groups. A map $f : G \to \tilde{G}$ is called *homomorphism*, if whenever $AB = C$ in the group $G$, it is true that $f(A)f(B) = f(C)$ in the group $G$. So the map must preserve the operation. The two groups $G$ and $\tilde{G}$ are then called *homomorphic*. Below we will consider a few examples that illustrate this concept.
Let us define $G = C_{3v}$ and $\tilde{G} = \{1\}$ is just unity with the operation of number product $(1 \cdot 1 = 1)$. This group is just one element group, the simplest group possible. If we now define for any element $A \in G$ $f(A) = 1 \in \tilde{G}$, this map will be a trivial homomorphism. Indeed, $f(A)f(B) = f(C)$ will look like $1 \cdot 1 = 1$ and will always hold true.

A bit less trivial example would appear if we define $G = C_{3v}$ and $\tilde{G} = \{1, -1\}$. For the group $\tilde{G}$ the operation is again the number product. We can construct a homomorphism $f$ by defining

$$f(I) = f(R^+) = f(R^-) = 1,$$
$$f(\sigma_1) = f(\sigma_2) = f(\sigma_3) = -1.$$ 

Constructed in this way $f$ will indeed be a homomorphism. We can see this, if we notice that in the group $C_{3v}$

1. the product of rotation by rotation is again a rotation,
2. the product of rotation by inversion is an inversion,
3. the product of inversion by inversion is a rotation.

Here the identity $I$ is also thought of as a rotation by 0 degrees. In some sense we can think of inversions and rotations to have a negative and positive signs respectively, and that is exactly what the homomorphism captures. From these three rules it follows that the map $f$ defined above indeed preserves the operation.

Remark 3. In general, homomorphism is a many to one correspondence, as we saw in the two examples above. Whenever it becomes a one to one correspondence, the corresponding homomorphic map is called isomorphism between two groups (for example, the group of space rotations is isomorphic to the group of $3 \times 3$ orthogonal matrices with unit determinant under the operation of matrix multiplication).

We now turn to the theory of group representations, the most important group theoretical tool in terms of its connection to the description of highly symmetric physical objects.

**Definition 5.** A group of square unitary matrices ($\Gamma$) with the operation of matrix multiplication, homomorphic to some group $G$ is called the representation of the group $G$. In other words, with each element from the group $G$ we associate a unitary matrix from $\Gamma$, such that $\Gamma(A)\Gamma(B) = \Gamma(AB)$ for any two elements $A, B$ from $G$. The dimension of the matrices is called the dimension of the representation.

We will present the theory of group representations as much as it is necessary to understand its relation to the physics of NV$^-$ centers. We will thus skip certain properties of the representations and all the theorems will be presented without prove. We refer the reader to [43] for a more thorough explanation.

Remark 4. If a representation $\Gamma$ of the group $G$ is found, then $S^{-1}\Gamma S$ with some matrix $S$ is also a group representation. Indeed, $S^{-1}\Gamma(A)SS^{-1}\Gamma(B)S = S^{-1}\Gamma(A)\Gamma(B)S = S^{-1}\Gamma(AB)S$. This transformation is called the similarity transformation and given a representation of the group $G$, we can construct infinitely many representations taking different matrices $S$.

To illustrate this concept, let us again return to the group $C_{3v}$. We already constructed two one dimensional representations of this group (we now name them $A_1$ for the one containing only the unity and $A_2$ for that with the elements $\{1, -1\}$), they are not related to each other through similarity transformation, as $-1$ can never be brought to $1$ in such
a way. Let us now construct a two-dimensional representation of this group. For that let us take a look at how the basis vectors along the \( x \)- and \( y \)-axes (\( e_x \) and \( e_y \)) transform under the operations of the group \( C_{3v} \) (Fig. 1.2 (b)). This leaves us with six \( 2 \times 2 \) matrices, whose left and right columns are the images of \( e_x \) and \( e_y \) respectively for the corresponding transformation. For example for the transformation \( R_+ : e_x \rightarrow -\frac{1}{2}e_x + \frac{\sqrt{3}}{2}e_y \) and \( e_y \rightarrow -\frac{\sqrt{3}}{2}e_x - \frac{1}{2}e_y \) or in matrix form \((e_x, e_y) \rightarrow (e_x, e_y) \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}\). We then obtain for all the \( C_{3v} \) elements

\[
E(I) = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad E(R_+) = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}, \quad E(R_-) = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix},
\]

\[
E(\sigma_1) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad E(\sigma_2) = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix}, \quad E(\sigma_3) = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}.
\] (1.1)

This is yet another representation of the group \( C_{3v} \), we call it \( E \). The vectors \( e_x \) and \( e_y \) are said to form a basis for the representation \( E \). In principal, the similarity transformation could transform these matrices to another form. But from the construction it is obvious that this would correspond just to a basis change, when instead of \( e_x \) and \( e_y \) to construct the representation we would use some other vectors \((e'_x, e'_y) = (e_x, e_y)S\). In fact similar arguments can always be made for the representations related by similarity transformation, that is why such representations are called equivalent.

At this point we would like to again explicitly write out the representations \( A_1 \) and \( A_2 \):

\[
A_1(I) = 1, \quad A_1(R_+) = 1, \quad A_1(R_-) = 1, \quad A_1(\sigma_1) = 1, \quad A_1(\sigma_2) = 1, \quad A_1(\sigma_3) = 1,
\]

\[
A_2(I) = 1, \quad A_2(R_+) = 1, \quad A_2(R_-) = 1, \quad A_2(\sigma_1) = -1, \quad A_2(\sigma_2) = -1, \quad A_2(\sigma_3) = -1.
\] (1.2)

Let us now assume that we found two matrix representations \((\Gamma_1 \text{ and } \Gamma_2)\) of the group \( G \). We can then build a third representation by using the block matrices \( \begin{pmatrix} \Gamma_1 & 0 \\ 0 & \Gamma_2 \end{pmatrix} \). In principal this block form could then be hidden by some similarity transformation. This brings us to the following definition.

**Definition 6.** A representation \( \Gamma \) of the group \( G \) is called reducible, if there exists a similarity transformation that brings all the matrices of this representation to block form (we then write \( \Gamma = \Gamma_1 \oplus \Gamma_2 \oplus \ldots \)). Otherwise the representation is called irreducible.

**Remark 5.** There can be infinitely many reducible representations, we can construct them using blocks. But fundamentally they all reduce to just a finite number of inequivalent irreducible representations. Knowing all of them, we can then construct any other or, vice versa, bring a given big representation into block form, where each block is an irreducible representation. We now formulate a few theorems, that allow one to identify all inequivalent irreducible representations.

**Theorem 1.** The number of inequivalent irreducible representations of a group \( G \) is equal to the number of classes of the group \( G \).

**Consequence.** The group \( C_{3v} \) contains exactly three inequivalent irreducible representations (this group has three classes).

**Theorem 2.** Let \( \Gamma_i \ (i \in \{1, \ldots, k\}) \) be all inequivalent irreducible representations of the group \( G \) and let \( l_i \) be the dimension of \( \Gamma_i \). Let \( h \) be the number of elements in the group \( G \), then \( \sum_{i=1}^{k} l_i^2 = h \).
Remark 6. The three inequivalent irreducible representations of the group $C_{3v}$ must have dimensions 1, 1 and 2. Indeed, there are 6 elements in $C_{3v}$, thus $l_1^3 + l_2^2 + l_3^2 = 6$. The only integer solution to this equation is 1, 1, 2.

For the group $C_{3v}$ we already found the three representations $A_1, A_2$ and $E$. The dimensions of these representations are exactly as they should be for all the inequivalent irreducible representations of the group $C_{3v}$. We are only left to show that $E$ cannot be reduced to the representations $A_1$ and $A_2$. Let us assume the opposite

$$S^{-1} E S = \begin{pmatrix} A_i & 0 \\ 0 & A_j \end{pmatrix} \quad (i, j \in \{1, 2\}).$$

Then $\text{tr} E = \text{tr} A_i + \text{tr} A_j$. This can never hold true, as $\text{tr} A_1(R_+) = \text{tr} A_2(R_+) = 1$, while $\text{tr} E(R_+) = -1$. We now see that $E$ must by itself be irreducible representation and that means we found all the inequivalent irreducible representations of $C_{3v}$ group.

We are now finally ready to apply the formalism above to the description of physical objects. The groups we are talking about now will always be groups of euclidean transformations (rotations, reflections in planes, inversions). Let us consider some transformation $T$. The action of this transformation on the physical world is that an object positioned at $r = (x, y, z)$ will be moved to $RTr$, where $RT$ is now a unitary matrix, that represents the transformation $T$ on a point object (in a similar way we built the matrix representation of $C_{3v}$ group, considering the transformation of basis vectors). The columns of this matrix are the images of the basis vectors along the coordinate axes.

Before we move on, let us remind that in quantum mechanics we usually deal with operators $\hat{V}(r_1, r_2, ...)$ and wave functions $\psi(r_1, r_2, ...)$. Now we are ready to introduce the induced transformation on the operators and wave functions.

**Definition 7.** A euclidean transformation $T$ induces the transformation $(\hat{O}_T)$ on the wave functions and operators in the following way

$$\hat{O}_T \psi(r_1, r_2, ...) = \psi'(r_1, r_2, ...) = \psi(R_{T}^{-1} r_1, R_{T}^{-1} r_2, ...),$$

$$\hat{O}_T \hat{V}(r_1, r_2, ...) \hat{O}_T^{-1} = \hat{V}'(r_1, r_2, ...) = \hat{V}(R_{T}^{-1} r_1, R_{T}^{-1} r_2, ...).$$

(1.3)

Though the use of inverse matrix $R_{T}^{-1}$ may seem counterintuitive, it is possible to convince oneself that it is true. By definition of wave function it is a probability amplitude in space. If our transformation $T$ transforms object at $r$ to $RT \mathbf{r}$, then the wave function after the transformation $\psi'$ should have the same value at $RT \mathbf{r}$ as $\psi$ had at $\mathbf{r}$, so it should be $\psi'(RT \mathbf{r}_1, RT \mathbf{r}_2, ...) = \psi(\mathbf{r}_1, \mathbf{r}_2, ...)$. Our definition of induced transformation makes this equation hold, indeed $\psi'(RT \mathbf{r}_1, RT \mathbf{r}_2, ...) = \psi(R_{T}^{-1} R_T \mathbf{r}_1, R_{T}^{-1} R_T \mathbf{r}_2, ...) = \psi(\mathbf{r}_1, \mathbf{r}_2, ...)$. The same arguments apply to induced transformations on operators. An operator represents a physical quantity, so after the transformation the value of $\hat{V}'$ for a particle at $RT \mathbf{r}$ must coincide with that of $\hat{V}$ for a particle at $\mathbf{r}$. This is indeed the case, as $\hat{V}'(RT \mathbf{r}_1, RT \mathbf{r}_2, ...) = \hat{V}(R_{T}^{-1} R_T \mathbf{r}_1, R_{T}^{-1} R_T \mathbf{r}_2, ...) = \hat{V}(\mathbf{r}_1, \mathbf{r}_2, ...)$.}

**Remark 7.** We also note that if the transformations $T_1, T_2, ......$ form a group, the induced transformations will be isomorphic to this group. Indeed, let us assume, that $T_2$ is performed after $T_1$ and the resulting transformation is $T_3$ ($T_3 = T_2 T_1$). Then

$$\hat{O}_{T_3} \hat{O}_{T_1} \psi(r_1, r_2, ...) = \hat{O}_{T_2} \psi(R_{T_1}^{-1} r_1, R_{T_1}^{-1} r_2, ...) = \psi(R_{T_2} R_{T_1}^{-1} r_1, R_{T_2} R_{T_1}^{-1} r_2, ...)$$

$$= \psi((R_{T_2} R_{T_1})^{-1} r_1, (R_{T_2} R_{T_1})^{-1} r_2, ...) (1.4)$$

$$= \psi((R_{T_3})^{-1} r_1, (R_{T_3})^{-1} r_2, ...).$$


looks as \((e_x, e_y, e_z) \rightarrow (e'_x, e'_y, e'_z) = (e_x, e_y, e_z)R_T\). If a vector has coordinates \(r = \begin{pmatrix} x \\ y \\ z \end{pmatrix}\)
in the basis \(e_x, e_y\) and \(e_z\), then \(r' = R_T^{-1}r\) are the coordinates of this vector in the basis \(e'_x, e'_y\) and \(e'_z\) \((xe_x + ye_y + ze_z = x'e'_x + y'e'_y + z'e'_z)\).

This remark may be helpful to understand how the operators transform. For example let us consider a momentum operator. In principal, we could treat this operator as a derivative of the coordinate and use the rules above to understand its transformation rules. But instead we may just write \(\hat{p}_x \rightarrow \hat{p}'_x\), where \(\hat{p}'_x\) is just the momentum operator along the axis \(e'_x\). If we say \(e'_x = \alpha e_x + \beta e_y + \gamma e_z\), then we can immediately write \(\hat{p}'_x = \alpha \hat{p}_x + \beta \hat{p}_y + \gamma \hat{p}_z\), where \(\alpha, \beta, \gamma\) form the first column of the matrix \(R_T\). Analogously for \(\hat{p}_y\) and \(\hat{p}_z\). We can now conclude that the momentum operator transforms under \(T\) as the basis vectors do. One has to be a bit careful though. This simple rule only works well for the real vectors and in general tensors. There are also axial vectors, such as angular momentum \(\hat{l}\), for which the inversion leaves them intact. In the case of an inversion it would be a mistake to assume \(\{\hat{l}_x, \hat{l}_y, \hat{l}_z\} \rightarrow \{\hat{l}_x, \hat{l}_y, \hat{l}_z\}\). Below we will return to this example and show how to get around this problem.

Let us now return to the \(C_{3v}\) group. We saw that its representation \(E\) has bases vectors \(e_x\) and \(e_y\), but after the above discussion we can say that \(\hat{p}_x\) and \(\hat{p}_y\) also form bases of this representation. This is the point where the link to physics becomes even stronger, as we now see that the operators can also form bases for the irreducible representation of some group of space transformations. The last and very important thing we need to understand is that the wave functions can also form bases of the irreducible representation. Let us consider the wave function \(\psi_x(x, y) = x\) and \(\psi_y(x, y) = y\). They are not normalized, but for now it is not important. We saw before that under the transformation \(T\) the coordinates in the arguments of functions transform in the following way

\[
\begin{pmatrix} x \\ y \end{pmatrix} \rightarrow \begin{pmatrix} x' \\ y' \end{pmatrix} = R_T^{-1} \begin{pmatrix} x \\ y \end{pmatrix} .
\]

\hspace{1cm} (1.5)

Now let us take a transpose of this equation and take into account that for unitary matrices \((R_T^{-1})^T = R_T\), we then obtain

\[
(x, y) \rightarrow (x', y') = (x, y)R_T .
\]

\hspace{1cm} (1.6)

This transformation has exactly the same form as the transformation of basis vectors \(e_x\) and \(e_y\), that means the wave functions \(x\) and \(y\) are also bases functions of the irreducible representation \(E\) of the group \(C_{3v}\) (one also says they belong to representation \(E\) of the group \(C_{3v}\)). The function \(x\) is called the partner of the function \(y\) and is said to transform according to the first row of irreducible representation \(E\) (one may argue first column could be more logical, but the convention is to say row). The function \(y\) is accordingly a partner of \(x\) and transforms according to the second row of the irreducible representation \(E\). These are of course not the only wave functions that form a basis of the irreducible representation \(E\) of the group \(C_{3v}\). In the following we switch gears away from \(C_{3v}\) and present a few general theorems about the bases functions of representations of general transformation groups (without prove). In general, the wave functions or operators \(\psi_1, \psi_2, ..., \psi_l\) are said to form a basis for the representation \(\Gamma\) (of dimension \(l\)) of the group \(G\), if they transform under the transformations \((T)\) induced by the group as

\[
\psi_i \rightarrow \sum_{j=1}^{l} \Gamma(T)_{ji}\psi_j
\]

\hspace{1cm} (1.7)
Theorem 3. Two wave functions which belong to different irreducible representation or to different rows of the same irreducible representation are orthogonal and their norm is the same for all the functions belonging to the same irreducible representation (provided they are partners)

$$\int d^3r (\phi_k^j)^* \psi_{k'}^j = M^j \delta_{j,j'} \delta_{k,k'}.$$  

Here \( j, j' \) mark the irreducible representations and \( k, k' \) are the indexes of the bases functions within the representation.

Theorem 4. If \( \Gamma_1, \Gamma_2, \ldots, \Gamma_c \) are all of the inequivalent irreducible representations of the group \( G \) (with dimensions \( l_1, l_2, \ldots, l_c \) respectively), then any function \( F(x,y,z) \) can be decomposed into a sum of the form

$$F = \sum_{j=1}^c \sum_{k=1}^{l_j} f_k^j(x,y,z),$$  

where \( f_k^j(x,y,z) \) belongs to the \( k \)th row of the \( j \)th irreducible representation. A simple illustration of this theorem is the case when \( G \) contains the identity operator and inversion. In that case there are two one-dimensional irreducible representations, the first one corresponding to symmetric functions and the second to antisymmetric functions. The decomposition then takes the form

$$F(x,y,z) = F(x,y,z) + F(-x,-y,-z) + F(x,y,z) - F(-x,-y,-z).$$

Theorem 5. Let \( \Gamma_1, \Gamma_2, \ldots, \Gamma_c \) be all of the inequivalent irreducible representations of the group \( G \) (with dimensions \( l_1, l_2, \ldots, l_c \) respectively). Let us introduce the operator

$$\hat{P}^j_{\lambda k} = \frac{\hbar}{i} \sum_{T \in G} \Gamma^j(T)_{\lambda k} \hat{O}_T,$$  

then

1. If \( f_k^j \) and \( f_\lambda^j \) belongs to the \( k \)th and \( \lambda \)th rows of the \( j \)th irreducible representation respectively and are partners, then

$$\hat{P}^j_{\lambda k} f_k^j = \delta_{k,k'} \delta_{j,j'} f_\lambda^j$$  

2. Let the decomposition of a function into symmetry components take the form \( F(x,y,z) = \sum_{j=1}^c \sum_{k=1}^{l_j} f_k^j \), then \( f_k^j = \hat{P}^j_{\lambda k} F \) and \( \hat{P}^j_{kk} \) is called the projection operator onto the \( k \)th row of the \( j \)th irreducible representation.

3. If \( f_k^j \) belongs to the \( k \)th row of the \( j \)th irreducible representation, then its partners can be generated as \( f_\lambda^j = \hat{P}^j_{\lambda k} f_k^j \) and \( \hat{P}_{\lambda k} \) is called the transfer operator.

The properties 2, 3 can be derived from 1.

Remark 8. We note that the application of transfer operator \( \hat{P}^j_{\lambda k} \) to \( F \) will generate the partner to its part \( f_k^j \), but this partner is not necessarily contained in \( F \) anymore (\( \hat{P}^j_{\lambda k} F \neq \hat{P}^j_{\lambda\lambda} F \)).

Remark 9. The last two theorems about the decomposition of a function into symmetry components and about partner generation are as much true for wave functions as for operators. Indeed, the operators can also form basis for irreducible representations (for example above we saw that the momentum operator transforms as unit vectors, and thus \( \hat{p}_x \) and \( \hat{p}_y \) are partners and belong to the representation \( E \) of the group \( C_{3v} \)). The only
difference we need to make is to use the induced transformation for operators instead of that for functions \(\Phi\), which corresponds to a replacement \(\hat{O}_T \rightarrow \hat{O}_T \hat{\sigma} \hat{O}_T^{-1}\) in the definition of \(\hat{P}_{\lambda k}\), where \(\hat{\sigma}\) stands for the operator to which the induced transformation is applied.

Before we proceed, it would be useful to consider some other examples of bases functions for the representations of the group \(C_{3v}\). In particular, we will be interested in the spin angular momentum operators \(\hat{S}_x, \hat{S}_y, \hat{S}_z\) (the same considerations are true for the orbital angular momentum). As we noted above, this is an axial vector, that does not transform under inversion. This is a problem for us because the group \(C_{3v}\) contains reflection planes. The operation of reflection can be thought of as a rotation in the reflection plane by 180° followed by an inversion. If a representation \(\Gamma\) is written in the bases of real vectors, that transform under inversion, the representation for axial vectors must coincide with it for all the rotations and contain additional minus sign in front of reflection matrices (to compensate the inversion). In \(C_{3v}\) group the real unit vector \(\mathbf{e}_z\) does not change under any of the group operations (Figure 1.2 (b). That means it forms a basis for \(A_1\) representation. All \(z\)-components of real vectors will have the same property. Then the \(z\)-component of the axial vector \(\hat{S}_z\) remains invariant for rotations and changes sign for inversions. That means it transforms according to \(A_2\) representation. The \(\hat{S}_x\) and \(\hat{S}_y\) components transform according to \(E\) representation

\[
\hat{E}(I) = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad \hat{E}(R_+) = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}, \quad \hat{E}(R_-) = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix},
\]

\[
\hat{E}(\sigma_1) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \hat{E}(\sigma_2) = \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}, \quad \hat{E}(\sigma_3) = \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix},
\]

that differs from \(E\) with the sign of the reflection matrices. This representation is still equivalent to \(E\) through a similarity transformation. That corresponds to a bases change form \(\hat{S}_x, \hat{S}_y\) to a new pair, that will transform as if they were components of a real vector. We can identify them using the following considerations. The similarity transformation must not change the rotation matrices, that means it is by itself a rotation by some angle around the \(z\)-axis. The \(\sigma_1\) reflection transforms \(\hat{S}_y\) exactly as \(\mathbf{e}_x\) and \(\hat{S}_x\) exactly as \(\mathbf{e}_y\). This implies that we should try a basis change \(\hat{S}_z \rightarrow -\hat{S}_y, \hat{S}_y \rightarrow \hat{S}_x\), which is a rotation by 90°. One can verify that this new pair of axial vector components \(\{-\hat{S}_y, \hat{S}_x\}\) transforms exactly as \(\{\mathbf{e}_x, \mathbf{e}_y\}\) and thus forms bases for the representation \(E\).

\[
\{-\hat{S}_y, \hat{S}_x\} \in E \\
\hat{S}_z \in A_2.
\]

That will be extremely important in the future when we will construct spin-spin and spin-orbit Hamiltonians, as well as consider interaction between spin and external fields. The last concept we need to introduce before we start speaking about the physics of NV centers are direct product representations within a group. Let us assume \(\phi_1, \phi_2, ..., \phi_l\) are basis functions of the representation \(\Gamma\) and \(\psi_1, \psi_2, ..., \psi_{l'}\) are basis functions of the representation \(\Gamma'\). At this point \(\psi\) or \(\phi\) can be either wave functions or operators. Then the functions \(\phi_i \psi_j\) will form a basis for an \(l \times l'\)-dimensional representation \(\Gamma\). This can be verified as for any transformation \(T\) these functions transform as

\[
\phi_i \psi_j \rightarrow \sum_{m=1}^{l} \sum_{n=1}^{l'} \Gamma_{mn}(T) \phi_m \Gamma'_{nj}(T) \psi_n = \sum_{m,n} \phi_m \psi_n \left[ \Gamma_{mn}(T) \Gamma'_{nj}(T) \right] = \sum_{m,n} \phi_m \psi_n \hat{\Gamma}(T)_{mn,ij},
\]

where \(\hat{\Gamma}(T) = \Gamma(T) \times \Gamma'(T)\). These direct product matrices form a representation based on the functions \(\phi_i \psi_j\).
Remark 10. Let us assume that one of the representations above is trivial (the one-dimensional representation that contains only a single number 1). The direct product representation then coincides with the second representation \((1 \times \Gamma' = \Gamma')\). A situation like this appears, for example, when an operator transforms according to a trivial representation. Its action on some wave function of a given symmetry (transforming according to a certain row of some irreducible representation) yields the function having the same symmetry then. If one combines this with the fact that wave functions of different symmetry are always orthogonal (the theorem 3), this immediately implies that this operator can have no matrix elements between the functions of different symmetry.

Remark 11. In general the direct product representations need not be irreducible any more. Indeed, if we recall the \(C_3v\) point group, obviously \(E \times E\) will be a four dimensional representation and thus it must be reducible. To illustrate the formalism above and in view of the future applications, it is instructive to reduce all possible tensor products of \(C_3v\) representations into irreducible representations. To do so, we start with two groups of functions that form bases for the corresponding representations of \(C_3v\):

1. \(\phi_{A_1} \in A_1, \phi_{A_2} \in A_2\) and \(\{\phi_x, \phi_y\} \in E\),
2. \(\psi_{A_1} \in A_1, \psi_{A_2} \in A_2\) and \(\{\psi_x, \psi_y\} \in E\).

Here \(\{\}\) means the corresponding functions on the left form bases for the representation on the right. \(\{\}\) means the functions inside are partners (for example the wave functions \(\phi_x, \psi_y\) are not partners, even though both of them are parts of the bases for the representation \(E\)). From now on we will assume that writing \(\Gamma_1 \times \Gamma_2 = \Gamma\) means that the equality holds up to a similarity transformation (that means a similarity transformation might be necessary to bring \(\Gamma_1 \times \Gamma_2\) to \(\Gamma\)). There are a few possibilities for the tensor products:

1. \(A_1 \times A_1 = A_1\) with the basis \(\phi_{A_1} \psi_{A_1} \in A_1\).
2. \(A_1 \times A_2 = A_2\) with the basis \(\phi_{A_1} \psi_{A_2} \in A_2\).
3. \(A_1 \times E = E\) with the basis \(\{\phi_{A_1} \psi_x, \phi_{A_1} \psi_y\} \in E\).
4. \(A_2 \times A_1 = A_2\) with the basis \(\phi_{A_2} \psi_{A_1} \in A_2\).
5. \(A_2 \times A_2 = A_1\) with the basis \(\phi_{A_2} \psi_{A_2} \in A_1\), this can be checked directly by calculating the tensor product.
6. \(A_2 \times E\). One can notice that this tensor product exactly coincides with \(\tilde{E}\) (Eq. 1.12). We considered this representation for the spin operators and arrived at the conclusion, that a similarity transformation, changing the bases \(\hat{S}_x \rightarrow -\hat{S}_y, \hat{S}_y \rightarrow \hat{S}_x\), brings \(\tilde{E}\) to \(E\). Analogously, we can now write \(A_2 \times E = E\) with the basis \(\{-\phi_{A_2} \psi_y, \phi_{A_2} \psi_x\} \in E\).
7. \(E \times A_1 = E\) with the basis \(\{\phi_x \psi_{A_1}, \phi_y \psi_{A_1}\} \in E\).
8. \(E \times A_2 = E\) with the basis \(\{-\phi_y \psi_{A_2}, \phi_x \psi_{A_2}\} \in E\), analogously to case 6.
9. \(E \times E = E \oplus A_1 \oplus A_2\) with the basis \(\{\phi_x \psi_x - \phi_y \psi_y, -\phi_x \psi_x + \phi_y \psi_y\} \in E, \frac{\phi_x \psi_x + \phi_y \psi_y}{2} \in A_1, \frac{\phi_x \psi_x - \phi_y \psi_y}{2} \in A_2\). We present a proof of this decomposition in Appendix A.1.

Let us illustrate these rules, by constructing the symmetry bases functions, quadratic in spin. We know that \(\{-\hat{S}_y, \hat{S}_x\}\) forms basis for the \(E\) representation and \(\hat{S}_z\) forms basis for the \(A_2\) representation. Then according to the rule five \(\hat{S}_z^2\) transforms as \(A_1\). According to the rules six and eight \(\{\hat{S}_x, \hat{S}_z\}, \{\hat{S}_y, \hat{S}_z\}\} \in E\), here \(\{\}\) means anticommutator of...
operators. According to the rule nine \(\{\hat{S}_y^2 - \hat{S}_x^2, \{\hat{S}_y, \hat{S}_x\}\} \in E\). These five operators are all relevant quadratic spin operators out of nine. Indeed, three more would look as commutators and are thus linear in spin operators \([\hat{S}_x, \hat{S}_y] = \hat{S}_z\). The last one \(\hat{S}_x^2 + \hat{S}_y^2\) is just \(\hat{S}^2\) and bears no new information as well. Thus, the five relevant quadratic operators are

\[
\hat{S}_z^2 \in A_1
\]

\[
\{\{\hat{S}_x, \hat{S}_z\}, \{\hat{S}_y, \hat{S}_z\}\} \in E
\]

(1.15)

These tensor product constructions will play a significant role in our future considerations, when we will discuss the eigenstates of the Hamiltonian of NV\(^-\) center. For now we have seen that operators and wave functions can form bases for the irreducible representations of the symmetry group. Of course this is also true for spinors, the vectors representing the spin. In general, description of half integer spin angular momentum requires the extension of the formalism above to the so called double groups \([43]\). Fortunately, the spin of NV\(^-\) is integer and thus it can be considered within the framework we already have. In general, rotations by \(\theta\) along the axis \(n\) act on the spin vectors according to \(\exp(-\frac{\theta}{\hbar} n \hat{S})\). The inversion does not change the spinor, that means reflection in a plane acts on spinors as rotations by 180\(^\circ\) in this plane (analogous to what we saw for spin operators). To construct the spinor bases for the irreducible representations, one could again use the projection operators. We perform this calculation in appendix A.2 and here just present the result for the \(C_{3v}\) group. We will only be interested in the total spin value 0 and 1, thus it can be thought of as a combined spin of two spin-1/2 particles (we associate the bases states \(|\uparrow\rangle\) and \(|\downarrow\rangle\) with each of them). The total spin zero state (spin singlet) \(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\sqrt{2}\) is the basis for \(A_1\) representation. The triplet spin state with zero spin projection \(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\sqrt{2}\) is the basis for \(A_2\) representation, while the triplet states \(\{\frac{|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle}{\sqrt{2}}, -i\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}\}\) form basis for the \(E\) representation

\[
\begin{align*}
|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\sqrt{2} & \in A_1 \\
|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\sqrt{2} & \in A_2 \\
\{\frac{|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle}{\sqrt{2}}, -i\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}\} & \in E
\end{align*}
\] (1.16)

We now have all the mathematical tools to analyze symmetries. But what is the symmetry group of a physical system. The answer is very simple, this is a group of operations \(T\) that leave the Hamiltonian of the system \(\hat{H}\) invariant

\[
\hat{O}_T \hat{H} \hat{O}_T^{-1} = \hat{H}.
\] (1.17)

It now follows that \(\hat{H}\) and \(\hat{O}_T\) commute

\[
\hat{O}_T \hat{H} = \hat{H} \hat{O}_T.
\] (1.18)

In the group theoretical language we can say that the Hamiltonian transforms according to the trivial representation. As we saw above, such an operator can have no matrix elements between states of different symmetry (remark 10). That allows us to simplify the eigenvalue problem \(\hat{H}\psi = E\psi\), as we know from the start that the Hamiltonian is non-diagonal only in the subspace of states that have the same symmetry (transform according to the same row of the same irreducible representation of the symmetry group). This consideration reduces the size of the eigenvalue problem we need to solve. Let us
now assume that we did the diagonalization for one symmetry block and that the state \( \psi_k \), that transforms according to the \( k \)th row of the irreducible representation \( \Gamma \), is the eigenvector of \( \hat{H} \) \( (\hat{H}\psi_k = E\psi_k) \). Then let \( T \) be operation from the symmetry group and let us consider the action of \( \hat{H} \) on \( O_T\psi_k \):

\[
\hat{H}O_T\psi_k = O_T\hat{H}\psi_k = E\hat{O}_T\psi_k.
\]

(1.19)

We see that \( \hat{O}_T\psi_k \) is also an eigenvector of \( \hat{H} \), corresponding to the same energy. Moreover, the functions \( \hat{O}_T\psi_k \) for all \( T \) from the symmetry group are linear combinations of the bases functions of the irreducible representation \( \Gamma \) (according to our definition of irreducible representation bases functions \( \hat{O}_T\psi_k = \sum_{i=1}^{\text{dim}\Gamma} \Gamma(T)_{ik}\psi_i \)). We can thus conclude that all the partners of \( \psi_k \) in the representation \( \Gamma \) are eigenvectors of \( \hat{H} \), corresponding to the same energy. We now fully understand the structure of the Hamiltonian with certain symmetry. All the eigenvectors of such a Hamiltonian can be associated to certain rows of irreducible representations of the symmetry group. Moreover, if one such eigenvector is found, then all of his partners that together form the bases for the irreducible representation of the symmetry group, must have the same energy. Usually that means that the number of degenerate levels coincides with the dimension of the corresponding irreducible representation. But in principal it can be larger. It can happen if, for example, two levels belonging to different irreducible representations happened to have the same energy. This degeneracy does not appear from symmetry and is thus called accidental.

1.2.2 NV\(^-\) center low temperature level structure

Our task now is to describe the energy levels of NV\(^-\) center in diamond, that arise due to different interactions present in this solid state system. In our consideration we will mostly follow the approach of [44]. We will completely skip certain important issues of the NV\(^-\) center physics, such as phonon sideband in the absorption and emission spectrum and Jahn-Teller interaction. We refer the reader to [45–47] to familiarize with these issues in more detail.

The figure 1.1 suggests that the operations of the group \( C_{3v} \), leave the defect invariant (transform it into itself). This immediately suggests that whichever interactions are present in this system, the Hamiltonian describing them must be invariant under the operations of \( C_{3v} \), which is now a symmetry group. This trigonal structure of the defect has been confirmed by EPR measurements [48] and numerous ab initio studies [6, 44]. As we already pointed out, the NV\(^-\) center consists of an absent carbon atom (vacancy) and a neighboring nitrogen, replacing another carbon (Fig. 1.1). The ab initio studies of the defect suggest that the electron density is highly localized on the atoms, that are closest to the vacancy. That means the electrons occupy the molecular orbitals of three carbon atoms and a nitrogen (Fig. 1.3). The orbitals, belonging to the carbons we call \( b_1 \), \( b_2 \) and \( b_3 \), while the nitrogen orbital is called \( b_n \). The molecular orbital method, that we are following here, assumes the electrons can only occupy one of these four orbits. That means that the orbital Hilbert space, the electrons are allowed to occupy, is four-dimensional. In Appendix A.3 we project these orbitals onto the irreducible representations of the group.
Figure 1.3: This figure represents the NV− center defect and the coordinate system that we associate with it. The six electrons occupy four molecular orbitals, that we name $b_1$, $b_2$, $b_3$ for those belonging to carbon atoms (C) and $b_n$ for the one belonging to the nitrogen atom (N).

$C_{3v}$ and construct the new orbitals $b_c$, $e_x$ and $e_y$, such that

\begin{align*}
    b_n &\in A_1, \\
    b_c &\in A_1, \\
    \{e_x, e_y\} &\in E, \\
    b_c &= \frac{b_1 + b_2 + b_3}{\sqrt{3}}, \\
    e_x &= \frac{2b_1 - b_2 - b_3}{\sqrt{6}}, \\
    e_y &= \frac{b_2 - b_3}{\sqrt{2}}.
\end{align*}

Effect of crystal field

Let us first consider the effect of crystal field. The most general symmetry allowed (transforming as $A_1$ representation) form it can have is

\begin{align*}
    \hat{H}_{cr} &= v_n |b_n\rangle \langle b_n| + \sum_{i=1}^{3} v_c |b_i\rangle \langle b_i| + \left[ \sum_{i=1}^{3} h_n |b_i\rangle \langle b_n| + h.c. \right] + \sum_{i\neq j} h_c |b_i\rangle \langle b_j|.
\end{align*}

Indeed, this Hamiltonian is invariant under the operations of the symmetry group $C_{3v}$. This can be checked either directly or by noticing the fact that this Hamiltonian can be rewritten as

\begin{align*}
    \hat{H}_{cr} &= v_n |b_n\rangle \langle b_n| + (v_c + 2h_c) |b_c\rangle \langle b_c| + \left( \sqrt{3}h_n |b_c\rangle \langle b_n| + h.c. \right) + (v_c - h_c) \left( |e_x\rangle \langle e_x| + |e_y\rangle \langle e_y| \right).
\end{align*}
In agreement with the remark\[10\] \(e_x\) and \(e_y\) are eigenstates of this Hamiltonian, as there are no other states of the same symmetry they could be coupled to. In contrast \(b_c\) and \(b_a\) have the same symmetry and are thus coupled with \(H_c\). Because the interaction of electrons and nuclei is attractive, the coupling coefficients \(w_n, v_c, h_c, h_n\) are negative. The coefficients \(h_c\) and \(h_n\) arise due to the interaction of orbitals, belonging to different atoms, that we assume to be quite small. In that case it should follow that \(h_n, h_c < v_c, v_n\) and we first neglect them. The DFT calculations reveal that \(|v_n| > |v_c|\). In this simplified picture the nitrogen orbital is lowest in energy \(W_n = v_n\). Then comes the orbitals \(b_c, e_x, e_y\) with the energy \(v_c\). This degeneracy becomes broken if we switch on the interaction \(h_c\). It pushes the energy of \(e_x, e_y\) up by \(h_c\) to the value \(W_{xy} = v_c - h_c\). The energy of \(b_c\) is lowered by \(2h_c\) to the value \(W_c = v_c + 2h_c\). If we finally switch \(h_n\) on, the nitrogen orbital \(b_n\) becomes hybridized with \(b_c\) (this new orbital we call \(\tilde{a}_1 = \alpha b_n + \beta b_c\)) and is pushed down in energy even further to the value \(W_{\tilde{a}_1} = \frac{1}{2}(v_c + 2h_c + v_n) - \frac{1}{2}\sqrt{(v_c + 2h_c - v_n)^2 + 12h_n^2}\). The orbital \(b_n\) also becomes hybridized with \(b_a\) (we call this new orbital \(a_1 = \alpha^*b_n - \beta^*b_a\)) and is pushed up in energy to the value \(W_a = \frac{1}{2}(v_c + 2h_c - v_n) + \frac{1}{2}\sqrt{(v_c + 2h_c - v_n)^2 + 12h_n^2}\). The values \(W_\tilde{a}, W_a\) one obtains after diagonalization of the Hamiltonian (1.22), neglecting the error arising from direct scalar product \(\langle b_n | b_c \rangle\) (diagonalization assuming these levels to be orthogonal, which can not be true exactly, as \(h_c, h_n\) are nonzero). The DFT calculations\[6\] reveal that this energy push is not sufficient to reach \(W_{xy}\), so we end up with the order of the single electron orbital levels as shown in Fig. 1.4 (a). Each of the carbon atoms, neighbouring to the vacancy, has one unpaired electron. The nitrogen has two unpaired electrons. In total there are five electron that can occupy four orbitals we have identified. In this configuration the NV center would be in the zero charge state. But one more electron comes from the environment, presumably form a substitutional nitrogen defect close to the NV\(^{-}\) center. These six electrons occupy six lowest orbitals in Figure 1.4 (a). That means in the ground state all symmetric orbitals \(a_1\) and \(\tilde{a}_1\) are occupied by four electrons in accordance with the Pauli principle and the remaining two electrons occupy the orbitals \(e_x\) and \(e_y\). Excited state of the system can then be thought of as if an electron is promoted from the level \(a_1\) to the orbital doublet \(\{e_x, e_y\}\). It is convenient though to notice that if two more electrons were added to the system, all four orbitals would be fully filled. The state would then be a spin singlet, a situation similar to the case of an atom with fully filled shells. These missing electrons can be thought of as holes that are added on top of the filled shells and in the ground state occupying the orbitals \(e_x\) and \(e_y\). The order of the levels in the hole picture is reversed with respect to that of the electron picture (Figure 1.4 (b)). From now on we will work in the hole picture, as it is simpler to deal with two fermionic particles, rather than with six of them. We will not consider
the states when a hole is excited to the highest orbital $\tilde{a}_1$, as this levels lie in the valence band and are irrelevant for the physics discussed in this thesis. We thus have the following electronic configurations: $e^2$, when two holes occupy the orbitals $e_x, e_y$, the configuration $ea_1$, when one hole occupies the orbital $a_1$ and the other hole occupies one of the orbitals $e_x, e_y$. The last configuration is $a_1^2$, when both holes occupy the orbital $a_1$. Our task now is to build two particle orbital wave functions, that transform according to the irreducible representations of the symmetry group. The last property is important for us, as only those functions can be eigenstates of the electron-electron interaction present in the system. Let us agree on the notation, for example $|e_x e_y\rangle$ means the first electron occupies the orbital $e_x$ and the second one occupies the orbital $e_y$ (this state is not symmetrized with respect to particle permutation). Now that we have developed the formalism of group theory, we can easily build the two particle wave functions based on the remark 11. Indeed, let us start with $e^2$ configuration. From rule 9 of the remark 11 we can immediately conclude that the following is true for the two particle wave functions

$$
\frac{|e_x e_x\rangle - |e_y e_y\rangle}{\sqrt{2}}, \quad \frac{|e_x e_y\rangle + |e_y e_x\rangle}{\sqrt{2}} \in E, \tag{1.23}
$$

$$
\frac{|e_x e_x\rangle + |e_y e_y\rangle}{\sqrt{2}} \in A_1, \quad \frac{|e_x e_y\rangle - |e_y e_x\rangle}{\sqrt{2}} \in A_2. \tag{1.24}
$$

Analogously, we can perform this analysis for the $ea_1$. Using the rules 3 and 7 of the remark 11 to reduce the tensor products, we obtain the states symmetric and antisymmetric with respect to particle permutations and that at the same time form bases for the irreducible representations of $C_{3v}$:

$$
\frac{|e_x a_1\rangle - |a_1 e_x\rangle}{\sqrt{2}}, \quad \frac{|e_y a_1\rangle - |a_1 e_y\rangle}{\sqrt{2}} \in E, \tag{1.25}
$$

$$
\frac{|e_x a_1\rangle + |a_1 e_x\rangle}{\sqrt{2}}, \quad \frac{|e_y a_1\rangle + |a_1 e_y\rangle}{\sqrt{2}} \in E.
$$

The $a_1^2$ configuration is the simplest

$$
|a_1 a_1\rangle \in A_1. \tag{1.25}
$$

To really calculate the eigenstates of the system, we still need to add the spin though. That means the full eigenstates we are interested in are combinations of the orbital functions (Eqn. 1.23,1.24,1.25) and the spinors (Eq. 1.16). As any fermionic wave functions, these combinations must be antisymmetric with respect to particle permutations (orbital singlet is combined with the spin triplet and vice versa). To make these new states be bases for the irreducible representations of $C_{3v}$, we again use the rules 1–9 for the tensor product reduction from the remark 11 (this time it is the tensor product of representations describing orbital states and spinors). We list the result of this procedure in Table 1.2.

**Effect of Coulomb interaction**

For now all the levels, belonging to the same orbital electronic configuration, have the same energy. This degeneracy can though be lifted, if one includes the electron-electron Coulomb interaction. At this point it is important to notice that electron-electron interaction obeys the $C_{3v}$ symmetry. That means it can have no matrix elements between levels of different symmetry in table 1.2. Within the same electronic configuration, the levels of the same symmetry can not be coupled by Coulomb interaction due to spin selection.
<table>
<thead>
<tr>
<th>Configuration</th>
<th>State (Orbit(\otimes)Spin)</th>
<th>Symmetry</th>
<th>Name</th>
</tr>
</thead>
</table>
| e^2(T)        | \(|e_x e_y - e_y e_x\rangle\otimes|\uparrow\downarrow + \downarrow\uparrow\rangle\) \(|\uparrow\uparrow - \downarrow\downarrow\rangle\) \(|\uparrow\uparrow + \downarrow\downarrow\rangle\) | A_1 \(\langle|e^2(A_{20})\rangle\) \(\langle e^2(A_{2x})\rangle\) |}
| e^2(S)        | \(|e_x e_x + e_y e_y\rangle\) \(|e_x e_x - e_y e_y\rangle\) \(|-e_x e_y + e_y e_x\rangle\) \(|\uparrow\downarrow - \downarrow\uparrow\rangle\) | A_1 \(\langle|e^2(S)_{A_1}\rangle\) \(\langle e^2(S)_{x}\rangle\) |}
| ea_1(T)       | \(|X\rangle \otimes|\uparrow\uparrow + \downarrow\downarrow\rangle\) \(|i|Y\rangle \otimes|\uparrow\uparrow - \downarrow\downarrow\rangle\) \(||X\rangle \otimes|\uparrow\uparrow - \downarrow\downarrow\rangle + |i|Y\rangle \otimes|\uparrow\uparrow + \downarrow\downarrow\rangle\) \(|i|X\rangle \otimes|\uparrow\uparrow - \downarrow\downarrow\rangle - |i|Y\rangle \otimes|\uparrow\uparrow + \downarrow\downarrow\rangle\) \(|-|Y\rangle \rangle \otimes|\uparrow\downarrow + \downarrow\uparrow\rangle\) | A_1 \(\langle A_{1}\rangle\) \(\langle|A_{2}\rangle\) \(\langle A_{2}\rangle\) \(\langle E_x, ms = \pm 1\rangle\) \(\langle E_y, ms = 0\rangle\) |}
| ea_1(S)       | \(|e_x a_1 + a_1 e_x\rangle \otimes|\uparrow\downarrow - \downarrow\uparrow\rangle\) \(|e_y a_1 + a_1 e_y\rangle \otimes|\uparrow\downarrow - \downarrow\uparrow\rangle\) | E_x \(\langle ea_1(S)_{x}\rangle\) \(\langle ea_1(S)_{y}\rangle\) |}
| a^2(S)        | \(|a_1 a_1\rangle \otimes|\uparrow\downarrow - \downarrow\uparrow\rangle\) | A_1 \(\langle a^2(S)_{A_1}\rangle\) |}

Table 1.2: This table lists all the energy levels, relevant in the coherent dynamics of NV-center. The left column marks the electronic configuration, here the letters stand for the orbitals occupied by the two holes and the letter in the brackets stands for the triplet or singlet spin state. The second column stands for the explicit expressions of the levels. The third column represents the symmetry of the levels, here the brackets mean that these levels are partners and form bases for the irreducible representation. The third column represents the symmetry of the coulomb interaction implies that partners for the corresponding state, a constant known as exchange energy, that is always positive for a repulsive interaction of electrons. We can now conclude, that the spin triplet e^2(T) lies lowest in energy, then comes the spin singlet orbital doublet \(|e^2(S)_{x}\rangle\) and \(|e^2(S)_{y}\rangle\) with the energy 2J. Finally, the state \(|e^2(S)_{A_1}\rangle\) lies highest in energy at 4J. Our conclusion
coincides with the Hunds rule, according to which a spin triplet is usually ground state of the system. Analogously, the Coulomb interaction places the doublet levels $ea_1(S)$ higher in energy than the six levels from $ea_1(T)$. Note that the degeneracy within each of these configurations can not be lifted by the Coulomb interaction, as those are formed by partner orbital functions, and as we know, the symmetric Hamiltonian leaves the partners degenerate. Moreover, for symmetry reasons the degeneracy of $ea_1(S)$ configuration can not be broken by any symmetric interaction Hamiltonian. This, however, is not true for the configuration $ea_1(T)$, as there we have the states of different symmetry and they can have different energy (the fact they are degenerate now we can treat as an accidental degeneracy). Analogously, the degeneracy within $e^2$ configuration is accidental and can be lifted, if we add additional interactions, that obey $C_{3v}$ symmetry.

**Effect of spin-orbit interaction**

The first such interaction we will consider will be spin-orbit interaction

$$
\hat{H}_{so} = \sum_{k} \frac{1}{2} \frac{e}{c^2 m_e} (\nabla_k \phi \times \hat{p}_k) \cdot \hat{s}_k.
$$

(1.28)

Here the sum is taken over the holes. $e$ and $m_e$ are the charge and the mass of the electron respectively. $\phi$ is the potential of the nuclei, $\hat{p}_k$ and $\hat{s}_k$ are the momentum and spin operators respectively for the $k$th hole. The sign of this interaction is reversed with respect to the conventional form of that for electrons, because we are working in the hole picture. The potential of the nuclei, $\phi$, is a scalar function that transforms according to the $A_1$ representation due to symmetry. The gradient $\nabla$ is a real vector, that means it transforms exactly as the bases vectors of the coordinate system (see remark 7) under the symmetry operations. That means $\{ \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \}$ form bases for the irreducible representation $E$ of the group $C_{3v}$ and $\frac{\partial}{\partial z}$ forms basis for the $A_1$ representation. Due to the rules 3, 7 of the remark 7 $\{ \frac{\partial \phi}{\partial x}, \frac{\partial \phi}{\partial y}, \frac{\partial \phi}{\partial z} \}$ also forms basis for $E$, while $\frac{\partial \phi}{\partial z}$ forms basis for $A_1$. Thus, $\nabla_k \phi$ transforms as a real vector under the operations of $C_{3v}$. The cross product $\nabla_k \phi \times \hat{p}_k$ then must transform as the an axial vector, according to the same representation $E$ (Eq. 1.12), as the angular momentum operator. This is intuitively clear, as cross product of two vectors is always an axial vector, but it can also be directly verified from the expression

$$
\nabla \phi \times \hat{p} = (\phi_y \hat{p}_z - \phi_z \hat{p}_y, \phi_z \hat{p}_x - \phi_x \hat{p}_z, \phi_x \hat{p}_y - \phi_y \hat{p}_x).
$$

(1.29)

using the rules 1 – 9 of the remark 11. The dot product of this axial vector with yet another axial vector $\hat{s}$ gives a scalar that transforms according to the $A_1$ representation, as should be for the Hamiltonian $H_{so}$. Let us compute all the allowed matrix elements of $\nabla \phi \times \hat{p}$ in the single particle orbital basis $e_x, e_y, a_1$. Some of the matrix elements are forbidden by symmetry. Indeed, the negative $y$–component of the axial vector transforms as $x$-component of the real vector (1.13). The operator, that transforms as $x$–component of the real vector can only take the form (see rules 1 – 9 of the remark 11 $\{ e_x, e_y \} \langle e_x | - | e_y \rangle \langle e_y |$ or $\alpha | a_1 \rangle \langle e_x | + \alpha^* \langle e_x | a_1 \rangle$. Although allowed by symmetry, the first possibility does not appear 14. Indeed, the matrix elements $\langle e_x | \phi_y \hat{p}_z - \phi_z \hat{p}_y | e_x \rangle = \langle e_y | \phi_y \hat{p}_z - \phi_z \hat{p}_y | e_y \rangle = 0$ under the assumption, that the orbitals $| e_x \rangle, | e_y \rangle$ can be made real. The equality must then hold as the matrix elements of the hermitian operator $\phi_y \hat{p}_z - \phi_z \hat{p}_y$ must be real, while the operator itself contains $i$. With real functions it must then yield 0. The second possibility can indeed be realized and we obtain for the negative $y$–component of $\nabla \phi \times \hat{p}$

$$
-(\phi_z \hat{p}_x - \phi_x \hat{p}_z) = iA |a_1 \rangle \langle e_x | + h.c.,
$$

(1.30)
where $iA = \langle a_1 \vert \phi_y \hat{p}_y - \phi_x \hat{p}_x \vert e_x \rangle$. The $x$–component of $\nabla \phi \times \hat{p}$ then takes the form of the partner of the expression above

$$\phi_y \hat{p}_y - \phi_x \hat{p}_x = iA |a_1 \rangle \langle e_y| + h.c. \tag{1.31}$$

The $z$–component of $\nabla \phi \times \hat{p}$ transforms as $A_2$ representation, meaning it can only take the form $|e_x \rangle \langle e_y| - |e_y \rangle \langle e_x|$. Introducing $iB = \langle e_x | \phi_x \hat{p}_y - \phi_y \hat{p}_x | e_y \rangle$, we obtain

$$\phi_x \hat{p}_y - \phi_y \hat{p}_x = iB |e_x \rangle \langle e_y| + h.c.. \tag{1.32}$$

The spin-orbit interaction (Eq. 1.28) for each hole then takes the form

$$\hat{H}_{so} = \frac{1}{2} \frac{iAe}{c^2 m_e^2} \left[ \begin{pmatrix} |a_1 \rangle \langle e_y| - |e_y \rangle \langle a_1| \\ - |a_1 \rangle \langle e_x| - |e_x \rangle \langle a_1| \end{pmatrix} \hat{s}_x \right]$$

$$+ \frac{1}{2} \frac{iBe}{c^2 m_e^2} \left[ \begin{pmatrix} |e_x \rangle \langle e_y| - |e_y \rangle \langle e_x| \end{pmatrix} \hat{s}_y \right]. \tag{1.33}$$

We note that the first two lines of this Hamiltonian, which we call transverse spin-orbit interaction (with a coupling constant $\lambda_\perp$), can not lift the degeneracy within the triplets $e^2(T)$ and $ea_1(T)$. Indeed, the transverse spin-orbit transforms by itself as an $A_1$ representation and its effect is in coupling $s^2(S)$ configuration to $ea_1(T)$ configuration. As always, only the levels of the same symmetry can be coupled through this Hamiltonian ($|e^2(S)_{A_1}\rangle$ to $|A_1\rangle$, $|e^2(S)_{S}\rangle$ to $|E_x, m_s = \pm 1\rangle$ and $|e^2(S)_{y}\rangle$ to $|E_y, m_s = \pm 1\rangle$). Note that this interaction changes the spin projection quantum number. The last line of the Hamiltonian (1.33), that we refer to as axial spin-orbit coupling (with a coupling constant $\lambda_z$), can only break degeneracy within $ea_1(T)$ configuration. Being spin conserving, it is unable to couple states of the same symmetry within $ea_1(T)$ configuration. So its action in the $ea_1(T)$ takes the form

$$\hat{H}_{so} = \lambda_z \left( |a_1 \rangle \langle A_1| + |A_2 \rangle \langle A_2| \right. \right.$$  

$$\left. - |E_x, m_s = \pm 1\rangle \langle E_x, m_s = \pm 1| - |E_y, m_s = \pm 1\rangle \langle E_y, m_s = \pm 1| \right), \tag{1.34}$$

where $\lambda_z = \frac{1}{4} \frac{Be}{c^2 m_e^2}$. We note that axial spin-orbit (Eq. 1.34) can be rewritten in a different form. If one introduces the states $|X\rangle = |e_x a_1 - a_1 e_x\rangle$ and $|Y\rangle = |e_y a_1 - a_1 e_y\rangle$ that form basis for the irreducible representation $E$ of the group $C_3v$, then $\hat{H}_{so}$ (Equation 1.34) takes the form

$$\hat{H}_{so} = i\lambda_z \left( |X\rangle \langle Y| - |Y\rangle \langle X| \right) \left( \hat{S}_z \right) \tag{1.35}$$

where $\hat{S}_z$ is a total z-spin projection operator of the two particles. Another effect of axial spin–orbit is coupling of triplets and singlet, in particular $|E_{x/y}, m_s = 0\rangle$ to $|ea_1(S)_{x/y}\rangle$ and $|^3A_{2g}\rangle$ to $|e^2(S)_{A_1}\rangle$. Within $e^2(T)$ electronic configuration the action of axial spin–orbit interaction is 0, as the matrix element of the Hamiltonian (1.33) is 0. The value of axial spin–orbit constant was measured to equal $\lambda_\perp = 5.3$ GHz [49, 60]. The transverse spin–orbit coupling manifests itself indirectly in the intersystem crossing processes (see 1.3) and the DFT predicts its value to equal $\lambda_\perp = 7.3$ GHz [44].
Effect of spin-spin interaction

We will now include the last intrinsic interaction, present in NV\textsuperscript{−} center, the spin-spin interaction. For the two holes it is described with the Hamiltonian
\[ \hat{H}_{ss} = -\frac{\mu_0 g_s^2 \mu_B}{4\pi} \left( \frac{\hat{S}_1 \cdot \mathbf{r} (\hat{S}_2 \cdot \mathbf{r})}{r^3} - \frac{\hat{S}_1 \cdot \hat{S}_2}{r^3} \right), \] (1.36)
where \( g \) is the electron Lande-factor, \( \mu_B \) is the Bohr magneton, \( \mu_0 \) is the vacuum permeability and \( \mathbf{r} \) is the vector connecting the holes. This Hamiltonian again transforms according to the \( A_1 \) representation. In principal, we could use this Hamiltonian to calculate the couplings between the levels in table 1.2 and express the coupling constants in terms of the matrix elements. That is why we will rewrite the Hamiltonian (1.36) using symmetry considerations and introducing the phenomenological couplings. The most important consequence of the spin-spin interaction is lifting the degeneracies within the spin triplet configuration tors. We must also remember that it transforms as an identity representation. Within the spin operators and is expressed as a sum of tensor products of spin and orbital operators. That is why we will rewrite the Hamiltonian (1.36) using symmetry considerations and introducing the phenomenological couplings. The most important consequence of the spin-spin interaction is lifting the degeneracies within the spin triplet configurations \( e^2(T) \) and \( ea_1(T) \). Generally, the spin-spin interaction must be quadratic in spin operators and is expressed as a sum of tensor products of spin and orbital operators. We must also remember that it transforms as an identity representation. Within the configuration \( e^2(T) \), the only orbital operator is \( |\beta A_2\rangle \langle \beta A_2| = |e_x e_y - e_y e_x\rangle \langle e_x e_y - e_y e_x| \) and it transforms as \( A_1 \) representation (a tensor product \( A_2 \times A_2 \)). The quadratic spin part of the interaction must then also transform as \( A_1 \). The only such spin configuration is \( S_z^2 \). The spin-spin interaction in the ground state then takes the form
\[ \hat{H}_{ss}^{gs} = \Delta_{gs} |\beta A_2\rangle \langle \beta A_2| \hat{S}_z^2 \]
\[ = \Delta_{gs} \left( |3^3 A_{2x}\rangle \langle 3^3 A_{2x}| + |3^3 A_{2y}\rangle \langle 3^3 A_{2y}| \right) \] (1.37)
and its effect is the splitting of the levels with spin projections \( \pm 1 \) from the level with spin projection 0. In the excited states there are more options. Based on the rules 1 – 9 of the remark 11\textsuperscript{[1]} we can construct the \( A_1 \) Hamiltonian using the right combinations of orbital and quadratic spin operators (1.15)
\[ \hat{H}_{ss}^{es} = \Delta_{es} \left( |X\rangle \langle X| + |Y\rangle \langle Y| \right) \hat{S}_z^2 \]
\[ + \frac{\Delta'}{2} \left( |X\rangle \langle X| - |Y\rangle \langle Y| \right) \left( \hat{S}_y^2 - \hat{S}_z^2 \right) - \left( |X\rangle \langle Y| + |Y\rangle \langle X| \right) \left( \hat{S}_x, \hat{S}_y \right) \]
\[ + \frac{\Delta''}{2} \left( |X\rangle \langle X| - |Y\rangle \langle Y| \right) \left( \hat{S}_x, \hat{S}_z \right) - \left( |X\rangle \langle Y| + |Y\rangle \langle X| \right) \left( \hat{S}_y, \hat{S}_z \right) \] (1.38)
A more careful inspection of Hamiltonian (1.36) shows that in addition to Equation (1.38) the whole \( ea_1(T) \) configuration is shifted down by \( \frac{\Delta}{2} \Delta_{es} \) (the operator \(|X\rangle \langle X| + |Y\rangle \langle Y| \) transforms as \( A_1 \) even without spin). Let us analyze the effect of the Hamiltonian (1.38). The first line splits the states with \(|E_{x/y}, ms = 0\rangle\) from the four other levels. The second line splits the levels \( A_1 \) and \( A_2 \). The third line changes the spin projection quantum number, so it mixes \(|E_{x/y}, ms = 0\rangle\) with \(|E_{x/y}, ms = \pm 1\rangle\). We can thus rewrite the Hamiltonian (1.38) in another form
\[ \hat{H}_{ss}^{es} = \frac{\Delta_{es}}{3} + \Delta' \left( |A_2\rangle \langle A_2| - |A_1\rangle \langle A_1| \right) \]
\[ - \Delta_{es} \left( |E_x, ms = 0\rangle \langle E_x, ms = 0| + |E_y, ms = 0\rangle \langle E_y, ms = 0| \right) \]
\[ + \Delta'' \left( i |E_x, ms = \pm 1\rangle \langle E_x, ms = 0| + i |E_y, ms = \pm 1\rangle \langle E_y, ms = 0| + h.c. \right) \] (1.39)
The energy diagram of the NV$^-$ center. The left part describes the spin triplet states. From left to right the splittings due to first Coulomb, then spin-orbit and finally spin-spin interactions are shown. The green circular arrow marks the spin mixing transitions due to spin-spin interaction. The right part of the figure marks the spin singlet states. With dashed lines we also show non-radiative transitions between triplets and singlets assisted with spin-orbit interaction.

The values of the spin-spin constants slightly vary from experiment to experiment. From the experiments of Ref. [49, 50] the values of $\Delta_{ss}$ and $\Delta'$ are 1.4 GHz and 1.5 GHz respectively, while the spin mixing constant $\Delta''$ is 154 MHz according to Ref. [50] and 200 MHz according to Ref. [49].

The effect of all the interactions described above is summarized in Figure 1.5. We now see clearly that inclusion of all interactions present in NV$^-$ center removes all the accidental degeneracies. Now only the partners from the irreducible representation $E$ still remain degenerate. These degeneracies can be removed though, if one applies external field to the system, that we will consider in the next section. Another important remark concerns the temperature dependence of the level structure of NV$^-$ centers. The structure considered above will be scrambled if the temperature rises high enough. This is a result of the thermal phonons, that induce transitions between the orbital levels $|X\rangle$ and $|Y\rangle$. These processes result in termal averaging of these states [45] and their indistinguishability. In other words, the width of the orbital levels becomes higher than the distance between them. As a result one has to deal with a spin-triplet level structure, similar to the one we observed for the ground state, where the orbital doublet behaves as one level. In the rest of the thesis, unless otherwise mentioned, we assume the temperature to be low enough, so the NV$^-$ center level structure can be well resolved.
1.2.3 Interaction of NV$^-$ center with external fields

The effect of external fields on the energy levels of the NV$^-$ center can as well be analyzed from symmetry point of view. The only remark we need to make here is that now the transformations of the symmetry group act not only on the degrees of freedom of the NV$^-$ center, but also on the external degrees of freedom as well. What it means is that if inside of the interaction Hamiltonain we have an external vector field with component $(f_x, f_y, f_z)$, then the symmetry group transforms these into $(f'_x, f'_y, f'_z)$, where $r'$ are the coordinates along the transformed axes as in the remark 7. For axial vectors the same is true, except that one manually has to take into account that the inversion leaves the axial vector intact. In other words, all vector fields transform as momentum operator, while all axial fields transform as angular momentum operator. A more interesting situation appears for the transformation of tensors. For the needs of this thesis we will only be interested in strain $\epsilon = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{pmatrix}$ and stress $\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$ tensors. These are symmetric second rank tensors with the following transformation rule induced on them by the operations $(T)$ of the group $C_{3v}$

$$\epsilon \rightarrow \epsilon' = \hat{O}_T \epsilon = R_T^{-1} \epsilon R_T,$$

(1.40)

where the square orthogonal matrix $R_T$ describes the transformation of the basis vectors of the coordinate system. This transformation just relates the components of the tensor in one coordinate system to those in the other coordinate system in exactly the same manner, as we saw it for vectors (remark 7). The strain tensor transforms in exactly the same way and from now on we will use this rule interchangably for the two tensors. Using the orthogonality of $R_T$ we have $R_T^{-1} = (R_T)^T$. It is then straightforward to write the rule in the form $\hat{O}_T \epsilon = R_T^{-1} \epsilon R_T = \sum_{i,j} \epsilon_{ij} (R_T)_{ik} (R_T)_{jk} \epsilon_{ij}$. If we introduce two sets of bases functions $\psi_x, \psi_y, \psi_z$ and $\phi_x, \phi_y, \phi_z$, that transform as bases vectors of the coordinate system (in other words transform as real vectors), this transformation rule will coincide with that of $\psi_i \phi_j$, if in all expressions we will substitute $\psi_i \phi_j \rightarrow \epsilon_{ij}$. From the remark 11 we know exactly which combinations of products $\psi_i \phi_j$ form the bases functions for the irreducible representations of the $C_{3v}$ group. We can then conclude

$$\epsilon_{xx} + \epsilon_{yy} \in A_1,$$

$$\left\{ \frac{\epsilon_{xx} - \epsilon_{yy}}{2}, \frac{\epsilon_{xy} + \epsilon_{yx}}{2} \right\} = \left\{ \frac{\epsilon_{xx} - \epsilon_{yy}}{2}, -\epsilon_{xy} \right\} \in E,$$

(1.41)

$$\epsilon_{zz} \in A_1,$$

$$\left\{ \epsilon_{xz}, \epsilon_{yz} \right\} \in E$$

In the second line we used the symmetry of the stress tensor. We note that in any symmetric real tensor only six components are independent and we now know according to which representation each of them transforms.

The effect of fields on the ground state

We begin our consideration with the effect of fields on the ground state. It is a spin triplet and so it does not couple directly to the electric field and strain (these effects though are present in the second order in spin and we will consider them in Chapter 2). One could argue that this coupling could happen indirectly through higher orbitals, but we disregard it as well, because all interactions in nature are described with Hamiltonians, that are real scalars. The product of spin operators and real field would always be an axial scalar though. But the spin can be coupled to magnetic field and the most general form of this
interaction, that transforms as a symmetric representation $A_1$ takes the form

$$H_{gs} = g_{gs} \mu_B (B_x \hat{S}_x + B_y \hat{S}_y) + g_{es} \mu_B B_z \hat{S}_z,$$

(1.42)

where $B$ is the magnetic field and $g_\perp, g_\parallel$ are axial ant transverse g-factors. We note that fundamentally this interaction should be symmetric with $g_\perp = g_\parallel = 2$, but because of the solid state environment indirect coupling through higher orbitals occurs, modifying g-factors and reducing the symmetry of the Hamiltonian from full rotation group to the $C_{3v}$ group. The measurement reveals that both $g_\perp$ and $g_\parallel$ are approximately 2, as in vacuum [53].

The effect of fields on the excited state spin triplet

We now consider the effect of fields on the excited state spin triplet $e^2(T)$. We will only be interested in the effect that can lift degeneracies within the excited state. We thus do not consider orbital operator $|X\rangle \langle X| + |Y\rangle \langle Y|$, that lifts all six levels as a whole. We actually did the same for the ground state as well. The complication in the excited state with respect to the ground state comes from the fact that there is also an orbital degree of freedom here. For the electric field $E = (E_x, E_y, E_z)$, the most general form of the interaction within the excited state takes the form

$$H_{es}^{ef} = d_{es}^\perp \left[ E_x \left( |X\rangle \langle X| - |Y\rangle \langle Y| \right) - E_y \left( |X\rangle \langle Y| + |Y\rangle \langle X| \right) \right],$$

(1.43)

where $d_{es}^\perp$ is the transverse dipole moment. From equations (1.41), the most general form in which strain can couple to the excited state is

$$H_{es}^{ef} = s_1 \left[ \epsilon_{xx} - \epsilon_{yy} \right] \left( |X\rangle \langle X| - |Y\rangle \langle Y| \right) + \epsilon_{xy} \left( |X\rangle \langle Y| + |Y\rangle \langle X| \right)$$

$$+ s_2 \left[ \epsilon_{xz} \left( |X\rangle \langle X| - |Y\rangle \langle Y| \right) - \epsilon_{yz} \left( |X\rangle \langle Y| + |Y\rangle \langle X| \right) \right].$$

(1.44)

Here $s_1$ and $s_2$ are strain coupling coefficients in the excited state. We note that it is not possible to distinguish the action on the excited state of those stress components, that have the same symmetry. We finally approach the action of the magnetic field on the excited state spin triplet. It should be noted that the magnetic field can couple not only to spin, but also to orbital angular momentum. The transverse orbital angular momentum operators could in principal be described with $|X\rangle \langle X| - |Y\rangle \langle Y|$ and $- \left( |X\rangle \langle Y| + |Y\rangle \langle X| \right)$. In reality these operators do not appear for the same reason as in the spin-orbit interaction we had no transverse coupling within the excited state. The orbital wave functions can be made real, while the angular momentum operators $\hat{l}_x, \hat{l}_y$ are imaginary and hermitian, thus $\langle X| \hat{l}_{x/y} |X\rangle = \langle X| \hat{l}_{x/y} |Y\rangle = 0$. Then the most general form of the interaction of magnetic field and the excited state spin triplet takes the form

$$H_{es}^{mf} = g_{es} \mu_B (B_x \hat{S}_x + B_y \hat{S}_y) + g_{es} \mu_B B_z \hat{S}_z + l_{es} \mu_B \left( |X\rangle \langle X| - |Y\rangle \langle Y| \right) B_z.$$

(1.45)

Here $g_{es}^\parallel = 2.15$ [50] and $g_{es}^\perp \approx 2$ are axial and transverse g-factors respectively, while $l_{es} = 0.1$ [51] describes the magnitude of the z-component of the orbital angular momentum.

The interactions we have considered by now are all direct couplings of electric field, strain and magnetic field to orbital and spin degree of freedom, that can lift the degeneracies within the excited and ground state spin triplets. The last remark we are going to make here is that there is a non zero dipole moment matrix element between
the state $|e_xe_y - e_ye_x\rangle$ (transforms as $A_2$) and the levels $|X\rangle$ and $|Y\rangle$. Indeed, from symmetry point of view (remark [11]) $\{-y|x|e_xe_y - e_ye_x\rangle, x|e_xe_y - e_ye_x\rangle\}$ form basis for the irreducible representation $E$. Then the matrix elements $\langle X|(-y)|e_xe_y - e_ye_x\rangle$ and $\langle Y|x|e_xe_y - e_ye_x\rangle$ are allowed to be nonzero. Moreover they can be shown to be equal. For that one has to notice that $\langle Y|(-y)|e_xe_y - e_ye_x\rangle = \langle X|x|e_xe_y - e_ye_x\rangle = 0$ from the orthogonality of functions belonging to different symmetries. On the other hand $\langle Y|(-y)|e_xe_y - e_ye_x\rangle + \langle X|x|e_xe_y - e_ye_x\rangle = 0$ transforms as the second row of the representation $E$. That means its partner $\langle X|(-y)|e_xe_y - e_ye_x\rangle - \langle Y|x|e_xe_y - e_ye_x\rangle$ is zero as well. It immediately follows that $\langle X|(-y)|e_xe_y - e_ye_x\rangle = \langle Y|x|e_xe_y - e_ye_x\rangle$.

This result can be put on more general grounds using Wigner-Eckart theorem [43], but we will not go deeper into this here. The presence of this dipole moment is one of the most important properties of an NV$^-$ center. First of all, it allows optical manipulation with the levels of the center, as the ground state spin triplet can be coherently coupled to the excited state spin triplet through a spin-conserving electric dipole transition with a laser of right frequency. The frequency of the zero-phonon line lies in the optical domain at 1.945 eV (632 nm) and it turns out it gives a simple way to initialize and read out the spin state of the system, as we will show in the next section.

1.3 Optical spin polarization and optically detected magnetic resonance (ODMR)

One of the key ingredients that makes the NV$^-$ center so attractive for quantum technology applications is the possibility to optically manipulate its spin state. In this section we will explain the key features that make such a manipulation possible. In general the dynamics of the NV$^-$ center under optical excitation is a complicated issue by itself and is not fully experimentally resolved by now. Apart from the effects considered above, one must also consider the vibrational degrees of freedom, that interact with the orbital degrees of freedom of the NV$^-$ center through Jahn-Teller interaction [46, 47]. We will not consider those here, but will present the mechanism in general, making remarks about what the inclusion of these interactions would bring. We will refer to levels and interactions as they are depicted in Figure 1.5, but for the sake of clarity we redraw this figure to contain only the levels relevant for the optical NV$^-$ dynamics (Figure 1.6). We will neglect the spin mixing ($\Delta^\prime$) spin-spin interaction, as it is an order of magnitude smaller that the gap between $m_s = 0$ and $m_s = \pm 1$ states. We will assume that the defect is subject to optical illumination, that excites the ground state triplet to the excited state triplet. Usually, the green laser is used, that also excites localized phonon modes (the vibrations of the atoms close to the NV$^-$ center). These phonon modes relax to the vibronic ground states in picoseconds (faster than any other relevant time scale in the system). The whole process of laser excitation then results into incoherent spin conserving excitation of ground state to the excited states. The system then ends up in the six levels of $e\alpha_1(T)$ manifold ($|A_1\rangle, |A_2\rangle, |E_{x/y}, m_s = 0\rangle, |E_{x/y}, \pm 1\rangle$). In principal another scheme exists, where the red laser is used, that is tuned in resonance with one of the transitions from ground to excited state (the frequency of the zero-phonon line) [52]. In that case one can also create coherence between ground and excited states as well as within the excited state manifold, but for now we will not be interested in this effect. If there were no singlet levels, the system would relax back to the ground state through a radiative orbital relaxation channel (blue errors in the left part of figure 1.6) with a relaxation time of approximately 12 ns [53]. All these processes we have described by now conserve spin and thus if the system starts in the incoherent mixture of different spin states we will not be able to
polarize the spin to one preferable direction. It turns out though that the presence of singlets allows for the process called intersystem crossing (ISC), when the excited spin triplet levels relax to the spin singlet manifold. Let us consider the level \( A_1 \) of the \( e_e(T) \) manifold. It turns out that it can relax to the level \( e^2(S)_{A_1} \) emitting a phonon (Figure 1.6). At first glance it seems to be impossible, as the electron-phonon interaction can not change the spin state of the defect. What happens is that the levels \( A_1 \) and \( e^2(S)_{A_1} \) become mixed through transverse spin-orbit interaction (dashed line in Figure 1.5). This mixing is enough for phonon emission matrix element to become nonzero. Other spin-orbit channels from figure 1.5 seem to be negligeable in this regard and we will not consider them here. This is the strongest non-radiative decay path for NV\(^-\) center, with the relaxation rate approximately half of that for the radiative decay \([5]\). From the level \( e^2(S)_{A_1} \) the system fastly (in less than 1 ns \([54]\)) decays to the level \( e^2(S)_{x/y} \) either through emitting a phonon or through emitting an infrared photon. In this orbital doublet the system gets trapped for approximately 375 ns \([55]\) at low temperature, until it relaxes back to the ground state manifold \( |^3A_{20}\rangle, |^3A_{2x}\rangle, |^3A_{2y}\rangle \). This transition is again forbidden and even spin-orbit interaction can not save the situation. To explain it one has to include mixing of the doublet \( e^2(S)_{x/y} \) with \( e^2(S)_{A_1} \) through Jahn-Teller interaction (lowers the symmetry of the system, thus allows coupling between levels of initially different symmetry) and with \( a^2(S)_{x/y} \) through electron-electron interaction \([47]\). The decay rates to each of the corresponding states \( |^3A_{20}\rangle, |^3A_{2x}\rangle, |^3A_{2y}\rangle \) are comparable and \( \Gamma_0/2\Gamma_\pm = 1.3 \) \([50, 55]\).
This closes the optical excitation cycle. The system initially brought with a laser to the excited state returns to the ground state. It is important to notice that the intersystem crossing is strongest for the \( A_1 \) level, that has a spin projection \( \pm 1 \). In this simple picture we see that it provides a spin flipping channel, when a \( \pm 1 \) spin projection is converted to 0. Many cycles of optical excitation will then polarize the spin to \( m_s = 0 \). Indeed, from spin 0 the transitions are spin conserving, while every time the population is in states with \( m_s = \pm 1 \) there is a non-zero probability it will convert to \( m_s = 0 \). This results in the biexponential decay of the system to the spin 0 state. A more rigorous analysis shows that ISC can also occur from the states with \( m_s = 0 \) because of Jahn-Teller interaction in the excited state spin triple. Still the rates for these ISC are smaller than for \( m_s = \pm 1 \) levels and polarization still takes place. This simple procedure initializes the spin with efficiency of more than 90% fidelity within a few optical cycles. The spin is then ready for further manipulations with microwave excitation. The discussion above suggests that whenever the spin is in \( \pm 1 \) state, the probability for a non-radiative decay is higher than that for the state \( m_s = 0 \). The radiative decay is then more probable for the state \( m_s = 0 \). In that case one will get higher luminescence signal whenever the system is in the state \( m_s = 0 \). This gives an efficient way to read out the state of the system. After all the necessary manipulations on the spin are done, one needs to perform the optical polarization procedure. Repeating this sequence many times and gathering statistics on the number of photons, emitted at time \( \tau \) after the optical pulse switching, one constructs the photoluminescence time trace and calculates the photoluminescence intensity as a function of \( \tau \). The intensity at \( \tau = 0 \) (right after switching the optical pulse on) contains information on whether the spin is in 0 or \( \pm 1 \) states.

This gives rise to the technique known as optically detected magnetic resonance (ODMR). One applies microwave excitation to drive transitions between different spin sublevels of an NV\(^-\) center. Once the frequency of the microwave drive coincides with the level splitting in the ground state, the coherent oscillations of spin occur, the effect known as magnetic resonance. That changes the occupation of \( \pm 1 \) and 0 spin sublevels, that can later be measured applying an optical pulse.

### 1.4 Quantum Information

The aim of this section is to briefly introduce the reader to the field of quantum information (QI) science. We will discuss the range of problems that QI science is trying to solve. We will not so much discuss the physical realizations of quantum hardware. In fact this thesis is about only one such realization, where the quantum bits (qubits) are encoded in the energy levels of a nitrogen-vacancy center in diamond. As it will be important for the future chapters, we will separately discuss the so called geometric quantum computing, that is resilient to certain types of noise and is a good alternative to conventional methods to do quantum computing.

#### 1.4.1 Basic notions of Quantum Information

In classical information theory a binary computation is used, and the information is encoded in bits, that can take only two values 0 and 1. Indeed, this is the most natural way to encode information in the classical physical systems, 0 can then correspond to absence of magnetization, current, voltage, magnetic flux etc., depending on the type of hardware that is used to store classical information. The logical value 1 then corresponds to the presence of the things listed above.

Quantum information is different from the above, as instead of bits it uses quantum bits (qubits), that are quantum two-level systems. These can also be in the states \(|0\rangle\) and \(|1\rangle\).
but these states are now quantum and thus any superposition state
\[ |\psi\rangle = \cos(\theta/2) |0\rangle + e^{i\phi} \sin(\theta/2) |1\rangle \]  

is also a physical state, that can exist in real world. Obviously, the ability of qubits to be in this superposition is their main difference from classical bits, as in classical physics, for example, we can not imagine to have a superposition of present and absent magnetization. As it is well known in quantum physics, the overall phase does not change the physical state, thus equation (1.46) is the most general form of the pure state of a two-level system. In order not to be concerned with an overall phase at all, one can also change the description of the system from states to density matrices
\[ \rho = |\psi\rangle \langle \psi| = \begin{pmatrix} \cos^2(\theta/2) & \cos(\theta/2) \sin(\theta/2) e^{-i\phi} \\ \cos(\theta/2) \sin(\theta/2) e^{i\phi} & \sin^2(\theta/2) \end{pmatrix}, \]  

written in the bases |0\rangle and |1\rangle. Introducing the Pauli matrix vector \( \sigma = (\sigma_x, \sigma_y, \sigma_z) \),
\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \]  

we can rewrite Eq. (1.47) in the following form
\[ \rho = \frac{1}{2}(1 + p \cdot \sigma). \]  

Here \( p = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \) is the unit vector called the Bloch vector. We thus see that any pure state of a two level system (Eq. 1.46) can be represented as a density matrix (Eq. 1.47), which in turn is uniquely represented with a vector of length one. In other words, each pure quantum state of a two level system corresponds to a point on the surface of the sphere of unit radius, called the Bloch sphere (Fig. 1.7). A two-level

Figure 1.7: A Bloch sphere of unit radius. Each point on its surface with the coordinates \( p = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \) represents a pure quantum state \( |\psi_{\theta,\phi}\rangle = \cos(\theta/2) |0\rangle + e^{i\phi} \sin(\theta/2) |1\rangle \). The points inside the Bloch sphere with \( |p| < 1 \) correspond to mixed state of the system.
so-called Bell states

Each of these bases states is a so-called product state \((1.49)\), but in that case the vector \(p\) has a norm smaller than unity \(|p| < 1\).

A superposition principle by itself, applied to a single particle, is almost useless, as the measurement would anyway yield either \(0\) or \(1\), as in the classical case. What really makes things different are the possible quantum correlation between different particles, that manifest themselves in the property known as entanglement. Indeed, if we have two two-level systems \(A\) and \(B\), the Hilbert space they live in is spanned by \(\{|00\rangle, \{01\rangle, \{10\rangle, \{11\rangle\}\}.\)

Each of these bases states is a so-called product state \((1.50)\), but in that case the vector \(p\) has a norm smaller than unity \(|p| < 1\).

\[
\psi^\pm = \frac{1}{\sqrt{2}} (|00\rangle \pm |11\rangle),
\]

\[
\phi^\pm = \frac{1}{\sqrt{2}} (|01\rangle \pm |10\rangle),
\]

they can by no means be written as a product \(|\psi\rangle_A \otimes |\psi\rangle_B\). This is an example of an entangled state, which plays a major role in the applications of quantum information and allows one to do things that would not be possible with classical information systems.

As a particular example of the concepts introduced above, let us consider the protocol of quantum teleportation \([56]\). We start with two parties, Alice and Bob, that share an entangled pair of qubits \(|\psi^-\rangle_{AB} = \frac{1}{\sqrt{2}}(|0\rangle_A |1\rangle_B - |1\rangle_A |0\rangle_B\). Alice has the qubit \(A\) in her disposition, while Bob has the qubit \(B\). Also Alice has an additional qubit in the unknown state \(|\phi\rangle_Z = \alpha |0\rangle_Z + \beta |1\rangle_Z\). She wants to teleport the state of this qubit to Bob. The allowed operations on the qubits are local gates and measurements. Also classical communication channels are allowed (the result of the measurement can be transmitted via phone or email). To understand how the protocol works, it is convenient to rewrite the full quantum state of the three qubits:

\[
|\psi\rangle_{total} = (\alpha |0\rangle_Z + \beta |1\rangle_Z) \otimes \frac{1}{\sqrt{2}}(|0\rangle_A |1\rangle_B - |1\rangle_A |0\rangle_B)
\]

\[
= \frac{1}{2} (|\phi^+\rangle_{ZA} [\alpha |1\rangle_B - \beta |0\rangle_B] + |\phi^+\rangle_{ZA} [\alpha |1\rangle_B + \beta |0\rangle_B] + |\phi^-\rangle_{ZA} [-\alpha |0\rangle_B + \beta |1\rangle_B] + |\phi^-\rangle_{ZA} [-\alpha |0\rangle_B - \beta |1\rangle_B]).
\]

Now the following steps are taken by Alice and Bob.

1. Alice performs a measurement in the Bell bases of the qubits \(Z\) and \(A\), that projects the qubits \(A\) and \(B\) to one of the four states \(|\phi^\pm\rangle\), \(|\psi^\pm\rangle\).

2. Alice communicates the outcome of the measurement to Bob via a classical channel.

3. Depending on the information obtained from Alice Bob performs a single qubit gate on the qubit \(B\), that is in his possession:

   - If Alice measured \(\phi^+\), Bob’s qubit is in the state \(\alpha |1\rangle_B - \beta |0\rangle_B\), so he performs an \(i\sigma_y\) gate on his qubit \([\alpha |1\rangle_B - \beta |0\rangle_B] \rightarrow i\sigma_y [\alpha |1\rangle_B - \beta |0\rangle_B] = [\alpha |0\rangle_B + \beta |1\rangle_B].\)

   - If Alice measured \(\phi^-\), Bob’s qubit is in the state \(\alpha |1\rangle_B + \beta |0\rangle_B\), so he performs a \(\sigma_z\) gate on his qubit \([\alpha |1\rangle_B + \beta |0\rangle_B] \rightarrow \sigma_z [\alpha |1\rangle_B + \beta |0\rangle_B] = [\alpha |0\rangle_B + \beta |1\rangle_B].\)

   - If Alice measured \(\psi^+\), Bob’s qubit is in the state \(-\alpha |0\rangle_B + \beta |1\rangle_B\), so he performs a \(\sigma_z\) gate on his qubit \([-\alpha |0\rangle_B + \beta |1\rangle_B] \rightarrow -\sigma_z [-\alpha |0\rangle_B + \beta |1\rangle_B] = [\alpha |0\rangle_B + \beta |1\rangle_B].\)
• If Alice measured $\psi^-$, Bob’s qubit is in the state $-\alpha |0\rangle - \beta |1\rangle$ that is a desired state up to an overall phase (which has no physical meaning).

We note that at the end of the protocol the unknown state of qubit $Z$ has been teleported to the qubit $B$. At the end of the protocol the qubit $Z$ is in the Bell state with the qubit $A$ and it has no memory of its initial state. This agrees with the non-cloning theorem, stating that an unknown state of the system can not be copied perfectly without destroying the source [57].

As we already saw, the operations on the quantum states are performed through the application of unitary operators. In the case of single qubit, these are $2 \times 2$ unitary matrices with unit determinant (this last property is not so important, as the overall phase of the gate has no physical meaning), that form a group $SU(2)$. It can be shown that an action of $SU(2)$ matrices on the states (1.46) is equivalent to a rotation on the Bloch sphere around certain axis. For example, the Pauli gates $\sigma_x, \sigma_y, \sigma_z$ are equivalent to rotations by $\pi$ around $x$-, $y$- and $z$-axes respectively. In general, rotation by $\alpha$ around an axis $n$ on the Bloch sphere corresponds to the unitary operation $\exp\left(-\frac{\alpha}{2} n \sigma\right)$. Another important single-qubit gates are Hadamard- and Phase-gates:

$$H = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix},$$

$$\Phi = \begin{pmatrix} 1 & 0 \\ 0 & e^{i\Phi} \end{pmatrix}.$$  \hspace{1cm} (1.52)

Hadamard gate can be thought of as a $\pi$–rotation around the axis, that is $45^\circ$ to the $x$– and $z$–axes. A $\Phi$-gate is a rotation by $\Phi$ around the $z$–axis of the Bloch sphere. For two qubit gates, unfortunately, there is no such simple interpretation. Two important examples of such gates are CPHASE and CNOT two-qubit gates:

$$\text{CPHASE} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & e^{i\phi} \end{pmatrix},$$

$$\text{CNOT} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}.$$  \hspace{1cm} (1.53)

Accomplishing a specific algorithm on a quantum platform requires performing the quantum gates in a specific order. Due to the fact that qubits are always realized on specific quantum platforms, that have certain form of interaction Hamiltonian, not every gate can be obtained as the exponent of this Hamiltonian. It is thus important to understand what is the minimal set of gates one needs to be able to run any algorithm. For a single qubit it is enough to be able to perform $H$– and $\Phi$–gates to generate any rotation on the Bloch sphere. If one adds a CNOT gate to this universal set of single qubit gates, it has been shown that any algorithm can be performed on such a quantum platform [58].

### 1.4.2 Applications of Quantum Information

**Quantum key distribution**

The security of information is one of the most important issues of our time. The situation is rather simple, Alice wants to share some information with Bob, so that Eve could not eavesdrop anything from that information. The ways to accomplish that are studied by the branch of mathematics called cryptography. The way most communication channels
are protected nowadays is based on the asymmetric encryption. It relies on the existence of private and public keys, that are generated by Bob. They are not independent, if one knows the private key, one can calculate the public key and vice versa. The asymmetry of the algorithm means that it takes little time to calculate public key with a private one, but it is computationally hard to compute a private key from the public one. For example, if the private key is a pair of big prime numbers and the public key is their product, factorization of this product takes exponential time with a classical computer. The messages are encrypted with a public key, but can only be decrypted with a private key. Bob then generates a private key, calculates a public key and makes this public key available to whoever wants to contact him. Alice then uses the public key to encrypt a message and sends it to Bob. Because no one, except for Bob, has the private key, Alice and Bob can be sure that their message is not read by Eve. The security of this algorithm relies on the mathematical complexity of certain operations, but it is not secure in the absolute sense. It is assumed, that it should take a lot of time to break the private key, but it does not mean it can not be broken. Besides, as we will see further, quantum computer could factorize the numbers a lot faster than the classical computer, which makes these algorithms vulnerable to future technologies.

The cryptographic algorithm, that can be proved secure from mathematical point of view, relies on the existence of the secret key that is shared between Alice and Bob prior to communication. This key is essentially a random number, as long as the message the parties are about to transmit. In classical communication theory, Alice and Bob have to first meet and share the key, before they transmit the message through the communication channel. This is hard to do in practice, as people do not always meet personally before they communicate. The quantum key distribution is a way to overcome this problem. A secret random key is generated by Alice and has to be sent to Bob in a secure way. Alice encodes this key in the state of some number of qubits and teleports them to Bob (she treats the states as unknown). As we saw before, it is not possible to copy the unknown state (non-cloning theorem). Thus either Bob receives the state Alice sends and Eve gets nothing or vice versa Eve has the state and Bob not. Non-cloning theorem suggests that the laws of quantum physics forbid Eve to spy and be unrevealed, only one party can get the information about the state. Alice and Bob then communicate classically to figure out whether Bob did receive the right state or not. If not, they detect that Eve got the state and this state is discarded. If the state was correct, they use it for the key, as they are sure Eve does not know it. The quantum key distribution thus allows secure communication between Alice and Bob, relying fully on the laws on nature.

Quantum Computation

A classical computer applies logical gates to classical bits to generate certain function \( f : \{0, 1\}^n \rightarrow \{0, 1\}^l \). For example a NOT operation corresponds to a function \( f(x) = (1 - x) \). A two-bit AND gate is described with a function \( f(00) = 0, f(01) = 0, f(10) = 0, f(11) = 1 \).

A quantum computer applies quantum gates instead. It turns out that the superposition principle and entanglement allow the quantum computer to solve certain tasks asymptotically faster than any classical computer would. Here we will briefly review the most well known algorithms that a universal quantum computer is supposed to perform. The first algorithm that had advantage over a classical computer was developed by David Deutsch in 1985 \[59\]. It shows an advantage of a quantum computer over a classical one when understanding whether a binary function is balanced or not.

Much later in 1997 a Grover search algorithm was invented \[60\]. The problem is that of finding a given number \( i \) in an unsorted list of \( N \) numbers. Classically, it would take \( O(N) \) queries to find this number (each query is a comparison operation between \( i \) and the
current number in the list). Grover’s algorithm can accomplish this task in $O(\sqrt{N})$ queries. It operates as follows. With each number in a list we associate a quantum state $|i\rangle$. First a superposition state $|\psi\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} |j\rangle$ is created. We also introduce a superposition of all the wrong results $|B\rangle = \frac{1}{\sqrt{N-1}} \sum_{j \neq i} |j\rangle$. Then

$$|\psi\rangle = \frac{1}{\sqrt{N}} |i\rangle + \frac{\sqrt{N-1}}{\sqrt{N}} |B\rangle = \sin(\phi) |i\rangle + \cos(\phi) |B\rangle,$$

where $\phi \simeq 1/\sqrt{N}$. We define two unitary gates

$$\hat{U}_1 = 1 - 2 |i\rangle \langle i|,$$

that requires one quantum comparison operation and is performed in $O(1)$ number of operations and

$$\hat{U}_2 = 2 |\psi\rangle \langle \psi| - 1,$$

known as Grover’s diffusion operator. A basic step of the Grover’s algorithm is application of $U_2U_1$ to the state of the system. It can be shown that one such iteration is equivalent to rotation by $2\phi$ in the plane with bases vectors $|i\rangle$ and $|B\rangle$. Applying this rotation approximately $\pi \sqrt{N}/4$ times rotates the state $\psi$ to the state $i$. The complexity of Grover’s quantum search algorithm is thus $O(\sqrt{N})$, which gives an advantage over classical search algorithms.

Another extremely important algorithm is a Shor’s algorithm. It allows to factor a big number $N$ into prime factors in time, that is polynomial in $N$, while all classical algorithms do it in time, that is exponential in $N$. It can be shown using group theory that this problem is equivalent to finding a period in $k$, such that $2^k \mod N$ are the same. It can easily be checked that indeed the same reminder appears periodically in $k$. A quantum computer uses quantum parallelism to solve this problem. The steps of the algorithm are the following

1. Initialize the input qubits in the superposition

$$|\psi\rangle = \frac{1}{2^{N/2}} \sum_{k=1}^{N} |2^k\rangle$$

2. Add the auxiliary qubits in $|0\rangle$ state

$$|\psi\rangle \otimes |0\rangle = \frac{1}{2^{N/2}} \sum_{k=1}^{N} |2^k\rangle \otimes |0\rangle$$

3. Apply a function $f$, that for an input state $|x\rangle$ returns $|f(x) = x \mod N\rangle$ in the auxiliary qubits. The state $|\psi\rangle \otimes |0\rangle$ then evolves to

$$|\psi\rangle \otimes |0\rangle \rightarrow \frac{1}{2^{N/2}} \sum_{k=1}^{N} |2^k\rangle \otimes |f(2^k)\rangle$$

4. Now one measures the auxiliary qubits in the natural basis ($|0\rangle$ and $|1\rangle$). It collapses the auxiliary qubits to some state, that corresponds to periodically separates input states. The total state of the system after the measurement is thus

$$|\phi_f\rangle = \frac{1}{\sqrt{[(N-a)/p]}} \sum_{k=1}^{[(N-a)/p]} |2^{a+ksp}\rangle \otimes |f(2^a)\rangle$$
5. From this final state $|\phi_f\rangle$ the period $p$ can be extracted through the application of the so called quantum Fourier transform, which we will not discuss here.

With this we would like to end the discussion about quantum computing. It should be noted, that performing any of the algorithms above requires the so called universal quantum computer, i.e. one needs to be able to perform a universal set of quantum gates (see discussion above). Besides, the computation should take shorter than the decoherence time of the system. The five criteria that a physical platform should satisfy in order to be the suitable for a universal quantum computer have been given by David DiVincenzo in the year of 2000 \[61\] and for now no platform has been able to meet all five of them at the same time. There is a lot of progress though in building rather small quantum machines, that can already simulate the complex quantum dynamics. These machines play the same role in quantum information as the analog computers played in classical one. They are thus capable of performing some specific task, can only run limited number of algorithms, unlike the universal quantum computer, that can solve any problem and run any algorithm. Needless to say, even this limited performance can give better results for certain classes of problems than the classical computer does and can help physicist simulate quantum materials with non trivial interactions.

1.4.3 Geometric Quantum Computation

As we saw before, for quantum computing to work, one must be able to efficiently manipulate the state of the quantum device with high gate fidelity in order to either perform sufficiently long quantum computations without error correction \[62\] or to allow for fault-tolerant quantum operation \[63\]. Most proposed and implemented quantum processors use dynamical protocols to manipulate the quantum state of the device by controlling a non-zero Hamiltonian $H(t)$ acting on the quantum register directly to generate the time evolution $U = T \exp(-i \int H(t) dt)$. Alternatively, geometric phases \[64\] and their non-Abelian generalizations arising after a cyclic adiabatic evolution of the system can be used to realize universal quantum gates \[65, 66\]. In this case the system is initialized in the dark subspace of its Hamiltonian and due to the adiabatic theorem remains there as the Hamiltonian is slowly changed in time. This method can provide an intrinsic tolerance against certain types of noise \[67, 68\] and was realized experimentally in NMR systems \[69\]. Later, proposals based on tripod systems \[70–72\] were experimentally applied to realize single qubit rotations in trapped ions \[73\]. There are other proposals to realize geometric gates in systems of superconducting qubits \[74\]. Geometric gates can also be constructed using non-adiabatic evolution \[75, 76\]. Relaxing the adiabaticity condition makes it simpler to perform gates, and non-adiabatic geometric gates have indeed been successfully realized with superconducting qubits \[77\], NMR systems \[78\] and with the electron spin of nitrogen-vacancy centers \[41, 79, 80\]. In this chapter we will quickly remind what the geometric phases are and how they are used to perform quantum gates. We will first consider the following example. Let the system be driven with a Hamiltonian $\hat{H}$ for a time $\tau$. Let the Hilbert space of the system be parametrized with a vector of parameters $\lambda$ as $|\phi(\lambda)\rangle$. The system evolves according to the Schrödinger equation $i\hbar \dot{\psi} = \hat{H} |\psi\rangle$. The solution to this equation can in general be written as

$$|\psi(t)\rangle = e^{i\gamma} |\phi(\lambda(t))\rangle.$$  \hspace{1cm} (1.61)

If we put this in the Schroedinger equation, one easily obtains for the phase $\gamma$ the following equation

$$\dot{\gamma} = i \langle \psi | \dot{\psi} \rangle - i \frac{\langle \psi | \hat{H} | \psi \rangle}{\hbar}, \hspace{1cm} \gamma = \int_0^\tau i \langle \phi | \dot{\phi} \rangle dt - \int_0^\tau dt \frac{\langle \psi | \hat{H} | \psi \rangle}{\hbar}. \hspace{1cm} (1.62)$$
The second term in the last equation is just the average energy of the system, integrated in time and the corresponding phase is called dynamic. The first term, on the contrary, has no explicit dependence on the system Hamiltonian and can be shown to depend only on the trajectory of the system in the Hilbert space. Indeed, this contribution can be transformed into a path integral as

$$
\gamma_g = \int_0^\infty i \langle \phi(t)|\dot{\phi}(t)\rangle dt = \int_0^\infty i \langle \phi(\lambda(t))|\dot{\phi}(\lambda(t))\rangle dt = \int \langle \phi(\lambda)|\nabla \phi(\lambda)\rangle d\lambda. \quad (1.63)
$$

The real physical meaning this phase acquires if the evolution turns out to be cyclic, i.e. \( \phi(\tau) = \phi(0) \). The expression for the geometric phase then takes the form

$$
\gamma_g = \oint_C \langle \phi(\lambda)|\nabla \phi(\lambda)\rangle d\lambda. \quad (1.64)
$$

In that case the geometric phase can be shown to be gauge invariant. Indeed, the choice of \( \phi(\lambda) \) is not unique, but is defined up to a phase factor \( \alpha(\lambda): \phi(\lambda) \rightarrow e^{i\alpha(\lambda)}\phi(\lambda) \). This is a gauge transformation and one can show that Eq. (1.64) is invariant under this transformation, unlike Eq. (1.63) that is not. Geometric phases do not depend on the Hamiltonian explicitly, but they do depend on the trajectory of the system in the Hilbert space. This makes them insensitive to the errors that do not affect the path dramatically, which in some cases has advantages over dynamical phases.

### Adiabatic geometric phases and quantum computing

As we have seen, cyclicity is essential for the geometric phase to be gauge invariant and thus have physical meaning (gauge dependent structures can not be measured). One way to assure cyclicity is to initialize the system in the eigenstate of some non-degenerate time-dependent Hamiltonian. The Hamiltonian then slowly changes in time, so that according to adiabatic theorem the sytem will always remain in the instantaneous eigenstate of the Hamiltonian

$$
\dot{H} \phi(\lambda(t)) = E(t)\phi(\lambda(t)). \quad (1.65)
$$

If the Hamiltonian is changed cyclically \( \dot{H}(0) = \dot{H}(\tau) \), then automatically it is true that \( \phi(0) = \phi(\tau) \) and the evolution of the system is also cyclic. This was first noticed by Berry [64] and gave rise to recognition of geometric phases in physics. What we have considered by now are the so called Abelian geometric phases. In this case the eigenstate of the Hamiltonian is non-degenerate and the geometric phase is just a number. This is not very useful for quantum computation, as in this case the geometric phase gives rise to the global phase only. A more interesting situation arises when the Hamiltonian has an \( n \)-fold degenerate space. If the Hamiltonian is parametrized with a vector of parameters \( \lambda, \dot{H}(\lambda) \), then its degenerate orthonormal eigenstates take the form \( \psi_1(\lambda), \psi_2(\lambda), \ldots, \psi_n(\lambda) \). The state of the system, when the Hamiltonian is changed adiabatically, takes the form

$$
\psi(t) = \sum_{i=1}^n c_i \psi_i(\lambda(t)). \quad (1.66)
$$

The energy of these levels is the same and can be put to 0 without loss of generality (we then call the subspace spanned by \( \psi_1(\lambda), \psi_2(\lambda), \ldots, \psi_n(\lambda) \) the dark subspace of the Hamiltonian \( \dot{H}(\lambda) \)). Demanding, that Eq. (1.66) be a solution of the Schrödinger equation, one obtains

$$
\frac{d}{dt} \psi(t) = \dot{H} \psi = 0. \quad (1.67)
$$

It then follows that

$$
\dot{c}_j = -\sum_{i=1}^n c_i \langle \psi_j|\hat{\psi}_i\rangle \quad (1.68)
$$
The solution to this equation yields

$$c_j(\tau) = \sum_{i=1}^{n} \hat{T} \exp \left( \int_{0}^{\tau} - (\psi_j | \dot{\psi}_i) \, dt \right) c_i(0), \quad (1.69)$$

where $\hat{T}$ means time ordering. In the case of adiabatic cyclic evolution (the Hamiltonian is changed slowly in a closed loop), this can be transformed into the path ordered closed loop integral

$$c_j(\tau) = \sum_{i=1}^{n} \hat{P} \exp \left( \oint_{C} - (\psi_j(\lambda) | \nabla \psi_i(\lambda)) \, d\lambda \right) c_i(0), \quad (1.70)$$

where $A_{ji} = - (\psi_j(\lambda) | \nabla \psi_i(\lambda))$ is called the non-Abelian Berry connection. Equation 1.70 defines a unitary, acting in the degenerate subspace of a time dependent Hamiltonian. If the logical space of the system (the states of the qubits) coincides with the degenerate subspace, Zanardi and Rasetti have shown that in this way a universal set of gates can be constructed on this space. In chapter 5 we will return to non-Abelian Berry connection and show that it is also possible to give an alternative formulation to the results presented in this section.

**Non-Adiabatic geometric phases and quantum computing**

The disadvantage of adiabatic quantum computing is that the evolution of the system takes too long. It is hard to preserve coherence during these time, that is why adiabatic quantum computation is hard to realize. Recently, another approach appeared, that uses geometric phases arising from non-Adiabatic evolution of quantum systems. More precisely, the condition that the system can not leave the degenerate eigenspace of the Hamiltonian is relaxed. The only condition that we still demand will be the absence of dynamical phase in equation (1.62),

$$\langle \psi | \hat{H} | \psi \rangle = 0. \quad (1.71)$$

In Ref. [81] a simple scheme to perform non-Adiabatic quantum computing using $\lambda$-system was introduced. We will present it here, as it will be the only non-adiabatic gate scheme we will discuss with respect to NV$^-$ centers. We first consider a system shown in Fig. 1.8 a). The level $|1\rangle$ is resonantly coupled to the level $|e\rangle$ with a Rabi frequency $\Omega$. The Hamiltonian of this interaction in the rotating frame takes the form

$$\hat{H}/\hbar = \Omega (|1\rangle \langle e| + |e\rangle \langle 1|). \quad (1.72)$$

Solving for the evolution of the state $|1\rangle$ we obtain

$$|1\rangle \rightarrow \cos(\Omega t) |1\rangle + \sin(\Omega t) |e\rangle. \quad (1.73)$$

If we evolve the system for the time $t = \pi/\Omega$, the state $|1\rangle$ will evolve into $-|1\rangle$. If we start with a superposition of $|0\rangle$ and $|1\rangle$ ($\alpha |0\rangle + \beta |1\rangle$), this transformation generates the following gate

$$\alpha |0\rangle + \beta |1\rangle \rightarrow \alpha |0\rangle - \beta |1\rangle, \quad (1.74)$$

that is equivalent to a $\pi$-rotation around z-axis (Fig. 1.9 a). Note that the energy of the level $|1\rangle$ during the evolution is exactly 0, so the origin of the gate is purely geometric phase. Let us consider a bit more complicated situation, shown in Fig. 1.8 b). Here the levels $|1\rangle$ and $|e\rangle$ are coupled non-resonantly, with a detuning $\Delta$ and a Rabi-frequency $\Omega$. The Hamitonian in the rotating frame takes the form

$$\hat{H}/\hbar = \Omega (|1\rangle \langle e| + |e\rangle \langle 1|) + \Delta |e\rangle \langle e|. \quad (1.75)$$
Figure 1.8: a) The levels $|1\rangle$ and $|e\rangle$ are resonantly coupled. The level $|1\rangle$ is excited and then deexcited, obtaining a geometric phase factor $-1$. This operation is equivalent to a $\pi$-rotation around the z-axis on the Bloch sphere, spanned with $\{ |0\rangle , |1\rangle \}$ (Fig. 1.9 a). b) Non-resonantly coupled $|1\rangle$ and $|e\rangle$ levels. The level $|1\rangle$ is excited and then deexcited, obtaining a geometric phase factor $\gamma$. This operation is equivalent to a rotation by $\gamma$ around the z-axis on the Bloch sphere, spanned with $\{ |0\rangle , |1\rangle \}$ (Fig. 1.9 b). c) The figure represents the non-resonant coupling of the levels $|0\rangle$ and $|1\rangle$ to the level $|e\rangle$ with two different lasers, but with the same detuning. In that case the bright ($|b\rangle$) and dark ($|d\rangle$) states can be introduced, that are superpositions of $|0\rangle$ and $|1\rangle$. The dark state can be shown to be decoupled from the lasers, while the bright state is coupled to $|e\rangle$ with a Rabi frequency $\sqrt{\Omega_1^2 + \Omega_2^2}$. This operation is equivalent to a rotation around the axis on the Bloch sphere, connecting $|b\rangle$ and $|d\rangle$ (Fig. 1.9 c).

Figure 1.9: a): a rotation by $\pi$ around z-axis of the Bloch sphere, corresponding to the transformation $\alpha |0\rangle + \beta |1\rangle \rightarrow \alpha |0\rangle - \beta |1\rangle$. b): a rotation by $\gamma = \pi - \pi \Delta \sqrt{\Delta^2 + 4\Omega^2}$ around z-axis of the Bloch sphere, corresponding to the transformation $\alpha |0\rangle + \beta |1\rangle \rightarrow \alpha |0\rangle + e^{i\gamma} \beta |1\rangle$. c): a rotation by $\gamma$ on the Bloch sphere, corresponding to the transformation $\alpha |d\rangle + \beta |b\rangle \rightarrow \alpha |d\rangle + e^{i\gamma} \beta |b\rangle$

This Hamiltonian generates the following evolution of the state $|1\rangle$

$$
|1\rangle \rightarrow e^{-i\Delta t/2} \left[ |1\rangle \cos(\omega t) + \left( \frac{\Omega}{\omega} |e\rangle - \frac{\Delta}{2\omega} |1\rangle \right) \sin(\omega t) \right],
$$

where we introduced $\omega = \sqrt{\Omega^2 + \Delta^2/4}$. After the time $t = \frac{2\pi}{\sqrt{\Delta^2 + 4\Omega^2}}$, the state $|1\rangle$ will evolve into

$$
|1\rangle \rightarrow e^{i\gamma} |1\rangle, \quad \gamma = \pi - \frac{\pi \Delta}{\sqrt{\Delta^2 + 4\Omega^2}}.
$$
If we start with a superposition $\alpha \ket{0} + \beta \ket{1}$, this transformation generates the following gate
\[
\alpha \ket{0} + \beta \ket{1} \to \alpha \ket{0} + e^{i\gamma} \beta \ket{1},
\]
that is equivalent to a rotation by the angle $\gamma$ around the $z$-axis (Fig. 1.9 b).

Finally, we would like to consider the $\lambda$-system coupling configuration shown in figure 1.8 c). Now both $\ket{0}$ and $\ket{1}$ are coupled to the excited state $\ket{e}$ with two different lasers, but with the same detuning from resonance.

The Hamiltonian of the system in the rotating frame reads
\[
\hat{H} = (\Omega_1 \ket{0} \bra{e} + \Omega_2 \ket{1} \bra{e} + h.c.) + \Delta \ket{e} \bra{e}.
\]

We can introduce the bright ($\ket{b}$) and dark ($\ket{d}$) states according to
\[
\ket{b} = \Omega_1 \ket{0} + \Omega_2 \ket{1},
\]
\[
\ket{d} = \Omega_2^* \ket{0} - \Omega_1^* \ket{1}.
\]

In this new basis the Hamiltonian takes the following form
\[
\hat{H} = \sqrt{\Omega_1^2 + \Omega_2^2} (\ket{b} \bra{e} + \ket{e} \bra{b}) + \Delta \ket{e} \bra{e},
\]
that is equivalent to the Hamiltonian 1.75, with the only difference that now $\ket{b}$ is coupled to the level $\ket{e}$, not the state $\ket{1}$. The only difference it will make will be the changed rotation axis (Figure 1.9 c). This gate is no longer a $z$-gate. Now the rotation happens around the axis that connects the bright and dark states on the Bloch sphere. The expression for the angle of rotation remains the same $\gamma = \pi - \frac{\pi \Delta}{\sqrt{\Delta^2 + 4\Omega^2}}$, where $\Omega = \sqrt{\Omega_1^2 + \Omega_2^2}$.

We note that in all the cases we have considered the dynamical phase was exactly 0 and the gates appear purely because of geometric phase. As we have seen, the relative phase and strength of the lasers ($\Omega_1$ and $\Omega_2$) define the bright state, which gives us the control over the qubit rotation axis on the Bloch sphere. The detuning $\Delta$ defines the rotation angle. Thus, this simple scheme allows for the universal control over the single qubit. In chapter 6 we will see that this procedure can be generalized to perform two-qubit gates as well, all one needs to do is to define the $\lambda$–system on the levels, that are the states of a coupled system.
Chapter 2

Spin-strain control of nitrogen-vacancy centers in diamond at ground state level anticrossing

In the introduction we considered the interaction of NV$^-$ with strain and argued that the ground state spin triplet does not couple directly to strain. This is true only in linear order in spin. The deformations of the diamond lattice lead to changes in the spin-spin interaction. Strain breaks the symmetry of the lattice, resulting in the new spin-spin tensor $\Delta$ (1.2.2), that can be numerically calculated using ab initio calculations [36, 82].

The interaction of the NV$^-$ ground state spin triplet with strain is thus quadratic in spin operators. In this chapter, we provide a theoretical description of this interaction. Even though in recent years it has been studied intensively [22–24, 83–86], to our knowledge the correct and complete form of the interaction Hamiltonian has only appeared in [36].

The chapter is structured in the following way. First we derive the symmetry-allowed form of the spin-strain interaction Hamiltonian, see Eq. (2.2). Then we propose a setup to measure the coupling-strength parameters of this Hamiltonian, that have not been experimentally characterized yet. Finally, we discuss how the spin-strain interaction can contribute to various applications of NVs in quantum information schemes.

We would like to point out that our group theoretical arguments and measurement schemes could apply more generally to other defects with $C_3v$ symmetry.

2.1 Preliminaries

We choose the cubic reference frame in exactly the same way, as it was done in the introduction in Figure 1.3. We start by writing without derivation the symmetry allowed interaction Hamiltonian of a homogeneous electric field $\mathbf{E} = (E_x, E_y, E_z)$ with the NV$^-$ spin:

$$H_E = H_{E0} + H_{E1} + H_{E2},$$

$$H_{E0}/\hbar = d_{||} S_z^2 E_z,$$

$$H_{E1}/\hbar = d_\perp \left[ \{S_x, S_z\} E_x + \{S_y, S_z\} E_y \right],$$

$$H_{E2}/\hbar = d_\perp \left[ (S_y^2 - S_x^2) E_x + \{S_x, S_y\} E_y \right].$$

These are quadratic in spin and have been theoretically and experimentally considered in [33, 34, 39]. The dipole moments $d_\perp = 17$ Hz cm/V and $d_{||} = 0.35$ Hz cm/V have been
measured in the experiment of Ref. [87]. To our knowledge, the coefficient \( d'_{\perp} \) has not been measured yet, nevertheless it is expected [83] to have the same order of magnitude as \( d_{\perp} \).

The form of \( H_{E1} \) suggests that it can couple the states with \( m_s = 0 \) to those with \( m_s = \pm 1 \). This means that coherent Rabi oscillations within the state pairs \( |0e\rangle \leftrightarrow |+1e\rangle \) and \( |0e\rangle \leftrightarrow |-1e\rangle \) can be driven by an ac electric field. Thus, any coherent-control experiment where these transitions are driven by ac magnetic field can also be done by replacing the ac magnetic field with an ac electric field (electrically driven spin resonance).

To our knowledge, this opportunity which is used in different solid-state spin platforms [89–92] has been with rare exceptions [82] overlooked in the context of the magnetically allowed transitions of NV\(^-\) centers and other defects with \( C_{3v} \) symmetry. Since electric control might bring significant advantages over magnetic control (simplified device layout, well-confined control fields allowing for local spin addressability, lower power requirements, etc), this observation provides a strong motivation to characterize the coupling-strength parameter \( d'_{\perp} \) of \( H_{E1} \) both experimentally and theoretically. The experimental setup we propose in Sec. 2.3 to measure spin-strain coupling-strength parameters can be easily adopted to measure \( d'_{\perp} \).

### 2.2 Spin-strain Hamiltonian

A central result we present here is the most general form of the interaction Hamiltonian between the spin triplet ground state of NV\(^-\) center and 3 \( \times \) 3 strain tensor. It can be constructed in a simple way using the group-theoretical tools we have developed in the introduction. We know that the interaction Hamiltonian must transform as \( A_1 \) irreducible representation of the \( C_{3v} \) group, must be linear in strain tensor components and quadratic in spin operators. We thus need to construct such combinations of the bases vectors [1.15] and [1.44] that will be bases for the \( A_1 \) representation. The rules one and nine of the remark [11] tell exactly which combinations must be taken and for the Hamiltonian one obtains:

\[
H_{\epsilon} = H_{\epsilon 0} + H_{\epsilon 1} + H_{\epsilon 2},
\]

\[
H_{\epsilon 0}/h = [h_{41}(\varepsilon_{xx} + \varepsilon_{yy}) + h_{43}\varepsilon_{zz}]S_z^2,
\]

\[
H_{\epsilon 1}/h = \frac{1}{2} \left[ h_{26}\varepsilon_{xx} - \frac{1}{2} h_{25}(\varepsilon_{xx} - \varepsilon_{yy}) \right] \{S_x, S_z\}
\]

\[
+ \frac{1}{2} \left( h_{26}\varepsilon_{yy} + h_{25}\varepsilon_{xy} \right) \{S_y, S_z\},
\]

\[
H_{\epsilon 2}/h = \frac{1}{2} \left[ h_{16}\varepsilon_{xx} - \frac{1}{2} h_{15}(\varepsilon_{xx} - \varepsilon_{yy}) \right] (S_y^2 - S_x^2)
\]

\[
+ \frac{1}{2} \left( h_{16}\varepsilon_{yy} + h_{15}\varepsilon_{xy} \right) \{S_x, S_y\},
\]

where \( \varepsilon_{ij} = (\partial u_i/\partial x_j + \partial u_j/\partial x_i)/2 \) denotes the strain tensor and \( u(r) \) denotes the displacement field. This Hamiltonian is characterized by six independent parameters \( h_{41}, h_{43}, h_{25}, h_{26}, h_{15}, h_{16} \) and is the most general form of the interaction allowed by the \( C_{3v} \) symmetry.

Note that the symmetry-allowed form of the spin-stress interaction, i.e., when the mechanical deformation is characterized by the 3 \( \times \) 3 stress tensor \( \sigma \) instead of strain \( \varepsilon \), is completely analogous to Eq. [2.2]. In what follows, we adopt a notation for the spin-stress...
Hamiltonian $H_\sigma$ that is analogous to Eq. (2.2), with the substitutions $\varepsilon \rightarrow \sigma$ and $h \rightarrow g$:

\begin{align}
H_\sigma &= H_{\sigma 0} + H_{\sigma 1} + H_{\sigma 2}, \\
H_{\sigma 0}/h &= [g_{41}(\sigma_{xx} + \sigma_{yy}) + g_{43}\sigma_{zz}]S_z^2, \\
H_{\sigma 1}/h &= \frac{1}{2} \left[ g_{26}\sigma_{xz} - \frac{1}{2} g_{25}(\sigma_{xx} - \sigma_{yy}) \right] \{S_x, S_z\} \\
&\quad + \frac{1}{2} (g_{26}\sigma_{yz} + g_{25}\sigma_{xy})\{S_y, S_z\}, \\
H_{\sigma 2}/h &= \frac{1}{2} \left[ g_{16}\sigma_{xx} - \frac{1}{2} g_{15}(\sigma_{xx} - \sigma_{yy}) \right] (S_y^2 - S_z^2) \\
&\quad + \frac{1}{2} (g_{16}\sigma_{yz} + g_{15}\sigma_{xy})\{S_x, S_y\}.
\end{align}

Many recent works (e.g., Refs. [22, 24, 84]) rely on a heuristic spin-strain Hamiltonians built on an unjustified analogy between strain and electric field. That approach does not take into account the $3 \times 3$ tensor structure of strain, therefore it provides an incorrect description of the spin-strain interaction, even in the absence of shear strain. A recent work[36] uses a spin-stress Hamiltonian based on the $3 \times 3$ stress tensor $\sigma$; their Hamiltonian includes 4 real parameters, $a_1$, $a_2$, $b$ and $c$. That Hamiltonian is equivalent to our $H_{\sigma 0} + H_{\sigma 2}$, but is incomplete as it lacks the symmetry-allowed term $H_{\sigma 1}$. This can be justified only as long as the NV$^-$ center is operated at low magnetic fields, where a large gap separates $m_s = 0$ from $m_s = \pm 1$. Otherwise this leads to an incorrect description of the system.

### 2.3 Methods to measure the spin-strain parameters

To the best of our knowledge, the spin-stress coupling parameters $g_{25}$ and $g_{26}$ have not yet been measured. This is no surprise considering that most of the experiments operate at low magnetic field. In this regime the $m_s = 0$ and $m_s = \pm 1$ levels in the ground state of the NV$^-$ are split by the zero field splitting $\Delta_{gs} = 2.88$ GHz (Eq. 1.37). If some constant stress is present in the sample, its effect through the Hamiltonian $H_{\sigma 1}$ will be suppressed due to this large zero field splitting. The situation will change if one applies external magnetic field that brings $m_s = -1$ close to $m_s = 0$ through Zeeman effect. In that case $H_{\sigma 1}$ will have a significant effect on the system. The DFT calculations predict the values of stress coupling coefficients $g_{25}$ and $g_{26}$ to be $-2.17$ MHz and $-2.58$ MHz respectively [36], that as we will argue is enough for them to be measured in an experiment (here we use the convention that negative stress corresponds to compression). In this section, we propose a method that allows to determine the stress coupling coefficients $g_{25}$ and $g_{26}$ in an experiment which combines the controlled application of mechanical stress and ODMR. The method is inspired by the experiment of Ref. [93] and requires a finite magnetic field along the NV axis, which tunes the system to the ground-state level anticrossing (GSLAC), where the $|−1e\rangle$ and $|0e\rangle$ electronic states are approximately degenerate, $B_{cr} \approx \Delta_{gs}/\gamma_e \approx 1024$ G. The anticrossing at that magnetic field arises due to hyperfine interaction of an NV$^-$ center with a nuclear spin ($I = 1$) of nitrogen-14 [94]. Mechanical stress can then induce strong mixing of the spin eigenstates of the coupled electron-nuclear system via the stress-coupling parameters $g_{25}$ and $g_{26}$. In turn, the spin dynamics governed by this mixing can be detected in a time-resolved fashion, via photoluminescence-based optical readout of the NV$^-$ spin system. First, in Section 2.3.1 we introduce our model, and show that the mechanical stress can be thought of as an extra contribution to the external magnetic field, see Eq. 2.6. Second, in Section 2.3.2 we describe an arrangement that can be used to determine the axial spin-stress coupling parameters $g_{41}$ and $g_{43}$. Third, in
where we introduced the effective fields and its interaction with stress are (Eq. 1.37, 2.3)

\[ P_{\{-1e,0e\}} H_z P_{\{-1e,0e\}} = P_{\{-1e,0e\}} \gamma_e \vec{B} \cdot \vec{S} P_{\{-1e,0e\}} = \gamma_e \begin{pmatrix} 0 & \frac{B_x - iB_y}{\sqrt{2}} \\ \frac{B_x + iB_y}{\sqrt{2}} & -B_z \end{pmatrix}. \] (2.4)

The symmetry allowed Hamiltonians describing the zero-field splitting of the center and its interaction with stress are (Eq. 1.37, 2.3)

\[
\begin{align*}
H_{ss} / \hbar &= DS_z^2, \\
H_{\sigma_0} / \hbar &= \left[ g_{11}(\sigma_{xx} + \sigma_{yy}) + g_{43}\sigma_{zz} \right] S_z^2, \\
H_{\sigma_1} / \hbar &= \frac{1}{2} \left[ g_{26}\sigma_{xz} - \frac{1}{2} g_{25}(\sigma_{xx} - \sigma_{yy}) \right] \{S_x, S_z\} \\
&\quad + \frac{1}{2} (g_{26}\sigma_{yz} + g_{25}\sigma_{xy}) \{S_y, S_z\}, \\
H_{\sigma_2} / \hbar &= \frac{1}{2} \left[ g_{16}\sigma_{xz} - \frac{1}{2} g_{15}(\sigma_{xx} - \sigma_{yy}) \right] (S_y^2 - S_x^2) \\
&\quad + \frac{1}{2} (g_{16}\sigma_{yz} + g_{15}\sigma_{xy}) \{S_x, S_y\}.
\end{align*}
\] (2.5)

Adding these interactions to the Zeeman Hamiltonian and projecting onto the space of \(|m_s = -1\rangle, |m_s = 0\rangle\), we obtain the effective Hamiltonian at GSLAC

\[
H_{\text{eff}} / \hbar = P_{\{-1e,0e\}} (H_z + H_{ss} + H_{\sigma_0} + H_{\sigma_1} + H_{\sigma_2}) P_{\{-1e,0e\}} / \hbar
= \begin{pmatrix} 0 & \frac{\Phi_x - i\Phi_y}{\sqrt{2}} \\ \frac{\Phi_x + i\Phi_y}{\sqrt{2}} & D - \gamma_e \Phi_z \end{pmatrix},
\] (2.6)

where we introduced the effective fields

\[
\begin{align*}
\Phi_x &= B_x + \frac{g_{25}}{4\gamma_e} (\sigma_{xx} - \sigma_{yy}) - \frac{g_{26}}{2\gamma_e} \sigma_{xz}, \\
\Phi_y &= B_y - \frac{g_{25}}{2\gamma_e} \sigma_{xy} - \frac{g_{26}}{2\gamma_e} \sigma_{yz}, \\
\Phi_z &= B_z - \frac{g_{41}}{\gamma_e} (\sigma_{xx} + \sigma_{yy}) - \frac{g_{43}}{\gamma_e} \sigma_{zz}.
\end{align*}
\] (2.7)

We see that the action of stress on the electronic spin of the NV$^-$ can be described by three effective fields $\Phi_x, \Phi_y, \Phi_z$, that incorporate both magnetic field and stress.

To have a precise description of the NV$^-$ center at GSLAC we need to include the nuclear spin into consideration. The quadrupole moment of the $^{14}\text{N} I = 1$ nuclear spin results in

\[
H_q / \hbar = Q t_z^2.
\] (2.8)
The Zeeman splitting of the nuclear spin we take into account by the Hamiltonian

\[ H_{zn}/h = -\gamma_n B_{cr} I_z, \]  

(2.9)

where \( B_{cr} \) is the axial magnetic field at the GSLAC \( B_{cr} = D/\gamma_e \). The hyperfine interaction between the electron and nuclear spins is given by the most general symmetry allowed Hamiltonian

\[ H_{hf}/h = A_|| S_z I_z + A_\perp (S_x I_x + S_y I_y). \]  

(2.10)

Equations (2.6−2.10) provide a good analytical description of the structure of the NV− center at GSLAC. The literature values of the coefficients are \( Q = -5.01 \) MHz, \( A_|| = -2.14 \) MHz, \( A_\perp = -2.7 \) MHz [48].

### 2.3.2 Magnetic resonance spectroscopy

#### ODMR signal contrast

In what follows we will describe the strategy to measure the stress coupling coefficients using an ODMR technique. We consider the system to be perfectly initialized in the \( |0e, 1n\rangle \) with an optical pulse [93]. Note that this state is not necessarily an eigenstate of the system. Then we model the resonant driving with the microwave or radiofrequency pulse. We assume the magnetic field in this pulse to point in the x direction in the NV coordinate frame. The strength of the pulse is described by

\[ b = (g\mu_B/h) \int_{-\infty}^{+\infty} B_x(\tau) d\tau, \]

where \( B_x \) is the magnetic field envelope in the rotating reference system in the rotating wave approximation. In our simulations we take \( b = \sqrt{2}/4 \), which corresponds to the \( \pi \)-pulse, when the electron spin is not mixed with the nuclear one. We also assume the integral to converge on a time scale much shorter than all dynamical time scales of the ground state of the NV−. The pulse induces coherent dynamics between 2 of the 9 eigenlevels of the 9 \( \times \) 9 Hamiltonian, which is then read out with one more optical pulse. Without the microwave pulse and right after the initialization, the readout pulse would result in the photoluminescence signal corresponding to the system being in the \( |0e\rangle \) electronic state. This signal is used as a reference. The coherent dynamics drives the system out of the \( |0e\rangle \) state and in an experiment that would correspond to a different photoluminescence response with respect to the reference signal. The result of the measurement is the contrast of the two signals. We model this ODMR contrast to be proportional to the factor \( 1 - P_0 \), which is the probability not to be in the \( |0e\rangle \) state. This factor is 0 whenever the dipole matrix element is 0, as no coherent dynamics is generated and the system remains in the \( |0e\rangle \) state. For a nonzero matrix element the transition does not always correspond to a perfect \( \pi \)-pulse, this is captured by solving the Schrödinger equation exactly for a pulse of given shape and magnitude. We also consider no other source of coherent evolution of \( |0e\rangle \) population rather than microwave or radiofrequency pulse. To show the ODMR contrast we scale the thickness of the lines for all the ODMR plots as \( 1 - P_0 \). Therefore, every point of the plot [2.2] has its own size revealing the ODMR contrast one should expect at that point.

#### Identification of axial stress coupling coefficients \( g_{41}, g_{43} \)

If the axial magnetic field \( B_z \) is swept, while keeping the other two fields and stress 0, the energy levels will shift as it is shown in the Fig. [2.1]. This shift can be measured by ODMR using an alternating magnetic field, but not all resonances can be detected. During the initialization procedure at the GSLAC the NV− center is efficiently initialized into the state \( |0e, 1n\rangle \) [93], thus only the transitions starting from \( |0e, 1n\rangle \) will look bright. As this level is unperturbed by the axial effective field, selection rules demand that one may only expect transitions to \( |-1e, 1n\rangle \) and \( |+1e, 1n\rangle \). But because the \( |-1e, 1n\rangle \) is mixed with
Figure 2.1: Level structure of the $^{14}$NV$^-$ at the GSLAC as a function of the axial magnetic field $B_z$. All the transverse fields and stress are kept zero, $B_x = B_y = 0$, $\sigma = 0$. The circle marks the crossing that serves to identify the stress coupling coefficients $g_{25}$, $g_{26}$. The levels split by the hyperfine interaction are shown with the same color. The arrows indicate the bright radiofrequency transitions at the corresponding values of the field. The dashed lines are invisible in the ODMR experiment in the absence of stress.

$|0e,1n\rangle$ at the GSLAC due to the hyperfine interaction, the first transition gives rise to two resonance frequencies

$$\omega_{1,2} = \frac{1}{2} \left(-A_{||} + D \left(1 + \frac{\gamma_m}{\gamma_e}\right) - Q - \gamma_e \Phi_z\right) \pm \sqrt{\frac{1}{4} \left(A_{||} - D \left(1 - \frac{\gamma_m}{\gamma_e}\right) - Q + \gamma_e \Phi_z\right)^2},$$

(2.11)

as shown in Fig. 2.1 with two black arrows around the field 1023.3 G. As the axial effective field is swept away from the GSLAC, one of the frequencies starts to correspond to a forbidden transition and thus vanishes. This is illustrated with one black arrow around the field 1026 G, corresponding to only one bright transition. The two resonant frequencies are plotted in the lower part of Fig. 2.2. Here the black curve describes the dependence of the resonance frequencies on the axial magnetic field without stress, while the orange curve describes the same but in the presence of $\sigma_{zz}$-stress of 1 GPa. The fact that the two curves are simply shifted with respect to each other illustrates that $\sigma_{zz}$-stress merely creates a shift to the axial effective field (Eq. 2.7).

The energy of $|+1e, 1n\rangle$ level at GSLAC can be obtained by projecting the Hamiltonians (2.3a) together with the Zeeman Hamiltonian onto the $|+1e\rangle$ electronic level

$$P_{\{+1e\}}(H_z + H_{ss} + H_{\sigma 0} + H_{\sigma 1} + H_{\sigma 2})P_{\{+1e\}}/h = (D + \gamma_e \Phi'_z)|+1e\rangle \langle +1e|,$$

(2.12)

where we introduced the effective field

$$\Phi'_z = B_z + \frac{g_{41}}{\gamma_e} (\sigma_{xx} + \sigma_{yy}) + \frac{g_{43}}{\gamma_e} \sigma_{zz},$$

(2.13)

and the projection operator $P_{\{+1e\}} = |+1e\rangle \langle +1e|.$

From this equation for the frequency of the $|0e, 1n\rangle$ to $|+1e, 1n\rangle$ microwave transition we obtain

$$\omega_3 = A_{||} + D + \gamma_e \Phi'_z.$$

(2.14)
The microwave transition and the dependence of its frequency on the magnetic field is illustrated in the upper part of figure 2.2 for the cases without stress and with $\sigma_{zz}$-stress of 1 GPa.

Detection of these transitions allows one to infer the stress coupling coefficients $g_{41}$, $g_{43}$, as long as the transversal effective field can be neglected. Though these coefficients have already been measured and are known in the literature [86], here we describe an alternative procedure to measure them at GSLAC. When one applies uniaxial stress along the z direction, the transverse fields are exactly zero and thus one can infer $g_{43}$ parameter from ODMR spectra using Eqs. (2.7), (2.11), (2.13), and (2.14). To measure $g_{41}$ coefficient one has to apply stress with nonzero $\sigma_{xx} + \sigma_{yy}$. Here we only consider uniaxial stress, as it is the simplest to apply experimentally. In that case the stress tensor is $\sigma_{ij} = n_i n_j \sigma$ and the transverse field is almost always nonzero, thus it will couple the levels shown on the Fig. 2.1. The effect of the transverse effective field becomes important only in the vicinity of the crossing point, marked with a circle in Fig. 2.1, and corresponding to zero transition frequency for the black and orange curves in Fig. 2.2. Further than 0.4 G away from this point at 1 GPa stress the transverse strain is small compared to the energy splittings of the Fig. 2.1 and thus it is possible to infer $g_{41}$ as we did with $g_{43}$. We only need to take into account that it is $\sigma_{xx} + \sigma_{yy}$ that contributes to axial effective fields to use the Eqs. (2.11) and (2.14).
Identification of transverse stress coupling coefficients $g_{25}$, $g_{26}$ using Larmor precession

The stress coupling coefficients $g_{25}$, $g_{26}$ contribute to the transverse effective fields, which leads to the coupling of the levels in Fig. 2.1. Therefore, in order to measure these coefficients efficiently, we need to tune the system to the crossing on the Fig. 2.1 marked with a circle. To analyze what happens at this point we derive an effective $2 \times 2$ Hamiltonian exactly at the crossing point, taking the crossing levels $|0e, 1n\rangle$ and $|-1e, 1n\rangle$ as a basis. Here mixing coefficient $\alpha = \frac{\gamma_e A_z}{Q_{0e} - Q_{1n}}$ is calculated through the diagonalization of the hyperfine Hamiltonian (2.10). The effective Hamiltonian then is

$$H_{\text{eff}} = \hbar \gamma_e \begin{pmatrix} 0 & \frac{\Phi_x - i \Phi_y}{\sqrt{2(1+\alpha^2)}} \\ \frac{\Phi_x + i \Phi_y}{\sqrt{2(1+\alpha^2)}} & \frac{\Phi_z - \Phi_0}{1+\alpha^2} \end{pmatrix},$$

(2.15)

where $\Phi_z$ is defined in Eq. (2.7) above and $\Phi_0$ denotes the crossing point. In what follows we will use $\delta \Phi_z = \Phi_z - \Phi_0$ and $\Phi^2_\perp = \Phi_x^2 + \Phi_y^2$ for simplicity.

Here we propose and quantitatively analyze a method for measuring the transverse stress coupling coefficients $g_{25}$, $g_{26}$, which works in a setting where the external magnetic field is tuned to the vicinity of the GSLAC. The method we propose is based on the experiment discussed and implemented in Section IV of Ref. [93], where Larmor-precession spin dynamics was used to precisely measure the magnetic-field component perpendicular to the NV axis. Here we focus on how to measure the coupling strengths $g_{25}$, $g_{26}$ in the case when the magnetic field is aligned with the NV axis. Our method relies on the observation of Larmor-precession spin dynamics, which is naturally affected by stress via the spin-stress interaction (2.3).

When the qubit is initialized in the first basis state $|0e, 1n\rangle$ of the Hamiltonian (2.15), then its dynamics governed by $H_{\text{eff}}$ is a simple Larmor precession. In particular, the time-dependence of the occupation probability of the first basis state is given by

$$P_{|0e, 1n\rangle}(t) = \frac{\delta \Phi_z^2 + (1 + \alpha^2) \Phi^2_\perp [1 + \cos \Omega t]}{\delta \Phi_z^2 + 2(1 + \alpha^2) \Phi^2_\perp},$$

(2.16)

where $\Omega = 2\pi \gamma_e \sqrt{\frac{\delta \Phi_z^2}{(1+\alpha^2)^2} + \frac{\Phi^2_\perp}{1+\alpha^2}}$.

The initialization, the Larmor-precession dynamics and the readout of this occupation probability was realized in Ref. [93]. We are now only interested in how the stress changes the transverse fields. To address this question in the most efficient way we propose to always keep the axial effective field at $\Phi_0$. This we can achieve for every value of stress by tuning the magnetic field in the way that leaves the axial effective field unchanged. In order to be able to do this, one has to know the magnitudes of the axial stress coupling coefficients $g_{41}$, $g_{43}$. We assume the uniaxial stress of magnitude $\sigma$ in the direction $(n_x, n_y, n_z)$ is applied and thus the stress tensor is $\sigma_{ij} = n_i n_j \sigma$. From the equations (2.7) it follows that the axial magnetic field should be changed by

$$\Delta B_z = \frac{g_{41}(n_x^2 + n_y^2) + g_{43}n_z^2}{\gamma_e} \sigma.$$

(2.17)

If one follows this procedure, the probability to be in $|0e, 1n\rangle$ equation (2.16) turns out to be

$$P_{|0e, 1n\rangle} = \frac{1 + \cos (\Omega t)}{2},$$

(2.18)
where Larmor frequency $\Omega$ becomes

$$\Omega = 2\pi \sqrt{\frac{g_{25}^2 n_1^4 + g_{26}^2 n_2^2 n_1^2 + g_{25}g_{26} n_x n_z(3n_y^2 - n_z^2)}{2(1 + A_\perp^2 \gamma^2/(Q_{\gamma e} - D_{\gamma n})^2)}} \sigma, \quad (2.19)$$

with $n_\perp = \sqrt{n_x^2 + n_y^2}$.

The formula (2.19) allows the identification of the coefficients $g_{25}$, $g_{26}$ by applying the stress in different directions and then observing the Larmor precession frequency. For example, $g_{25}$ can independently be measured by applying the uniaxial stress in the direction $(1, 1, 0)$. In that case from Eq. 2.19 the Larmor frequency dependence on stress is

$$\Omega = 2\pi \sqrt{\frac{|g_{25}|}{8(1+A_\perp^2 \gamma^2/(Q_{\gamma e} - D_{\gamma n})^2)}} \sigma.$$ Analogously, $g_{26}$ can then be measured if one applies stress in another direction and detects the arising Larmor precession. It is important to note that this procedure only allows us to determine the stress coupling coefficients up to a sign. Indeed, Eq. 2.19 is invariant under a sign change of the stress coupling coefficients and thus cannot be used to define it. Nevertheless, it is straightforward to generalize the above procedure to determine the signs of the coefficients: one has to add a finite transverse magnetic field. Indeed, let us assume that we apply compressive uniaxial stress $\sigma < 0$ along $\vec{n} = (1, 1, 0)/\sqrt{2}$. If the sign of $g_{25}$ is indeed negative, as indicated by the DFT results in Ref. [36], then the transverse effective field components read $\Phi_x = 0$ and $\Phi_y = B_y - p|\sigma|$ with $p > 0$. Thus, according to Eq. 2.19 the Larmor precession is slowed down gradually as a magnetic field component along the y axis is switched on. On the other hand, if the sign of $g_{25}$ is positive, then a small y-directional magnetic field will speed up the Larmor precession.

#### 2.4 Discussion

We have established the spin-strain and spin-stress interaction Hamiltonians for the NV− ground state, that depend on the 6 independent parameters. Focusing on the new Hamiltonian term $H_{e1}$, that has been overlooked in the literature, we proposed an experimental setup in which the yet unknown spin-stress coupling coefficients can be measured. Our findings suggest that coherent mechanical or electrical spin control of the magnetically allowed spin transitions can be achieved. All qualitative considerations of this work should hold for the whole family of defects with $C_{3v}$ symmetry and spin-1 electronic ground states.

Coherent spin control in NVs via ac mechanical deformation has been demonstrated with $\sim 1$ MHz Rabi frequency for the magnetically forbidden $|\not{1e}\rangle \leftrightarrow |\not{+1e}\rangle$ transition [23]. Our results imply that the other two, magnetically allowed transitions, $|0e\rangle \leftrightarrow |\pm1e\rangle$, can also be driven in a similar manner. It is thus possible to completely substitute the ac magnetic field by ac mechanical driving for the spin control in NV− ground state. From the spin-strain Hamiltonian $H_e$ of Eq. (2.2), we estimate that an ac strain $\varepsilon_{xx}$ with an amplitude of 0.01 can provide mechanically induced Rabi oscillations for the magnetically allowed transitions with a Rabi frequency of $\sim 5$ MHz, if one assumes the DFT values [36] for the spin-stress coupling coefficients $g_{25}$ and $g_{26}$. As discussed above, the spin-strain (spin-stress) coupling-strength parameters of $H_{e1}$ ($H_{\sigma1}$), namely $h_{25}$ and $h_{26}$ ($g_{25}$ and $g_{26}$), are yet to be characterized experimentally. Similarly, the corresponding spin-electric coupling-strength coefficient $d_{\perp}$ in Eq. (2.1) is yet to be measured.
Chapter 3

Long distance addressability of NV\textsuperscript{−} centers using spin waves in YIG

As we have already mentioned before, the spin state of the NV\textsuperscript{−} center can be manipulated with oscillating magnetic fields, that cause transitions between the levels of the spin triplet. In most of the experiments this oscillating field was generated by an antenna placed in the vicinity of the center, which raises the issue of addressability for many NV\textsuperscript{−} centers when the antenna can no longer be placed close to each of them. Recently an experiment was reported in which the NV\textsuperscript{−} center was placed on top of a ferromagnetic material (YIG) that can host propagating spin waves \cite{38}. Using an antenna as a source of the spin waves in this material, one can couple distinct NV\textsuperscript{−} centers to it just like dialog partners are connected by a signal line. In this chapter we theoretically treat the coupling of the spin waves to the NV\textsuperscript{−} centers for a special geometry of the device described below. We provide an analytical expression for the spin wave field and determine the coupling enhancement that it produces with respect to the field of the antenna only, when spin waves are absent.

3.1 Setup

We calculate the effect of spin wave excitation inside ferromagnetic thin films as used in the experiment of Ref. \cite{38}. Spin waves in YIG provide an additional component of the driving field on top of the pure antenna field. In that way, spin wave excitation inside a ferromagnetic material affects the coupling between the driving field and the given quantum system. In the experimental realization of Ref. \cite{38} the quantum system consisted of defect spins inside a group of nanodiamonds patterned on the surface of the magnetic material as depicted in Fig. 3.1 (a). A single nanodiamond hosts an ensemble of \(~500\) NV\textsuperscript{−} centers with an isotropic electron g-factor of \(g \approx 2\) \cite{45} (here we neglect the anisotropy due to the symmetry of the \(C_{3v}\) group). The nanodiamond is embedded in a polydimethylsiloxane (PDMS) film, which is on top of a layered structure of YIG and gadolinium gallium garnet (GGG). Since YIG is a ferromagnetic material with ultra-low spin wave damping, it is perfect for the usage as the spin wave medium. An ac current flowing through a microstrip line (MSL) deposited on the surface of the YIG generates a microwave driving field, penetrating the materials and denoted as the antenna field in Fig. 3.1 (a). For a theoretical description of the system we use the coordinate system and the defining parameters sketched in Fig. 3.1 (b). Assuming the YIG film to have a thickness \(d\) and to lie in the \(xy\)-plane, the MSL orientation can be set as the \(y\)-axis and the center of the MSL is the origin of the coordinate system. Further, the MSL has a width \(w\) and the probed nanodiamond is located in the \(xz\)-plane at \(x_{NV}\). Based on realistic dimensions
Figure 3.1: (a) Electron spin resonance in NV\(^-\) spins driven by spin waves demonstrated in Ref. [38]. An array of nanodiamonds is patterned inside a polydimethylsiloxane (PDMS) film layered on top of a yttrium iron garnet (YIG) thin film. From a distant microstripline (MSL) deposited on the YIG the antenna field propagates through the PDMS and couples to NV\(^-\) centers. Inside the YIG the microwave field of the MSL excites the spin waves propagating in the plane. Given the relevant dimensions of the problem, the theoretical treatment can be reduced to a two-dimensional coordinate system as shown in (b), which is a cross section of the setup in (a). The layered structure lies in the \(xy\)-plane and the center of the MSL of width \(w\) marks the origin of the coordinate system and is oriented along the \(y\)-direction.

Of experimental systems, some assumptions concerning the boundary conditions of the system are reasonable. In Ref. [38], the YIG film is only 3.08 \(\mu\)m thick, which is very thin compared to its dimensions of about 10 mm along the \(x\)- and \(y\)-axes [38]. Thus, the film can be assumed to be infinite in the \(xy\)-plane. The GGG substrate and the PDMS layer are a few hundreds of \(\mu\)m thick, so that they are treated as infinite in the \(z\)-direction and the only boundary conditions to be fulfilled are those at the YIG interfaces, where both surrounding layers in regions I and III are approximated as non-magnetic. This assumption is justified due to their magnetic permeabilities being isotropic and close to unity [95, 96]. The MSL has a width of \(w = 5\mu\)m, making its height of about 200 nm negligible. Overall, due to the spatial expansion of the system along the \(y\)-direction and the invariance of the system under \(y\)-translation, we assume that all fields are independent of \(y\) and the problem is treated in two dimensions.

### 3.2 Driven Spin Waves

In order to calculate the spin wave spectrum of a ferromagnetic thin film and the resulting field amplitude, we start from Maxwell’s equations (MEs). If there is an external magnetic \(H\)-field, a magnetization field \(M\) is built up in the magnetic film. In general, the external \(H\)-field can be decomposed into a static part \(H_0\) and a time-dependent component \(h(t)\) originating from the microwave antenna field. Consequently, the magnetization inside the material depends on the driving frequency \(\omega\) and will also have a time-dependent component \(m(t)\). The relation between both time-varying components is given by the constitutive equation \(m = Xh\), where material properties and the geometry of the system enter via the susceptibility tensor \(X\). In case of a strong static bias field \(H_0\) along the \(y\)-direction, the magnetic film is tangentially magnetized and the static component of magnetization \(M_0\) saturates. Under these conditions, \(X\) takes the form of the Polder
susceptibility
\[ X = \begin{pmatrix} \chi & 0 & -i\kappa \\ 0 & 1 & 0 \\ i\kappa & 0 & \chi \end{pmatrix}, \quad (3.1) \]
with the frequency-dependent entries \( \chi = \omega \omega_M / (\omega^2 - \omega^2) \) and \( \kappa = \omega_0 \omega_M / (\omega_0^2 - \omega^2) \). The parameters \( \omega_0 = \gamma \mu_0 H_0 \) and \( \omega_M = \gamma \mu_0 M_S \) account for the characteristics of the material in an external field \( H_0 \). Here, \( \gamma \) and \( M_S \) denote the gyromagnetic ratio and the saturation magnetization of the film and \( \mu_0 \) denotes the vacuum permeability. Using the Polder tensor (3.1) and assuming the electric permittivity of the materials to be 1 for simplicity, the single components of the four MEs in two dimensions form a system of eight coupled differential equations for the magnetic and electric field components \( H_i(x, z) \) and \( E_i(x, y, z) \) (\( i = x, y, z \)) in each region I-III in Fig. 3.1 (b). Since the MSL is located right at the PDMS-YIG interface and is assumed to be infinitesimally thin, the flowing current is non-zero only at the boundary between the two upper layers I and II, whereas inside the bulk regions there are no free currents \( j \) flowing, and thereby, no additional source terms. Referring to that, the fields inside the bulk regions I-III are obtained by solving the system of homogeneous MEs with \( j = 0 \) separately and the MSL current is included by matching the boundary conditions at \( z = 0 \) and \( z = -d \) afterwards.

Performing a one dimensional Fourier transform of the \( x \)-coordinate yields a system of ordinary differential equations in the \( k_x \)-\( z \)-space, where only one equation actually has to be solved,
\[ \partial^2_{t} H_x(k_x, z) + a^2 H_x(k_x, z) = 0. \quad (3.2) \]
Here \( a^2 = ((1+\chi)^2 - \kappa^2)k_0^2/(1+\chi) - k_x^2 \) and \( k_0 = \omega/c \). The other non-zero field components \( H_z(k_x, z) \) and \( E_y(k_x, z) \) can be expressed in terms of the solution \( H_x(k_x, z) \) of (3.2) and its derivative \( \partial_z H_x(k_x, z) \),
\[
H_z(k_x, z) = \frac{i\kappa k_0^2 H_x(k_x, z) - ik_x \partial_z H_x(k_x, z)}{k_x^2 - (1+\chi)k_0^2}, \quad (3.3)
\]
\[
E_y(k_x, z) = \frac{\omega}{k_x} (ik_x H_x(k_x, z) + (1+\chi)H_z(k_x, z)). \quad (3.4)
\]
Since the PDMS as well as the GGG layer are assumed to be infinite in positive and negative \( z \)-directions respectively, there are no incoming waves in these regions, which could be caused by reflections at any surfaces. Thus, the ansatz
\[
H_x^1(k_x, z) = C_1 e^{ia_{PDMS} z},
H_x^{II}(k_x, z) = C_2 e^{ia_{YIG} z} + C_3 e^{-ia_{YIG} z},
H_x^{III}(k_x, z) = C_4 e^{-ia_{PDMS} z}, \quad (3.5)
\]
is chosen, where the superscripts I-III refer to the regions and \( a_i \) corresponds to \( a \) in Eq. (3.2) in the corresponding material \( i \). In order to obtain the actual amplitude of the magnetic field, the coefficients \( C_1-C_4 \) have to be derived, so one needs to include the boundary conditions, arising at the two interfaces. In the absence of any surface currents, the parallel component of the \( \mathbf{H} \)-field and the orthogonal component of the \( \mathbf{B} \)-field are continuous at an interface. But since this is only the case for the lower interface at \( z = -d \), the upper boundary condition for the parallel \( H \)-field component has to be considered more carefully. The field component \( H_z \) is not continuous at \( z = 0 \), where the step between both regions equals the current density at the boundary. Hence, the proper boundary condition at the I-II interface is
\[
H_z^1(k_x, 0) - H_z^{II}(k_x, 0) = j(k_x) \quad (3.6)
\]
in the $k_{x}z$-space. The current density function $j(x, z)$ describes the total current $I_{0}$ flowing through the infinitesimally thin MSL of width $w$, that can be expressed as $j(x, z) = I_{0}/w\delta(x/w - 2)\delta(z)$ and the corresponding Fourier transform is $j(k_{x}, z) = j_{0}\sin(k_{x}w/2)\delta(z)$ with $j_{0} = (2/\pi)^{1/2}I_{0}/w$. The Fourier component of the linear current density, $j(k_{x})$, that enters the boundary conditions (Eq. [3.6]), is given by $j(k_{x}) = j_{0}\sin(k_{x}w/2)/k_{x}$.

Combining this discontinuity of the parallel $H$-field at the upper interface with the known continuity condition at the lower interface and the continuity of the orthogonal $B$-field at both interfaces provides four boundary conditions in total. Inserting the ansatz (3.5) finally leads to a system of linear equations determining the coefficients $C_{1} - C_{4}$. As long as the interacting quantum system is located above the magnetic thin film, we only require the solution for positive $z$-values, as only the field amplitude in region I is playing a role for any coupling processes. Hence, it is sufficient to concentrate only on the coefficient $C_{1}$.

The system of equations can be further simplified by introducing approximations relying on the realistic experimental values [38]. We take the saturation magnetization $M_{S}$ of the ferromagnetic material to be $M_{S} = 1850$ G and to be achieved in an external magnetic field $B_{0}$ of $\sim 10^{5}$ G. Hence, the assumption $\omega_0^2 \ll \omega^2$ is justified for microwave excitation frequencies $\omega$ in the GHz range and susceptibility parameters $\chi$ and $\kappa$ are of the order of $10^{-1}$ and $10^{0}$ respectively. Further, the wave vectors of microwaves of about $k_{0} \approx 10^{4}$ m$^{-1}$ in vacuum are much smaller than the experimental wave vectors $k_{x} \approx 10^{5}$ m$^{-1}$, i.e. $k_{0}^2 \ll k_{x}^2$. It follows then that the parameter $a$ in (3.2) can be approximated independently from the material as $a^{PDMS} \approx a^{GGG} \approx a^{YIG} \approx ik_{x}$. Hence, the result for $C_{1}$ only depends on $k_{x}$,

$$C_{1}(k_{x}) \approx j_{0}\sin(k_{x}w/2)/k_{x} \left[\omega_{M}(\omega_{0} + \omega_{M} + \omega) - e^{2k_{x}d}(\omega_{0} + \omega_{M} - \omega)(2\omega_{0} + \omega_{M} + 2\omega)/\omega_{M}^2 + e^{2k_{x}d}(4\omega^2 - (2\omega_{0} + \omega_{M})^2)\right].$$

(3.7)

The full solution for the magnetic field $H$ in the region I is given by

$$\begin{pmatrix} H_{1}^{I} \\ H_{2}^{I} \end{pmatrix} \approx \begin{pmatrix} 1 \\ i \end{pmatrix} C_{1}(k_{x}) e^{-k_{x}z} \equiv \begin{pmatrix} 1 \\ i \end{pmatrix} H_{s}^{I}(k_{x}, z)/\sqrt{2},$$

(3.8)

where the amplitude function $H_{s}^{I}(k_{x}, z)$ is introduced. From equation (3.8) as a function of $k_{x}$ and $z$, the allowed spin wave modes inside the ferromagnetic film can be derived by determining the zeroes of the denominator. This yields the dispersion relation

$$\omega(k_{x}) = \frac{1}{2}\sqrt{(2\omega_{0} + \omega_{M})^2 - \omega_{M}^2 e^{-2k_{x}d}},$$

(3.9)

that matches exactly the so called Damon-Eshbach surface waves (DESW), which exist in ferromagnetic thin films in the absence of any surface currents [38] in the magnetostatic regime. Hence, the solution of the modified system with non-zero current is peaked around the DESW modes, which is reasonable against the background of made approximations.

An important feature of the calculated spin wave modes is that for large $k_{x}$ the frequency in (3.9) saturates to a value that depends on the external magnetic field $B_{0}$. Thus, at a fixed magnetic field, spin wave excitations are limited to a fixed range of frequencies between the limiting cases $k_{x} = 0$ and $k_{x} \to \infty$,

$$\sqrt{\omega_{0}(\omega_{0} + \omega_{M})} \leq \omega \leq \omega_{0} + \omega_{M}/2.$$

(3.10)

The lower bound at $k_{x} = 0$ corresponds to the so called uniform precession mode, where all the spins inside the material precess in phase, so that there is an oscillating magnetization,
but no spatial wave propagation. Even in a strong external magnetic field of 200 G as used, for example, in Ref. [38], the uniform precession mode of the considered YIG film oscillates at about 1.6 GHz, which is far too small to stimulate magnetic dipole transitions in the spin triplet of the NV$^-$ center. In contrast, the upper limit $\omega_{\text{sw}}^{\text{max}} = \omega_0 + \omega_M/2$ is reached for the same magnetic field at $\sim 3.1$ GHz, which lies within the range of NV$^-$ resonances, as will be important later.

After deriving the driven spin wave modes, we are interested in the real space solution of the magnetic field to be able to model the interaction with an NV$^-$ ensemble and to give a quantitative expectation of the coupling strength. Therefore, the magnetic field $H^1$ in (3.8) has to be Fourier transformed back into real space using the explicit form of the coefficient $C_1(k_x)$ in (3.7). The field can be written as

$$H^1(x, z) = \left(\frac{1}{i}\right) H^1(x, z)/\sqrt{2}$$

with the Fourier transform of the amplitude function

$$H^1(x, z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} H^1(k_x, z) e^{ik_xx} \, dk_x.$$  

In order to calculate this integral, the denominator of Eq. (3.7) is expanded to first order in $k_x$ around its zero $k_x'$, which corresponds to the resonant wave number defined by (3.9),

$$k_x' = \frac{1}{2d} \ln \left(\frac{\omega_M^2}{4\omega^2 - (2\omega_0 + \omega_M)^2}\right).$$

The remaining integral can be analytically evaluated assuming that before the current in the MSL was switched on there were no spin waves. This adds an infinitesimally small imaginary to the denominator of Eq. (3.7) and imposes the rule how to go around the pole in the integral above. Applying the Sokhotski-Plemelj theorem in case of a real line integral and restricting ourselves to the far field regime, where for all relevant $k_x$ the condition $x \gg (k_x - k_x')^{-1}$ holds, the amplitude function $H^1(x, z)$ in real space is

$$H^1(x, z) \approx i\sqrt{2} \frac{I_0}{w} \frac{\sin(k_x'w/2)}{k_x'd} \left[ \frac{\omega_M(\omega_0 + \omega_M + \omega)}{4\omega^2 - (2\omega_0 + \omega_M)^2} e^{-2k_x'd} + \frac{\omega_0 + \omega_M - \omega}{2\omega_0 + \omega_M - 2\omega} e^{-k_x'z} e^{ik_x'x},
$$

which is one of our main results. Based on this complex field amplitude, the magnetic field above the ferromagnetic film is known explicitly. The factor before the square brackets in this expression takes into account the geometry of the MSL. The expression inside the square brackets gives the frequency dependence of the coupling between the current in the MSL and the spin wave mode of a given frequency. There is no way one can predict this dependence based on the Damon-Eshbach spectra only. Note, however, that the calculated solution only holds for frequencies within the range (3.10). The assumptions, which were made in order to solve the integral above, are not valid outside this frequency range, where the solution of (3.14) at frequencies above $\omega_{\text{sw}}^{\text{max}}$ does not exist. Hence, the given solution (3.14) is only valid for $\sqrt{\omega_0(\omega_0 + \omega_M)} \leq \omega \leq \omega_0 + \omega_M/2$ and is set to 0 otherwise, which corresponds to the absence of spin waves.

### 3.3 Magnetically driven NV$^-$ spins

The spin wave propagation through the magnetic thin film can increase the interaction between the external field and a quantum system. As a consequence, the driving of magnetic dipole transitions of NV$^-$ centers in diamond can be performed more efficiently. In order to model the coupling strength and to simulate the resulting transition spectrum, we have to distinguish whether a single NV$^-$ center or an NV ensemble in single crystal diamond is probed.
Figure 3.2: (a) Possible orientation of NV$^-$ centers inside the diamond structure. The arrows start at the vacancy and end at four possible sites a substitutional nitrogen can take, marked with different colors of the arrows. This leads to four different angles $\theta_{Bi}$ between the magnetic field and the possible NV-axes $\hat{c}_i$. (b) Resonance frequencies of the magnetic dipole transitions within the ground state triplet of an ensemble of NV$^-$ centers embedded in single crystal diamond. Each of the four possible NV$^-$ center orientations $\hat{c}_i$ contributes two resonances at $\omega^\pm$, marked with the same color. The resonances depend on the alignment of the magnetic field.

3.3.1 Single NV$^-$

The ground state of the NV$^-$ center is a spin triplet, which is split into the $m_S = 0$ and $m_S = \pm 1$ sublevels (see sec. 1.2.2 of the introduction). The Hamiltonian of the spin triplet is

$$\hat{H}_0 = \Delta_{gs} \hat{S}_z^2 + g \mu_B B_0 \cdot \hat{S}, \quad (3.15)$$

where the second term accounts for the Zeeman splitting with an external magnetic field $B_0 = (B_x, B_y, B_z)$. In cases where the magnetic field is not aligned with the NV-axis $\hat{c}$, the Hamiltonian (3.16) can be written as

$$\hat{H}_0 = D \hat{S}_z^2 + g \mu_B B_0 (\sin \theta_B \hat{S}_x + \cos \theta_B \hat{S}_z), \quad (3.16)$$

where the relative angle $\theta_B$ quantifies the orientation of the external magnetic field in the frame of the NV center. Here we assume the local NV$^-$ $x$–axis to be in the plane, formed by magnetic field direction and the NV$^-$ axis. This does not agree with the convention we used in previous chapters, when the $x$–axis was fixed by the crystal structure. But as now we are only interested in the interaction of the ground state spin with magnetic field and this interaction is invariant under rotations in the $xy$–plane, we can change the bases for simplicity here. Another way to say it would be that the energy splittings of the NV$^-$ ground state spin depend only on the relative angle of the magnetic field with respect to symmetry axis and choosing the $x$–axis freely we disregard the information about the actual spin direction, corresponding to the eigenstates. Since the Hamiltonian (3.16) depends explicitly on $\theta_B$, the corresponding eigenenergies and, consequently, the frequencies $\omega_{\theta_B}^\pm$ of the dipole transitions $|0\rangle \leftrightarrow |\pm 1\rangle$ vary for different orientations of the magnetic field with respect to the NV-axis. Hence, the transition spectrum of a single NV$^-$ center consists of two frequency branches $\omega_{\theta_B}^\pm$, whose behavior with respect to varying bias field $B_0$ is determined by the given value of $\theta_B$. It is worth pointing out that when the magnetic field has non-axial component, the levels $|0\rangle$ and $|\pm 1\rangle$ become mixed. This effect is not too strong due to a large zero-field splitting $\Delta_{gs}$, that is why we will still address the spin states as ($|0\rangle$, $|-1\rangle$ and $|1\rangle$).
3.3.2 NV ensemble in single crystal diamond

In case of an NV ensemble every single of the numerous NV\(^-\) centers contributes two branches to the transition spectrum. If the single NV centers were randomly oriented, all branches would combine to a blurred spectrum. But due to the symmetry of the diamond crystal, the actual transition spectrum of an NV ensemble inside a single crystal consists of single branches. For a single crystal diamond, the lattice has a fixed orientation in the lab frame, but inside the diamond structure the actual orientation of an NV\(^-\) center is not controllable during fabrication. Thus, the NV axis can be aligned along the four crystal directions shown in Fig. 3.2 (a), which are at a tetrahedral angle of \(\theta_t = 109.5^\circ\) to each other. A single nanodiamond contains NV centers with orientations equally distributed over these four directions. Accordingly, for a fixed \(B_0\)-field orientation, the magnetic field is aligned at a different angle with respect to each of these four directions. Thus, each of the four possible NV-axis orientations gives rise to two resonances and in total there are eight resonances for an NV ensemble.

In order to describe the expected magnetic resonances with a formula, the NV center orientation is expressed in terms of the relative angles \(\theta_{B_i}\) between the possible NV-axis and the magnetic field as shown in the Fig. 3.2 (a). Choosing one of the NV-axes, \(\hat{c}_0\), to define the \(z\)-direction and one of the carbon atoms to lie on the \(x\)-axis, the normalized magnetic field vector and the four NV-axes \(\hat{c}_i\) are parameterized in spherical coordinates as \(\hat{B} = (\sin \theta_B \cos \varphi_B, \sin \theta_B \cos \varphi_B, \cos \theta_B)\) and \(\hat{c}_i = (\sin \theta_i \cos \varphi_i, \sin \theta_i \cos \varphi_i, \cos \theta_i)\) with \(\theta_0 = 0, \theta_{1,2,3} = \theta_t, \varphi_{0,1} = 0\) and \(\varphi_{2,3} = 2\pi/3, 4\pi/3\). The introduced coordinate system is thus fixed to the crystal lattice. Based on these vectors, the angles \(\theta_{B_i}\) between the single NV-axes and the magnetic field in Fig. 3.2 are related to the corresponding scalar product as

\[
\cos \theta_{B_i} = \hat{B} \cdot \hat{c}_i = \sin \theta_B \sin \theta_i \cos(\varphi_B - \varphi_i) + \cos \theta_B \cos \theta_i. \tag{3.17}
\]

From experimental data of the eight different magnetic resonance frequencies in a nanodiamond of known crystal orientation, the angles \(\theta_B\) and \(\varphi_B\) can be calculated or, in turn, from a known magnetic field alignment, the crystal directions of a nanodiamond can be derived. Hence, the resonance experiment can be used to sense a probe magnetic field resolving its direction on the one hand and to measure the crystal structure of a nanodiamond indirectly on the other hand [99, 100].

3.4 Enhancement

Due to the presence of spin waves inside the magnetic film, the magnetic field coupling to an NV ensemble is enhanced compared to the amplitude of a pure antenna field. Moreover, the spin wave field has the great advantage of longer decay length, which becomes apparent when inspecting the explicit dependencies of the spin wave field in (3.14). The lack of \(x\)-dependence of the field amplitude indicates a very important difference from a pure antenna driving field. The microwave field of the antenna decays as \(1/x\), so that the coupling strongly depends on the position of the interacting NV\(^-\) center. In a system of defect spins addressed or read out with an oscillating magnetic field, information can be transferred over a distance, at which the field amplitude is strong enough. Hence, the \(x\)-independent spin wave field amplitude in (3.14) appears to lead to a constant coupling over a large distance. Realistically, the coupling decays due to the neglected exchange energy terms in the susceptibility tensor. Regarding the corresponding terms would give rise to a magnetic amplitude damping in (3.14) along the \(x\)-coordinate. But YIG has a particularly low damping parameter and the excited spin waves propagate at low \(k\), thus justifying the made approximation. Along the \(z\)-direction, \(\tilde{C}_1\) decays exponentially with the distance to the surface, i.e. the spin wave modes are confined to the surface of the thin
film. This guarantees a highly localized field, so that the effect of spin wave enhancement is only present in the vicinity to the magnetic film.

Using the obtained result for the spin wave field allows us to investigate the enhancement of the coupling strength $\Omega_R$ with respect to the case of no spin wave excitation. The enhancement factor is defined as $\eta_{\text{eff}} \equiv \frac{\Omega_{\text{sw}}}{\Omega_{\text{ant}}}$, where $\Omega_{\text{sw}}$ denotes the Rabi frequency in the case of spin wave excitation and $\Omega_{\text{ant}}$ is the same quantity for the pure antenna driving, obtained at the same current through the MSL. We want to adapt our result to the experimental method described in [38], where the resonance between the same levels is measured twice in the different driving regimes (the antenna driving and the spin wave driving regimes). To measure both regimes at the same frequency, a resonance has to lie once above the maximal excitation frequency of spin waves and once below, so that the different regimes can be tuned by the bias magnetic field. For the realization of such a measurement, the orientation of the bias field has to be non-collinear to the NV-axis, whereby the states $|0\rangle$ and $|\pm 1\rangle$ become coupled and the energy splitting does not depend linearly on the magnetic field. Thus, the resonance branches are tilted as plotted in Fig. 3.3 (a). The plot shows the NV resonances in the case of the NV-axis being aligned in the $xy$-plane of the YIG (Fig. 3.1) at an angle of $\theta_B = 78^\circ$ with respect to the bias magnetic field (pointing along the y-axis in Fig. 3.1). In Fig. 3.3 (a) only six resonances are visible, because the magnetic field encloses the same angle with two of the possible crystal directions leading to these resonances being two-fold degenerate. An excitation frequency of 2.86 GHz hits the resonance at the bias field $B_{\text{ant}} = 15$ G in the antenna driving regime, which is marked by the black dot in Fig. 3.3 (a). A second resonance (black dot) occurs in the regime of spin wave excitation at $B_{\text{sw}} = 145$ G. Equation (3.9) shows that the corresponding spin wave has a $k$-vector ($k'_x$) of 0.346 $\mu$m$^{-1}$.

Both quantities, the spin wave and the antenna Rabi frequencies, depend on the angle between the magnetic field and the NV$^-$ center symmetry axis, which is non-zero in the general case. In a coordinate system $S'$ with $z'$-axis parallel to the NV-axis $\hat{c}$, the direction of the linearly polarized antenna magnetic field can be parametrized in spherical coordinates as $B_{\text{ant}} = B_{\text{ant}}(\sin \theta_{\text{ant}} \cos \varphi_{\text{ant}}, \sin \theta_{\text{ant}} \sin \varphi_{\text{ant}}, \cos \theta_{\text{ant}})$, where $\theta_{\text{ant}}$ denotes the angle between the field and the $\hat{c}$-axis. Let us assume that the antenna field amplitude is $B_{\text{ant}} \cos(\omega t)$. The driving Hamiltonian arises due to off-diagonal term in $B_{\text{ant}} \cdot \sigma$ and
\[ \hat{H}_d = g\mu_B B_{\text{ant}} \cos(\omega t) \sin \theta_{\text{ant}} \left( \cos \varphi_{\text{ant}} \hat{S}_x + \sin \varphi_{\text{ant}} \hat{S}_y \right). \]  

(3.18)

The linearly polarized field is a superposition of two circularly polarized fields of equal amplitudes and only one of those can excite the dipole spin resonance (the other one is counter-rotating to the free spin precession and its effect can be neglected), the Rabi frequency for the antenna field is then given by

\[ \Omega_{R\text{ant}} = \frac{1}{2} g\mu_B B_{\text{ant}} \sin \theta_{\text{ant}}. \]  

(3.19)

The antenna field amplitude is calculated without regarding the stray field of the YIG, which is reasonable in the regime of no spin wave excitation, since the thin film is located in an approximately homogeneous magnetic field and due to its small height the influence on the antenna field becomes negligible. In that case we can approximate the antenna field at large distances as the field of the wire

\[ B_{\text{ant}} = \frac{\mu_0 I_0}{2\pi x}, \]  

(3.20)

where \( x \) is the distance from the NV to the MSL (we assume it to be much larger than the width of the MSL). In this approximation the antenna field points along the \( z \)-axis in Fig. 3.1 and the angle \( \theta_{\text{ant}} \) is taken to be 90°. One finally obtains for the Rabi-frequency in the antenna driving regime

\[ \Omega_{R\text{ant}} = g\mu_B \frac{\mu_0 I_0}{4\pi x}. \]  

(3.21)

The spin wave field is circularly polarized and its explicit time and space dependence obtained from Eq. (3.14) and (3.12) is

\[ B_{\text{sw}}(x, z, t) = B_{\text{sw}}(z) \begin{pmatrix} \sin(\omega t - k'_x x) \\ -\cos(\omega t - k'_x x) \end{pmatrix}, \]

\[ B_{\text{sw}}(z) = \mu_0 \frac{I_0}{w} \frac{\sin(k'_x w/2)}{k'_x d} \begin{pmatrix} \omega_M(\omega_0 + \omega_M + \omega) \\ 4\omega^2 - (2\omega_0 + \omega_M)^2 \end{pmatrix} e^{-2k'_x d} + \begin{pmatrix} \omega_0 + \omega_M - \omega \\ 2\omega_0 + \omega_M - 2\omega \end{pmatrix} e^{-k'_x z}. \]  

(3.22)

Projecting this field on the plane perpendicular to the NV-axis \( \hat{c} \) and again writing the time dependent driving Hamiltonian, one calculates the Rabi frequency as the amplitude of the circularly polarized field, that rotates clockwise with respect to the bias field. The Rabi amplitude then yields

\[ \Omega_{R\text{sw}} = \frac{1 - \cos \theta_B}{2} g\mu_B B_{\text{sw}}(z). \]  

(3.23)

Inserting this into the enhancement ratio yields

\[ \eta_{\text{eff}} = 2\pi (1 - \cos \theta_B) \frac{\sin(k'_x w/2)}{k'_x d} \left( \frac{\omega_M(\omega_0 + \omega_M + \omega)}{4\omega^2 - (2\omega_0 + \omega_M)^2} e^{-2k'_x d} + \frac{\omega_0 + \omega_M - \omega}{2\omega_0 + \omega_M - 2\omega} e^{-k'_x z} \right) \frac{x}{w}. \]  

(3.24)

With this expression, we are able to make a theoretical prediction of the enhancement for an NV\(^-\) center located at \( x_{\text{NV}} \). Since the far field approximation was made, the condition \( x \gg k^{-1} \) has to be fulfilled and for wave numbers of the excited spin waves in Ref. [38] of the order of \( \sim 10^5 \) m\(^{-1}\), the expression (3.24) applies for distances above 10 \( \mu \)m. For example, for a nanodiamond at \( x_{\text{NV}} = 20 \mu \)m driven by a microwave field at frequency 2.86 GHz, the enhancement factor of the coupling between the defect spin and the driving field is \( \eta_{\text{eff}} \approx 119 \) (we assume the nanodiamond to be close to the surface of the YIG, so that \( z \approx 0 \)), which is close to the experimentally measured enhancement \( \eta_{\text{eff}} \approx 100 \) detected via Rabi experiments [38]. Moreover, when distance \( x \) in expression (3.24) is varied, the
enhancement factor \( \eta_{\text{eff}} \) behaves as plotted in Fig. 3.3 (b), along with the experimental data of Ref. [38]. The theoretical prediction matches the experimental behavior, although the experimental data are slightly shifted to lower enhancement values with respect to the predicted theory curve. Nevertheless, the linear \( x \)-dependence of \( \eta_{\text{eff}} \) not only shows good agreement with the trend of experimental data, but also an achievable enhancement factor of more than 400 at distances above 70 \( \mu m \), that emphasizes the great advantage of spin wave excitation inside the magnetic film. For low magnetic damping the spin waves do not decay as fast as the microwave field leading to a large enhancement far away from the antenna.

3.5 Discussion

We have presented a theoretical model that provides a complete description of real experimental hybrid systems consisting of driven spin waves coupled to NV\(^{-} \) spins. All results are obtained analytically and especially the description of spin wave modes follows a fundamental approach from the basics of Maxwell’s equations. In that way, we derive an analytical solution for the magnetic field amplitude, which allows a theoretical calculation of the coupling to an NV ensemble. Therefore, we regard every possible spatial orientation of an NV center in a real nano-diamond, thus obtaining the full spectrum capturing all eight resonances.

The derived enhancement factor \( \eta_{\text{eff}} \) is strongly dependent on the distance between the source of the microwave field and the NV ensemble. Accordingly, the magnetic field at the NV\(^{-} \) spin can be enhanced by two orders of magnitude and the predicted behavior for longer distances is in good agreement with recent experiments\([38]\) indicating the strength of our model as well as the applicability of the related assumptions and approximations. The presented solutions are obtained using the far field approximation, which holds for distances above \( \sim 10 \mu m \). This regime is of particular interest for technical realizations, since it is a general problem to couple a sensitive quantum system to a microwave antenna across distances of more than a few \( \mu m \) in view of the rapidly decaying antenna field. In contrast, we show that the spin wave field is very stable along these distances, enabling a coupling to NV\(^{-} \) centers far away from the antenna by using a magnetic thin film.

If one is interested in the enhancement effect over a long distance, the approximations made are reasonable and the model provides good results. But in case of a modified system operating at a different conditions, possibly the limits of our theoretical model could be reached. If a nanodiamond is positioned very close to the antenna, there is need of a solution outside the far field regime, that can be applicable for short distances. An exemplary real system would be an array of nanodiamonds, where the antenna is not deposited besides but in between the array, so that the NV\(^{-} \) centers are partly in the near field and partly in the far field regime. Strictly speaking, this would require a mid field solution as well.

Further unconsidered effects, which had to be taken into account in order to optimize the presented model, are additional boundary effects caused by the surrounding material being non-perfect magnetic vacuum or spin wave reflections in case of the film having finite expansion in the \( xy \)-plane. A refinement of the model considering those aspects would lead to important insights with respect to new applications of a spin wave mediated coupling. Since the spectrum of the spin waves is mainly determined by the shape of the ferromagnetic sample, the driven spin wave modes could be adapted by shaping, for example, a ferromagnetic sphere or a disk. In this way, the technique of the experiment of Ref. [38] could be transferred to various magnetic resonance experiments by changing the driven spin wave modes to be in resonance with other defect spins like different color centers in diamond or vacancies in silicon carbide. The usage of a spin wave resonator, which
has already been experimentally realized[101], would lead to an additional improvement of spin wave excitation. This provides an outlook towards the possible long-term goal of achieving a coherent coupling between single magnons and single defect spins, thus entering the quantum regime.
Chapter 4

Designing a cavity-mediated quantum CPHASE gate between NV spin qubits in diamond

One of the remaining challenges on the way towards diamond-based quantum computation is scaling the system up. This requires a possibility for distant NV centers to interact in a controlled way. As we argued before, it is enough to show that controlled-phase (CPHASE) or controlled-not (CNOT) gate between any pair of qubits can be realized. This in combination with single-qubit gates forms a universal set of quantum gates. Controlled operations between the NV electron spin and nearby nuclear spins can now be performed on a routine bases [33, 35]. Entanglement generation can be achieved between the electron spins of two nearby NV centers on the basis of static dipolar interactions [15], and between NV center spins separated by several meters via a non-deterministic coincidence measurement protocol [102]. The latter is most frequently used in quantum teleportation NV-based experiments. Here, we propose and theoretically analyze a fully controllable and switchable coupling between the spins of distant NV centers coupled to the same mode of a surrounding optical cavity (Fig. 4.1).

![Figure 4.1](image.png)

Figure 4.1: Two nitrogen-vacancy centers in diamond located in an optical cavity and coupled to a common cavity mode with frequency $\omega_C$ (shown schematically). The NV centers are excited by off-resonant laser fields (frequencies $\omega_{L1}$). Spin-dependent scattering of laser photons off the NV center into the cavity mode and back allows for a coupling of the two NV spins which produces the universal CPHASE quantum gate.

A variety of optical cavity systems for cavity quantum electrodynamics (QED) coupled to defect centers in diamond exist. An important example in this regard are photonic crystals fabricated within the diamond crystal [103, 105] or on top [106] of it. They
allow for the embedding of the NV centers directly into the optical cavity structure, but comprise (so far) somewhat lower $Q$ factors. Recently, two SiV centers have been shown to successfully interact through such a cavity \[107\]. The architecture we discuss here can in principle be used with any realization of NV-cavity coupling, provided sufficiently high $Q$ and the ability of NV to relax emitting a photon into the cavity.

The basic working principle of the quantum gate operation proposed here is as follows. We assume the sample to be highly strained and for simplicity only assume $\epsilon_{xz}$ strain component to be nonzero. In that case, as suggested by the Hamiltonian (1.44), the states $|X\rangle$ and $|Y\rangle$ will split apart. For a sufficiently high strain, this splitting can reach up to 20 GHz \[49, 50\] and becomes the dominant energy scale within the excited state. One can then neglect the spin-orbit interaction (Eq. 1.35 with $\lambda = 5.3$ GHz), as it tends to mix the orbital states and they are now separated by large strain. For the spin-spin interaction (Eq. 1.38) we can only keep the secular terms, that do not couple $|X\rangle$ to $|Y\rangle$. We then effectively end up with an NV level scheme, shown in Figure 4.2. The excited state is represented with only one spin triplet (that is subject to spin-spin interaction), the second one we assume to be much higher in energy and thus never occupied, so its effect can be neglected. We focus on only two of the three ground state (GS) spin triplet states, $m_s = 0$ and $m_s = -1$, which will serve as the qubit bases in our scheme (Fig. 4.2). For this approximation to be valid, we apply a magnetic field of about $B_0 \sim 1000$ G, so that $m_s = 0$ and $m_s = -1$ are nearly degenerate, while $m_s = 1$ is approximately $2\Delta_{gs} \simeq 5.7$ GHz away from them. We further assume the GS-ES transition to be detuned from the cavity resonance frequency. As shown in the Figure 4.1 we need to fulfill these conditions for two NV centers and place them inside of the same cavity. We then drive GS-ES transition of each NV with lasers, that are again off resonant to both the cavity and the GS-ES transitions. This procedure generates the processes, in which a laser photon is first absorbed by the first NV, scattered into the cavity and then reabsorbed by the second NV, ending with a relaxation of the second NV. This is a fourth order process in perturbation theory (see appendix B.2). The off-resonant coupling is the main distinguishing feature from resonant schemes which are limited by spontaneous emission and Purcell effect \[108\].

One final feature, that makes this scheme generate entanglement between qubits, is the spin-photon locking, i.e. the scattering of photons into the cavity is spin dependent due to the difference in zero-field splittings in the GS and ES. More specifically, the $m_s = 0$ and $m_s = -1$ states in the ES are not degenerate at $B_0$, which leads to unequal scattering matrix elements for the $m_s = 0$ and $m_s = -1$ states. To produce an entangling quantum gate between two NV spin qubits, we find it to be sufficient if the laser-cavity photon scattering rate is different for the two spin states. We show that this virtual photon exchange generates a conditional phase shift. Once the accumulated phase amounts to $\pi$, a CPHASE gate on the two NV spin qubits has been achieved.

Earlier works on cavity-mediated quantum gates for defect qubits in diamond make use of spectral hole burning \[109\] or a series of $\Lambda$ systems\[110\]. The latter requires a sequence of at least three two-color pulses, while our scheme manages on just one single-color laser pulse for a CPHASE gate. A model for three NV centers coupled to a whispering-gallery mode in a silica microsphere cavity using polarized excitation has been studied with the goal of achieving a three-qubit CPHASE gate \[111\]. Our scheme relies on spectral selectivity and thus does not require polarized excitation. The effect studied here produces an elementary, universal two-qubit CPHASE gate.
Figure 4.2: GS and ES energy levels as a function of the magnetic field $B$. In the ES, only one orbital triplet is shown. The effect of the spin-spin interactions $\Delta_{gs/es}$ is shown schematically by the dotted lines.

### 4.1 Single NV center in a cavity

The NV center in its ground state (GS) and excited state (ES) spin triplet will be described by the Hamiltonian

$$H_{NV} = g_e \mu_B BS_z + \left( \frac{E_g + D_{es} S_z^2}{g_L e^{i \omega_L}} \right) \left( \frac{D_{gs} S_z^2}{g^*_L e^{i \omega_L}} \right),$$

where the first term describes the Zeeman splitting of the spin $S = (S_x, S_y, S_z)$ with eigenvalues $m_s = -1, 0, 1$ in a magnetic field applied along the NV ($z$) axis with identical electronic Landé g-factor $g_e = 2$ for the GS and ES ($\mu_B$ denotes the Bohr magneton). For now we will neglect the non-axial spin-spin interaction in the excited state, but we will include it further below. We as well neglect the differences between $g||$ and $g\perp$. The transverse magnetic field is assumed to be 0, see Appendix B.1 for a discussion of a possible magnetic field misalignment. The second term in Eq. (4.1) includes the GS-ES energy gap $E_g = 1.945 \text{eV}$ and the distinct GS and ES zero-field spin splittings $\Delta_{gs} = 2.88 \text{GHz}$ and $\Delta_{es} = 1.44 \text{GHz}$. The off-diagonal terms describe laser excitation at a frequency $\omega_L$, with the spin-independent dipole matrix element $g_L$. Taking only one orbital ES into account, we can view the Hamiltonian $H_{NV}$ in Eq. (4.1) as a 6x6 matrix consisting of four 3x3 blocks. The Zeeman splitting described by the first term in Eq. (4.1) is independent of the orbital state. Using Pauli matrices $\tau_i$ to describe the GS-ES orbital state, i.e., $\tau_z = +1$ for the GS and $\tau_z = -1$ for the ES, and working in a rotating frame with the frequency $\omega_L$, we can write

$$H_{NV} = g \mu_B BS_z + D S_z^2 + \frac{\Delta}{2} S_z^2 \tau_z + g_L \tau_z + g^*_L \tau_z,$$

where $D = (\Delta_{gs} + \Delta_{es})/2 = 2.16 \text{GHz}$ and $\Delta = \Delta_{gs} - \Delta_{es} = 1.44 \text{GHz}$ denote the mean and difference between the GS and ES zero-field splittings, $\tau_z = (\tau_z \pm i \tau_y)/2$ describe transitions between the GS and ES, and $\delta_L = E_g - \omega_L$ is the laser detuning.

We now consider a single NV center coupled to a near-resonant mode of a surrounding optical cavity which we describe, using the rotating-wave approximation, with the following Hamiltonian,

$$H = H_{NV} + \delta_C a^\dagger a + g_C \left( \tau_+ a + \tau_- a^\dagger \right),$$

where $a$ and $a^\dagger$ are creation and annihilation operators of the cavity mode, $g_C$ is the cavity coupling constant, and $\delta_C$ is the cavity detuning.
where $\delta_C = \omega_C - \omega_L$ denotes the detuning of the cavity mode from the laser excitation frequency and $a^\dagger$ ($a$) creates (annihilates) a cavity photon. The dipole matrix element $g_C$ of the cavity field can be made real-valued by an appropriate phase convention in the excited state. However, $g_L$ can in general not be made real-valued at the same time; its phase $\phi$ depends on the phase of the laser field.

The magnetic field is chosen at a working point around the GS level crossing $B_0 = D_{gs}/g_e\mu_B$ where we focus our description on the nearly degenerate $m_s = -1$ and $m_s = 0$ levels (the $m_s = +1$ level will be included further below together with the spin-spin interaction). We describe here the situation of an initially empty cavity, which subsequently holds at most one virtual photon.

### 4.2 Two NV centers coupled to a common cavity mode

The scattering of a photon from the laser to the cavity field and vice versa, conditional on the spin (qubit) state of an NV center can be used to construct a cavity-photon mediated quantum gate between two NV spin qubits coupled to a common cavity mode. Starting from two NV centers ($i = 1, 2$), each coupled to the same cavity mode as described above (Fig. 4.1), we derive the effective coupling Hamiltonian for two NV spins by eliminating the virtual cavity photon. It is important to recognize that the cavity mediated interaction between the NV centers is a fourth-order process in the coupling strengths. In order to systematically account for all contributions up to the fourth order, we apply a fourth-order perturbation theory to the Hamiltonian describing two NV centers coupled to a common cavity mode.

$$H = H_0 + H_{\text{int}},$$
$$H_0 = \delta_C a^\dagger a + \sum_{i=1,2} \left[ \frac{1 + \tau_i}{2} (\delta_{Li} + \Delta \hat{S}_{zi}) + \delta B_i \hat{S}_{zi} \right],$$
$$H_{\text{int}} = \sum_{i=1,2} g_{Li} \tau_i^z + g_C a^\dagger \tau_i^z + h.c..$$

(4.4)

As this Hamiltonian commutes with the operators $\hat{S}_{z1}$ and $\hat{S}_{z2}$ of the NV centers, we can treat it separately for each of the four ground-state spin configurations, which represent the logical basis for our two-qubit system.

For each spin configuration, we consider the five states $|GG0\rangle$, $|GG1\rangle$, $|EG0\rangle$, $|EG0\rangle$, and $|EE0\rangle$, where $|X_1X_2\rangle$ denotes the state with NV $i$ ($i = 1, 2$) in the ground ($X_i = G$) or excited ($X_i = E$) state, while the cavity mode is occupied with $n$ photons.

To describe the combined action of the coupling between the NV center and the laser and cavity fields we treat $H_{\text{int}}$ in Eq. (4.4) as a perturbation and eliminate the ES in order to derive an effective interaction using the Schrieffer-Wolff transformation [112, 113],

$$H_{\text{eff}} = e^S H e^{-S} = H + [S, H] + \frac{1}{2} [S, [S, H]] + \frac{1}{6} [S, [S, [S, H]]] + \frac{1}{24} [S, [S, [S, [S, H]]]] + \ldots$$

(4.5)

The matrix $S$ is expanded in a series $S = S_1 + S_2 + S_3 + S_4 + \ldots$, where each term $S_i$ is derived using Eq. (4.5) under the requirement that there is no coupling between the $|GGn\rangle$ ($n = 0, 1$) subspace and the excited states of the NV centers up to $i$-th order in the coupling constants $g_L$ and $g_C$. In the sum Eq. (4.5), we then calculate all the residual terms and obtain the effective Hamiltonian in the bases of $|GG0\rangle$, $|GG1\rangle$,

$$H_{\text{eff}} = \begin{pmatrix}
W_{GG0} + |\tilde{g}|^2/\delta_C \\
\tilde{g} \\
W_{GG1} - |\tilde{g}|^2/\delta_C
\end{pmatrix}.$$  

(4.6)
Introducing the phase of the lasers by the equation $g_{Li} = |g_{Li}|e^{i\phi_i}$, for the eigenenergies of this effective Hamiltonian we find

$$W_{GG0} = \sum_{i=1,2} \delta B_i m_{si} - \sum_{i=1,2} \frac{|g_{Li}|^2}{\delta_{Li} + \Delta m_{si}} + \sum_{i=1,2} \frac{|g_{Li}|^4}{(\delta_{Li} + \Delta m_{si})^3}$$

and $W_{GG1} \approx \delta_c + \sum_{i=1,2} \delta B_i m_{si}$, whereas for the offdiagonal matrix element we obtain

$$\tilde{g} = -\sum_{i=1,2} e^{i\phi_i} g_{Ci} |g_{Li}|(\delta_{Li} + \Delta m_{si} - \delta_C / 2).$$

We present $W_{GG0}$ only up to the fourth order corrections, as only these terms will be important for the following discussion. We have also calculated $W_{GG0}$ using conventional perturbation theory, rather than a Schrieffer-Wolff transformation, with identical results (see Appendix B.2). The expression for $W_{GG0}$ in Eq. (4.7) consists of nine terms, where the first eight terms each depend on the spin state of only one NV center and thus can only lead to single qubit dynamics. The entanglement arises when we consider the last term of Eq. (4.7),

$$\epsilon_{m_{s1},m_{s2}} = -\frac{2|gL_i gL_j gC_i gC_j| \cos (\phi_1 - \phi_2)}{\delta_{Li1} + \Delta m_{s1} \delta_{Li2} + \Delta m_{s2} \delta_C},$$

as it depends on the spin state of both NV centers. Calculating this term for each spin configuration $|m_{s1},m_{s2}\rangle = \{|-1,-1\rangle, |-1,0\rangle, |0,1\rangle, |0,0\rangle\}$ leaves us with the diagonal spin Hamiltonian

$$H_{2q} = \begin{pmatrix} \epsilon_{-1,-1} & 0 & 0 & 0 \\ 0 & \epsilon_{-1,0} & 0 & 0 \\ 0 & 0 & \epsilon_{0,-1} & 0 \\ 0 & 0 & 0 & \epsilon_{0,0} \end{pmatrix}.$$  \hspace{1cm} (4.10)

This Hamiltonian generates a quantum gate $\exp(-itH_{2q})$ which up to single-qubit operations, is the CPHASE gate $U = \text{diag}(1,1,1,\epsilon^{i\gamma})$ with

$$\gamma = \frac{2|gL_i gL_j gC_i gC_j| \Delta^2 \cos (\phi_1 - \phi_2)}{\delta_C \delta_{Li1} \delta_{Li2} \delta_{Li1} - \Delta}.$$  \hspace{1cm} (4.11)

Equation (4.11) proves that the interaction of two NVs through the cavity can give rise to entangling gate. This gate can be controlled by both the amplitude $|g_{Li}|$ and phase $\phi_i$ of the lasers and by the detuning of the laser frequency from the cavity mode $\delta_{Li}$. This gate also gives rise to local single qubit operations, which depend on both the parameters of the lasers and on the magnetic field $\delta B_i$ and are fully described by the first eight terms of Eq. (4.7).

The results of this section can only be considered a qualitative proof of the entangling gate. They are valid as long as the perturbation analysis works, which implies that the couplings $g_{Li}, g_{Ci}$ are much smaller than the detunings $\delta_C, \delta_{Li}$. Moreover, to make predictions one should take into account the spin-spin interaction in the excited state of the NVs, which will be done in the next section in the description of our numerical results.
4.3 Spin-spin interaction

To make quantitative predictions, we need to include the spin-spin interactions (see introduction 1.2.2) in the ES which have been studied both experimentally \[49, 50, 114\] and theoretically \[44, 115\]. Under the assumption of $\epsilon_{zz}$ strain, the nonaxis part of the spin-spin interaction from Eq. 1.38 takes the form

$$H_s = \frac{1}{2} (1 + \tau_z) \left[ \frac{\Delta_1}{2} (S_y^2 - S_x^2) + \frac{\Delta_2}{\sqrt{2}} (S_x S_z + S_z S_x) \right],$$  \tag{4.12}

where $\Delta_1 = 1.55 \text{ GHz}$ and $\Delta_2 \simeq 0.15 \text{ GHz}$.

The Hamiltonian of the system will then take the form

$$H = H_0 + H_{\text{int}} + H_s,$$  \tag{4.13}

where $H_0$ and $H_{\text{int}}$ have been introduced in the previous section. In the spin Hamiltonian the $\Delta_1$ term mixes the spin states $m_s = -1$ and $m_s = 1$, while the $\Delta_2$ term mixes $m_s = -1$ and $m_s = 0$, as well as $m_s = 0$ and $m_s = 1$. Therefore, we can no longer treat each of the four logical states separately.

It is important to note that both cavity photon creation and spin-spin interaction are only possible when one of the NVs is in the excited state. To achieve this and thus create a quantum gate, laser excitation can be used to transform the initial ground state of the NVs. But it is also important that after the excitation is switched off, the system should remain in a final state that is the coherent superposition of the logical basis states. Thus the probability to have an excited NV after the laser pulse is turned off should be very low. This will be the case if the intensity of the lasers changes very slowly, such that the adiabatic theorem guarantees that the system never leaves the ground space of the time-dependent Hamiltonian. The final state of the system after the pulse is turned off will correspond to the ground state of the NVs and zero cavity photons — the logical bases of the two qubit system.

We now introduce our numerical results obtained for this system, including spin-spin interactions. The laser detuning $\delta_L$ and the cavity detuning $\delta_C$ are assumed to be 1640 MHz and 400 MHz respectively. The distance between the ground state and the lower excited state of the NV would then be $\delta_L - \Delta = 200 \text{ MHz}$ for $m_s = -1$ spin state and $\delta_L = 1640 \text{ MHz}$ for $m_s = 0$ spin state. The energy of the cavity excitation would be $\delta_C = 400 \text{ MHz}$. The inverses of these values (5 ns, 0.6 ns, 2.5 ns respectively) define the internal dynamical rate of the system, with respect to which one has to choose the ramp time of the pulse. To stay within the adiabatic regime we took the pulse to be a convolution of a Gaussian and a rectangle with the widths 56.7 ns and 20 ns respectively. The coupling $g_L$ at the maximum of the pulse is assumed to be 25 MHz. The coupling between the NV and the cavity is assumed to be $g_C = 100 \text{ MHz}$. For simplicity we consider both NVs to be identical and driven by two identical and synchronized lasers with the same amplitude, phase and the pulse form described above. Under these assumptions we numerically propagate each of the four logical states of the system. This results in a $4 \times 4$ Hamiltonian in the logical space of the two-qubit system, corresponding to a CNOT gate, as shown by the Makhlin invariants $G_1$ and $G_2$ (Fig. 4.3), for which the values 1 and 0 respectively were obtained, which is a characteristic of a CNOT gate \[116\].

4.4 Discussion

We have shown that virtual exchange of photons in an optical cavity can mediate the two-qubit CPHASE gate between two NV spin qubits in diamond. Combined with single-qubit operations, produced by rf excitation or by laser fields \[117\], the CPHASE gate allows for
Figure 4.3: The dependence of Makhlin invariants $G_1$ and $G_2$ on time during the operation of a cavity mediated two qubit gate. Before the lasers are turned on $G_1 = 1$ and $G_2 = 3$, which corresponds to the identity operation and absence of entanglement. When the lasers are turned on, the two NVs start to interact through the cavity, which leads to the appearance of entanglement and change of Makhlin invariants. After the lasers are turned off the final state of the system is related to the initial one by a CNOT operation, characterized with Makhlin invariants $G_1 = 0$ and $G_2 = 1$.

arbitrary (universal) quantum computations. Therefore, optical cavity QED with NV centers in diamond represents a realistic path towards spin-based quantum information processing.

As a further prerequisite for the scheme to work, the NV spin coherence time and average time between cavity photon loss must be longer than the gate operation time $t \sim 100 \text{ ns}$. The NV spin coherence time can reach $1/\gamma_2 = T_2 \sim 10 \mu s$, even at elevated temperatures. The photon loss rate can be estimated as $\tau^{-1} \sim (g/\delta_C)^2 \omega_C/2\pi Q$ where $(g/\delta_C)^2 \sim 10^{-3}$ is the probability for the cavity mode to be occupied by a virtual photon during the gate operation, and $\kappa = \omega_C/2\pi Q$ is the photon loss rate in the cavity with quality factor $Q$. For the parameters used above, a Q factor of $Q \sim 10^5$ is needed to achieve $\tau \sim 200 \text{ ns}$. Because $\tau \sim \delta_C^2$ while $t \sim 1/g_{12} \sim \delta_C$, increasing the detuning $\delta_C$ allows the use of cavities with lower $Q$ at the expense of slower gates, which in turn are admissible for sufficiently long $T_2$. The limit of this scaling can be described in terms of a (coherent) cooperativity factor $C_2 = g/\sqrt{\kappa \gamma_2} \gg 1$.

Finally, we expect this scheme to work below a temperature of about 20 K where the excited state levels are stable. It is an open question whether a variation of this scheme will also work at higher temperatures.

In a scalable qubit architecture, pairs of qubits need to be selectively coupled within a large array. A possible architecture comprises single NV centers in optical cavities linked via optical fibers [119]. The coupling mechanism described here lends itself to another architecture where many NV centers are embedded in a single cavity. In an array with separations between NV centers on the order of 10 to 100 nm, selective pairwise coupling can be accomplished with a combination of spatial and spectral selectivity of the laser excitation.
Chapter 5

Effective Hamiltonian description of adiabatic evolution of quantum systems

In this chapter we consider the adiabatic time evolution of a quantum system initialized in the instantaneous dark subspace of its time-dependent Hamiltonian (zero-energy subspace), as required for adiabatic geometric quantum computation [1.4.3]. A conventional way to describe the dynamics of such systems would be to find a bases in the instantaneous dark subspace, compute the non-Abelian Berry connection [1.70] using this bases [120, 121], and subsequently evaluate the path-ordered exponential of the line integral of the obtained Berry connection along the path in the Hamiltonian parameter space. We show that it is possible to describe the evolution of this system without explicitly calculating the Berry connection, but by introducing an effective Hamiltonian and then solving the Schrödinger equation instead. The Hamiltonian used for this procedure acts in a Hilbert space large enough to contain the instantaneous dark subspace at any moment in time. It may coincide with the full Hilbert space of the system, but can also be smaller if the dark subspace never involves some of the system’s levels. Our approach suggests that instead of computing a bases in the instantaneous dark subspace of the time dependent Hamiltonian one can identify its bright states and use them to construct an effective Hamiltonian that contains all the information about the adiabatic evolution of the dark subspace. That means that a complicated procedure of finding the orthonormal bases in the possibly very large dark subspace of the system can be avoided, which makes the numerical description of the system dynamics much less demanding.

5.1 System description.

We first consider a generalized Lambda system with \( n + 1 \) levels, for which the first \( n \) levels, forming a Hilbert space \( \mathcal{H} \) are separated from the remaining level with the energy \( \omega \) and are resonantly coupled to it by oscillating fields \( \Omega_i e^{i\omega t} \) (Fig. 5.1). From here on, we use units in which \( \hbar = 1 \). The detailed description of the adiabatic evolution of this system, obtained with the formalism of the non-Abelian Berry connection, is well known in the literature [122]. The Hamiltonian of such a system in the rotating frame is

\[
\hat{H} = \sum_{i=1}^{n} \left( \Omega_i \ket{i}\bra{e} + \Omega_i^* \ket{e}\bra{i} \right), \tag{5.1}
\]

where \( \Omega_i \) is the complex coupling amplitude (Rabi frequency) of the \( i^{th} \) level \( \ket{i} \) to the excited state \( \ket{e} \) (Fig. 5.1). It should be noted here that the form of the Hamiltonian [5.1]
Figure 5.1: Energy level diagram of the generalized Lambda-system. The lower $n$ states $|i\rangle$ ($i = 1, ..., n$) are coupled to the excited state $|e\rangle$. The system has an instantaneous $(n-1)$-dimensional dark subspace, in which it remains due to the adiabatic theorem.

does not require the ground states to be degenerate. It suffices that each ground state level $|i\rangle$ is coupled to $|e\rangle$ resonantly. This is the reason why the rotating frame Hamiltonian (5.1) can arise in many different multilevel systems, the requirement being the absence of parasitic coupling between the ground states.

We introduce the mean Rabi frequency $\Omega = \sqrt{\sum_{i=1}^{n} \Omega_i^2}$ and parametrize the coupling coefficients as $\Omega_i / \Omega = r_i e^{i\phi_i}$, so that the Hamiltonian (5.1) can be rewritten as

$$\hat{H} = \Omega \sum_{i=1}^{n} r_i \left( e^{i\phi_i} |i\rangle \langle e| + e^{-i\phi_i} |e\rangle \langle i| \right).$$

(5.2)

Here $r_i$ are positive numbers obeying the property $\sum_{i=1}^{n} r_i^2 = 1$. By introducing the normalized bright state,

$$|B\rangle = \sum_{i=1}^{n} r_i e^{i\phi_i} |i\rangle,$$

(5.3)

the Hamiltonian of the system can be rewritten as

$$\hat{H} = \Omega (|B\rangle \langle e| + |e\rangle \langle B|).$$

(5.4)

The values of the $n$ amplitudes and $n$ phases of the excitation fields determine the bright state, thus defining a Hamiltonian that acts trivially on the orthogonal complement of the space spanned by $|B\rangle$ in the Hilbert space $\mathcal{H}$. These $n-1$ states form the so-called dark subspace, such that for any state $\psi$ in this subspace $\hat{H}\psi = 0$. If the bright state is specified, one can uniquely define the dark subspace as its orthogonal complement. The global phase of the bright state is not important for the identification of the dark subspace; if one also takes into account the normalization condition for the $r_i$, one concludes that one has $2n - 2$ independent parameters that define the dark subspace of the Hamiltonian $\hat{H}$. Considering a time-dependent excitation with $r_i(t)$ and $\phi_i(t)$, the evolution of the system is governed by a time dependent Hamiltonian $\hat{H}(t)$, whose dark subspace is now time dependent and describes a path in the $(2n-2)$-parametric space. In the adiabatic regime, where the parameters are changed slowly with respect to $1/\Omega$, it is known that if the system starts in the dark subspace, it will remain there during the evolution [123].

The initialization of the system in the dark subspace is by itself an interesting issue and strongly depends on the system. In the case when the state $|e\rangle$ has a short lifetime a way to initialize the system would be to use coherent population trapping (CPT) [124]. If we do not restrict the Hamiltonian to contain the couplings to the state $|e\rangle$ only, but
allow couplings between the ground states as well, we can construct a Hamiltonian that contains only one dark state, for example $|1\rangle$. If the system does not start in the state $|1\rangle$, it will be pumped with such a Hamiltonian to $|e\rangle$, from which it may either decay to $|1\rangle$ or to some other ground state and then the process will repeat. After many cycles the system will be trapped in the state $|1\rangle$. Then one can switch off the couplings between the ground states and return to the case of the Hamiltonian (5.4), assuming the system is initialized in its dark subspace. The standard way to describe the adiabatic evolution of this subspace would be to write down the basis vectors in the dark subspace, that depend on the $2^n - 2$ independent parameters and then calculate the Berry connection. The path ordered exponential of the line integral of the Berry connection will then define the evolution operator of the system. In what follows we will present a different formalism to analyze the evolution of the system based on the construction of an effective Hamiltonian in the whole Hilbert space $\mathcal{H}$ and discuss the purposes to which it could be applied.

5.2 Effective Hamiltonian.

Let $|\psi_1(t)\rangle$, $|\psi_2(t)\rangle$, $\ldots$, $|\psi_{n-1}(t)\rangle$ be orthonormal basis in the dark subspace of the system at time $t$. We assume the system to be initialized in an instantaneous dark state of its Hamiltonian and to subsequently evolve in the adiabatic regime, so at any time moment $t$ the state of the system is $|\psi_s\rangle = \sum_{i=1}^{n-1} c_i(t) |\psi_i(t)\rangle$. Let us now concentrate on how this general state evolves due to the Hamiltonian $\hat{H}(t)$ during an infinitesimal time interval $dt$.

In Appendix C.1 we show that

$$|\psi_s\rangle \rightarrow \hat{U} |\psi_s\rangle,$$  \hspace{1cm} (5.5)

where the unitary operator $\hat{U}$ acts in the whole Hilbert space $\mathcal{H}$ and is given by

$$\hat{U} = \hat{1} + \left[ |\hat{B}\rangle \langle B| - |B\rangle \langle \hat{B}| \right] dt,$$  \hspace{1cm} (5.6)

where $\hat{1}$ is the projection operator on the Hilbert space $\mathcal{H}$, acting as identity in this space. Since the operator $\hat{U}$ generates the correct evolution of the states in the dark subspace of the system, we can view the evolution of the state in the dark subspace in the adiabatic regime as if a time dependent effective Hamiltonian $\hat{H}_{\text{eff}}$ was acting in the Hilbert space $\mathcal{H}$.

In terms of the laser coupling coefficients $r_i, \phi_i$ ($i = 1, \ldots, n)$, using equation (5.3), the effective Hamiltonian (5.7) can be rewritten in the original basis $|i\rangle$ ($i = 1, \ldots, n$) as

$$\hat{H}_{\text{eff}} = i \left( |\hat{B}\rangle \langle B| - |B\rangle \langle \hat{B}| \right).$$  \hspace{1cm} (5.7)

In Appendix C.3 we show that this Hamiltonian can describe the same universal set of gates as the non-Abelian Berry connection, demonstrating that the two approaches are indeed equivalent.

5.3 Generalizations.

Let us now consider a more general Hamiltonian of the form

$$\hat{H} = \sum_{i,j=1}^{k} \left( g_{ij} |B_i\rangle \langle B_j| + g_{ij}^* |B_j\rangle \langle B_i| \right),$$  \hspace{1cm} (5.9)

where $g_{ij}$ are the laser coupling coefficients and $B_i$ are the basis states. The evolution of the system in this case can be described by the effective Hamiltonian (5.7) with $\hat{U}$ replaced by the path ordered exponential of the line integral of the Berry connection.

In what follows we will present a different formalism to analyze the evolution of the system based on the construction of an effective Hamiltonian in the whole Hilbert space $\mathcal{H}$ and discuss the purposes to which it could be applied.
acting in some Hilbert space $\mathcal{H}$ of dimension $n$, where $|B_i\rangle$ are time dependent states in this Hilbert space, forming an orthonormal set of vectors at any instant in time. Note that the Hamiltonian (5.4) is a special case of (5.9), with two bright states, one of them being constant. We point out that the Hamiltonian (5.9) can always be brought into a diagonal form with appropriately chosen bright states, but for our purposes it is not necessary to assume this.

From now on we will assume that the instantaneous eigenvalues of the Hamiltonian (5.9) in the subspace spanned by the vectors $|B_i\rangle$ are nonzero and that the adiabatic condition with respect to these eigenvalues is fulfilled. Thus, if the system starts in the instantaneous dark subspace of this Hamiltonian, it never leaves it, in accordance with the adiabatic theorem.

In full analogy to the case of equation (5.6), in Appendix C.2 we show that one can build the unitary transformation acting in the Hilbert space $\mathcal{H}$ and describing correctly the transformation of the dark subspace of Hamiltonian (5.9) during the infinitesimal time interval $dt$

$$\hat{U} = \hat{1} + \sum_{i=1}^{k} \left[ |\dot{B}_i\rangle \langle B_i| - |B_i\rangle \langle \dot{B}_i| \right] dt,$$

We now conclude that the evolution of the dark subspace of the Hamiltonian (5.9) in the adiabatic regime can be described with the effective Hamiltonian

$$\hat{H}_{\text{eff}} = \sum_{i=1}^{k} i \left[ |\dot{B}_i\rangle \langle B_i| - |B_i\rangle \langle \dot{B}_i| \right] = \sum_{i=1}^{k} \hat{H}_i,$$

acting in the Hilbert space $\mathcal{H}$. Here $\hat{H}_i$ $(i = 1, ..., k)$ is a Hamiltonian equivalent to (5.7).

Another approach exists to describe the adiabatic evolution of quantum systems using a transitionless driving Hamiltonian [125, 126]. Both transitionless driving Hamiltonian and Equations (5.7) and (5.11) describe the evolution of the states from the dark subspace as a solution of the Schrödinger equation with the corresponding Hamiltonian. The main difference between the two approaches is that the transitionless driving Hamiltonian requires the eigenbasis in the dark subspace, while in our approach we construct the effective Hamiltonian using the bright states only, thus avoiding the procedure of orthogonalization of the dark subspace. Later we discuss the cases when our formalism will be simpler to apply than the Berry connection or the transitionless driving Hamiltonian.

Now we will discuss the systems to which our formalism can be applied. One of the simplest cases when the systems’ dynamics in the Hilbert space of dimension $n$ is controlled with a Hamiltonian (5.9), $k < n$, is depicted in Fig 5.2.

Here all the states of $r$–fold degenerate ground space are coupled to all the states of the $m$–fold degenerate excited space with the same excitation frequency. Performing the Morris-Shore transformation [127] and assuming $r \geq m$, the system is brought to at most $m$ coupled pairs. All the other states turn out to be isolated and thus can be associated with the dark states. Going to the frame rotating with the frequency of the excitation and applying the rotating wave approximation, we can describe the system exactly with the Hamiltonian (5.9) with $n = r + m$ and $k \leq 2m$. Here the bright states $|B_i\rangle$, $(1 = 1, ..., k)$ as well as the couplings $g_i$ between pairs will depend on the excitations between the ground and excited states. If one now allows the couplings in the rotating frame to change slowly, so that the adiabatic condition is fulfilled, the states from the dark subspace will evolve according to the effective Hamiltonian (5.11). The criterion for the adiabaticity can be formulated as, firstly, the conservation of the number of coupled pairs. In other words, the coupling for any of the pairs never becomes 0. Secondly, the couplings between the ground and excited states should change much more slowly than the inverse of the smallest
Figure 5.2: (a) A system having an $r$-fold degenerate ground state and an $m$-fold degenerate excited state. Each arrow denotes the coupling between the corresponding levels. All ground states are coupled to all excited states with the same detuning from the resonance. (b) Under the rotating wave approximation the Morris-Shore transformation \[127\] brings this system to at most $m$ driven two-level systems and $r - m$ decoupled dark states (assuming $r \geq m$). The Hamiltonian of this system will then have the form \[(5.9)\].

coupling strength among the pairs, arising after the Morris-Shore transformation. Let us assume that the number of bright states is the greatest possible, $k = 2m$. As the excited states are always bright and do not change in time, to construct the effective Hamiltonian one only needs to find the other $m$ bright states from the ground space. This will be easier than finding the basis in the dark subspace if the number of dark states $r - m$ is greater than $m$. Thus the effective Hamiltonian approach will be advantageous over the Berry connection if $r > 2m$. Apart from the Lambda system, for which the Berry connection can be calculated analytically, the smallest possible system when that will be the case is when 5 ground states are coupled to 2 excited states.

We would like to stress that the Hamiltonian \[(5.9)\] with $k < n$ need not arise necessarily in the system in Fig. 5.2. One may start with the most general case when all $n$ states of the Hilbert space $\mathcal{H}$ are coupled in the rotating frame. In general this Hamiltonian will have no dark states, but if additional conditions are imposed on the couplings, the Hamiltonian may become reducible to the case of the formula \[(5.9)\] with $k < n$. In the case of Fig. 5.2 this reducibility arises from the absence of couplings in the excited and ground state manifolds.

### 5.4 Description of quantum gates using effective Hamiltonian.

Let us now go back to the original Lambda system in Fig. 5.1. We will assume that the system’s logical space coincides with the first $n - 1$ levels of the ground state space and the system is initialized in this space. To encode the states of $m$ qubits in this logical space we need $n - 1 = 2^m$. Then the state $|k\rangle$ corresponds to the qubit state, which is the binary representation of $k$. For example the state $|4\rangle = |00\ldots0011\rangle$, which means that only two last qubits are excited and all other qubits are in the ground state. We would like to perform a geometric adiabatic gate on the logical space of the system. For that we first switch on only the $n$th coupling $\Omega_n$, so that the bright state initially coincides with the level $|n\rangle$. The logical space is thus the dark space of the Hamiltonian at the
Figure 5.3: A Bloch sphere that represents a state space spanned with the states $|n\rangle$ and $|\psi\rangle$. The system is initialized in the dark state $|\psi\rangle$ and the blue line shows the adiabatic evolution of the dark state along a closed path in a two dimensional Hilbert space. At the end of the evolution the system acquires a geometric phase that is equal to $\Phi$, half of the solid angle enclosed by the trajectory.

beginning of the gate. Let us choose the arbitrary state $|\psi\rangle$ as a linear combination of $|1\rangle, |2\rangle, \ldots, |n-1\rangle$ and adiabatically change the couplings in the way that the bright state follows a three-piece trajectory from $t = 0$ to $t = t_1$, from $t = t_1$ to $t = t_2$ and from $t = t_2$ to $t = t_3$:

1. $|B(t)\rangle = \sin(\theta(t)/2) |\psi\rangle + \cos(\theta(t)/2) |n\rangle$
   \[\theta(0) = 0, \; \theta(t_1) = \pi\]

2. $|B(t)\rangle = e^{i\phi(t)} |\psi\rangle$
   \[\phi(t_1) = 0, \; \phi(t_2) = \Phi\]

3. $|B(t)\rangle = e^{i\Phi} \sin(\theta(t)/2) |\psi\rangle + \cos(\theta(t)/2) |n\rangle$
   \[\theta(t_2) = \pi, \; \theta(t_3) = 0\]

Note that the second stage just changes the global phase of the bright state and thus its only meaning is to make the bright state continuous, it does not affect the system that lies in the dark subspace. Therefore this stage can be performed arbitrarily fast without breaking the adiabaticity condition. The trajectory of the state of the system is shown in the Fig. 5.3.

We can now use the formula (5.7) to calculate the effective Hamiltonian for each stage, together with the corresponding unitary $T e^{-i \int_{\text{start}}^{\text{end}} H_{\text{eff}}(t) dt}$ and obtain:

1. $\hat{H}_{\text{eff}} = \frac{\dot{\theta}}{2} (|\psi\rangle \langle n| - |n\rangle \langle \psi|)$
   \[\hat{U}_1 = e^{\frac{\pi}{2} (|\psi\rangle \langle n| - |n\rangle \langle \psi|)}
   = 1 - |\psi\rangle \langle \psi| - |n\rangle \langle n| + |\psi\rangle \langle n| - |n\rangle \langle \psi|\]

2. $\hat{H}_{\text{eff}} = -2\dot{\phi} |\psi\rangle \langle \psi|$
   \[\hat{U}_2 = e^{2i\phi |\psi\rangle \langle \psi|} = 1 - |\psi\rangle \langle \psi| + e^{2i\Phi} |\psi\rangle \langle \psi|\]

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3. \( \hat{H}_{\text{eff}} = \frac{\dot{\theta}}{2} (i \cos(\Phi)(|\psi\rangle \langle n| - |n\rangle \langle \psi|) \\
- \sin(\Phi)(|\psi\rangle \langle n| + |n\rangle \langle \psi|) \)

\[
\hat{U}_3 = \hat{1} - |\psi\rangle \langle \psi| - |n\rangle \langle n|
- \cos(\Phi)(|\psi\rangle \langle n| - |n\rangle \langle \psi|)
- i \sin(\Phi)(|\psi\rangle \langle n| + |n\rangle \langle \psi|)
\]

We note that after the third stage the bright state returns back to \(|n\rangle\), which indicates that the dark subspace at the end of the gate coincides with the logical space. Combining the action of the three stages we obtain

\[
\hat{U} = \hat{U}_3 \hat{U}_2 \hat{U}_1 = \hat{1} - |\psi\rangle \langle \psi| - |n\rangle \langle n| + e^{-i\Phi} |\psi\rangle \langle \psi| + e^{i\Phi} |n\rangle \langle n|
\]

The action on the state \(|n\rangle\) is irrelevant as the effective Hamiltonian only describes the evolution of the vectors from the dark subspace correctly. The state \(|\psi\rangle\) on the other hand obtains a phase factor \(-\Phi\). This phase factor is equal to half of the solid angle the trajectory of the state \(|\psi\rangle\) traces on the Bloch sphere in Fig. 5.3, that coincides with the classical result [64, 121].

If \(n = 3\) the gate above is a single qubit gate on the levels \(|1\rangle, |2\rangle\). If one displays the state space, spanned with these two levels, using a Bloch sphere representation, this gate can be thought of as rotation by the angle \(\Phi\) around an axis on this sphere, that passes through the center of the sphere and the point that corresponds to \(\psi\). If \(n = 5\) the gate above is a two qubit gate, as the dimension of the logical space is four. If also \(|\psi\rangle = |4\rangle\), this is a CPHASE gate, which in combination with the universal single qubit gates gives a complete set of gates in the space of two qubits. We also note that if one does not restrict oneself to closed trajectories, the effective Hamiltonian describes the STIRAP process.

5.5 Discussion.

We have shown that the adiabatic dynamics of a state from the dark subspace of the Hamiltonian (5.9) can be described with an effective Hamiltonian (5.11). Due to the presence of derivatives in this Hamiltonian, the equation of motion for the wave function turns out to be invariant with respect to the reparametrization of time \(\tau = f(t)\), which reflects the geometric nature of the evolution. We stress that the calculation of the effective Hamiltonian (5.11) requires that one brings the initial dynamical Hamiltonian to the form (5.9), which involves the identification of the instantaneous orthonormal bright states of the system. But for this, it is not necessary to compute the bases in the dark subspace. For large dimensionalities of the Hilbert space one often encounters a situation, when the number of dark states is much greater than the number of bright states. If the Hamiltonian (5.9) takes the simplified form of (5.1) with two bright states and one of them constant, it is possible to easily parametrize all the dark states using the coordinates on the sphere [122]. But if the situation is more complicated with two or more bright states changing in time, one can no longer easily parametrize the dark subspace. This would involve the Gram-Schmidt orthogonalization procedure which is a recursive process that can take a long time even with the use of powerful computers. In that case the effective Hamiltonian will be very useful because it allows to avoid this procedure.

In this chapter we do not discuss the fidelities of the quantum gates obtained through the geometric evolution, but instead give an alternative description of the latter. The effects of noise on the adiabatic evolution were extensively studied theoretically [128], recent experimental results show evidence for a selectivity of noise, which the system is
sensitive to [129]. A description of noise within our effective Hamiltonian formalism is out of scope of this work and will be addressed in the future research.
Chapter 6

Non-adiabatic geometric gates in diamond

6.1 Nonadiabatic optical holonomic gates with NV$^-$ ground state spin

In this section we theoretically analyze the optical non-adiabatic holonomic gates, recently realized experimentally [41] on the logical space of the NV$^-$ ground spin states $\ket{-1}$ and $\ket{1}$ with spin projections $-1$ and $1$ respectively. The scheme is the same as described in Ref. [81] and in section 1.4.3 of the introduction. This approach is different from similar experiments that use the microwave excitation [79, 80] in that now the couplings are realized purely using short optical pulses. This on the one hand significantly reduces the gate time to the order of $\sim 10$ ns, but on the other hand requires the orbital excitation of the NV$^-$ center, which in turn leads to fast decoherence channels, that we take into account to calculate theoretical gate fidelities.

6.1.1 System description

We are considering the NV$^-$ center, cooled to approximately 5 K, so that its fine structure can be well resolved (1.2.2). We assume that two lasers coherently couple the NV$^-$ ground states $\ket{m_s = -1}$ and $\ket{m_s = 1}$ to the excited state $\ket{A_2}$ with Rabi frequencies $\Omega_1$ and $\Omega_2$ and a common detuning $\Delta$ (In Fig. 1.8 one would have to replace $\ket{0} \rightarrow \ket{-1}$ and $\ket{e} \rightarrow \ket{A_2}$). For this scheme to work we need to make sure that the lasers can couple $\ket{m_s = \pm 1}$ selectively to $\ket{A_2}$, so that one laser will not couple two different spin states at the same time. This we achieve by assuming the magnetic field of 261 G in the direction of the NV symmetry axis, that splits $\ket{m_s = 1}$ and $\ket{m_s = -1}$ by 1.461 GHz (see equation 1.42). Then the resonance frequencies are very different for the two transitions $\ket{m_s = -1} \leftrightarrow \ket{A_2}$ and $\ket{m_s = 1} \leftrightarrow \ket{A_2}$, so if one laser is close to resonance for one of the transitions, it is far off-resonant for the other and this last coupling can be neglected. This is different from a similar scheme, where the selectivity is achieved through the control of the laser polarization instead of its frequency [130]. Strickly speaking, the presence of magnetic field of 261 G in the direction of the symmetry axis affects not only the ground state, but also the excited state. Indeed, its Hamiltonian $g_\mu B_z \hat{S}_z$ transforms as $A_2$ irreducible representation (in the same way as $S_z$), which means that the $\ket{A_2}$ level becomes coupled to $\ket{A_1}$ (from the rules two and four of the remark 11 an $A_2$ operator couples a wave function of symmetry $A_1$ to the wave function of symmetry $A_2$). This level will still be highest in energy and we will still address it as $A_2$, however we have to remember about the mixing effect of the magnetic field, as it will be important when we will consider the decoherence channels of the $A_2$ level.
Because the lasers use an electric dipole transition to couple the ground state to the orbital excited state, that is 1.945 eV in energy, one can apply the rotating wave approximation and in the rotating frame the Hamiltonian takes a simple form

$$\hat{H}(t)/\hbar = \left( \Omega_1(t) \langle A_2 \rangle \langle -1 \rangle + \Omega_2(t) \langle A_2 \rangle \langle 1 \rangle + h.c. \right) + \Delta \langle A_2 \rangle \langle A_2 \rangle . \quad (6.1)$$

We now assume that the two lasers are locked, so that

$$\Omega_1(t) = \Omega \sin(\theta/2)$$
$$\Omega_2(t) = -\Omega \cos(\theta/2)e^{-i\phi} . \quad (6.2)$$

We assume $\Omega$ is a constant pulse amplitude, that can instantaneously be switched on and off. If one now introduces the bright ($|b\rangle$) and dark ($|d\rangle$) states according to

$$|b\rangle = \sin(\theta/2) | -1 \rangle - \cos(\theta/2) e^{i\phi} | 1 \rangle ,$$
$$|d\rangle = \cos(\theta/2) | -1 \rangle + \sin(\theta/2) e^{i\phi} | 1 \rangle , \quad (6.3)$$

the Hamiltonian (6.1) takes the form

$$\hat{H}(t)/\hbar = \Omega \left( |A_2\rangle \langle b| + |b\rangle \langle A_2| \right) + \Delta |A_2\rangle \langle A_2| . \quad (6.4)$$

This is exactly the same Hamiltonian we considered in section 1.4.3 of the introduction (Eq. 1.81). So we may expect that if we switch the Hamiltonian (6.4) for a time

$$t = \frac{2\pi}{\sqrt{4\Omega^2 + \Delta^2}} , \quad (6.5)$$

the bright state will undergo an excitation and deexcitation cycle and obtain a geometric phase factor $e^{i\gamma}$ with

$$\gamma = \pi \left( 1 - \frac{\Delta}{\sqrt{4\Omega^2 + \Delta^2}} \right) . \quad (6.6)$$

This induces a gate operation

$$\beta |d\rangle + \alpha |b\rangle \rightarrow \beta |d\rangle + e^{i\gamma} \alpha |b\rangle \quad (6.7)$$
in the subspace of $| -1 \rangle$ and $| 1 \rangle$.

We would like to point out that the duration of the pulse implies that the pulse area $\sqrt{\Omega^2 + \Delta^2/4} * t$ equals exactly $\pi$.

### 6.1.2 Environmental effects and full process tomography

For now we have only considered the ideal case, when no dissipation and dephasing processes are present in the system. This can not be true, as we excite the NV$^-$ center to the orbital state $|A_2\rangle$, that has a very short life time. Indeed, the orbital $|A_2\rangle$ level can orbitally relax to the states $| -1 \rangle$ and $| 1 \rangle$. Moreover, due to the nonzero magnetic field mixing, $A_2$ level is mixed with the $|A_1\rangle$ level as described above. This in turn means we have one more relaxation channel through the intersystem crossing (see section 1.3 of the introduction). Through this channel the system can relax not only to $| 1 \rangle$ and $| -1 \rangle$, but also to $| 0 \rangle$. For complete description, one also needs to include the dephasing in the excited state $|A_2\rangle$, that does not lead to energy relaxation, but destroys coherence between the ground and excited states. Our gate realization relies on the fact that the bright state $|b\rangle$ is excited to $|A_2\rangle$ and then deexcited back to $|b\rangle$. If dephasing in $A_2$ is too strong and no relaxation from $A_2$ happens, the laser excitation will just bring half of the population of
$|b\rangle$ to $A_2$. One can think of it as of stimulated emission process, where the emission rate is equal to the excitation rate. In the absence of spontaneous emission in the steady state these processes must have the same rate (detailed equilibrium), which immediately leads to equal populations in $|A_2\rangle$ and $|b\rangle$. Thus, unlike most of the works where coherence between excited and ground states is not important, here we need to consider that as well.

In principal we could model the relaxation and dephasing rates in the system using our knowledge about the fine structure of the defect and how it is affected by magnetic field. But as the work we are describing here analyzes particular experimental conditions of Ref. [41], we can describe these processes phenomenologically with certain rates, that were measured in a separate experiment [131] and are listed in table 6.1. Using these rates, environmental effects can now be taken into account in the framework of a 4−level model ($|A_2\rangle$, $|-1\rangle$, $|1\rangle$ and $|0\rangle$) using a Lindblad equation [132]. In the rotating frame, where all the ground state levels have the same energy and $|A_2\rangle$ has an energy $\Delta$, the Lindblad equation for the 4 × 4 density matrix takes the form

$$\frac{d\rho}{dt} = -i[\hat{H},\rho] + \sum_k [\hat{O}_k \rho \hat{O}_k^+ - \frac{1}{2}(\hat{O}_k^+ \hat{O}_k, \rho)].$$

The first term here describes coherent evolution of the system with the Hamiltonian (6.4), while the sum over $k$ runs over the decoherence processes:

- Spontaneous decay from $|A_2\rangle$ to $|0\rangle$ at the rate $\Gamma_0$ with the jump operator $O_0 = \sqrt{\Gamma_0}|0\rangle \langle A_2|$, 
- spontaneous decay from $|A_2\rangle$ to $|-1\rangle$ at the rate $\Gamma_{-1}$ with the jump operator $O_{-1} = \sqrt{\Gamma_{-1}}|-1\rangle \langle A_2|$, 
- spontaneous decay from $|A_2\rangle$ to $|1\rangle$ at the rate $\Gamma_1$ with the jump operator $O_1 = \sqrt{\Gamma_1}|1\rangle \langle A_2|$, 
- orbital dephasing of the level $|A_2\rangle$ at the rate $2\Gamma_{orb}$ with the jump operator $O_{orb} = \sqrt{\Gamma_{orb}}|A_2\rangle \langle A_2|$. 

The coherent part of the Lindblad equation is designed in the way to generate the desired gate in the absence of decoherence processes. That means we need to choose the angles $\theta$ and $\phi$, that define the desired bright and dark states and to switch this Hamiltonian only for a time $t$, given by the equation (6.5). Once the coherent interaction is designed, we numerically solve the Lindblad equation to obtain the final density matrix when the lasers are switched off and all residual population decayed from the excited $|A_2\rangle$ level back to the ground state. To be even more accurate we include the effect of spectral hopping.

<table>
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<th>$\sigma/2\pi$</th>
<th>$\Gamma_0/2\pi$</th>
<th>$\Gamma_{-1}/2\pi$</th>
<th>$\Gamma_1/2\pi$</th>
<th>$\Gamma_{orb}/2\pi$</th>
</tr>
</thead>
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<tr>
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<td>1.6 MHz</td>
<td>8.5 MHz</td>
<td>4.3 MHz</td>
<td>8.8 MHz</td>
</tr>
</tbody>
</table>

Table 6.1: The values for the spectral hopping and the decoherence rates used to obtain the final density matrix after the excitation pulse.

This effect usually appears in experiments, because experimental data are almost never obtained in single shot. One needs to reinitialize the NV− center and repeat the experiment again and again. The reinitialization is usually done using a strong green laser (excites the NV− center orbitally together with localized phononic modes). This laser can affect the environment of the NV−, thus changing local electric field. This field then changes the gap between orbital ground and excited states (the electric field along the NV axis, $E_z$, transforms as $A_1$ irreducible representation and can move triplet states with respect to each other through the operator $|X\rangle \langle X| + |Y\rangle \langle Y| - |3A\rangle \langle 3A|$). Thus, in different runs
of the same experiment the detuning $\Delta$ fluctuates, which means our time of the gate (Eq. 6.5) becomes incorrect. This leads to additional errors in the gate operation. We include this effect into the model by propagating the Lindblad equation for different values of $\Delta$, calculating the resulting $\rho_\Delta$ as described above and then averaging this matrix over $\Delta$, which we believe to obey a Gaussian distribution. The result for the final density matrix, obtained in the presence of decoherence and spectral hoping takes the form

$$\rho_{\text{final}} = \int_{-\infty}^{\infty} d\Delta \exp\left(-\frac{(\Delta - \Delta_0)^2}{2\sigma^2}\right) \rho_\Delta,$$

(6.9)

where $\Delta_0$ is the detuning value to which the lasers were initially set. The dispersion $\sigma$ we restrict to the value that gives the best fit to the experimental data of Ref. [41], which is around 15 MHz. The Rabi frequencies we assume are an order of magnitude larger than this, so the effect of spectral hoping can be neglected. We will discuss this issue below in more detail.

Now we have the tools to compute the environment affected density operators at the end of the gate, if we know the initial state of the system. But we are still missing the measure of the quality of our single qubit gates, i.e. the fidelity. These should be independent of the initial state of the system to be a proper measure of errors. We first notice that every noisy single qubit gate can be characterized in terms of a linear quantum process [133], acting on the qubit’s $2 \times 2$ initial state according to

$$\rho_{\text{final}} = \sum_{i,j=1}^{4} \chi_{ij} E_i \rho_{\text{initial}} E_j,$$

(6.10)

where $E_1 = I$, $E_2 = \sigma_x$, $E_3 = -i\sigma_y$, $E_4 = \sigma_z$ are given in terms of identity and Pauli matrices. The corresponding $\chi$-matrix completely describes the process and thus can be used to characterize the gates (it is independent of the initial states). It is Hermitian $4 \times 4$ matrix and thus has 16 independent coefficients. In order to determine those, we compute $\rho_{\text{final}}$ for four different initial conditions ($\rho_{\text{initial}} = I/2, (I + \sigma_x)/2, (I + \sigma_y)/2, (I + \sigma_z)/2$) using the procedure above. Each initial condition leads to a final density matrix with four coefficients each, that means in total we have 16 independent equation for the $\chi$-matrix, that are exactly enough to determine it uniquely. This procedure is called the full process tomography. Because our $\chi$-matrix includes the effects of environment, we refer to it as a $\chi_{\text{real}}$. Next we compute the ideal $\chi$-matrix, that one would obtain purely from coherent Hamiltonian dynamics, when no environment is present, that we refer to as $\chi_{\text{ideal}}$. The fidelity of the gate we then define as

$$F = Tr(\chi_{\text{real}} \chi_{\text{ideal}}).$$

(6.11)

### 6.1.3 Results

We first analyze the resonant Z-gate ($\Delta = 0$), when only one laser is switched on ($\theta = 0, \phi = \pi$), that couples $|b\rangle = |1\rangle$ to $|A_2\rangle$. This corresponds to a $\pi$-rotation around the Z-axis on the Bloch sphere, as shown in the left side of Figure 6.1 a).

Ideally without environment, this gate should have the $\chi$-matrix $\chi_{\text{ideal}} = \text{Diag}(0, 0, 0, 1)$, that corresponds to a transformation of the initial density operator $\rho_{\text{initial}}$ according to $\rho_{\text{final}} = \sigma_z \rho_{\text{initial}} \sigma_z$. We now compute the real $\chi$-matrix of the gate, affected by the environment and extract the gate fidelity according to the procedure described above. The dependence of the fidelity on the Rabi frequency of the drive, $\Omega$, entering the Hamiltonian (6.4) is plotted in the figure 6.1 b). Here we investigate different decoherence channels and their effect on the gate fidelity. The dots are experimental results of Ref. [41]. The blue line shows a theoretical dependence, when only relaxation channel is taken into account.
Figure 6.1: a) The figure demonstrates the $\pi$-rotation on the Bloch sphere, that occurs when $|1\rangle$ is resonantly coupled to $|A_2\rangle$. b) The plot shows the fidelity of the $\pi$-rotation with respect to coupling Rabi frequency $\Omega$, that enters the Hamiltonian (6.4). Here we investigate different decoherence channels and their effect on the gate fidelity. The dots are experimental results of Ref. [H]. The blue line shows a theoretical dependence, when only relaxation channel is included. The yellow line also takes into account the dephasing in the excited state $|A_2\rangle$. Finally, the green line fits the experimental data including the spectral hoping of 15 MHz on top of the decoherence processes.

The yellow line also takes into account the dephasing in the excited state $|A_2\rangle$ in addition to relaxation. Finally, the green line also includes the spectral hoping of 15 MHz, that gives the best fit to the experimental data at low optical powers. At high powers the experimental fidelities saturate due to cross talk between the levels [H], so our theoretical description does not capture the fidelities in that range. This fixes the value of spectral hoping. We see that it is one order of magnitude smaller than the optical powers used in the experiment of Ref. [H], so we can neglect its effect when analyzing fidelities.

We now proceed to the non-resonant $Z$-gate, when the rotation angle on the Bloch sphere is smaller than $\pi$, shown in figure 6.2 a). The dependence of the rotation angle

Figure 6.2: a) The figure demonstrates the $\gamma$-rotation on the Bloch sphere, that occurs when $|1\rangle$ is non-resonantly coupled to $|A_2\rangle$ with a detuning $\Delta$. b) The plot shows the fidelity of the rotation by the angle $\gamma$ as a function of the detuning $\Delta$. The dots are experimental results from Ref. [H]. The solid lines are theoretical dependences. The blue color corresponds to $\Omega/2\pi = 252$ MHz, the orange color corresponds to $\Omega/2\pi = 134$ MHz.
on the detuning $\Delta$ is given with the expression $\text{(6.6)}$. It is interesting to check whether this expression still holds in the presence of environment. In general, we can think of environmental errors as leading to two different effects. The first one is the leakage error, when after the optical pulse the population ends up in state $|0\rangle$. The second effect is scrambling of the ideal density matrix in the logical space. To calculate the environment affected rotation angle, we do the following procedure. We assume the system is initialized in the $X$-state ($|\pm 1\rangle + |1\rangle$). We perform numerically our rotation around the $Z$-axis, as described before, using the Lindblad equation. We take the final density matrix in the logical space (that now has non-unit trace due to the leakage error), and normalize it to have a unit trace. Next we compute the the $X$- and $Y$-components of the final Bloch vector, that we obtain after the gate is performed. Finally, we compute the angle it makes with the $X$-axis of the Bloch sphere (that coincides with the initial Bloch vector). The result is shown in Figure 6.3 with dots for the two values of the optical powers ($\Omega/2\pi = 134$ MHz and $\Omega/2\pi = 252$ MHz respectively). We compare this result to the equation $\text{(6.6)}$, that is shown in Fig. 6.3 with solid lines. The perfect agreement between the two indicates that the orbital decay and dephasing channels can only reduce the length of the Bloch vector, but do not change its orientation. In these considerations we neglected the spectral hoping, as we argued before. The ideal $\chi$-matrix for $Z$-gates as a function of $\gamma$ is given

\[
\chi_{\text{ideal}}^{Z} = \begin{pmatrix}
\cos^2(\gamma/2) & 0 & 0 & I \sin(\gamma)/2 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
-I \sin(\gamma)/2 & 0 & 0 & \sin^2(\gamma/2)
\end{pmatrix}
\] (6.12)

Using this and the procedure described above, we plot the theoretical fidelity of the detuned $Z$-gate as a function of the detuning ($\Delta$) in the figure 6.2 b) (solid lines). The results of the experiment of Ref. 41 are shown there with dots. We see that the two agree reasonably well, indicating that our theoretical model manages to capture the main sources of gate errors.

Finally, we present the full process tomography on the three important resonant gates $X, Y$ and Hadamard ($H$). The corresponding rotations on the Bloch sphere are plotted in Figure 6.4. We obtain the gate fidelities of 0.8 for $X$- and $Y$-gates and 0.79 for the Hadamard gate. These are slightly higher than those obtained in the experiment of Ref. 41 (0.75, 0.78 and 0.74 for the $X$, $Y$- and $H$-gates respectively).

Ideally, the gate operation requires that all the pulses are flat. In reality this is not

Figure 6.3: This plot compares the rotation angle, generated when the state $|1\rangle$ is coupled to $|A_2\rangle$ with detuning in a numerical experiments (denoted with dots), to the ideal angle, given with expression $\text{(6.6)}$ (denoted with solid lines). The agreement between the two clearly states that the orbital decay and dephasing channels can only reduce the length of the Bloch vector, but do not change its orientation. The grey line corresponds to the Rabi frequency $\Omega/2\pi = 252$ MHz, while the blue line corresponds to $\Omega/2\pi = 134$ MHz.
the case and we include this in our simulations, assuming that the pulses have a ramp time of 1.2 ns (linear increase and decrease), as it was in experiment of Ref. [41]. We restrict our pulses to have the same area of $\pi$ as the ideal pulse, which for resonant gates means the nonideality of the pulse has no effect on the gate [81]. For nonresonant gates, the situation is a bit more complicated, as even without the decoherence and spectral hopping, the Hamiltonian described above would not generate an ideal gate on the logical subspace, if it contains pulse ramps. It is possible to show that some residual population may still remain in the $|A_2\rangle$ excited state after the pulse is turned off. This effect we include in the fidelity because for the nonresonant case we define the ideal gate as the one we would have without decoherence and spectral hopping if the pulse was flat and had an area of $\pi$. It is worth checking how big the effect of the pulse form is. If it affects the fidelity more or at least as much as the environment does, then one would have to optimize the experiments to undo this effect. Figure 6.5 compares the fidelities of the $Y(\pi/2)$ gates (rotations by $\pi/2$ around the Y-axis on the Bloch sphere) if we use an ideal rectangular pulse and a real trapezoid pulse. Here we plot the fidelity versus vacuum Rabi frequency in the maximum of the pulse. One can infer that below 600 MHz the fidelity is mostly defined by spectral hopping and decoherence, while the effect of the pulse form in that range is negligible.

![Figure 6.4](image_url)

**Figure 6.4:** a) Rotation around the X-axis on the Bloch sphere by $\pi$, generated when the bright state coincides with $|1\rangle - |\rangle$ ($\theta = \pi/2$, $\phi = 0$). b) Rotation around the Y-axis on the Bloch sphere by $\pi$, generated when the bright state coincides with $|\rangle - i|1\rangle$ ($\theta = \pi/2$, $\phi = \pi/2$). c) Hadamard gate rotation, generated when the bright state coincides with $\sin(3\pi/8)|\rangle - \cos(3\pi/8)|1\rangle$ ($\theta = 3\pi/4$, $\phi = 0$).

![Figure 6.5](image_url)

**Figure 6.5:** Power dependence of the $Y(\pi/2)$ gate fidelity on the vacuum Rabi frequency at pulse maximum. The yellow curve corresponds to the rectangular pulse, the blue one-for the real pulse with 1.2 ns ramp times.
6.2 All-microwave geometric control in registers of coupled NV− centers and 13C nuclear spin

Recently fault tolerant universal geometric single-qubit gates [81] have been achieved both using optical [41, 130] and microwave [79, 80] control of the spin. Scaling up to many NV− spins is still an issue, as it is challenging to couple the defect spins together [15, 39, 102]. On the other hand, numerous experiments have been performed on multiqubit registers that include the NV− center electron spin coupled to the nearby 13C nuclear spins through the hyperfine interaction [26, 31]. Such a configuration allows the use of the longer coherence time of the nuclear spin to preserve the quantum state during times exceeding the $T_2^*$ of the electron spin. This can then be used for distributed quantum computation with electron-nuclear quantum registers [134] or to gain increased sensitivity in metrological applications of NV− centers [25]. From this perspective the feasibility of universal control of the state of such registers becomes important. The existing experiments described in the literature [135] allow fast microwave control of the electron spin, as well as fast entangling CNOT or CPHASE gates controlled with the state of the nuclear spin. At the same time performing single qubit gates on the nuclear spins that are relatively close to the electron spin still required radio frequency pulses, that weakly couple to the nuclear spins due to their low gyromagnetic ratio [136].

Our work is motivated by the fact that the hyperfine interaction between the nearest neighbour 13C nuclear spin and an NV− center provides a nuclear spin splitting of the order of 130 MHz [48, 137], which allows for universal holonomic [81] single and two-qubit gates on the two-qubit register, assisted by hyperfine interaction. The key enabling idea is to use a magnetic field to mix the electronic states $|−1\rangle$ and $|0\rangle$. In this case the quantization axis for the nuclear spin will depend on the state of the electron spin. We will show that this implies that electronic transitions between different hyperfine levels are no longer forbidden by nuclear spin selection rules and can efficiently be driven by microwaves. This should result in a speed-up compared to the existing schemes and provide universal control of the register, requiring application of microwave-only pulses and making use of the relatively stronger electron magnetic dipolar transitions.

This chapter is structured as follows. In subsection 6.2.1 we will consider our scheme in the leading order of perturbation theory, providing a more detailed treatment in the Appendix D.1. In subsection 6.2.2 we will discuss how one could initialize and read out the state of the two-qubit register. Section 6.2.3 will be concerned with the construction of the pulses for universal quantum computing on the two-qubit system.

6.2.1 System and operating regime

The Hamiltonian describing the ground state of the NV− interacting with the nuclear spin of a nearby 13C is

$$\hat{H}_{gs} = \hat{H}_e + \hat{H}_n + \hat{H}_{hf},$$

$$\hat{H}_e = D_{gs} \hat{S}_z^2 + \gamma_e B \cdot \hat{S},$$

$$\hat{H}_n = \gamma_n B \cdot \hat{I},$$

$$\hat{H}_{hf} = \sum_{i,j=x,y,z} A_{ij} \hat{S}_i \hat{I}_j.$$  \hspace{1cm} (6.13)

Here $D_{gs} = 2.88$ GHz is the ground state zero-field splitting, $\gamma_e = g \mu_B = 2.8$ MHz/G is the electronic gyromagnetic ratio and $\gamma_n = 0.001$ MHz/G is the nuclear gyromagnetic ratio. The values for the hyperfine tensor $A_{ij}$ are taken from [137]. This tensor is approximately diagonal in the basis, where the z-axis coincides with the direction connecting the vacancy

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to the $^{13}$C atom. The eigenvalue corresponding to this axis amounts to 201 MHz for a $^{13}$C atom in the first coordination shell, while the other two eigenvalues are 120 MHz. In our simulations we do a basis change to obtain the values of the tensor in the NV-axial basis. In what follows we will neglect the splittings arising due to the Zeeman Hamiltonian $\hat{H}_n$, as they are much smaller than those arising from hyperfine interaction for the $^{13}$C atom in the first coordination shell of an NV$^-$ center.

Let us first treat the electronic part of the Hamiltonian \[ (6.13) \], later we will add the hyperfine interaction as a perturbation. We first assume magnetic field $B_z = D_{gs}/\gamma_c$ in the direction of the NV symmetry axis, so that the levels $|\pm\rangle$ and $|0\rangle$ are degenerate. Now we also assume a magnetic field $B_\perp$ in the direction perpendicular to the symmetry axis, and write the magnetic field as $B_z + iB_y = B_\perp e^{i\phi}$. The coupling of $|1\rangle$ to $|0\rangle$ is suppressed due to a large energy gap $2D_{gs}$ between them, therefore, in this subsection we neglect this coupling. Thus the eigenvectors of the Hamiltonian will be $|\pm\rangle = \left( e^{i\phi/2} |0\rangle + e^{-i\phi/2} |-1\rangle \right)/\sqrt{2}$ and $|-\rangle = \left( e^{i\phi/2} |0\rangle - e^{-i\phi/2} |-1\rangle \right)/\sqrt{2}$ with the energies $\pm|\Omega|$ respectively, with $|\Omega| = \gamma_c B_\perp/\sqrt{2}$. Now we add the hyperfine interaction $\hat{H}_{hf}$ to the system. Assuming $||A|| \ll |\Omega|$, we can restrict our analysis to the secular terms of the hyperfine interaction, that do not flip the electron spin. Then for each electronic level we can describe the hyperfine interaction in terms of the Knight field $h_j$, acting on the nuclear spin $I_j$,

\[
\hat{H}_{hf} = \sum_{e=\{+,-,1\}} \sum_{j=x,y,z} |e\rangle \langle e| h_j^e \hat{I}_j,
\]

\[
h_j^e = \sum_{i=x,y,z} A_{ij} \langle e| \hat{S}_i |e\rangle. \tag{6.14}
\]

One of the key ingredients of the current proposal is the fact that the Knight field turns out to point in different directions for each of the three electronic levels, resulting in the level structure of the defect’s ground state shown in Fig. \[6.6\]. We can thus conclude that transitions between all eigenlevels of the system are now allowed by the nuclear spin selection rules and can be driven with a microwave field, oriented in the direction perpendicular to the symmetry axis of the defect. Let us number the levels in the figure from bottom to the top with $1, \ldots, 6$. For a given direction of the microwave field, resonant with the transition from level $i$ to level $j$, the Hamiltonian of the microwave field takes the form

\[
\hat{H}_{mw} = g_{ij} \left( s_{ij} e^{i\omega_{ij} t} |i\rangle \langle j| + h.c. \right).
\]

Here $\omega_{ij} = E_i - E_j$ is the energy splitting between levels $i$ and $j$, $s_{ij}$ is the matrix element, describing the strength of the corresponding microwave transition, $g_{ij}$ is the amplitude of the microwave pulse, proportional to the magnetic field amplitude. In the simple picture described above, that neglects all nonsecular terms, one calculates $w_{ij}$ as the difference between eigenvalues of the Hamiltonian \[6.13\], that includes only the secular terms

\[
\hat{H} = \left( -|\Omega| + \sum_{j=x,y,z} h_j^- \hat{I}_j \right) |\pm\rangle \langle \pm|,
\]

\[
+ \left( |\Omega| + \sum_{j=x,y,z} h_j^+ \hat{I}_j \right) |\pm\rangle \langle \pm|,
\]

\[
+ \left( 2D_{gs} + \sum_{j=x,y,z} h_j^1 \hat{I}_j \right) |1\rangle \langle 1|.
\]

\[85\]
Figure 6.6: Energy level structure of the ground state of the NV$^-$ center in diamond coupled to a nearby $^{13}$C nuclear spin when a nonparallel magnetic field mixes the electronic levels $|0\rangle$ and $|-1\rangle$. The states $|+\rangle$, $|-\rangle$ and $|1\rangle$ to the left of the dashed line are the eigenstates of the electron spin without hyperfine interaction (hyperfine tensor $A = 0$), the direction of the black arrows to the right of the dashed line indicates the quantization axis of the nuclear spin and $|\psi_{p,m}\rangle$ ($e \in \{+, -, 1\}$) mark the corresponding hyperfine eigenstates. $D_{gs}$ is the NV$^-$ ground state zero field splitting, while $|\Omega|$ marks the splitting that arises between $|+\rangle$ and $|-\rangle$ when nonparallel magnetic field mixes $|0\rangle$ and $|-1\rangle$.

To parametrize $h^e_j$, $e \in \{+,-,1\}$, we introduce $\theta^\pm, \phi^\pm, \theta^1, \phi^1$ according to

$$h^e_j = (h^e_x, h^e_y, h^e_z) = |h^e| (\sin \theta^e \cos \phi^e, \sin \theta^e \sin \phi^e, \cos \theta^e), \quad (6.17)$$

for $e \in \{+,-,1\}$.

The eigenstates of the system in Fig. 6.6 will take the form

$$\psi_{p}^e = |e\rangle \left( \begin{array}{c} \cos(\theta^e_2) \cos(\phi^e_2) \\ \sin(\theta^e_2) \sin(\phi^e_2) \end{array} \right),$$

$$\psi_{m}^e = |e\rangle \left( \begin{array}{c} \sin(\theta^e_2) \cos(\phi^e_2) \\ - \cos(\theta^e_2) \sin(\phi^e_2) \end{array} \right), \quad (6.18)$$

with the eigenvalues being $E_{1,2} = -|\Omega| \pm |h^-|/2$, $E_{3,4} = |\Omega| \pm |h^+|/2$, $E_{5,6} = 2D_{gs} \pm |h^1|/2$.

The state with index $p$ corresponds to the upper state of the hyperfine doublet, with index $m$-to the lower one. If the system is driven with a microwave field pointing in the y-direction, $s_{ij}$ from equation (6.15) can be explicitly calculated using the states (6.18). For example $s_{26}$ will take the form

$$s_{26} = \langle \psi^-_p | S_y | \psi^1_p \rangle = \langle -|S_y|1\rangle \left[ \cos(\theta^1_2) \cos(\phi^1_2) + \sin(\theta^1_2) \sin(\phi^1_2) \right]. \quad (6.19)$$

The last factor here comes from the scalar product of two nuclear spin wave functions and its absolute value is $\cos (\alpha) = (h^- \cdot h^1)/(|h^-||h^1|)$.

To gain universal control over the system we propose to use eight microwave pulses, that couple the levels 1, 2, 3, 4 to the levels 5, 6 (Fig. 6.6). The control Hamiltonian will
then contain eight copies of (6.15) with \(i \in \{5, 6\}, j \in \{1, 2, 3, 4\}\). If we change into a rotating frame, in which all the six levels have the same energy, the control Hamiltonian will take the form

\[
\hat{H}_{\text{mw}} = \sum_{i \in \{5, 6\}, j \in \{1, 2, 3, 4\}} g_{ij} s_{ij} |i\rangle \langle j| + \text{h.c.} \quad (6.20)
\]

Adjusting the two amplitudes \(g_{61}, g_{62}\), we can couple any superposition of levels \(|1\rangle, |2\rangle\) to the state \(|6\rangle\). Let us now choose any pair of orthogonal nuclear spin states \(|0_n\rangle, |1_n\rangle\), then

\[
|-, 0_n\rangle = \alpha |1\rangle + \beta |2\rangle, \\
|-, 1_n\rangle = -\beta^* |1\rangle + \alpha^* |2\rangle. \quad (6.21)
\]

If we now apply the two pulses simultaneously, one coupling the level 1 to the level 6 and one coupling the level 2 to 6, such that \(g_{61} = g\alpha^*/s_{61}, g_{62} = g\beta^*/s_{62}\), the control Hamiltonian will take the form \(\hat{H}_{\text{mw}} = g |6\rangle \langle 6| + \text{h.c.}\). Analogously, if we define \(g_{61} = -g\beta^*/s_{61}, g_{62} = g\alpha^*/s_{62}\), we will obtain the control Hamiltonian \(\hat{H}_{\text{mw}} = g |6\rangle \langle -1_n| + \text{h.c.}\). These pairs of pulses are the new control pulse protocols that can couple \(|-, 0_n\rangle\) and \(|-, 1_n\rangle\) to the level \(|6\rangle\). Similarly, we can define in total eight new control pulse protocols that will couple the levels \(|-, 0_n\rangle, |-, 1_n\rangle, |+, 0_n\rangle, |+, 1_n\rangle\) to the levels \(|5\rangle\) and \(|6\rangle\). We name these new pulse protocols \(p_1, p_2, \ldots, p_8\) and show them in the Fig. 6.7. Each of these pulses has a magnitude \(|p_i|\) and a phase \(f_i\). In the rotating frame all states have the same energy, but in a real system the possibility to apply each of the given pulse protocols separately is based on the fact that the energy differences between levels 1, 2, 3, 4 and the levels 5, 6 in Fig. 6.6 have eight different values and the corresponding transitions can be resolved. In Fig. 6.6 the transition from level 1 to level 5 and from level 2 to level 6 are closest to each other. Choosing the parameters as discussed in Appendix D.2, we numerically diagonalize the Hamiltonian (6.13) and find that the closest resonance frequencies differ by 36 MHz, which suffices to resolve them.

In this subsection we based our description on the simplified Hamiltonian (6.16), that neglects the nonsecular interaction of the electron spin with nonparallel magnetic field and nonsecular hyperfine interaction terms. The same arguments can be given if one uses a more rigorous effective Hamiltonian (D.10), that we derive in the Appendix D.1. This Hamiltonian takes into account the nonsecular interaction terms and is valid to second order perturbation theory.

### 6.2.2 Initialization and Readout

In this subsection we show how to perform initialization and readout of the system in the regime, suggested in the previous subsection, when \(B_z = D_{gs}/\gamma_e\) and \(|\Omega| \gg ||A||\). Our proposal to perform initialization and readout of the system is based on coherent population trapping (CPT) [124] and resembles the scheme used in Ref. [52]. Figure
Figure 6.8: State initialization protocols. Optical pulses (red) pump the electronic states $|1\rangle$ and $|+\rangle$ to the NV$^-$ excited state manifold. An additional simultaneous microwave tone (blue arrow) pumps one of the two lowest hyperfine sublevels. Green arrows illustrate incoherent mechanisms that return the population to the ground state. After many excitation cycles the system becomes trapped in the lower hyperfine level (black dot).

6.8 shows the procedure. Here the excited state manifold consists of an orbital doublet, spin triplet and a hyperfine doublet, thus forming a twelve-dimensional space. The exact Hamiltonian, governing the dynamics of the excited state manifold will be given in the Appendix D.2. The electronic levels $|1\rangle$, $|+\rangle$ are coupled to the excited state manifold through optical excitation, shown as red arrows in the Fig. 6.8. The frequencies of the optical fields are such that the level $|\rangle$ is out of resonance, while the other two levels $|1\rangle$, $|+\rangle$ are coupled close to resonance. In Appendix D.2 we show that one can achieve this with a single frequency optical field in the relevant magnetic field regime. In order to initialize the system in the lowest level of Fig. 6.8 an additional microwave pulse is required, shown as a blue arrow in Fig. 6.8. Whenever the lowest level is not populated, it will be brought to the excited state manifold through a combination of microwave and optical pulses. From there, the population will incoherently decay back to the ground state manifold through the channels marked with green arrows in the Fig. 6.8. Then the process repeats itself until after many cycles of optical and microwave excitation the population becomes trapped in the lowest level of Fig. 6.8. We performed a numerical simulation of this initialization procedure and showed that in 100 $\mu$s the system can be initialized with a fidelity of 98%, in agreement with the results obtained for a similar procedure in [52]. The details of the simulation and the relevant parameters are given in Appendix D.2.

Read out can be performed in a similar manner. Let us assume that we want to know whether the system is in a state $\psi$. We first perform a gate that takes $\psi$ to the lowest level of Fig. 6.8, followed by the initialization procedure. The absence of luminescence
intensity indicates the system was initially in the state $\psi$, the presence of luminescence intensity indicates the opposite measurement result.

### 6.2.3 Universal set of holonomic gates

We now show how to construct a universal set of gates to control the two-qubit register in the magnetic field regime given in subsection 6.2.1, when $B_z = D_{gs}/\gamma_e$ and $|\Omega| \gg ||A||$. Universal control requires that one can perform each of the eight microwave tones $p_1, p_2, \ldots, p_8$, without driving any other transitions. Our proposal is to perform nonabelian holonomic gates \[8\] using the setup described in the previous subsections. Each step of such a gate requires the identification of a $\Lambda$-system, built from two lower and one upper state from Fig. 6.7 (see section 1.4.3 of the introduction). The lower states are coupled to the excited state with two different lasers, that are both detuned from resonance by the same value $\Delta$, as shown in Fig. 6.9.

![Figure 6.9: Energy levels in $\Lambda$-configuration. Two different lasers with amplitudes $u_0$ and $u_1$ and a common detuning $\Delta$ couple the ground states $|0\rangle$ and $|1\rangle$ to the same excited state $|e\rangle$. This generates nontrivial unitary operation on the lower levels, when the system is driven to the $|e\rangle$ state and back.](image)

The $\Lambda$-system Hamiltonian reads

$$\hat{H}_\Lambda = \sum_{k=1}^{2} \left( u_k |k\rangle \langle e| + u_k^* |e\rangle \langle k| \right) + \Delta |e\rangle \langle e|$$

and as shown in \[8\], can be used to perform universal set of gates on the levels $|0\rangle$ and $|1\rangle$, if one can control the complex amplitudes $u_1$ and $u_0$ and the detuning $\Delta$ and the lasers are switched on for the duration $\tau = 2\pi/\sqrt{\Delta^2 + 4|u_0|^2 + 4|u_1|^2}$.

Figure 6.7 suggests different ways to identify such a $\Lambda$-system. Using the pulses $p_1$ and $p_3$ we can create a $\Lambda$-system that allows one to perform universal gates on the nuclear spin controlled by the state of an electron spin. More precisely, the nuclear spin state is flipped only if the electron spin is in the state $|+\rangle$. Analogously, using the pulses $p_5$ and $p_7$ one arrives at gates on the nuclear spin, controlled with the $|-\rangle$ state of the electron spin. Performing the same gate first using the pulses $p_1$ and $p_3$ and then the pulses $p_5$ and $p_7$, one performs universal single qubit gates on the nuclear spin. In exactly the same way, gates on the electron spin controlled with the state of a nuclear spin can be performed combining pulses $p_1$ with $p_5$ and $p_3$ with $p_7$. Thus, universal holonomic computation with the two-qubit register can be achieved.

For example, the CPHASE gate can be performed if the control pulse protocol $p_8$ is switched on with zero detuning for the time $\tau = \pi/|p_8|$. That is equivalent to switching two laser pulses that resonantly couple the levels 1 and 2 to the level 6 (Fig. 6.6). The
amplitudes and phases of the lasers are adjusted such that the microwave Hamiltonian takes the form

\[ \hat{H}_{mw} = |6\rangle \langle g_{61}s_{61}|1\rangle + g_{62}s_{62}|2\rangle + h.c. \]
\[ = p_8|6\rangle \langle -, 1_n| + h.c. \] 

(6.23)

**6.2.4 Discussion**

In this work we have shown how to perform universal quantum computing on a two qubit register, consisting of the electron spin of a negatively charged nitrogen-vacancy center in diamond and the nuclear spin of a nearby $^{13}$C atom. Although we only considered the carbon atom of the shell closest to the vacancy due to the strong hyperfine interaction, our method can be extended to control the carbon atoms further away. We estimate that the magnitude of the dipole-dipole hyperfine interaction for $^{13}$C atoms that are twice as far from the vacancy as the closest carbon is such that the transitions $|1\rangle$ to $|5\rangle$ and $|2\rangle$ to $|6\rangle$ can still differ by 1 MHz and thus the register can be manipulated using microwave transitions only. The density functional theory calculations [6] that also take into account the Fermi contact term reveal there are approximately 40 carbon atoms around the vacancy with hyperfine constants greater that 2 MHz, which suggests that there are more than 3 closest $^{13}$C atoms, to which our method can be applied. It is still possible to perform universal gates on these atoms until the electron spin decoheres, but in that case one also has to include the nitrogen nuclear spin into consideration. Our method can readily be extended to include the nitrogen nuclear spin through the hyperfine interaction Hamiltonian

\[ \hat{H}_N = A_{\parallel} \hat{S}_z \hat{I}_z + A_{\perp} (\hat{S}_x \hat{I}_x + \hat{S}_y \hat{I}_y), \]

(6.24)

with the hyperfine constants being $A_{\parallel} = -2.16$ MHz, $A_{\perp} = -2.6$ MHz [138]. Using this Hamiltonian, the Knight field acting on the nitrogen nuclear spin can be calculated in the same way as it was done for the closest shell carbon atom. Other proposals exist to perform universal microwave control on the registers of coupled nuclear and electron spins [139, 140]. They differ from our method in the sense that their gates are not geometric and universality in those schemes requires an external magnetic field acting on the nuclear spins to add up with the hyperfine Knight field and thus create two nonparallel axes of rotation, while in our scheme we only rely on the hyperfine field, that is stronger than the external magnetic field. Strong hyperfine interaction has its disadvantages in that it decoheres the nuclear spin very fast. Going to a rotating frame picture reveals that the nuclear spin is not affected by the dephasing in the ground state space of the electron spin ($T_2$), but the relaxation processes ($T_1$), as well as reinitialization of the electron spin affect the nuclear spin dramatically [27]. Still our scheme can be used to perform universal quantum computation, for example, to gain increased sensitivity of an NV$^-$ based quantum sensor [25]. We also note that although we only considered our scheme applied to the nuclear spin strongly coupled to the electronic spin, it would also be possible to consider it with respect to weakly coupled nuclear spins. A lot of research is done on the control of these registers [32, 35] and configuration, in which the levels $|0\rangle$ and $|−1\rangle$ are mixed due to nonparallel magnetic field could offer new pathways to control such registers.
Chapter 7
Conclusion

A lot of experimental and theoretical studies suggest that an NV$^-$ center is a promising platform for quantum information science. Its long ground state spin coherence time, as well as optical interface for state initialization and read out make this point defect in diamond extremely useful for applications, ranging from quantum sensing to quantum communication and possibly computation. In this thesis we have considered several problems relevant for the application of NV$^-$ centers in quantum information.

In chapter 2 we considered the interaction of the NV$^-$ center with mechanical strain. We derived all three symmetry-allowed interaction Hamiltonians, with a special emphasis on the one that was previously overlooked in the literature. We conclude that if the values of the coupling parameters are of the same order of magnitude, as those of the other two Hamiltonians, mechanical strain can be used to drive spin transitions, that by now could only be driven with magnetic field. This paves the way to full mechanical control of NV$^-$ centers, without the need to fabricate microwave antennas. This strategy could then be used to optimize the experiments and simplify the setup needed to efficiently control the NV$^-$ centers.

In chapter 3 we theoretically consider the benefits one obtains when coupling the NV$^-$ centers to spin waves, rather than to the microwave antenna. This has recently been realized experimentally and we show that our theory quantitatively agrees with experiment in the coupling enhancement one obtains with respect to pure antenna driving. We predict several hundred times enhancement for an NV$^-$ placed 50 $\mu$m way from the antenna, which means this approach can sufficiently simplify the control of multiple NV$^-$ centers by reducing the number of microwave antennas needed to control them. Moreover, we expect that reducing the size of magnetic material, that hosts spin-waves, it should be possible to observe coherent excitation exchange between NV$^-$ centers and magnonic cavities, that is the aim of the future experimental and theoretical research.

In chapter 4 we discuss the very important issue, related to NV$^-$ based quantum devices, scalability. We develop a protocol for entanglement generation between two NV$^-$ centers, coupled to a common optical mode of a high Q cavity. It turns out that a CNOT gate can be generated in approximately $\sim 100$ ns and at a fidelity, that would be sufficient for quantum error correction schemes. This paves the way for universal quantum computing with NV$^-$ centers, provided good optical cavities compatible with diamond technology can be fabricated.

In the chapter 5 we present an effective Hamiltonian description of adiabatic geometric gates, alternative to conventional Berry connection approach. This is an analytical formalism, that does not require the diagonalization of the dark subspace, that is necessary for the Berry connection approach. It turns out that for big dimensions of the Hilbert space of the system, our analytical method may still work, while the Berry connection would require numerical calculations with identical results, which is clearly an advantage.
of our method. Recently, the adiabatic Berry phase has been observed in NV$^-$ centers \[129\], so we expect our method could be useful in the description of similar experiments with multiple coupled NV$^-$ spins.

In the chapter \[6\] we describe non-adiabatic geometric gates with NV$^-$ centers. We show that for the optical gates, that require excitation of NV$^-$ to its orbital excited state, the decoherence is limited by orbital relation and dephasing processes \[41\]. When driven with detuning, the fidelity of these gates increases, as the NV$^-$ spends less time in the excited state. These gates are thus a compromise of fast ($\sim 10$ ns) gate time and low fidelity. If one needs gates with really high fidelity, one must remain within the ground state space of NV$^-$ center. We show that with microwaves only it is still possible to perform non-adiabatic geometric gates not only on the electron spin of an NV$^-$ center, but also on the nuclear spin, that is hyperfine couple to it. It turns out that our scheme allows one to realize a universal set of two-qubit gates on such small register, with possibility of generalization to a higher number of nuclear spins.

Despite existing issues with scalability, NV$^-$ centers are a promising platform for quantum information purposes. The issues we discussed in this thesis are important for any application NV$^-$ may have in the future and open new opportunities for the NV$^-$ based research.
Appendix A

Appendix

A.1 Reduction of $E \times E$ representation of the group $C_{3v}$

In this appendix we show how to reduce the tensor product representation $E \times E$ into irreducible representations of $C_{3v}$ group. This is a four dimensional representation in the space of vectors $\{\phi_x \psi_x, \phi_x \psi_y, \phi_y \psi_x, \phi_y \psi_y\}$ and we will reduce it using the projection operators. Let us assume the vector $\phi_x \psi_x$ contains a symmetry component, that transforms according to $A_1$ representation. To identify, whether it is true or not, we need to project out the corresponding symmetry component using the projection operator $\hat{P}^{A_1} = \frac{1}{6} \sum_{T \in G} A_1(T) \hat{O}_T$.

We omitted the indexes of the matrix because the representation is one-dimensional and obtain

\[
\hat{P}^{A_1}(\phi_x \psi_x) = \frac{1}{6} \sum_{T \in G} A_1(T) \hat{O}_T(\phi_x \psi_x) = \frac{1}{6} \left( \hat{O}_E - \hat{O}_{R_+} + \hat{O}_{R_-} + \hat{O}_{\sigma_1} + \hat{O}_{\sigma_2} + \hat{O}_{\sigma_3} \right) (\phi_x \psi_x)
\]

\[
= \frac{1}{6} \left( \phi_x \psi_x + (-\frac{1}{2} \phi_x + \frac{\sqrt{3}}{2} \phi_y)(-\frac{1}{2} \psi_x + \frac{\sqrt{3}}{2} \psi_y) + (-\frac{1}{2} \phi_x - \frac{\sqrt{3}}{2} \phi_y)(-\frac{1}{2} \psi_x + \frac{\sqrt{3}}{2} \psi_y) 
+ \phi_x \psi_x + (-\frac{1}{2} \phi_x - \frac{\sqrt{3}}{2} \phi_y)(-\frac{1}{2} \psi_x - \frac{\sqrt{3}}{2} \psi_y) + (-\frac{1}{2} \phi_x + \frac{\sqrt{3}}{2} \phi_y)(-\frac{1}{2} \psi_x + \frac{\sqrt{3}}{2} \psi_y) \right)
\]

\[
= \frac{\phi_x \psi_x + \phi_y \psi_y}{2} \tag{A.1}
\]

Let us continue to work with the vector $\phi_x \psi_x$. We will now assume that it has a component that transforms as $e_x$, according to the first row of the representation $E$. To identify this component we will apply the projection operator $\hat{P}^E_{11}$ on $\phi_x \psi_x$ and obtain

\[
\hat{P}^E_{11}(\phi_x \psi_x) = \frac{2}{6} \sum_{T \in G} E(T)_{11} \hat{O}_T(\phi_x \psi_x) = \frac{1}{3} \left( \hat{O}_E - \frac{1}{2} \hat{O}_{R_+} - \frac{1}{2} \hat{O}_{R_-} + \hat{O}_{\sigma_1} - \frac{1}{2} \hat{O}_{\sigma_2} - \frac{1}{2} \hat{O}_{\sigma_3} \right) (\phi_x \psi_x)
\]

\[
= \frac{1}{3} \left( \phi_x \psi_x + \frac{1}{4} \phi_x - \frac{\sqrt{3}}{4} \phi_y)(-\frac{1}{2} \psi_x + \frac{\sqrt{3}}{2} \psi_y) + \frac{1}{4} \phi_x + \frac{\sqrt{3}}{4} \phi_y)(-\frac{1}{2} \psi_x + \frac{\sqrt{3}}{2} \psi_y) 
+ \phi_x \psi_x + \frac{1}{4} \phi_x + \frac{\sqrt{3}}{4} \phi_y)(-\frac{1}{2} \psi_x - \frac{\sqrt{3}}{2} \psi_y) + \frac{1}{4} \phi_x - \frac{\sqrt{3}}{4} \phi_y)(-\frac{1}{2} \psi_x + \frac{\sqrt{3}}{2} \psi_y) \right)
\]

\[
= \frac{\phi_x \psi_x - \phi_y \psi_y}{2} \tag{A.2}
\]

Indeed this symmetry component is nonzero. If we would obtain zero we would have to use the projectors $\hat{P}^E_{22}$ and $\hat{P}^{A_2}$ to split $\phi_x \psi_x$ into symmetry components. Now we need to generate a partner of $\frac{\phi_x \psi_x - \phi_y \psi_y}{2}$ in the representation $E$. For that we need to apply the
transfer operator $\hat{P}_{21}^E$ to the function $(\phi_x \psi_x)$ and we obtain

$$\hat{P}_{21}^E(\phi_x \psi_x) = \frac{2}{6} \sum_{T \in G} E(T)_{21} \hat{O}_T(\phi_x \psi_x)$$

$$= \frac{1}{3} \left( \frac{\sqrt{3}}{2} \hat{O}_{R+} - \frac{\sqrt{3}}{2} \hat{O}_{R-} - \frac{\sqrt{3}}{2} \hat{O}_{\sigma_2} + \frac{\sqrt{3}}{2} \hat{O}_{\sigma_3} \right) (\phi_x \psi_x)$$

$$= \frac{1}{3} \left( \frac{\sqrt{3}}{2} \left( -\frac{1}{2} \phi_x + \frac{\sqrt{3}}{2} \phi_y \right) \left( -\frac{1}{2} \psi_x + \frac{\sqrt{3}}{2} \psi_y \right) - \frac{\sqrt{3}}{2} \left( -\frac{1}{2} \phi_x - \frac{\sqrt{3}}{2} \phi_y \right) \left( -\frac{1}{2} \psi_x - \frac{\sqrt{3}}{2} \psi_y \right) \right)$$

$$= \frac{1}{\sqrt{2}} \left( \phi_x \psi_y - \phi_y \psi_x \right). \quad (A.3)$$

The three functions we have identified span almost the whole vector space of $E \times E$. The last function we are still missing is $\phi_x \psi_y - \phi_y \psi_x$. We can in principal apply projection operators to find the representation to which it belongs to, but now it is possible to use a shortcut. This function can not be transformed by symmetry operations to other three, as it is not part of their representations. That means this function must be a basis vector for a one-dimensional representation of $C_{3v}$. Applying the transformation $\hat{O}_{\sigma_1}$, we see, that $\phi_x \psi_y - \phi_y \psi_x \rightarrow \frac{-\phi_x \psi_y + \phi_y \psi_x}{2}$. That means this vector is a basis for $A_2$ irreducible representation.

### A.2 Construction of spinor bases functions for the irreducible representations of the group $C_{3v}$

In this appendix we will construct the spinor bases functions for the irreducible representations of the $C_{3v}$ group. We will only be interested in the cases when the total spin is 0 and 1. We can think of these cases as the states of two spin-1/2 particles. With each such particle we associate the Hilbert space spanned by $|\uparrow\rangle$ and $|\downarrow\rangle$, which are the states with spin projections $\pm 1/2$ along the symmetry z-axis (Fig. 1.2 (b)). The total Hilbert space of two particles is thus spanned by $\{ |\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle \}$. In general, rotations by $\theta$ along the axis $\mathbf{n}$ act on the two-component spin vector of each particle according to

$$\exp(-\frac{i\theta}{\hbar} \mathbf{n} \hat{S}) \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \exp(-\frac{i\theta}{\hbar} \mathbf{n} \mathbf{\sigma}) \begin{pmatrix} \alpha \\ \beta \end{pmatrix},$$

where

$$\mathbf{\sigma} = \{ \sigma_x, \sigma_y, \sigma_z \} = \{ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \} \quad \text{(A.4)}$$

The inversion does not affect the spinor, that means reflection in a plane acts on spinors as rotations by 180° in this plane (analogous to what we saw for spin operators). The action of the transformations of the $C_{3v}$ group on two particle four component spinor is
just the tensor product of the transformations for the single particles

$$O_I = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix},$$

$$O_{R_+} = e^{-i \frac{\pi}{3} \sigma_z} \times e^{-i \frac{\pi}{3} \sigma_z} = \begin{pmatrix} e^{-i \frac{2\pi}{3}} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$O_{R_-} = e^{i \frac{\pi}{3} \sigma_z} \times e^{i \frac{\pi}{3} \sigma_z} = \begin{pmatrix} e^{i \frac{2\pi}{3}} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$O_{\sigma_1} = e^{-i \frac{\pi}{2} \sigma_y} \times e^{-i \frac{\pi}{2} \sigma_y} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix},$$

$$O_{\sigma_2} = e^{-i \frac{\pi}{4} (\sigma_x + \frac{3}{2} \sigma_y)} \times e^{-i \frac{\pi}{4} (\sigma_x + \frac{3}{2} \sigma_y)} = \begin{pmatrix} 0 & 0 & \frac{1}{4}(1 + i \sqrt{3})^2 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$O_{\sigma_3} = e^{-i \frac{\pi}{4} (\sigma_x - \frac{3}{2} \sigma_y)} \times e^{-i \frac{\pi}{4} (\sigma_x - \frac{3}{2} \sigma_y)} = \begin{pmatrix} 0 & 0 & \frac{1}{4}(1 - i \sqrt{3})^2 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$  \hspace{1cm} (A.5)

Now we can construct the projectors onto the irreducible representations. In full analogy to [A.1], we construct the operators

$$\hat{p}_{A_1} = \frac{1}{6} \left( \hat{O}_E + \hat{O}_{R_+} + \hat{O}_{R_-} + \hat{O}_{\sigma_1} + \hat{O}_{\sigma_2} + \hat{O}_{\sigma_3} \right) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1/2 & -1/2 \\ 0 & -1/2 & 1/2 \end{pmatrix},$$

$$\hat{p}_{A_2} = \frac{1}{6} \left( \hat{O}_E + \hat{O}_{R_+} + \hat{O}_{R_-} - \hat{O}_{\sigma_1} - \hat{O}_{\sigma_2} - \hat{O}_{\sigma_3} \right) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1/2 & 1/2 \\ 0 & 1/2 & 1/2 \end{pmatrix},$$

$$\hat{p}_{\pi_1} = \frac{1}{3} \left( \hat{O}_E - \frac{1}{2} \hat{O}_{R_+} - \frac{1}{2} \hat{O}_{R_-} + \hat{O}_{\sigma_1} - \frac{1}{2} \hat{O}_{\sigma_2} - \frac{1}{2} \hat{O}_{\sigma_3} \right) = \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 0 & 0 \\ 1/2 & 0 & 0 \end{pmatrix},$$

$$\hat{p}_{\pi_2} = \frac{1}{3} \left( \sqrt{3}/2 \hat{O}_{R_+} - \sqrt{3}/2 \hat{O}_{R_-} - \sqrt{3}/2 \hat{O}_{\sigma_2} + \sqrt{3}/2 \hat{O}_{\sigma_3} \right) = \begin{pmatrix} -i/2 & 0 & 0 \\ 0 & 0 & 0 \\ i/2 & 0 & 0 \end{pmatrix}. $$  \hspace{1cm} (A.6)

Applying the operator $\hat{p}_{A_1}$ to $|\uparrow \downarrow \downarrow \downarrow \rangle_{\sqrt{2}}$, we see that it remains invariant and thus is the basis for $A_1$ representation. Applying the operator $\hat{p}_{A_2}$ to $|\uparrow \downarrow \downarrow \downarrow \rangle_{\sqrt{2}}$, we see that it remains invari-
ant and thus is the basis for $A_2$ representation. The remaining states \( \{ |↑↑⟩ + |↓↓⟩ \}/\sqrt{2}, \{- |↑↑⟩ - |↓↓⟩ \}/\sqrt{2} \) form the bases for the $E$ representation (the first vector is projected out using \( \hat{P}_E^{11} \) and his partner is generated using the transfer operator \( \hat{P}_E^{21} \)).

### A.3 Molecular orbital bases for the irreducible representations of the $C_{3v}$ group

In this appendix we construct the molecular orbitals that are basis functions for the irreducible representations of the group $C_{3v}$. We start with the orbitals $b_1$, $b_2$, $b_3$, $b_n$ in Fig. 1.3. The operations of the group $C_{3v}$ leave the orbital $b_n$ invariant. We can thus immediately conclude that this orbital transforms according to the trivial representation $A_1$. Other orbitals do change under the operations of the group. Let us construct a representation $\Gamma$ in the bases of orbitals $b_1$, $b_2$ and $b_3$. The corresponding $3 \times 3$ matrices will take the form

\[
\begin{align*}
\Gamma(I) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \\
\Gamma(R+) &= \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \\
\Gamma(R-) &= \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \\
\Gamma(\sigma_1) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \\
\Gamma(\sigma_2) &= \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \\
\Gamma(\sigma_3) &= \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.
\end{align*}
\]  

(A.7)

Analogously to what we have done for the spinors, we can construct the projectors onto the rows of the irreducible representations of the group $C_{3v}$ and obtain

\[
\begin{align*}
\hat{P}^{A_1} &= \frac{1}{6} \left( \hat{O}_E + \hat{O}_{R_+} + \hat{O}_{R_-} + \hat{O}_{\sigma_1} + \hat{O}_{\sigma_2} + \hat{O}_{\sigma_3} \right) = \begin{pmatrix} 1/3 & 1/3 & 1/3 \\ 1/3 & 1/3 & 1/3 \\ 1/3 & 1/3 & 1/3 \end{pmatrix}, \\
\hat{P}^{A_2} &= \frac{1}{6} \left( \hat{O}_E + \hat{O}_{R_+} + \hat{O}_{R_-} - \hat{O}_{\sigma_1} - \hat{O}_{\sigma_2} - \hat{O}_{\sigma_3} \right) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\
\hat{P}^{E}_{11} &= \frac{1}{3} \left( \hat{O}_E - \frac{1}{2} \hat{O}_{R_+} + \frac{1}{2} \hat{O}_{R_-} + \hat{O}_{\sigma_1} - \frac{1}{2} \hat{O}_{\sigma_2} - \frac{1}{2} \hat{O}_{\sigma_3} \right) = \begin{pmatrix} 1/3 & -1/6 & -1/6 \\ -1/6 & 1/12 & 1/12 \\ -1/6 & 1/12 & 1/12 \end{pmatrix}, \\
\hat{P}^{E}_{21} &= \frac{1}{3} \left( \frac{\sqrt{3}}{2} \hat{O}_{R_+} - \frac{\sqrt{3}}{2} \hat{O}_{R_-} - \frac{\sqrt{3}}{2} \hat{O}_{\sigma_2} + \frac{\sqrt{3}}{2} \hat{O}_{\sigma_3} \right) = \begin{pmatrix} 0 & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{2\sqrt{3}} & -\frac{1}{2\sqrt{3}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{2\sqrt{3}} & -\frac{1}{2\sqrt{3}} \end{pmatrix}.
\end{align*}
\]  

(A.8)

We can apply this projectors, for example, to the the orbital $b_1$. Its projection will be the first column of the matrices above (A.8). Normalizing the resulting projections we obtain

\[
\begin{align*}
b_c &\in A_1, \\
\{e_x, e_y\} &\in E, \\
b_c &= b_1 + b_2 + b_3, \\
b_c &= \frac{\sqrt{3}}{\sqrt{6}}, \\
e_x &= \frac{2b_1 - b_2 - b_3}{\sqrt{6}}, \\
e_y &= \frac{b_2 - b_3}{\sqrt{2}}.
\end{align*}
\]  

(A.9)
Appendix B

Appendix

B.1 Magnetic field alignment

In our model, we have so far assumed that the magnetic field is perfectly aligned with the NV axis of both defects involved in the CPHASE gate. This raises two important issues: (1) how to treat NV centers with different orientations with respect to the diamond crystal, and (2) to what extent will the CPHASE operation be disturbed by any small misalignment of the magnetic field? As for (1), we note that there are four distinct NV orientations (up to small misalignments which we discuss below). Only the NV centers with their orientation along the external B field will be near resonance and will participate in the CPHASE gate operation while the NV centers oriented along the three other axes can be safely ignored. Regarding (2), the field misalignment will add a term $g\mu_B B_x S_x$ to the Hamiltonian Eq. (4.1) where $B_x = B \tan \phi \approx B\phi$ is the transverse (misalignment) field (chosen to point in $x$ direction) and $\phi \ll 1$ denotes the misalignment angle. The effect of the misalignment field is small if $B_x \ll \delta B$. For a misalignment of one degree, the NV center should be operated at least $\delta B \approx 20\, \text{G}$ away from the level anticrossing.

B.2 Perturbation analysis

In this section we will give an alternative derivation of equation (4.7), using conventional time independent perturbation theory. We are interested in the shift of the ground state of $H_0$, induced by the perturbation $H_{\text{int}}$. The matrix element of $H_{\text{int}}$, that causes the transition from the initial state $|i\rangle$ to the final state $|f\rangle$, is

$$H_{\text{int}}^{i\rightarrow f} = \langle f | H_{\text{int}} | i \rangle.$$  \hspace{1cm} (B.1)

Thus, the matrix elements of the perturbation are:

$$H_{\text{int}}^{GG0 \rightarrow EG0} = H_{\text{int}}^{GE0 \rightarrow EE0} = g_{L1},$$

$$H_{\text{int}}^{GG0 \rightarrow GE0} = H_{\text{int}}^{EG0 \rightarrow EE0} = g_{L2},$$

that account for the interaction between the NVs and the laser, and

$$H_{\text{int}}^{EE0 \rightarrow GG1} = g_{C1},$$

$$H_{\text{int}}^{EG0 \rightarrow GG1} = g_{C2},$$

that account for the interaction between the NVs and the cavity. There are also six inverse transitions with the conjugate matrix elements. We consider only the first five
energy levels of $H_0$, as we are going to use fourth order perturbation theory and higher energy levels are not excited under this approximation.

One can think of the perturbation to the particular eigenenergy level of $H_0$ as arising from transitions that start and end at this level. First order processes are thus absent as we have no diagonal terms in the perturbation. Second order processes are

\[
|GG0\rangle \rightarrow |EG0\rangle \rightarrow |GG0\rangle,
|GG0\rangle \rightarrow |GE0\rangle \rightarrow |GG0\rangle,
\]

and the second order energy correction will be

\[
\delta E_2 = -\frac{|g_{L1}|^2}{\delta L_1 + \Delta m_{s_1}} - \frac{|g_{L2}|^2}{\delta L_2 + \Delta m_{s_2}}.
\]

We have no third order processes that would start and end at the ground state, so the third order correction to the energy is zero. Now we include all of the fourth order processes, described by the formula

\[
\delta E_4 = -\sum_{i,j,k\neq GG0} H^G_{int} \frac{H^{i\rightarrow j}H^{j\rightarrow k}H^{k\rightarrow GG0}}{\langle i|H_0|i\rangle \langle j|H_0|j\rangle \langle k|H_0|k\rangle} - \delta E_2 \sum_{i\neq GG0} H^G_{int} \frac{H^{i\rightarrow GG0}}{\langle i|H_0|i\rangle^2}.
\]

Here we have omitted all the terms that contain the diagonal perturbation elements, as those are zero for our system. The first term in this equation contains all eight fourth order processes that exist for this system. The second term is responsible for renormalization of the perturbed wavefunction. After the calculation we have

\[
\delta E_4 = \frac{|g_{L1}|^4}{(\delta L_1 + \Delta m_{s_1})^3} + \frac{|g_{L2}|^4}{(\delta L_2 + \Delta m_{s_2})^3} - \frac{|g_{L1}|^2|g_{c1}|^2}{(\delta L_1 + \Delta m_{s_1})^2\delta c} - \frac{|g_{L2}|^2|g_{c2}|^2}{(\delta L_2 + \Delta m_{s_2})^2\delta c} - \frac{2|g_{L1}g_{L2}|g_{c1}g_{c2}\cos(\phi_1 - \phi_2)}{(\delta L_1 + \Delta m_{s_1})(\delta L_2 + \Delta m_{s_2})\delta c}.
\]

It can easily be seen that $\delta B_1 m_{s_1} + \delta B_2 m_{s_2} + \delta E_2 + \delta E_4$ coincides with the result (4.7) obtained in the section 4.2.

### B.3 Makhlin invariants

We are interested in producing a two-qubit gate (e.g. $U_{\text{CPHASE}}$) only up to single-qubit operations, i.e.,

\[
U(t) = \exp(-2\pi itH_{2q}) = (W_1 \otimes W_2)U_{\text{CPHASE}}(V_1 \otimes V_2),
\]

with $V_i$ and $W_i$ arbitrary single-qubit unitaries. To test whether $U(t)$ and $U_{\text{CPHASE}}$ are equivalent in this sense, one can use two invariants $(G_1, G_2)$ of a two-qubit unitary $U$, defined as

\[
G_1 = (\text{tr} U)^2 / 16 \det U,
G_2 = ((\text{tr} U)^2 - \text{tr} U^2) / 4 \det U.
\]

For the identity operation $U(0) = 1$, we find $G_1 = 1$, $G_2 = 3$, whereas the CPHASE gate lies in the same class as the CNOT gate, with $G_1 = 0$, $G_2 = 1$. Finding the latter values for $G_1$ and $G_2$ with $U(t)$ for some time $t > 0$ therefore proves that we have generated the CPHASE gate (and with this also CNOT gate) up to single-qubit operations.
Appendix C

Appendix

C.1 Effective Hamiltonian for a generalized Lambda system

In this section, we derive Eqs. (5.6) and (5.7) of the main text. We consider a generalized Lambda system with \( n + 1 \) levels, for which the first \( n \) levels, forming a Hilbert space \( \mathcal{H} \) are resonantly coupled to the remaining level (Fig. 5.1). The Hamiltonian of such a system in the rotating frame is

\[
\hat{H} = \Omega \sum_{i=1}^{n} r_i \left( e^{i\phi_i} |i\rangle \langle e| + e^{-i\phi_i} |e\rangle \langle i| \right).
\]  

By introducing the bright state \( |B\rangle = \sum_{i=1}^{n} r_i e^{i\phi_i} |i\rangle \) the Hamiltonian may be rewritten as

\[
\hat{H} = \Omega \left( |B\rangle \langle e| + |e\rangle \langle B| \right),
\]  

The \( n - 1 \) states spanning the Hilbert space \( \mathcal{H} \) are eigenvectors of this Hamiltonian with zero eigenvalue, thus forming the dark subspace of this Hamiltonian. We assume that Hamiltonian (C.2) is time dependent, such that the dark subspace also depends on time and is defined with a time dependent orthonormal basis \( |\psi_1(t)\rangle, |\psi_2(t)\rangle, \ldots, |\psi_{n-1}(t)\rangle \).

We assume the system to be initialized in an instantaneous dark state of its Hamiltonian and to subsequently evolve in the adiabatic regime, so at any time \( t \) the state of the system can be expressed as

\[
|\psi\rangle = \sum_{i=1}^{n-1} c_i(t) |\psi_i(t)\rangle + p |B\rangle.
\]

According to the Schrödinger equation

\[
\frac{i\hbar}{\partial t} \left( \sum_{i=1}^{n-1} c_i(t) |\psi_i(t)\rangle + p |B\rangle \right) = p \hat{H} |B\rangle,
\]  

because the Hamiltonian acts trivially on the dark states. In other words, one may write

\[
\sum_{j=1}^{n-1} \left( \hat{c}_j(t) |\psi_j(t)\rangle + c_j(t) |\dot{\psi}_j(t)\rangle \right) + p |B\rangle + p \hat{B} = p \hat{H} |B\rangle.
\]  

Multiplying this equation by \( \langle \psi_i | \) from the left we obtain

\[
\dot{c}_i(t) = -\sum_{j=1}^{n-1} c_j(t) \langle \psi_i | \dot{\psi}_j(t) \rangle - p \langle \psi_i | \hat{B} \rangle.
\]  

In the adiabatic limit \( p \to 0 \), we find

\[
\dot{c}_i(t) = -\sum_{j=1}^{n-1} c_j(t) \langle \psi_i | \dot{\psi}_j(t) \rangle.
\]
Let us now concentrate on the evolution of the dark subspace during an infinitesimal time interval $dt$. A general state of the system in the adiabatic limit $|\psi_s\rangle = \sum_{i=1}^{n-1} c_i(t) |\psi_i(t)\rangle$ evolves into

$$
|\psi_s\rangle = \sum_{i=1}^{n-1} c_i(t) |\psi_i(t)\rangle \rightarrow \sum_{i=1}^{n-1} c_i(t + dt) |\psi_i(t + dt)\rangle = \sum_{i=1}^{n-1} (c_i(t) + \dot{c}_i(t) dt) (|\psi_i(t)\rangle + |\dot{\psi}_i(t)\rangle dt),
$$

which using Eq. (C.6) up to the linear terms in $dt$ becomes

$$
\sum_{i=1}^{n-1} \left( c_i(t) |\psi_i(t)\rangle + c_i(t) |\dot{\psi}_i(t)\rangle dt \right) - \sum_{i,j=1}^{n-1} c_j(t) \langle \psi_i(t) | \dot{\psi}_j(t) \rangle |\psi_i(t)\rangle dt.
$$

Introducing the operator

$$
\hat{O}_D(dt) = \sum_{i=1}^{n-1} |\psi_i(t)\rangle \langle \psi_i(t)| + dt \sum_{i=1}^{n-1} |\dot{\psi}_i(t)\rangle \langle \psi_i(t)|
$$

$$
- dt \sum_{i,j=1}^{n-1} \langle \psi_i(t) | \dot{\psi}_j(t) \rangle |\psi_i(t)\rangle \langle \psi_j(t)|,
$$

it follows that

$$
|\psi_s\rangle \rightarrow \hat{O}_D(dt) |\psi_s\rangle.
$$

Here the dark states form an $(n-1)$-dimensional subspace of the $n$-dimensional Hilbert space $\mathcal{H}$. Therefore $\hat{O}_D(dt)$ can be viewed as an operator acting in the space $\mathcal{H}$. Introducing the projector onto the dark space

$$
\hat{P}_D = \sum_i |\psi_i(t)\rangle \langle \psi_i(t)|,
$$

we arrive at

$$
\hat{O}_D = \hat{P}_D + \hat{P}_D \hat{P}_D dt.
$$

The expression for $\hat{O}_D$ can be even further simplified, if one uses the fact that $\hat{P}_D = \mathbb{1} - \hat{P}_B$, where $\mathbb{1}$ is the identity operator acting in the Hilbert space $\mathcal{H}$ and $\hat{P}_B = |B\rangle \langle B|$. We obtain

$$
\hat{O}_D = \mathbb{1} - \hat{P}_B - \hat{P}_B (\mathbb{1} - \hat{P}_B) dt = \mathbb{1} - \hat{P}_B + \left[ (\hat{B}|B\rangle \langle B| - |B\rangle \langle B| \hat{B} \right] dt.
$$

This operator transforms the basis vectors of the dark subspace and because it arose from the Schrödinger equation with the Hamiltonian $H$ in the adiabatic limit, we can conclude that the orthonormal basis vectors from the dark subspace, corresponding to time $t$, are transformed into orthonormal vectors from the dark subspace, corresponding to time $t + dt$. $\hat{O}_D$ is not unitary, as it takes the bright state to 0, whereas we can make $\hat{O}_D$ unitary if we complement it with an operator performing the following transformation

$$
e^{i\alpha(t)} |B(t)\rangle \rightarrow e^{i\alpha(t+dt)} |B(t + dt)\rangle.
$$

In analogy with the dark subspace, the operator performing this transformation is

$$
\hat{O}_B = \hat{P}_B + \left[ i\alpha(t) |B\rangle \langle B| + |\hat{B}\rangle \langle B| \right] dt,
$$

100
Now we can define the unitary transformation $\hat{U}$, acting in the whole Hilbert space $\mathcal{H}$, such that it yields the correct evolution of the vectors in the dark subspace

$$\hat{U} = \hat{O}_D + \hat{O}_B = \hat{1} + \left[ |\hat{B}\rangle \langle B| - |B\rangle \langle \hat{B}| \right] dt + \left( i\dot{\alpha}(t) + \langle \hat{B}|B\rangle \right) |B\rangle \langle B| dt.$$

(C.16)

The operator $\hat{U}$ is not uniquely defined as there is still some freedom left in defining $\dot{\alpha}(t)$. From the normalization condition $\langle B|B\rangle = 1$ it follows that $\langle \hat{B}|B\rangle$ is purely imaginary; furthermore we can define $\dot{\alpha}(t)$ such that

$$i\dot{\alpha}(t) + \langle \hat{B}|B\rangle = 0.$$

We then obtain the unitary

$$\hat{U} = \hat{1} + \left[ |\hat{B}\rangle \langle B| - |B\rangle \langle \hat{B}| \right] dt,$$

(C.17)

which acts in the whole space $\mathcal{H}$ and generates the correct evolution in the dark subspace. Using the relation $\hat{U} = e^{-i\hat{H}dt} = \hat{1} - i\hat{H}dt$, we can view the evolution of the state in the dark subspace in the adiabatic regime as if a time dependent effective Hamiltonian

$$\hat{H}_{\text{eff}} = i \left[ |\hat{B}\rangle \langle B| - |B\rangle \langle \hat{B}| \right]$$

(C.18)

was acting in the Hilbert space $\mathcal{H}$. We assume $\hbar = 1$.

### C.2 Effective Hamiltonian for a general quantum system with a dark space

In this section, we derive Eqs. (5.10) and (5.11) of the main text. Let us now consider a more general Hamiltonian of the form

$$\hat{H} = \sum_{i,j=1}^{k} g_{ij} |B_i\rangle \langle B_j| + g_{ij}^* |B_j\rangle \langle B_i|,$$

(C.19)

acting in some Hilbert space $\mathcal{H}$ of dimension $n$, where $|B_i\rangle$ are time dependent states in $\mathcal{H}$, forming an orthonormal set of vectors at any instant in time. Note that the Hamiltonian (C.2) is a special case of (C.19), with two bright states, one of them being time-independent. We point out that the Hamiltonian (C.19) could always be brought to diagonal form with appropriately chosen bright states, but for our purposes it is not necessary to assume this.

From now on we will assume that the eigenstates of the Hamiltonian (C.19) in the subspace spanned by the vectors $|B_i\rangle$ have nonzero instantaneous eigenvalues and that the adiabatic condition with respect to these eigenvalues is fulfilled. Thus, if the system starts in the instantaneous dark subspace of this Hamiltonian, it remains in the dark subspace, in accordance with the adiabatic theorem. Equations (C.10), (C.11) and (C.12) remain unchanged with the number of bright states increasing, while equation (C.13) is replaced by

$$\hat{O}_D = \hat{1} - \sum_{i=1}^{k} \hat{P}_{B_i} - \left( \sum_{i=1}^{k} \hat{P}_{B_i} \right) \left( \hat{1} - \sum_{i=1}^{k} \hat{P}_{B_i} \right) dt$$

$$= \hat{1} - \sum_{i=1}^{k} \hat{P}_{B_i} + \left[ \sum_{i,j=1}^{k} |\hat{B}_i\rangle |B_j\rangle \langle B_j| |B_i\rangle - \sum_{i=1}^{k} |B_i\rangle \langle \hat{B}_i| \right] dt.$$

(C.20)
This operator is again non-unitary in exactly the same sense as the operator in equation (C.13). To make $\hat{O}_D$ unitary we can complement it with an operator, performing in general the following transformation

$$|B_i(t)\rangle \rightarrow \sum_{j=1}^{k} \tilde{U}_{ij}(dt) |B_j(t + dt)\rangle,$$  \hspace{1cm} (C.21)

where $\tilde{U}_{ij}(dt)$ is an arbitrary infinitesimal unitary transformation in the subspace spanned by the vectors $|B_j(t + dt)\rangle$. If we introduce a general Hermitian matrix $A_{ij}$, we can write

$$\tilde{U}_{ij}(dt) = e^{iA_{ij}dt} \approx \delta_{ij} + iA_{ij}dt$$  \hspace{1cm} (C.22)

and thus equation (C.21) takes the form

$$|B_i(t)\rangle \rightarrow |B_i(t)\rangle + |\dot{B}_i(t)\rangle dt + i \sum_{j=1}^{k} A_{ij} |B_j\rangle dt.$$  \hspace{1cm} (C.23)

The operator performing this transformation is

$$\hat{O}_B = \sum_{i=1}^{k} \hat{P}_{B_i} + \sum_{i=1}^{k} |\hat{B}_i(t)\rangle \langle B_i| dt + i \sum_{i,j=1}^{k} A_{ij} |B_j\rangle \langle B_i| dt.$$  \hspace{1cm} (C.24)

In full analogy to (C.16), we can build the unitary transformation acting in the Hilbert space $\mathcal{H}$ by adding $\hat{O}_B$ and $\hat{O}_D$

$$\hat{U} = \hat{O}_D + \hat{O}_B = \hat{1} + \sum_{i=1}^{k} \left[ |\hat{B}_i\rangle \langle B_i| - |B_i\rangle \langle \hat{B}_i| \right] dt +$$

$$\sum_{i,j=1}^{k} (iA_{ji}(t) + \langle \hat{B}_i|B_j\rangle) |B_i\rangle \langle B_j| dt.$$  \hspace{1cm} (C.25)

The arbitrariness in $A_{ij}(t)$ can be removed if we choose $A_{ji}(t) = i \langle \hat{B}_i|B_j\rangle$. Note that this definition is consistent with the Hermitian property of $A$, as

$$i \langle \hat{B}_i|B_j\rangle = -i \langle B_i|\hat{B}_j\rangle = -i \langle B_j|B_i\rangle^* = (i \langle \hat{B}_j|B_i\rangle)^*.$$  \hspace{1cm} (C.26)

For the unitary operator $\hat{U}$ we then obtain

$$\hat{U} = \hat{1} + \sum_{i=1}^{k} \left[ |\hat{B}_i\rangle \langle B_i| - |B_i\rangle \langle \hat{B}_i| \right] dt.$$  \hspace{1cm} (C.27)

We now conclude that the evolution of the dark subspace of the Hamiltonian (C.19), acting in the Hilbert space $\mathcal{H}$ can be described with the effective Hamiltonian

$$\hat{H}_{\text{eff}} = \sum_{i=1}^{k} i \left[ |\hat{B}_i\rangle \langle B_i| - |B_i\rangle \langle \hat{B}_i| \right] = \sum_{i=1}^{k} \hat{H}_i,$$  \hspace{1cm} (C.28)

acting in the Hilbert space $\mathcal{H}$. Here $\hat{H}_i$ ($i = 1, ..., k$) is a Hamiltonian equivalent to (C.18).
C.3 Comparison of Non-Abelian Berry connection to the effective Hamiltonian

In this section we will consider the system shown in figure (5.1) with three ground states \( n = 3 \) and show that the universal set of single-qubit gates on two of them can be equivalently described either with the language of non-Abelian Berry connection or with the effective Hamiltonian.

The dark states of the Hamiltonian (5.2) can be parametrized with the angles of the sphere \( \theta_1, \theta_2 \), if one parametrizes coupling coefficients \( r_i \) as [122]

\[
\begin{align*}
    r_1 &= \sin(\theta_1), \\
    r_2 &= \cos(\theta_1) \sin(\theta_2), \\
    r_3 &= \cos(\theta_1) \cos(\theta_2).
\end{align*}
\]

For the dark states one then obtains [122]

\[
\begin{align*}
    |d_1\rangle &= \cos(\theta_1) |1\rangle - \sin(\theta_1) (e^{i\phi_2} \sin(\theta_2) |2\rangle + e^{i\phi_3} \cos(\theta_2) |3\rangle), \\
    |d_2\rangle &= e^{i\phi_2} \cos(\theta_2) |2\rangle - e^{i\phi_3} \sin(\theta_2) |3\rangle.
\end{align*}
\]

Treating \( \theta_1, \theta_2, \phi_2, \phi_3 \) as parameters \( (\lambda_k, k = \{1, 2, 3, 4\}) \) and calculating the Berry connection \( A_k = \langle d_i | \frac{\partial}{\partial \lambda_k} | d_j \rangle \) one obtains [122]

\[
\begin{align*}
    A_{\theta_1} &= \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}, \\
    A_{\theta_2} &= \begin{pmatrix} \sin(\theta_1) \\ -\sin(\theta_1) \end{pmatrix} \\
    A_{\phi_2} &= i \begin{pmatrix} \sin^2(\theta_1) \sin^2(\theta_2) & \sin(\theta_1) \sin(\theta_2) \cos(\theta_2) \\ \sin(\theta_1) \sin(\theta_2) \cos(\theta_2) & \cos^2(\theta_2) \end{pmatrix}, \\
    A_{\phi_3} &= i \begin{pmatrix} \sin^2(\theta_1) \cos^2(\theta_2) & -\sin(\theta_1) \sin(\theta_2) \cos(\theta_2) \\ -\sin(\theta_1) \sin(\theta_2) \cos(\theta_2) & \sin^2(\theta_2) \end{pmatrix}.
\end{align*}
\]

We assume a loop that starts with the parameters \( \theta_1 = \theta_2 = \phi_2 = \phi_3 = 0 \), such that the dark subspace is spanned by \( \{|1\rangle, |2\rangle\} \). If we perform a closed loop in parameter space, forcing the dark subspace to undergo a closed loop in the Hilbert space, a unitary on the dark subspace will be induced, that in the basis \( \{|1\rangle, |2\rangle\} \) takes the form

\[
U = \hat{P} \exp \left( - \oint \sum_{k=1}^{4} A_k d\lambda_k \right),
\]

where \( \hat{P} \) corresponds to the operation of path ordering.

If we only vary the two parameters \( \theta_1 \) and \( \theta_2 \), Eq. (C.32) takes the form

\[
U_y = \exp \left( -i \int \sin(\theta_1) d\theta_2 \right),
\]

where \( \sigma_y \) is the Pauli matrix.

If we only vary \( \theta_2 \) and \( \phi_3 \), Eq. (C.32) takes the form

\[
U_z = \exp \left( -i \oint \begin{pmatrix} 0 & 0 \\ 0 & \sin^2(\theta_2) \end{pmatrix} d\phi_3 \right).
\]
These two types of loops generate rotations around \(Y\) and \(Z\) axes respectively. Thus, the two operations do not commute and are sufficient to generate a universal set of gates.

We can alternatively analyze these loops using the effective Hamiltonian, equation (5.8). Given the loop in the parameter space \((\theta_1(t), \theta_2(t), t = [0, T])\), using the equations (5.8), (C.29) one can construct the effective Hamiltonian

\[
\hat{H}_{\text{eff}} = i \sum_{i,j} (r_j \dot{r}_i - r_i \dot{r}_j) |i\rangle \langle j|
\]

\[
= i (\sin(\theta_2) \dot{\theta}_1 - \sin(\theta_1) \cos(\theta_2) \dot{\theta}_2) (|1\rangle \langle 2| - |2\rangle \langle 1|)
+ i (\cos(\theta_2) \dot{\theta}_1 + \sin(\theta_1) \cos(\theta_2) \dot{\theta}_2) (|1\rangle \langle 3| - |3\rangle \langle 1|)
+ i \cos^2(\theta_1) \dot{\theta}_2 (|2\rangle \langle 3| - |3\rangle \langle 2|).
\]

(C.35)

We numerically solved the Schrödinger equation to obtain the final unitary

\[
U = \hat{T} \exp \left( - \int_0^T \hat{H}_{\text{eff}}(t) dt \right).
\]

(C.36)

Restricted to the space of \{\(|1\rangle, |2\rangle\}\}, the result exactly coincides with the unitaries obtained with Eqs. (C.33), (C.34) obtained for the Berry connection. We also did the same check for the \(U_z\) gates with the same results.

We note that although in our example the Berry connection approach did not require integration and thus is easier to implement, it relies on the explicit parametrization of the dark states, Eq. (C.30). In contrast, the effective Hamiltonian (5.8) does not require explicit parametrization of the coupling parameters and thus could be used without it, given only the dependence of the couplings on time. This will still hold in more general cases, when the number of bright states is larger than one and the dark subspace cannot be parametrized so easily. Then the effective Hamiltonian would allow to calculate the unitary arising from purely geometric evolution with much lower numerical cost, without the necessity to numerically orthogonalize the dark subspace.
Appendix D

Appendix

D.1 Effective Hamiltonian for hyperfine interaction in each electronic level, valid to second order perturbation theory

In this appendix we treat the coupled nuclear and electron spin system in the presence of nonparallel magnetic field in a rigorous way. We fix $B_z = D_{gs}/\gamma_e$ and introduce the phase factor $\phi$ according to the equation $B_x - iB_y = B_\perp e^{i\phi}$. At this field and in this notation one obtains

$$\hat{H}_e = D_{gs} \hat{S}_z^2 + \gamma_e \left( B_x \hat{S}_x + B_y \hat{S}_y + B_z \hat{S}_z \right) = 2D_{gs}|1\rangle\langle 1| + \frac{\gamma_e}{2} B_\perp \left( e^{i\phi} \hat{S}_+ + e^{-i\phi} \hat{S}_- \right).$$

We further introduce $\Omega = \frac{e^{3i\phi/2}}{2\gamma_e} B_\perp$ and the new basis states

$$|+\rangle = \frac{1}{\sqrt{2}} \left( e^{i\phi/2} |0\rangle + e^{-i\phi/2} |-1\rangle \right),$$

$$|-\rangle = \frac{1}{\sqrt{2}} \left( e^{i\phi/2} |0\rangle - e^{-i\phi/2} |-1\rangle \right),$$

so the Hamiltonian $H_e$ takes the form

$$\hat{H}_e = \hat{H}_0^0 + \hat{H}_e^2,$$

$$\hat{H}_0 = 2D_{gs}|1\rangle\langle 1| + \Omega (|+\rangle\langle +| - |-\rangle\langle -|),$$

$$\hat{H}_e^2 = \Omega (|+\rangle\langle +| + |-\rangle\langle -|) + \Omega^* (|+\rangle\langle 1| + |-\rangle\langle 1|).$$

We now introduce the hyperfine and the nuclear spin Zeeman interactions $\hat{H}_{hf}, \hat{H}_n$ into the system. We split the hyperfine interaction into secular and nonsecular terms as

$$\hat{H}_{hf} = \hat{H}_{hf}^1 + \hat{H}_{hf}^2,$$

$$\hat{H}_{hf}^1 = \sum_{k=\{1,+,-\}} |k\rangle\langle k| \sum_{i,j=\{x,y,z\}} A_{ij} \hat{I}_j \langle k|\hat{S}_i|k\rangle,$$

$$\hat{H}_{hf}^2 = \sum_{k \neq k'} |k\rangle\langle k'| \sum_{i,j=\{x,y,z\}} A_{ij} \hat{I}_j \langle k'|\hat{S}_i|k\rangle.$$

Our aim now is to obtain an effective Hamiltonian in each of the three electronic subspaces. We achieve this using the formalism of the Schrieffer-Wolf transformation [112, 113]. The basic idea is to find a basis change that brings to zero non-secular terms $\hat{H}_e, \hat{H}_{hf}^2$ up to a
certain order of magnitude. In order for this procedure to work we have to assume that $|\Omega| \ll 2D_{gs}$, $||A_{ij}|| \ll 2\Omega$. Following this procedure, we introduce an antihermitian matrix $S$, that obeys the equation

$$SH^0 - H^0 S = -\hat{H}_{hf}^2 - \hat{H}_c^2.$$  \hfill (D.5)

After performing this procedure, we obtain

$$S = \frac{\Omega}{2D_{gs} - |\Omega|} |1\rangle \langle + | + h.c. + \frac{\Omega}{2D_{gs} + |\Omega|} |1\rangle \langle - | + h.c. - \sum_{k \neq \tilde{k}} \frac{\sum_{ij} A_{ij} \hat{I}_j \langle k | S_i | \tilde{k} \rangle}{W_k - W_k},$$  \hfill (D.6)

where $W_1$, $W_+$ and $W_-$ are $2D_{gs}$, $|\Omega|$ and $-|\Omega|$ respectively. Now we can calculate the effective Hamiltonian in each of the three electronic subspaces

$$\hat{H}_{eff} = \hat{H}_e^0 + \hat{H}_n + \hat{H}_{hf}^1 + \frac{1}{2} \left[ S, \hat{H}_{hf}^2 + \hat{H}_c^2 \right].$$  \hfill (D.7)

From this expression it follows that the interaction of the electron spin with the transverse magnetic field leads to the renormalization of the energies of the bare electronic states $D_{gs}$, $|\Omega|$, $-|\Omega|$ to the new values

$$\tilde{D}_{gs} = D_{gs} \left( 1 + \frac{2|\Omega|^2}{4D_{gs}^2 - |\Omega|^2} \right)$$
$$\Omega_\pm = |\Omega| \left( 1 \mp \frac{|\Omega|}{2D_{gs} \mp |\Omega|} \right).$$  \hfill (D.8)

Let us also introduce the corrections to hyperfine terms due to the interaction of electron spin with the transverse magnetic field

$$C_\pm = \frac{2\mathrm{Re} [\Omega \langle \pm | S_i | 1 \rangle]}{2D_{gs} \mp |\Omega|}.$$  \hfill (D.9)

For the effective Hamiltonian we then obtain

$$\hat{H}_{eff} = 2\tilde{D}_{gs} |1\rangle \langle 1 | + \Omega_+ |+\rangle \langle + | - \Omega_- |\rangle \langle - |$$
$$+ \sum_{ij} A_{ij} \hat{I}_j \left( |1\rangle \langle S_i | 1 \rangle + C_+ + C_- \right) |1\rangle \langle 1 |$$
$$+ \sum_{ij} A_{ij} \hat{I}_j \left( |+\rangle \langle S_i | + \rangle + C_+ \right) |+\rangle \langle + |$$
$$+ \sum_{ij} A_{ij} \hat{I}_j \left( |\rangle \langle S_i | \rangle - C_- \right) |\rangle \langle - |$$
$$+ \frac{1}{2} \sum_{ij} A_{ij} A_{ij} \frac{\left( |+\rangle \langle S_i | + \rangle \langle + | + \rangle \hat{I}_j \hat{I}_j |+\rangle \langle + | + \rangle \hat{I}_j \hat{I}_j \right)}{2|\Omega|}$$
$$- \frac{1}{2} \sum_{ij} A_{ij} A_{ij} \frac{\left( |\rangle \langle S_i | \rangle \langle + | + \rangle \hat{I}_j \hat{I}_j \right)}{2|\Omega|} + \hat{H}_n.$$  \hfill (D.10)
The first line here arises due to the interaction of the electron spin with magnetic field. Lines two to four describe the secular terms of the hyperfine interaction corrected due to nonsecular terms of the electron spin interaction with the magnetic field. Lines five and six take into account nonsecular part of the hyperfine interaction, that mixes the electron spin states $|+\rangle$, $|–\rangle$. We neglect the effect of this interactions that mixes $|+\rangle$, $|–\rangle$ with $|1\rangle$, because it is small compared to all other effects.

### D.2 Details of the dynamics simulation

In this appendix we give details of the simulation we performed to model the initialization fidelity. The ground state of the NV is an orbital singlet, spin triplet and we describe it with the Hamiltonian (6.13). The excited state is treated as an orbital doublet, spin triplet and we describe it with the following Hamiltonian (see the introduction 1.2.2)

\[
\hat{H}_{es} = g_s^x \mu_B B \hat{S}_z \hat{S}_z + 2 \mu_B \left( B_x \hat{S}_x + B_y \hat{S}_y \right) \\
- \lambda s \hat{S}_z + l \mu_B B_s \sigma_y \\
+ D_{zz} \left( \hat{S}_z^2 - \frac{1}{3} S(S+1) \right) \\
+ D_{xy} \left( \sigma_z(\hat{S}_y^2 - \hat{S}_z^2) - \sigma_x \{\hat{S}_x, \hat{S}_y\} \right) \\
+ D_{xz} \left( \sigma_z \{\hat{S}_x, \hat{S}_z\} - \sigma_x \{\hat{S}_y, \hat{S}_z\} \right) \\
+ \sum_{i,j=x,y,z} A_{ij} \hat{S}_i \hat{I}_j, \\
+ \gamma_n B \cdot \hat{I}
\]  

(D.11)

Here $\sigma_x$, $\sigma_y$, $\sigma_z$ are Pauli matrices that act in the bases of $|X\rangle$ and $|Y\rangle$ of the orbital doublet. The first line describes the Zeeman interaction, the second line takes into account spin-orbit coupling and the interaction of magnetic field with the orbital angular momentum $\hat{L}$ (described with an operator $\sigma_y$ in the relevant subspace). Lines three, four and five describe the spin-spin interaction. The sixth line takes into account the hyperfine interaction in the excited state. The seventh line gives the Zeeman interaction for the nuclear spin. The strength of the corresponding interactions is taken from Ref. [50] and is listed in Table [D.1]. The strength of the hyperfine interaction is given in the basis when z-axis coincides with the direction from the vacancy to the $^{13}C$ atom. In this basis the hyperfine tensor is diagonal, with the biggest eigenvalue ($A_{rx}^{es}$) corresponding to the vector along z-direction. The excited orbital states can decay to the ground state through a spin-conserving photon emission with the rate $\Gamma_{ge}$ each. The corresponding decay operators are $O_x = |A_2\rangle \langle E_x|$ and $O_y = |A_2\rangle \langle E_y|$, where $|A_2\rangle$ is the ground state orbital singlet. The excited state $|A_1\rangle$, that is the eigenstate of the spin-orbit and spin-spin part of the Hamiltonian (D.11), can also decay to the singlet level $|s\rangle$ with the rate $\Gamma_{xe}$. The corresponding decay operator is $O_3 = |s\rangle \langle A_1|$. The singlet state can decay to the ground states through three channels, to the state with spin 0 at the rate $\Gamma_{0s}$ and corresponding decay operator $O_4 = |A_2, m_s = 0\rangle \langle s|$ or to the states with spins $\pm 1$ with the rate $\Gamma_{pms}$ and corresponding decay operators $O_5 = |A_2, m_s = +1\rangle \langle s|$ and $O_6 = |A_2, m_s = -1\rangle \langle s|$. In our model we replace all spin singlet levels with only one orbital level, that is placed between the triplets. The values of the decay rates are taken from Ref. [50] and are listed in Table [D.1]. We assumed the z-component of the magnetic field to be $D_{gs}/\gamma_e$. The transverse magnetic field is assumed to point in the x-direction and have the value of 500 G. We show that at this magnetic field one optical field is enough to couple the electronic levels $|+\rangle$ and $|1\rangle$ to the excited states close to resonance (Figure 6.8), while leaving $|–\rangle$
out of resonance. The microwave magnetic field pulse in Fig. 6.8 is assumed to point in the y-direction. The corresponding optical and microwave Rabi frequencies $\Omega_o$ and $\Omega_{mw}$ respectively are given in Table D.1. The optical and microwave driving Hamiltonians are given by

$$\hat{H}_o = \Omega_o (|E_x\rangle \langle A_2| e^{i\omega_1 t} + |A_2\rangle \langle E_x| e^{-i\omega_1 t}),$$

$$\hat{H}_{mw} = \Omega_{mw} \hat{S}_y \sin(\omega_2 t).$$

We solve the Lindblad equation

$$\dot{\rho} = -\frac{i}{\hbar} [\hat{H}_{gs} + \hat{H}_{es} + \hat{H}_o + \hat{H}_{mw}, \rho] + \sum_{i=1}^{6} \Gamma_i \left( \hat{O}_i \rho \hat{O}_i^\dagger - \frac{1}{2} \hat{O}_i^\dagger \hat{O}_i \rho - \frac{1}{2} \rho \hat{O}_i^\dagger \hat{O}_i \right),$$

assuming the duration of the optical and microwave pulses of 100 $\mu$s. Our simulation reveals that assuming the system to be initially in equal superposition of the six ground states, after such procedure the system will be trapped in the lowest ground state with the probability 97%.

Table D.1: The values used to simulate the initialization fidelity.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>$g$-factor $g_{es}$</td>
<td>2.15</td>
</tr>
<tr>
<td>spin-orbit constant $\lambda$</td>
<td>5.33 GHz</td>
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<tr>
<td>$l$</td>
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</tr>
<tr>
<td>axial spin-spin constant $D_{zz}$</td>
<td>1.44 GHz</td>
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<tr>
<td>transverse spin-spin constant $D_{xy}$</td>
<td>1.54/2 GHz</td>
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<tr>
<td>transverse spin-spin constant $D_{xz}$</td>
<td>$154/\sqrt{2}$ MHz</td>
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<tr>
<td>$A_{e\parallel}^{es}$</td>
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<tr>
<td>$A_{e\perp}^{es}$</td>
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<tr>
<td>$\gamma_n$</td>
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<td>$\Gamma_{ge}$</td>
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<td>$\Gamma_{pm}$</td>
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<tr>
<td>$\Omega_o$</td>
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<tr>
<td>$\Omega_{mw}$</td>
<td>10 MHz</td>
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Bibliography


